

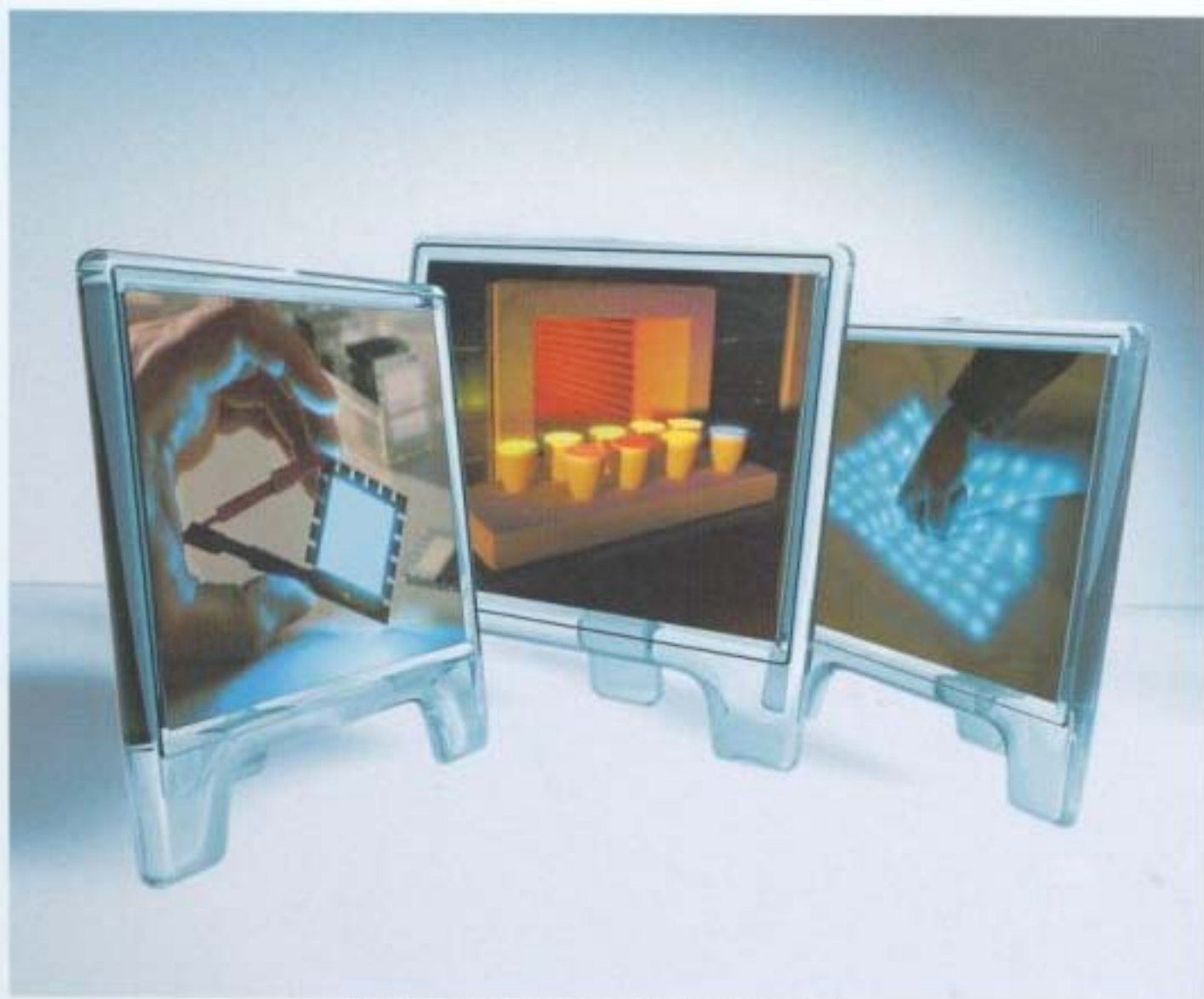
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Luminescence

From Theory to Applications

With a Foreword by Sailing He



Luminescence

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Luminescence

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Cees Ronda



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Foreword

Since Joseph Swan in Britain and Thomas Edison in the USA invented the light bulb independently in 1879, illumination technology has become indispensable in our daily lives. In the 20th century, more efficient illumination technologies of gas discharge lamps, halogen tungsten lamps and LEDs were commercialized for lighting. Liquid crystal displays and plasma display panels have become the most promising technologies for display screens. Excellent luminescent materials have been developed for lighting and display with greater performance in brightness, color gamut, efficiency, and lifetime. Therefore, it is critical to understand the mechanism behind the new technologies of luminescence.

The book you are about to read addresses this need. It contains 9 chapters. From Chapter 1 to Chapter 8, each chapter is on one kind of phosphors, while Chapter 9 is on experimental techniques. The authors describe clearly the physical principles, related backgrounds and research directions for almost every popular luminescent material. Various subjects are covered, such as physics, nonlinear optics, chemistry, quantum mechanism and spectroscopy. Many clear diagrams and illustrations are given to help readers understand and remember the principles well. Definitions are made precisely and much attention has been paid to the differences (even small) among various concepts. All the equations used in this book are very basic as the authors want to give readers a clear insight into the related physics. No puzzling mathematics or complicated calculations are involved. The book is easy to read and thus very suitable for students who want to get an overall picture of luminescence. Cees Ronda is both an academic professor and a research fellow of Philips. He has given a series of excellent lectures on luminescence in our center during the past several years and we enjoyed very much his style of making everything crystal clear. His personal experience and contacts in industry and academia are essential in putting together such an impressive book. Each theory explained here has practical applications. Many classical papers and books have been cited, as well as the latest developments. R & D histories, current markets and future trends and challenges in luminescence technology are given. Therefore, the book is also very suitable for researchers.

My students and I enjoyed very much in reading this book. I am sure you will also enjoy it.

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July 2007

Contents

	Foreword	V
	Preface	XIII
	List of Contributors	XV
1	Emission and Excitation Mechanisms of Phosphors	1
	<i>Cees R. Ronda</i>	
1.1	Introduction	1
1.2	General Considerations – Fluorescent Lamps	1
1.3	General Considerations – Cathode Ray Tubes	2
1.4	Luminescence Mechanisms	3
1.4.1	Center Luminescence	4
1.4.2	Charge Transfer Luminescence	8
1.4.3	Donor Acceptor Pair Luminescence	8
1.4.4	Long Afterglow Phosphors	11
1.5	Excitation Mechanisms	12
1.5.1	Optical Excitation of Luminescence and Energy Transfer	12
1.6	Energy Transfer Mechanisms between Optical Centers	14
1.6.1	Mechanisms Underlying Energy Transfer	14
1.6.2	Energy Transfer Governed by Electrostatic Interaction	15
1.6.3	Energy Transfer by Higher-order Coulomb Interaction	18
1.6.4	Energy Transfer Governed by Exchange Interactions	19
1.6.5	Cross-relaxation and Energy Transfer	19
1.6.6	Practical Implications	20
1.7	Excitation with High-energy Particles	21
1.8	Electroluminescence (EL)	24
1.8.1	High-voltage Electroluminescence	24
1.8.2	Low-voltage Electroluminescence	26
1.9	Factors Determining the Emission Color	27
1.10	Energy Efficiency Considerations of Important Luminescent Devices	29
1.11	Luminescence Quantum Yield and Quenching Processes	29

- 1.11.1 The Energy does not Reach the Luminescent Ion 31
- 1.11.2 The Absorbed Energy Reaches the Luminescent Ion but there are Nonradiative Channels to the Ground State 31
- 1.11.3 The Luminescence Generated is Absorbed by the Luminescent Material 33
- 1.12 Acknowledgement 34

2 Quantum Dots and Nanophosphors 35

Cees R. Ronda and Thomas Jüstel

- 2.1 Introduction 35
 - 2.1.1 Optical Properties of Quantum Dots 35
 - 2.1.2 Particle in a One-dimensional Potential Well 36
 - 2.1.3 Particle in Three-dimensional Potentials 40
 - 2.1.3.1 Particle in a General Three-dimensional Potential 40
 - 2.1.3.2 Electron in a Coulomb Potential 41
 - 2.1.3.3 The Hydrogen Atom 42
- 2.2 Density of States in Low-dimensional Structures 43
- 2.3 Electrons, Holes, and Excitons 45
- 2.4 Low-dimensional Structures 46
 - 2.4.1 The Weak Confinement Regime 46
 - 2.4.2 The Strong Confinement Regime 47
- 2.5 Quantum Confinement in Action 49
- 2.6 Photoluminescence of Quantum Dots Prepared by Wet-chemical Precipitation 52
- 2.7 Photoluminescence from Doped Quantum Dots 53
- 2.8 Luminescence of Nano Particles of Rare-Earth Phosphors 55
- 2.9 Nanoscale Particles for Molecular Imaging 56
- 2.10 Conclusions 58
- 2.11 Acknowledgements 58

3 Phosphors for Plasma Display Panels 61

Thomas Jüstel

- 3.1 Introduction 61
- 3.2 Principle of Operation of Plasma Display Panels 61
- 3.3 Performance of Applied Phosphors in PDPs 65
 - 3.3.1 Phosphor Efficiency 66
 - 3.3.2 Electronic Transitions Involved in Europium Luminescence 68
 - 3.3.3 Color point and efficiency of the red phosphors 68
 - 3.3.4 Stability and Color Point of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ 70
- 3.4 Summary and Prospects 72

4 Quantum-Splitting Systems 75

Alok M. Srivastava and Cees R. Ronda

- 4.1 Introduction 75

4.2	Quantum-splitting Phosphors Based on Pr ³⁺ -activated Fluoride Materials	76
4.3	Quantum-splitting Phosphors Based on Pr ³⁺ -activated Oxide Materials	82
4.3.1	SrAl ₁₂ O ₁₉ : Pr ³⁺	83
4.3.1.1	LaMgB ₅ O ₁₀ and LaB ₃ O ₆ Doped with Pr ³⁺	85
4.4	The Quantum Efficiency of the Quantum-splitting Process	88
4.5	Limitations of Pr ³⁺ -based Quantum-splitting Phosphors	91
4.6	Quantum-splitting Phosphors Based on Gd ³⁺ and Rare Earth Ion-Activated Fluoride Materials	92
4.6.1	The Electronic Energy Level Structure of the Gd ³⁺ Ion	92
4.6.2	Quantum Splitting in the Gd ³⁺ -Eu ³⁺ System	94
4.6.3	Quantum Splitting in the Er ³⁺ -Gd ³⁺ -Tb ³⁺ System	97
4.7	Multiphoton Emission through High-energy Excitation	98
4.8	Applications of Quantum-splitting Phosphors	99
4.9	Conclusions	100
4.10	Acknowledgements	101
5	Scintillators	105
	<i>Cees R. Ronda and Alok M. Srivastava</i>	
5.1	Introduction	105
5.2	Positron Emission Tomography and Computed Tomography	106
5.2.1	Physical Principles of Positron Emission Tomography (PET)	106
5.2.2	Computed Tomography (CT)	107
5.3	General Requirements for Scintillating Materials used in Medical Imaging	107
5.4	Scintillators for Pet Application	112
5.4.1	General Description of Phosphors for PET Scintillators	112
5.4.2	Scintillating Composition Used in PET	114
5.4.2.1	Bi ₄ Ge ₃ O ₁₂ (BGO)	115
5.4.2.2	NaI:Tl ⁺	116
5.4.2.3	Lu ₂ SiO ₅ :Ce ³⁺ (LSO)	116
5.4.2.4	Lu ₂ Si ₂ O ₇ :Ce (Lutetium Pyrosilicate, LPS)	117
5.4.2.5	LaBr ₃ :Ce	118
5.4.2.6	LuI ₃ :Ce	119
5.4.3	Other PET Scintillators	119
5.5	Scintillators for CT Application	120
5.5.1	General Description of Scintillators for CT	120
5.5.2	Scintillating Compositions Used in CT	120
5.5.2.1	CdWO ₄	120
5.5.2.2	(Y,Gd) ₂ O ₃ :Eu ³⁺	121
5.5.2.3	Gd ₂ O ₂ S:Pr ³⁺ (GOS)	122
5.6	X-ray Intensifying Screens	123
5.6.1	General Description of Scintillators for Intensifying Screens	123
5.6.2	Phosphor Compositions for Use in X-ray Intensifying Screens	123

- 5.7 FDXD Detectors 124
- 5.8 Storage Phosphors 124
- 5.8.1 General Description of Storage Phosphors 124
- 5.9 Semiconductor Scintillators 127

- 6 Upconversion Phosphors 133**
J. Freek Suijver
- 6.1 Introduction 133
- 6.2 Theory of Upconversion 137
 - 6.2.1 Absorption and Excitation Spectroscopy 139
 - 6.2.2 Time Evolution of UC Emission 143
 - 6.2.3 Power Dependence of Upconversion 146
 - 6.2.4 Photon Avalanche Effects in Upconversion 150
 - 6.2.5 Determination of the Upconversion Efficiency 153
- 6.3 Examples 154
 - 6.3.1 Rare Earth Upconverters 155
 - 6.3.2 Transition Metal Upconverters 162
 - 6.3.3 Mixed Rare Earth/Transition Metal Upconverters 165
 - 6.3.4 Organic Upconverters 169
 - 6.3.5 Nanocrystalline Upconverters 171
- 6.4 Conclusions and Outlook 175
- 6.5 Acknowledgements 176

- 7 Luminescent Materials for Phosphor-Converted LEDs 179**
Thomas Jüstel
- 7.1 Inorganic Light-Emitting Diodes (LEDs) 179
- 7.2 White and Colored LEDs 180
- 7.3 Phosphor-Converted LEDs 183
- 7.4 Future Trends 188

- 8 Organic Electroluminescence 191**
Joseph J. Shiang and Anil R. Duggal
- 8.1 Introduction 191
- 8.2 OLED Fundamentals 192
- 8.3 Key OLED Trends and Innovations 197
 - 8.3.1 Electroluminescence from Vapor-deposited Organic Films 197
 - 8.3.2 Electroluminescence from Solution-Deposited Organic Films 202
- 8.4 Prospects for General Illumination 207
 - 8.4.1 A First OLED Lighting Demonstration 208
 - 8.4.1.1 Downconversion for White Light Generation 209
 - 8.4.1.2 Scattering for Outcoupling Efficiency Enhancement 210
 - 8.4.1.3 A Scalable Monolithic Series Architecture 211
 - 8.4.2 Efficiency Challenge for General Illumination 212
- 8.5 Conclusions 213
- 8.6 Acknowledgements 214

9	Experimental Techniques	219
	<i>Peter Vergeer</i>	
9.1	Introduction	219
9.2	Energy of Optical Transitions: Absorption, Excitation, and Emission Spectroscopy	220
9.2.1	Broadband Light Sources	223
9.2.2	Dispersing Elements	224
9.2.2.1	Gratings	224
9.2.2.2	Interferometers	227
9.2.3	Detectors	229
9.3	The Transition Dipole Moment: Absorption Strengths and Luminescence Lifetimes	233
9.3.1	Lasers	235
9.3.2	Luminescence Lifetimes	237
9.4	Quantum Efficiency and Nonradiative Relaxation	238
9.5	Homogeneous Broadening and Dephasing	240
9.6	Detection of Luminescence from Individual Optical Centers	244
9.7	Acknowledgement	248
	Index	251

Preface

Modern society relies heavily on mankind's ability to produce light. In the early days, light was produced by chemical means. Though this is a rather inefficient way, the heat produced also enabled our predecessors to develop metal tools and to cook their foods. This is a very early demonstration how increased technological capabilities improved people's life. Later on, dedicated light sources were developed, such as candles and oil lamps.

Electrically generated light is only a few centuries old and the developments in these light sources is a beautiful example of how our increased understanding of physical and chemical processes led to new light generation principles.

In incandescent lamps, in which light generation is still rather inefficient, a conducting body is heated and the spectrum of the radiation generated corresponds to the temperature of the heated body (black body radiation). It is also interesting to note that understanding the operation principles of incandescent lamp requires quantum mechanics and in fact black body radiation played a very important role in the early development of quantum mechanics. The large-scale introduction of incandescent lamps in addition required glass- and vacuum technology and metallurgy. Finally, the availability of electricity was a decisive prerequisite. The vacuum technology developed was very important in the development of valves, X-ray tubes, gas discharge lamps and picture tubes later on.

In gas discharge lamps, light is generated by exciting atoms or molecules in the gas phase. Gas discharge lamps require knowledge of electronic states of individual excited atoms or molecules, which reflects our increased understanding of electronic states in these moieties. In addition, they use emitters (materials releasing electrons), developed to certain maturity in the early 20th century. Many gas discharge lamps use luminescent materials, which absorb light generated by the discharge and convert it to light with a different frequency. The development of luminescent materials, also called phosphors, requires high purity materials and sophisticated materials science. Very important is the description of electronic states of ions interacting with their environment. This reflects a further increased understanding of the electronic states in matter: ions, which interact with their environment. It is this level of understanding, which has also enabled the development of solid-state lasing materials.

Also in the first half of the 20th century luminescent materials, excitable with electron beams with large kinetic energy or with high-energy photons were developed. Application areas are picture tubes and detection of X-rays or γ -rays. These achievements were instrumental in reaching our current level of medical care and our current ability to distribute and receive information. Understanding the excitation mechanism of this kind of emission requires some knowledge of the electronic band structure, the electronic states of the emitting ions and of lattice vibrations (phonons) in luminescent materials.

In the same period, Destriau discovered high voltage electroluminescence¹. High voltage electroluminescence has a number of applications, mainly in displays. The materials properties that govern high voltage electroluminescence are not yet well understood, but they also involve electronic band states and electronic states of the emitting ions.

A further increase of our understanding of electronic states has led to emission in quantum dots and in materials showing electroluminescence under low voltage excitation. In quantum dots, the electronic states depend on the size of the particles. Quantum dots typically have a diameter between 1–10 nm. Application opportunities are in e.g. molecular imaging. Low voltage electroluminescence involves charge transport in extended molecular orbitals and recombination in such states or on e.g. ions.

In this book, the luminescence mechanisms underlying important applications will be dealt with. This makes this book very interesting for people working in both an academic and an industrial environment. Experts in their respective fields have written the chapters. All chapters start at a fundamental level and finally deal with the state of the art. This also makes this book very useful for teaching purposes.

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¹G. Destriau, J. Chem. Phys. 33, 620 (1936).

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1

Emission and Excitation Mechanisms of Phosphors

Cees R. Ronda

1.1

Introduction

In this chapter, basic concepts involved in luminescence will be discussed. We will take a closer look at a number of excitation mechanisms which are involved in generating luminescence and processes which lead to luminescence, taking illustrative examples from luminescent materials applied in fluorescent lamps and cathode ray tubes. With respect to fluorescent lamps, we will restrict ourselves to discharge lamps based on the low-pressure Hg discharge. Other applications will be treated more extensively in separate chapters. A separate chapter in this book is devoted to scintillators, used in medical detectors. Here the excitation mechanism strongly resembles the one in cathode ray phosphors. Phosphors for Light-Emitting Diodes (LEDs) and phosphors for Plasma Display Panels (PDPs) are treated separately as well, the processes leading to excitation and emission being comparable to those in fluorescent lamps.

Possible ways to influence the emission color will be discussed, this being of strong relevance for applications. We will also give an overview of the most popular devices that rely on luminescent materials, and finally we will touch upon processes that result in nonradiative recombination.

Recently, organic luminescent materials have attracted considerable interest in view of their application in organic light-emitting diodes. In this chapter, however, we discuss inorganic phosphors only.

1.2

General Considerations – Fluorescent Lamps

On passing a current through an Hg discharge, UV light is generated as a consequence of electronic transitions on the Hg atoms. In low-pressure Hg discharge, the main emission line is located at 254 nm. This light is invisible and harmful; therefore it has to be converted into visible light. This is done by the application of luminescent materials. These materials have to show a strong absorption at 254 nm and have to convert this into visible light very efficiently. In most of the fluorescent lamp phosphors, the optical

processes leading to luminescence do not involve host lattice states, implying that the energy gap is at least 4.9 eV, this being the energy of a photon with wavelength 254 nm. Therefore, the luminescent materials applied in fluorescent lamps are insulators.

The conversion efficiency of luminescent materials is very high: about 90 % of the UV photons are absorbed, and also about 90 % of the absorbed photons are converted into visible light. This implies that such materials cannot be improved any further in terms of conversion efficiency unless materials can be found that generate more than one visible photon after absorption of a UV photon. This is the subject of a separate chapter in this book.

An elementary calculation shows that, even though fluorescent lamps are the most efficient white light sources, the overall energy efficiency is nevertheless rather limited: only about 25 %. The percentage energy efficiency is calculated as follows:

$$\eta = \eta_{\text{disch}} \cdot \eta_{\text{phos}} \cdot (254/550) \cdot 100 \quad (1)$$

in which 254 nm is the wavelength of the exciting Hg radiation in nm and 550 nm is the mean wavelength of the light emitted. As in current fluorescent lamp phosphors only one visible photon per absorbed UV photon is generated, the difference in photon energy represents energy loss. The discharge efficiency (η_{disch}) of the Hg discharge is about 70 % and the conversion efficiency (η_{phos}) of the phosphors (on a photon basis) is about 80 %. Insertion of these numbers leads to the overall efficiency of about 25 %. In view of the very high Hg discharge efficiency, here also hardly any significant improvement can be expected. This implies that this lamp concept has reached physical limits in terms of energy efficiency.

Compact fluorescent lamps have a lower light generation efficiency (only 15 %). As the luminescent materials applied are the same or very similar, this must be due to the lower discharge efficiency in these devices, which, in turn, is due to the smaller diameter of the lamp envelope and therefore to the increased wall losses: excited Hg atoms reach the ground state on interacting with the lamp wall without generating UV light: energy and momentum can be conserved by interaction of excited species with the wall without generation of light.

1.3

General Considerations – Cathode Ray Tubes

Though the importance of cathode ray tubes is rapidly decreasing, we will treat the luminescence mechanism in these materials in view of its historical importance. In addition, the excitation mechanism that comprises excitation with high-energy particles (electrons, X-ray photons, or γ -rays) is also operative in phosphors used in scintillators for, e.g., medical applications.

Luminescent materials applied in cathode ray tubes in general differ from those applied in fluorescent lamps. Excitation proceeds via the band gap. To achieve high efficiencies, small values for the band gap are needed, as will be elucidated below. For this reason, quite a few luminescent materials applied in cathode ray tubes are semiconductors.

The luminescence mechanism operating in the blue and green emitting phosphors applied in cathode ray tubes is a beautiful example of luminescence involving defect states in semiconductors. We will therefore also discuss this mechanism in some detail.

The maximum energy efficiency of the cathode ray phosphors is relatively low, at most about 25 %, as will be outlined in this chapter. Also for these phosphors, the maximum efficiencies have been reached.

In the next sections, we will deal with luminescence and excitation mechanisms.

1.4 Luminescence Mechanisms

Luminescent materials, also called phosphors, are mostly solid inorganic materials consisting of a host lattice, usually intentionally doped with impurities (see Fig. 1.1). The impurity concentrations generally are low in view of the fact that at higher concentrations the efficiency of the luminescence process usually decreases (concentration quenching, see below). In addition, most of the phosphors have a white body color. Especially for fluorescent lamps, this is an essential feature to prevent absorption of visible light by the phosphors used. The absorption of energy, which is used to excite the luminescence, takes place by either the host lattice or by intentionally doped impurities. In most cases, the emission takes place on the impurity ions, which, when they also generate the desired emission, are called activator ions. When the activator ions show too weak an absorption, a second kind of impurities can be added (sensitizers), which absorb the energy and subsequently transfer the energy to the activators. This process involves transport of energy through the luminescent materials. Quite frequently, the emission color can be adjusted by choosing the proper impurity ion, without changing the host lattice in which the impurity ions are incorporated. On the other hand, quite a few activator ions show emission spectra with emission at spectral positions which are hardly influenced by their chemical environment. This is especially true for many of the rare-earth ions.

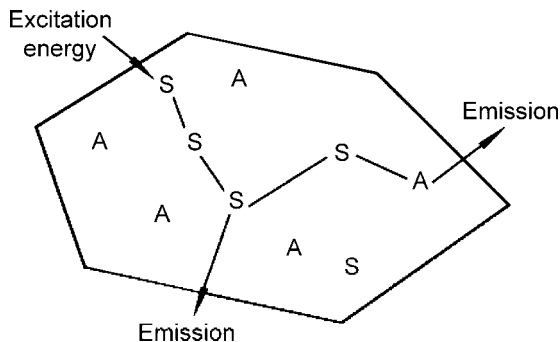


Fig. 1.1 Luminescent material containing activator ions A (ions showing the desired emission) and sensitizing ions S (on which, e.g., UV excitation can take place).

1.4.1

Center Luminescence

In the case of center luminescence, the emission is generated on an optical center, in contradiction to, e.g., emission, which results from optical transitions between host lattice band states or from a transition between two centers. Such an optical center can be an ion or a molecular ion complex.

One speaks of characteristic luminescence when, in principle, the emission could also occur on the ion in a vacuum, i.e. when the optical transition involves electronic states of the ion only. Characteristic luminescence can consist of relatively sharp emission bands (spectral width typically a few nm), but also of broad bands, which can have widths exceeding 50 nm in the visible part of the spectrum. Broad emission bands are observed when the character of the chemical bonding in the ground and excited state differs considerably. This goes hand in hand with a change in equilibrium distance between the emitting ion and its immediate chemical environment and is commonly explained with the configuration coordinate diagram (Fig. 1.2).

In this diagram, Q_g and Q_e represent the metal-ligand distances in the ground and excited states, respectively. E_a and E_e are the energies at which the absorption and emission bands have their maximum intensity, respectively. Δ is the energy of the so-called zero phonon line; this transition involves completely relaxed excited and ground states, and no excited phonon states are involved – hence the name of this kind of transitions. The phonon frequencies in the ground and excited state are given by $\hbar\omega_g$ and $\hbar\omega_e$, respectively. The relaxation energies in the ground and excited states can be expressed as a product of the phonon energy and the so-called Huang-Rhys factors. The Huang-Rhys factors S_e and S_g in the ground and excited state (being pure numbers), respectively, give the mean number of phonons involved in the absorption and emission processes, respectively. In the harmonic approximation, the curvature of the parabolic band (determined by the bond strength), the phonon frequencies, and the Huang-Rhys factors are the same in the ground and excited state. This picture

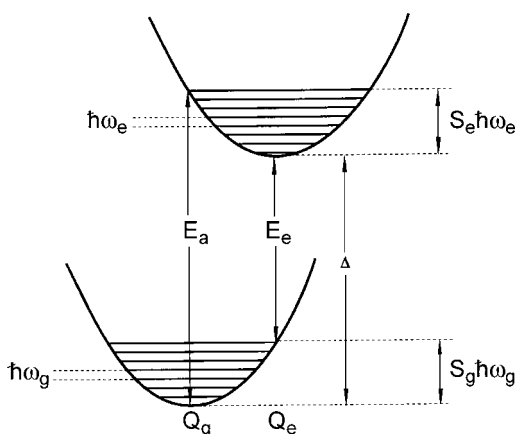


Fig. 1.2 Configurational coordinate diagram.

is very elementary. For example, it does not describe thermal expansion of the lattice. However, it does give a lot of insight. It can, e.g., be used in showing that a larger Stokes Shift is expected on increasing lattice relaxation and also in the description of thermal quenching of the emission (see further below).

Broad bands are observed for many optical transitions in the partly filled d-shell of transition metal ions ($d \rightarrow d$ transitions), but also for transitions between the 5d shell and the 4f shell of rare-earth ions ($d \rightarrow f$ transitions) and for emission on s^2 ions (these ions possess a “lone pair” of s electrons), like Tl^+ , Pb^{2+} , or Sb^{3+} . Sharp emission bands are characteristic of optical transitions between electronic states with chemical bonding character (almost) the same for ground and excited state, and for the same reason also of optical transitions between electronic states that hardly participate in the chemical bonding (e.g., $f \rightarrow f$ transitions on rare-earth ions).

In the case of optical processes involving electronic states which participate in the chemical bonding, the nature of the bonding (covalent, ionic) and the symmetry of the site at which the emitting ion is incorporated play a very important role. This is generally described by the ligand field theory, which we do not treat here. We will use the term symbols for the description of the electronic transitions which arise from the site symmetry of the ions of interest, however.

An example of a broad $d \rightarrow d$ emission band (in the green part of the spectrum) is the emission of Mn^{2+} in $BaMgAl_{10}O_{17}$: Eu, Mn, see Fig. 1.3.

The green emission is generated by a $d \rightarrow d$ optical transition on the Mn^{2+} ion with high spin d^5 electronic configuration (all electrons have their spin oriented in the same direction). The optical transition leading to emission is ${}^4T_{1g} \rightarrow {}^6A_{1g}$. The electronic configurations in the ground and excited state are $(t_{2g})^3 (e_g)^2$ and $(t_{2g})^4 (e_g)^1$, respectively. The emission generated reflects how the optical properties of the ion depend on its chemical environment. This luminescent material can be applied as green phosphor in very high-quality fluorescent lamps and also in plasma display

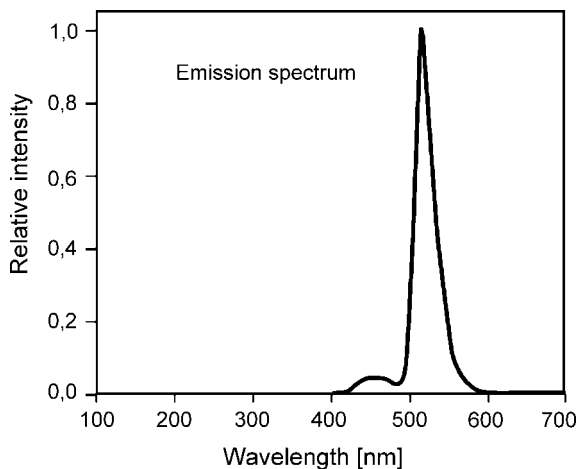


Fig. 1.3 Mn^{2+} emission in $BaMgAl_{10}O_{17}$:Eu,Mn.

panels. Its quantum efficiency is very high (90 %), and it shows a very good absorption at 254 nm, the absorption taking place on the Eu^{2+} ion, followed by energy transfer to Mn^{2+} . This process is elucidated further below. The composition without Mn^{2+} shows efficient blue Eu^{2+} emission; this emission is responsible for the shoulder at 450 nm and is used as blue emitting phosphor in high-quality fluorescent lamps. The emission stems from the optically allowed $5d-4f$ transition on Eu^{2+} , which is consequently very fast (decay time about 1 μs). $\text{Sr}_5(\text{PO}_4)_3\text{Cl}:\text{Eu}$ shows virtually the same emission band, and is used in high-quality fluorescent lamps as well.

An example of $d \rightarrow d$ emission, consisting of a few relatively sharp bands, is the emission of Mn^{4+} in $\text{Mg}_4\text{GeO}_{5.5}\text{F}:\text{Mn}$ (see Fig. 1.4). Please note that the emitting ion is the same; only its charge (and therefore its electronic configuration) is different. In this case, the optical transition consists of a spin-flip transition within the t_{2g}^3 manifold (${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition), i.e. hardly changing the character of the bonding. This manifests itself in relatively narrow emission bands. The spectral structure encountered reflects electron-phonon coupling: the electronic states are coupled to lattice vibrations, which slightly modifies the optical transition energies. This phosphor can be used as red primary in fluorescent lamps. It enables the reproduction of deep red colors. Also in this case, the emission process involves energy transfer. Here, the lattice absorbs the energy, followed by energy transfer to the emitting Mn^{4+} ions. This phosphor is one of the few phosphors applied which are sensitized by the host lattice absorption.

The $d-d$ optical transitions, discussed above, are spin and parity forbidden and consequently rather slow (decay time in the order of ms).

Most rare earth ions show sharp emission bands due to optical transitions within the f -manifold, e.g., Tb^{3+} ($4f^8$ -configuration) and Eu^{3+} ($4f^6$ -configuration). See Figs. 1.5 and 1.6 in which the emission spectra of $(\text{Ce},\text{Tb})\text{MgAl}_{11}\text{O}_{19}$ and $\text{Y}_2\text{O}_3:\text{Eu}$ are reproduced. Both phosphors are applied in high-quality fluorescent lamps, and $\text{Y}_2\text{O}_3:\text{Eu}$ is also used in projection television based on cathode ray tubes. In such

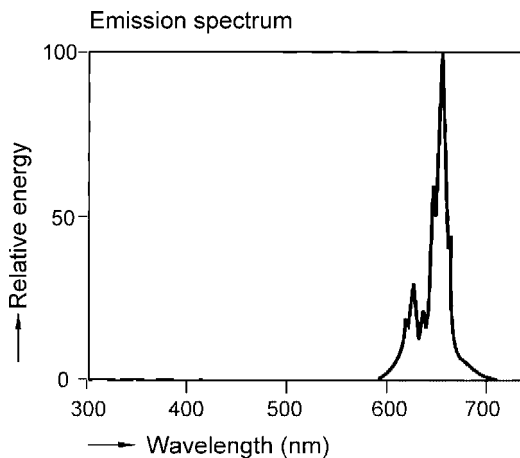


Fig. 1.4 Mn^{4+} emission in $\text{Mg}_4\text{GeO}_{5.5}\text{F}$.

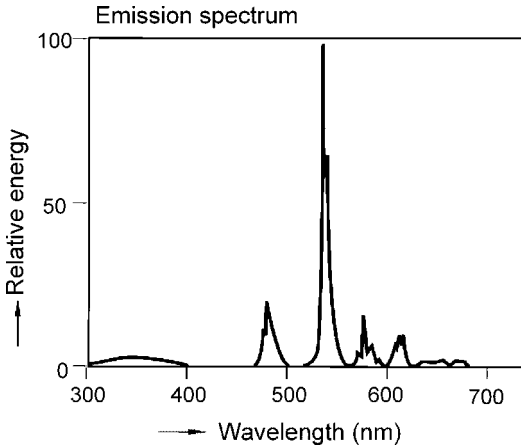


Fig. 1.5 Emission spectrum of $(\text{Ce,Tb})\text{MgAl}_{11}\text{O}_{19}$.

projection televisions, small cathode ray tubes are used, the images of which are projected onto a large screen.

There are a few green Tb^{3+} based phosphors suitable for application in fluorescent lamps (see Table 1.2).

Especially Eu_2O_3 is rather expensive, but despite intensive research, no less expensive substitute for $\text{Y}_2\text{O}_3:\text{Eu}$ with the same properties has been found, leaving it the only red primary applied with line emission at about 611 nm.

Width and position of the emission bands originating from optical transitions within the f-electronic shell are almost independent of the chemical environment. The relative intensity of the separate bands, however, depends on the crystal lattice. The transitions on many rare-earth ions are spin and parity forbidden and therefore

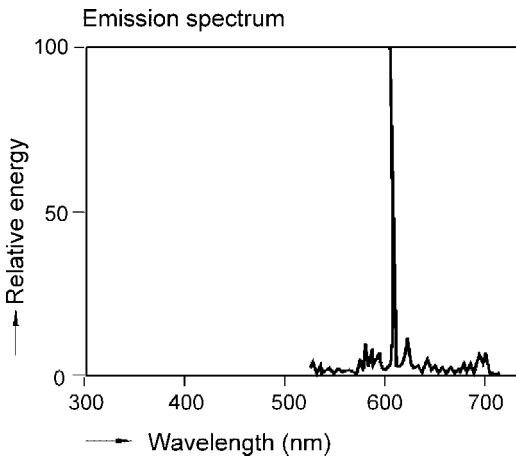


Fig. 1.6 Emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}$.

rather slow (in the ms range). However, for a number of rare-earth ions, broad emission bands are also known, due to $d \rightarrow f$ emission, e.g., Eu^{2+} ($4f^7$ -configuration) or Ce^{3+} ($4f^1$ -configuration). These transitions are allowed and consequently very fast (in the μs range or even faster).

Quite a few very important commercial phosphors are based on rare-earth ions. Rare-earth based phosphors are frequently applied in very demanding applications.

1.4.2

Charge Transfer Luminescence

In the case of charge transfer, the optical transition takes place between different kinds of orbitals or between electronic states of different ions. Such an excitation very strongly changes the charge distribution on the optical center, and consequently the chemical bonding also changes considerably. In these cases, therefore, very broad emission spectra are expected.

A very well-known example is CaWO_4 , used for decades for the detection of X-rays, which shows luminescence originating from the $(\text{WO}_4)^{2-}$ group (see Fig. 1.7). A similar compound, also showing blue emission, was used in early generations of fluorescent lamps: MgWO_4 . The transition involves charge transfer from oxygen ions to empty d-levels of the tungsten ion.

In this material no intentional dopant is introduced, and for this reason it is also called self-activated.

1.4.3

Donor Acceptor Pair Luminescence

This luminescence mechanism is found in some semi-conducting materials doped with both donors and acceptors. The mechanism is depicted in Fig. 1.8, in which

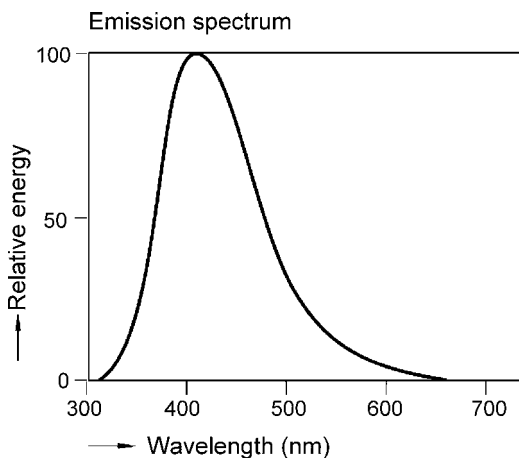


Fig. 1.7 Emission spectrum of CaWO_4 .

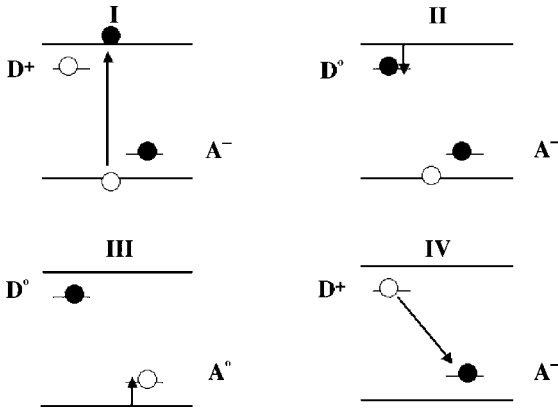


Fig. 1.8 Processes leading to donor-acceptor pair luminescence.

step 4 results in luminescence. Electrons that are excited into the conduction band are captured by ionized donors, and the resulting holes in the valence band are captured by ionized acceptors. The emission involves electron transfer between neutral donors and neutral acceptors. The final state (with ionized donors and acceptors) is Coulomb stabilized. Therefore, the spectral position of the emission generated on a donor-acceptor pair depends on the distance between the donor and the acceptor in a pair: the smaller the distance, the higher the energy of the photon generated.

The energies involved in these processes are:

1. The absorption of energy with the band gap energy, energy involved:

$$-E_g \quad (2)$$

2. Neutralization of the ionized donor, energy involved:

$$E_D - e^2/(4\pi\epsilon_0\epsilon R) \quad (3)$$

in which R is the distance between donor and acceptor involved in the emission process. The Coulomb term originates from the electrostatic interaction between ionized donor and acceptor.

3. Neutralization of the ionized acceptor, energy involved:

$$E_A \quad (4)$$

4. The luminescence process, energy involved:

$$E_g - (E_A + E_D) + e^2/(4\pi\epsilon_0\epsilon R) \quad (5)$$

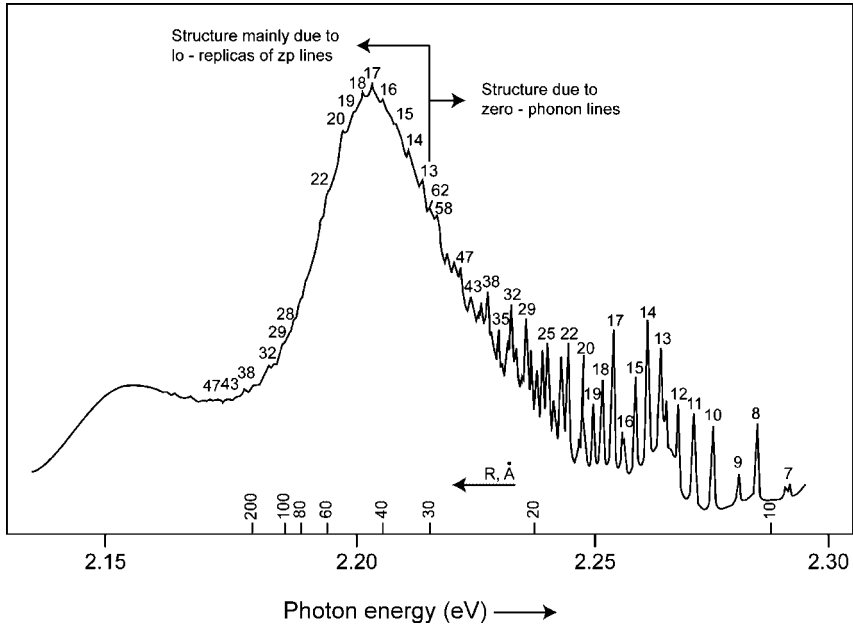


Fig. 1.9 Donor-acceptor pair luminescence of GaP doped with ZnS.
From A. T. Vink, thesis, Technical University Eindhoven, 1974.

In the phosphor crystal lattice, many different donor-acceptor distances are possible, but they are restricted by the ionic positions in the lattice. When the interaction of the excited state with the lattice is small, a spectrum with many sharp emission lines occurs. See Fig. 1.9, which shows the emission of GaP doped with ZnS. The numbers in the spectra indicate the donor-acceptor distances (the distance increasing with increasing number associated to the lines). The structure in the right hand part of the spectrum is due to zero-phonon lines, i.e. the emission takes place between the completely relaxed ground and excited state. The structure in the left hand part of the spectrum is due to coupling to host lattice vibrational modes, in this case longitudinal optical phonons.

At larger distances (lower energies), the energy separation between the emission of each of the individual donor-acceptor pairs decreases; as a result, at lower energy a broad emission band is found. The width of the emission band in the case of small interaction with the lattice is given by the Coulomb term. Whether the donor-acceptor mechanism is operative can be deduced easily by a number of techniques:

- Measuring the temporal evolution of the luminescence signal.
No single exponential decay is expected, as pairs at larger distance will show a smaller radiative recombination rate. For this reason, the decay gets slower as a function of time accompanied by a red shift of the emission spectrum.
- Increasing the excitation density will result in a blue shift of the emission spectrum. This is a consequence of the fact that

emissions at short donor-acceptor pair distances, which have the highest photon energy, have the shortest decay time. The more distant pairs decay much more slowly than the pairs at short distances. Consequently, the more distant pairs saturate, i.e. contribute less to the emission, which rationalizes the blue shift.

This mechanism is operative in the blue and green emitting phosphors, which are used in color television picture tubes (ZnS:Ag,Cl and ZnS:Cu,Au,Al , respectively). In these materials, broad emission bands are found, which are due to a strong electron-phonon coupling of the electronic defect states to vibronic lattice states (see Fig. 1.10).

1.4.4

Long Afterglow Phosphors

In long afterglow phosphors, optical excitation energy is stored in the lattice by trapping of photo excited charge carriers. The most prominent example is $\text{SrAl}_2\text{O}_4:\text{Eu,Dy}$: after optical excitation of Eu^{2+} , Eu^{2+} is oxidized to Eu^{3+} and Dy^{3+} is reduced to Dy^{2+} . Thermal excitation of Dy^{2+} to Dy^{3+} , followed by capture of the electron by Eu^{3+} and subsequent Eu^{2+} emission, results in time-delayed Eu^{2+} emission. The thermal excitation process of Dy^{2+} determines the time delay. This particular material still generates visible emission after several hours in the dark.

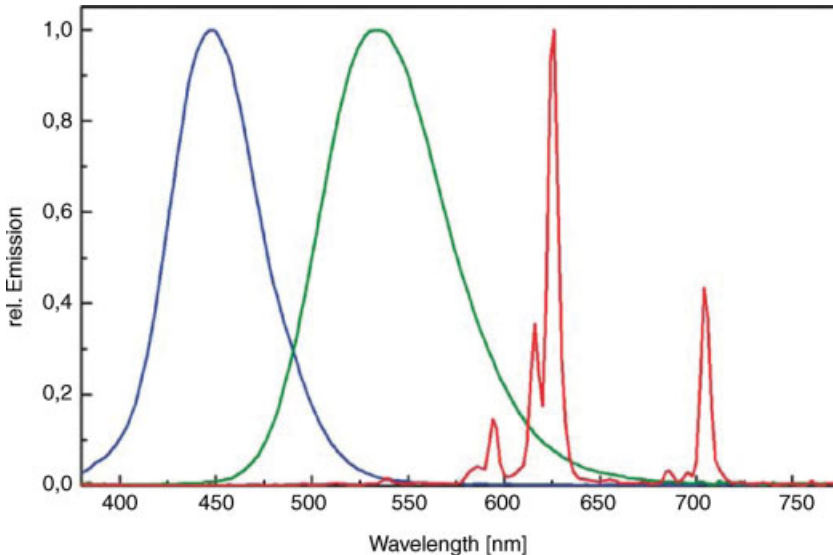


Fig. 1.10 Emission spectra of ZnS:Ag,Cl (blue-emitting phosphor), ZnS:Cu,Au,Al (green-emitting phosphor), and $\text{Y}_2\text{O}_2\text{S:Eu}$ (red-emitting phosphor). The emission of the ZnS phosphors mentioned is of the donor-acceptor pair emission type.

The same mechanism also leads to (undesired) afterglow in scintillating materials, e.g., in $\text{Gd}_2\text{O}_2\text{S}:\text{Pr,Ce}$, which is used in Computer Tomography (CT) equipment.

Long afterglow phosphors can be used in watch fingers, but also in safety applications, e.g., in exit signs which still operate in case of a current blackout. Other long afterglow materials are, e.g., $\text{ZnS}:\text{Cu}$ and $\text{SrS}:\text{Bi}$.

When the energy involved in reversing the trapping process thermally is too high, IR-light absorption might be used to generate visible luminescence. This is the mechanism underlying the use of $\text{BaFBr}:\text{Eu}$ as X-ray phosphor, as will be discussed in the chapter on scintillators.

1.5 Excitation Mechanisms

1.5.1 Optical Excitation of Luminescence and Energy Transfer

When absorption of UV or even visible light leads to emission, one speaks of optical excitation of luminescence. This process takes place in, e.g., fluorescent lamps and phosphor-converted LEDs, in which phosphors are used to at least partly change the wavelength of the radiation emitted by the LED. Optical absorption can take place on the already discussed impurities (optical centers), being either the activator ions or the sensitizer ions. Sensitizer ions are used when the optical absorption of the activator ions is too weak (e.g., because the optical transition is forbidden) to be useful in practical devices. In such a case, energy transfer from the sensitizer ions to the activator ions has to take place. The optical absorption leading to emission can also take place by the host lattice itself (band absorption). In this case one speaks of host lattice sensitization. Energy transfer from host lattice states to the activator ions (in some cases also involving sensitizers) has to take place.

In the blue emitting luminescent material $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$, both the absorption and the emission processes originate from optical transitions between the 4f and 5d levels of the Eu^{2+} ion. As the transition leading to optical absorption is allowed, a relatively small Eu^{2+} concentration (10 % of the Ba^{2+} ions are replaced by Eu^{2+} ions) is sufficient to adjust a sufficiently strong absorption in practical devices. The excitation spectrum of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$ is given in Fig. 1.11.

One observes a strong broad absorption spectrum in the UV part of the spectrum as the excited 5d state of the Eu^{2+} ion is split by ligand field interaction with the oxygen ions surrounding it. In addition, one observes that the absorption extends into the near UV/blue part of the optical spectrum; this makes this material also suitable for application with near UV LEDs. Phosphors for LEDs are treated in a dedicated chapter in this book.

The excitation spectrum of the Mn^{2+} spectrum in $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu,Mn}$ is, in the UV, very similar to the excitation spectrum of the compound without Mn^{2+} . Here we encounter an example of Eu^{2+} -sensitized emission of Mn^{2+} , as proven by the similarity of the excitation spectrum of both the Eu^{2+} and the Mn^{2+} emission. The very localized excitation (exciton) of Eu^{2+} is transferred to the Mn^{2+} ion. The

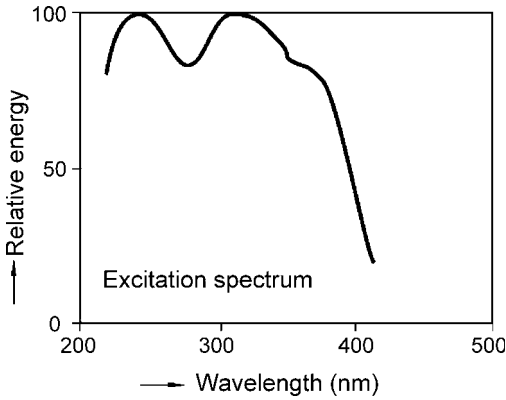


Fig. 1.11 Excitation spectrum of the Eu^{2+} emission in $\text{BaMgAl}_{10}\text{O}_{17}$.

energy transfer process might involve more than only one Eu^{2+} ion. The energy transfer proceeds via the Eu^{2+} sub lattice and does not involve charge transport; the underlying mechanism relies on exciton diffusion.

Mn^{2+} emission can also be sensitized by other ions like Sb^{3+} in the well-known white emitting material $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl}):\text{Sb},\text{Mn}$. Here, orange emission is generated by Mn^{2+} and blue emission by the Sb^{3+} . This material is applied widely in fluorescent lamps. The emission of this material is perceived as white. Its emission spectrum is given in Fig. 1.12.

Please note that the emission spectrum depends on the Sb^{3+} and Mn^{2+} concentrations. By adjusting these concentrations, the color temperature of the emission can be varied.

Another well-known sensitizer-activator pair is the $\text{Ce}^{3+} - \text{Tb}^{3+}$ couple (see Fig. 1.5 and Table 1.4 below). All green emitting phosphors applied in high-quality fluorescent lamps are based on this combination.

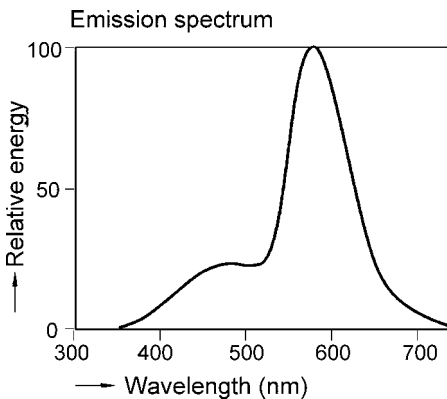


Fig. 1.12 Emission spectrum of $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl}):\text{Sb},\text{Mn}$.

1.6 Energy Transfer Mechanisms Between Optical Centers

Energy transfer between a sensitizer ion (S) and an activator ion (A) can be written as a chemical reaction:



where the asterisk indicates the excited state.

We remark that sensitization can involve even more ions, as in (Ce,Gd,Tb)Mg-B₅O₁₀:Mn (a green and red emitting luminescent material applied in fluorescent lamps with a very high color rendering), where the energy is transferred from the Ce³⁺ ions to the Tb³⁺ and the Mn²⁺ ions via the Gd³⁺ ion sub lattice. The emission spectrum is given in Fig. 1.13. We observe green Tb³⁺ emission, red Mn²⁺ emission, and a trace of Ce³⁺ emission in the UV, indicating that the energy transfer efficiency is almost completely unity.

1.6.1 Mechanisms Underlying Energy Transfer

For energy transfer, the sensitizer ion and the activator ion have to show physical interaction. This energy transfer can find its origin in electrostatic and exchange interaction. In addition, the emission spectrum of the sensitizer ion and the absorption spectrum of the activator ion have to show spectral overlap, for energy conservation reasons.

The probability W_{et} for energy transfer is given by the following term:

$$W_{et} = 2\pi/\hbar(\rho)[\varphi_i|H|\varphi_f]^2 \quad (7)$$

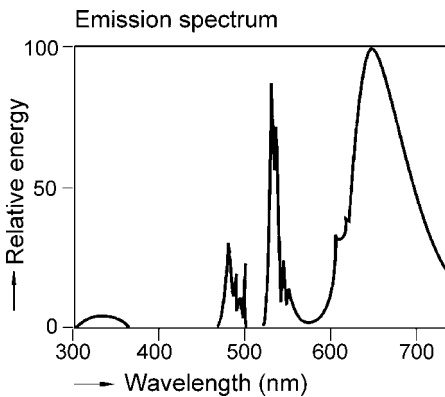


Fig. 1.13 Emission spectrum of (Ce,Gd,Tb)(Mg,Mn) B₅O₁₀.

In this term, φ_i is the wave function of the initial state, φ_f is the wave function of the final state, ρ is a measure for the density of initial and final states capable of interaction, and H is the operator coupling the initial and final state. ρ is given by

$$\rho = \int g_s(E)g_A(E)dE \quad (8)$$

representing the spectral overlap between sensitizer and activator ions. $g_s(E)$ and $g_A(E)$ are the normalized optical line shape functions for the sensitizer and the activator ions, respectively.

In this treatment we distinguish between two kinds of interactions: electrostatic interaction given by H_c and exchange interaction described by H_e . The probability per unit time for energy transfer then can be written as

$$W_{et} = 2\pi/\hbar(\rho)\{[\varphi(S^*)\varphi(A)|H_c|\varphi(S)\varphi(A^*)]^2 + [\varphi(S^*)\varphi(A)|H_e|\varphi(S)\varphi(A^*)]^2\} \quad (9)$$

The matrix elements for Coulomb interaction represent the repulsive electrostatic interaction between the electronic charge distributions in the initial and final state, respectively, and have the following shape:

$$Q_i^C = \varphi_{s^*}(1)\varphi_A(2) \text{ and } Q_f^C = \varphi_s(1)\varphi_{A^*}(2) \quad (10)$$

The matrix elements for exchange interaction represent the repulsive electronic interaction of the electronic charge distributions, and have the following shape:

$$Q_i^e = \varphi_{s^*}(1)\varphi_A(2) \text{ and } Q_f^e = \varphi_s(2)\varphi_{A^*}(1) \quad (11)$$

In Fig. 1.14, electronic energy transfer by Coulomb and exchange interaction are compared. In the case of Coulomb interaction, the electrons initially on the excited donor stay there, and the electrons initially on the acceptor also remain there. This interaction does not require physical contact between the interacting partners; it is sufficient that the excited sensitizer ion induces a dipole oscillation on the activator ion. In the case of energy transfer governed by exchange interaction, the way the energy is transferred can be visualized by a double electron substitution reaction: the excited electron on S^* travels to A, whereas one electron on A goes to S. This type of interaction requires overlap of the electronic charge distribution, i.e. physical contact between the sensitizer ion and the activator ion.

1.6.2

Energy Transfer Governed by Electrostatic Interaction

In this section, we discuss, using a simple model, the factors governing the magnitude of the electrostatic interaction and how they relate to the rate of energy transfer.

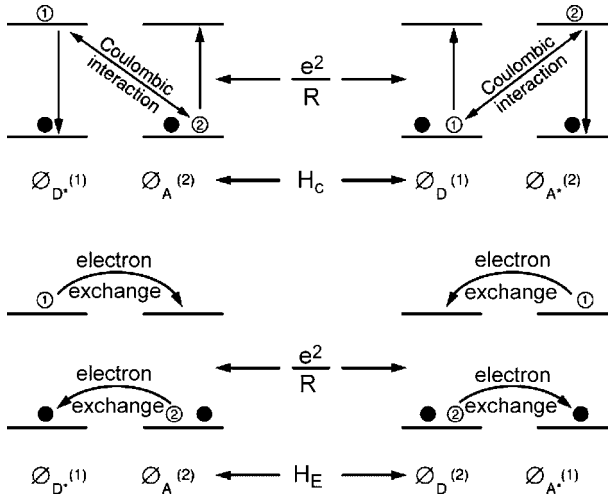


Fig. 1.14 Visualization of energy transfer by Coulomb interaction (a) and exchange interaction (b) between two ions.

The interaction energy E_{SA} between two dipoles is given by the magnitude of the two dipoles (μ_S and μ_A , respectively) and the distance R_{SA} between them:

$$E_{SA} \propto \mu_S \mu_A / R_{SA}^3 \quad (12)$$

Förster [1–3] has identified μ_S and μ_A , respectively, with the oscillator strength for the radiative transitions $S^* \leftrightarrow S$ and $A^* \leftrightarrow A$, respectively. We will now treat energy transfer more quantitatively.

The power irradiated by an oscillating dipole $\mu \cos \omega t$ is given by

$$P = 4\omega |\mu|^2 / 3c^3 \quad (13)$$

The result obtained is a factor of 4 larger than in classical electrodynamics, to differentiate between photons absorbed and emitted.

The rate of decay A is given by Eq. (14) (energy emitted per unit time divided by the photon energy $\hbar\omega$):

$$A = 1/\tau_0 = (4\omega |\mu|^2 / (3c^3)) / (\hbar\omega) \quad (14)$$

in which τ_0 is the radiative lifetime.

We obtain for $|\mu|^2$:

$$|\mu|^2 = 3hc^3 / (8\pi\omega^3 \tau_0) \quad (15)$$

The oscillator strength for an optical transition is related to $|\mu|^2$ in the following way:

$$f = 2m\omega|\mu|^2/(3\hbar e^2) \quad (16)$$

$|\mu|^2$ is thus given by

$$|\mu|^2 = (3\hbar e^2)f/(2m\omega) \quad (17)$$

Apart from some numbers we are now able to calculate the rate of energy transfer from sensitizer ions to activator ions, being the product of equation (14) for the sensitizer and (17) for the activator ion divided by the distance R_{SA}^6 (see above, the transition rate contains the matrix element for the energy squared):

$$W_{SA} \propto 3\hbar c^3/(8\pi\omega^3\tau_{0S})(3\hbar e^2)f_A/(2m\omega R_{SA}^6) \quad (18)$$

Or, after some rearrangements and inclusion of the numbers mentioned above (which partly originate from the expansion of the interaction Hamiltonian in spherical harmonics), the following equation is obtained [4]:

$$W_{SA} = 2\pi/\hbar/R_{SA}^6 \cdot 3e^2c^3\hbar^6/4m \cdot f_A/\tau_S \cdot \eta \cdot \int g_S(E)g_A(E)/E^4 dE \quad (19)$$

In this equation, τ_S is the decay time of the sensitizer ion and η is the quantum efficiency of the sensitizer ion.

Equation (19) can also be written as:

$$W_{SA} = 1/\tau_S \cdot (R_0/R_{SA})^6 \quad (20)$$

where R_0 is the distance at which the transfer rate to the activator is equal to the decay rate of the sensitizer and is given by:

$$R_0^6 = \eta f_A (3e^2c^3\hbar^5\pi/2m) \int g_S(E)g_A(E)/E^4 \cdot dE \quad (21)$$

Inspection of the equations derived shows that energy transfer, governed by Coulomb interaction, is favored by a large spectral overlap, a small value of the intrinsic decay time of the sensitizer ion, a large absorption strength of the activator ion, and a small distance between the sensitizer and activator ion.

In practice, it is of more importance to determine the efficiency of the energy transfer process than the rate.

The decay of the sensitizer ion is given by:

$$1/\tau_S = 1/\tau_0 + 1/\tau_S \cdot R_0^6/R_{SA}^6 \quad (22)$$

The yield η_{SA} for energy transfer is therefore given by:

$$\eta_{SA} = 1/\tau_S \cdot R_0^6/R_{SA}^6/(1/\tau_S) \quad (23)$$

the energy transferred per unit time divided by the total amount of energy emitted per unit time.

For the efficiency of the energy transfer process η_{SA} , we therefore find the following proportionality:

$$\eta_{SA} = (R_0/R_{SA})^6 \quad (24)$$

Please note that the quantum efficiency of the sensitizer ion is contained in R_0 [see Eq. (21)]. For a distance R_{SA} between the sensitizer ion and the activator ion smaller than R_0 , energy transfer will dominate; in the opposite case, inherent decay of the sensitising ion S^* is the most important process. Moreover, though the energy transfer rate increases with decreasing τ_S , the same applies to the sensitizer emission probability. Therefore, the transfer yield is independent of τ_S .

1.6.3

Energy Transfer by Higher-order Coulomb Interaction

Apart from dipolar interaction, higher-order interaction may also result in energy transfer. In Table 1.1, the distance dependence of interaction involving dipoles and quadrupoles is summarized for the case that the optical transitions involved are spin allowed:

A more quantitative analysis, using the expressions derived above, shows that in the case of electric dipole interaction:

- Energy transfer from a broad-band emitter to a line absorber only occurs between nearest neighbors.
- Energy transfer from a line emitter to a broad-band absorber is possible for distances up to about 2 nm.
- Energy transfer from a broad-band emitter to a broad-band absorber is possible for distances as large as about 3.5 nm.
- Dipole-dipole interactions and dipole-quadrupole interactions can result in energy transfer in solids: both interactions can take place over metal ion–metal ion distances which are observed in solids.
- Interactions between electric quadrupoles are not expected to play an important role in solids in view of the very short interaction range.

Tab. 1.1 Equations for energy transfer governed by Coulomb interaction as a function of the type of interaction for spin-allowed transitions.

Interaction type	Equation form	Range (nm)
Electric dipole – electric dipole	$W_{SA} = (1/\tau_S) (R_0/R_{SA})^6$	3.5
Electric dipole – electric quadrupole	$W_{SA} = (1/\tau_S) (R_0/R_{SA})^8$	0.8
Electric quadrupole – electric quadrupole	$W_{SA} = (1/\tau_S) (R_0/R_{SA})^{10}$	0.2

1.6.4

Energy Transfer Governed by Exchange Interactions

Dexter has formulated a theory describing energy transfer by exchange interaction [5]. The rate constant for energy transfer is written as

$$W_{SA} = KJ \exp(-2R_{SA}/L) \quad (25)$$

In equation (25), K is a constant determined by the interaction between the orbitals involved in the energy transfer process, J is determined by the spectral overlap integral, normalized for the absorption strength of the activator ion, and L is determined by the van der Waals radii of the interacting ions. The exponential dependence is due to the fact that the electron density in general falls off exponentially with the distance between the electron and the nucleus.

As the energy transfer process does not involve electric dipole interaction, no dependence of the magnitude of the electric dipoles on the sensitizer and activator ions is expected. In view of the relationship between the magnitude of the electric dipoles and the oscillator strength (see above), therefore, no relation between the oscillator strength of the optical transitions on sensitizer and activator ion is expected. In fact, for exchange interaction, there is no relation between the interaction between the ions and any spectroscopic characteristic of the sensitizer or activator ions.

Another difference between energy transfer governed by Coulomb and exchange interaction is the distance dependence. The rate of energy transfer shows an R_{SA}^{-n} dependence in the case of Coulomb interaction and an $\exp(-R_{SA}/L)$ dependence in the case of energy transfer by exchange interaction. In the case of energy transfer by exchange interaction, the rate drops very quickly for distances R_{SA} greater than about 1 nm.

Finally, exchange interaction, due to the requirement of wave function overlap, has a pronounced angular dependency and is also dependent on covalence.

1.6.5

Cross-relaxation and Energy Transfer

A phenomenon not discussed until now is cross-relaxation. In such a process, which can also be looked upon as energy transfer, the excited ion transfers only part of its energy to another ion. For two Tb^{3+} ions, the process is depicted in Fig. 1.15. In this case, the energy difference between the 5D_3 and 5D_4 excited states matches approximately the energy difference between the 7F_6 ground state and higher 7F_j states. As in the energy transfer processes discussed above, at large Tb-Tb distances, the process of cross-relaxation has a low rate. In many host lattices, therefore, at low Tb concentration, emission from both the 5D_3 and 5D_4 excited states is observed (unless the gap between these two states is bridged by phonon emission, for which relatively high-energy phonons are required, which is, for example, the case with $InBO_3:Tb$). The resulting emission spectrum has emission from the near UV into the red part of

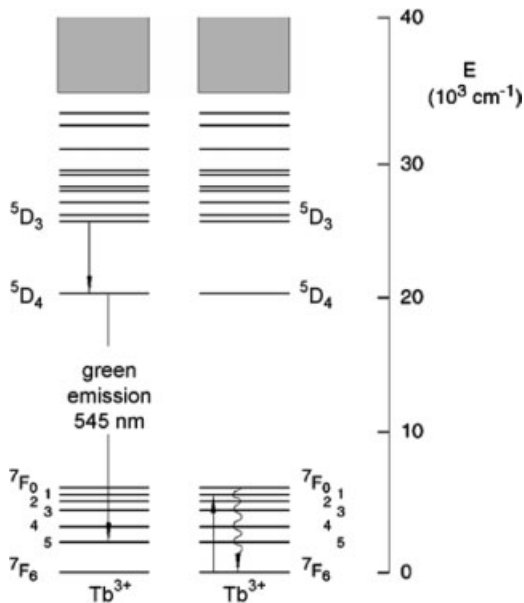


Fig. 1.15 Cross-relaxation between two Tb^{3+} ions.

the optical spectrum. At higher Tb concentrations (in the order of five percent), cross-relaxation quenches the emission from the ${}^5\text{D}_3$ level in favor of emission originating from the ${}^5\text{D}_4$ level, implying that it is not possible to obtain blue Tb^{3+} emission in luminescent materials with higher Tb^{3+} concentrations.

Cross-relaxation also occurs for other ions. It quenches blue Eu^{3+} emission even at relatively low Eu^{3+} concentrations (<1%) in favor of the well-known red emission. In case of ions like Sm^{3+} and Dy^{3+} , cross-relaxation leads to quenching of the visible emission. This seriously limits the applicability of these ions.

1.6.6

Practical Implications

Of course, the arguments developed above have practical implications. In general, the activator ions used in luminescent materials are rather expensive. This implies that the concentration of the activator ions should be as low as possible. When energy transfer processes are important, the smallest activator concentrations are possible for the case of broadband-emitting sensitizers and broadband-absorbing activators. On the other hand, for high-quality fluorescent lamps, line emitters are required to obtain an optimized adaptation of the emission spectrum to the human eye with respect to the amount of visible light generated and the need to reproduce all colors in a natural way. As discussed above, this requires that sensitizer ion and activator ion are nearest neighbors, i.e. at least one of the two kinds of ions should be present in relatively high concentrations.

When optical absorption on the activator ions is forbidden at the energy where the sensitizer ion emits (the activator ions, however, should have an excited state there), in principle there are nevertheless two options to obtain energy transfer:

- Coulomb interaction exploiting the quadrupole of the activator ion. This is the mechanism underlying the fluorescent lamp phosphors $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu},\text{Mn}$ [6] and $(\text{Ce},\text{Tb})\text{MgAl}_{11}\text{O}_{19}$ [7]. Because of the vanishingly small spectral overlap between the Ce^{3+} absorption and the emission bands, no energy migration between the Ce ions takes place. This requires not only short Ce-Tb distances in this luminescent material, but also relatively high Tb concentrations, to prevent Ce emission from occurring.
- Exchange interaction between sensitizer and activator ion. As shown above, this mechanism does not require allowed optical transitions. This is the mechanism which is operative in the one-component white fluorescent lamp phosphor $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{Cl}):\text{Sb},\text{Mn}$, as deduced from an analysis of the decay curve for some Mn^{2+} concentrations [8]. The same study did not reveal evidence for energy transfer between antimony ions, indicating the necessity of nearest neighbor Sb-Mn interaction, which is a prerequisite for energy transfer via exchange interaction. Please note, in addition, that in view of the large Stokes shift between absorption and emission on the Sb^{3+} ion in this lattice, no energy transfer between the antimony ions is expected.

Both for electric dipole – electric quadrupole and exchange interaction, the distance between sensitizer ion and activator ion has to be rather small, not larger than about 1 nm. This requires high activator and/or sensitizer ion concentrations, which is a disadvantage, considering the high costs of these materials.

1.7

Excitation with High-energy Particles

After absorption of electrons or high-energy photons (e.g., X-ray quanta) impinging on the phosphor material, primary electrons and holes in very deep shells are created. Whereas the holes are tightly bound, the electrons can move in the lattice (and a fraction of the electrons generated can leave the material). The primary ionization event is followed by radiative decay (secondary X-rays, the basis for EDAX), non-radiative decay (the generation of secondary electrons by Auger processes), and inelastic electron-electron scattering. These processes are very fast and occur typically in the 10^{-15} – 10^{-13} s regime after the primary absorption. During these processes, many electrons are excited.

When the energy of the electrons generated is lower than the ionization threshold, the hot electrons and holes thermalize by intraband transitions and electron-optical

phonon interaction. Also during this process, activator or sensitizer ions may be excited by impact excitation by hot electrons, by sequential excitation by capture of mobile charge carriers (electrons and holes), and by excitons. These processes typically occur in a time frame 10^{-12} – 10^{-8} s and may therefore lead to a clearly visible rise time of the emission.

In the last step, luminescence can occur in a time frame of 10^{-9} s for very fast allowed optical transitions up to ms or even longer times for forbidden transitions.

Robbins has treated these processes more quantitatively [9]. In this chapter, we only outline this excellent treatment. The more interested reader is referred to the original paper.

The energy efficiency of the overall process is given by

$$\eta = (1 - r)[h\nu]/(\beta E_g) \cdot \eta_t \eta_{act} \eta_{esc} \quad (26)$$

in which r is the backscatter coefficient, expressing the fact that not all high-energy particles enter the material, $[h\nu]$ is the mean photon energy of the photons emitted, βE_g the energy needed to generate a thermalized electron-hole pair (β being a pure number and E_g being the band gap energy), η_t is the transfer efficiency of electron-hole pairs to activators or sensitizers, η_{act} is the quantum efficiency of the activator ions (which gives the ratio of the number of photons emitted divided by the number of photons absorbed), and finally η_{esc} is the ratio between photons leaving the material and photons generated in the material (escape probability).

Backscattering is negligible for X-rays, whereas for electrons the backscatter coefficient r generally has values between 0.1 and 0.2.

For applications, phosphors operating at physical limits are of interest only. This means that the transfer efficiency, the activator efficiency, and the escape probability have to be unity. Equation (26) then simplifies to

$$\eta = (1 - r)[h\nu]/\beta E_g \quad (27)$$

Inspection of this equation shows that the energy efficiency is determined by the mean energy of the photons emitted by the activator ions and by the product βE_g . The primary particles, eventually generating the luminescence, lose their energy by impact ionization and generation of optical phonons. In what follows, we discuss this mechanism in some more detail. It is important to note that the description boils down to calculating what fraction of the energy that impinges on the material is used to create electron-hole pairs with energy (almost) equal to the band gap energy. The energy might be slightly smaller than the band gap energy, as the electron and the hole can attract each other by Coulomb interaction. In such a case an exciton is formed. Further, the reader should carefully note that this treatment gives the maximum efficiencies only.

In Chapter 5, which deals with scintillating materials, we will use expression (27) in a slightly different form. In scintillator physics, the light yield is generally expressed in the units [photons/MeV of excitation energy]. Scintillating materials can generate more than 70 000 photons per MeV of excitation energy. For scintillators, the light

yield is more useful than the energy efficiency in view of the fact that photons are to be detected.

The average energy needed to create an electron-hole pair can be written as

$$\beta E_g = E_i + E_{op} + 2E_f \quad (28)$$

In this expression, E_i is the ionization threshold, E_{op} the average energy lost in generating optical phonons, and E_f is the threshold energy for the generation of electron-hole pairs.

The ratio of the energy needed to generate optical phonons with frequency $\hbar\omega_{LO}$ and impact ionization is proportional to R , which in turn is given by

$$R = (1/\varepsilon_\infty - 1/\varepsilon_0)(\hbar\omega_{LO})^{1.5}/(1.5 E_g) \quad (29)$$

in which ε_∞ and ε_0 are the optical and static dielectric constants of the phosphor host lattice, respectively. The dependence of β on R is given in Fig. 1.16, in which a slightly different notation for the expression dealing with the dielectric constants is used.

The value of β is found to vary between about 2.5 and 10 for a number of host lattices. We observe that in order to obtain host lattices with small β , resulting in highly efficient phosphors, the value of R should be small as well. This condition implies a low optical phonon frequency or a small difference between the optical and the static dielectric constant. In Table 1.2, the relevant data are given for a number of well-known phosphor materials. We observe a good agreement between the energy efficiencies observed and the maximum efficiencies predicted.

Please note that this treatment deals with host lattice properties only, i.e. it is the host lattice properties which decide whether the impinging energy is efficiently converted into energy gap excitations. This is in line with observations: quite a few host lattices show efficient cathode rays from X-ray excited luminescence when doped with different activators. Examples are ZnS, CaS (see Table 1.2) and the rare

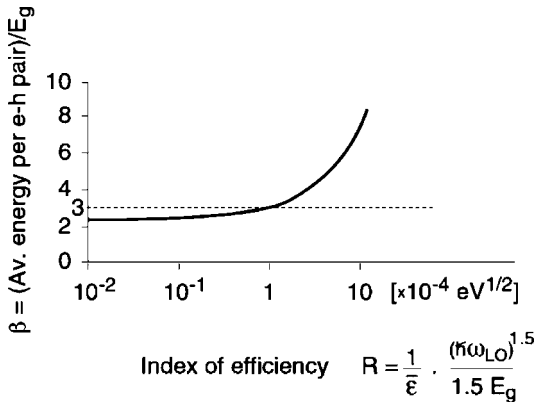


Fig. 1.16 Dependence of β on R .

Tab. 1.2 Physical constants of a number of efficient host lattice-excited phosphors. η_{the} is the maximum efficiency calculated, η_{exp} is the energy efficiency observed experimentally.

Phosphor	$\hbar\omega_{\text{LO}}$ (eV)	E_g (eV)	$[\hbar\nu]$ (eV)	β	η_{the}	η_{exp}
CsI:Tl	0.011	6.4	2.25	2.5	0.14	0.14
ZnS:Ag	0.044	3.8	2.75	2.9	0.25	0.20
ZnS:Cu	0.044	3.8	2.3	2.9	0.21	0.17
CaS:Ce	0.047	4.8	2.3	3.0	0.16	0.22
CaS:Mn	0.047	4.8	2.1	3.0	0.15	0.16
La ₂ O ₂ S:Eu	0.057	4.4	2.0	3.9	0.12	0.11
Y ₂ O ₃ :Eu	0.068	5.6	2.0	4.6	0.07	0.08
YVO ₄ :Eu	0.116	3.7	2.0	7.5	0.07	0.07

earth oxysulfides (like Gd₂O₂S, which shows efficient emission when doped with Pr³⁺, Eu³⁺ or Tb³⁺).

The mechanism discussed above involves efficient energy transfer from host lattice states to localized states. This mechanism also occurs in some luminescent materials applied in Xe-discharges. The Xe-discharge generates radiation in the VUV part of the spectrum. In these materials, the host lattice itself acts as sensitizer.

We remark that an alternative description for the generation of electron-hole pair generation has been formulated [10]. In this model, β can be much smaller than the values derived by Robbins (close to unity and virtually material independent). In this model, transfer from host to activator ions is the energy efficiency determining step. Interesting feature of this model is that also ionic materials could have very high photon yields.

1.8 Electroluminescence (EL)

1.8.1 High-voltage Electroluminescence

High-voltage electroluminescence relies on an electrical breakthrough in a semi-conducting material, which rationalizes the necessity to use rather high voltages. Generally speaking, the lifetime of such electroluminescent devices can be long but the efficiencies are rather low (in the order of one percent, see below) and consequently applications are found in segments where reliability is an issue and efficiency considerations are not very important (emergency signs, exit signs, and interestingly ceiling illumination in the Maybach premium car). Prominent materials are ZnS:Mn, ZnS:Cu, and SrS:Ce, although oxides are under investigation as well.

The luminescent materials are used in thin layers (in the order of 1 μm) generated by techniques like atomic- or molecular beam epitaxy, although powder EL is also known. The materials are subjected to high electric fields, and electrons are accelerated in the materials. The electrons excite the activator ions by impact excitation. At present, there is no general picture of the mechanism(s) underlying high-voltage electroluminescence.

We will give a very elementary treatment, which yields the energy efficiency to be expected, without considering the mechanism(s) in detail.

The maximum efficiency η is given by:

$$\eta = E_{\text{em}}\sigma N/eF \quad (30)$$

in which E_{em} is the photon energy of the emitted radiation, σ the cross-section for impact excitation, N the optimum concentration of luminescent centers, and F the electric field applied. Dimensional analysis shows that $(\sigma N)^{-1}$ has the units [m]. The physical meaning of $(\sigma N)^{-1}$ is the mean distance that an electron travels through the luminescent material between two excitation events.

The cross-section is not known *a priori*. In the case of ZnS:Mn (the most efficient ACTFEL material known), we approximate it by using atomic dimensions, i.e. $\sigma = 10^{-16} \text{ cm}^2$ (the Mn^{2+} ions has the same charge and approximately the same size as the Zn^{2+} ion). The other typical values are: $E_{\text{em}} = 2 \text{ eV}$, $N = 10^{20} \text{ cm}^{-3}$ and $F = 10^6 \text{ V cm}^{-1}$. It follows that the energy efficiency equals about 2 %, which is in very good agreement with experiment. In this treatment, however, we have used a number of simplifications. We did not account for the Stokes shift. Moreover, we neglected light-trapping effects in the thin layers. All these phenomena further reduce the energy efficiency. However, the energy efficiency is not likely to be improved significantly. This is mainly because of the low value for the cross-section, because N cannot be chosen to be too large in view of concentration quenching.

The mean energy that the charge carrier has taken up from the electric field between two impact excitation events equals $eF/\sigma N$, neglecting any losses due to phonon emission. The minimum pathway that an electron has to travel to be able to excite an activator ion L_{crit} equals $L_{\text{crit}} = E_{\text{exc}}/eF$, where E_{exc} is the energy needed for the excitation of the luminescence. Please note that L_{crit} is dependent on the electric field strength. Incorporation of L_{crit} in Eq. (30) yields

$$\eta = E_{\text{em}}/E_{\text{exc}} \cdot \sigma N \cdot L_{\text{crit}} \quad (31)$$

In the case of excitation of luminescence via host-lattice states (see above), the luminescence efficiency can be written very generally as

$$\eta = E_{\text{em}}/E_{\text{exc}} \cdot \eta_t \cdot \eta_{\text{act}} \cdot \eta_{\text{esc}} \quad (32)$$

In this expression η_t is the probability of energy transfer from the host lattice to the activator ions, η_{act} is the quantum efficiency of the activator, and finally η_{esc} is the escape probability – the ratio between the number of photons leaving the material and the number of photons generated in the material. On assuming η_{act} and η_{esc} to be unity, the maximum energy efficiency for the ACTFEL process is given by:

$$\eta = E_{\text{em}}/E_{\text{exc}} \cdot \eta_t \quad (33)$$

Inspection of Eqs. (31) and (33) leads to the conclusion that $\sigma N \cdot L_{\text{crit}}$ is the transfer efficiency. In case of cathode ray excitation, this figure can be unity. In case of

ZnS:Mn, its optimal value is calculated to be about 0.02 only. The low transfer efficiency of energy from host lattice states to activator states is the main reason for the low energy efficiency of this material, but still it is the most efficient one known! Please note that this equation shows that the maximum efficiency of EL phosphors is determined by both host-lattice and dopant properties.

1.8.2

Low-voltage Electroluminescence

The advent of the blue light-emitting diode (LED) and of organic electroluminescent structures has strongly revitalized interest in this luminescence mechanism. For the first time, efficient light-emitting structures can be realized which do not require either high or low pressure. In addition, luminescent devices have always hitherto used a cascade – in fluorescent lamps, first a discharge is generated and the resulting invisible radiation is converted into visible light, resulting in a (considerable) energy loss. In cathode ray tubes, first an electron beam consisting of electrons with rather high kinetic energy is generated, which subsequently impinges on the luminescent material. In the phosphors, electron bombardment finally leads to excitations where electrons in the conduction band are coupled to holes in the valence band (excitons). These excitons are transferred to activator ions. As a result, there are no white light-emitting devices with energy efficiency greater than 50%. Low-voltage electroluminescent devices might be a way out here. In such devices, the step leading to emission is the recombination of electrons in conduction band states with holes in valence band states, and in principle only the band gap energy is required to excite the luminescence. Within limits, the color of the emission can be selected by choosing the appropriate semiconductor. The generation of luminescence can be very energy efficient; the main issue is getting the light out of the emitting device. LEDs are available with wall plug efficiency approaching 70%.

Apart from efficiency, the power dissipated by LEDs is also an important driver, as it contributes to the light output that such a device can generate. Lighting applications generally require a light output of 1 W and above. LEDs with input power of 30 W and external energy efficiency of about 10% have been demonstrated by the Japanese company Nichia and Philips Lumileds.

In this book, luminescent materials that can be used in inorganic low-voltage electroluminescent devices are discussed in a separate chapter. Phosphors are used for two reasons:

- Inorganic LEDs generally generate narrow line emission. Combination of LEDs emitting in different spectra regions to generate white light therefore results in white light of low quality: it cannot reproduce all colors in a natural way.
- Efficient LEDs are not yet available in all colors required. Especially green is a concern.

Phosphors for LEDs have to fulfill rather harsh conditions. The Stokes shift must be small, the absorption must be high, and, in addition, as the excitation densities are

in the order of 20 W cm^{-2} (the area which emits light is much smaller than, e.g., in fluorescent lamps), the luminescent materials must remain efficient up to high temperatures, should not show saturation (meaning a less than linear increase in output power with input power at high excitation densities), and must be radiation stable.

1.9 Factors Determining the Emission Color

Many luminescent ions show emission at different wavelengths in different host lattices. This phenomenon, once understood, opens up the possibility to change, within certain limits, the emission color. In this way, the emission spectra (and excitation spectra) can be tuned toward the specifications required.

In cases where at least one of the electronic states is involved in the chemical bonding, the coupling to the lattice has to be taken into account. This situation is encountered for many transition metal ions, for the s^2 ions, and for rare-earth ions showing $d \rightarrow f$ emission.

In Fig. 1.17, this situation is illustrated for $d \rightarrow f$ optical transition on Eu^{2+} .

Other rare-earth ions showing $d \rightarrow f$ emission are Ce^{3+} , Pr^{3+} , Nd^{3+} and Er^{3+} , albeit for the last three ions only in the UV.

The energy difference between the d- and f-electrons is modified by the covalence of the Eu^{2+} -ligand bond and the crystal field strength. An increase of the covalence of the Eu^{2+} -ligand bond results in a lower energy difference of the $4f$ - $5d$ energy separation (due to the nephelauxetic effect). This elementary treatment considers the shift of the center of gravity (also called barycenter) of the d-electron level (also called centroid shift), i.e. any splitting is not yet taken into account. The crystal field

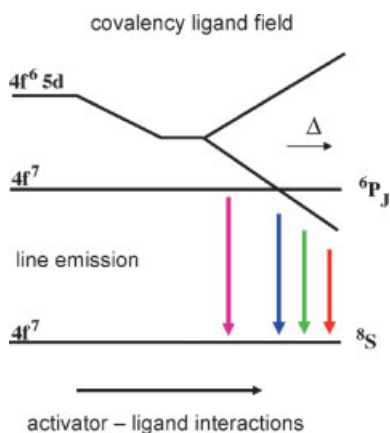


Fig. 1.17 Energy separation of the $4f^7$ and $4f^6 5d^1$ bands as a function of covalence and ligand field strength. The arrows indicate different emission colors.

Tab. 1.3 Spectral position of the emission band of Eu^{2+} in some representative lattices.

$\text{SrB}_4\text{O}_7:\text{Eu}$	368 nm
$\text{Sr}_2\text{P}_2\text{O}_7:\text{Eu}$	420 nm
$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}$	453 nm
$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$	490 nm
$\text{Ba}_2\text{SiO}_4:\text{Eu}$	505 nm
$\text{SrGa}_2\text{S}_4:\text{Eu}$	535 nm
$\text{Sr}_2\text{SiO}_4:\text{Eu}$	575 nm
$\text{SrS}:\text{Eu}$	615 nm

interaction splits the d-level, depending on symmetry and crystal field strength. In this way, e.g., for Eu^{2+} , emission can be obtained extending from the UV part of the optical spectrum (where even line emission is possible [11]) to the red part (see Table 1.3). Both are easily accessible by choosing appropriate host lattices, and for this reason broad-band emitters can in general be tuned within a large spectral range and can be adapted to the application needs.

The spectral position of the emission lines due to transitions between f-electronic states does not vary very much on changing the host lattice. However, the relative emission intensity of the several possible optical transitions does vary considerably.

As general remark, one can state that in cases where the rare-earth ion occupies a site with inversion symmetry, the selection rule states: $\Delta J = 0, 1$. In cases where $\Delta J = 0$, any transition to another state with $J = 0$ is forbidden as well. In such a case, $\Delta|J|$ is necessarily $+1$. These are all magnetic dipole transitions. In lattices without inversion symmetry there is also electric dipole emission. For these transitions, the selection rule is: $\Delta|J| \leq 6$. Here again, for initial or final states with $J = 0$, other selection rules are operative. In such a case, for electric dipole transitions, $\Delta|J| = 2, 4$, or 6 . We observe that the presence of an inversion center opens up the possibility to tune the emission spectrum to a small extent. For Eu^{3+} with excited state ${}^5\text{D}_0$, the emission can be tuned from orange (590 nm, with inversion symmetry, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition) to red (610 nm, without inversion symmetry, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition). More generally, these effects can be described by the Judd-Ofelt theory [12,13]. As a function of three parameters, all possible spectra can be calculated. However, a direct coupling to the chemical environment is lacking. Nevertheless, such calculations are useful. Apart from being able to calculate the relative intensities, these calculations can also be used to calculate subsequent optical transitions, i.e. quantum cutters. For Pr^{3+} , in principle a quantum efficiency of 198 % can be obtained in the visible. The same kind of calculation has shown that for Tm^{3+} , no quantum cutter, a yield of two visible photons can be obtained [14].

Finally, in the case of donor-acceptor pair luminescence, both the donors and the acceptors and the magnitude of the band gap strongly influence the spectral position of the emission color to be obtained. $\text{ZnS}:\text{Ag}$ and $\text{ZnS}:\text{Cu,Au}$ (blue- and green-emitting phosphors, respectively, nicely illustrate this).

1.10

Energy Efficiency Considerations of Important Luminescent Devices

As argued above, in general, the luminescent materials applied operate at physical limits in terms of absorption of the exciting radiation and the quantum efficiency (number of visible photons generated divided by the number of photons absorbed) with which luminescence is generated. In cathode ray tubes, the energy efficiency of the phosphors used is at maximum (up to about 25 %, see above), and the quantum efficiency of the luminescent centers is almost 100 %.

In plasma display panels, fluorescent lamps, and LEDs, the quantum efficiency amounts about 100 %, and the absorption coefficient is also very high. Nevertheless, the energy efficiency of luminescent devices is rather low (see Table 1.4) in which the energy loss is factorized. The phosphor energy loss factor in this table is mainly determined by the Stokes shift (the difference in photon energy of radiation absorbed and emitted). This results in energy loss, which can be significant even when the quantum efficiency is 100 %.

We observe that, although the phosphors operate at physical limits, nevertheless the energy efficiency of the devices is rather low, especially in display applications.

Finally, Table 1.5 gives a survey of luminescent materials with popular applications.

1.11

Luminescence Quantum Yield and Quenching Processes

In this section, we deal with energy loss processes, to throw some light on the question why all phosphors do not have a quantum efficiency of unity and what the loss processes are. We base this discussion on Eq. (26). We also briefly discuss degradation processes in luminescent materials, which quite frequently occur during the operation of devices utilizing phosphors and which have a negative effect on the performance of such devices. The influence on device performance can be considerable, especially in case of

Tab. 1.4 Energy efficiencies of important luminescent devices and a breakdown into the most important energy loss factors.

Device	Cathode ray tube	Plasma display panel	Fluorescent lamp	Phosphor-converted LED lamp
Energy efficiency (%)	1–2	2	Straight fluorescent: 25 Compact: 15	50
Major energy loss factors (%)	Shadow mask: 70–90 Phosphors: 80 Deflection yoke: 50	Discharge: 90 Phosphors: 70	Phosphors: 55 Discharge: 30 (Straight) Discharge: 40 (Compact)	LED: 40 Phosphors: 25

Tab. 1.5 Prominent phosphors and their applications.

Emission color	Application			
	Cathode ray tubes and projection television tubes (PTV)	Plasma display panels	Fluorescent lamps	X-ray detectors
UV			Ba ₂ SiO ₅ :Pb ²⁺ (sun tanning) CeMgAl ₁₁ O ₁₉ (sun tanning) LaPO ₄ :Ce ³⁺ (sun tanning) SrB ₄ O ₇ :Eu ²⁺ (sun tanning, photo copiers)	
Blue	ZnS:Ag ⁺ ,Cl ⁻ ZnS:Ag ⁺ ,Al ³⁺	BaMgAl ₁₀ O ₁₇ :Eu ²⁺	BaMgAl ₁₀ O ₁₇ :Eu ²⁺ Sr ₄ Al ₁₄ O ₂₅ :Eu ²⁺ Sr ₅ (PO ₄) ₃ Cl:Eu ²⁺	NaI:Tl ⁺ Ba(F,Br):Eu ²⁺ (storage phosphor) LaBr ₃ :Ce ³⁺ Bi ₄ Ce ₃ O ₁₂ Gd ₂ SiO ₅ :Ce ³⁺ Lu ₂ SiO ₅ :Ce ³⁺ LuAlO ₃ :Ce ³⁺ YTaO ₄ :Nb ⁵⁺
Green	ZnS:Cu ⁺ ,Au ⁺ ,Al ³⁺ ZnS:Cu ⁺ ,Al ³⁺ Zn ₂ SiO ₄ :Mn ²⁺ (PTV) Y ₂ SiO ₅ :Tb ³⁺ (PTV) InBO ₃ :Tb ³⁺ (PTV) LaOCl:Tb ³⁺ (PTV)	(Y,Gd)BO ₃ :Tb BaAl ₁₂ O ₁₉ :Mn ²⁺ Zn ₂ SiO ₄ :Mn ²⁺ BaMgAl ₁₀ O ₁₇ :Eu ²⁺ ,Mn ²⁺	GdMgB ₅ O ₁₀ :Ce ³⁺ ,Tb ³⁺ LaPO ₄ :Ce ³⁺ ,Tb ³⁺ CeMgAl ₁₁ O ₁₉ :Tb ³⁺ Zn ₂ SiO ₄ :Mn ²⁺	CsI:Tl ⁺ Gd ₂ O ₃ :Tb ³⁺ Gd ₂ O ₃ :Pr ³⁺
Yellow			Y ₃ Al ₅ O ₁₂ :Ce ³⁺	(Y,Cd) ₃ Al ₅ O ₁₂ :Ce ³⁺
Red	Y ₂ O ₃ :Eu ³⁺ Y ₂ O ₃ :Eu (PTV)	Y ₂ O ₃ :Eu ³⁺ (Y,Gd)(P,V)O ₄ :Eu ³⁺	Y ₂ O ₃ :Eu ³⁺	(Y,Gd) ₂ O ₃ :Eu ³⁺ , Pr ³⁺ CaS:Eu
White	ZnS:Ag ⁺ + (Zn,Cd)S:Ag ⁺		Ca ₅ (PO ₄) ₃ (F,Cl):Sb ³⁺ ,Mn ²⁺	

cathode ray tubes, where phosphor degradation can contribute to an efficiency loss up to 30–50% during the operational lifetime. In fluorescent lamps, the maintenance of the phosphors is in general much better, and the efficiency loss over the operational lifetime can be less than 10%.

Looking at the expression in Eq. (26), we distinguish the following loss processes:

1. The absorbed energy does not reach the luminescent ions (η_i).
2. The absorbed energy reaches the luminescent ions but there are nonradiative channels to the ground state (η_{act}).
3. The luminescence generated is absorbed by the luminescent material (η_{esc}).

In what follows, the underlying mechanisms will be treated in more detail.

1.11.1

The Energy does not Reach the Luminescent Ion

When there is more than one origin of optical absorption at the wavelength at which the excitation takes place, the quantum efficiency can be less than unity, even if the ion showing luminescence has a quantum efficiency of one. This is, e.g., the case if both the luminescent ion and the host lattice show optical absorption at the excitation wavelength, or the energy transfer probability of the host lattice to the luminescent ions is smaller than unity. Comparing the absorption or reflection spectra with the excitation spectra can disentangle the different contributions to the absorption.

Degradation of luminescent materials can be due to creation of additional absorption centers in the spectral range where the activators or sensitizers also absorb.

1.11.2

The Absorbed Energy Reaches the Luminescent Ion but there are Nonradiative Channels to the Ground State

The transition rate (units s^{-1}) is given by k . If only emission occurs, k is written as k_r . If the transition involves radiative and nonradiative contributions, k is written as

$$k = k_r + k_{nr} \quad (34)$$

We observe that k increases in the case of nonradiative contributions to the transition rate. For this reason, the emission decay time (being $1/k$) decreases in such cases. Using this expression, it is easily shown that the quantum yield can be determined by measuring the decay time (τ) if the decay time without nonradiative transitions (τ_0) is known:

$$QE = \tau/\tau_0 \quad (35)$$

The proof of this equation is left to the reader.

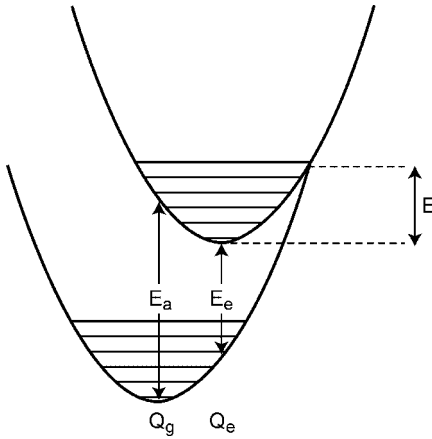


Fig. 1.18 Crossing of parabolas describing ground and excited states, leading to thermal quenching characterized by the activation energy E .

Very frequently, the luminescent ion can reach the ground state via thermal quenching (see Fig. 1.18). This is the case when the excited state and the ground state energy curves cross at an energy which is thermally accessible from the relaxed excited state. For this reason, this process is called thermal quenching. Using the rate equations again, and assuming that the nonradiative rate k_{nr} can be written as

$$k_{nr} = A \cdot \exp(-E/kT) \quad (36)$$

in which A is a constant (units s^{-1}) and E is the energy difference between the energy of the relaxed excited state and the energy at which the ground and excited states cross (Fig. 1.18).

The quantum efficiency is given by

$$QE = 1/(1 + C \cdot \exp(-E/kT)) \quad (37)$$

in which C is a dimensionless constant.

We observe that an increase in temperature results in a lower value for the quantum efficiency. The energy involved in the thermal quenching process is easily determined by measuring the decay time of quantum efficiency as a function of the temperature.

Of course, the elementary treatment leading to Eq. (37) describes quenching due to any thermally activated process, e.g., also thermal quenching due to photoionization. In this process, excited activator ions ionize thermally activated. This process is very important in, e.g., scintillators.

Another quenching process is related to energy transfer. If the concentration of luminescent ions chosen is too high, energy transfer occurs over the luminescent

ions until the energy reaches a center where a nonradiative transition occurs. Two remarks have to be made here:

- Energy transfer underlies sensitization schemes, in which case energy transfer is a useful process. Though the sensitizer emission is quenched, the activator emission appears. This allows practical application of sensitization schemes.
- In general the centers for nonradiative recombination are not known. In many cases, therefore, the possibility to increase the concentration of luminescent ions is limited. The mechanism leading to quantum yield loss is called concentration quenching. Whether or not this mechanism takes place can be easily deduced by investigating the quantum efficiency or the decay time of the emission as a function of the activator concentration.

Please note that a large difference between absorption and emission wavelength (Stokes shift) reduces energy transfer and therefore concentration quenching. On the other hand, a very large Stokes shift increases the probability for thermal quenching, as the ground state parabola will cross the excited state parabola at a lower energy, allowing the ground state parabola to be reached without emission of a photon. This is a direct consequence of the quadratic dependence of the potential energy of the electronic states on the metal-ligand distance, as the reader can easily verify. For the same reason, thermal quenching becomes less probable when the emission energy increases.

Degradation of luminescent materials can be due to additional centers to which energy can be transferred, without efficient photon generation by these centers (killing centers, killers, centers for nonradiative recombination). Such centers can be, e.g., vacancies generated as a consequence of the operation of the device or sensitizer or activator ions that have changed their valence during operation of the device.

1.11.3

The Luminescence Generated is Absorbed by the Luminescent Material

Finally, even if all the absorbed energy is converted into emission, the quantum efficiency is not necessarily one. For example, this is the case when the host lattice itself shows optical absorption in the spectral range where emission occurs. This is easily determined by measuring the absorption or reflection spectra of the host material.

Self-absorption is also an important loss factor in luminescent structures which do not effectively scatter the luminescence light. This is the case, e.g., in organic or inorganic LEDs, where trapping of light in the luminescent structure, followed by absorption of the light emitted in the luminescent material, strongly reduces the light output. In such a case, additional scattering, e.g., by applying scattering layers to such structures or applying photonic structures such that light is generated in desired directions only, can be a way out.

Degradation of luminescent materials (resulting in a loss of photon generating efficiency) is often due to additional absorption bands which are not present in the virgin material. Absorption or reflection spectroscopy therefore are important techniques in understanding the physical origin of light generation losses of phosphors.

1.12

Acknowledgement

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2

Quantum Dots and Nanophosphors

Cees R. Ronda and Thomas Jüstel

2.1

Introduction

In this section we will discuss the electronic properties of quantum dots and nanocrystalline luminescent materials. The topics treated will be illustrated using selected examples from research literature dealing with absorption and emission of quantum dots and luminescence of nano particles of conventional phosphors. While the optical properties of quantum dots are governed by size-dependent quantum confinement, the luminescence spectra of, e.g., rare earth or transition metal ion activated nano phosphors are, if at all, hardly dependent on the particle size. Quantum dots and nano phosphors generally have shortcomings in terms of luminous efficiency; they are nevertheless of strong interest, both from a theoretical, as well as an applied point of view. Theoretically, quantum dots are very suitable to study the effect of dot size on the electronic states with, e.g., spectroscopic techniques. Potential applications of quantum dots and nano crystalline phosphors are in lighting or displays but also in the biochemical and medical field. Very small particles can be modified at their surfaces easily and are therefore ideally suited for, e.g., applications in molecular medicine. Beyond the scope of this book are potential applications in nano crystal electronics in which the quantum properties of electrons come into play.

2.1.1

Optical Properties of Quantum Dots

One speaks of quantum dots when the electronic properties of very small particles depend on the size of the particle. This occurs in the nano-size regime, and for this reason the terms quantum dots and nano particles are frequently used to describe the same kind of particles. We do not do this here: we use the term nano particles solely for particles for which the electronic properties are independent of the particle size.

In this section, we describe elementary quantum mechanical treatments describing particles in a number of different environments. We need this treatment

in our section on quantum dots. There are many textbooks on this subject. A recommended one is Ref. [1], although our treatment is more elementary than this, and emphasis is on generating insight by using very simple arguments whenever this is thought possible. Please note that our treatment follows the same lines as [1]. For a number of readers, the results of the treatment may be well known. Readers are nevertheless advised to appreciate this section, as it might give them a lot of insight. We start with a description of a particle in potential well.

2.1.2

Particle in a One-dimensional Potential Well

For a particle in a one-dimensional potential well, the time-independent Schrödinger equation is given by

$$-(\hbar^2/2m)\partial^2\psi(x)/\partial x^2 + U(x)\psi(x) = E\psi(x) \quad (1)$$

In this equation, m is the mass of the particle, the potential is given by $U(x)$ and E is the energy of the particle with wave function $\psi(x)$.

First we describe the case of a well with width a and with a potential $U(x)$ for $|x| \leq a/2$ and infinite otherwise. This means that the energies found are the kinetic energies of the particles described. It is important to realize that the quantized solutions we will find are solely due to the requirement that the probability to find the particle is zero outside the box and at the boundary of the box. This results in important boundary conditions for the wave functions. As we are only interested in solutions for which there is a particle in a box, the wave functions should generate values which differ from zero in the box. In finding the solutions, we also have to fulfil the condition that the wave functions have to be able to be differentiated at least twice, as follows from Eq. (1). In addition, we assume that the probability of finding the particle (given by the square of the wave function) is symmetric around the center of the box. These conditions are fulfilled by goniometric functions. The goniometric functions have to be chosen such, that the amplitude is zero at the box boundary; this can be achieved with an infinite number of goniometric functions. The more nodes the goniometric function has, the higher its energy will be. Please note that we can introduce a counter, which we call n , which is quantized and which we define to be equal to the number of nodes + 1. For the state with the lowest energy, $n = 1$. Next we introduce the wave vector k , which is general is given by $2\pi/\lambda$, λ being the wavelength of the particle. The state with the lowest energy has wave vector $k = 2\pi/2a = \pi/a$ (the state with the lowest energy has wavelength $2a$: the boundary condition is that the probability of finding the particle at the boundary of the box, there is no requirement to the phase of the particle at the boundary of the box, see also Fig. 2.1). The next state has $n = 2$, the corresponding wave function has wavelength a . For this state we can write k as $2\pi/a$ or for the general case:

$$k = n\pi/a \quad (2)$$

This equation shows that the wave vector k is quantized, the quantization being solely due to the boundary condition that the probability of finding a particle at the box boundaries is zero. For this case, we need only one quantum number (n).

Using the classical relation between the kinetic energy and the momentum p and the quantum mechanical relation between the momentum p and the wave number k and on inserting (2):

$$E = p^2/2m; \quad p = \hbar k \quad (3)$$

We find for the energy of a particle in a box

$$E_n = (\pi^2 \hbar^2 / 2ma^2)n^2 \quad (4)$$

We observe that also the energy is quantized and that only one quantum number (again n) is necessary to characterize the states. Please also note the shape of the second of the two equations labeled Eq. (3), which relates this “particle” property (p) to a “wave” property (k) and therefore beautifully illustrates the dualistic character of nature.

We are now in a position to solve Eq. (1). Already from the treatment given above, we know the nature of the solutions, which are also given graphically in Fig. 2.1. In finding the mathematical shape of the solutions, we have to realize that physics requires the solutions to be normalized, to account for the fact that we calculate the probability to find one particle only.

From Fig. 2.1, we deduce that we find 2 kinds of solutions, one given by cosine functions (with odd n) and one given by sine functions (with even n). Recall that we start counting in the center of the box. Again using Fig. 2.1, we deduce that we can write the goniometric functions as:

$$\psi_{\text{odd}} = 1/N \cos(kx) \quad (5)$$

and

$$\psi_{\text{even}} = 1/N \sin(kx) \quad (6)$$

in which N^2 is the normalization constant and $|x| \leq a/2$. Outside of this range, the wave functions are zero.

On inserting k , we find using Eqs. (3) and (4):

$$\psi_{\text{odd}} = (1/N) \cos(1/\hbar \cdot \sqrt{(2mE)}x) \quad (7)$$

and

$$\psi_{\text{even}} = (1/N) \sin(1/\hbar \cdot \sqrt{(2mE)}x) \quad (8)$$

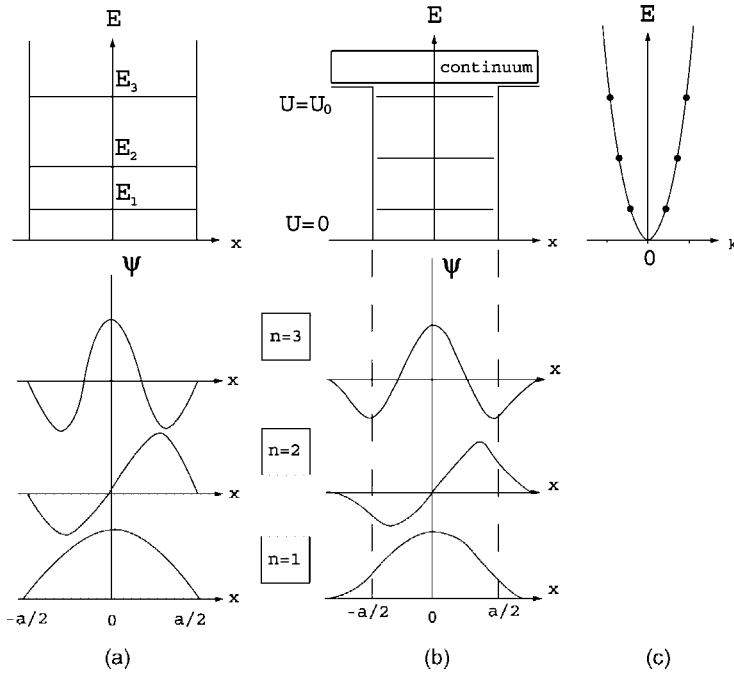


Fig. 2.1 Energy levels and wave functions for (a) particle in a well with infinitely high walls, and (b) particle in a well with finite height. (c) The dispersion curve for a free particle. The dots on these curves are the quantized energy values for a particle in a box. In case of a finite well, above U_0 the dispersion curve for a free particle is obtained.

And finally, the normalized wave functions read

$$\psi_{\text{odd}} = \sqrt{2/a} \cos(1/\hbar \cdot \sqrt{2mE}x) \quad (9)$$

for odd expressions and

$$\psi_{\text{even}} = \sqrt{2/a} \sin(1/\hbar \cdot \sqrt{2mE}x) \quad (10)$$

for even expressions

The reader can easily verify this, by inserting these equations in Eq. (1). The reader then also observes that normalization is achieved by the factor $\sqrt{2/a}$.

The energy separation between two subsequent levels is given by:

$$E_n = \pi^2 \hbar^2 (2n + 1) / 2ma^2 \quad (11)$$

So the energy difference between subsequent levels increases on increasing n .

The wave functions vanish at $x > a$. When a particle exists in the well, the product $\psi^*\psi$ must be nonzero somewhere. The minimum energy of a particle ($n = 1$) is therefore nonzero and given by (see (4)):

$$E_1 = (\pi^2 \hbar^2 / 2ma^2) \quad (12)$$

Eq. (12) can also be derived (apart from a constant) from the Heisenberg uncertainty relation.

$$\Delta p \Delta x \geq \hbar/2 \quad (13)$$

with $\Delta x = a$, it follows for the energy:

$$\Delta E = \Delta p^2 / 2m = \hbar^2 / 8ma^2 \quad (14)$$

For potential wells with walls with a finite height, the nature of the solutions obtained are almost the same, there are, however, a few differences. Above a certain value for the kinetic energy (U_0 , corresponding to the height of the well), the states form a continuum. In addition, the probability to find a particle outside the box is larger than zero and the probability increases with increasing n . The number of states inside the well is given by the following expression:

$$a\sqrt{(2mU_0)} > \pi\hbar(n - 1) \quad (15)$$

for $n = 1$, this condition always holds and therefore, there is at least one state inside the well. The number of states within the well corresponds to the value for n for which Eq. (15) still holds.

For a particle in a potential well, the dispersion relation (which gives the kinetic energy of the particle as a function of k) consists of points on a parabola, as the energy increases with k^2 . The so-called dispersion relation, which relates k to E , is given by (equations (3)).

$$E = \hbar^2 k^2 / 2m \quad (16)$$

Below U_0 , the solutions are quantized, as is the case for any energy level in the case of a particle in a potential well with infinitely high walls. Above U_0 , any value of k is possible, and the dispersion curve is a continuous curve, quadratically dependent on k .

In Fig. 2.1, the results obtained are summarized. In Fig. 2.1 and from Eq. (16), the reader will also note that the energy Eigenvalues are generated for different values of k . This will have an impact for the optical selection rules, as we will see below.

Please note that Eq. (16) can also be used in defining the “mass” of the particle governed by this dispersion relation. Eq. (16) is valid for a free particle. In the solid state, in general dispersion relations differing from Eq. (16) apply and consequently the particle can be thought of to behave as if it had a different mass, which

in addition can be different in different directions. The different mass is called “effective mass”, it finds its origin in interaction of the particle with the solid state.

2.1.3

Particle in Three-dimensional Potentials

In the next sections we discuss, without deriving them, results for particles in a spherically symmetric potential, a three-dimensional Coulomb potential and the hydrogen atom.

2.1.3.1 Particle in a General Three-dimensional Potential

In three dimensions, the wave function are written as a product of a radial part and an angular dependent part. Three quantum numbers are needed (without the spin), in contrast to the one-dimensional case, to characterize the wave functions:

- The principal quantum number n
- The orbital quantum number l
- The magnetic quantum number m

The principal quantum number n equals $n_r + 1 + 1$. It has as minimum value 1. n_r determines the number of nodes of the corresponding wave function. For any value of n , n states exist, which differ in l and l runs from 0 to $(n - 1)$.

The orbital number determines the angular momentum L :

$$L^2 = \hbar^2 l(l + 1), l = 0, 1, 2, 3, \dots \quad (17)$$

The magnetic quantum number (m) determines the component of L parallel to the quantization axis, usually chosen as the z -axis:

$$L_z = \hbar m, m = 0, \pm 1, \pm 2, \dots \pm l \quad (18)$$

The states with different l values are usually denoted as s, p, d, f, \dots states. Every state l is $(2l + 1)$ fold degenerate, as follows from Eq. (18). The parity of the wave functions is determined by l ; this is important for the optical selection rules. Wave functions with even l values have even parity, with odd l values they have odd parity.

Taking again a potential well with an infinite barrier, as in the previous section, we obtain for the energy values of this system:

$$E_{n,l} = (\hbar^2/2ma^2)\chi_{nl}^2 \quad (19)$$

where χ_{nl} are roots of the spherical Bessel functions with n the number of the root and l the order of the function. For $l = 0$, Eq. (19) is equal to Eq. (4).

When the potential well is finite with potential U_0 , Eq. (19) is a good approximation only for

$$U_0 \gg (\pi^2 \hbar^2 / 8ma^2) \quad (20)$$

As only for values of U_0 much larger than given by the uncertainty principle, the values of the energy $E_{n,l}$ are determined by the system.

The smallest value for the energy is obtained for the state with $l = 0$ and $n = 1$. For this case, the energy $E_{1,0}$ is given by

$$E_{1,0} = (\pi^2 \hbar^2 / 8ma^2) \quad (21)$$

For $U_0 = (\pi^2 \hbar^2 / 8ma^2)$, no state exists within the well, in contrast to the one-dimensional problem.

Until now, we have derived our equations without knowing exactly the form of the potential. Solutions were nevertheless obtained which were found to depend on the system chosen. For a particle in a one-dimensional quantum well, the state of the system can be described by one quantum number only; for a particle in a spherically symmetric potential, three quantum numbers are needed. In the next part we will extend our treatment to two physically defined systems.

2.1.3.2 Electron in a Coulomb Potential

The Coulomb potential is given by (throughout this chapter we do not include the term $4\pi\epsilon_0$ in the expressions):

$$U(r) = -e^2/r \quad (22)$$

For the energy, the solution reads:

$$E = -E_0 / (n_r + 1 + 1)^2 \equiv -E_0 / n^2 \quad (23)$$

in which

$$E_0 = e^2 / 2a_0 \approx 13.6 \text{ eV} \quad (24)$$

in which

$$a_0 = \hbar^2 / (m_0 e^2) \approx 5.29 \cdot 10^{-2} \text{ nm} \quad (m_0 \text{ being the electron mass}) \quad (25)$$

So in contrast to the particle in a box, the difference between two subsequent energy levels decreases with increasing n .

For $n = 1$ and $l = 0$ (1s-state), the wave function has spherical symmetry with a_0 corresponding to the most probable distance (from the center from which the Coulomb potential originates) where the electron can be found (Bohr radius). For $E > 0$, the particle can have any energy.

2.1.3.3 The Hydrogen Atom

So far, we have dealt with one-particle problems. The simplest real quantum mechanical topic that can be treated is that of the hydrogen atom: a particle with a positive charge (proton, mass M_o) and a particle with a negative charge (electron, mass m_o).

The Schrödinger equation describing this system is a two-particle equation and therefore consists of three terms, one term for each particle and a term describing the interaction between the particles, the latter term finding its origin in Coulomb interaction:

$$H = -[(\hbar^2/2M_o)\nabla_p^2 + (\hbar^2/2m_o)\nabla_e^2 + e^2/|\mathbf{r}_p - \mathbf{r}_e|] \quad (26)$$

In this equation, the proton and electron position vectors are given by \mathbf{r}_p and \mathbf{r}_e , respectively. In what follows, we write \mathbf{r} for $\mathbf{r}_p - \mathbf{r}_e$ and \mathbf{R} for:

$$\mathbf{R} = (m_o\mathbf{r}_e + M_o\mathbf{r}_p)/(m_o + M_o) \quad (27)$$

For the masses, we write

$$M = m_o + M_o; \mu = m_oM_o/(m_o + M_o) \quad (28)$$

We now write Eq. (26) as:

$$H = -[(\hbar^2/2M)\nabla_R^2 + (\hbar^2/2\mu)\nabla_r^2 + e^2/r] \quad (29)$$

It is very instructive to look at Eq. (29) in some more detail. Eq. (29) describes a Hamiltonian of a free particle with mass M and a Hamiltonian of a particle with reduced mass μ in the potential $-e^2/r$. The first term is that of the center of mass motion of the complete hydrogen atom (nucleus and electron) that describes motion that is not quantized; the other two terms generate internal states, the energies of which are:

$$E_n = -Ry/n^2 \text{ for } E < 0 \quad (30)$$

$$\text{in which } Ry = e^2/2a_B \text{ and } a_B = \hbar^2/\mu e^2 \quad (31)$$

Ry is the Rydberg constant ($Ry = 13.6 \text{ eV}$), which corresponds to the ionization energy of the hydrogen atom, counting from the lowest state, and a_B is the Bohr radius of the hydrogen atom. As in the previous case, the energy difference between neighboring levels decreases with increasing n , and for $E > 0$ the states of the electron and proton are not quantized.

Eq. (25) and (31) differ only by μ/m_e . Please note that Eq. (25) has been derived in a single particle problem. μ/m_e has, for the hydrogen atom, a value of 0.9995, justifying that for the hydrogen atom also the single particle equations can be used.

Although rather elementary, the equations discussed will accompany us further. The single-particle problem is used in the description of an electron and a hole in

nano particles, whereas the two-particle equations are important in the description of excitons (an interacting electron-hole pair). Finally, our discussion of the two-particle system has shown that mass renormalization, using the reduced mass instead of the individual particle masses, can be used to treat the problem as a single particle problem, albeit at the cost of differentiation between center of mass translational motion and single-particle motion in an effective field.

2.2

Density of States in Low-dimensional Structures

In this part, we quantitatively evaluate the density of states (DOS) as a function of the dimensionality of the structure. Knowledge of the density of states is important in understanding the spectroscopic properties of, e.g., quantum dots. We first derive the number of states as a function of k and then calculate the DOS function as a function of E . For a beautiful review, see [2].

It follows from the periodic boundary condition of a one-dimensional crystal that $k = 2\pi n/L$, n being the number of atoms and L the length of the crystal. Please note the difference between this and the particle in a box case, where we found $k = \pi n/a$, with a being the size of the box: in the one-dimensional crystal the *phase* of the wave function has to be the same at the two ends of the crystal, in the particle in a box case *only the probability of finding the particle at the box boundaries has to be zero*.

For the one-dimensional crystal, this means that n is given by $kL/(2\pi)$. With arbitrary dimensionality (D), this equation reads:

$$n = k_D(L/2\pi)^D \quad (32)$$

The number of states per energy interval (dn/dE) can be written as:

$$dn/dE = dn/dk \cdot dk/dE \quad (33)$$

Insertion of (32) leads to:

$$dn/dE = (L/2\pi)^D \cdot dk_D/dE \quad (34)$$

Assuming free particles, for which the relationship between k and E is known [16], we now write:

$$dk/dE = m/(\hbar^2 k) \quad (35)$$

After doing some mathematics and normalizing by dividing by the volume, we obtain

$$\text{DOS}(E) = 1/L^D \cdot (L/2\pi)^D m/(\hbar^2 k) \cdot dk_D/dk \quad (36)$$

in which the D in k_D refers to the dimensionality of the electronic system for which the density of states is calculated.

For three dimensions, we obtain (the states are in a sphere with radius k):

$$\text{DOS}_3(E)dE = 1/4\pi^2 \cdot (2m/\hbar^2)^{3/2}(E - E_g^0)^{1/2}dE \quad (37)$$

(in which we used $E = E_g^0 + \hbar^2 k^2/2m$)

Please note that the number of electron states is twice as large.

The results for two dimensions (the states are in a circle with radius k) and one dimension (the states are on a line with length k) are

$$\text{DOS}_2(E) dE = 1/\pi \cdot m/\hbar^2 dE \quad (38)$$

$$\text{DOS}_1(E)dE = 1/(2\sqrt{2\pi}) \cdot 1\hbar/m^{1/2} \cdot (E - E_g^0)^{-1/2}dE \quad (39)$$

Finally, in a zero-dimensional system, the $\text{DOS}(E)$ is described by a set of δ - functions. The results are summarized in Fig. 2.2.

The shape of the dependence of the density of states on the energy depends on the dimensionality of the system. In different dimensions, the states are described by equations which a different dependence on k , whereas the expression for the energy always contains k^2 .

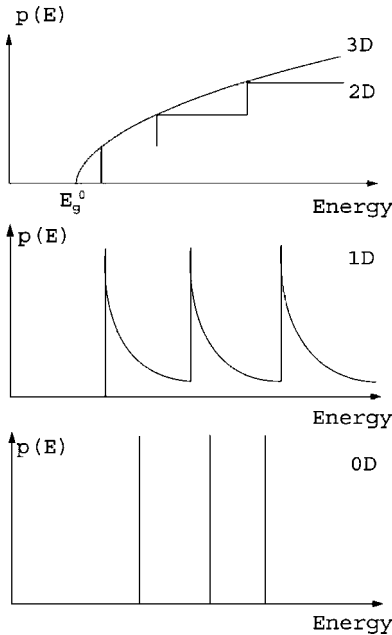


Fig. 2.2 Density of states for 3, 2, 1, and zero dimensional systems.

2.3

Electrons, Holes, and Excitons

We treat holes in the valence band and electrons in the conduction band as elementary excitations. We will obtain an approximate solution in terms of a small number of non-interacting particles. These so-called quasi particles represent excitations of the system, which consists of real particles. The ground state of the system contains no electrons in the conduction band and no holes in the valence band. The first excited state is the state with one electron in the conduction band and one hole in the valence band. Such a transition can, e.g., be induced by photon absorption. On applying energy and momentum conservation, we obtain:

$$\hbar\omega = E_g + E_{\text{kin,e}} + E_{\text{kin,h}} \quad (40)$$

in which $\hbar\omega$ is the photon energy, E_g is the band gap energy, $E_{\text{kin,e}}$ is the kinetic energy of the electron in the conduction band, and $E_{\text{kin,h}}$ is the kinetic energy of the hole in the valence band.

Also

$$\hbar \mathbf{k} = \hbar \mathbf{k}_e + \hbar \mathbf{k}_h \quad (41)$$

in which $\hbar \mathbf{k}$ is the momentum of the photon, $\hbar \mathbf{k}_e$ is the momentum of the electron and $\hbar \mathbf{k}_h$ is the momentum of the hole.

The momentum of the photons is very small; therefore in the absorption process only so-called vertical transitions are possible, without a change in momentum, when no other processes (like electron-phonon interaction, using which the momentum of phonons can also be included in (41)). The reverse process is also possible, e.g., leading to luminescence. Please note that momentum conservation results in an optical selection rule.

We now extend our treatment to interacting electrons and holes and add an interaction term to the Hamiltonian. The resulting quasi particle is called an exciton and, in the framework of almost free electrons and holes, corresponds to the hydrogen atom:

$$H = -[(\hbar^2/2m_e)\nabla_e^2 + (\hbar^2/2m_h)\nabla_h^2] - e^2/\epsilon|\mathbf{r}_e - \mathbf{r}_h| \quad (42)$$

Which essentially is the same equation as Eq. (29), with adaptation of the masses and insertion of the dielectric constant ϵ of the crystal. We therefore obtain:

$$a_B = \epsilon \hbar^2 / (\mu e^2) = \epsilon m_0 / \mu \cdot 0.592 \text{ \AA} \quad (43)$$

for the Bohr radius of the exciton.

For the reduced mass we obtain:

$$\mu^{-1} = m_e^{*-1} + m_h^{*-1} \quad (44)$$

For the Rydberg energy of the system we find:

$$Ry^* = e^2 / (2\epsilon a_B) = \mu e^4 / (2\epsilon^2 \hbar^2) = \mu / m_0 \cdot 1 / \epsilon^2 \cdot 13.6 \text{ eV} \quad (45)$$

We observe that the expressions for the energy [Eq. (45)] contain the dielectric constant squared, the expression for the Bohr radius [Eq. (43)] contains the dielectric constant linearly.

2.4

Low-dimensional Structures

In a semi-conducting material, the wavelength electron and holes, or the Bohr radius of an exciton, can be much larger than the lattice constant a_L . On decreasing the dimensions of a structure, we may enter the regime in which at least one of the dimensions is in the same order of magnitude or even smaller than the wavelength of the electron, hole or Bohr radius of the exciton, but still larger than a_L . In such a structure, the elementary excitations we discussed above will be quantum confined. The result is a quantized motion in the direction of the confinement axis and continuous motion in the other directions.

Confinement in one direction results in a quantum well, which we have treated. Confinement in two directions results in a quantum wire. Confinement in three directions results in an effectively zero-dimensional system: a quantum dot.

In what follows we will treat the electron and hole states in a quantum dot. We will discuss two limiting cases, the weak confinement regime and the strong confinement regime. In both cases we will assume that we can use the effective mass approximation for the electrons and the holes. We will derive the energy states and the optical spectra. As is the case in other branches of spectroscopy, optical selection rules apply. The selection rules obtained for the quantum dots will be compared to selection rules known for optical transitions on ions and in conventional solid-state physics.

We will deal with the quantum dot adopting a three-dimensional quantum well with an infinite potential and electrons and holes with an isotropic effective mass.

2.4.1

The Weak Confinement Regime

Weak confinement occurs when the radius (a) of the nano-particle is a few times larger than the exciton Bohr radius (a_B). In this case, the exciton center of mass motion is confined. We can easily derive the energy of the exciton from the results already derived in the previous chapter. The kinetic energy of the exciton is obtained from the dispersion law of an exciton in a crystal in which the kinetic energy of the free exciton is

replaced by the solution for a particle in a box (we have discussed these expressions already; we take the band gap energy as reference for the exciton energy):

$$E_{nml} = E_g - Ry^*/n^2 + (\hbar^2/2Ma^2)\chi_{ml}^2 \quad (46)$$

The quantum number n describes the internal exciton states, which originate from the Coulomb interaction between electron and hole in the exciton. The two additional numbers m and l describes the states connected to the center of mass motion in the presence of the external barrier. Both sets of numbers have states $1s, 2s, 2p$, etc., those for the internal exciton states are written in capitals.

The lowest state is given by $n = 1, m = 1$ and $l = 0$ (please note that m has taken the position of n in Eq. (19)). Its energy is given by:

$$E_{1S1s} = E_g - Ry^* + \pi^2\hbar^2/(2Ma^2) \quad (47)$$

which can be written as, using the relations derived above,

$$E_{1S1s} = E_g - Ry^*(1 - (\mu/M)(\pi a_B/a)^2) \quad (48)$$

The last part of the expression gives the blue shift of the first exciton absorption as a function of the particle size. When $a \gg a_B$, this shift is small compared to Ry^* .

As photons have almost zero momentum, optical absorption can only connect states exciton with $l = 0$, as the $\Delta l = \pm 1$ part is already included in the optical transition which connects the p -like valence band states to the s -like conduction band states. This means that the absorption spectrum is given by Eq. (46) with χ_{m0} , which is πm (this being a property of the roots of the equations originating from the Bessel functions):

$$E_{nm} = E_g - Ry^*/n^2 + \pi^2\hbar^2/(2Ma^2) \cdot m^2 \quad (49)$$

This indicates that the energy differences between subsequent states decreases with increasing m .

2.4.2

The Strong Confinement Regime

In the strong confinement regime, the radius (a) of the nano-crystal is much smaller than the exciton Bohr radius (a_B): $a \ll a_B$; in this case the confinement also has impact on the electron and hole states.

In this situation, the zero-point kinetic energy is much larger than the Ry^* value. The electron and the hole do not have bound states corresponding to the hydrogen-like exciton. Therefore, in this physical limit, the electron and hole motion may be treated as uncorrelated, and the Coulomb interaction between electron and hole is ignored. Please note that the Coulomb interaction energy by no means vanishes; its contribution to the ground state energy is even higher than in the bulk crystal. In the

strong coupling limit, the Coulomb energy of a free electron-hole pair is unequal to zero, but the zero-point kinetic energy is even much larger.

The energy spectrum of electron and hole are given by, respectively:

$$E_c^{nl} = E_g + (\hbar^2/2m_e a^2)\chi_{nl}^2 \quad (50)$$

and

$$E_h^{nl} = -(\hbar^2/2m_h a^2)\chi_{nl}^2 \quad (51)$$

in which we started counting from the state belonging to valence band-like states with the highest energy.

Please note that the electron and hole states are described by orbital quantum numbers only (n and l), reflecting the description of an uncorrelated electron and hole. Taking the selection rules into account, in the optical absorption spectra we obtain discrete bands, peaking at

$$E^{nl} = E_g + (\hbar^2/2\mu a^2)\chi_{nl}^2 \quad (52)$$

indicating that only optical transitions are allowed between electron and hole states with the same n and l values. Again the electric-dipole selection rule is obeyed, taking the valence and conduction band character underlying the excitonic transition into account. As can be judged from Fig. 2.1, states with different n will have different k positions in the dispersion curve, this generates the selection rule $\Delta n = 0$.

Here, there is a clear parallel to atoms. In the strong coupling limit, the optical spectrum is determined by the number of atoms (via the size of the quantum dot). An atom has a discrete spectrum, dependent on its atomic number.

As mentioned above, the electron and the hole in the quantum dot show Coulomb interaction. The Hamiltonian describing this system is given by:

$$H = -[(\hbar^2/2m_e)\nabla_c^2 + (\hbar^2/2m_h)\nabla_h^2] - e^2/\epsilon|\mathbf{r}_e - \mathbf{r}_h| + U(\mathbf{r}) \quad (53)$$

In which the third term gives the Coulomb interaction between the electron and the hole and the last term the potential describing the confinement. Please note the difference between this Eq. (42). The potential U(r) prevents us from using mass renormalization. This problem has been treated by several authors [3–5]. The result for the electron-hole pair in the ground state is:

$$E_{1s1s} = E_g + \pi^2\hbar^2/(2\mu a^2) - 1.786 e^2/\epsilon a \quad (54)$$

The last term describes the Coulomb interaction between electron and hole. The exciton Rydberg energy is $e^2/2\epsilon a_B$, and, as $a \ll a_B$, this means that the Coulomb energy does not vanish as already stated above. For other optical transitions, the parameter 1.786 has slightly different values.

2.5

Quantum Confinement in Action

In this section, we will describe experimental results of optical investigations. First we will shortly discuss some important techniques for the preparation of the nano-materials. We will then deal with optical properties of compound quantum dots and of doped nanoscale materials.

Quantum confinement studies are done on semi-conductor crystals (in contrast to insulators) in view of the fact the exciton radii are large in semi-conductors (large dielectric constants and small effective mass). Quantum confinement studies are done on semi-conductor crystals typically in the range below 10 nm in size. At larger sizes, no quantum size effects are observed. This can be understood relatively easily: for a dielectric constant ≥ 10 and reduced effective masses in the order of $0.01 - 0.01 m_0$, the exciton radii are in the order of 1–10 nm and their binding energies vary between $0.1 - 10^{-3}$ eV, as can be estimated with Eqs. (43) and (45).

There are many techniques to prepare quantum dots, and all techniques have their own advantages and disadvantages. Wet chemical precipitation methods are used, and in recent years have resulted in relatively narrow particle size distributions. In these methods, the starting materials are dissolved in a liquid and reacted, and the resulting nano-particles are not soluble in this liquid. Changing the reaction conditions can vary the size of the particles. In general, the quantum dots have to be protected from agglomerating with each other or from uncontrolled growth. This is achieved by capping, e.g., by application of a coating on top of the quantum dots. Although the particle size distribution obtained can be rather small ($\pm 10\%$), nevertheless the emission spectra of such materials still show broad spectral features. Sharp spectral features have been obtained by using quantum dots obtained via epitaxial techniques. There are several different methods; some of them will be discussed:

- Growth of islands on a substrate with lattice mismatch (Volmer-Weber)
- Growth of a layer, which subsequently forms islands (Stranski-Krastanow), due to lattice mismatch.
- Self-organized growth of quantum dots, as found by Nötzel [6].
Using this method, quantum dot structures can be obtained with both a vertical and a lateral ordering in some III-V material systems, also exploiting lattice mismatch. It is an interesting feature of this method that the quantum dots bury themselves in the substrate layer and that one can study the effect of contact between the individual quantum dots.

Laser ablation techniques are also used. Another interesting technique is the incorporation of small particles in zeolites.

Luminescence studies require rather perfect materials with a well-defined surface. In addition, as stated above, the quantum dots should not agglomerate to larger units. This can be achieved by surface treatments with stabilizing agents. Interestingly,

size-selective precipitation can also be used to achieve narrower size distributions of the very small particles. See, e.g., Ref. [7].

In general, the optical absorption spectra are richer than the luminescence spectra. In the absorption spectra, absorption features reflecting many excited states are observed. The luminescence spectra discussed here are due to the lowest excited state. Emission from higher excited states is generally absent, due to a rapid relaxation to the lowest excited state. In addition, in many cases near energy gap emission is observed and emission with a much larger Stokes Shift, this latter emission generally being due to lattice defects.

Quantum dots can be charged electrically, e.g., by putting them between two electrodes which are at different potentials. In this way, one or more electrons can be transferred to the nano particles, and consequently their spectroscopy can be studied. In case of ZnO, quite a few electrons can be stored on the particles, depending on the size, up to virtually 10 electrons. Optical transitions between conduction band states of the ZnO nano crystals can then be observed (see Ref. [8]). As we have derived before, electron states, belonging to the nano particles, of s, p, d, etc. character are expected. The wave functions belonging to these states are delocalized over the complete quantum dot. Optical transitions between these conduction band-like states are expected, obeying the usual parity selection rule, i.e. s-p, p-d optical transitions, etc. are allowed.

In Fig. 2.3 the optical absorption due to transitions between conduction band-like states in ZnO nano particles with a mean diameter of 4.3 nm is given. An experimental complication is that there is not only a size variation but also an occupancy variation (with electrons) in the quantum dots. All these factors have been taken into account. The spectra obtained can be deconvoluted, and the contribution of

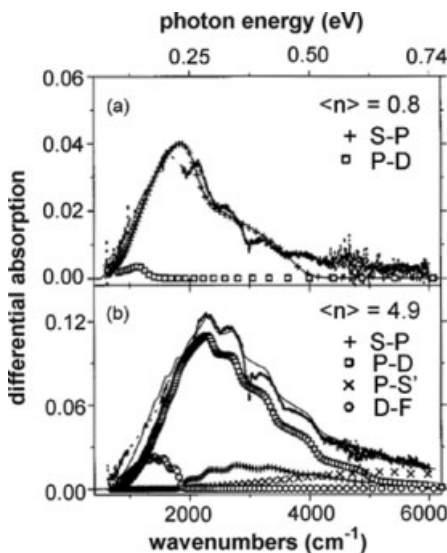


Fig. 2.3 Absorption spectra (black lines) and corresponding fits (thin black lines) for ZnO quantum dot thin films (200 nm) with mean size 4.3 nm at low and high orbital occupancy. The dip at 3000 cm^{-1} is due to the electrolyte used (propylene carbonate).

each individual peak can be compared to results of tight binding calculations in terms of spectral position and intensity. The agreement obtained is quite good; the interested reader is referred to Ref. [8].

Fig. 2.3a shows the result for quantum dots with a low mean occupation number. This is also reflected in the spectra: the shoulder on the right hand side is assigned to particles with one electron; the left hand part is due to particles with two electrons. A very small proportion of the particles also has one electron in a p state as deduced from the observed p-d absorption.

Larger mean sizes allow a higher number of electrons to be stored on the quantum dots – in the example given in Fig. 2.4 up to almost 9 electrons. In this way, the relative contributions of the different transitions to the spectrum can be varied (see Figs. 2.3 and 2.4). In the larger quantum dots with higher occupation numbers, even f states are involved in the optical absorption process.

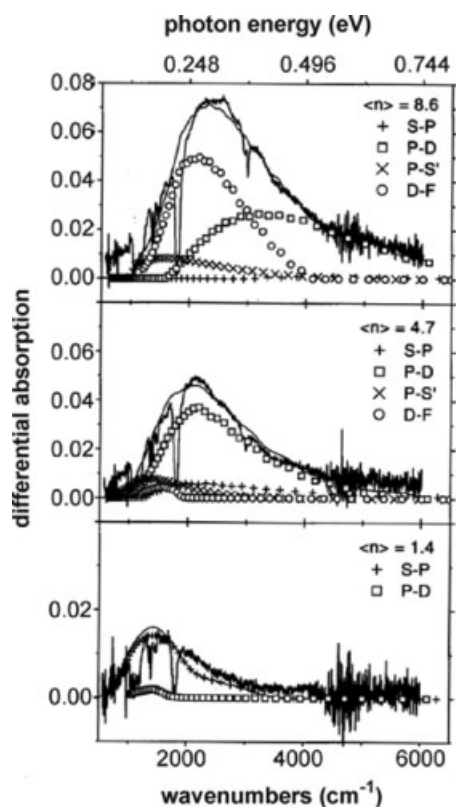


Fig. 2.4 Absorption spectra (black lines) and corresponding fits (thin black lines) for ZnO quantum dot thin films (200 nm) with mean size 5.2 nm at low and high orbital occupancy. The sharp spectral features are due to the electrolyte used (propylene carbonate). From A. Roest, thesis, University of Utrecht, 2003.

2.6

Photoluminescence of Quantum Dots Prepared by Wet-chemical Precipitation

Highly efficient luminescence for InP quantum dots has been reported by Micic et al. [9] with a relatively high quantum efficiency of up to 60 % at 10 K and 30 % at 300 K. Absorption and emission spectra of HF etched samples, which produce high quantum efficiencies, are given in Fig. 2.5. Again a considerable blue shift of the quantum dot emission with decreasing particle size, as bulk InP has a band gap of 1.35 eV (corresponding to 918 nm), is observed. When the quantum dots are not treated with HF, they also show an emission in the deep red part of the optical spectrum, with a wavelength greater than 850 nm; after the HF treatment, this emission is virtually gone. This observation again underlines the importance of surface treatments of nano-particles.

The quantum efficiencies in this material are already rather high and are beginning to approach the range where they are becoming interesting for practical applications. Mimic et al. have also found energy transfer between InP nano particles of a different size when they are in close contact (see Fig. 2.6), i.e. in a closed-packed film [10]. In accordance with expectations, energy transfer from smaller particles to larger particles takes place. Using Förster-Dexter theory (see Chapter 01), the characteristic radius was found to be 90 Å, quite a large value.

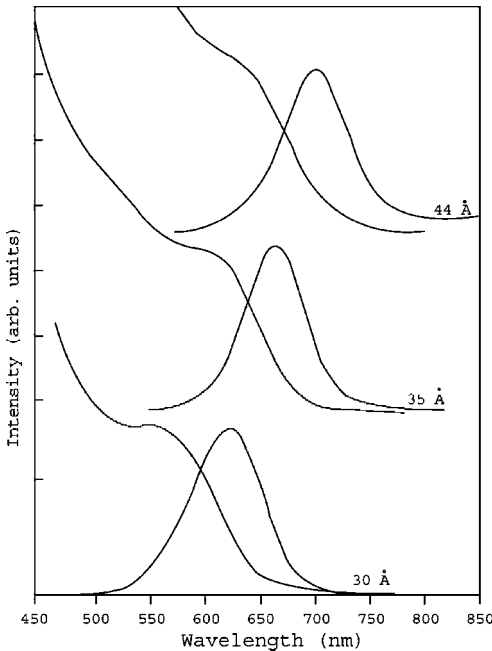


Fig. 2.5 Absorption and emission spectra of InP particles treated with HF as a function of the particle size. The spectra were recorded at 300 K.

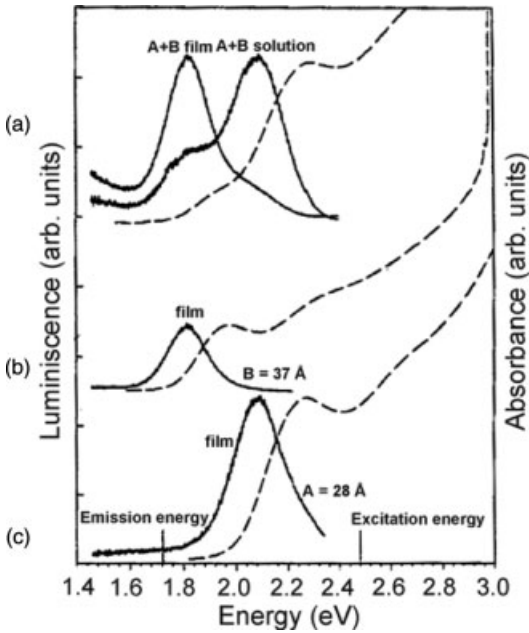


Fig. 2.6 Absorption and emission spectra (excited at 500 nm) of InP quantum dots with (a) two sizes (2.8 and 3.7 nm) in closed-packed films and a mixed solution, (b) 3.7-nm quantum dots only, and (c) 2.8 nm quantum dots only.

2.7 Photoluminescence from Doped Quantum Dots

Apart from emission of the quantum dots themselves, it is also interesting to study the luminescence properties of doped quantum dots. In the early 1990s, there were a number of publications dealing with ZnS:Mn, claiming highly efficient Mn^{2+} emission and a large decrease in decay time of the emission [11]. Already at that time, these findings were being discussed controversially.

Bhargava et al. argued that, because of interaction of Mn^{2+} states with ZnS host lattice states, the optically forbidden transition becomes allowed, this being the reason for the strong decrease in the emission decay time (about a factor of 10^5). There are a few points here: the optical transition on Mn^{2+} is spin forbidden and in principle parity allowed as the Mn^{2+} ion incorporates on a site without inversion symmetry. In addition, the position of the Mn^{2+} emission band hardly shifts, as compared to bulk ZnS:Mn, which is difficult to understand in view of the strong interaction of Mn^{2+} states with ZnS host lattice states that is needed to make the optical transitions allowed. Finally, Bhargava et al. only performed decay time measurements in the ns range.

These observations attracted the attention of many other researchers, and this particular example was even mentioned in a number of textbooks on optical

properties of quantum dots [1] or on luminescence, mentioning this discovery as one of the most important ones in this field in this decade [12,13]. But is it true?

The emission spectrum of ZnS:Mn consists of two bands: one at about 420 nm, which is also observed in undoped ZnS:Mn, and one at about 590 nm, which is due to the ${}^4T_1 \rightarrow {}^6A_1$ transition on Mn^{2+} . Bol et al. [14] have measured the emission spectrum of nanocrystalline ZnS:Mn as a function of the delay time between the laser pulse and the emission measurement. The results are given in Fig. 2.7. As is clearly visible, the fast emission is the emission centered at 420 nm and the Mn^{2+} emission is still very slow.

The results obtained by Bol and Meijerink imply that the fast emission, with a decay time of 20 ns, is not due to emission of Mn^{2+} but due to the emission on the ZnS host, which extends, albeit at low intensity, into the region where Mn^{2+} shows its orange emission. These observations clearly show that there is no combination of a high luminescent efficiency of Mn^{2+} with a very short decay time (in the ns range) of the emission on this ion.

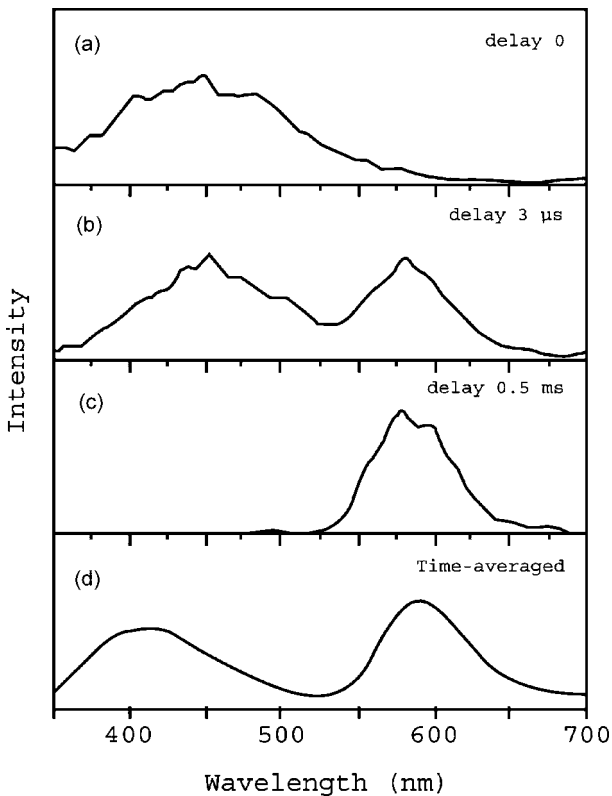


Fig. 2.7 Emission spectra of ZnS:Mn as a function of the delay time and gate width. The delay times and gate widths applied are: (a) ~ 0 and 2 μs , (b) 3 μs and 200 μs , (c) 0.5 and 1 ms, and finally (d) the time-averaged spectrum. All spectra were recorded at 300 K.

2.8 Luminescence of Nano Particles of Rare-Earth Phosphors

In recent years, research on nano particles of commercially applied lamp phosphors has also been performed. We briefly discuss $\text{LaPO}_4\text{:Ce,Tb}$, $\text{YVO}_4\text{:Eu}$, and $\text{Y}_2\text{O}_3\text{:Eu}$ as examples. The main advantage of *ortho*-phosphates and vanadates over oxides is that these compounds can crystallize at room temperature, thus opening the way toward their synthesis as nano particles through colloidal chemistry and preventing agglomeration of nano particles at higher reaction temperatures. Therefore, highly efficient luminescent materials, consisting of nano-particles, have been obtained in *ortho*-phosphates and vanadates crystallizing in the monazite or zircon structure.

The work on the green-emitting fluorescent lamp phosphor $\text{LaPO}_4\text{:Ce,Tb}$ concentrated on the absorption on Ce^{3+} and emission on Tb^{3+} , i.e. on localized states [15]. As such, the optical transitions studied are not dependent on the particle size. However, the nonradiative transitions, which involve host lattice states, likely are. This can, e.g., be due to energy transfer to the surface, the probability depending on the ion-particle surface distance. The system $\text{LaPO}_4\text{:Ce,Tb}$ is therefore of particular interest, as energy transfer is needed to feed the Tb^{3+} emission. Haase et al. succeeded in obtaining nano particles by synthesis in non-aqueous solution with a quantum efficiency greater than 60 % (sum of Ce and Tb emission), even though the relative contribution of Ce^{3+} emission (in the UV) is larger than that in microcrystalline $\text{LaPO}_4\text{:Ce,Tb}$.

$\text{YVO}_4\text{:Eu}$ is applied as a UV converter in high-pressure Hg discharge lamps with an enhanced color rendition. The high luminescence quantum yield of more than 70 % is essentially the consequence of the efficient energy transfer from the vanadate host lattice to the localized states of the doping ion Eu^{3+} , which obviously occurs in the microscale material before any nonradiative recombination takes place at the surface [16].

In contrast, nanoscale $\text{YVO}_4\text{:Eu}$ particles having a mean diameter of 10–50 nm, as made by the groups of Haase and Boilot [17,18], have a quantum yield of only ca. 15 %. It has been shown by the latter group that the quantum efficiency can be improved by a factor of two by simply stirring the particles in D_2O [18]. The strong increase in the quantum yield has been attributed to the decrease in the number of OH groups on the surface, these groups being well known to be very efficient quenchers of the luminescence of lanthanide elements through multiphonon relaxation [19]. From these findings, it can be concluded, that the optimization of the quantum yield of nanoscale phosphors must deal with the deactivation of surface quenching, which is, e.g., promoted by high-energy phonons of surface-bound species, such as OH or NH groups. This is confirmed by investigations on core-shell particles, i.e. by the growth of a silicate shell around the $\text{YVO}_4\text{:Eu}$ particles. This measure decreases the optimum europium concentration, showing that energy transfer within the nano particles is limited by the quenching of the excited states of the vanadate groups [19]. Even though the chemical nature of the passivation of the surface by the silicate shell has not yet been clarified, it might be attributed to the formation of V–O–Si bonds, which will be less active luminescence quenchers than V–OH groups.

Since $\text{Y}_2\text{O}_3:\text{Eu}$ is a lamp and display phosphor of quite some importance, many publications have dealt with the luminescence of Eu^{3+} doped, undoped, microscale, and nanoscale Y_2O_3 (yttria). The luminescence properties of cubic yttria in dependence on the particle size from 10 nm to 10 μm were determined quite recently [20]. It was demonstrated that nanocrystalline cubic yttria samples showed an emission band at 3.6 eV (around 340 nm) due to the recombination emission of bound excitons. The emission band position is equal to that found in microscale yttria. Therefore quantum confinement is not of importance in such oxidic nanophosphors, which can be expected from the Bohr radius, as argued above.

Eu^{3+} doped Y_2O_3 nano phosphors have been made by a large number of techniques, e.g., by solvothermal synthesis or sol-gel chemistry [21,22]. It was found that the nature of the solvent plays an important role in determining the morphology and chemical composition of the precipitates. Moreover, the photoluminescence efficiency of phosphors prepared in non-aqueous media is improved compared to those phosphors made in water [21]. This points again to the impact of surface-bound OH-groups on the quenching of the excited state of Eu^{3+} , since the surface of $\text{Y}_2\text{O}_3:\text{Eu}$ nanoscale particles made in non-aqueous solution is partly coordinated to solvent molecules. This reduces the number of coordinated OH groups and thus the efficiency of surface quenching.

From these examples it can be concluded that the main drawback of nanoscale phosphors is their lower quantum efficiency compared to microscale particles. This is attributed to the large surface area, which amplifies quenching processes. Therefore, research activities aiming at the application of these materials concentrate on the deactivation of surface quenching, which might be achieved by coordinating the surface to ligands having low-phonon frequencies or by the application of a passivating shell.

2.9 Nanoscale Particles for Molecular Imaging

In medical and biochemical research, organic fluorescent compounds are extensively used, e.g., as optical markers for proteins or nucleic acids in the study of molecular and cellular processes [23–25]. Since organic chromophores typically undergo rapid photo bleaching, quantum dots have been proposed as alternative fluorescent labels [26,27] and have already led to very promising results [28–32]. One of the major drawbacks of Cd(S,Se) or InP quantum dots is their high toxicity, which is an obstacle for their *in vivo* application. *In vitro* applications of quantum dots are often hampered by their complex water solubilization and their fluorescence intermittency. However, despite these problems, quantum dots have already been applied as luminescent biolabels, since beyond their higher stability compared to organic fluorophores they offer further advantages such as rather narrow emission bands, including their suitability for color multiplexing, i.e. detecting several analytes by different emission colors at the same time.

Recently, lanthanide ion-doped oxide nano particles have been proposed as biological fluorescent labels [33], since they exhibit strong fluorescence and a large

Stokes Shift, their emission spectrum is characterized by narrow emission bandwidths independent of their particle size, and their colloidal synthesis is well described. Moreover, they exhibit long luminescence lifetimes, which enable time-gated detection (the detection of the luminescence signal starts a predetermined time after the excitation pulse) and discrimination of the background fluorescence stemming from the biological matrix.

The application of oxidic inorganic nano particles doped by lanthanides is thus an interesting alternative to the use of organic fluorophores and quantum dots for many application areas, e.g., in medical diagnostics, in biological sensors, and in fluorescence marking of biological probes for high throughput screening.

By combining a given host lattice with different activators (lanthanide ions) it is possible to synthesize nanoscale oxidic phosphors with several emission colors. As shown in Fig. 2.8, by the incorporation of different lanthanide ions into a given host, e.g., YPO_4 , nanoscale particles with emission colors from UV-A to red can be achieved.

The application of Eu^{3+} -doped Gd_2O_3 nano particles for the visualization of protein micro patterns (proteins printed onto a wafer) has been recently demonstrated [34]. To this end, the nanoparticles were coated with avidin (a glycoprotein found in white of egg) through physical adsorption, avidin having a very strong affinity to biotin. Biotin (vitamin H, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$) can be covalently bound to proteins, e.g., to bovin serum albumin (BSA), and the biotinylated protein (P-biotin), i.e. biotin covalently bound to BSA, is subsequently printed onto a silicon wafer. Once the wafer is incubated in a solution of the avidin-labelled nano particles, fluorescence microscopy reveals that the nano particles linked to avidin are organized onto a designated area, as defined by the microcontact printing process as depicted in Fig. 2.9.

The linking of oxidic luminescent nanoparticles to organic moieties undergoing specific antigen-antibody reaction is a powerful tool that is likely to become a standard

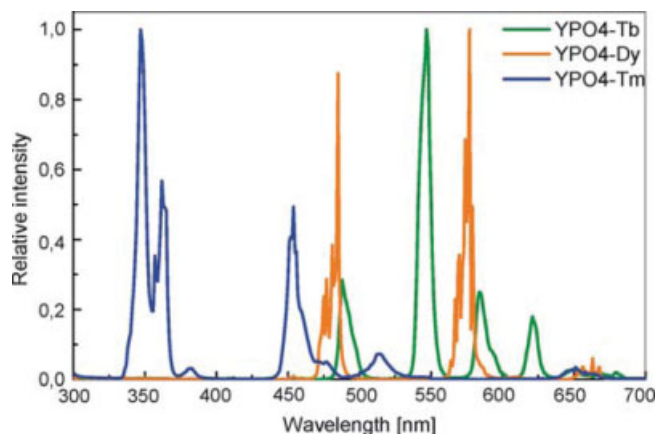


Fig. 2.8 Emission spectra of a YPO_4 host lattice doped with Tm^{3+} , Tb^{3+} , or Dy^{3+} .

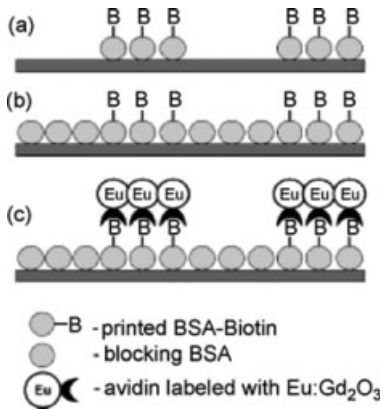


Fig. 2.9 Schematic representation of microcontact printing of biotin onto a silicon wafer (a), blocking with BSA (bovine serum albumin) (b), and specific interaction of biotin with avidin-Gd₂O₃-Eu (c).

technique in biochemical and medical imaging by fluorescent labels. However, luminescent oxidic nanoparticles are not only confined to this application field, since materials based on Gd³⁺-comprising host lattices, e.g., Gd₂O₃ or GdPO₄, can lead to the development of contrast and therapeutic agents because of their magnetic properties (Gd³⁺ has the electron configuration [Xe]4f⁷). The large neutron capture cross-section of gadolinium could make it interesting for nuclear therapy too. The ability of such multifunctional particles to perform both diagnosis (luminescence, magnetic resonance contrast enhancement) and therapy (Gd-neutron capture therapy) at the same time is an up-coming research area.

2.10

Conclusions

In this chapter, we have discussed the electronic properties of confined particles and quantum dots in the weak and strong quantization limit. Examples of absorption and emission spectra of quantum dots have been given. We have also treated luminescence properties of nano phosphors and the application of quantum dots and nano phosphors.

2.11

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3

Phosphors for Plasma Display Panels

Thomas Jüstel

3.1

Introduction

Displays are key devices of the information age, acting as the final interface between information providers such as computers, the internet, or TV, and the human visual system. Starting more than 100 years ago with the “Braun tube”, many different display technologies have been developed. The “Braun tube”, also known as the cathode ray tube (CRT) was for a very long time the most frequently used display principle. At present, we are living in a transition period toward flat panel displays, and CRTs are being more and more replaced by other technologies, in particular, liquid crystal displays (LCDs) and plasma display panels (PDPs). The most promising technology for screen sizes larger than 40 inch is the PDP. However, their future market penetration and share will heavily depend on their performance relative to other technologies. As an emissive display technology, PDPs rely on luminescent materials, and this means that many performance criteria, e.g., brightness, color gamut, efficiency, and lifetime will be determined by these functional materials.

In this contribution we concentrate on the most important aspects of PDP phosphors and the demands defined by the PDP technology. Therefore, a brief introduction to the display principle and the physical aspects of light generation (generation of plasma discharges and phosphor emission) are considered. Special attention is finally paid to currently applied phosphor materials and their main problem areas.

3.2

Principle of Operation of Plasma Display Panels

Displays based on plasma discharges have been known since the early 1950s [1]. In principle, all plasma displays employ a simple neon glow discharge. A sealed glass envelope is filled with neon or a rare-gas mixture (e.g., 10 % Xe, 90 % Ne) and a plasma is ignited by applying a sufficiently high voltage between two electrodes. Both, DC and AC discharges were used in PDPs [2]. Initially, the orange/red light generated

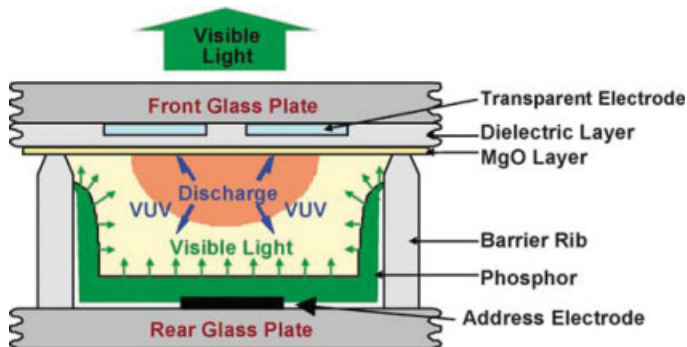


Fig. 3.1 Schematic drawing of a discharge cell in a state-of-the-art AC surface discharge type PDP. In this sketch the front plate electrodes are drawn in the same direction

as the address electrode on the rear plate for visibility. In real panels the transparent discharge electrodes are perpendicular to the address electrode.

in the neon glow discharge was used directly for monochrome display purposes. A breakthrough for this display technology was achieved by applying the so-called AC surface discharge principle illustrated in Fig. 3.1. A dielectric barrier AC discharge is sustained on the surface of a front-glass plate of a display by applying a high frequency voltage of several hundred volts between two transparent electrodes embedded in the glass. Typically, a mixture of 3–15% xenon in neon is used at a pressure of about 600 mbar. In the discharge, Xe atoms are excited to generate vacuum UV (VUV) radiation. This radiation is converted into visible light by a phosphor layer deposited on the rear glass substrate. Visible light leaves the panel through the front glass. This so-called “reflective mode AC surface discharge design” has significant advantages [3] over DC discharges or vertical AC discharges where the plasma is sustained between electrodes located on the front and back plate.

A three-dimensional schematic picture of the complete 3-electrode color AC surface PDP as used in state-of-the-art products [3,4] is shown in Fig. 3.2 and is described in detail later in this chapter. On the rear, so-called barrier ribs form glass substrate channels. The depth of such channels is typically 100–200 μm , and the channels are most commonly formed by powder blasting in a low-melting-point soft glass layer. The channel width determines the resolution of the display. For a 107 cm diagonal display with W(wide)-VGA resolution of 852*480 pixels, the channels are about 300 μm wide. On the bottom of each channel, a metal address electrode is positioned and covered by a dielectric. Sets of 3 channels are then covered with a red-, green-, and blue-emitting phosphor layer, respectively forming color pixels. The front plate electrodes usually consist of Indium-Tin-Oxide (ITO), which is a conductive transparent material. However, since the peak currents in AC-PDPs are very high, the conductivity of the ITO is insufficient, and small extra (bus) electrodes made from copper or silver are applied on top of the ITO. On each intersection of a pair of display electrodes with an address electrode, an addressable pixel is formed. This pixel is selected by an appropriate voltage pulse applied between address electrode and the

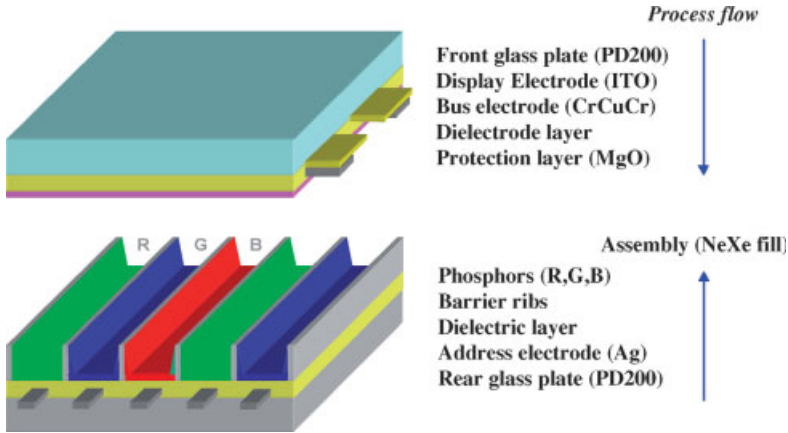


Fig. 3.2 Schematic drawing of a 3-electrode AC-surface discharge type color PDP.

display electrodes, which are also often referred to as sustain electrodes. After addressing, light pulses are generated by an AC voltage of some hundred Volts applied between the sustain electrodes.

The basics of gas discharges are described in several textbooks, and in the case of PDP discharges, the book by Raizer [5] is a good starting point.

In single-element gas discharges, e.g., in a discharge using just Ne gas, ions are typically generated by electron impact ionization, thus releasing a second free electron:



The second electron is also accelerated in the applied electric field and may generate further ions on its path to the anode, thus generating an avalanche process that results in a self-sustaining discharge. The generated ions are accelerated and neutralized at the cathode where they can release secondary electrons. Hence a high secondary electron emission coefficient of the cathode surface material is very important for the firing of the discharge. Generally, generating secondary electrons is very important to obtain an efficient discharge. However, not all electron energy is used for ionization processes. Part of the energy is consumed in order to generate excited (metastable) atoms, e.g.,



These metastable atoms usually relax by emitting a photon. Furthermore, electrons from the surface may also be released by photo-effect or by de-excitation of metastable species. If specific additional other species, e.g., argon atoms, are present in the gas phase, the called Penning ionization process may play an important role. Energy may

then be transferred from excited atoms to such species, resulting in ionization of the additional gas. Mixing, e.g., Ne and Ar results in



Penning ionization occurs only in certain gas mixtures, e.g. Ne/Ar, and leads to the efficient conversion of Ne metastables to Ar ions plus electrons, thus decreasing the required discharge firing voltage. In present-day AC-PDPs, Ne/Xe mixtures are used in order to optimize the generation of VUV-radiation rather than minimizing the plasma firing voltage. VUV light is generated by excited Xe atoms and dimers in the Ne/Xe discharges used. Fig. 3.3 depicts the relevant energy levels and a typical emission spectrum for a low-pressure Xe/Ne discharge.

For the excitation of the phosphors, which subsequently emit the visible light, the resonant radiation at 147 nm and the dimer radiation around 172 nm are most important. In the discharge, Xe is excited by e-impact into the resonant $^3\text{P}_1$, the metastable $^3\text{P}_2$, or a highly excited Xe^{**} state:



By emitting infrared photons, Xe^{**} can be de-excited:



The $^3\text{P}_1$ state can relax to the ground state by emitting a 147 nm photon

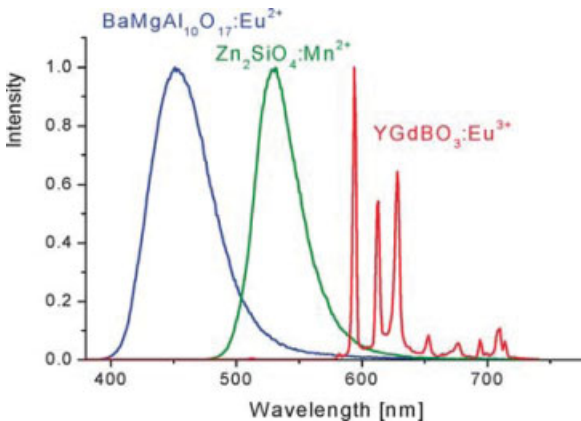


Fig. 3.3 Energy levels of Xe and Xe^{*} and typical emission spectrum of low-pressure discharge [3].

or an excimer state is formed in the case of three-body collisions with an Xe atom and any third atom (M):



The excimer dissociates and emits a photon at about 150 nm (1st continuum) or 172 nm (2nd continuum).

3.3

Performance of Applied Phosphors in PDPs

In a PDP, luminescent materials have to convert vacuum UV (VUV) photons emitted by the Xe/Ne discharge between 147 nm to 190 nm into visible light. Materials applied today are closely related to those materials applied in fluorescent lighting. However, phosphors used in conventional cathode ray tubes still outperform current PDP phosphors in TV display applications with respect to red and blue color purity and operational lifetime.

In fluorescent lighting, UV-C light from an Hg discharge (wavelength 254 nm) penetrates the whole phosphor grain. VUV light in PDPs is absorbed via band gap absorption, with a penetration depth of about 100 nm, which compares with the electron range for voltages used in high-voltage Field Emission Displays (FEDs). Therefore, the phosphor surface and the limited excitation volume play an important role in the light emission process and phosphor efficiency.

Apart from the VUV conversion, the phosphor layer in a PDP has not only to be geometrically dense to fully absorb the VUV radiation but also highly reflective for visible light, demanding low optical absorption for the emitted light.

Table 3.1 summarizes the most relevant phosphor materials with their specific problem areas for the application in PDPs. Most PDPs nowadays use $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor as green primary. Although this phosphor has an intrinsically long decay time due to strictly spin-forbidden optical transitions within the d-shell of the Mn^{2+} ion, phosphors can be fabricated with compositions that relax the spin selection rule sufficiently to achieve decay time constants below 10 ms suitable for display

Tab. 3.1 PDP phosphor materials and their problem areas.

Phosphor composition	Emission color	Problem area
$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$	Blue	Lifetime, processing stability
$\text{Y}(\text{V},\text{P})\text{O}_4$	Blue	Efficiency
$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$	Green	Decay time
$\text{BaAl}_{12}\text{O}_{19}:\text{Mn}^{2+}$	Green	Lifetime
$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+},\text{Mn}^{2+}$	Green	Decay time, lifetime
$(\text{Y},\text{Gd})\text{BO}_3:\text{Eu}^{3+}$	Red	Color point
$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$	Red	Efficiency
$(\text{Y},\text{Gd})(\text{V},\text{P})\text{O}_4:\text{Eu}^{3+}$	Red	Efficiency

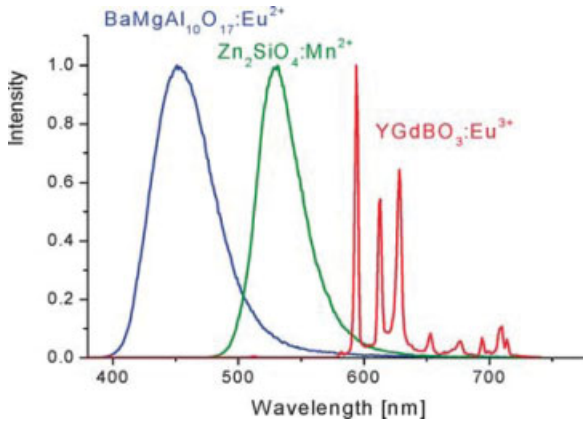


Fig. 3.4 Emission spectra of the red-, green-, and blue-emitting VUV phosphors used by most PDP manufacturers.

applications [6]. The blue-emitting $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM) phosphor has the desired luminescence properties, but phosphor lifetime and also stability during the high-temperature processing steps applied during PDP fabrication ($>400^\circ\text{C}$) are the subject of ongoing investigations. The red phosphor, used mostly for efficiency reasons, $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$, does not have the deep red emission desired for emissive displays.

Fig. 3.4 shows emission spectra for those phosphors mostly applied in PDPs today.

3.3.1

Phosphor Efficiency

In photoluminescence, the so-called quantum efficiency $\text{QE}(\lambda)$ at the excitation wavelength λ is defined as the ratio of emitted quanta and the number of absorbed quanta at excitation wavelength λ . It is measured as light output LO with known reflectivity R according to Eq. (8). Absolute values for the quantum efficiency QE are obtained after determination of the reflectivity R in comparison with the light output for a given phosphor with a reference phosphor of known quantum efficiency.

$$\text{LO}(\lambda) = \text{QE}(\lambda) \cdot (1 - R(\lambda)) \quad (8)$$

Figures 3.5–3.7 show the wavelength-dependent reflectivity, light output, and quantum efficiency for the PDP phosphors shown in Fig. 3.4. All phosphors exhibit a high light output between 147 and 190 nm, as required for PDP application. In this wavelength range, the amount of reflected light is rather low because of strong band gap absorption, and the quantum efficiency is close to the light output of the phosphor.

The quantum efficiencies displayed in Figs. 3.5–3.7 are below unity over the entire spectral range (this is true for all phosphors listed in Table 3.1, although, energetically, below 200 nm, the photon energy of the exciting photons would be high enough to

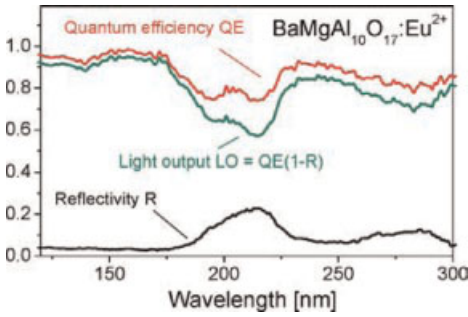


Fig. 3.5 Reflectance, light output, and quantum efficiency of $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM) as a function of wavelength. The reflection spectrum is determined by band absorption below 180 nm (6.9 eV). Above 200 nm light is absorbed by the Eu^{2+} ions via $4f^7 \rightarrow 4f^65d^1$ transitions.

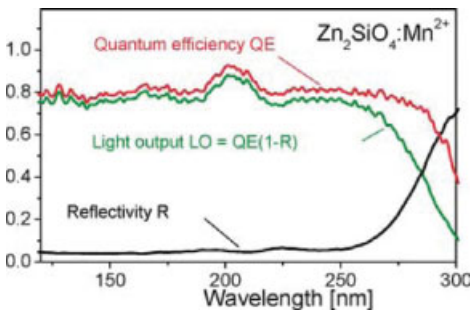


Fig. 3.6 Reflectance, light output, and quantum efficiency of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ as a function of wavelength. The reflection spectrum is determined by band absorption below 220 nm (5.6 eV). Above 220 nm light is absorbed by the Mn^{2+} ions via charge transfer and 3d inner shell transitions.

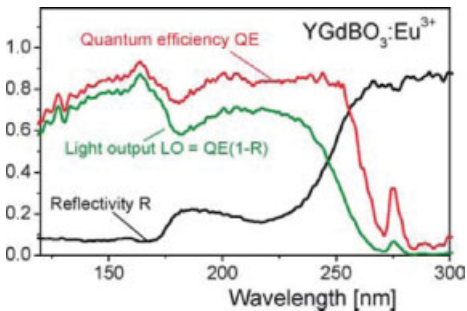


Fig. 3.7 Reflectance, light output, and quantum efficiency of $\text{YGdBO}_3:\text{Eu}^{3+}$ as a function of wavelength. The reflection spectrum is determined by band absorption below 175 nm (7.1 eV).

Above 175 nm light is absorbed by the Eu^{3+} ions via charge transfer transitions, $4f^62p^n \rightarrow 4f^72p^{n-1}$ (a 2p electron from the surrounding oxygen ions is excited into the 4f shell of Europium).

produce two visible photons. In principle, such a down conversion process can be observed for a few activators in fluoridic or oxidic systems in this wavelength regime, but, until now, it is not applicable practically [7].

In general, the light output and quantum efficiency of all phosphors decrease when the photon energy surpasses the band gap energy, as can be seen in Fig. 3.7 for the red-emitting phosphor. It must be noted that the PDP phosphors shown here are selected because of their extraordinarily high efficiency for band gap excitation and that phosphors with a high band gap energy show indeed the highest efficiency for VUV excitation.

Although the quantum efficiency of PDP phosphors is rather high, the energy efficiency of PDP phosphors only reaches 25–30%. However, CRT phosphors have an even lower energy efficiency, which on average is less than 20%.

3.3.2

Electronic Transitions Involved in Europium Luminescence

Fig. 3.8 displays the energy level diagram of Europium ions, which play an important role in phosphors for the lighting and display industry. An understanding of the spectral properties associated with the emission spectra, as described in detail in the legend of Fig. 3.8, is crucial for phosphor development and the understanding of effects relevant to the application of PDP phosphors in PDPs.

3.3.3

Color point and efficiency of the red phosphors

Emissive full color displays (like PDPs) aim at a high luminance (luminous efficacy) and a so-called large color gamut. The color gamut is the range of colors that may be reproduced by the combination of the three applied primary colors. In the 1931 CIE diagram, the color gamut is formed by the area covered by the triangle defined by the color points of the red-, green-, and blue-emitting phosphors. For color television, it was predicted as early as 1955 that for the red primary, the above-mentioned requirements could only be met with a phosphor emitting a line around 610 nm. Meanwhile it has become clear that only the Eu^{3+} ion is able to satisfy this requirement [8].

The CIE color point of the $(\text{Y,Gd})\text{BO}_3:\text{Eu}$ phosphor of $x = 0.640$ and $y = 0.360$ is not as deeply red as the red-emitting CRT phosphor $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$ with $x = 0.660$ and $y = 0.340$. The difference in color co-ordinates is rather small. However, the numerical difference in this chromaticity system does not reflect the human perception in color difference. The emission color of the $(\text{Y,Gd})\text{BO}_3:\text{Eu}$ is perceived as somewhat orange compared to the deep red emission of $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$.

The orange appearance of the emission color of the $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$ phosphor is caused by the relatively intense line at 594 nm, which corresponds to a magnetic dipole transition ${}^5\text{D}_0 - {}^7\text{F}_1$, while the emission lines for the electric dipole transitions ${}^5\text{D}_0 - {}^7\text{F}_2$ at 612 and 627 nm are weaker (see Fig. 3.9).

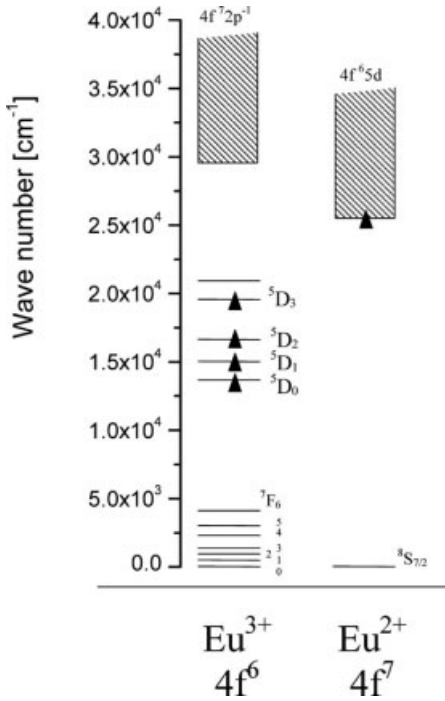


Fig. 3.8 Energy level diagram of Eu^{3+} and Eu^{2+} . The energy axis (in cm^{-1}) is representative for ions in oxidic lattices. Horizontal lines represent narrow energy states of 4f levels. Shaded areas represent broad charge transfer states in the case of Eu^{3+} and $4f^6 5d^1$ states for Eu^{2+} . Triangles indicate levels from which radiative transitions can occur. For Eu^{2+} the 5d band covers almost all 4f levels, leading to a broad emission spectrum found in many lattices, covering the whole visible spectrum and even extending into the UV. The emission wavelength is determined by the position of the $4f^6 5d^1$ levels, which is a function of the crystal field. Eu^{3+} emission usually consists of narrow lines in the red spectral range. Most of the lines

belong to transitions from the $^5\text{D}_0$ level to the $^7\text{F}_j$ ($j=0,1,2,3,4,5,6$) levels, although transitions from other ^5D -levels are frequently observed. The $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions are ideally suited for determination of the lattice site symmetry. For a position with inversion symmetry, electric dipole transitions between the 4f levels are strictly forbidden. In that case only magnetic dipole transitions with the selection rules $\Delta j = 0, \pm 1$ ($j=0$ to $j=0$ forbidden). Without inversion symmetry, electric dipole transition becomes allowed and some transitions with $\Delta j = 0, \pm 2$ appear and dominate the spectrum for even small deviations from inversion symmetry.

The spectrum can be understood from the site symmetry of the Eu^{3+} (Fig. 3.9) in the $(\text{Y,Gd})\text{BO}_3:\text{Eu}$ lattice. Eu^{3+} ions occupy two sites with C_3 symmetry with a very small deviation from a local S_6 symmetry with inversion symmetry. Therefore, electric dipole transitions ($^5\text{D}_0 - ^7\text{F}_2$) are almost forbidden. Figure. 3.9 shows emission spectra of the $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$ phosphor in comparison to alternative red-emitting phosphors in which the Eu^{3+} ions is located on lattice sites without inversion symmetry inducing electric dipole transitions [8,9].

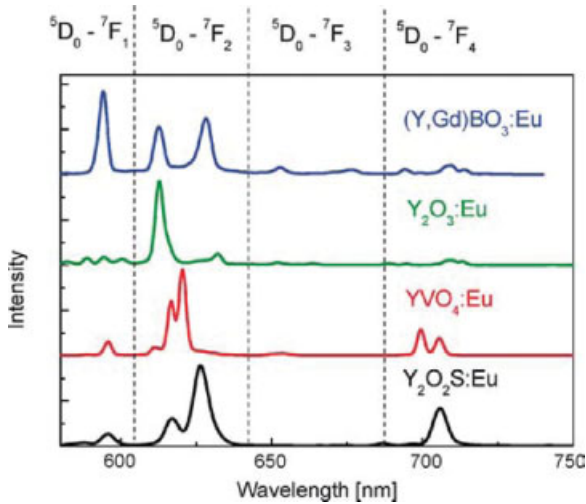


Fig. 3.9 Emission spectra of different Eu³⁺ phosphors. (Y,Gd)BO₃:Eu³⁺, mainly used in PDPs, has a color point of $x = 0.640$ and $y = 0.360$. The color point of Y₂O₃:Eu is $x = 0.641$ and $y = 0.344$. The color point of YVO₄:Eu is $x = 0.645$ and $y = 0.343$. The color point of Y₂O₂S:Eu is $x = 0.660$ and $y = 0.330$.

The ${}^5D_0 \rightarrow {}^7F_1$ levels to which the transitions can be assigned are indicated for the corresponding spectral regions in the top of the figure (compare also Fig. 3.9). Although differences in color points are small, they are clearly perceived by the human eye.

The reason for the wide application of (Y,Gd)BO₃:Eu³⁺ in PDPs is illustrated in Fig. 3.10, where the light output for the phosphors discussed above is displayed as a function of the excitation wavelength. The light output of all alternative red-emitting phosphors is inferior to that of the (Y,Gd)BO₃:Eu³⁺ phosphor for excitation in the vacuum UV spectral range of 147–175 nm, the emission regime of the Ne/Xe gas discharge.

3.3.4

Stability and Color Point of BaMgAl₁₀O₁₇:Eu

The most vulnerable material with respect to panel processing and degradation during operation is the blue-emitting BaMgAl₁₀O₁₇:Eu²⁺ (BAM) phosphor. Degradation effects are related to its host lattice and the Eu²⁺ activator ion. Figure. 3.11 shows the light output measured on a commercial BAM batch as a function of the annealing temperature for excitation at 147 nm and 254 nm, after annealing in ambient air. With increasing temperature the light output (and also the quantum efficiency) decreases significantly, starting at a lower temperature for the shorter wavelength (147 nm) excitation. The main reason for the drastic decrease in light output is the oxidation of the Eu²⁺ ion that was also observed by Oshio et al. [10]. They confirmed the formation of EuMgAl₁₁O₁₉, in which the europium is trivalent,

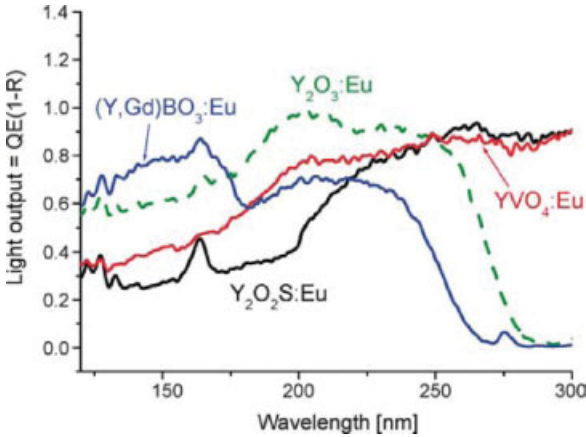


Fig. 3.10 Light output as a function of the excitation wavelength of the red-emitting phosphors depicted in Figure. 3.9.

In the wavelength range of the Xe/Ne discharge emission (145–175 nm), $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$ has a distinctly higher light output than that of all alternative phosphors.

which is very inefficient in this lattice and thus hardly visible in the emission spectrum.

Not only does the Eu^{2+} oxidation decrease the light output of the phosphor, the Eu^{2+} emission itself can also be affected during PDP processing and panel operation. Figure. 3.12 shows emission spectra for different excitation wavelengths of BAM phosphor layers after annealing in ambient air at 550°C , i.e. at a temperature which is reached during PDP processing. In particular, under excitation by short wavelength

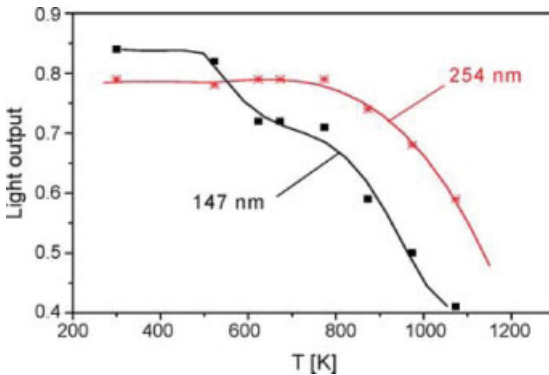


Fig. 3.11 Light output of BAM phosphor powders as a function of annealing temperature for excitation at 147 and 254 nm as indicated in the figure. Annealing was done in ambient air.

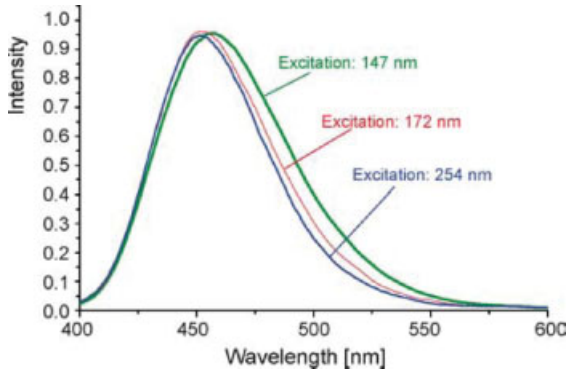


Fig. 3.12 Luminescence spectra of a processed BAM phosphor layer for different excitation wavelengths indicated in the figure. The phosphor layers were baked in ambient air at 550 °C for 1 h. With decreasing excitation wavelength, the green emission intensity increases. The green emission is due to the formation of $\text{Ba}_{0.75}\text{Al}_{11}\text{O}_{17.25}:\text{Eu}$ at the particle surface, which emits at 495 nm.

radiation, additional green emission occurs, resulting in a broadening of the emission spectra at the low-energy edge. As discussed above, the crystal field determines the position of the Eu^{2+} emission band. The spectra depicted in Fig. 3.12 can be fitted quantitatively using an additional emission term centered at around 495 nm, which can be associated with the formation of $\text{Ba}_{0.75}\text{Al}_{11}\text{O}_{17.25}:\text{Eu}$ [11].

From these findings it is concluded that BAM particles have to be single-phase with an optimal stoichiometric composition. An excess of Al_2O_3 during BAM synthesis should be avoided, since additional Al_2O_3 -rich phases, e.g., $\text{Ba}_{0.75}\text{Al}_{11}\text{O}_{17.25}:\text{Eu}$, are a source of the additional emission band peaking at 495 nm. Recent experiments indicate that a small excess of Mg^{2+} used during BAM synthesis yields powders with enhanced photo and thermal stability [12].

3.4 Summary and Prospects

Today, AC-PDPs are the leading technology for large and flat displays, and the dream of a flat TV hanging on the wall is now a reality. Although the performance is already good enough to fulfill most consumer desires, further improvement is necessary to withstand the competition from LCD displays, which are already available in sizes larger than 40 inch.

Since luminescent materials are key components in PDPs, all major phosphor suppliers, display manufacturers, and many university groups are conducting research in the field of PDP phosphors. Although state-of-the-art materials fulfill most of the requirements, improvements are still necessary to further boost the PDP screen efficiency from currently about 2 lm/W to 5 lm/W or higher and to improve color gamut, contrast, and lifetime. It is not very likely that luminescent materials will

be found which perform much better than the already established PDP phosphors. Therefore, future research projects will concentrate on the improvement of the above-mentioned standard materials in terms of particle morphology and surface properties. The latter will imply the optimization of the interaction at the plasma phosphor interface, reduction of phosphor degradation, improvement of light out-coupling from the phosphor grains, and in the long term the development of color filters to improve display contrast.

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4

Quantum-Splitting Systems

Alok M. Srivastava and Cees R. Ronda

4.1

Introduction

According to the US Department of Energy, lighting accounts for 14 % of the total energy used in the United States and 21 % of the electricity consumed in the building sector. With the emphasis on reducing lighting energy use and concurrently reducing pollution from fossil fuel power plants, there is an interest in improved general-purpose illumination technologies. The quantum efficiencies of the phosphor coatings in current “state-of-the-art” fluorescent lamps generally exceed 90 %. Further major improvements in fluorescent lighting efficiency may be sought in the development of more efficient means of generating visible photons from phosphors. The development of practical multiphoton-emitting phosphors, which produce more than one visible photon per incident ultraviolet photon using a controlled photon cascade process, can significantly improve the overall energy conversion of fluorescent lamps. We refer to such phosphors as “quantum-splitting phosphors” (QSPs). The development of suitable quantum-splitting phosphors can also lead to the development of new technologies such as mercury-free fluorescent lamps with an overall energy conversion efficiency that is comparable to existing low-pressure mercury-based lamps.

The purpose of this chapter is to introduce the concept of quantum-splitting or multiphoton-emitting phosphors and their practical importance to the lighting and display industries and to describe the recent significant efforts to develop so-called quantum-splitting phosphors.

The hypothetical energy level diagrams of Fig. 4.1 show two situations which in the archival literature have been found to be suitable for obtaining quantum splitting of a VUV photon. In the energy level diagram of Fig. 4.1a, there is an intermediate state (I) between the ground (G) and the excited (E) states of the luminescent ion. When an electron is raised from the ground state to the excited state via the optical transition $G \rightarrow E$, the system can relax to the ground state through two radiative transitions $E \rightarrow I$ and $I \rightarrow G$, thereby completing the optical cycle. Since the emission process is a composite of two radiative returns, the activator ion produces two visible photons per absorbed ultra-violet photon (quantum efficiency = 2).

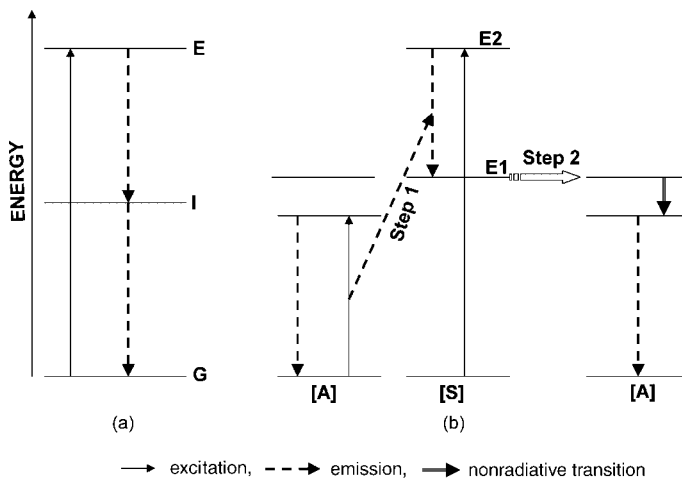


Fig. 4.1 Hypothetical energy level diagrams which generate multiphoton emission; see text.

A more complex situation capable of generating more than one visible photon per incident ultraviolet photon is illustrated in Fig. 4.1b. This mechanism is based on sensitizer (S)-activator (A) interaction. In this scheme, the incident photon is absorbed by the sensitizer ion S. The sensitizer energy levels are such that the radiative transition $E2 \rightarrow E1$ excites the emission of the intentionally added activator ion A via a cross-relaxation process. This process, denoted by Step 1, yields the first visible photon. A second photon is generated when the energy localized on the E1 excited state of the sensitizer ion is transferred to a second activator ion by an energy transfer process.

In the archival literature there is a third process by which multiphoton emission in the visible can be achieved. This pertains to excitation of the phosphor by very high-energy photons. We describe this process in detail in Section 4.7.

4.2

Quantum-splitting Phosphors Based on Pr^{3+} -activated Fluoride Materials

The mechanism of quantum splitting as proposed in Fig. 4.1a, under proper conditions, is fulfilled by the Pr^{3+} ($4f^2$) ion. There have been several demonstrations of Pr^{3+} -activated phosphors, which on average produce more than one visible photon for each incident ultraviolet photon. About thirty years ago, two research groups at industrial laboratories (GE and Philips) reported the observation of two photon emission processes in fluoride-based materials [1,2]. A material comprising 0.1% Pr^{3+} in a matrix of YF_3 was shown by Piper, DeLuca, and Ham to generate more than one visible photon for every absorbed ultraviolet photon when excited with 185 nm

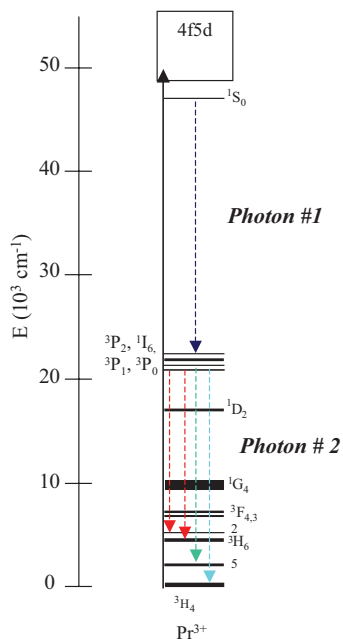


Fig. 4.2 The energy level diagram of the Pr^{3+} ion and the quantum splitting process.

radiation. The phosphor was shown to emit 1.4 visible photons per incident 185 nm ultraviolet photon.

The process of quantum splitting can be described using Fig. 4.2, which shows the electronic energy structure of the Pr^{3+} ion.

Incident UV photons (185 nm) are absorbed by Pr^{3+} from its ground state ($^3\text{H}_4$) into the $4f^15d^1$ configuration. Since this transition is allowed, the incident VUV photons are strongly absorbed. Next, the excitation decays to the $^1\text{S}_0$ level by nonradiative transitions. The transition probability is then such that the $^1\text{S}_0$ level decays radiatively to the $^1\text{I}_6$ level, resulting in the generation of the first photon. A second transition that connects the upper ^3P levels with several ground state levels yields the second photon. The resulting emission spectrum is shown in Fig. 4.3, and the quantum efficiencies of all the relevant optical transitions are listed in Table 4.1. It is seen that the total quantum efficiency (this is the sum of the quantum yields of all transitions in the specified spectral range) of the phosphor greatly exceeds unity. The quantum efficiency for the visible transitions sum to 1.4 (± 0.15), and if we include the UV photons originating from the $^1\text{S}_0$ state, the quantum yield increases to 1.76.

Quantum splitting in a Pr^{3+} -activated phosphor is only realized when the crystal field split components of the $\text{Pr}^{3+} 4f^15d^1$ configuration occur above the $^1\text{S}_0$ state. The free ion energy levels of the $\text{Pr}^{3+} 4f^15d^1$ configuration have been determined by

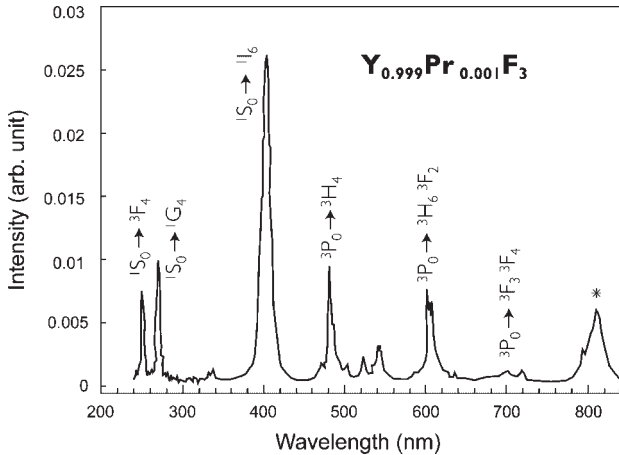


Fig. 4.3 Room temperature emission spectrum of $\text{YF}_3:\text{Pr}^{3+}$ ($\lambda_{\text{ex}} = 185 \text{ nm}$).

Sugar [3]. If the lowest energy component of the $\text{Pr}^{3+} 4f^1 5d^1$ configuration is located below the $^1\text{S}_0$ state, the transition probabilities are such that the initial radiative transitions terminate in the lower energy $4f^2$ levels ($^3\text{H}_4$, $^3\text{H}_5$, $^3\text{H}_6$, $^3\text{F}_2$). Most of these transitions are allowed by the electric-dipole selection rule. In this situation it is impossible to generate two visible photons from the $4f^1 5d^1 \rightarrow 4f^2$ radiative decay. Hence, an efficient quantum-splitting process for the generation of visible photons requires that the crystal field split components of the $\text{Pr}^{3+} 4f^1 5d^1$ configuration occur above the $^1\text{S}_0$ state.

The position of the lowest energy $\text{Pr}^{3+} 4f^1 5d^1$ level relative to $^1\text{S}_0$ depends critically on both the centroid shift and the total crystal field splitting of the $4f^1 5d^1$ band. In highly covalent (such as sulfides) surroundings, the relatively large centroid shift

Tab. 4.1 Optical transitions and quantum efficiency of the $\text{YF}_3:\text{Pr}^{3+}$ phosphor

Transition	Wavelength (nm)	Quantum efficiency
$^1\text{S}_0 \rightarrow ^3\text{H}_4$	215.2	0.007
$^1\text{S}_0 \rightarrow ^3\text{H}_5$	225.4	0.001
$^1\text{S}_0 \rightarrow ^3\text{H}_6$	236.8	0.007
$^1\text{S}_0 \rightarrow ^3\text{F}_4$	251.7	0.053
$^1\text{S}_0 \rightarrow ^1\text{G}_4$	272.7	0.128
$^1\text{S}_0 \rightarrow ^3\text{D}_2$	338.2	0.015
$^1\text{S}_0 \rightarrow ^1\text{I}_6$	405.3	0.789
$^3\text{P}_0 \rightarrow ^3\text{H}_4$	484.3	0.210
$^3\text{P}_0 \rightarrow ^3\text{H}_5$	531.9	0.068
$^3\text{P}_0 \rightarrow ^3\text{H}_6, ^3\text{F}_2$	610.3	0.266
$^3\text{P}_0 \rightarrow ^3\text{F}_3, ^3\text{F}_4$	704.7	0.114

locates the center of gravity of the Pr³⁺ 4f¹5d¹ configuration at lower energies (nephelauxetic effect). Consequently, it is necessary to maintain low covalency of the Pr³⁺-ligand bond. The total splitting of the 4f¹5d¹ state is determined by the strength of the crystal field, which in turn depends on the shape and size of the coordination polyhedra [4]. A weak crystal field results in a high-energy position of the Pr³⁺ 4f¹5d¹ level. These important principles for generating two-photon emission in Pr³⁺-activated materials are relatively more easily satisfied in fluorides (for example, the centroid shift of the Pr³⁺ 4f¹5d¹ configuration is small because of the high electronegativity of the F⁻ ion).

As an example, in YF₃:Pr³⁺, the lowest energy 4f¹5d¹ level is located at a rather high energy value (~51 300 cm⁻¹) and therefore singularly isolated from the ¹S₀ state, which is located at ~47 000 cm⁻¹[5]. The Y³⁺ ions in YF₃ are present in nine-fold coordination with an average metal-to-ligand distance of 2.32 Å [6]. These structural factors satisfy the condition for quantum splitting in the YF₃:Pr³⁺ system. Similarly, in LaF₃, the large La³⁺ ions are present in eleven-fold coordination, with an average metal-to-ligand distance of 2.59 Å [7]. The lowest energy Pr³⁺ 4f¹5d¹ level is located at high energy (~52 400 cm⁻¹) and is therefore isolated from the ¹S₀ state [8]. The ¹S₀ state in LaF₃ is located at 46 961 ± 5 cm⁻¹[9–11]. Consequently, it is not surprising that most efforts have concentrated on fluorides as host lattices for developing quantum-splitting phosphors.

It is instructive to further examine the optical properties of the YF₃:Pr³⁺ system. For low concentrations of the Pr³⁺ activator ion YF₃, a temperature-independent (from room temperature to 450 K) decay time of 523 ± 4 ns was determined for the ¹S₀ → ¹I₆ transition (405 nm). The decay was found to be single exponential (see Fig. 4.4a).

This short lifetime, which is uncharacteristic of a typical 4f-4f optical transition, is due to the mixing of the ¹S₀ wave function with that of the close-lying 4f¹5d¹ state. The mixing relaxes the parity selection rule, which increases the transition probability and hence shortens the decay time. We note that attempts made to calculate the ¹S₀ radiative decay rate by the Judd-Ofelt theory has not met with success because of the close proximity of the ¹S₀ level to the 4f¹5d¹ configuration. Thus, the calculated radiative lifetime of 3.6 μsec for the ¹S₀ state in LaF₃:Pr³⁺ is five times the measured value of 710 ± 10 ns [9]. The possible nature of this admixing is discussed in Section 4.3.

The almost temperature-independent emission lifetime points to negligible nonradiative transition probability from the ¹S₀ state. This is not unexpected since the next electronic manifold is located at ~24 000 cm⁻¹ lower energy, and this large energy gap prevents the quenching of the ¹S₀ state through multiphonon relaxation (MPR). Hence, in the absence of any other quenching pathway (such as energy transfer to defect centers or other luminescent ions), the decay of the ¹S₀ state is mainly radiative. The radiative decay rate of the ¹S₀ state in YF₃ is thus 1.9 × 10⁶ s⁻¹. In Fig. 4.4b, we have shown the rise time of the ³P₀ state in YF₃:Pr³⁺. The rise time was determined to be 453 ± 63 ns and thus similar to the decay time of the ¹S₀ state. This confirms the sequential photon emission process, because under ³H₄ → 4f¹5d¹ excitation the ¹S₀ → ¹I₆ radiative decay populates the ³P₀ level [12].

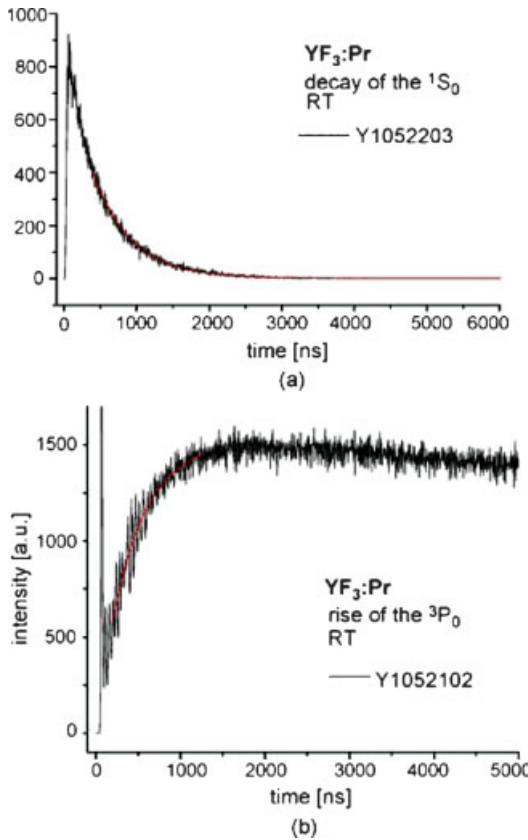


Fig. 4.4 Room temperature luminescence decay curve of $\text{Pr}^{3+}{}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ (a) and rise time of ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ (b) in $\text{YF}_3:\text{Pr}^{3+}$.

It is of interest to note that the ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ optical transition has also been observed in the room temperature emission spectrum of pure PrF_3 [5]. This indicates that the lowest energy level of the $\text{Pr}^{3+} 4f^15d^1$ configuration is located above the ${}^1\text{S}_0$ state. In many materials, such as La_2O_3 , the excitation band shifts to lower energy with increasing Pr^{3+} concentration [13]. This shift to lower energies indicates that the $4f^15d^1$ energy levels of coupled Pr^{3+} ions are different from their energy levels when the ions are isolated at low concentrations. This is apparently not the case in concentrated PrF_3 . The quantum efficiency was determined to be 120 %, which is less than the efficiency in the diluted material (see Table 4.1). The absence of emission from the ${}^3\text{P}_0$ state in PrF_3 is attributed to efficient cross-relaxation between the Pr^{3+} ions [5].

We now proceed to briefly review the quantum-splitting behavior of the Pr^{3+} ion in various fluoride lattices that have been recently reported in the literature. Vink et al. [14] have demonstrated quantum splitting in $\text{SrAlF}_5:\text{Pr}^{3+}$ and evaluated the optical properties of this material under VUV (direct excitation of the Pr^{3+} ion via the

³H₄ → 4f¹5d¹ transition) and X-ray excitation (indirect excitation via band gap excitation). The lowest energy component of the Pr³⁺ 4f¹5d¹ configuration is located at ~49 550 cm⁻¹ and is thus isolated from the ¹S₀ state. Under VUV excitation, strong ¹S₀ → ¹I₆ transition and complete absence of interconfigurational 4f¹5d¹ → ³H_J transitions are noted in the room temperature emission spectrum. This suggests that the levels of the Pr³⁺ 4f¹5d¹ configuration are indeed located well above the energy position of the ¹S₀ state in this host lattice.

It is more instructive to compare the emission spectrum of Pr³⁺ under VUV and X-ray excitation, since such studies indicate some of the major effects, e.g., the variation in the emission characteristics with alterations in the energy of the exciting photon [14]. At low temperatures (T < 150 K) and under band gap excitation (X-ray excitation), the Pr³⁺ ion emits predominantly from the ³P₀ and ¹D₂ states. This is unlike the emission observed under ³H₄ → 4f¹5d¹ excitation, where the emission is dominated by luminescence from the ¹S₀ state. The dominance of emission from the ³P₀ and ¹D₂ states under X-ray excitation is explained as follows. Band gap excitation results in the formation of a self-trapped exciton (STE) whose emission band (maximum at 350 nm) exhibits favorable spectral overlap with the Pr³⁺ ³H₄ → ³P₀, ¹D₂ ¹D₂ absorption transitions. The energy of the STE emission is not sufficient to excite the Pr³⁺ ³H₄ → 4f¹5d¹ (¹S₀) transitions. At low temperatures, the “sensitization” of the Pr³⁺ ion is due to energy transfer from the STE to the Pr³⁺ ³P₀, ¹D₂ states. With increasing temperature, the number of energy transfer events from STE to Pr³⁺ increases since the STE becomes mobile. This results in further enhancement of the ³P₀, ¹D₂ emission intensity.

The absence of ¹S₀ emission at low temperatures in SrAlF₅:Pr³⁺ is due to the fact that this emission is mainly excited by the direct recombination of an electron-hole pair on the Pr³⁺ ion. At low temperatures (T < 150 K), the Pr³⁺ has captured holes from the top of the valence band to form Pr⁴⁺ (Pr³⁺ + h → Pr⁴⁺) but the electrons are not available for the recombination process since they are strongly bound at shallow traps (these shallow traps are unavoidable imperfections in the host lattice). Consequently, under X-ray excitation and for T < 150 K, the overall emission spectrum is dominated by Pr³⁺ ³P₀, ¹D₂ → ³H_J optical transitions (see above). With increasing temperature, the trapped electrons are thermally released from the shallow traps and their recombination with the trapped holes on the Pr³⁺ ion results in emission from the ¹S₀ state.

In this respect it is interesting to note that experiments with YF₃:Pr³⁺ excited by X-ray excitation have shown the prevalence of emission from the ¹S₀ state at room temperature [15]. It is possible that either the exciton in YF₃ (which has not been observed at room or low temperatures; see reference [16]) is energetically resonant with the Pr³⁺ ³H₄ → 4f¹5d¹ (¹S₀) transitions or that at room temperature the electrons bound at shallow traps in the host lattice are released to recombine with the holes previously trapped by the Pr³⁺ ion in a process similar to that described for the SrAlF₅:Pr³⁺ system. It is also instructive to note that variation in the emission characteristics with alterations in the energy of the primary photons (VUV and X-ray excitation) has also been reported in the case of LaF₃:Pr³⁺ [17]. However, in the case of LaF₃:Pr³⁺ the STE emission has been observed (unlike the case of YF₃:Pr³⁺). It is a

broad band extending from about 250 nm ($40\,000\text{ cm}^{-1}$) to 450 nm ($22\,222\text{ cm}^{-1}$) with a maximum at 332 nm ($30\,120\text{ cm}^{-1}$) [18]. Hence, in $\text{LaF}_3:\text{Pr}^{3+}$, the energy of the STE is sufficient to excite the $\text{Pr}^{3+} {}^3\text{P}_0$ emission, so that under X-ray excitation, the emission is dominated by transitions emanating from this level, whereas for VUV excitation the dominance of luminescence from the ${}^1\text{S}_0$ state is observed.

Kück et al. have recently studied the quantum-splitting emission of Pr^{3+} in a large number of fluoride host lattices. The VUV excited luminescence of $\text{LuF}_3:\text{Pr}^{3+}$ (isostructural with YF_3) shows strong emission from the ${}^1\text{S}_0$ state [19]. The quantum efficiency of this phosphor was determined to be 160 % (all transitions included). In BaMgF_4 , the large Ba^{2+} ion is present in eight-fold coordination with an average metal-to-ligand distance of 2.32 Å [20]. The lowest-energy $\text{Pr}^{3+} 4f^15d^1$ configuration is located at rather high energy ($\sim 52\,000\text{ cm}^{-1}$) and the room temperature emission spectrum is dominated by the optical transitions from the ${}^1\text{S}_0$ state. The quantum efficiency of this phosphor was determined to be 130 % [19].

Spectroscopic properties of Pr^{3+} -activated complex fluorides such as K_2YF_5 , KYF_4 , LiKYF_5 , and $\text{Cs}(\text{Y,Gd})_2\text{F}_7$ under synchrotron and F_2 excimer laser excitation have recently been reported in the literature [21]. In the case of K_2YF_5 , KYF_4 , and LiKYF_5 , the crystal field split components of the $\text{Pr}^{3+} 4f^15d^1$ configuration occur below the ${}^1\text{S}_0$ state, and the emission spectrum is characterized by the broad-band $4f^15d^1 \rightarrow 4f^2$ interconfigurational transitions with fast decay time (20–30 ns). However, under VUV excitation, weak $\text{Pr}^{3+} {}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ transition is observed in the visible. This is attributed to a quantum-splitting process in which the optical transitions of the $4f^15d^1 \rightarrow {}^1\text{I}_6, {}^3\text{P}_{0,1,2}$ type populates the ${}^3\text{P}_j$ states from which the second photon is generated. The $4f^15d^1 \rightarrow {}^1\text{I}_6, {}^3\text{P}_{0,1,2}$ emission transition manifests itself as a weak broad band centered at ~ 440 nm. It is obvious that the efficiency of this quantum-splitting process will be exceedingly low because of the strong probability that the $4f^15d^1$ level will decay radiatively to states that are located well below the ${}^1\text{I}_6$ and ${}^3\text{P}_{0,1,2}$ levels.

The emission of Pr^{3+} -activated CsY_2F_7 is characterized by the simultaneous occurrence of interconfigurational (broad-band) $4f^15d^1 \rightarrow 4f^2$ transitions and sharp line luminescence from the ${}^1\text{S}_0$ state. This dual nature of the emission is attributed to the occupation of Pr^{3+} in two distinct crystallographic sites with varying crystal field strength in the host lattice (there are at least eight different sites for the Y^{3+} ion in this lattice whose coordination polyhedra differ considerably) [22].

It is rather unfortunate that the practical use of fluorides in mercury-based fluorescent lamps is not straightforward for several reasons. First, the material is not stable in the presence of a rare-gas/mercury discharge used in conventional low-pressure mercury. Second, the manufacture of fluorinated materials is difficult because of environmental concerns and the reactivity of fluorides.

4.3

Quantum-splitting Phosphors Based on Pr^{3+} -activated Oxide Materials

The aforementioned problem in the practical implementation of fluorides led GE Global Research to pursue the development of oxide host lattices that support

quantum splitting. The oxide lattices are generally compatible with operations in Hg plasma and existing manufacturing. We have noted earlier the possible reasons for QSPs not easily being realized in oxides. The larger nephelauxetic effect and the larger crystal field in oxides relative to that in fluorides generally results in the lower limit of the Pr³⁺ 4f¹5d¹ configuration being situated below the ¹S₀ state. This usually results in broad-band interconfigurational luminescence from the 4f¹5d¹ level to the ³H_J ground states.

However, since the strength of the crystal field decreases with increasing Pr³⁺-ligand bond distance, quantum splitting in oxides may be favored in structures that offer high coordination number for the Pr³⁺ ion. To demonstrate, quantum splitting is observed in SrAl₁₂O₁₉ [23], LaMgB₅O₁₀ [24], and LaB₃O₆ [25], where the Pr³⁺ ions are coordinated to twelve and ten nearest-neighbor oxygen ions, respectively. This constituted the first observation of quantum splitting in oxide-based materials. Below, we examine the salient features of the emission and excitation spectra of Pr³⁺-doped oxidic systems, which support emission from the ¹S₀ state at room and/or low temperatures.

4.3.1

SrAl₁₂O₁₉: Pr³⁺

The SrAl₁₂O₁₉ material crystallizes in the magnetoplumbite (PbFe₁₂O₁₉) structure with the space group P6₃/mmc. The Pr³⁺ ions substitute for the Sr²⁺ ions, which are present in twelve-fold coordination [26]. The nearest-neighbor oxygen ions are located at relatively large distances (2.75–2.785 Å), resulting in a low crystal field splitting of the Pr³⁺ 4f¹5d¹ excited configuration. The splitting of about 6300 cm⁻¹ is one of the smallest observed in an oxide material. From the room temperature excitation spectrum, the lowest energy Pr³⁺ 4f¹5d¹ configuration is located at ~50 550 cm⁻¹ [23]. The energy position of the ¹S₀ state was determined to be 46 490 ± 10 cm⁻¹ [27]. We, therefore, expect emission from the ¹S₀ level, and this is indeed observed in the room temperature emission spectrum (Fig. 4.5).

The spectral lines at 215 nm (46 512 cm⁻¹), 255 nm (39 216 cm⁻¹), 275 nm (36 364 cm⁻¹), 345 nm (28 985 cm⁻¹) and 405 nm (24 691 cm⁻¹) are assigned to optical transitions from the ¹S₀ level to the ³H₄, ³F₂, ¹G₄¹D₂ and ¹I₆ states, respectively. Note the strong intensity of the ¹S₀ → ¹G₄ emission transition. This observation will become important when we discuss the visible quantum efficiency of this material (Section 4.4).

At room temperature, the emission lifetime of the ¹S₀ → ¹I₆ transition, under synchrotron radiation, is 330 ± 10 ns and ~400 ns at T = 14 K [28]. Under 193 nm excitation, we have measured a decay time of 520 ns for the same transition in SrAl₁₂O₁₉:Pr³⁺. In Ref. [27], a lifetime of 658 ns has been reported. The mixing of the Pr³⁺ 4f¹5d¹ configuration into the ¹S₀ level has been examined. The crystal field mixes the ¹S₀ state with the 4f¹5d¹ ¹F₃ and ¹H₅ levels. The spectroscopic properties of the ¹S₀ level can be explained qualitatively through this admixture. The ¹S₀ → ¹G₄, ³F₄ transitions are zero phonon line dominated, while the ¹S₀ → ¹I₆ optical transition is vibronic in nature [25,29].

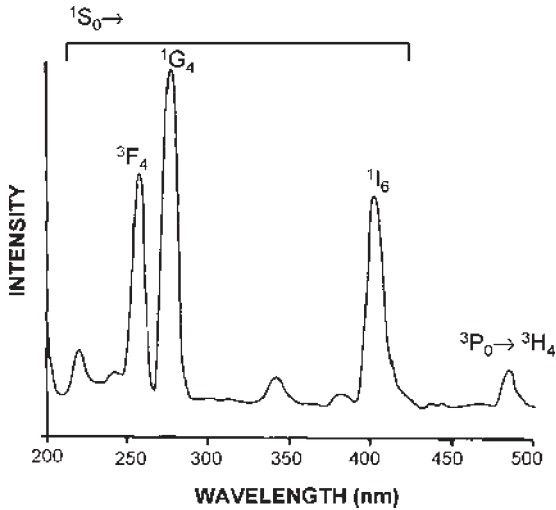


Fig. 4.5 Room temperature emission spectrum of $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ ($\lambda_{\text{ex}} = 193 \text{ nm}$).

Rodnyi et al. [28] have investigated the luminescence of this material under vacuum ultraviolet and X-ray excitation. Briefly, at low temperatures and under band gap excitation (the band gap of $\text{SrAl}_{12}\text{O}_{19}$ was determined to be 7.6 eV), the created electron-hole pairs preferentially transfer their energy to the $\text{Pr}^{3+} {}^3\text{P}_0$ state rather than to the ${}^1\text{S}_0$ state. The experimental data reveals negligible intensity for the ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ optical transition below 130 K, while strong emission from the ${}^3\text{P}_0$ state is observed. This is explained as follows. The emission energy of the exciton created by the capture of the electron (in the conduction band) by the self-trapped hole is resonant with the excitation of the $\text{Pr}^{3+} {}^3\text{P}_0$ emission but not with the ${}^1\text{S}_0$ state. Hence, the $\text{Pr}^{3+} {}^3\text{P}_0$ emission retains high intensity even at low temperatures because of this energy transfer process. It is speculated that the emission of the ${}^1\text{S}_0$ state is activated by trapped holes whose mobility decreases with decreasing temperature. Hence, at low temperatures the trapped holes are unable to excite the $\text{Pr}^{3+} {}^1\text{S}_0$ emission efficiently. At higher temperatures, the trapped holes become mobile, so that their capture by the Pr^{3+} ion results in emission from the ${}^1\text{S}_0$ state.

The first observation of quantum splitting in nanocrystalline $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ nanocrystals was reported recently [30]. High-quality nanocrystals with thickness between 30 and 60 nm were synthesized by using a surfactant-templated-assisted route. The quantum-splitting properties of the material were fully retained in the nanocrystalline particles and no significant differences between the optical properties of nanocrystals and the micron-sized material were observed. Quenching of the luminescence in nanoparticles due to surface loss mechanisms was not competitive with the radiative decay of the $\text{Pr}^{3+} {}^1\text{S}_0$ state. This was attributed to the careful synthesis process that reduced the concentration of the surface defect states.

4.3.1.1 $\text{LaMgB}_5\text{O}_{10}$ and LaB_3O_6 Doped with Pr^{3+}

The $\text{LaMgB}_5\text{O}_{10}$ host material crystallizes in the (monoclinic) structure with the space group P121/C1. The La^{3+} ions (site symmetry C_1) are twelve-coordinated; the ten nearest neighbor oxygen ions are located between 2.3979 and 2.961 Å, and two other oxygen ions are located at ~ 3.67 Å [31]. The LaB_3O_6 host material also crystallizes in the monoclinic structure (site symmetry C_2) with the space group I12/C1. The La^{3+} ions are ten-coordinated; the nearest neighbor oxygen ions are located between 2.4291 and 2.8457 Å [32]. Both host lattices offers a single site for the dopant ion, and the incorporation of the trivalent praseodymium ion does not require charge compensation.

The large coordination polyhedral around the Pr^{3+} ion in the two host lattices results in a low crystal field splitting of the $\text{Pr}^{3+} 4f^15d^1$ configuration. The room temperature excitation spectrum reveals that the lowest energy $\text{Pr}^{3+} 4f^15d^1$ levels in $\text{LaMgB}_5\text{O}_{10}$ and LaB_3O_6 are located at approximately $49\,000\text{ cm}^{-1}$ and $49\,270\text{ cm}^{-1}$, respectively [24,25]. Consequently, quantum splitting is expected in these materials. As shown in Fig. 4.6, the room temperature emission spectrum of $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$ is indeed dominated by the $^1\text{S}_0 \rightarrow ^1\text{I}_6$ optical transition.

Let us examine the room temperature emission spectrum of quantum-splitting phosphor, $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$ (Fig. 4.6). As previously discussed, the first photon in the quantum-splitting process is generated by the $^1\text{S}_0 \rightarrow ^1\text{I}_6$ transition and the second photon by the efficient radiative decay to the ground state of the $^3\text{P}_0$ intermediate level. However, in striking contrast to $\text{YF}_3:\text{Pr}^{3+}$ and $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$, the luminescence of $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$ (and $\text{LaB}_3\text{O}_6:\text{Pr}^{3+}$) shows the near absence of emission from the $^3\text{P}_0$ state. Instead, the second photon transition produces weak emission in the red

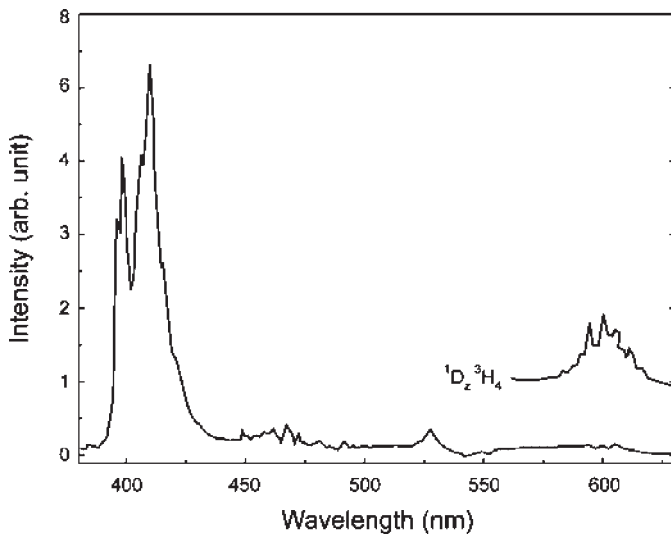


Fig. 4.6 Room temperature emission spectrum of $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$ ($\lambda_{\text{ex}} = 185\text{ nm}$).

when excited with UV at room temperature. It is possible to associate this luminescence with the radiative return of the $\text{Pr}^{3+}{}^1\text{D}_2$ state to the ground states; practically identical line spectra of luminescence is observed when exciting with photons of wavelength resonant with the $\text{Pr}^{3+}{}^3\text{H}_4 \rightarrow {}^1\text{D}_2$ absorption transition. We further note that the ${}^3\text{P}_j$ levels appear in the excitation spectrum of the ${}^1\text{D}_2$ fluorescence.

These results indicate that the intermediate ${}^3\text{P}_0$ level in $\text{LaMgB}_5\text{O}_{10}$ relaxes by multi-phonon relaxation to the ${}^1\text{D}_2$ state. The interaction of Pr^{3+} ion with the host lattice phonons is responsible for the ${}^3\text{P}_0 \Rightarrow {}^1\text{D}_2$ nonradiative relaxation process. The multiphonon relaxation rate can be given by the modified exponential energy gap law of Van Dijk and Schuurmans [33–35]:

$$W_{\text{NR}}(T = 0 \text{ K}) = \beta_{\text{el}} \exp[-\alpha(\Delta E - 2\hbar\omega_{\text{max}})] \quad (1)$$

where β_{el} and α are constants for a given host lattice, ΔE is the energy gap, and $\hbar\omega_{\text{max}}$ is the highest fundamental phonon frequency. For borate glasses, $\beta_{\text{el}} = 16.8 \times 10^7 \text{ s}^{-1}$, $\alpha = 4.43 \times 10^{-3} \text{ cm}$. With $\Delta E \approx 3300 \text{ cm}^{-1}$ and $\hbar\omega_{\text{max}} = 1400 \text{ cm}^{-1}$ [36], we obtain $W_{\text{NR}} \approx 10^7 \text{ s}^{-1}$. Since the characteristic decay rate of the ${}^3\text{P}_0$ fluorescence in diluted systems (isolated Pr^{3+} ions) is $\sim 10^5 \text{ s}^{-1}$, the ${}^3\text{P}_0 \Rightarrow {}^1\text{D}_2$ nonradiative relaxation process can compete with the radiative decay of the ${}^3\text{P}_0$ level. In $\text{YF}_3:\text{Pr}^{3+}$ where $\hbar\omega_{\text{max}}$ is of the order of $500\text{--}600 \text{ cm}^{-1}$ [37], $W_{\text{NR}} \approx 10^2 \text{ s}^{-1}$, and so the ${}^3\text{P}_0 \Rightarrow {}^1\text{D}_2$ nonradiative relaxation through multiphonon relaxation process is improbable in this case. Hence, the effectiveness of the ${}^3\text{P}_0 \Rightarrow {}^1\text{D}_2$ nonradiative relaxation process in $\text{LaMgB}_5\text{O}_{10}$ (and LaB_3O_6) can be attributed to the high effective phonon energy ($\hbar\omega_{\text{max}}$) of the borate host lattice.

As we discuss in Section 4.4, the probability that the system generates lighting-useful visible photons from the ${}^1\text{D}_2$ state is lower than the probability of generating visible photons from the ${}^3\text{P}_0$ state. Thus far, no useful quantum-splitting phosphors have been made from borates or phosphates because their lattices tend to exhibit high effective phonon energy, so that a small number of phonons are required to bridge the ${}^3\text{P}_0 - {}^1\text{D}_2$ energy gap via the multiphonon nonradiative process.

$\text{LaPO}_4:\text{Pr}^{3+}$ [38] We briefly review the optical properties of this interesting system, since there is the occurrence of both the ${}^1\text{S}_0$ and the $4f^15d^1$ emission from the single optical center at low temperatures. The host material crystallizes in the (monoclinic) monazite structure. The La^{3+} ions (site symmetry C_1) are nine-coordinated; eight oxygen ions located between 2.4 and 2.7 Å and the ninth located at ~ 3.0 Å. In the monazite structure the largest A-O bond distance is always 0.2–0.3 Å greater than the other A-O bond distances [39–41]. The host lattice offers a single site for the dopant ion, and the incorporation of the trivalent praseodymium ion does not require charge compensation.

From the room temperature excitation spectrum, the lowest energy $4f^15d^1$ excitation band is placed at about $48\,870 \text{ cm}^{-1}$, which is thus higher than the energy position of the ${}^1\text{S}_0$ state ($46\,500 \text{ cm}^{-1}$). Hence, we expect the system to exhibit the process of quantum splitting. This, however, is not the case, and at room temperature the luminescence is completely dominated by interconfigurational $4f^15d^1 \rightarrow 4f^2$ optical transitions [42].

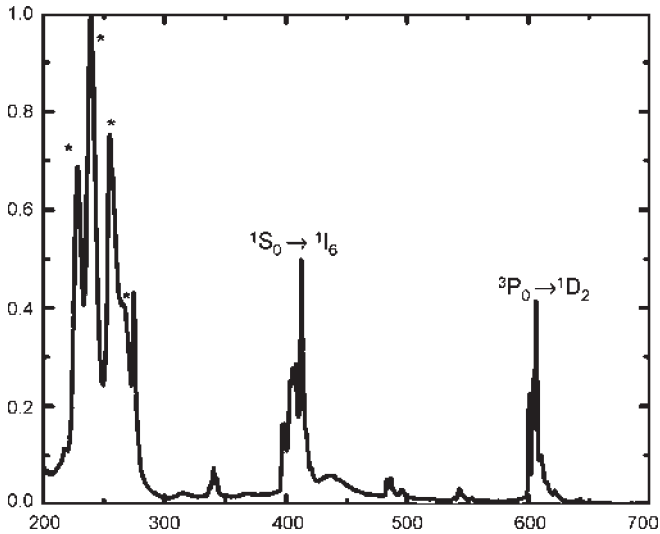


Fig. 4.7 Emission spectrum of $\text{LaPO}_4:\text{Pr}^{3+}$ at $T = 1.6 \text{ K}$ ($\lambda_{\text{ex}} = 185 \text{ nm}$); peaks labeled with an asterisk are transitions from the $\text{Pr}^{3+} 4f^1 5d^1$ configuration.

Fig. 4.7 shows the emission spectrum of $\text{LaPO}_4:\text{Pr}^{3+}$ ($\lambda_{\text{ex}} = 193 \text{ nm}$) at $T = 1.6 \text{ K}$. Clearly, the situation changes dramatically at low temperature. In addition to the interconfigurational transitions, sharp line emission emanating from the $^1\text{S}_0$ state is clearly observed (Fig. 4.7). Note that the $^1\text{S}_0 \rightarrow ^1\text{I}_6$ transition dominates the emission spectrum.

The lifetime and the intensity of the $^1\text{S}_0 \rightarrow ^1\text{I}_6$ transition remain constant in the range of 1.6–25 K. The radiative lifetime of the $^1\text{S}_0$ state is determined to be 145 ns. This fast decay time indicates that the $^1\text{S}_0$ state is strongly perturbed by the close-lying $4f^1 5d^1$ states. The lifetime shortens rapidly as the temperature is raised beyond 25 K, which indicates the onset of nonradiative transitions within the $^1\text{S}_0$ state. The activation energy for temperature quenching was determined to be 164 cm^{-1} . Since $kT \approx 200 \text{ cm}^{-1}$ at room temperature it is clear that there is a very high probability of classically mounting the potential barrier of 164 cm^{-1} . This explains the absence of $^1\text{S}_0$ emission at room temperature. It was determined that with increasing temperature, the $^1\text{S}_0$ state simply depopulates into the lowest energy $4f^1 5d^1$ state, which explains the intensity and lifetime quenching of the $^1\text{S}_0$ state. It also explains the observation that the total quantum efficiency ($^1\text{S}_0 + 4f^1 5d^1$ emission intensity) remains fairly constant through the temperature range.

Detailed analysis of the optical spectra of $\text{LaPO}_4:\text{Pr}^{3+}$ suggests that the relaxed excited state of the $4f^1 5d^1$ configuration is located below that of the $^1\text{S}_0$ level. It is not often that we encounter a situation where the $^1\text{S}_0$ emission is observed when the (relaxed) $4f^1 5d^1$ state is energetically below the $^1\text{S}_0$ level. The reason for the positioning of the relaxed $4f^1 5d^1$ state below that of the $^1\text{S}_0$ level is the following. As previously noted, the excitation spectrum (unrelaxed state) shows that the lowest energy component of the $4f^1 5d^1$ state is

located energetically above the 1S_0 state. In the excited $4f^15d^1$ state, the geometry of the Pr^{3+} site relaxes significantly, as evidenced by the rather large Stokes shift ($\sim 5000 \text{ cm}^{-1}$) of the Pr^{3+} emission. The large Stokes shift results in a significant lowering of the Pr^{3+} $4f^15d^1$ edge, which results in the $4f^15d^1$ level being located below the 1S_0 state. Hence, it is the large Stokes shift of the Pr^{3+} emission which is responsible for the positioning of the $4f^15d^1$ level below that of the 1S_0 level. It is this placement of the 1S_0 and $4f^15d^1$ energy levels in the relaxed excited state that gives rise to the interesting temperature dependence of the Pr^{3+} luminescence in the LaPO_4 host lattice.

4.4

The Quantum Efficiency of the Quantum-splitting Process

In this section we examine the important factors that determine the visible quantum efficiency obtained in the quantum-splitting process. It is important to emphasize that the simple observation of quantum splitting by a Pr^{3+} -activated phosphor does not necessarily imply visible quantum efficiency in excess of unity. As we will show, high quantum efficiency requires the proper site symmetry around the Pr^{3+} ion to be chosen so as to maximize the desired transition rate.

Taking the 1S_0 state as the initial excited state, we wish to estimate the probability that, in the radiative decay to the Pr^{3+} 3H_4 ground state, two photons are emitted. We see from Fig. 4.2 (and Table 4.1) that the transitions to any of the levels 1I_6 , 3P_J ($J=0,1,2$) will generate a useful visible photon, but photons resulting from transitions to any of the levels lying below the aforementioned states and including 1D_2 are “lost” since they are of too high energy for lighting application. We must also take into account the fact that even though the photon resulting from the $^1S_0 \rightarrow ^1D_2$ optical transition is not useful, the highest energy transition originating from the 1D_2 state ($^1D_2 \rightarrow ^3H_4$, emission near 600 nm) will generate a useful visible photon (all other transitions from the 1D_2 to the ground states are in the infrared and therefore of no interest for lighting applications).

In Fig. 4.8, let η_1 represent the probability that the initial radiative transition from the 1S_0 state will yield a visible photon ($^1S_0 \rightarrow ^1I_6, ^3P_2$ are the only two optical transitions that generate useful photons), let η_2 represent the probability that subsequent radiative transition from the 3P_0 state will yield a visible photon, let p_d represent the probability of the $^1S_0 \rightarrow ^1D_2$ transition, and let η_3 represent the probability of $^1D_2 \rightarrow ^3H_4$ (the only transition that generates a useful visible photon). The total quantum efficiency η_T of the conversion of the VUV photon to useful visible radiation is then given by [43].

$$\eta_T = \eta_1(1 + \eta_2) + p_d\eta_3 \quad (2)$$

Continuing with the general requirements for obtaining greater than unity visible quantum efficiency, we see that since the 1S_0 and 1I_6 states are predominantly singlet states with $S=0$, the transition probability $^1S_0 \rightarrow ^1I_6$ is overwhelmingly favored over

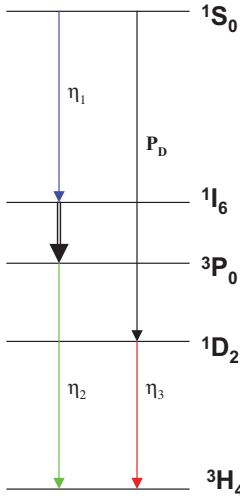


Fig. 4.8 Schematic energy level diagram of the Pr^{3+} ion for estimating the efficiency of the quantum splitting process; see text.

the ${}^1\text{S}_0 \rightarrow {}^3\text{P}_j$ transition probability because the former transition satisfies the $\Delta S = 0$ selection rule. Similarly, the optical transition with the highest probability emanating from the ${}^1\text{S}_0$ state and terminating in states below the ${}^1\text{I}_6$ state is the ${}^1\text{S}_0 \rightarrow {}^1\text{G}_4$ transition.

It is thus clear that optical transitions of the type ${}^1\text{S}_0 \rightarrow {}^1\text{G}_4$, which convert the incident UV photon into another UV photon and an IR photon should be minimized in favor of the ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transition. In the Judd-Ofelt theory, the strength of the ${}^1\text{S}_0 \rightarrow {}^1\text{G}_4$ transition depends on the Ω_4 parameter, while Ω_6 determines the strength of the ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transition. Hence, for quantum yields in excess of unity, Ω_6 must dominate over Ω_4 and Ω_2 . In other words, the quantum yield for the first step is low unless the condition $\Omega_6 \gg \Omega_4, \Omega_2$ is satisfied [1,44].

The foregoing discussions shows that the condition for greater than unity quantum yield is: $\Omega_2/\Omega_6 = \Omega_4/\Omega_6 = 0$ and $\Omega_6 \neq 0$. An example of this is seen in the visible quantum yield of Pr^{3+} -activated YF_3 (quantum efficiency = 1.46) and LaF_3 (quantum efficiency = 0.83). Table 4.2 shows that the relative size of the Ω_k values indeed determine whether a quantum-splitting phosphor will exhibit greater than unity quantum yield. It is clear that the much reduced efficiency in the case of $\text{LaF}_3:\text{Pr}^{3+}$ is due to the presence of the Ω_4 term. The ratio Ω_2/Ω_6 is satisfactorily small (<0.25) but the value of $\Omega_4/\Omega_6 = 0.37$ is still too large. The predicted yield for the ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transition in LaF_3 is only 0.44 (in YF_3 it is 0.79, see Table 4.1), and since the overall yield is dependent on the ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$ transition (first photon emission) it is not surprising that the visible quantum efficiency of this phosphor does not exceed unity [44]. We therefore conclude that the site symmetry properties offered by the YF_3 host

Tab. 4.2 Judd-Ofelt intensity parameters (Ω_k) for Pr^{3+} -activated YF_3 and LaF_3 .

Materials	Ω_2	Ω_4	Ω_6	Visible quantum yield
YF_3	0.13	0.70	10.00	1.46
LaF_3	0.12	1.77	4.78	0.83

are apparently sufficient for generating high quantum efficiency of luminescence. In the extreme case in which only the Ω_6 term is non-zero, we would anticipate $\eta_1 \approx 1$ and $\eta_2 \approx 1$, so that $\eta_T \approx 2$ [see Eq. (1)], and hence the quantum-splitting process would be 100% efficient.

For the oxide quantum-splitting phosphor, $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$, the Judd-Ofelt ratios Ω_2/Ω_6 (0.23) and Ω_4/Ω_6 (0.59) have been determined from the single-crystal absorption measurements [45]. These ratios have been used to estimate a maximum visible quantum efficiency of only 50% under VUV excitation. The rather poor performance of $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ occurs as a result of having a large Ω_4/Ω_6 ratio relative to that in YF_3 . It is clear from the emission spectrum that the $^1\text{S}_0 \rightarrow ^1\text{G}_4$ ($^1\text{S}_0 \rightarrow ^3\text{F}_4$) optical transition dominates the emission spectrum (Fig. 4.5). As previously discussed, the strength of this transition depends on the Ω_4 parameter. Hence, the rule for obtaining quantum yield in excess of unity (Ω_6 should dominate over Ω_4 and Ω_2) is not satisfied in this host lattice. Consequently, it is not surprising that visible quantum efficiency in excess of unity is not achieved in this material.

Experimentally, the room temperature quantum efficiency of $\text{SrAl}_{12}\text{O}_{19}:\text{Pr}^{3+}$ measured relative to $\text{YF}_3:\text{Pr}^{3+}$ is only 27%, and hence there is an apparent discrepancy between this and the estimation from the Judd-Ofelt theory. This strongly suggests that the assumption that nonradiative decay from the $^1\text{S}_0$ level does not occur is incorrect, at least for this host lattice. Experimentally, we find that the decay of the $^1\text{S}_0$ state in $\text{SrAl}_{12}\text{O}_{19}$ at $T = 10$ K is a single exponential with a decay time of ~ 600 ns (radiative decay rate of $1.66 \times 10^6 \text{ s}^{-1}$) [30]. However, as the temperature is raised from 10 K to room temperature, the lifetime of the $^1\text{S}_0$ state shortens and at room temperature a lifetime of ~ 500 ns is measured. The onset of lifetime quenching (and hence the onset of nonradiative transitions) is observed at about 100 K. At the present time it is not possible to give a quantitative explanation for this quenching. As previously discussed, MPR of the $^1\text{S}_0$ level cannot compete with the radiative relaxation, so we can rule out this mechanism as the culprit in the shortening of the lifetime. We speculate that energy transfer from the $^1\text{S}_0$ state to unavoidable lattice defect sites in $\text{SrAl}_{12}\text{O}_{19}$ is responsible for the quenching of $^1\text{S}_0$ luminescence.

In $\text{LaMgB}_5\text{O}_{10}:\text{Pr}^{3+}$, the branching ratio for the $^1\text{S}_0 \rightarrow ^1\text{I}_6$ transition is favorable, but the relative quantum efficiency (relative to $\text{YF}_3:\text{Pr}^{3+}$) is only 42%. The chief reason for this low quantum yield is the very efficient MPR of the $^3\text{P}_0$ state to the $^1\text{D}_2$ state (as previously discussed) and this combined with the low visible quantum efficiency of $^1\text{D}_2$ emission results in a relative poor quantum yield for the quantum-splitting process. A similar observation is made in the case of $\text{SrB}_4\text{O}_7:\text{Pr}^{3+}$ [46]. We

restate for the purpose of emphasis that no useful quantum-splitting phosphors are anticipated in borates or phosphates host lattices because their lattices tend to exhibit high effective phonon energy so that a small number of phonons are required to bridge the $^3P_0 - ^1D_2$ energy gap via the MPR process.

Kück et al. [47] have investigated quantum splitting in a large number of Pr³⁺-activated fluorides and have estimated the visible quantum efficiency (defined as the number of emitted photons in the 390–750 nm spectral range per absorbed ultra-violet photon) and the relevant Ω_2/Ω_6 and Ω_4/Ω_6 parameters. It again becomes clear from their work that the relative magnitude of Ω_2/Ω_6 and Ω_4/Ω_6 ratios is the principal factor determining the efficiency of the quantum-splitting process. The optimum theoretical efficiency of two can only be obtained when Ω_6 is non-zero. These authors have also investigated the dependence of quantum efficiency on structural parameters such as the coordination number and the effective metal-to-ligand bond distance (R_{eff}). R_{eff} is defined as $R_i - 0.6\Delta R$, where R_i is the metal-to-ligand bond distance and ΔR is the difference between the ionic radii of the Pr³⁺ ion and the ion that it substitutes for in the host lattice. Thus, R_{eff} takes into account the lattice relaxation upon the introduction of Pr³⁺ ion into the host lattice. They conclude that all lattices supporting quantum splitting offer an eight-coordinated site for the Pr³⁺ ion. They further conclude that the highest quantum efficiency is obtained in materials in which the condition $2.1 \text{ \AA} < R_{\text{eff}} < 2.5 \text{ \AA}$ is satisfied.

It is clear from the foregoing discussions that the quantum-splitting process in Pr³⁺-based systems is only efficient if the values of the three Judd-Ofelt parameters fall within a limited range, and this fundamental rule restricts the selection of the host lattice. In fact it goes to exclude a number of possible host lattices.

4.5

Limitations of Pr³⁺-based Quantum-splitting Phosphors

The visible emission that results from the quantum splitting of the VUV photon by the Pr³⁺ ion is not directly suitable for use as a white light source. As shown in Fig. 4.3, the emission consists of a strong line in the deep blue near 405 nm from the initial radiative decay in the quantum-splitting process ($^1S_0 \rightarrow ^1I_6$) and several weaker lines in the 484 nm and 610 nm (emission from the 3P_0 state), which are perceived by the human eye as blue and red, respectively. The overall phosphor emission is thus lacking in the green, and the strong emission near 405 nm is essentially wasted because the human eye is virtually insensitive to that wavelength. An ideal improvement to the phosphor is to somehow shift the emission near 405 nm close to the peak of the eye sensitivity curve, around 555 nm (in the green).

Attempts have been made to shift the emission near 405 nm to the green by means of energy transfer processes. For example, the $^1S_0 \rightarrow ^1I_6$ emission transition at 405 nm in YF₃ (and other fluorides such as SrAlF₅, CaF₂, LiBaF₃, and SrY₂F₈) exhibits a strong spectral overlap with the Mn²⁺ $^6A_1 \rightarrow ^4A_1, ^4E$ absorption transitions [48,49]. The Mn²⁺ ion in these fluorides emits in the green via the $^4T_1 \rightarrow ^6A_1$ optical transition (emission maximum near 500 nm). We would therefore anticipate

efficient $\text{Pr}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer and the conversion of 405 nm radiation to useful green light. However, it has been found experimentally that this energy transfer is very inefficient. For example, the decay of the $\text{Pr}^{3+} \ ^1\text{S}_0 \rightarrow \ ^1\text{I}_6$ emission transition in YF_3 (590 ns; single exponential) is unaltered upon the introduction of Mn^{2+} ion in rather high concentrations (5 mol %) [49]. This indicates that the $\text{Pr}^{3+} \rightarrow \text{Mn}^{2+}$ energy transfer is inefficient despite the favorable spectral overlap. At the present time it is not possible to give a quantitative explanation for this observation in terms of either the nature of energy transfer (dipole-dipole or exchange interaction) or the chemical composition and crystal structure of the host lattice.

4.6

Quantum-splitting Phosphors Based on Gd^{3+} and Rare Earth Ion-Activated Fluoride Materials

4.6.1

The Electronic Energy Level Structure of the Gd^{3+} Ion

The mechanism of quantum splitting as proposed in Fig. 4.1b is satisfied in concentrated Gd^{3+} -based luminescent materials. Before describing this mechanism of quantum splitting, it will be beneficial to discuss the “extended” energy level diagram of the Gd^{3+} ion. In 1967, Piksís et al. determined the Gd^{3+} energy levels in hexagonal LaCl_3 , up through $^6\text{D}_{7/2}$ level ($40\,590\text{ cm}^{-1}$) [50]. In a more recent study, Wegh et al. have extended and surveyed the Gd^{3+} energy levels in the vacuum-ultraviolet spectral region ($50\,000\text{--}70\,000\text{ cm}^{-1}$) [51]. They have also carried out detailed calculations of energy levels on the $\text{Gd}^{3+} 4f^7$ configuration and assigned all the experimentally observed spectral lines to free-ion term symbols. The most interesting result of their study is the identification of $^6\text{G}_J$ levels around $50\,000\text{ cm}^{-1}$ (see Fig. 4.9).

The energy separation between the $^6\text{G}_J$ and the $^6\text{P}_J$ level (the first excited level of Gd^{3+}) is about $16\,500\text{ cm}^{-1}$. This large energy separation ensures that MPR cannot quench the luminescence of the $^6\text{G}_J$ manifold. In fact, it suggests the possibility of $^6\text{G}_J \rightarrow ^6\text{P}_J$ radiative relaxation with narrow line emission in the orange-red spectral region. This is in fact observed experimentally (see Fig. 4.10) and constitutes the first observation of visible emission from the Gd^{3+} ion.

Note that the subsequent $^6\text{P}_J \rightarrow ^8\text{S}_{7/2}$ emission (in the ultra-violet, line emission near 310 nm) represents the sequential emission of photons ($^6\text{G}_J \rightarrow ^6\text{P}_J + ^6\text{P}_J \rightarrow ^8\text{S}_{7/2}$), which is exactly described by the hypothetical energy level diagram of Fig. 4.1a. Hence, this quantum-splitting process results in the generation of an orange-red and an ultra-violet photon. However, the visible quantum yield for this process is exceedingly low because of the strong probability of the $^6\text{G}_J$ level decaying radiatively to the $^8\text{S}_{7/2}$ ground state. As a concluding note to the energy level structure of Gd^{3+} , we draw attention of the reader to a recent study where excited-state excitation (resonant two-photon excitation) from the $^6\text{P}_{7/2}$ level is shown to identify the Gd^{3+} levels located beyond $50\,000\text{ cm}^{-1}$ with high resolution [52,53]. Luminescence from Gd^{3+} levels

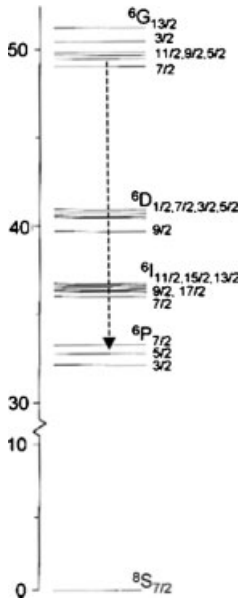


Fig. 4.9 Energy level diagram of Gd^{3+} in fluoride lattice; note the possibility of visible emission through the ${}^6G_J \rightarrow {}^6P_J$ optical transition (adapted from Ref. [71]).

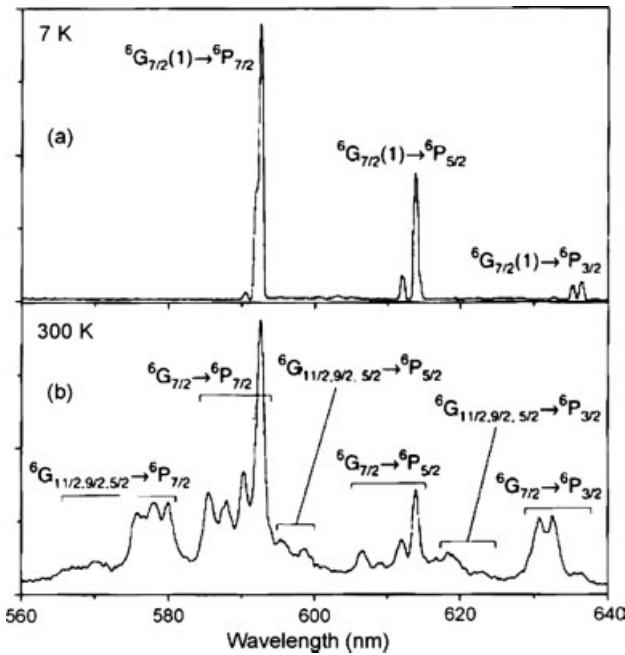


Fig. 4.10 Orange-red emission (${}^6G_J \rightarrow {}^6P_J$) of Gd^{3+} in $LiYF_4$ at (a) $T = 7\text{ K}$ and (b) $T = 300\text{ K}$ (adapted from Ref. [71]).

lying near $60\,000\text{ cm}^{-1}$ after one- and two-photon excitation has been reported in oxyfluoroborate glass [54].

4.6.2

Quantum Splitting in the $\text{Gd}^{3+}\text{-Eu}^{3+}$ System

The $\text{Gd}^{3+}{}^6\text{G}_J$ manifold can be used as the starting point for a quantum-splitting process which generates two red photons. Wegh et al. [55,56] have attained a quantum yield near 200 % in Eu^{3+} -doped LiGdF_4 (and GdF_3) when the Gd^{3+} ions of the host lattice were excited by VUV light in a process labeled quantum splitting via down-conversion. Fig. 4.11 shows the electronic energy structure of Gd^{3+} and Eu^{3+} ions and the energy transfer processes that result in the emission of two (red) photons. The incident VUV photons are absorbed by the ions via the transition ${}^8\text{S}_{7/2} \rightarrow {}^6\text{G}_J$; the $\text{Gd}^{3+}{}^6\text{G}_J$ states occur at about $50\,000\text{ cm}^{-1}$. As previously discussed, the ${}^6\text{G}_J \rightarrow {}^6\text{P}_J$ radiative decay results in line emission near 590 nm (see Fig. 4.10). Alternatively, this energy can be transferred to the Eu^{3+} ion, because this emission is in near-resonance with the $\text{Eu}^{3+}{}^5\text{D}_0 \rightarrow {}^5\text{D}_3$ absorption transition. The radiative decay of the $\text{Eu}^{3+}{}^5\text{D}_0$ state to the ground states generates the first photon through this cross relaxation process (step 1 in Fig. 4.11). Further, the migrating energy over the $\text{Gd}^{3+}{}^6\text{P}_J$ state is captured by a second Eu^{3+} ion to produce the second photon in the quantum-splitting process (step 2 in Fig. 4.11). In this way, two red photons are produced per incident VUV photon. In theory, an overall quantum yield as high as 200 % is attainable by this process.

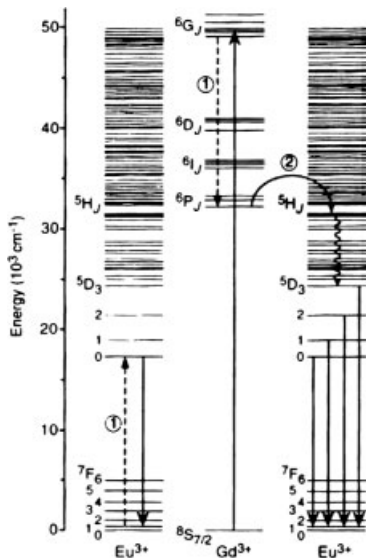


Fig. 4.11 Energy level diagram of $\text{Gd}^{3+}\text{-Eu}^{3+}$ couple showing the process of quantum splitting through the ${}^6\text{G}_J$ state (adapted from Ref. [71]).

The efficiency of the quantum-splitting process can easily be determined from the emission spectrum by exciting the sample at two different wavelengths, (a) at 202 nm, which corresponds to the ${}^8S_{7/2} \rightarrow {}^6G_J$ transition and (b) at 273 nm, which corresponds to the ${}^8S_{7/2} \rightarrow {}^6I_J$ transition. Note from Fig. 4.11 that the latter excitation transfers energy to the Eu^{3+} ion through the 5H_J levels. After multiphonon relaxation, Eu^{3+} luminescence from the 5D_3 , 5D_2 , 5D_1 , and 5D_0 levels is observed. This is the normal emission of the Eu^{3+} ion in $LiGdF_4$. Excitation into the 6G_J level leads to the cross relaxation process, and this results in an increase in the 5D_0 emission intensity relative to the 5D_3 emission intensity. Figure 4.12 shows the emission spectrum of $LiGdF_4:Eu^{3+}$ under the two different excitation wavelengths.

Indeed, the ${}^5D_0/{}^5D_1$ emission intensity ratio is higher for ${}^8S_{7/2} \rightarrow {}^6G_J$ excitation, which confirms the cross relaxation path (step 1 in Fig. 4.11). The visible quantum efficiency can be estimated from the integrated emission intensities by assuming that all Gd^{3+} ions excited in the 6G_J and 6I_J levels transfer their energy to the Eu^{3+} ion, which results in ${}^5D_{0,1,2,3}$ emission [55]:

$$P_{CR}/(P_{CR} + P_{DT}) = [R({}^5D_0/{}^5D_{1,2,3})]^G - [R({}^5D_0/{}^5D_{1,2,3})]^I / [R({}^5D_0/{}^5D_{1,2,3})]^I + 1 \quad (3)$$

where P_{CR} and P_{DT} are the probabilities of cross relaxation and direct transfer from the $Gd^{3+}{}^6G_J$ level to the Eu^{3+} ion, and $[R({}^5D_0/{}^5D_{1,2,3})]^G$ and $[R({}^5D_0/{}^5D_{1,2,3})]^I$ are the ${}^5D_0/{}^5D_{1,2,3}$ emission intensity ratios after excitation into the $Gd^{3+}{}^6G_J$ and 6I_J levels, respectively. Note that direct energy transfer from the $Gd^{3+}{}^6G_J$ level to the Eu^{3+} ion

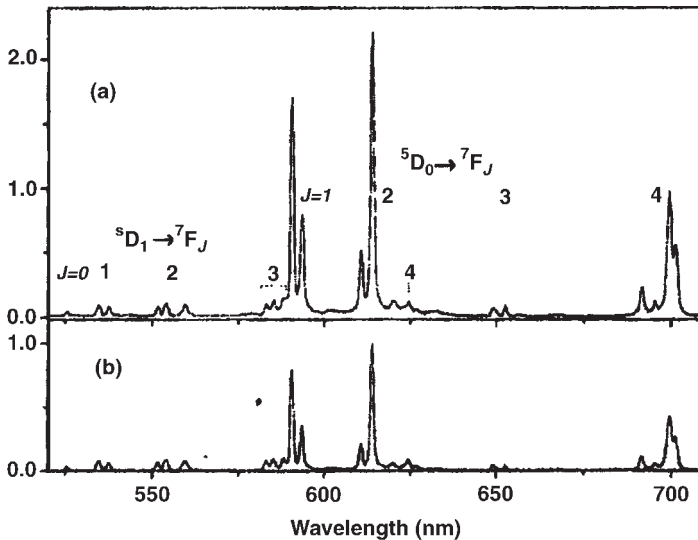


Fig. 4.12 Room-temperature emission spectrum of $LiGdF_4:Eu^{3+}$ under (a) ${}^8S_{7/2} \rightarrow {}^6G_J$ excitation ($\lambda_{ex} = 202$ nm) and (b) ${}^8S_{7/2} \rightarrow {}^6I_J$ excitation ($\lambda_{ex} = 273$ nm); the spectra are scaled to the ${}^5D_1 \rightarrow {}^7J_1$ emission intensity (adapted from Ref. [71]).

is possible and has been observed [55,56]. Therefore, not all the $\text{Eu}^{3+5}\text{D}_0$ emission intensity originates from the cross relaxation process. However, the ${}^5\text{D}_0/{}^5\text{D}_{1,2,3}$ emission intensity increases by a factor of 2.3 when exciting into the ${}^6\text{G}_J$ level relative to ${}^6\text{I}_J$ excitation. Proper integration of the emission intensity yields $P_{\text{CR}}/(P_{\text{CR}} + P_{\text{DT}}) = 0.90$. This means that 90 % of the Gd^{3+} ions excited into the ${}^6\text{G}_J$ level relax via the two-step energy transfer process, and in the absence of any other nonradiative processes, the quantum efficiency upon excitation into the ${}^6\text{G}_J$ level is approximately 190 %.

We stress that this high quantum efficiency value reflects an internal yield because it only describes the process of converting the energy of $\text{Gd}^{3+} {}^6\text{G}_J$ states into visible photons. In other words, the internal quantum efficiency refers to those absorbed photons which result in the population of the $\text{Gd}^{3+6}\text{G}_J$ state. Any competitive absorption process that would not result in the population of the $\text{Gd}^{3+6}\text{G}_J$ state is not taken into account. Any such parasitic absorption (for example, due to defects in the host lattice) will certainly reduce the external quantum efficiency of the phosphor.

This brings us to the work of Feldmann et al. [57], who have measured the external quantum yield of the down-conversion phosphor $\text{LiGdF}_4:\text{Eu}^{3+}$. Based on the integrated intensity in the emission spectra, they have indeed confirmed an internal quantum efficiency of 195 % when exciting directly into the $\text{Gd}^{3+6}\text{G}_J$ states. The external quantum efficiency and the absolute light output (the light output is defined as the number of emitted photons expressed as a percentage of the number of incident photons) has been determined relative to the standard $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphor. We encourage the reader to consult Ref. [57] for the experimental details. This measurement yielded an external quantum efficiency of only 32 %, which included the effect of quantum splitting (excitation under 202 nm; ${}^8\text{S}_{7/2} \rightarrow {}^6\text{G}_J$). The external quantum efficiency drops to 16 % if the quantum-splitting effect is ignored.

The reason for the rather low (and disappointing) external quantum efficiency is that a substantial amount of incident photons are absorbed by defect centers in the host lattice. The onset of a broad absorption band near 350 nm is observed, and the reflectance of pure LiGdF_4 (a material with a band gap of about 10 eV) at 202 nm was only about 50 %. The broad absorption band was attributed to the presence of defect center(s) in the host lattice. It is thus clear that the competitive absorption of the incident photons by the host lattice defect center(s) and its subsequent nonradiative relaxation depletes the population of $\text{Gd}^{3+6}\text{G}_J$ state. This results in a very low external quantum efficiency of $\text{LiGdF}_4:\text{Gd}^{3+}$. It is thus imperative that the synthesis of the fluoride-based quantum-splitting material is optimized to reduce the lattice defect concentration.

Another issue arising in quantum-splitting phosphors that are centered on the Gd^{3+} ion is the rather poor absorption of the incident radiation because the intraconfigurational transition ${}^8\text{S}_{7/2} \rightarrow {}^6\text{G}_J$ is both spin and parity forbidden. Hence, the Gd^{3+} ion will not efficiently absorb radiation produced by any discharge source. Consequently, the use of a sensitizer that will efficiently absorb the discharge radiation and transfer the energy to the $\text{Gd}^{3+6}\text{G}_J$ state

is required. Note that the sensitizer energy level structure should be such that it does not interfere with the quantum-splitting behavior of the (Gd^{3+} - Eu^{3+}) pair. A US patent application advocates the use of ions with ns^2 electronic configuration (Tl^+ , Pb^{2+} , and Bi^{3+}) as sensitizing ions for the absorption into the $Gd^{3+}6G_J$ state [58].

4.6.3

Quantum Splitting in the Er^{3+} - Gd^{3+} - Tb^{3+} System

Wegh et al. [59,60] have also demonstrated higher than unity quantum yield (internal quantum efficiency) in the phosphor conversion of VUV excitation into green light by a similar scheme. This process, which involves three ions Er^{3+} , Gd^{3+} , and Tb^{3+} is shown in Fig. 4.13.

The investigated host lattice was $LiGdF_4$. Several $Er^{3+} 4f^{10}5d^1 \rightarrow 4F_J, 4G_J$ optical transitions exhibit strong spectral overlap with the Gd^{3+} absorption transitions ($8S_{7/2} \rightarrow 6P_J, 6I_J, 6D_J$). Therefore, efficient energy transfer from Er^{3+} to Gd^{3+} is expected due to a cross relaxation process after excitation takes place in the $Er^{3+} 4f^{10}5d^1$ level. This cross relaxation process populates the $Er^{3+}4S_{3/2}$ state (the cross relaxation populates Er^{3+} energy states between the $4S_{3/2}$ and $4G_{11/2}$ levels, and efficient multiphonon relaxation populates the $4S_{3/2}$ level). The emission transition $4S_{3/2} \rightarrow 4I_{15/2}$ produces the first green photon (near 550 nm; step 1 in Fig. 4.13). The $4f^{10}5d^1 \rightarrow 4S_{3/2}$ optical transition further excites the $Gd^{3+}8S_{7/2} \rightarrow 6P_J, 6I_J, 6D_J$ transitions. Multiphonon relaxation populates the lowest energy $Gd^{3+}6P_J$ multiplet. Because of the high Gd^{3+} concentration, the energy migrates rapidly over the $Gd^{3+}6P_J$ state. The intentionally added acceptor Tb^{3+} ions act as traps for the

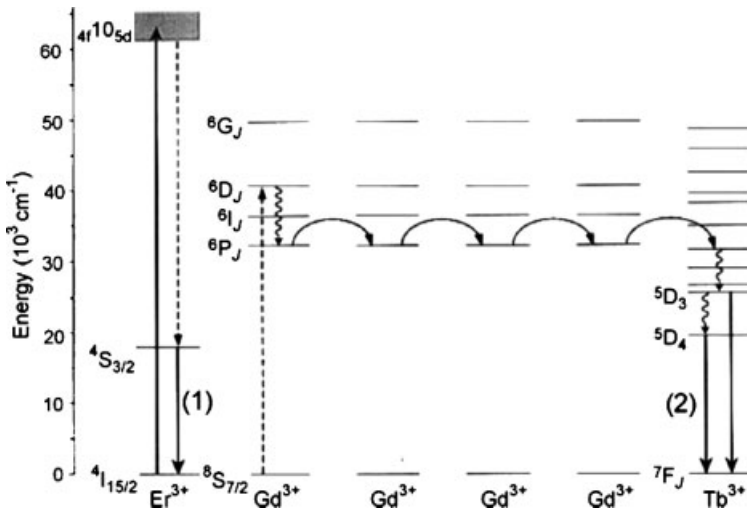


Fig. 4.13 The process of quantum splitting in $LiGdF_4:Er^{3+},Tb^{3+}$ (adapted from Ref. [71]).

migrating energy. This sensitization process results in the generation of a second green photon through the Tb^{3+} ion ${}^4\text{D}_J \rightarrow {}^7\text{F}_J$ emission transitions (step 2 in Fig. 4.13). The visible quantum efficiency of this system is estimated to be some 110%.

The main drawback of this mechanism is that the concentration of the activator ion (Tb^{3+}) must be very low to (a) prevent the direct absorption of the VUV photon by the Tb^{3+} ion, (b) prevent additional nonradiative relaxation due to cross relaxation within the ($\text{Er}^{3+} + \text{Tb}^{3+}$) system and (c) prevent direct energy transfer from the Er^{3+} $4f^{10}5d^1$ to the Tb^{3+} ion. Thus, in LiGdF_4 , the nominal concentrations are ~ 1.5 mol% Er^{3+} and 0.3 mol% Tb^{3+} , respectively. At these low Tb^{3+} concentrations, the optical transitions from the $\text{Tb}^{3+}5\text{D}_3$ state (in the blue-green) dominate the emission spectrum. Thus, it is difficult to realize phosphors with higher than unity quantum efficiency and the desired green color. Direct sensitization of the Dy^{3+} ion via the Er^{3+} $4f^{10}5d^1$ state has also been observed in CsGd_2F_7 [61].

Another drawback of this system that may limit the visible (green) quantum efficiency is the back transfer of the migrating excitation energy from the $\text{Gd}^{3+} {}^6\text{P}_J$ states to the $\text{Er}^{3+} {}^2\text{P}_{3/2}$ state. This results in strong emission at 401 nm and 469 nm, respectively [61]. We note that the external quantum efficiency of $\text{LiGdF}_4:\text{Er}^{3+}, \text{Tb}^{3+}$ has not been determined.

4.7

Multiphoton Emission through High-energy Excitation

Multiphoton emission processes in standard commercial phosphors such as $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ were reported by Ilmas and Savikhina [62]. Later, Berkowitz and Olsen, utilizing synchrotron radiation, confirmed and extended the work [63]. The mechanism underlying the generation of more than one photon is schematically shown in Fig. 4.14.

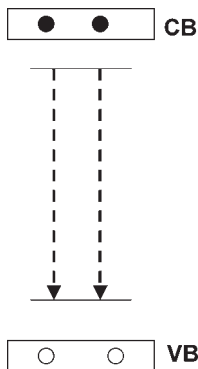


Fig. 4.14 Schematic energy level diagram showing the emission of two photons by the luminescent ion through the interband Auger process; VB = host lattice valence band; CB = host lattice conduction band; open circles are the holes in the VB, and filled circles are the electrons in the CB.

The incident photons must have energy which is at least twice the band gap energy of the host lattice. Through the interband Auger process, in which secondary electron-hole pairs are produced from the primary electron-hole pair (formed by the incident photon), two or more electron-hole pairs are created. The consequence of the eventual recombination of these electron-hole pairs at the luminescent ion site is multiphoton emission and hence a quantum efficiency exceeding unity. The threshold energy for multiphoton emission due to the interband Auger process occurs at energy values greater than integral multiples of the band gap energy.

The published aspects of this work report the quantum efficiency of a variety of phosphor materials on exciting by photons with energies in the 5–21 electron volts range. Quantum yields in excess of unity were indeed observed in certain phosphor materials but under very high-energy photon excitation, indicating that the process is driven by the interband Auger transitions, as previously discussed. For example, the quantum yield of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (standard red emitting phosphor, band gap of 5.6 eV) phosphor material rises to 2.39 (± 0.38) when exciting by photons with energies of 17–25 electron volts, suggesting the emission of at least two photons. Band structure calculations have proven to be useful in providing a satisfactory explanation of the quantum yield beyond the threshold energy [64]. However, the energy loss for such energetic ultraviolet photons is severe, implying that the phosphor must have a very high quantum efficiency for practical application. As a practical matter, no such sufficiently high quantum efficiency has been demonstrated, and arguments have been developed that this mechanism for quantum splitting cannot further increase the energy efficiency of luminescent devices [65].

4.8 Applications of Quantum-splitting Phosphors

Conventional low-pressure fluorescent lamps employ mercury as the active species for generating the ultraviolet radiation. Environmental issues regarding the disposal of these fluorescent lamps in solid-waste landfills has provided the impetus for developing a mercury-free replacement for conventional fluorescent lamps. One can envision a fluorescent lamp where a low-pressure xenon discharge (emitting at 147 nm) excites suitable phosphors to generate white light. However, the lamp efficiency issue prevents any consideration of conventional phosphors as white light-generating materials in such a fluorescent lamp.

The overall conversion efficiency of a fluorescent lamp can be written very approximately as

$$\eta_{\text{lamp}} \approx \eta_{\text{dis}} [\varepsilon_{\text{vis}} / \varepsilon_{\text{uv}}] \text{QE} \quad (4)$$

where η_{dis} is the discharge efficiency for converting electric power to ultraviolet power, ε_{vis} is the weighted average energy of the spectrum of visible photons emitted by the phosphor (555 nm), ε_{uv} is the energy of the photon emitted by the discharge and absorbed by the phosphor, and QE is the quantum efficiency of the phosphor. The efficiency of conventional mercury based fluorescent lamp is (very approximately):

0.25~0.65 [254 nm/555 nm] 0.85. These figures do not seem clear.→. The relatively low overall conversion efficiency of 25 % is due to the large energy loss denoted in Eq. (4) by the ratio $[\epsilon_{\text{vis}}/\epsilon_{\text{uv}}]$, which accounts for the fact that each ultraviolet photon incident on the phosphor carries nearly 5 eV of energy, while each emitted photon by the phosphor carries barely more than 2 eV of energy. This single process is responsible for nearly 55 percent of the energy loss in conventional fluorescent lamps.

If we wish to reproduce the energy conversion efficiency of conventional fluorescent lamp but with a Xe discharge emitting mainly at 147 nm, the higher energy loss (in the conversion of 147 nm photons to visible radiation at 555 nm) can be offset by higher phosphor quantum efficiency. The energy conversion efficiency of a fluorescent lamp with a practical quantum-splitting phosphor with a quantum efficiency of 140 percent is: 0.25~0.65 [147 nm/555 nm] 1.40. Hence one can immediately recognize the benefit of a quantum-splitting phosphor in devices that employ VUV emission of rare gas discharge as the primary exciting source.

A color plasma flat-panel display consists of an intermittent atmosphere pressure xenon discharge, which excites red, green, and blue phosphors to form color images. The desirable 147 nm and 173 nm VUV radiation is produced when the electronically excited Xe monomers and excimers, respectively, decay radiatively to the ground state. Relative to the mercury discharge in low-pressure mercury fluorescent lamps, the discharge conversion efficiency of electric power to VUV radiation in PDPs is rather inefficient – about 6 %. This inefficiency is related to the cell geometry. In PDPs, nearly 70 % of the input power will be lost when the phosphor converts each 7 eV (172 nm) Xe photon to a visible photon with an average energy of about 2 eV. Further, nearly 75 % of the energy is lost in the conversion of an incident 147 nm xenon photon into a ~555 nm visible photon. Clearly, any development of a practical quantum-splitting phosphor would be of great interest to the manufacturers of PDPs.

4.9 Conclusions

The foregoing discussions show that the phosphor, which appeared as a weak link in the energy conversion process, can be improved by developing quantum-splitting phosphors. The breakthrough in new materials for making practical quantum-splitting phosphors could lead to the development of mercury-free fluorescent lamps; it is reasonable to envision the development of such lamps with an overall conversion efficiency of 25 %, which is comparable to that of existing mercury-based lamps. Any new quantum-splitting material must be compatible with traditional lamp/display device fabricating conditions and must satisfy the various requirements for use in the proposed device. We note that no such material has been turned into a commercially viable phosphor, although significant effort continues in the development of such phosphors because of the game-changing technologies that become possible with this interesting class of luminescent materials. We hope that this chapter serves to illustrate the thinking processes that go into the development of

energy-efficient light sources and highlights the important role of fundamental research as a route to major advances in lighting and display technologies.

Finally, there are some useful articles that the reader may consult for general background and some additional information specific to the quantum-splitting phosphor technology [66–73].

4.10

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5

Scintillators

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5.1

Introduction

In this chapter, we discuss high-density luminescent materials which convert X-rays and gamma rays directly into visible light. These materials are known as scintillators, and although they may be in the form of glasses, liquids, and gases, this review focuses only on inorganic solids that can have commercial application as scintillators. This field is quite extensive and diverse, as these materials find increasing scientific and commercial use in such diverse fields as medical imaging, industrial inspections, security applications, and high-energy physics calorimetry, to name only a few. The visible light generated by the scintillators may be detected by photosensitive devices such as photodiodes (for example, silicon diodes), charge-coupled devices (CCDs), and photomultiplier tubes (PMTs).

In the following discussions, the background review which is presented is common knowledge to those associated with scintillating materials. There are a number of useful references which one may consult for general background and on existing commercial functional devices incorporating these materials. Strongly recommended are the monographs by Blasse and Grabmaier [1] and Rodnyi [2], the Phosphor Handbook [3], and books edited by Kitai [4].

Among the numerous useful applications are the very important scintillator materials for medical imaging that form an essential part of these life-saving diagnostics tools. It is the purpose of this article to discuss the salient features of the scintillators that have been developed for Positron Emission Tomography (PET) and Computed Tomography (CT). Scintillating compositions for some other applications (such as X-ray intensifying screen and storage phosphors) will be discussed briefly. The chapter ends with a section on semiconducting scintillating materials.

5.2

Positron Emission Tomography and Computed Tomography

5.2.1

Physical Principles of Positron Emission Tomography (PET)

In positron-emission tomography, the patient is injected with a radioactive material that emits positrons. The positrons rapidly thermalize within the body tissue, and the annihilation of each positron by an electron produces two 511 keV gamma rays in opposite directions (angle close to 180°). Only in this way can both energy and momentum be conserved in the annihilation process. As shown in Fig. 5.1, the pair of photons is detected in coincidence by opposing detectors, which surround the patient. The patient is moved through the detector in a direction perpendicular to the plane described by the detector ring. In this way cross-sectional images of the human body can be generated.

Spatial resolution is obtained by detecting photons in coincidence. Each photon pair detected in coincidence gives a (virtual) straight line (line of coincidence) on which the position where the positron-electron annihilation event has taken place is located (Fig. 5.1). As the γ -ray photon pairs leave the position where they were generated in all directions, the point where all these virtual lines cross is the position where the annihilation process has taken place. Factors such as the range of positron and the fact that the two gamma rays are emitted less than 180 degree apart can contribute to loss in spatial resolution. However, further spatial resolution can be obtained by measuring the difference in time at which the two photons hit the

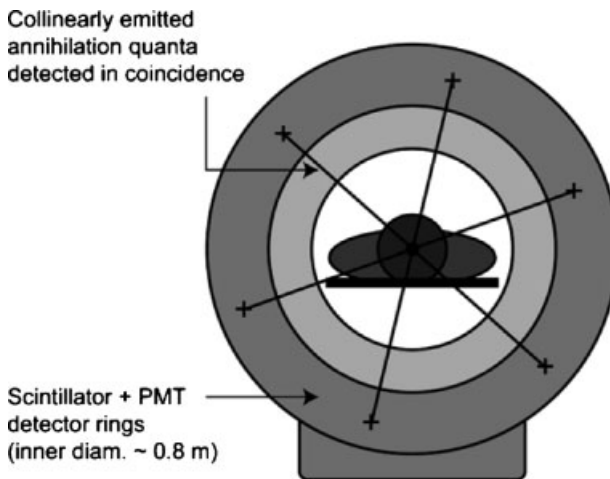


Fig. 5.1 Principle of operation of PET. The object in the middle symbolizes the patient. The scintillator crystals (several thousands) are contained in the outer ring. Adapted from C.W.E. van Eyk, *Phys. Med. Biol.* **47** (2002) 85–106.

scintillator. In this way, information is obtained about the position on the line at which the annihilation process took place. Philips has recently introduced such machines on the market (2006).

This chapter provides both an overview of existing materials and a review of recent developments in new materials that are based on the luminescence of the trivalent cerium ion (Ce^{3+}) in rare earth halide materials for PET application.

5.2.2

Computed Tomography (CT)

In CT, the attenuation of X-rays through the body is measured as the source-detector rotates through 360° in a plane around the patient (Fig. 5.2). The X-ray tube and the detectors are rigidly coupled, and the tube-detector generally executes the 360° rotation within 1–2 s. The fan beam consists of as many individual beams as there are detectors. A planar fan shaped beam of X-rays passes through a cross-sectional slice of the patient and strikes the detector.

5.3

General Requirements for Scintillating Materials Used in Medical Imaging

In PET and CT applications, the scintillator material is in the form of single crystals or (almost) transparent polycrystalline pieces of sintered material (ceramic scintillators). Especially when single crystals are used, the cost involved is mainly

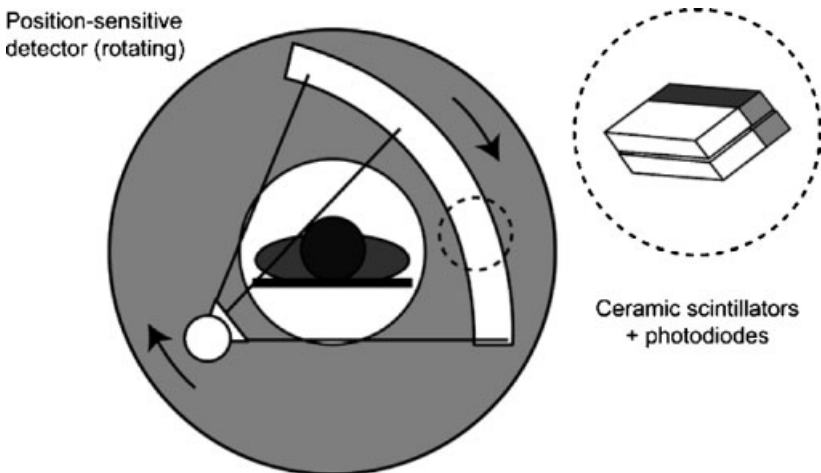


Fig. 5.2 Schematic outline of a CT machine. The object in the middle symbolizes the patient. The small circle at the left is the X-ray source which generates a fan-shaped beam; on the right hand side is the position-sensitive detector containing the scintillating ceramics. Adapted from C.W.E. van Eyk, *Phys. Med. Biol.* **47** (2002) 85–106.

determined by the cost associated with the growth process itself and less by materials costs. The following requirements must be satisfied when selecting a particular material for single-crystal growth or sintering the material to transparency (ceramic scintillators).

In the case of single crystals grown from the melt, the material should not decompose (incongruent melting), and the crystal structure should not change between the melting point and room temperature. Care must be taken to obtain materials in which the activator concentration is distributed uniformly along the growth axis. The variation in the activator concentration (inhomogeneities) along the growth axis is due to different solubility of the activator ions in the liquid and solid phase.

In the case of ceramic scintillators, the material is preferably cubic to prevent scattering due to differences in refractive index in the principal lattice directions. In general, ceramic scintillators do not show problems related to inhomogeneities in the concentration of activator ions [5]

We continue this section by defining the most important physical parameters that make luminescent materials a good scintillator for medical imaging modalities. These are:

- high physical density and high stopping power of the host lattice
- high light yield from the scintillation process for good energy, timing, and spatial resolution
- fast decay time of the luminescent ion for good timing resolution
- a low value for the afterglow
- linearity of the light output as a function of the excitation energy for good energy resolution
- ease of machinability
- hardness
- spectral match with photo detectors.

High Physical Density and High Stopping Power of the Host Lattice The need to stop the highly penetrating primary radiation within short distances requires that the host lattice have high physical density (ρ) and contain a large proportion of elements with high atomic number (high Z elements). The data in the archival literature indicates that stopping power of the host lattice is proportional to $\rho Z^3 - \rho Z^4$. High physical density also reduces the detector size.

High Light Yield In almost all applications, a high light yield of the scintillator is desired. High light yield from the scintillation process can be used to reduce the exposure of patients to the harmful radiation.

In order to understand the physical mechanism responsible for the scintillator light yield, it is necessary to understand the processes which excite the luminescence of the scintillating ions embedded in the solid. As discussed in Chapter 1, the scintillation process strongly resembles the process leading to cathode ray emission. We will not repeat the treatment of cathode ray emission here but will only focus on

aspects which are specific for scintillators. The overall light yield (LY) of the scintillator can be written as

$$LY = [10^6/\beta E_g] \cdots S \cdots QE \quad (1)$$

where β is a constant, E_g is the band gap of the solid, S characterizes the transfer of electron-hole pairs to the scintillating ion, and QE is the quantum efficiency of the luminescence. The factor βE_g is the average energy required to produce one thermalized electron-hole pair. In general, the energy needed to create one electron-hole pair is roughly 2–3 times the band gap of the solid. If the transfer efficiency (S) and quantum efficiency (QE) are set to unity, then the light yield is determined by the factor in brackets in Eq. (1). This factor gives the number of photons generated after excitation with photons with energy 1 MeV. It is easily derived from the Robbins equation, which was discussed in Chapter 1.

It is therefore clear that the product of β and the scintillator band gap (E_g) essentially defines the number of electron-hole pairs that are produced upon band gap excitation. For a high light yield, therefore, material with a small band gap is desirable. Small band gap materials are generally found among covalent compounds, and such materials generally also have small β values (see Chapter 1). Indeed, the most efficiently scintillating materials have small values for the band gap (see Fig. 5.3). Please note the low efficiency of the oxides.

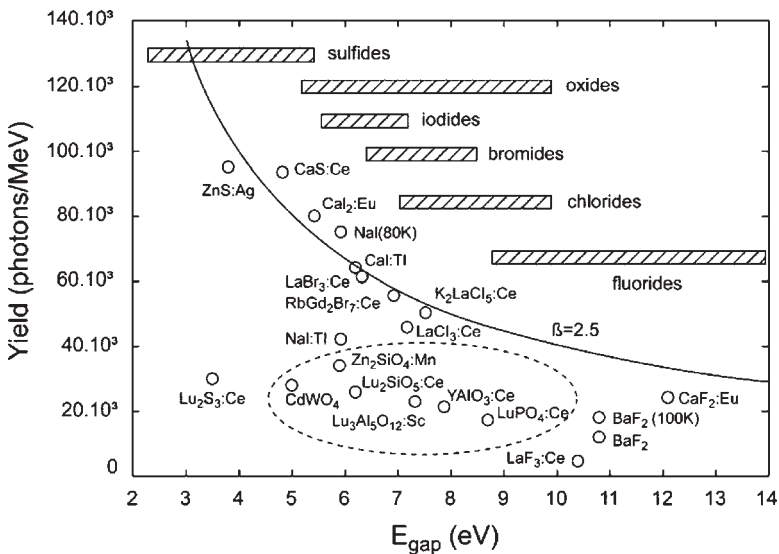


Fig. 5.3 Relationship between band gap and light yield of scintillating materials. The hatched bars give the energy range in which band gaps are found for the materials classes mentioned. Adapted from: P. Dorenbos, *Nucl. Instr. and Methods in Phys. Res. A* **486** (2002) 208–213.

We note that the host lattice-dependent variations in the transfer efficiency [S in Eq. (1)] are not clearly understood. However, the factors that influence the quantum efficiency of the luminescent centre in a given host lattice are understood more or less. As far as the quantum efficiency of the luminescent centre is concerned, we would point out that in small band gap materials (a desirable property for obtaining high scintillating light yield), the scintillating emission efficiency of several activator ions may not be efficient. There are two main reasons for this. First, if the emission energy is greater than the band gap of the material, the emitted photons will be absorbed by the crystal (host lattice) itself and never exit the crystal. A second factor that decreases the efficiency of the luminescent centre in small band gap materials is photoionization. In photoionization, the electron in the excited state of the activator ion is injected back into the conduction band by thermal activation. This condition happens when the activator excited state and the bottom of the conduction band are in close proximity. For example, in Lu_2O_3 , all the $\text{Ce}^{3+} 5d^1$ states are located within the conduction band of the solid and the cerium luminescence is totally quenched [6]. This is proved by photoconductivity experiments where the onset of photoconductivity coincides with the onset of the lowest Ce^{3+} absorption band. The sole reason for the light yield being essentially zero at room temperature in $\text{LaI}_3: \text{Ce}^{3+}$ is because the lowest excited $\text{Ce}^{3+} 5d$ level is $\sim 0.1\text{--}0.2\text{ eV}$ (or less) below the bottom of the conduction band [7]. In both cases, there is no way to excite the emission efficiently, if at all.

This excludes the use of most of the known activator ions in scintillating materials with a band gap smaller than about 4 eV. Since the minimum value for β appears to be 2.5, this implies a maximum light yield of about 100 000 photons/MeV for a scintillator in which the luminescence is generated by intentionally added activator ions.

Short Decay Time In almost all applications, a high light yield of the scintillator is desired. As pointed out in Ref. [8], the accuracy of a physical quantity is better (or improved) if a large number of photons (N) are emitted during the scintillation process.

It is imperative that for good timing resolution, such as in PET, the radiative lifetime (τ) of the luminescent center be as short as possible. The short lifetime of the luminescent center becomes important in high count rate situations. Fast rise in the scintillating signal (fast response), which is limited by energy transport and migration of host lattice excitation to the luminescent center [factor S in Eq. (1)], is also important for good timing resolution. For example, the development of time-of-flight PET requires that the scintillator exhibit short rise times (the increase of the emission intensity immediately after the excitation pulse) [9].

According to Ref. [8], the timing resolution is proportional to τ/\sqrt{N} if the response is fast and the decay time short. Here, N is the number of photoelectrons detected by the photosensor. As is further discussed below, the spin- and parity-allowed optical transitions of the $4f5d$ type, which are generated by ions such as Ce^{3+} and Pr^{3+} , exhibit a typical decay time in the 10–60 ns range. These are thus ideally suitable for the attainment of good timing resolution.

In the case of CT, materials with a long decay time limit the rotation speed of the X-ray source and the detector unit around the patient. The same applies to afterglow (see below). CT application, however, poses less stringent requirements on the decay time of the scintillating materials than PET. Decay times in the order of milliseconds are already short enough.

Low Value for the Afterglow Many luminescent materials show a time-dependent luminescence with a higher intensity than would be expected based on the decay time of the luminescent activator ions. Afterglow is defined as the fraction of scintillating light present for a certain period of time after the ionizing radiation has been shut off. Afterglow is mainly a result of charge trapping by the lattice defects. Such lattice defects can be intrinsic or can be created by the ionizing radiation. Excitonic effects can also induce afterglow in a scintillator. In all circumstances, afterglow must be minimized or eliminated altogether.

In the case of CT, afterglow reduces the rotation speed which can be used. In case of PET, afterglow increases the time needed to discriminate between two incident γ -photons. In addition, it leads to enhanced pile-up: a specific scintillator crystal (or a small group, coupled to a photomultiplier) cannot be used to detect the next γ -photon when photons from a previous event are still being detected. In time-of-flight PET, the first photons detected trigger the counting electronics as soon as the trigger threshold is surpassed. Afterglow necessarily increases the trigger level and therefore decreases the timing resolution.

Linearity of the Light Output In the ideal case, every incident γ -photon will result in the generation of the same number of photons. In practice, this is not the case, e.g., if high-energy photons leave the crystal after having transferred only part of their energy to the crystal. In addition, inhomogeneities in the μ -structure of the scintillator may lead to spatial differences in conversion efficiencies. Finally, Compton scattering (interaction of the γ -photons with the scintillator) produces electrons which vary in energy, and consequently different amounts of energy are transferred to the scintillator host lattice, resulting in different amounts of low-energy photons.

An important aspect of a gamma detector is the ability to discriminate between gamma photons with slightly different energies. This is called the energy resolution of the system (scintillator plus photodiode) and is defined by the full width at half maximum of the photopeak at a certain energy divided by this energy. Apart from the factors given above, the energy resolution is also a function of the light yield of the scintillator and the number of photons that are detected by the photodiode: the energy resolution varies as $1/\sqrt{N}$, N being the number of photons detected.

Proportionality is very important for energy resolution, as any deviations in light yield from proportionality will degrade the energy resolution of the scintillator. In recent years, as is discussed in this chapter, there has been renewed interest in obtaining materials with energy resolution in the 2–3% range. For example, the detection and identification of radioisotopes for security applications requires the use of an ambient-temperature, efficient, fast, low-cost gamma detector with energy resolution of <2% FWHM at 662 keV (originating from ^{137}Cs).

Ease of Machinability The materials should be machinable, as the crystals have to be built into the imaging machines in units with a well-defined geometry and orientation. This generally excludes the existence of planes in the scintillator materials along which cleavage is easy. Such planes in principle would allow very effective machining, but it is imperative that this be in the correct directions.

Hardness Important additional factors are chemical, mechanical, and radiation hardness of the material.

Spectral Match with Photodetector To maximize the detection of the scintillating photons, the emission wavelength of the scintillator must overlap maximally with the sensitivity spectrum of the chosen photo detector.

With the above background, we now discuss the salient properties of scintillators for PET and CT applications.

5.4 Scintillators for Pet Application

5.4.1 General Description of Phosphors for PET Scintillators

Modern PET machines have several thousands of single crystals (typical volume 1–4 cm³). The scintillator requirements for PET are (a) short decay time, (b) short attenuation length for 511 keV gamma photons, (c) high photon yield (>8000 photons/MeV), (d) emission wavelength that is well matched with the PMT spectral sensitivity, and (e) low cost.

Scintillators used for PET have to be very fast, because this enables many photons to be measured in coincidence per time interval. Consequently, the optical transitions involved in generating the luminescence have to be spin- and parity-allowed. The radiative transition rate is given by

$$1/\tau = n/\lambda^3 \cdot [(n^2 + 2)/3]^2 \cdot \sum_f \cdot |\langle f|\mu|i \rangle|^2 \quad (2)$$

where n is the refractive index, λ is the emission wavelength, and μ is the electric dipole operator which couples the final states (f) to the initial state (i).

The requirement for a fast emission can be fulfilled by the spin- and parity-allowed $d \rightarrow f$ transitions of certain rare earth ions (such as Ce³⁺, Pr³⁺, and Nd³⁺) or by the $np \rightarrow ns$ transitions of ns^2 ions such as Bi³⁺ and Tl⁺. Choosing hosts, which allows for a short emission wavelength and/or a large value for the refractive index, can further reduce the emission decay time. However, as can be judged from Eq. (2), faster transitions are characterized by shorter emission wavelengths.

The use of very fast ultraviolet (UV)-emitting rare-earth ions like Ce³⁺ or even Pr³⁺ and Nd³⁺ requires materials with a large band gap and low phonon frequencies. The band gap has to be greater than the energy of the photons emitted, otherwise the light

will be absorbed by the host lattice. The lattice phonon frequencies should be low to prevent intra-ionic relaxation of the d-state into the f-levels, which would result in too slow f-f emission.

As previously discussed, the use of ions that occur in more than one valence state (such as Ce^{3+} and Pr^{3+}) can induce photoionization, and this creates an additional requirement to the energy gap. As a rule of thumb, the energy separation between the excited state of the activator ion and the host lattice states must be at least ca. 0.5 eV to avoid photoionization. The considerations given above give rise to some conflicting requirements:

- The band gap has to be large to be able to use fast-emitting ions.
- The band gap has to be small for a high light yield.
- The refractive index must be large, which is generally true for covalent lattices, which quite frequently have a small band gap.

The coincidence timing resolution is a critical factor determining the performance of a PET system, more particularly for time-of-flight (TOF) PET. In order to obtain improved image quality, timing resolution of less than 1 nanosecond is generally required. The scintillator rise time can significantly change the timing resolution of fast scintillators with short decay times. The “slow” rise time can be a result of some of the physical processes given below:

- The activator concentration is too low, and the build-up in the luminescence signal reflects the diffusion of electron-hole pairs toward the activator ions (see also Chapter 1).
- The electron and the hole show interaction with the lattice and the corresponding exciton traps itself (self-trapped exciton). The self-trapped exciton has a low mobility, which delays the activation of the luminescent center; this occurs quite frequently and can be tested by, e.g., measuring the emission spectrum of undoped materials or by performing low-temperature luminescence measurements.

Scintillators which satisfy the requirements of the PET scanners can be divided into two classes. Members of the first class operate on the luminescence of ions with mercury-like ns^2 electronic configuration. Examples include $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) and $\text{NaI}:\text{Tl}^+$, where the luminescent species Bi^{3+} and Tl^+ have the $6s^2$ electronic configuration.

The ground state of the free ion with the $6s^2$ electronic configuration is 1S_0 , whereas the $6s6p$ excited states give rise to the triplets levels [3P_0 , 3P_1 , 3P_2] and the 1P_1 singlet state (see Fig. 5.4). The $^1S_0 \rightarrow ^3P_1$ transition (A-band) becomes allowed as a result of spin-orbit coupling, whereas the $^1S_0 \rightarrow ^3P_2$ transition (B-band) is forbidden (by parity) but can be induced by coupling with unsymmetrical lattice vibrational modes. The $^1S_0 \rightarrow ^1P_1$ transition (C-band) is an allowed transition, but the $^1S_0 \rightarrow ^3P_0$ is strongly forbidden. In addition to the above transitions, another optical transition (a “D-band”) appears in the optical spectra of the Bi^{3+} ions. The D-bands are presumed to be ligand-to-metal charge transfer transitions, although an earlier view ascribed the band to a perturbed exciton [10].

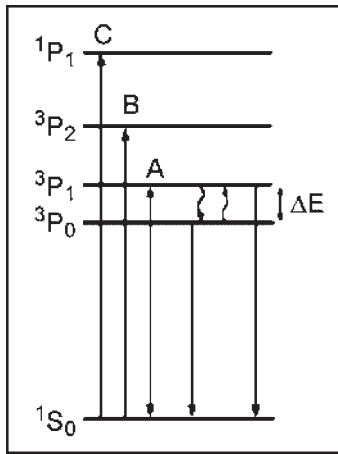


Fig. 5.4 Electronic configuration of ns^2 ions.

Since the $3P_0$ state is the lowest energy state, the emission at low temperature of ions with the $6s^2$ electronic configuration is dominated by the forbidden $3P_0 \rightarrow 1S_0$ transition. However, as the temperature increases, the emission originates from the thermal population of the $3P_1$ state by overcoming the energy barrier of ΔE , as shown in Fig. 5.4. The corresponding $3P_1 \rightarrow 1S_0$ transition is partially allowed.

The second class of PET scintillators is based on the luminescence of Ce^{3+} . The free-ion ground state configuration of Ce^{3+} ions consists of a xenon-like core of 54 electrons and a valence shell containing one 4f electron only $\{[Xe] 4f^1\}$. Spin-orbit coupling interaction splits the $4f^1$ ground state into $2F_{7/2}$ and $2F_{5/2}$ levels, separated by 2253 cm^{-1} (0.28 eV). The first excited configuration of the Ce^{3+} ion is formed when the single 4f electron is promoted to the 5d energy level. The 5d energy level is also split by the spin-orbit coupling interaction into the $2D_{3/2}$ and the $2D_{5/2}$, which are located at $49\,737 \text{ cm}^{-1}$ (6.16 eV) and $52\,226 \text{ cm}^{-1}$ (6.47 eV) in the free ion, respectively. The centroid (the barycenter, the center of gravity) of the $5d^1$ level is 6.32 eV. The 6s level is located at $86\,600 \text{ cm}^{-1}$ (10.74 eV) [11]. The optical transitions on the Ce^{3+} ion are of the electric dipole $4f^1 \leftrightarrow 5d^1$ type. Since the transitions are parity- and spin-allowed, the use of Ce^{3+} ion provides for the development of scintillators with fast decay.

5.4.2

Scintillating Composition Used in PET

In view of the physical dimensions of the scintillating crystals, they have to be transparent; otherwise, light scattering will significantly reduce the amount of light which arrives at the photo detectors. Many materials optimized for PET applications have a high melting point and are not cubic (see below). This means that very high temperatures are needed to produce single crystals, contributing significantly to PET equipment costs.

5.4.2.1 $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO)

Current PET scanners use BGO as the detector of the 511-keV gamma rays. The density of this scintillator is 7.1 g cm^{-3} , and the Z_{eff} is 75, which is the highest Z_{eff} value of all the scintillator materials commonly used in PET scanners. Note that the Z_{eff} is driven by the high atomic number of Bi ($Z = 83$). The material is non-hygroscopic, crystallizes in the cubic space group, and has a low melting point (approximately 1050°C). Hence, the growth of large single crystals of BGO is relatively easily accomplished. Further, the peak emission wavelength is 480 nm (Fig. 5.5) and the Stokes shift ($14\,000 \text{ cm}^{-1}$) is large, which results in minimal self-absorption. Therefore, the crystal is transparent to its own emission, which allows for the use of thin detectors. The main drawback of this scintillator is the rather low light yield of only 9000 photons/MeV at room temperature. The dependence of the emission intensity and lifetime on temperature indicates that nonradiative decay becomes important at a temperature of $\sim 250 \text{ K}$ [12]. The large Stokes shift of emission is responsible for the low quantum efficiency of BGO at room temperature. As a result, the energy efficiency of BGO only amounts to 2% as compared to 12% for NaI:Tl. Also, the lifetime of this scintillator is rather long (300 ns). The peak emission wavelength of 480 nm is not particularly well matched with the spectral sensitivity of PMT, so that the relative yield with standard photocathodes is only 10–15% relative to NaI:Tl. The energy resolution of the BGO is rather poor ($>10\%$ at 662 keV FWHM) because of the low light yield and the long lifetime [13].

BGO crystallizes with the eulytite structure [12,14]. The Bi^{3+} ion is coordinated by six oxygen ions in a highly asymmetrical geometry, with the $\text{Bi}^{3+}\text{-O}^{2-}$ bond distance being 2.16 Å on one side and 2.60 Å on the other. This highly asymmetrical and one-sided

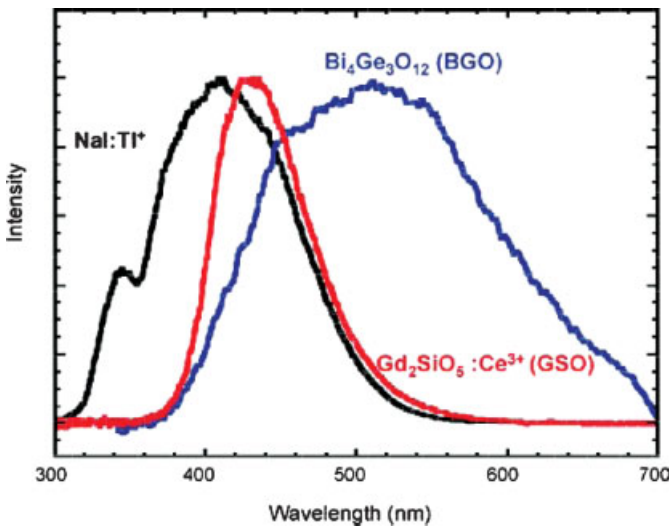


Fig. 5.5 X-ray excited emission spectra of PET scintillators.

coordination is typical of ions with the ns^2 (lone electron pair) electronic configuration. It has been suggested in the literature that the luminescence of BGO is not simply associated with optical transitions of the $6s^2 \rightarrow 6s6p$ type, but involves a charge transfer transition between the Bi^{3+} ion and the germanate group. *Ab initio* study pertaining to the absorption and emission properties of BGO indicate that the large Stokes shift can be connected to a highly deformed excited state geometry where one of the oxygen ions is displaced away from the Bi^{3+} ion (the $\text{Bi}^{3+}\text{-O}^{2-}$ bond elongates by as much as 42 %), while the Bi^{3+} ion shifts towards the center of the cluster [15].

5.4.2.2 NaI:Tl⁺

Another commonly used PET scintillator works on the luminescence of Tl^+ ion in NaI. The density of this scintillator is 3.86 g cm^{-3} and the Z_{eff} is 51, both figures being lower than the corresponding figures for the BGO scintillator. The light yield of the scintillator is 40 000 photons/MeV, with a emission decay time of 230 ns. At 662 KeV, an energy resolution of 7.5 % FWHM has been reported [13]. The scintillator suffers from non-proportionality of the light yield as a function of energy; in the 60–1275 keV range, the non-proportionality in the light yield is $\sim 20\%$. The emission peak wavelength is at 415 nm. The chief reason for the popularity of this scintillator is the ease and the low cost of manufacturing large single crystals. The crystals must be hermetically sealed to prevent attack by moisture, as sodium iodide is hygroscopic. The emission spectrum of this scintillator under X-ray excitation is shown in Fig. 5.5.

NaI crystallizes in face-centered cubic symmetry in which the Na^+ ions are octahedrally coordinated by six chlorine ions and vice versa.

5.4.2.3 $\text{Lu}_2\text{SiO}_5\text{:Ce}^{3+}$ (LSO)

This scintillator exhibits physical and optical properties that are very well suited for PET application. The density and Z_{eff} are 7.4 g cm^{-3} and 66, respectively. The Z_{eff} is the second highest of all the commonly used scintillator materials and displays only 1.5 times lower sensitivity than BGO for the detection of coincident 511-keV gamma rays. The melting point of LSO is 2100°C , and large crystals have been grown by the Czochralski technique. The light yield of the scintillator is 25 000 photons/MeV [16]. The timing resolution of LSO has been measured to be 160 ps [17]. The main scintillator emission wavelength is 420 nm, with a decay time of about 40 ns. The Stokes shift of the Ce^{3+} emission is $\sim 2800 \text{ cm}^{-1}$. At 662 KeV, energy resolution of 8.6 % FWHM has been reported [16]. The rather poor energy resolution can be partially explained on the basis of strong non-proportionality response of the scintillator [18]

Crystals of $\text{Lu}_{1.8}\text{Y}_{0.20}\text{SiO}_5$ [LYSO] activated with Ce^{3+} have also been investigated for scintillation. A light yield of 33 800 photons/MeV, an energy resolution between 9.5 and 12.5 %, and a decay time of 41 ns have been reported [19]. Both LSO and LYSO suffer from significant afterglow.

It is instructive to examine the temperature quenching behavior of the Ce^{3+} emission in LSO. Although the room temperature efficiency of the Ce^{3+} luminescence is high, the luminescence intensity starts to quench very rapidly above room

temperature and approaches values close to zero at only 425 K [20]. The results of photoconductivity measurements on single crystals of LSO have been reported in the literature [6,21]. At room temperature the photoconductivity curve closely follows the absorption curve, indicating that electrons are transferred from the lowest energy $\text{Ce}^{3+} 4f5d$ band (located at 360 nm) to the conduction band by thermal activation. At liquid nitrogen temperatures, the photoconductivity signal at 360 nm drops by three orders of magnitude. This indicates that the lowest energy $\text{Ce}^{3+} 4f5d$ band is located just slightly below the bottom of the conduction band of the solid. The activation energy of ~ 0.28 eV, derived from the thermal quenching of the Ce^{3+} lifetime, thus represents the energy separation of the lowest-energy $\text{Ce}^{3+} 5d$ state from the bottom of the conduction band.

Lu_2SiO_5 crystallizes in monoclinic symmetry with space group $C2/c$ [22]. In the crystal structure, infinite chains of Lu_4O tetrahedra, which are joined by SiO_4 tetrahedra, run along the c -axis. The non-Si-bonded O atoms are surrounded by four Lu atoms in a distorted tetrahedral coordination. There are two crystallographically distinct sites of the Lu^{3+} ion, i.e. with coordination numbers of 6 and 7, respectively. Luminescence from the activator Ce^{3+} ion occupying the two sites has been observed and characterized in the literature [23].

5.4.2.4 $\text{Lu}_2\text{Si}_2\text{O}_7:\text{Ce}$ (Lutetium Pyrosilicate, LPS)

LPS crystallizes in monoclinic symmetry with the space group $C2/m$. There is only one crystallographic site for the Lu^{3+} ion, and this has the coordination number of 6 (distorted octahedral) [24]. This scintillator also exhibits physical and optical properties that are very well suited for PET application [19]. The density and Z_{eff} are 6.2 g cm^{-3} and 64, respectively. The melting point of LPS is 1900°C , and large crystals have been grown by the Czochralski technique. The light yield of the scintillator is 26 300 photons/MeV. The energy resolution is between 7.5 and 9.5%. The timing resolution is 253 ps. The main scintillator emission wavelength is 385 nm, with a decay time of about 38 ns. The Stokes shift of the Ce^{3+} emission is $\sim 2200 \text{ cm}^{-1}$. The activation energy of ~ 0.68 eV derived from the thermal quenching of the Ce^{3+} lifetime, which represents the energy separation of the lowest-energy $\text{Ce}^{3+} 5d$ state from the bottom of the conduction band is higher for LPS when compared with the activation energy of 0.28 eV for LSO. Indeed, the quenching temperature of the Ce^{3+} emission occurs at a higher temperature than that for LSO. In contrast to LSO, LPS does not exhibit thermoluminescence.

It is interesting to note that the lifetime of the Ce^{3+} emission in LPS crystals with a nominal concentration of Ce^{3+} of 0.5% increases from 32 ns at 50 K to 40 ns at 450 K [19]. This is attributed to self-absorption caused by the spectral overlap between the excitation and the emission bands. With increasing temperature, the bands broaden, increasing the self-absorption of the emitted light. It is well known that this lengthens the lifetime of the luminescent species. The effect of self-absorption on the Ce^{3+} lifetime is stronger in LPS than in LSO because the Stokes shift of LSO exceeds that of LPS, which results in reduced spectral overlap between the excitation and emission bands in LSO.

5.4.2.5 LaBr₃:Ce

Let us now discuss the properties of Ce³⁺-activated LaBr₃, a new and promising scintillator material with outstanding light yield, enhanced energy resolution, and timing features. The light yield of LaBr₃:0.5% Ce³⁺ approaches 60 000 photons/MeV [25]. The radiative decay time of this scintillator, which is independent of the Ce³⁺ concentration, is 25 ns (primary decay constant). Because of the fast decay time, the material is suitable for PET modality. The room temperature emission spectrum of LaBr₃:Ce³⁺ matches well with the sensitivity of commercially available PMTs (see Fig. 5.6).

The energy resolution of this scintillator is less than 3%. At 662 keV, energy resolution of 2.6% FWHM has been reported [26]. As previously discussed, the proportionality of the scintillating light yield as a function of the incident energy contributes to the energy resolution. The non-proportionality in the scintillating light yield of this scintillator in the energy range 60–1275 keV is about 6% as compared to 20% for commercial NaI:Tl and CsI:Tl scintillators [27]. This remarkable non-proportionality combined with a very high light yield makes LaBr₃:0.5% Ce³⁺ the best scintillator for energy resolution. Hence, the combination of high light yield, excellent energy resolution, and fast timing properties makes LaBr₃ the leading candidate for the time-of-flight (TOF) whole-body PET camera. However, the chief drawback of this scintillator in PET application is the low stopping power and photo-fraction, both of which effect the sensitivity and spatial resolution. Another drawback of this scintillator is that it is highly hygroscopic and therefore difficult to handle.

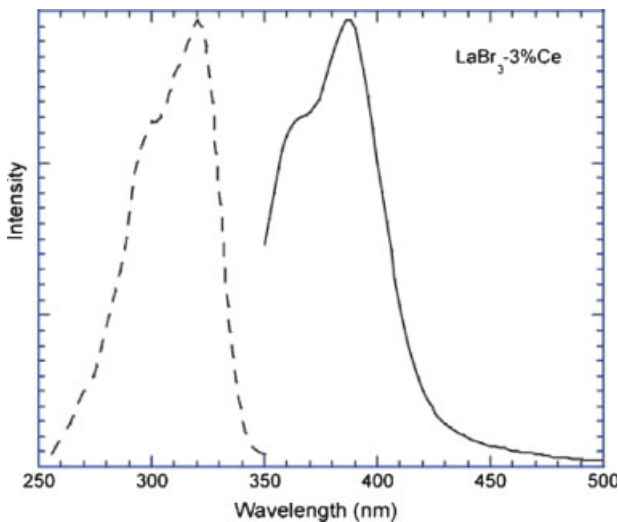


Fig. 5.6 The UV excitation (dotted line; $\lambda_{em} = 390$ nm) and the emission spectra (bold line; $\lambda_{ex} = 320$ nm) of LaBr₃: 3% Ce³⁺.

The crystal structures of the compounds LaX_3 ($\text{X}=\text{Cl}, \text{Br}$) are known to be of the UCl_3 type (space group $\text{P6}_3/\text{m}$). The La^{3+} ion is present in a nine-fold coordination of the halide anions. These nearest neighbours lie in a configuration with C_{3h} symmetry [28].

5.4.2.6 $\text{LuI}_3:\text{Ce}$ [29–31]

The light yield of this recently discovered scintillator [$\text{LuI}_3:5\% \text{Ce}$] is remarkably high, 75 000 photons/MeV. The density and Z_{eff} are 5.6 g cm^{-3} and 61, respectively. For low concentrations of Ce^{3+} , the emission band can be resolved into two overlapping bands, centered at 472 nm and 535 nm, respectively. The Stokes shift of the Ce^{3+} emission is $\sim 2623 \text{ cm}^{-1}$. About 60 % of the photons are emitted in the primary scintillation decay time of 24 ns. The melting point of LuI_3 is 1050°C , and large crystals can be grown by the Bridgman and Czochralski techniques because it melts congruently. At 662 keV, an energy resolution of 3.3 % FWHM has been reported. The non-proportionality in the scintillating light yield of this scintillator in the energy range 60–662 keV is about 10 %. The timing resolution of $\text{LuI}_3:\text{Ce}$ has been measured to be 210 ps. The drawback of this scintillator is that it is highly hygroscopic, and crystals can be easily cleaved because of its layered structure.

Lutetium iodide crystallizes in the layered structure of BiI_3 with hexagonal symmetry and space group R-3. There is only one crystallographic site for the Lu^{3+} ion; this has a distorted octahedral coordination [32]

5.4.3

Other PET Scintillators

The scintillation properties of orthorhombic perovskites such as YAlO_3 and LuAlO_3 (LuAP) activated with Ce^{3+} have been extensively investigated [33,34]. For LuAP , the density and Z_{eff} are 8.3 g cm^{-3} and 65, respectively. The melting point of LuAP is 1960°C . The light yield of the scintillator is only 11 300 photons/MeV, which is about three times less than that of LSO . The main scintillator emission wavelength is 365 nm, with a decay time of about 18 ns. The Stokes shift of the Ce^{3+} emission is large, $\sim 4091 \text{ cm}^{-1}$. A timing resolution as short as 160 ps has been reported. The scintillation mechanism and thermoluminescence, which indicate the presence of complex electron trapping centers, have been investigated [35]. LuAP has been investigated for small animal imaging PET systems that are based on photodiodes [36].

$\text{Gd}_2\text{SiO}_5:\text{Ce}^{3+}$ (GSO) has also been investigated for PET application [37]. GSO crystallizes in a structure that is different from that of LSO . However, as in LSO , there are two crystallographically distinct sites of the Gd^{3+} ion, with coordination numbers of 8 and 7, respectively [38]. The density and Z_{eff} are 6.71 g cm^{-3} and 59, respectively. The melting point of GSO is $\sim 1900^\circ\text{C}$, and large crystals have been grown by the Czochralski technique. The light yield of the scintillator is only 9000 photons/MeV. The main scintillator emission wavelength is 440 nm (Fig. 5.5), with a decay time of about 60 ns. The Stokes shift of the main Ce^{3+} emitting center is large -5511 cm^{-1} . The intrinsic energy resolution of GSO is 9 %, similar to that of NaI:Tl^+ . It is also

interesting to note that the Ce^{3+} scintillation decay in this material is lengthened because of energy transfer from Gd^{3+} to Ce^{3+} [39]. Lutetium gadolinium orthosilicate ($\text{Lu}_{0.4}\text{Gd}_{1.6}$) SiO_5 [LGSO] has also been investigated for PET application. The energy resolution has been measured at 8.3%. The light yield of the scintillator is 23 000 photons/MeV [40].

5.5 Scintillators for CT Application

5.5.1 General Description of Scintillators for CT

As previously discussed, in CT one measures the attenuation of X-rays through the body: an X-ray source and an opposed detector rotate 360 degrees in a plane around the patient. The scintillators employed in CT must be capable of measuring attenuation differences of 1 part in 1000, must be stable under ionizing radiation conditions over the time of an extended scan, and must show little or no afterglow.

For CT applications, the requirements placed on the emission decay time are not as high as in case of PET. This relaxes the selection criteria for the emitting ions, and, for this reason, ions emitting in the complete visible range and also ions showing forbidden optical transitions, e.g., f-f optical transitions, can be used.

The physical dimensions of CT scintillators are much smaller than those of PET scintillators and are typically in the order of 1 mm^3 . For this reason, CT scintillators do not need to be completely transparent.

5.5.2 Scintillating Compositions Used in CT

5.5.2.1 CdWO_4 [41–43]

This material crystallizes in the wolframite (monoclinic) structure, with tetrahedral tungstate groups [44]. The intrinsic emission of this scintillator is a broad band centered at 480 nm. The density of the scintillator is 7.99 g cm^{-3} . The light yield of this scintillator is 30% of that of CsI:Tl^+ , with a decay time of $8.9 \mu\text{s}$. Although the scintillator exhibits low afterglow, short decay time, and relatively high light yield, the toxicity associated with cadmium and the fact that the single crystals have a tendency to crack along the cleavage plane [the (010) crystallographic plane] during machining limits the practical application of this scintillator [45,46]. Early crystals of CdWO_4 also suffered from radiation damage, which had to be compensated for during image reconstruction. However, advances in the crystal growth and, in particular, the control of defect concentration and the control of the vacancies created by the evaporation of CdWO_4 at high temperatures [47] have led to significant improvements in controlling the radiation damage in this scintillator.

The electronic structure and the approximate optical properties of CdWO_4 have been studied within the framework of density-functional theory [48]. The Cd 4d states

are located near the bottom of the valence band formed by the oxygen 2p orbitals. The conduction band is mainly composed of the W 5d states. The valence band width is determined to be 5.3 eV and the minimum band gap is estimated to be 2.9 eV. Experimentally, these authors have estimated the interband edge of 4.4 ± 0.3 eV for CdWO_4 . It is clear, from the band structure calculations, that the optical properties of CdWO_4 cannot simply be described in terms of a charge transfer of the O^{2-} (2p) to W^{6+} (5d) type but the must also include the contribution of Cd^{2+} 4d states that are located in a narrow band near the top of the valence band.

5.5.2.2 $(\text{Y,Gd})_2\text{O}_3:\text{Eu}^{3+}$ [5]

The solid solution of $\text{Y}_2\text{O}_3\text{-Gd}_2\text{O}_3$ with the added activator Eu^{3+} is an efficient red-emitting scintillator with a density of 5.91 g cm^{-3} , a light yield of about 67 % of that of CsI:Tl^+ , and a decay time of $1000 \mu\text{s}$. This scintillator has been commercialized by the General Electric Company under the trade name of HiLight. The HiLight scintillator has more than twice the light output of the CdWO_4 scintillator previously discussed. The material crystallizes in the cubic system with the space group $\text{Ia}\bar{3}/\text{T}_h^7$. There are two different sites for the Eu^{3+} ion, with C_2 and C_{3i} (centrosymmetric) site symmetry. A sharp peak at 611 nm, which corresponds to the electric dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ on the Eu^{3+} ion, dominates the emission spectrum. This emission, which emanates from the Eu^{3+} ions occupying C_2 sites, can be detected efficiently by photodiodes.

The melting point of 2439°C makes single crystal growth rather difficult, and so ceramists have developed techniques of fabricating these materials as polycrystalline ceramics that are sintered to transparency. The isotropic optical properties of the $\text{Y}_2\text{O}_3\text{-Gd}_2\text{O}_3$ cubic structure allows for sintering to complete transparency (Fig. 5.7). For the purposes of controlling the afterglow and radiation damage, the

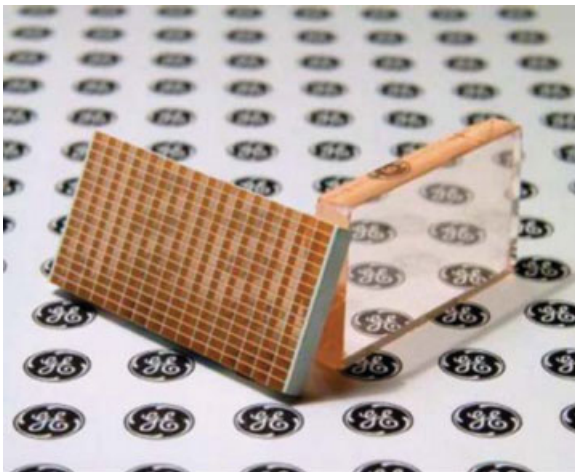


Fig. 5.7 The GE HiLight sintered $(\text{Y, Gd})_2\text{O}_3:\text{Eu}^{3+}$ ceramic scintillator.

scintillator composition also incorporates ppm of Pr and Tb. As an example, the incorporation of these ions in the 100-ppm range reduces the afterglow by more than an order of magnitude. Although the presence of these ions decreases the light yield of the scintillator, the initial high intrinsic efficiency of the scintillator allows for this trade-off. The main drawback of this scintillator is the rather slow decay time of ~ 1 ms.

More recently, Eu^{3+} -activated Lu_2O_3 (cubic) has also been developed as a ceramic scintillator [49]. The high density of 9.42 g cm^{-3} makes it an attractive candidate for CT application. The light yield is comparable to that of CsI:Tl^+ . Persistent afterglow attributed to hole traps in the ceramic scintillator probably limits the practical application of this material in its current form [50,51].

5.5.2.3 $\text{Gd}_2\text{O}_2\text{S:Pr}^{3+}$ (GOS) [52]

This material has also been commercialized as a polycrystalline ceramic scintillator for CT applications. The scintillating ion is Pr^{3+} , which emits at 510 nm corresponding to the ${}^3\text{P}_0 \rightarrow {}^3\text{H}_1, {}^3\text{F}_1$, with a decay constant of about $3 \mu\text{s}$. The light yield of the scintillator is 75 % of that of CsI:Tl^+ . The density of the scintillator is 7.34 g cm^{-3} . The scintillator is intentionally doped with F and Ce to improve the light yield and to reduce the afterglow that is caused by intrinsic traps in the host lattice.

The material crystallizes with hexagonal symmetry (space group P3-m1). Since this material does not have cubic symmetry, it cannot be formed into a fully transparent ceramic. In the literature, hot isostatic pressing of the material with traces of Li_2GeF_6 as a sintering aid has been shown to result in a translucent ceramic scintillator.

The X-ray excited emission spectra of the CT scintillators discussed in this section are shown in Fig. 5.8.

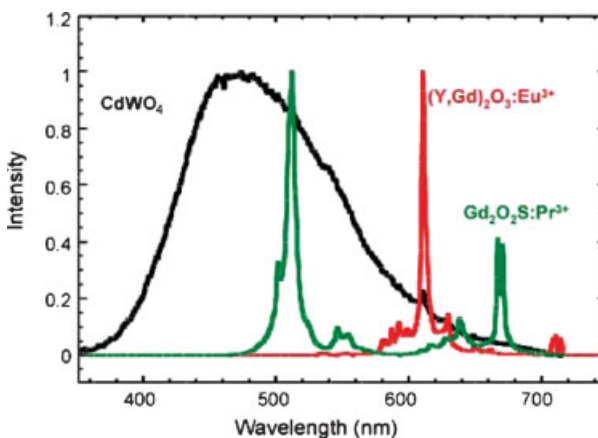


Fig. 5.8 X-ray-excited emission spectra of CT scintillators.

5.6 X-ray Intensifying Screens

5.6.1 General Description of Scintillators for Intensifying Screens

X-ray intensifying screens are used to convert X-ray radiation into photons for which photographic material has a high sensitivity. In contrast to PET and CT, in this application, powders can be used. In a cartridge, a photographic film is sandwiched between two sheets of X-ray phosphors. The patient is placed between the X-ray source and the cartridge. The phosphor strongly absorbs the incoming X-ray photons and converts it to visible light with efficiency as high as 20%. The photographic film then absorbs the light emitted by the phosphor, forming an image on the film. The chief aim of using the phosphor is to reduce the dosage of X-rays to the patient. In this way, one obtains the necessary sensitivity required for medical applications, but because of light scattering by the phosphor particles, the high spatial resolution of the original X-rays is lost.

Since such systems are not suitable for time-resolved detection, efficiency and spatial resolution are the more important parameters. The thickness of the phosphor screen determines the sharpness or the resolution of the X-ray image. Thin films with dense packing of the phosphor particles increase the spatial resolution. Hence, the phosphor particle size and the morphology play a significant role in determining the optimum phosphor coating densities. Typical values are a layer thickness of 200–400 μm , a phosphor grain size of 3–10 μm , and a packing density of 30–60%. Phosphors with very low afterglow are required in order to minimize blurring or fogging, which results in ghost images of one patient onto another on subsequent film exposure.

Issler and Torardi have reviewed the phosphors used in intensifying screens [53].

5.6.2 Phosphor Compositions for Use in X-ray Intensifying Screens

CaWO_4 (scheelite structure) with tetrahedral $[\text{WO}_4]^{2-}$ groups was one of the first luminescent materials to be proposed in 1896 as a scintillator for the conversion of X-rays to visible light in X-ray intensifying screens. The blue luminescence of this phosphor is due to charge transfer transitions within the tetrahedral $[\text{WO}_4]^{2-}$ groups (see also Chapter 1). The main disadvantages of this phosphor are the low X-ray absorptivity in the 30–80 keV energy range, its long persistence of emission, and the rather poor X-ray-into-visible photon conversion efficiency.

The CaWO_4 phosphor has been essentially replaced by more efficient phosphors such as LaOBr:Tm^{3+} (blue-emitting), $\text{Gd}_2\text{O}_2\text{S:Tb}^{3+}$ (green-emitting), and YTbO_4 (UV-emitting). The $\text{Gd}_2\text{O}_2\text{S:Tb}^{3+}$ phosphor has a strong X-ray absorption at the Gd K-edge (50 KeV, in the middle of the diagnostic X-ray energy range), very high light yield (of the order of 40 000 photons/MeV), and efficient green emission. Further, the phosphor crystallizes in perfect polyhedra, which is an important parameter for

reaching high spatial energy resolution. This is in fact one of the disadvantages of LaOBr:Tm^{3+} , which crystallizes in a plate-like morphology because of its layered structure. This plate-like morphology results in poor packing in screens, and the phosphor has a tendency to “light-pipe” toward the side of the plates.

In Table 5.1 we summarize the properties of the important X-ray intensifying phosphors.

5.7

FDXD Detectors [54]

FDXD detectors are very important in cardiac applications. The acronym stands for Flat Dynamic X-ray Detector. Using a sufficiently fast phosphor system coupled to a matrix array of photodiodes, dynamic pictures can be obtained in real time, which are very important in, e.g., heart inspection and treatments. Typical detector dimensions are $40 \times 40 \text{ cm}^2$, consisting of $2 \text{ k} \times 2 \text{ k}$ pixels (Fig. 5.9).

A commonly used phosphor is CsI:Tl^+ , the emission spectrum of which is given in Fig. 5.10. This figure also shows the good match of the emission spectrum with the sensitivity spectrum of a common detector used. The Tl^+ -ion belongs to the class of s^2 ions, which was previously discussed.

In CsI:Tl , the emission behavior is unfortunately somewhat more complicated than would be expected based on the energy level scheme of an ns ion (Fig. 5.4). At ambient temperature, two emission bands are observed, one at 400 nm which originates from the Tl^+ ion and one at 550 nm which is due to a strongly perturbed Tl-related bound exciton center. The relatively low emission energy is due to strong relaxation, in line with the strong perturbation. At low temperatures (liquid nitrogen), emission which originates from a weakly perturbed Tl-bound state is observed. This emission disappears at higher Tl concentrations and at higher temperatures.

CsI:Tl has the interesting property that during evaporation it grows in column-like structures with typical dimensions $3 \times 3 \times 500 \mu\text{m}^3$, which has a beneficial influence on the spatial resolution of the FDXD detectors. CsI:Tl shows, apart from its fast intrinsic decay, a lag in the 1000 ms regime.

5.8

Storage Phosphors

5.8.1

General Description of Storage Phosphors

In the case of storage phosphors, the luminescence generated during X-ray irradiation is not used. Part of the X-ray energy is used to store electrons and holes in traps. Optical stimulation leads to the liberation of one of the charge carriers, which recombines with the charge carriers of opposite charge, resulting in luminescence. Storage phosphors therefore rely on the presence of both electron traps and hole

Tab. 5.1 Important X-ray-intensifying phosphors and their properties (E is the energy conversion efficiency as a percentage; ρ is the density).

Phosphor	E(%)	$\rho(\text{g cm}^{-3})$	Speed (s)	Emission	Comments
CaWO ₄	5	6.12		Broad blue (430 nm)	<ul style="list-style-type: none"> - Limited by strong afterglow; mechanism not understood - Inferior X-ray absorption relative to other new materials - Poor X-ray-to-light conversion efficiency
BaFBr:Eu ²⁺	16	4.56	800×10^{-9}	Broad UV/ blue (390 nm)	<ul style="list-style-type: none"> - Plate-like morphology which packs poorly; spray drying improves morphology - Limited by low density but has much higher conversion and speed relative to CaWO₄
Gd ₂ O ₃ :Tb ³⁺	19	7.34	3×10^{-3}	Line/green (540 nm)	<ul style="list-style-type: none"> - Excellent phosphor in combination with green-sensitive film - High density with Gd K-edge (50 keV) in the middle of X-ray energy range - Although the material has a layered structure, proper synthesis can result in well-faceted round crystallites
LaOBr:Tm ³⁺	18	6.10		Line UV/blue	<ul style="list-style-type: none"> - Isostructural with BaFCl but with higher density and higher X-ray absorption - Limited by plate like morphology
M' YTaO ₄	8	7.57	3×10^{-3}	Broad/UV (330 nm)	<ul style="list-style-type: none"> - Higher X-ray absorption than CaWO₄
M' YTaO ₄ :Nb ⁵⁺	8	7.57	3×10^{-3}	Broad/blue (410 nm)	<ul style="list-style-type: none"> - Emission efficiency twice that of CaWO₄ - Speed twice or three times that of CaWO₄

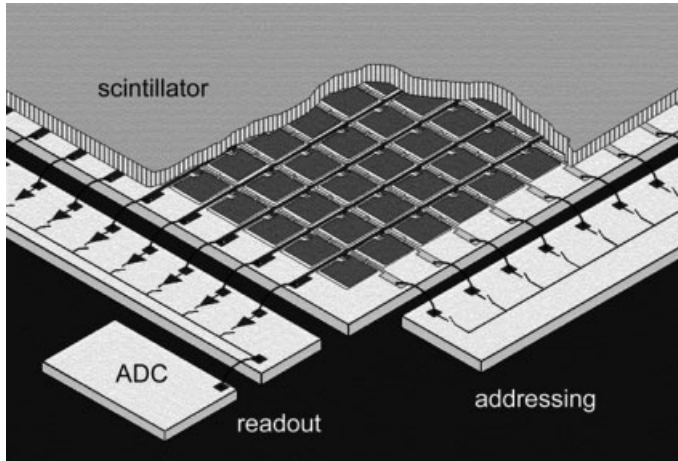


Fig. 5.9 Principle and layout of the FDXD detector. The light generated by the scintillators is detected by a two-dimensional array of photodiodes.

traps, which is completely opposite to phosphors used in CT and PET, where the influence of electron and hole traps has to be minimized. The intensity of the photostimulated luminescence is proportional to the X-ray dosage, which in turn is proportional to the density of the trapped carriers. As in the case of PET and CT

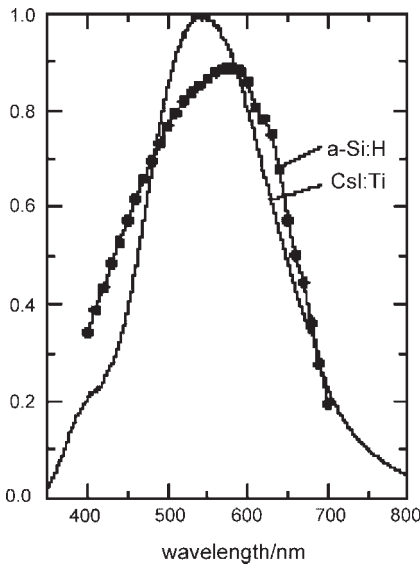


Fig. 5.10 Emission spectrum of CsI:Tl and the sensitivity spectrum of a common photodetector. Taken from C.W.E. van Eyk, *Phys. Med. Biol.* **47** (2002) 85–106.

systems, a photo detector measures the emission. Spatial resolution is obtained by using a scanning laser beam.

It is instructive to consider the trapping/direct emission ratio in storage phosphors. If the trapping probability is too high, the emission intensity is reduced, also during optical read out. On the other hand, a high luminescence probability will prevent effective trapping. For this reason, the ratio should be about unity when the traps are not yet occupied, i.e. in the initial irradiation phase.

The best example of a storage phosphor, introduced in the 1980s, is BaFBr:Eu²⁺ [55]. Upon X-ray irradiation, the created holes in the valence band are trapped by the Eu²⁺ ions, resulting in Eu³⁺, while the electrons in the conduction band are trapped by Br⁻ ion vacancies, resulting in the formation of F-centers. The illumination of the storage phosphor by red laser light provides a sufficient amount of energy to stimulate the release of the trapped electrons. The subsequent recombination of the electrons with the trapped holes at the Eu³⁺ yields Eu²⁺ in the excited state. The resulting emission is a broad band centered at 390 nm which corresponds to the well-known Eu²⁺ 4f⁶5d → 4f⁷ optical transition. As pointed out in Ref. [1], the physical mechanism behind the operation of a storage phosphor is complicated and not completely understood.

Other storage phosphors that have been investigated are RbBr:Tl⁺ [56], Ba₅(Ge,
Si)O₄Br₆: Eu²⁺ [57,58], and Y₂SiO₅:Ce³⁺, Sm³⁺ [59,60].

5.9 Semiconductor Scintillators

In this section, we discuss scintillators in which the luminescence mechanism is determined by the band structure of the luminescent material. The recent past has seen an interest in the development of extremely fast and potentially very bright scintillators that are based on the luminescence of semiconductors with small band gap (<3 eV). Consider, for example, the case of direct-gap materials such as PbI₂ (band gap 2.55 eV) [61–64] and HgI₂ (band gap 2.1 eV) [64,65]. These materials can be classified as having moderate densities of 6.16 g cm⁻³ and 6.36 g cm⁻³, respectively. The emission of these materials is of the donor-acceptor recombination type. In both materials, the emission is dominated by near band edge emission and broad bands shifted to lower energies, which are attributed to the donor-acceptor recombination. We consider the case of PbI₂, where the near band edge emission occurs at 495 nm, corresponding to free and bound excitons, and a broad asymmetrical band in the region of 510–530 nm, which is attributed to the donor-acceptor recombination. The interesting aspect of this material is the measured decay constants. At 10 K, the scintillation exhibits an extremely fast nonexponential decay with 1/e decay times of 0.55, 2.4, 3.7, and 5.6 ns. The light yield of this scintillator is 3000 photons/MeV at 10 K. This is about 0.4 times the light yield of BGO at room temperature. Increasing the temperature to 165 K results in a dramatic decrease in the light yield (the luminosity decrease by a factor of 27). This decrease is much faster than the decrease in the decay lifetime. It is then concluded that the reduction in light yield with

increasing temperature is not due to thermal quenching of the excited state, but is mainly due to thermally activated trapping of the charge carries on nonradiative recombination centers. It is estimated that if the PbI_2 were made defect-free, then the light yield of the scintillator would be about 200 000 photons/MeV with a decay constant of 1 ns: the band gap is only 2.55 eV, and this may result in a value for β of only about 2.

The luminescence of $\text{ZnO}:\text{Ga}$ was investigated in the 1960s. ZnO is a direct-gap material. The Ga^{3+} ions act as shallow donors when substituting for the tetrahedrally coordinated Zn^{2+} ions (n-type). At 0.3 % doping level, a degenerate donor band that overlaps with the bottom of the conduction band of ZnO is formed. At 12 K, the luminosity of $\text{ZnO}:\text{Ga}$ is twice that of BGO at room temperature. The principal decay time at low temperature is 0.41 ns. Increasing the temperature to 365 K decreases the luminosity by a factor of 33 while decreasing the decay lifetime from 0.41 ns to 0.21 ns [65]. Similar observations are made in the case of the direct band gap scintillator, $\text{CdS}:\text{In}$ [63, 65].

One last example that we discuss in this section is the presence of isoelectronic impurity in semiconductors. Consider the example of $\text{CdS}:\text{Te}$ [$\text{CdS}_{1-x}\text{Te}_x$] [63]. The scintillation emission spectrum of this material is a broad band with maximum at 640 nm. The light yield at room temperature is 17 000 photons/MeV and thus twice that of BGO. The decay time behavior is quite complex, with the decay time

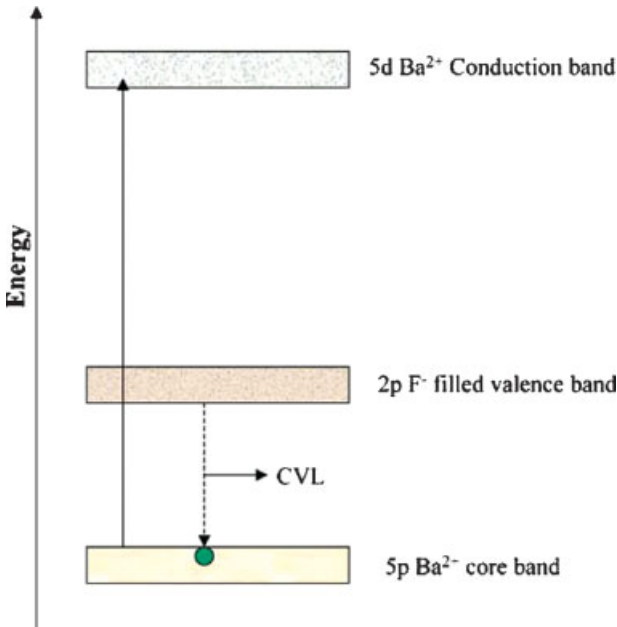


Fig. 5.11 A schematic representation of cross-over luminescence or cross valence luminescence (CVL) for BaF_2 . The hole in the Ba^{2+} 5p core state can be filled by an electron from the F^- 2p state, yielding luminescence.

components of 18 ns, 270 ns, and 3.0 μ s. The latter two are the main decay components. The scintillating mechanism is the following. Because of the large difference in electronegativity (between S and Te), the Te ions act as isoelectronic hole traps in CdS. The subsequent capture of the electrons results in the strongly Stokes-shifted emission at 640 nm. The low temperature band gap of CdS is 2.50 eV, yielding a Stokes shift of \sim 0.5 eV. The large Stokes shift is a result of the lattice relaxation that is induced by the presence of the local hole.

It is clear that the potential of direct band gap scintillators is based on the extremely fast decay lifetime (<1 ns) and a light yield which is close to the fundamental limit. This will, however, require the understanding and elimination of nonradiative centers that quench the luminescence in these materials. Please note that activator ion luminescence is a very elegant way to circumvent this problem: in most cases, the activator ions trap the excitation energy very fast, thereby eliminating luminescence quenching by nonradiative recombination centers. This is the main reason why the

Tab. 5.2 Overview of important commercial scintillators.

Material	Density [g/cm ³]	Index of refraction (at λ_{max})	Crystal system	Emission max. [nm]	Light output [photons/ MeV]	Decay time [ns]
NaI:Tl	3.67	1.85	Cubic	415	62 000	230
CsI:Tl	4.51	1.79	Cubic	550	66 000	600, 3400
CsI:Na	4.51	1.84	Cubic	420	40 000	630
CsI	4.51	1.95	Cubic	315	2000	16
CaF ₂ :Eu	3.18	1.44	Cubic	435	24 000	940
CsF	4.64	1.48	Cubic	390	2000	3–5
BaF ₂	4.88	1.54, 1.50	Cubic	220, 315	11 000	0.8, 630
LuAlO ₃ :Ce	8.34	1.94	Cubic	365	12 000	18
YAlO ₃ :Ce	5.55	1.95	Orthorhombic	350	17 000	27
Gd ₂ SiO ₅ :Ce	6.71	1.85	Monoclinic	440	8000	60
Lu ₂ SiO ₅ :Ce	7.40	1.82	Monoclinic	420	30 000	40
Bi ₄ Ge ₃ O ₁₂	7.13	2.15	Cubic	480	9000	300
CdWO ₄	7.90	2.3	Monoclinic	470, 540	28 000	10, 5000
ZnWO ₄	7.62	2.32	Monoclinic	490	9500	20 000
Lu ₃ Al ₅ O ₁₂ :Ce	6.90	1.85	Cubic	520	5600	58
Y ₃ Al ₅ O ₁₂ :Ce	4.57	1.82	Cubic	550	14 000	70
Lu ₂ Si ₂ O ₇ :Ce	6.20		Monoclinic	380	30 000	30
LuPO ₄ :Ce	6.53		Tetragonal	360	17 000	25
LuBO ₃ :Ce	7.40		Trigonal	410	10 000	39
LuF ₃ :Ce	8.3		Orthorhombic	310	8000	23
LaCl ₃ :Ce	3.86		Hexagonal	330	49 000	26
LaBr ₃ :Ce	5.29		Hexagonal	358	61 000	35
LaI ₃ :Ce	5.6		Hexagonal	472, 535	95 000	24
Gd ₂ O ₂ S:Pr,Ce,F	7.34	2.2	Trigonal	510	40 000	3000
Gd ₂ O ₂ S:Tb	7.34	2.2	Trigonal	510	40 000	\sim 10 ⁶
(Y,Gd) ₂ O ₃ :Eu	5.90	1.90	Cubic	610	19 000	\sim 10 ⁶

majority of applied luminescent materials consist of a host lattice with intentionally doped impurities.

For faster decay constants, we could use luminescent materials which show cross-over luminescence (or cross valence luminescence) [66]. In such materials, emission occurs involving electron transitions between the valence band and an incompletely filled core state (Fig. 5.11). Such transitions are generally very fast, albeit not very efficient. A prominent example of a material showing this kind of emission is BaF₂. This material shows cross-over luminescence at 220 nm, with a decay time of 800 ps. The light yield of 11000 photons/MeV is for the cross-over luminescence and the excitonic luminescence at 315 nm which has a much longer decay time: 630 ns (see Table 5.2).

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6

Upconversion Phosphors

J. Freek Suijver

6.1

Introduction

This chapter deals with phosphors that are capable of absorbing photons of a certain energy E_1 and emitting photons with another energy E_2 , such that $E_2 > E_1$. Many fascinating applications have been suggested for these materials, known as upconversion phosphors, which are capable of converting e.g. near-infrared radiation to visible wavelengths, although the actual applicability will depend on the conversion mechanism. Several examples will be given and discussed at the end of this section. Note that there exist a multitude of processes that result in the conversion of photons of a given wavelength into shorter-wavelength ones. Therefore, it is useful to first divide them into different types, according to the underlying physical mechanisms. Physically, these conversion processes can most straightforwardly be divided into two types: single-photon or multi-photon processes. The most famous single-photon conversion process is anti-Stokes emission, where one photon is absorbed and subsequently emitted at higher energy. The additional energy is usually provided by the lattice, in the form of the annihilation of one or more phonons. The anti-Stokes emission bands are typically investigated when performing Raman spectroscopy, as they occur at very specific energies that are dictated by the phonon spectrum of the host lattice. Furthermore, the anti-Stokes emission is usually in a relatively dark spectral range, as only a few processes result in emission at higher energy than the excitation energy, and these are typically not very efficient.

In the class of multi-photon processes, two or more incident photons are converted into one emitted photon of (substantially) higher energy. Many such processes exist, and the most well-known ones will be described and compared here briefly. After this comparison, the remainder of this chapter will focus exclusively on photon upconversion. Figure 6.1 shows an overview of the relevant (idealized) energy level structures of luminescent materials in accordance with the multi-photon emission schemes that will be described below, as well as the most important energy transfer processes.

Figure 6.1(a) describes an often-used, though rather inefficient, process: anti-Stokes Raman emission. Here, a vibronic excited state of the ground state is the initial

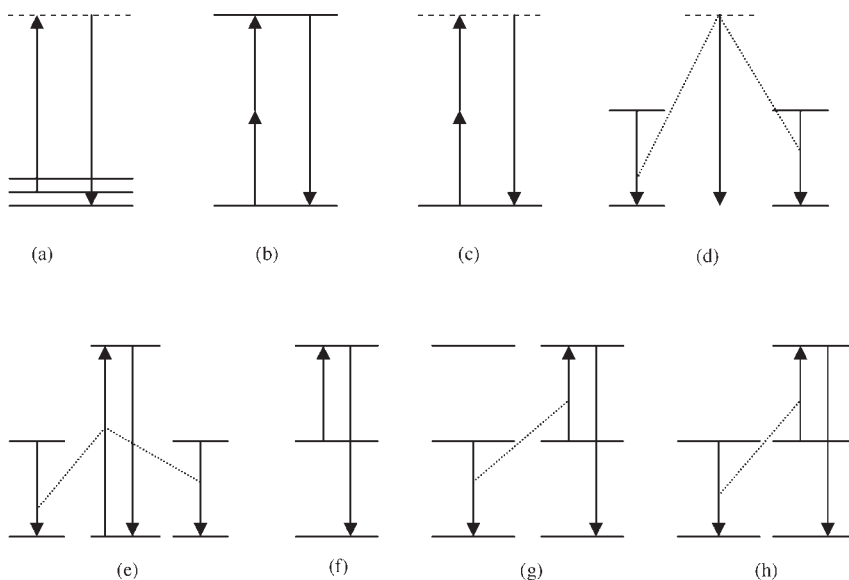


Fig. 6.1 Eight of the most relevant processes that convert long-wavelength excitation light into shorter-wavelength emission light. The processes are (a) anti-Stokes Raman emission, (b) 2-photon excitation, (c) second harmonic generation, (d) cooperative luminescence, (e) cooperative sensitization, (f) excited state

absorption, (g) energy transfer upconversion, and (h) sensitized energy transfer upconversion. The dotted lines indicate nonradiative energy transfer processes, the dashed horizontal lines indicate virtual states, and the arrows indicate excitation (upward) or emission (downward) transitions.

state. After absorption of an excitation photon, emission occurs from a virtual excited state down to the real ground state. As a result, the emission energy lies at somewhat higher level than the excitation energy, and the energy difference is given by the phonon spectrum of the material. Typically, the emission occurs at $100\text{--}1000\text{ cm}^{-1}$ higher energy than the excitation. Because of the (often) well-defined phonon energies, precisely determined emission photons are recorded, and from their increase in energy the phonon spectrum of the material is determined. A typical example of this process can be found in silicon. Silicon shows anti-Stokes Raman emission with an efficiency of $\sim 10^{-13}\text{ cm}^2\text{ W}^{-1}$ when one uses sub-band-gap laser light. From the energy differences between the emitted and excitation radiation, one can determine (some of) the Si phonon modes.

Figure 6.1(b) schematically indicates the process of two-photon absorption (TPA). In this case the intermediate state is still a virtual one, but now both the ground state and the excited state are real. TPA occurs when a single excitation photon cannot bridge the gap between the ground state and the excited state, but two excitation photons can. It is not required that the two excitation photons be of the same wavelength or that they be coherent, although this is often the case. Very intense excitation is required, as simultaneous absorption of two excitation photons is the

underlying process, which is intrinsically much less efficient than single-photon absorption. For example, $\text{CaF}_2:\text{Eu}^{2+}$ shows two-photon absorption with an efficiency of $\sim 10^{-12} \text{ cm}^2 \text{ W}^{-1}$. Under red-light excitation of a pulsed ruby laser, blue two-photon emission of Eu^{2+} can be detected.

Figure 6.1(c) illustrates second harmonic generation (SHG) such as may occur in, e.g., the green 532 nm emission observed from KNbO_3 crystals under 1064 nm excitation. As indicated in the figure, only the ground state is a real level. Both the intermediate and the excited states are virtual. This implies that the two excitation photons must coincide and must also be coherent. Furthermore, because of the prerequisite of simultaneous absorption of the two excitation photons, the oscillator strength for this transition is very low. Finally, due to the fact that the excited state is a virtual one, the lifetime of the excited state will be zero (to within the uncertainty principle). KH_2PO_4 crystals show second harmonic generation with an efficiency of $\sim 10^{-11} \text{ cm}^2 \text{ W}^{-1}$. In this material, two near-infrared photons (typically 1064 nm from an $\text{Nd}^{3+}:\text{YAG}$ laser) undergo sum-frequency mixing, generating one green (532 nm) photon. This material is extensively used in modern-day lasers.

Figure 6.1(d) shows the cooperative luminescence process. Here, two excitation photons are sequentially absorbed by two different active ions, bringing both of them into their excited states. Next, both excited ions simultaneously decay to their ground states with emission of a single photon that contains the combined energy of both ions. As the cooperative emission occurs from a virtual state, the emission probability is rather low. Also, since only one of the two excited ions needs to decay to its ground state to prohibit cooperative emission, the lifetime of the cooperative emission is given by exactly half of the lifetime of the excited state of the single ions when they are in the same excited states. Note that the two absorbing ions do not need to be of the same species, or be in the same excited states, although this is often the case. Generally speaking, when two ions are in excited states with lifetimes τ_1 and τ_2 , then their cooperative luminescence will have a lifetime that is given by

$$\tau_{\text{Coop}} = ((\tau_1)^{-1} + (\tau_2)^{-1})^{-1}. \quad (1)$$

A well-known example is $\text{YbPO}_4:\text{Yb}^{3+}$, which shows cooperative luminescence with an efficiency of $\sim 10^{-8} \text{ cm}^2 \text{ W}^{-1}$. Two excited Yb^{3+} ions generate one photon at double the energy, in the green part of the spectrum.

Figure 6.1(e) depicts cooperative sensitization, a process that is quite similar to that shown in Fig. 6.1(d). In this process, again two excitation photons are sequentially absorbed by two different active ions, bringing both of them into their excited states. However, now the energy of the two excited ions is transferred to another ion, bringing it from its ground state into an excited state at an energy resonant with the sum of the two excitation energies. As the final state is a real one, in contrast to the case of cooperative luminescence, the cooperative sensitization is generally speaking considerably more efficient than cooperative luminescence. Again, the two ions absorbing the initial radiation need not be the same species or in the same excited states. $\text{YF}_3:\text{Yb}^{3+}, \text{Tb}^{3+}$ shows cooperative sensitization of Tb^{3+} from the Yb^{3+} ions

with an efficiency of $\sim 10^{-6} \text{ cm}^2 \text{ W}^{-1}$. Here the two excited Yb^{3+} ions simultaneously transfer their energy to Tb^{3+} , bringing it into an excited state at $\sim 20\,000 \text{ cm}^{-1}$.

Figure 6.1(f–h) show the two-photon upconversion (UC) processes that are relevant for the remainder of this chapter. They are excited-state absorption, energy transfer upconversion, and sensitized energy transfer upconversion, respectively [1]. The most important difference between upconversion and the other processes shown in Fig. 6.1(a–e) is that UC depends on a real intermediate state. This state must have a finite lifetime that is long enough for an excitation to be stored there for such a time as to allow a second excitation photon to further excite the phosphor into the higher-lying excited state. Typically, as a rule of thumb, the intermediate excited state should have at least a microsecond lifetime to allow enough time for upconversion. Due to the fact that in photon upconversion all relevant energy levels are real, (very) high excitation powers are now no longer required in order to observe this effect. Experimental data showing upconversion at excitation powers that are 5–10 orders of magnitude lower than those required for second harmonic generation or two-photon absorption are routinely available.

Typical examples of the three-photon upconversion processes are found among the rare-earth doped fluorides. Excited state absorption has been recorded in $\text{SrF}_2:\text{Er}^{3+}$ crystals, yielding an efficiency of $\sim 10^{-5} \text{ cm}^2 \text{ W}^{-1}$. Here, up to three $1\text{-}\mu\text{m}$ wavelength photons can be absorbed by Er^{3+} sequentially, allowing it to emit in the red, green, or blue spectral regions. $\text{YF}_3:\text{Er}^{3+}$ shows energy transfer upconversion with an efficiency of $\sim 10^{-3} \text{ cm}^2 \text{ W}^{-1}$. One Er^{3+} ion transfers its energy to another already excited Er^{3+} ion, allowing $1.5\text{-}\mu\text{m}$ wavelength photons to be converted to the green spectral range. Finally, $\text{NaYF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ shows sensitized energy transfer upconversion with an efficiency of $\sim 10^{-1} \text{ cm}^2 \text{ W}^{-1}$. Three or four near-infrared excitations of Yb^{3+} are transferred one by one to Tm^{3+} , resulting in emission in the violet and ultraviolet spectral ranges.

To end this section, an overview is presented of the examples showing the different mechanisms discussed here. In order to get a feeling for the relative efficiencies of all these processes, their efficiencies have been converted to a standard unit, and saturation effects are ignored. The relevant processes are shown in Fig. 6.1 and were described previously in some more detail. The summary of the most important data is indicated in Table 6.1. Needless to say, rather large variations in efficiencies can be found for each of these mechanisms (i.e., there exist ESA phosphors with much lower efficiencies, as well as higher). The values indicated are simply reasonable averages.

The remainder of this chapter will deal exclusively with upconversion. After a somewhat detailed discussion of some of the most important theory related to upconversion emission, several examples of well-known as well as obscure upconversion phosphors will be described in more detail in Section 6.3. At the end of that section, the young field of nano-scale upconverters will also be visited. The reason that many research groups are studying upconversion phosphors is that a huge body of literature has now emerged describing the properties and uses of upconversion materials in (possible) future devices. A few of such applications are, for example, diode-pumped all-solid-state visible lasers [2,3], next-generation lighting or three-dimensional displays based on a diode-pumped 3-dimensional imaging

Tab. 6.1 Typical examples of the mechanisms in which higher-energy emission light is generated from the original excitation light. The processes are schematically shown in the parts of Fig. 6.1 as indicated, and are further discussed in the text.

Fig. 6.1	Mechanism	Typical example	Efficiency
(a)	Anti-Stokes Raman	Silicon crystals	$\sim 10^{-13} \text{ cm}^2 \text{ W}^{-1}$
(b)	2-Photon excitation	$\text{CaF}_2:\text{Eu}^{2+}$	$\sim 10^{-12} \text{ cm}^2 \text{ W}^{-1}$
(c)	SHG	KH_2PO_4 crystals	$\sim 10^{-11} \text{ cm}^2 \text{ W}^{-1}$
(d)	Cooperative luminescence	$\text{YbPO}_4:\text{Yb}^{3+}$	$\sim 10^{-8} \text{ cm}^2 \text{ W}^{-1}$
(e)	Cooperative sensitization	$\text{YF}_3:\text{Yb}^{3+}, \text{Tb}^{3+}$	$\sim 10^{-6} \text{ cm}^2 \text{ W}^{-1}$
(f)	ESA	$\text{SrF}_2:\text{Er}^{3+}$	$\sim 10^{-5} \text{ cm}^2 \text{ W}^{-1}$
(g)	ETU	$\text{YF}_3:\text{Er}^{3+}$	$\sim 10^{-3} \text{ cm}^2 \text{ W}^{-1}$
(h)	Sensitized ETU	$\text{NaYF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$	$\sim 10^{-1} \text{ cm}^2 \text{ W}^{-1}$

technique [4], near-infrared photon detection devices based on avalanche quantum counting [5], high-power fiber upconversion lasers [6], and nanometer-sized biological labels [7]. All these applications are based on near-infrared to visible upconversion excitation schemes. Such wide and diverse bodies of fascinating applications of upconversion phosphors clearly warrant the significant scientific attention that the field has received in recent years.

6.2 Theory of Upconversion

Usually one distinguishes between two different types of upconversion: the single-ion excited-state absorption process and the two-ion (sensitized) energy transfer upconversion process. The boundary between these two processes can sometimes be a little blurred, as will become clear from some examples of mixed rare earth/transition metal upconverters, described later in this chapter. For both types of upconversion, the phosphor has to sequentially absorb two excitation photons, followed by the emission of a photon of higher energy. Note that this does not imply that the ion only absorbs two excitation photons before any emission of a photon, as often there is an intermediate nonradiative relaxation step between the absorption of the two excitation photons and the emission. In the examples shown later in this chapter, such intermediate relaxation steps frequently occur. However, as this does not bring new physics relevant for the upconversion mechanism, these obscuring relaxation steps are ignored here.

For the remainder of this chapter, four main processes must first be described. These processes are schematically depicted in Fig. 6.2. The first and second processes, as indicated in Fig. 6.2 (a) and (b), show what happens when the material is excited from its ground state or from an excited state, respectively. In the case that two ions are both in an excited state, energy transfer upconversion can take place, as is shown in Fig. 6.2(c). As a result of this process, one ion is de-excited to a lower-energy state (though not necessarily the ground state), while the second is excited to a

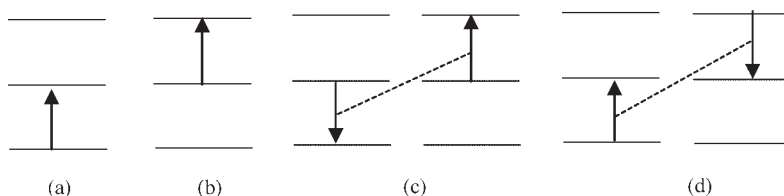


Fig. 6.2 The four main energy transfer processes that are important for upconversion. They are (a) ground-state absorption (GSA), (b) excited-state absorption (ESA), (c) energy transfer upconversion (ETU), and (d) cross-relaxation.

higher-energy state. The fourth process, cross-relaxation, is the reverse of energy transfer upconversion: one ion is excited to a higher-energy state, while the second is de-excited to a lower-energy state (though not necessarily the ground state). This process is shown in Fig. 6.2(d). The distinction between these last two processes lies in the highest excited state: if, after the process, one of the ions is in a higher excited state than either of the ions was before the process, one speaks of energy transfer upconversion. If this is not the case, one speaks of cross-relaxation. Typically for upconverting phosphors, energy transfer upconversion is a wanted process while cross-relaxation is considered a loss process. However, there are exceptions to this rule of thumb, as will become clear in the discussion of avalanche upconversion in Section 6.2.4. Note that for both energy transfer upconversion and cross-relaxation it is not required that the two ions be identical. However, as these processes are two ion pair processes, they must be in close proximity to each other, and experimentally it was found that the rate constants governing these processes are strongly concentration dependent.

To complete the list of relevant energy transfer processes, two additional (trivial) ones should be included here. These are photon emission and nonradiative multiphonon relaxation, respectively. Clearly, the first process (when occurring from a high, upconversion excited state) is desired, while the second is generally not. The majority of compounds that are able to perform UC involve trivalent lanthanides (Ln^{3+}). Examples of such phosphors will be described in Section 6.3.10. The lanthanide ions commonly have more than one metastable level (with the exception of Yb^{3+}), the basic requirement for UC. This is due to the fact that the spectroscopically active 4f electrons are well shielded from their chemical environment by the outer-lying 5s and 5p electrons, resulting in particularly small electron–phonon coupling strengths for the various excited f–f states. As a consequence, luminescence processes are much more competitive with multiphonon relaxation in lanthanides compared to other ions, and their excited state lifetimes are typically in the range of 10^{-6} – 10^{-2} s. In lanthanide centered f–f transitions there is only a small displacement between the ground state and the excited state along any relevant configurational coordinate. In this so-called weak coupling case, the multiphonon relaxation rate constant is described by the energy gap law,

$$k_{\text{NR}} \propto \exp[-\beta g] \quad (2)$$

indicating that the nonradiative rate constant k_{NR} decreases exponentially with increasing energy gap. Here, β is a specific constant of the material and g is the reduced energy gap in units of the highest-energy vibrational mode $\hbar\omega_{\text{max}}$ and the total energy gap ΔE that is to be breached,

$$g = \frac{\Delta E}{\hbar\omega_{\text{max}}} \quad (3)$$

As a rule of thumb for f-electron systems, radiative relaxation is dominant when the reduced energy gap to the next lower energy level is greater than five times the highest-energy phonons available (i.e.: $g > 5$), while for smaller gaps nonradiative multiphonon emission becomes the dominant depopulation mechanism. However, for d metals, where Eq. (4) cannot be used, gaps as large as 10–20 times the maximum phonon energy can be breached because of the large offset between the ground state and the excited state parabolas (e.g., due to the large Huang-Rhys factor in such materials). Examples of d metal upconversion phosphors will be given in Sections 6.3.2.7 and 6.3.3.8.

6.2.1

Absorption and Excitation Spectroscopy

In the absorption spectroscopy of rare earth ions, typically the well-known Judd-Ofelt theory is used in order to calculate the absorption strengths of the relevant $4f \rightarrow 4f$ transitions. Especially in the case of upconversion phosphors, where direct measurement of excited state absorption strengths may not be possible, Judd-Ofelt theory can be extremely useful. In this theory, the initial and final states of an absorption transition are written as $|SLJ\rangle$ and $|S'L'J'\rangle$, respectively. Here S , L , and J denote the quantum numbers for the total spin, orbital angular momentum, and total angular momentum, respectively. Judd and Ofelt derived independently that the oscillator strength for an inter-4f transition can be written as [8]

$$f = \frac{8\pi^2 m \nu \chi}{3h(2J+1)} \sum_{k=2,4,6} \Omega_{(k)} |\langle SLJ || U^k || S'L'J' \rangle|^2 \quad (4)$$

where the most significant parameters are the parameter χ that is related to the refractive index of the material, ν which describes the energy of the excitation light (usually denoted in wavenumbers), and the tensor operators U^k that are used in the calculation of the reduced matrix elements that describe the electrostatic and spin-orbital interactions. A detailed derivation and discussion of Eq. (4) can be found in many fundamental textbooks on spectroscopy (e.g., Ref. [8]). The relevant fitting parameters are the set of $\Omega_{(k)}$, and these are found by fitting Eq. (4) to available absorption data. Subsequently, for the same ion in a slightly different host lattice, one uses the known $\Omega_{(k)}$ to get a (quite accurate) estimation of where certain absorption features may be found. Clearly Judd-Ofelt theory can be very useful when investigating upconversion phosphors, especially when the ground state absorption and excited state absorption steps do not coincide at the same

excitation energy. In such a case, two-color excitation spectroscopy becomes required, and it really helps the experimenter if a reasonable first estimate of the excitation energies are known.

In the case of ground state absorption $|0\rangle \rightarrow |1\rangle$ followed by excited state absorption $|1\rangle \rightarrow |2\rangle$, the luminescent ion simply absorbs two excitation photons before returning to its ground state. This process is usually denoted by GSA/ESA and is schematically shown by the combination of Figs. 6.2 (a) and 6.2(b). Since both excitation steps are required before emission from $|2\rangle$ can be observed, the excitation cross-section for the upconversion emission can be written as the product of the two separate cross-sections

$$\sigma_{\text{GSA/ESA}} = \sigma_{\text{GSA}} \cdot \sigma_{\text{ESA}} \quad (5)$$

where σ_{GSA} and σ_{ESA} indicate the cross-sections for the $|0\rangle \rightarrow |1\rangle$ and $|1\rangle \rightarrow |2\rangle$ excitation steps, respectively. It is important to remember that both these cross-sections can be strongly wavelength dependent, which allows for interesting two-color experiments, as will be discussed later.

Figure 6.3(a) shows the (one-color) excitation spectrum of an upconversion emission that is excited via a GSA/ESA sequence. Note that beside the multitude of satellite peaks a main excitation maximum is found at $\sim 10\,450\text{ cm}^{-1}$. When this excitation spectrum is compared with the absorption cross-section (i.e., the ground state \rightarrow intermediate state excitation spectrum) as shown in Fig. 6.3(b), it is clear that this main excitation maximum does not correspond to a strong ground state absorption feature. However, using the previously mentioned Judd-Ofelt theory, one can calculate the intermediate state \rightarrow excited state excitation spectrum, which is shown in Fig. 6.3(c). It is clear from comparison of Figs. 6.3(b) and 6.3(c) that the GSA and ESA spectra are indeed quite different. On multiplication of these spectra, in accordance with Eq. (5), the spectrum in Fig. 6.3(a) was obtained. This example demonstrates that in the case of (one-color) excitation spectra of GSA/ESA upconversion emission bands, large and unexpected excitation features can be observed that cannot be attributed to individual transitions but rather to combinations of more than one energy transfer step.

When the dominant upconversion process is (sensitized) energy transfer upconversion, the excitation cross-section for the upconversion emission can be written exclusively in terms of the GSA cross-section. Since each of the n excitation photons are absorbed on the sensitizer ion (via the same excitation transition) and subsequently transferred to the acceptor ion (note that in the case of non-sensitized ETU both these ions are of the same species), the total excitation cross-section becomes straightforwardly

$$\sigma_{\text{GSA/ETU}} = (\sigma_{\text{GSA}})^n \quad (6)$$

in the case that n ground state absorption steps are required for excitation of the upconversion emission.

Graphically, one can see the effects of Eq. (6) in Fig. 6.4, where the excitation spectrum of a hypothetical ion capable of sensitized upconversion is shown. It is

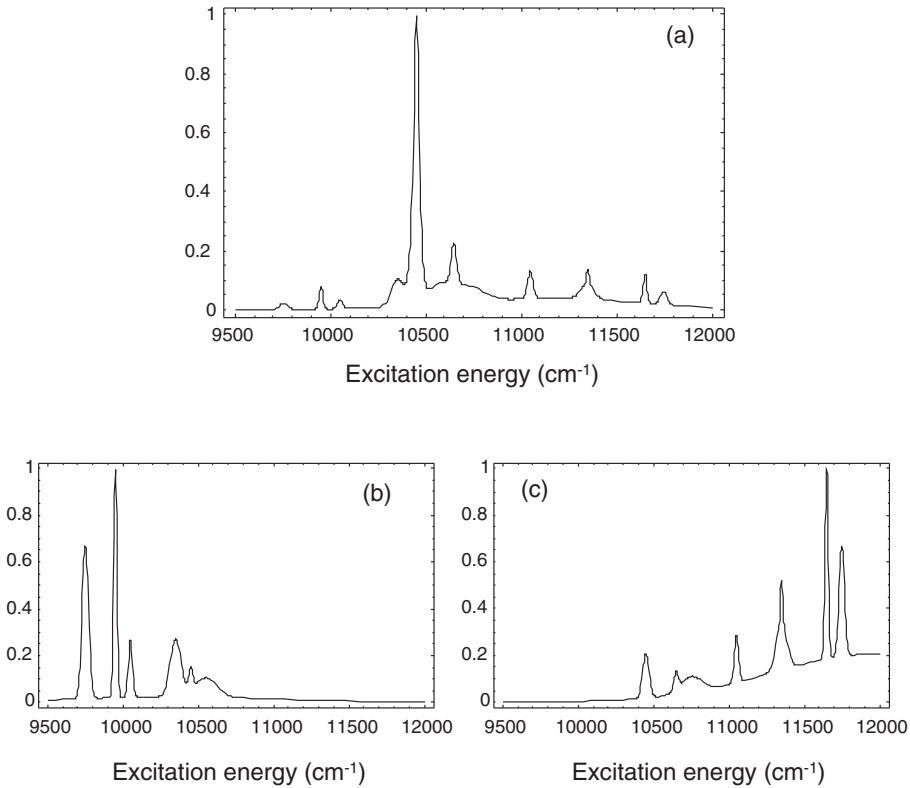


Fig. 6.3 (a) Excitation spectrum of the upconversion emission of a hypothetical upconversion phosphor. The (b) ground state absorption step and (c) excited state absorption step are indicated separately. The spectrum shown in (a) was calculated from those in (b) and (c) using Eq. (5). Relative intensities cannot be compared.

assumed that the whole fine structure of the excitation spectrum is due to the transition from the ground state of the sensitizer ion to its excited state, and that subsequent energy transfer from this sensitizer ion brings the acceptor ion into increasingly higher excited states ($n = 1, 2, 3, 4$) from where emission is observed. Depending on the number of excitation photons required to observe the emission spectrum, one clearly sees that the highest intensity excitation lines (most notably the 12 000, 12 500, and 13 500 cm^{-1} ones) become considerably more pronounced. Typically, when a sharp-line feature is superimposed on a broad-band background, observing the excitation spectrum of higher-energy emissions will allow one to resolve these sharp-line features in much more detail. A typical example of this effect can be seen in $\text{YF}_3:\text{Er}^{3+}$. In this material under 6500 cm^{-1} excitation, the upconversion occurs via a GSA/ETU sequence, and emission is observed all the way up to the ultraviolet spectral range. The excitation spectra of the ${}^4\text{I}_{13/2}$ ($\sim 6500 \text{ cm}^{-1}$), ${}^4\text{I}_{11/2}$

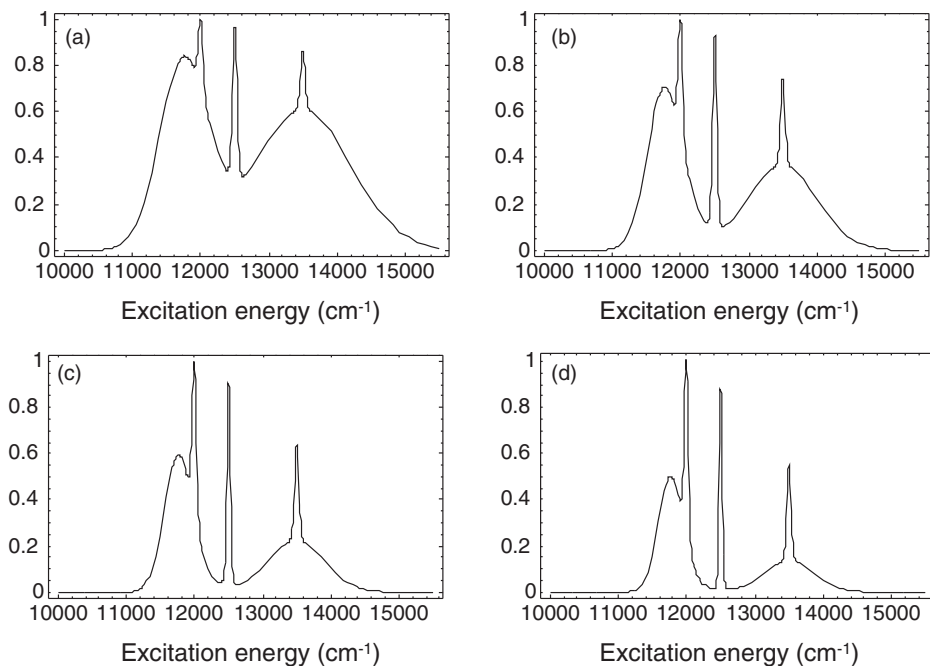


Fig. 6.4 Excitation spectra for a hypothetical upconversion emission transition when the dominant excitation mechanism is sensitized energy transfer upconversion. The upconversion emission requires an n -photon process, where (a) $n = 1$, (b) $n = 2$, (c) $n = 3$, and (d) $n = 4$ and the spectra were calculated in accordance with Eq. (6). Relative intensities cannot be compared.

($\sim 10\,000\text{ cm}^{-1}$), ${}^4\text{F}_{9/2}$ ($\sim 13\,000\text{ cm}^{-1}$), ${}^4\text{S}_{3/2}$ ($\sim 18\,000\text{ cm}^{-1}$), and ${}^2\text{H}_{9/2}$ ($\sim 24\,000\text{ cm}^{-1}$) emissions all follow the absorption spectrum of the ${}^4\text{I}_{13/2}$ to the power 1, 2, 3, 4, and 5, respectively, as follows from Eq. (6). Naturally, such clear examples are rather rare, as often more than one upconversion mechanism is active in a phosphor with so many different emission features.

An interesting extension of the normal excitation spectroscopy, as mentioned in this section, is the field of two-color excitation experiments. In such experiments, one often limits oneself to a system with a dominant and well-defined upconversion process in order to allow interpretation of the data. The principle is based on using two different wavelengths to excite the phosphor and varying one while keeping the other fixed. The reason to use two-color excitation is straightforward when one considers a GSA/ESA-type phosphor, as shown in Fig. 6.3. In a normal one-color experiment, both the GSA and ESA steps need to be resonant with the excitation energy, implying that the energy gaps that are breached must be of comparable sizes. When a two-color experiment is performed, this limitation is nullified. By varying the two wavelengths separately, one can maximize the upconversion emission

intensity. At the same time, this procedure results in the measurement of the (wavelength-dependent) excitation cross-sections for both the GSA and ESA steps separately. Such results can be used as a vindication (albeit after the fact) of the Judd-Ofelt theory described in the beginning of this section. A rough estimation reveals that using a two-color excitation scheme for the phosphor shown in Fig. 6.2 [excitation at 9950 and 11650 cm^{-1} , according to Figs. 6.3 (b) and 6.3 (c)] would result in a gain of more than an order of magnitude of the upconversion emission intensity over excitation at the highest-intensity wavelength according to the one-color excitation spectrum excited at 10450 cm^{-1} and shown in Fig. 6.3(a).

A particularly beautiful example of two-color excitation spectroscopy can be found in $\text{Cs}_3\text{Tb}_2\text{Br}_9:\text{Yb}^{3+}$, where exchange-coupled $\text{Tb}^{3+}\text{-Yb}^{3+}$ dimers are responsible for the GSA/ESA upconversion mechanism that results in green/blue emission under near-infrared excitation [9]. With one excitation color, the Yb^{3+} ion is excited from its ground state into its excited state. The second color excitation photon excites the $\text{Tb}^{3+}\text{-Yb}^{3+}$ dimer from its Yb^{3+} -dominated $|^2\text{F}_{5/2}(0), ^7\text{F}_6\rangle$ intermediate excited state into the higher-lying, and Tm^{3+} -dominated $|^2\text{F}_{7/2}(i), ^5\text{D}_4\rangle$ multiplet. Transitions to all different Yb^{3+} ground states ($i=0, 1, 2,$ and 3) were identified separately as contributing to the excited-state absorption step. Depending on the excitation wavelength in the ESA step, a strong shift in the emission color from green to blue was observed, which can be explained through a competition between an upconversion mechanism related to Tb^{3+} only and one due to the total $\text{Tb}^{3+}\text{-Yb}^{3+}$ dimer.

6.2.2

Time Evolution of UC Emission

Here, a useful technique to gain insight into the underlying energy transfer dynamics of an ion capable of upconversion is discussed. The technique that is used here is based on very fast excitation of the upconversion phosphor. When one monitors the temporal evolution of the upconversion emission intensity, a clear distinction between excited state absorption and energy transfer upconversion can be made.

Clearly, when ESA is the dominant excitation pathway for the upconversion emission, both the ground state absorption and the excited state absorption must occur within the excitation time. Therefore, after the fast (typically $\sim 5\text{--}10$ ns) excitation pulse is over, only depopulation processes can occur for the excited state. When one denotes by $N_2(t)$ the population of the upper excited state (i.e. the state capable of upconversion emission) and by k_{UC} the decay rate from this state (i.e. the reciprocal of the lifetime), then, in the case of excited state absorption

$$N_2^{\text{ESA}}(t) \propto \exp[-k_{UC}t] \quad (7)$$

corresponding to a single exponential decay with a lifetime that is given by the natural lifetime of the upper excited state.

In the case where energy transfer upconversion is the dominant excitation process, a distinctly different result will be found, as will be derived here. Let $N_1(t)$ and $N_2(t)$

denote the populations of the intermediate and upper excited states, respectively. Furthermore, the three relevant energy transfer processes have accompanying rate constants that are written as k_R (emission from the intermediate state to the ground state), k_T (ETU from the intermediate state to the upper excited state), and k_{UC} (emission from the upper excited state to the ground state), respectively. With these definitions, the two relevant rate equations that govern the excited state dynamics are

$$\frac{\partial N_1(t)}{\partial t} = -k_R N_1(t) - 2k_T [N_1(t)]^2 \quad (8)$$

and

$$\frac{\partial N_2(t)}{\partial t} = +k_T N_1(t) - k_{UC} N_2(t) \quad (9)$$

where the factor 2 and the square in Eq. (8) are due to the fact that in the ETU step two ions are both in their first excited states and they transfer their energy simultaneously to yield one ion in its second excited state and one in its ground state.

The boundary conditions, determined by the excitation cross-section σ and the laser power P , are subsequently imposed on the set of coupled differential equations,

$$N_1(t=0) = \sigma P \quad (10)$$

$$N_2(t=0) = 0 \quad (11)$$

These boundary conditions imply a (physically reasonable) delta-type excitation pulse, coupled with a negligible population in the upper excited state. Because of their non-linear nature, Eqs. (8)–(11) do not have a closed form solution for the second excited state. However, in the limit where the excitation density remains small, one can make the approximation

$$2(N_1(t))^2 \approx N_1(t) \quad (12)$$

which results in

$$N_1(t) \propto \exp[(k_T - k_R)t], \quad (13)$$

and

$$N_2^{\text{ETU}}(t) \propto (1 - \exp[(k_T + k_{UC} - k_R)t])\exp[-k_{UC}t]. \quad (14)$$

Note that the prefactors are not included explicitly, as an arbitrary scaling of the intensity axis is always allowed with the experimental data (for example by changing the slit widths or the excitation intensity).

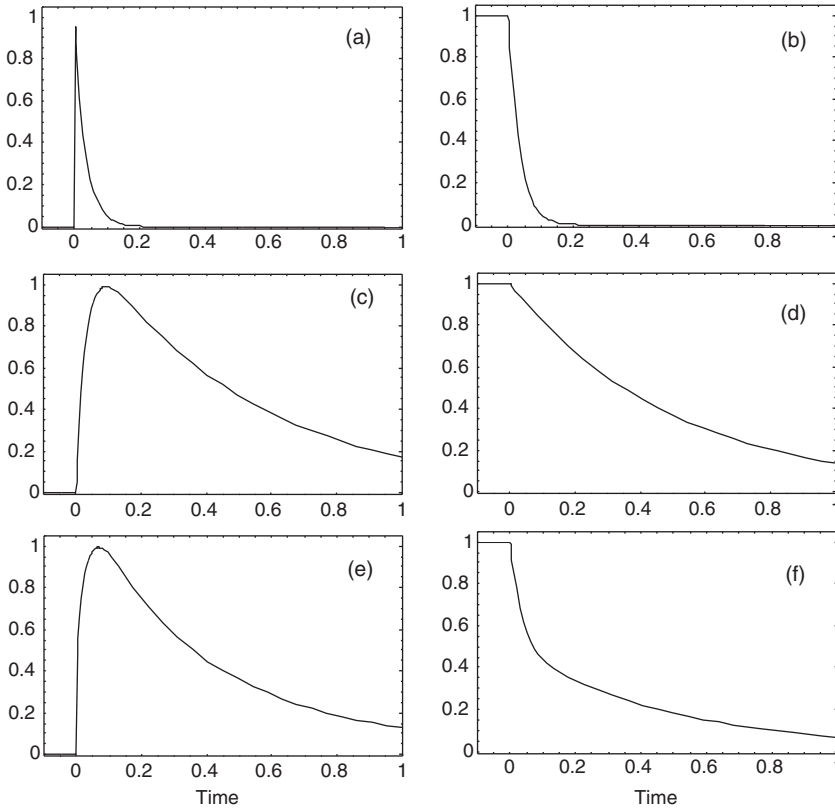


Fig. 6.5 Temporal evolution of the upconversion emission intensity resulting from (a, c, e) using a very short excitation pulse or (b, d, f) using a square wave excitation pulse. The upconversion mechanisms are (a, b) excited state absorption, (c, d) energy transfer

upconversion, and (e, f) a mixed situation with 40% ESA and 60% ETU, as given in Eq. (15). For these calculations, numerical integration of the relevant rate equations was used rather than the approximations shown in Eqs. (13) and (14).

On comparing $N_2^{\text{ESA}}(t)$ with $N_2^{\text{ETU}}(t)$ it can be seen that the time evolution of the population in the excited state clearly depends on whether ESA or ETU is the dominant excitation mechanism for the upconversion emission. In the case of ESA, a simple single exponential decay is measured, as is shown in Fig. 6.5(a). However, when ETU is responsible for the upconversion excitation there is zero initial intensity, followed by a rise in the emission intensity and a subsequent exponential decrease at longer times. This behavior is graphically shown in Fig. 6.5(c).

Based on the clear distinction between the transients shown in Figs. 6.5(a) and (c), one can directly discern which mechanism is responsible for the upconversion excitation. However, in practice both ESA and ETU are often present. In this case, one finds a convolution of the transients shown in Figs. 6.5(a) and (c): the initial intensity after the excitation pulse is not zero, but continues to rise nonetheless.

After rising to a maximum at some time after the excitation pulse, the long time limit comparable to the ETU-only result is reached. When fitting such a transient using a function like

$$N_{\text{Total}}(t) = fN_2^{\text{ESA}}(t) + (1 - f)N_2^{\text{ETU}}(t) \quad (15)$$

one can determine the fraction f of all ions that are excited through an ESA mechanism and the fraction $(1 - f)$ that is excited via ETU. An example of a mixed ESA/ETU signal is shown in Fig. 6.5(e), where $f = 0.4$.

Note that in the derivation presented here, it is assumed that short excitation pulses are used. However, one can also use square-wave excitation, where the excitation time is long compared to all the time constants for the energy transfer processes. In this case one will find a single exponential decay in the case of ESA, as well as in the case of ETU, as shown in Figs. 6.5(b) and (f). The different decay rates in the two figures are related to fact that after the excitation is finished, further energy transfer upconversion can occur in the case of ETU, which is not the case for excited-state absorption. When both the ESA and the ETU mechanisms are present, a double exponential signal is observed, as shown in Fig. 6.5(f). Similarly to what was shown above, the fraction f of all ions that are excited through an ESA mechanism and the fraction $(1 - f)$ that is excited via ETU can be determined using a double-exponential fit. The derivation of this result is the goal of Exercise 3.

6.2.3

Power Dependence of Upconversion

Three main types of upconversion need to be separated when one wishes to discuss the excitation power dependence of the upconversion emission intensity. These three are (a) excited-state absorption, (b) energy transfer upconversion on a single type of ion, and (c) sensitized energy transfer upconversion where two types of ions are involved: a sensitizer ion that absorbs the excitation radiation and another species of ion that is capable of upconversion through energy transfer upconversion. These three types of upconversion are schematically indicated in Fig. 6.6.

Theoretically, one needs to distinguish between these types of upconversion, as the underlying energy transfer mechanisms are fundamentally different. Clearly, one needs to distinguish between excited-state absorption and energy transfer upconversion. However, also within ETU, two different types must be treated separately: ETU on a single type of ion, and ETU where the excitation is absorbed on a sensitizer ion and subsequently transferred to an acceptor ion responsible for the actual upconversion.

For simplicity, we will only derive the power-dependent emission intensity for sensitized upconversion here. The other results can be found in the literature [10]. In order to simplify the calculation, we will assume two types of ions: a sensitizer ion and an acceptor ion. The sensitizer ion has only one excited state, with a population density of N_s , where all excitation photons are absorbed. Further, we assume a

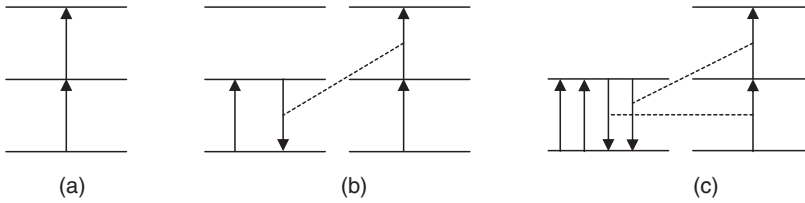


Fig. 6.6 Schematic representation of the three main types of upconversion that are relevant for this section. They are (a) ground state absorption/excited state absorption, (b) ground state absorption/energy transfer upconversion, (c) sensitized energy transfer upconversion. The processes involve (a) a single upconverting ion, (b) two identical upconverting ions, or (c) a non-upconverting sensitizer ion and a different ion capable of energy transfer upconversion.

(non-physical) perfect ladder of states $|0\rangle, |1\rangle, |2\rangle, \dots$ on the acceptor ion, where the energy difference between two subsequent states is fixed and is the same as the gap between the ground state and the excited state of the sensitizer ion. The populations of these states are denoted by N_0, N_1, \dots, N_n . Here n denotes the highest energy state of the ion. Note that often $n \rightarrow \infty$, as usually a continuum of states is found at high energy. To further simplify the derivation, we assume that all the energy transfer upconversion steps begin by exciting the sensitizer ion, and that the acceptor ion only has emission transitions to its ground state. Note that these simplifications are actually not required and that the same low- and high-power limits can be derived without them. Let W_i denote the upconversion rate constant associated with energy transfer upconversion from state $|i\rangle$ to state $|i+1\rangle$ and let R_i be the relaxation rate constant from state $|i\rangle$ to the ground state. With these definitions, we can directly write down the rate equation governing the population density of any state $|i\rangle$ on the acceptor ion,

$$\frac{\partial N_i(t)}{\partial t} = W_{i-1}N_{i-1}(t)N_s(t) - R_iN_i(t) - W_iN_i(t)N_s(t) \quad (16)$$

assuming that $i \neq 0$ and $i < n$ (if n is finite).

The time dependence in Eq. (16) is explicitly incorporated, which results in the fact that this non-linear differential equation cannot be solved in the general case.

However, when one is only interested in the steady state result (where $\partial N_i(t)/\partial t = 0$) the calculation becomes straightforward and its result is

$$N_i = \frac{W_{i-1}N_{i-1}N_s}{R_i + W_iN_s}. \quad (17)$$

In order to utilize this result, one must first realize that $N_s \propto P$ (the excitation laser power). Note that, by construction, the state $|1\rangle$ associated with N_1 lies at the same energy as the sensitizer state associated with the population density N_s . This implies that $N_1 \propto P$, because $N_s \propto P$, regardless of the excitation power used.

When the influence of upconversion is small, one can say that the main depopulation process for a given excited state is emission to the ground state. This implies that $R_i \gg W_i N_s$ and results in Eq. (17) simplifying to

$$N_i = \frac{N_{i-1} W_{i-1} N_s}{R_i} \propto (N_s)^i \propto P^i \quad (18)$$

where P remains the excitation power. The first equivalence is due to the fact that one can rewrite N_{i-1} as a prefactor times $N_{i-2} N_s$ and so on down the ladder of states on the acceptor ion. Since $N_1 \propto P$, regardless of the excitation power used, the second equivalence in Eq. (18) becomes straightforward.

When, on the other hand, the influence of upconversion is large, one can say that the main depopulation process for a given excited state is energy transfer upconversion to the next higher-lying excited state. This implies that $W_i N_s \gg R_i$ and results in

$$N_i = \frac{W_{i-1}}{W_i} N_{i-1} \propto N_s \propto P^1 \quad (19)$$

Clearly, in the high-power limit, the population in any state $|i\rangle$ becomes linearly dependent on the population density of the state lying directly below it. As one can repeat this argument for any lower-lying excited state, the only conclusion must be that the population of any excited state of the acceptor ion scales linearly with the population of the sensitizer ion (i.e., the excitation power).

Similarly to the calculation shown above, one can derive the expected power dependencies in the low- and high-power limits when the main upconversion mechanism is excited-state absorption or non-sensitized energy transfer upconversion. In these cases the result will be different. The three possible mechanisms and their power-dependencies are listed in Table 6.2. Clearly, when one is able to measure

Tab. 6.2 Theoretically derived power dependencies of the upconversion emission intensities for ions that abide by the three different types of upconversion discussed in the text. Note that in all cases the high-power limit (defined by a large influence of upconversion) differs when the ion is in its highest excited state compared to any lower-lying state. The graphical analog of this table is shown in Fig. 6.7. The data are taken from the literature [10,11].

Upconversion mechanism	Influence of upconversion	Transition from state	Power dependence
ESA	Small	$ i\rangle$	$N_i \propto P^i$
	Large	$ i\rangle, i < n$	$N_i \propto P^0$
	Large	$ i\rangle, i = n$	$N_i \propto P^1$
ETU	Small	$ i\rangle$	$N_i \propto P^i$
	Large	$ i\rangle, i < n$	$N_i \propto P^{1/2}$
	Large	$ i\rangle, i = n$	$N_i \propto P^1$
Sensitized	Small	$ i\rangle$	$N_i \propto P^i$
	Large	$ i\rangle, i < n$	$N_i \propto P^1$
	Large	$ i\rangle, i = n$	$N_i \propto P^2$

the excitation power dependence of a few upconversion emission bands, one can use the power dependence to distinguish between any of these three upconversion mechanisms. Experimentally, one usually measures a series of emission spectra of an upconversion phosphor while varying the excitation power over several orders of magnitude using neutral density filters. After converting the emission data to photon flux per constant energy interval, the integral of the relevant emission bands is plotted versus the excitation power density using a double-logarithmic representation. In such graphs, the slope of a straight line fitted through the data directly gives the power-dependence. Theoretical examples of all three upconversion mechanisms are shown in Fig. 6.7.

Clearly, the graphs shown in Fig. 6.7(a)–(c) differ strongly from each other. Therefore, one can use power-dependent emission spectroscopy to gain valuable information about the underlying energy transfer mechanisms that are active in an upconversion

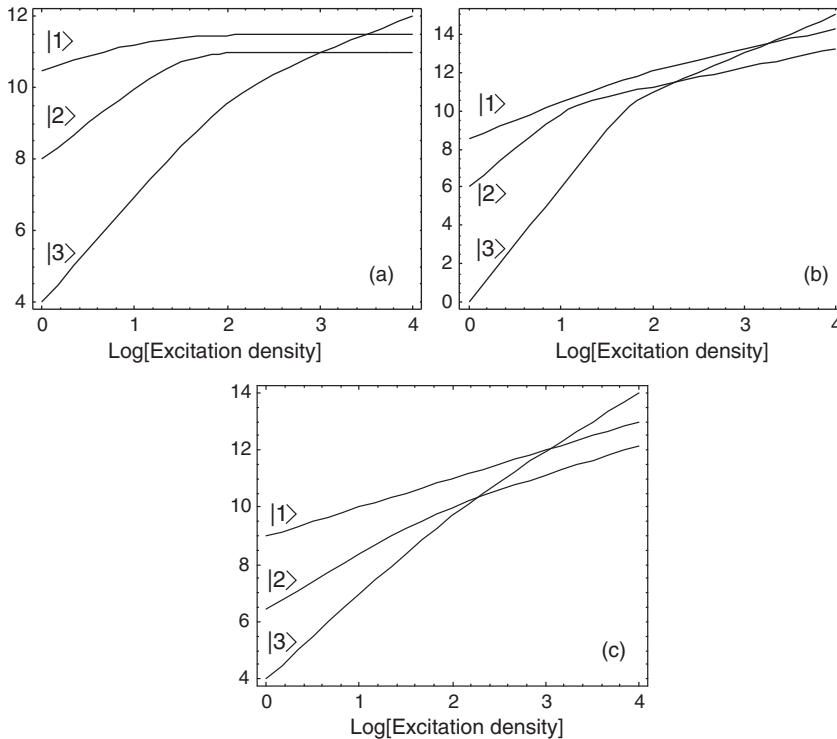


Fig. 6.7 Theoretically determined dependencies of the upconversion emission intensity of an ion with three excited states ($n=3$) as a function of excitation density for (a) excited-state absorption, (b) energy transfer upconversion, and (c) sensitized upconversion. The emission intensities

of the three states of an upconverting ion are indicated. The analytical expressions behind the graphs shown here are listed in Table 6.2. Note the double-logarithmic axes. Relative intensities between different emissions within the same graph cannot be compared.

phosphor. Not only is the number of excitation photons required to observe emission from any band directly experimentally accessible (by measuring the power-dependent emission data for the low-power regime), but also, by measuring in the high-power regime, one can determine unequivocally what the actual upconversion mechanism is. Especially for phosphors where time-resolved data may be hard to obtain, for example because of very fast energy transfer rates, this method can be indispensable for deriving fundamental knowledge about the precise workings of the phosphor.

6.2.4

Photon Avalanche Effects in Upconversion

A logical extension of the field of power-dependent spectroscopy that was described in the previous section is in the direction of so-called avalanche upconversion effects. This effect, though relatively rare, occurs through an interesting interplay between several competing absorption and energy transfer processes.

Figure 6.8 shows a schematic three-level system that demonstrates avalanche upconversion. Three special conditions are required for this effect to be observed. First, the excitation radiation must not be resonant with the absorption transition from the ground state to the intermediate excited state $|0\rangle \rightarrow |1\rangle$, but must rather be at a somewhat higher energy. Second, the excitation radiation must be resonant with the absorption transition from the intermediate excited state to the upper excited state $|1\rangle \rightarrow |2\rangle$. Third, there must be a relatively strong cross-relaxation process $|0,2\rangle \rightarrow |1,1\rangle$ that can compete with radiative relaxation from the upper excited state $|2\rangle \rightarrow |0\rangle$.

In order to derive the avalanche effect, we define the following: let P denote the laser power, N_i the population density of state $|i\rangle$, σ_0 the (small) absorption cross-section for the ground state absorption $|0\rangle \rightarrow |1\rangle$, and σ_1 the (comparatively larger) absorption cross-section for the excited state absorption $|1\rangle \rightarrow |2\rangle$. The radiative rate

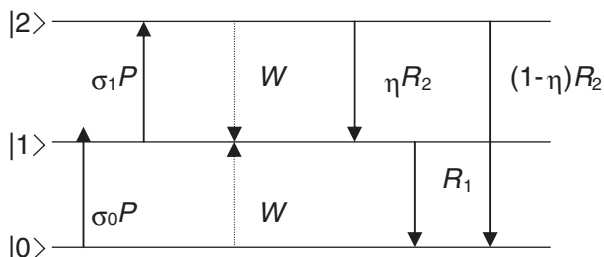


Fig. 6.8 Schematic energy level diagram for an ion with three electronic states that is capable of avalanche upconversion. The upward arrows indicate absorption transitions, the downward arrows indicate emission transitions, and the set of dotted arrows indicates the cross-relaxation process.

for the transition $|2\rangle \rightarrow |1\rangle$ is written as ηR_2 , while the radiative rate for the transition $|2\rangle \rightarrow |0\rangle$ is written as $(1 - \eta)R_2$, where η is the branching ratio which is normalized to 1. The radiative rate for the transition $|1\rangle \rightarrow |0\rangle$ is written as R_1 . Finally, W denotes the cross-relaxation rate constant. With these definitions, the system of rate equations describing the populations of all three states becomes

$$\frac{\partial N_0}{\partial t} = -\sigma_0 P N_0 - W N_0 N_2 + R_1 N_1 + (1 - \eta) R_2 N_2, \quad (20)$$

$$\frac{\partial N_1}{\partial t} = \sigma_0 P N_0 - \sigma_1 P N_1 + 2W N_0 N_2 - R_1 N_1 + \eta R_2 N_2, \quad (21)$$

$$\frac{\partial N_2}{\partial t} = \sigma_1 P N_1 - W N_0 N_2 - R_2 N_2. \quad (22)$$

Note that the factor 2 in Eq. (21) is a direct consequence of the two-ion cross-relaxation process $|0,2\rangle \rightarrow |1,1\rangle$.

Under steady state conditions ($\partial N_i(t)/\partial t = 0$) the solutions of this system of rate equations become

$$N_2 = \frac{\sigma_1 P}{W N_0 + R_2} N_1 \approx \frac{\sigma_1 P}{W + R_2} N_1 \quad (23)$$

and

$$N_1 = \frac{\sigma_0 P N_0}{R_1} + \frac{W N_0 - (1 - \eta) R_2}{R_1} N_2 \approx \frac{\sigma_0 P}{R_1} + \frac{W - (1 - \eta) R_2}{R_1} N_2 \quad (24)$$

when using $N_0 \approx 1$ for the approximations. This assumption implies that no ground state bleaching is taken into consideration, which is reasonable in a sub-avalanche situation. When one incorporates Eq. (24) into Eq. (23) without the assumption, the result obtained is

$$N_2 = \frac{\sigma_0 \sigma_1 P^2 N_0}{R_1 (W + R_2) - \sigma_1 P (W - (1 - \eta) R_2)}. \quad (25)$$

Note that this implies that there is a critical power P_C ,

$$P_C = \frac{R_1 (R_2 + W)}{\sigma_1 (W - (1 - \eta) R_2)} \quad (26)$$

for which Eq. (25) diverges and a photon avalanche occurs. Graphically, this divergence and the subsequent avalanche effect can be seen in Fig. 6.9.

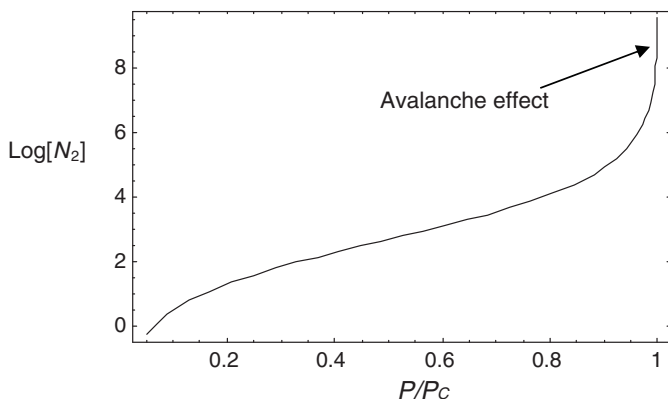


Fig. 6.9 Population of the upconversion state $|2\rangle$ as a function of normalized excitation power. The avalanche effect can be seen for powers approaching $P \approx P_C$, in accordance with Eqs. (25) and (26).

As can be seen from Eq. (26), a divergence of the population of the upconverting state will occur when the magnitude of W is at least comparable to R_2 . There are a variety of ions capable of upconversion where this criterion is met, most noticeably the rare-earth ions (where the radiative relaxation rates from the upper excited states are typically within the range 10^4 – 10^6 s⁻¹ and the cross-relaxation rate may even be as large as 10^7 s⁻¹ in some cases). When W is much smaller than R_2 , the competition between radiative decay from the upper excited state and cross-relaxation will favor radiative emission. Nevertheless, no strong upconversion emission will be observed in this case, as in such a case the avalanche threshold is not reached. The general requirements for photon avalanche upconversion phosphors (namely the sizeable gap between $|1\rangle$ and $|2\rangle$ where no absorption occurs) also favors mixed rare-earth/transition metal systems. For example, based on the energy level structure of the Yb³⁺, Mn²⁺ codoped system discussed in Section 6.3.3, it is expected that such phosphors show avalanche upconversion as well, although no experimental verification has been performed so far.

In one of the most extreme cases of power-dependent upconversion properties, so-called “optical bistability” may occur. This effect is very rare and is characterized by a hysteresis loop in the power dependence of the optical absorption cross-section as well as the emission intensity. The effect is schematically illustrated in Fig. 6.10, and has been observed for example in Yb³⁺-doped crystals of Cs₃Lu₂Br₉ or Cs₃Y₂Br₉ at temperatures below ~ 30 K. In these materials both the normal (downconverted) luminescence intensity as well as the upconverted (green, cooperative luminescence) intensity suddenly and sharply increase after the excitation power has been increased to 1.9 kW cm⁻². However, on decreasing the excitation power, the jump back to lower emission intensities does not occur until an excitation power of 1.6 kW cm⁻² is reached [12]. In parallel to these jumps in the cooperative emission intensity, there is an equal but opposite jump in the transmittance of the crystals (i.e. the transmittance

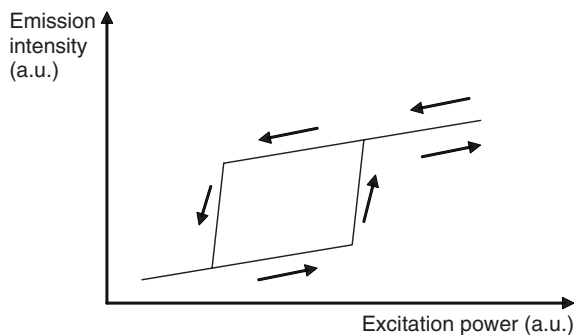


Fig. 6.10 Schematic representation of the power-dependent luminescence intensity that can be seen in the optical bistability effect. The size of the hysteresis loop is strongly dependent on temperature and laser power.

sharply decreases above excitation powers of 1.9 kW cm^{-2} , but does not recover until the excitation power has been decreased to 1.6 kW cm^{-2}). The range of excitation powers that make up this hysteresis loop varies with temperature, and the effect is more pronounced at lower temperatures. The effect has basically been explained through the temperature dependence of the heat capacity of the material in combination with the temperature dependence of the excitation cross-section. For an extensive description as well as a full semiclassical theory of optical bistability, the interested reader is referred to the literature [13].

6.2.5

Determination of the Upconversion Efficiency

While it may seem a straightforward assignment to find “the upconversion efficiency” of a given phosphor, it turns out that many different, and sometimes incorrect, definitions are used throughout the literature. A simple example will demonstrate the error that is most often made: suppose that one has an upconversion phosphor, and its transition spectrum shows two emissions of equal intensity, one band related to the upconversion and one assigned to downconversion, and that no nonradiative transition occurs to the ground state. Naively, one might assume that this implies that the upconversion efficiency is simply $1/2 = 50\%$. However, this is incorrect. The reason for the error is twofold: First, intensity is not the same as photon flux, but this is easily converted. The real underlying problem lies in the fact that two excitation photons are required to observe one upconversion emission photon, while at the same time one excitation photon will allow for the emission of one downconversion emission photon. As a result, in this example, the total number of excitation photons that must have been absorbed is given by $3/2$ times the number of emission photons. Therefore, the actual upconversion efficiency of this phosphor will be equal to $2/3 = 66.7\%$, as this is the fraction of all excitation photons that are used to generate the upconversion emission.

In order for one to determine the correct value, several steps must be undertaken. First, the emission spectrum of the phosphor must be recorded at a well-defined excitation power (as discussed previously, the upconversion characteristics are all non-linear with respect to the excitation power, implying that the efficiency of the phosphor will be power dependent when the high-power limit is not yet reached). Second, the luminescence emission spectra must be corrected for the instrument response and the refractive index of air, and must subsequently be displayed as a photon flux per constant energy interval [14]. This representation is required because only in this representation will the integral of a certain emission band be a true measure of the number of photons emitted (i.e. the population of the excited state) in that band. Third, one must determine p_i , the number of near-infrared excitation photons required to induce emission for each of the emission bands i (the values of p_i are often determined through power-dependent spectroscopy, as explained in Section 6.3). Furthermore, Φ_i , the number of photons emitted in band i must be calculated via integration of the emission spectrum. With these definitions,

$$T \equiv \sum_{\forall j} p_j \Phi_j \quad (27)$$

denotes the (minimum) number of excitation photons required to induce the full emission spectrum. Ideally, it should be found that T is independent of temperature when corrected for the temperature-dependence of the excitation cross-section. This implies that no significant nonradiative multiphonon relaxation to the ground state occurs, because such nonradiative processes would depend on the sample temperature. Therefore, each photon absorbed must contribute to the emission of a photon, and from this it can be seen that

$$R_i \equiv p_i \Phi_i / \sum_{\forall j} p_j \Phi_j \quad (28)$$

will be the fraction of absorbed infrared photons emitted in band i . The R_i give a measure for the true efficiency of the upconversion phosphor, and their values can be determined for different excitation powers and/or temperatures.

Note that one important assumption has been made in Eq. (28), namely that the inter-excited state emissions do not present a significant contribution to the total emission spectrum. This assumption is usually expected to be valid. However, in specific cases where this is not the case (e.g., the 4-photon intra-excited state transition $^1D_2 \rightarrow ^3F_4$ in the Tm^{3+} -doped upconversion phosphors that is discussed in Section 6.3.1), the reader can easily extend Eq. (28) to include this effect, since it is only influenced by one additional process. This extension is the goal of Exercise 5.

6.3 Examples

In the second part of this chapter, several characteristic examples of upconversion phosphors are described. However, it is not the aim of this part to present an

exhaustive overview of the complete literature on upconversion spectroscopy. There exist several review papers that do aim at presenting as far as possible a complete overview of the present state of knowledge of the field. The interested reader is therefore strongly urged to read the two excellent review papers by Auzel [1], the very clear one by Gamelin [16], or a recent one by the present author [17].

The principal strategies for obtaining new UC compounds involve two steps: (a) variation of the host lattice and (b) variation of the dopant metal ions in the lattice. Changing the host lattice may dramatically influence the radiative and nonradiative (multiphonon relaxation as well as energy transfer) properties, leading to entirely different upconversion luminescence behavior. For example, one can reduce the efficiency of multiphonon relaxation processes by changing from a lattice having high phonon energies (oxide, fluoride) to one having low phonon energies (chloride, bromide, iodide), with the drawback that most of these compounds are hygroscopic. Choosing a host with specific optical and/or magnetic properties may also influence the upconversion emission properties of a dopant ion through sensitization or perturbation by exchange interactions. A change in the metal dopant ions has a dramatic effect on the emission properties of a compound. The most obvious effect is a change in the color of the emitted light. The freedom of choice for the host lattice, dopant and (possibly) codopant covers a very broad spectrum of possibilities in the development of compounds with new and unprecedented upconversion properties, leaving much to the imagination and creativity of the researcher. The remainder of this chapter will focus separately on rare earth upconverters, transition metal upconverters, mixed rare earth/transition metal systems, and nanocrystalline upconverters.

6.3.1

Rare Earth Upconverters

Most of the well-known upconverting phosphors contain trivalent rare earth ions as the active components, typically Pr^{3+} , Nd^{3+} , Er^{3+} , Tm^{3+} , or Yb^{3+} , though others occur too. Also the actinide ions U^{3+} and U^{4+} have been studied in some detail for their upconversion properties. The reason that the vast majority of all the work in the field has been devoted to this relatively small collection of ions lies in the fact that for these ions their inner 4f (or 5f in the case of uranium) shell contains the spectroscopically relevant electronic states. As their outer 5s and 6p (6s and 6p for uranium) shells are involved with the bonding, the f states are rather insensitive to the precise nature of the surrounding host lattice (i.e. the exact crystal field and, to a lesser extent, the local site symmetry). As a result, a significant number of the excited f states have lifetimes that are long enough to allow for upconversion processes to play a role. Not surprisingly, rare earth ions were also the first ions in which upconversion was observed, discovered by Auzel [15] and independently by Ovsyankin and Feofilov [18] in the mid-1960s.

Figure 6.11 shows the near-infrared and visible part of the energy level structure of trivalent erbium, ytterbium, and thulium (a so-called Dieke diagram). These are some of the most frequently used ions in upconversion phosphors. Typically, one can

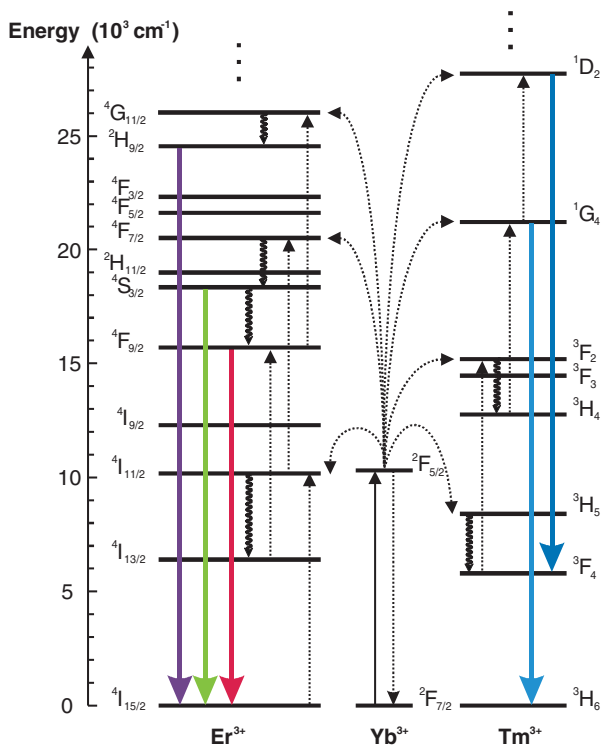


Fig. 6.11 Energy level scheme of Yb^{3+} , Er^{3+} , and Tm^{3+} , some of the most common ions to be found in upconversion phosphors. The colored downward arrows denote strong upconversion emissions that lie in the visible spectral range. The dotted arrows on Er^{3+} and

Tm^{3+} describe strong excited-state absorption steps, and those from Yb^{3+} to Er^{3+} or Tm^{3+} indicate energy transfer steps that may occur in codoped systems. The curly downward arrows indicate nonradiative multiphonon relaxation steps.

distinguish three main types of (bulk) host materials that are used in the application of upconversion phosphors. These are single crystals, optical fibers, and glasses, respectively. Rather than immediately describing specific materials, let us first draw some general observations from the energy level diagram shown in Fig. 6.11.

When we limit ourselves to the often used $\sim 10\,000\text{ cm}^{-1}$ excitation energies, it is clear that only the $\text{Yb}^{3+} \ ^2\text{F}_{5/2}$ and $\text{Er}^{3+} \ ^4\text{I}_{11/2}$ states are at such energies that direct excitation into these states is possible. Given that the excitation cross-section for $\text{Yb}^{3+} \ ^2\text{F}_{7/2} \rightarrow \ ^2\text{F}_{5/2}$ contains the full f-f oscillator strength, while the $\text{Er}^{3+} \ ^4\text{I}_{15/2} \rightarrow \ ^4\text{I}_{11/2}$ transition contains only a part of the oscillator strength, a reasonable estimate is that (at room temperature) the majority of the excitation photons will be absorbed by Yb^{3+} . As Yb^{3+} has no higher-lying excited states than the $\ ^2\text{F}_{5/2}$, this ion must perform energy transfer upconversion with another species (e.g. Er^{3+} or Tm^{3+}) in order for visible emission to occur. Within the energy range shown in Fig. 6.11, Yb^{3+} has several energy transfer possibilities to both other ions, as indicated by the dotted arrows. When no strong multi-phonon relaxation is taken into account, there are three

energy transfer possibilities from Yb^{3+} to Er^{3+} (to induce the Er^{3+} transitions ${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{11/2}$, ${}^4\text{I}_{11/2} \rightarrow {}^4\text{F}_{7/2}$, and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{G}_{11/2}$, respectively) and four to Tm^{3+} (to induce the transitions ${}^3\text{H}_6 \rightarrow {}^3\text{H}_5$, ${}^3\text{F}_4 \rightarrow {}^3\text{F}_2$, ${}^3\text{H}_4 \rightarrow {}^1\text{G}_4$, and ${}^1\text{G}_1 \rightarrow {}^1\text{D}_2$, respectively). However, on inclusion of multiphonon relaxation (or strong cross-relaxation) a fourth energy transfer path to Er^{3+} is opened up: after, e.g., the nonradiative transition ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$, the Er^{3+} transition ${}^4\text{I}_{13/2} \rightarrow {}^4\text{F}_{9/2}$ becomes possible via energy transfer upconversion. This is significant, since it implies that there are now two distinctly different Er^{3+} states (the ${}^4\text{F}_{9/2}$ and ${}^4\text{S}_{3/2}$) that are both populated via a 2-photon energy transfer upconversion process. However, as the rate constants for these two processes are not the same (partly because of the additional relaxation step required for reaching the ${}^4\text{F}_{9/2}$), the excitation powers required for reaching the high-power limit will not generally be identical for these two states. Remember from Section 6.2.3 that in the low-power limit the emission intensity of a state excited via a two-photon process will scale with the laser power squared, while in the high-power limit it will be linear with the laser power. As a result, in the intermediate-power regime, the populations of the ${}^4\text{F}_{9/2}$ and ${}^4\text{S}_{3/2}$ states will have a somewhat different power dependence. This implies, in this regime, the red to green emission ratio of any upconversion phosphor that has a ${}^4\text{I}_{13/2} \rightarrow {}^4\text{F}_{9/2}$ excitation pathway will depend on the excitation power. Clearly this opens up interesting possibilities, because this way one can tune the emission color of an upconversion phosphor simply by varying the excitation power.

Another interesting observation that can be made from the Dieke diagram of Er^{3+} shown in Fig. 6.11 is that there is almost an energetically equidistant ladder of states in Er^{3+} that allows a whole series of excited-state absorption steps: after ${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{13/2}$ ground state absorption, ESA can occur to the ${}^4\text{I}_{11/2}$, from which subsequent ESA steps will reach the ${}^4\text{F}_{9/2}$, ${}^4\text{F}_{5/2}$, and ${}^4\text{G}_{11/2}$ states. This way indeed, 5-photon upconversion in $\text{YF}_3:\text{Er}^{3+}$ has been observed experimentally, resulting in emission up to the ultraviolet spectral range under near-infrared excitation at 6500 cm^{-1} .

When a powder of NaYF_4 (containing micrometer-sized single crystals) doped with Yb^{3+} and Er^{3+} is excited in the near-infrared spectral range, a rich emission spectrum can be recorded, as is shown in the top panel of Fig. 6.12. For this measurement, the excitation power was $\sim 60\text{ W cm}^{-2}$, which is in the high-power limit of this particular phosphor. As explained previously, when a lower excitation power is used, the red to green emission intensity becomes strongly power-dependent: typically there is ~ 4 times as much green emission at low powers, while there are roughly equal amounts of red and green emission at high excitation powers, as can be seen from Fig. 6.12. From the emission spectrum, one can determine that (in the high-power limit) $\sim 32\%$ of all photons emitted by this phosphor are in the visible spectral range [19]. This implies that nearly 50% of all near-infrared excitation photons have undergone photon upconversion, as can be calculated using Eq. (28). Clearly this is a truly spectacular number. The fact that the NaYF_4 crystal is such a good host lattice for photon upconversion is related to the very low energy phonon modes in this material (the dominant phonon modes are found at $\sim 350\text{ cm}^{-1}$ [20]). So far, no phosphor has been found that is a more efficient upconverter than $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$. As the power required to reach the high-power limit is acceptably low and this phosphor operates at room temperature, this suggests that application of $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$ (e.g., in

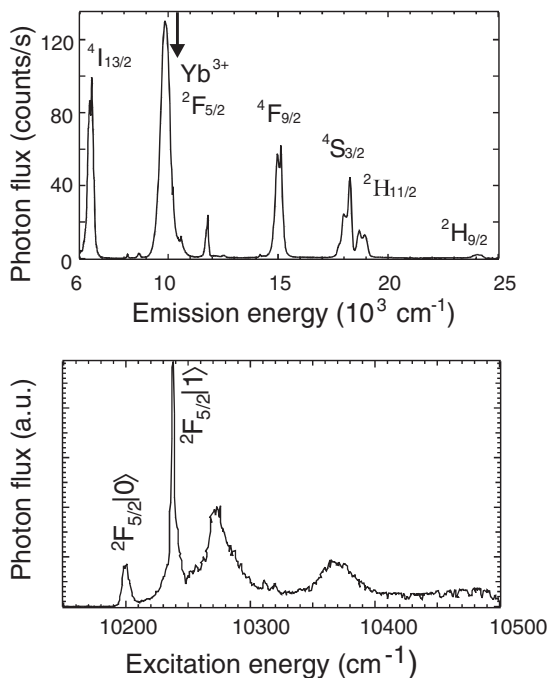


Fig. 6.12 (top) Upconversion and downconversion emission spectrum of an $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$ sample under $10\,238\text{ cm}^{-1}$ excitation (indicated by the arrow) with an excitation density of 60 W cm^{-2} . The data were recorded at room temperature and the laser excitation line was removed manually. (bottom)

Excitation spectrum of the $18\,200\text{ cm}^{-1}$ upconversion emission recorded at 5 K in the low-power limit. The two states that are indicated correspond to the lowest-energy crystal field components of the Yb^{3+} excited state multiplet.

displays, lasers, phosphors, etc.) may not be far-fetched. In all the low-temperature excitation spectra (a representative example is shown in the bottom panel of Fig. 6.12), a clear Yb^{3+} signature is recognized. This directly proves that the excitation of all the upconversion emission bands in this phosphor is sensitized via Yb^{3+} .

Another strong piece of evidence for the sensitized nature of the upconversion emissions in the $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$ phosphor can be seen in Fig. 6.13. In this figure, the excitation power dependence of four different emission bands is plotted using double-logarithmic axes. On comparison of the data with the calculations shown in Fig. 6.7 (or the functional forms in Table 6.2), it is clear that only sensitized energy transfer upconversion is capable of explaining the observed trends. It is clear from the lines in Fig. 6.13 that the model described in Section 6.2.3 explains the experimental data very well for all emission bands. Furthermore, it is also clear that the power density required to observe a crossover in the upconversion emission intensities (from a slope greater than 1 to a slope of 1) is different for the different emission bands. This fact proves that this crossover cannot be related to sample heating in the

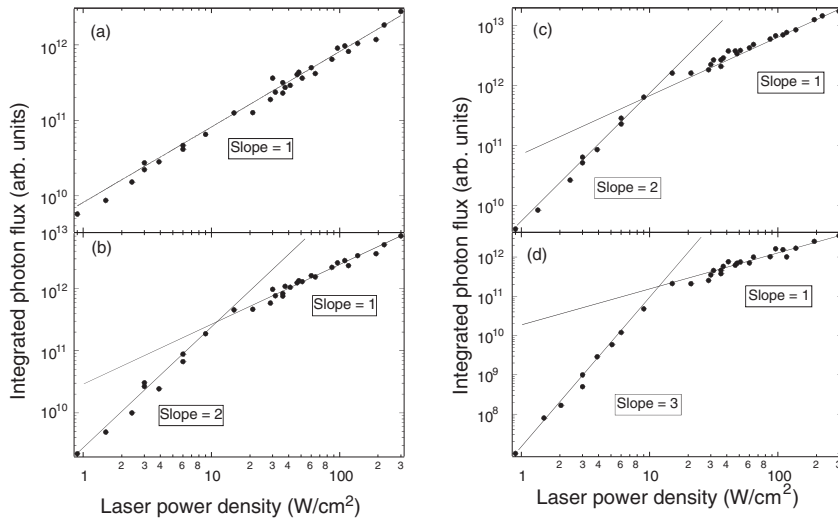


Fig. 6.13 Excitation power dependence of four Er^{3+} -related emission bands in an $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$ sample under $10\,238\text{ cm}^{-1}$ excitation. The data were recorded at room temperature, and the emissions relate to the transitions (a) ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$, (b) ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$,

(c) ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$, and (d) ${}^2\text{H}_{9/2} \rightarrow {}^4\text{I}_{15/2}$, respectively. Note the double-logarithmic representation. The lines through the data are calculations using Eqs. (18) and (19) for the low- and high-power limits, respectively.

high-power limit. Therefore, it must be attributed to an excitation power-induced change in the net excited-state dynamics. This results in a change of the dominant depopulation process for the specific excited state under investigation. The actual power density for the crossover point from the low- to the high-power behavior is determined by a complex interplay between the relevant energy transfer processes: upconversion, cross-relaxation, and radiative and nonradiative decay. Clearly, from Fig. 6.13, it can be seen that the red to green emission ratio is dependent on power, as was noted earlier.

The specific example of the fluoride NaYF_4 has been described in some detail because this material is a highly efficient upconverter (related to the low phonon energy of the host lattice in combination with the well-defined crystal structure) and serves as a single example covering most of the theory described in Section 6.2. Most other upconverters are significantly less efficient, which is mainly related to a greater energy mismatch between excited states, the site symmetry of the upconverting ion, and the higher-energy phonons available in such systems.

Typically, fluoride and germanate glasses serve as host materials for upconverting ions such as Pr^{3+} and Nd^{3+} . These glasses can be in bulk form or drawn into optical fibers. Partly because of the availability of high-power diode laser rods lasing at $\sim 800\text{ nm}$, a fair amount of research on upconversion in Nd^{3+} systems has been devoted to excited-state absorption studies from the ${}^4\text{F}_{5/2}$ state to the ${}^4\text{G}_{7/2}$ state (allowing for red, orange, and green emission transitions to lower-lying states). As

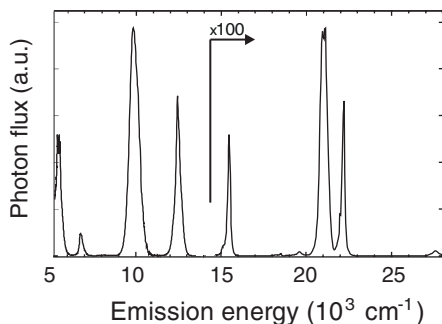


Fig. 6.14 Emission spectrum of $\text{NaYF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$ under $10\,238\text{ cm}^{-1}$ excitation and in the high-power limit. The data were recorded at room temperature. Note the vertical scaling in the high-energy segment of the spectrum.

one can draw fibers of these materials, lasing and light amplification experiments have also been performed. Further upconversion in Nd^{3+} -doped chalcogenide, fluoroarsenate, and fluoroindate glasses mainly results in ${}^2\text{P}_{1/2}$ and ${}^2\text{P}_{3/2}$ emission (in the violet) under ${}^4\text{F}_{9/2}$ excitation. The upconversion mechanism is a two-ion $|{}^4\text{F}_{9/2}, {}^4\text{F}_{9/2}\rangle \rightarrow |{}^4\text{I}_{9/2}, {}^2\text{P}_{3/2}\rangle$ energy transfer upconversion, resulting in a strong concentration dependence of the upconversion efficiency. Pr^{3+} is mainly used as a two-photon near-infrared ($10\,200\text{ cm}^{-1}$ into the ${}^1\text{G}_4$ state) to blue ($20\,300\text{ cm}^{-1}$ emission from the ${}^3\text{P}_0$ state to the ground state) upconverter, where the dominant emission occurs from the ${}^3\text{P}_0$, and the excitation pathway is usually predominantly via excited-state absorption. Neither Pr^{3+} nor Nd^{3+} (similarly to Gd^{3+} , Dy^{3+} , and Ho^{3+}) has been investigated in a great variety of host lattices because of their inefficient upconversion, undesired emission wavelengths, and synthetic difficulties.

Together with Er^{3+} , the upconversion properties of trivalent thulium (see Fig. 6.11 for the Dieke diagram) have been investigated in a large number of different host materials. Figure 6.14 shows the emission of the upconversion phosphor $\text{NaYF}_4:\text{Tm}^{3+}, \text{Yb}^{3+}$. This phosphor is evidently a very good upconverter; $\sim 40\%$ of all near-infrared excitation photons are upconverted (in the high-power limit). However, the energy level structure of the Tm^{3+} ion is such that it requires at least three $10\,238\text{ cm}^{-1}$ excitations (sensitized energy transfer upconversion via Yb^{3+}) in order to obtain one visible Tm^{3+} emission. As a result, the near-infrared to visible upconversion efficiency of the phosphor is only $\sim 2\%$, which is still considerable for a room-temperature upconversion phosphor. These emissions are mainly into the two blue/violet emission bands: the 3-photon ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ and the 4-photon intra-excited state transition ${}^1\text{D}_2 \rightarrow {}^3\text{F}_4$. Most of the upconversion emission (consisting of $\sim 35\%$ of all absorbed excitation photons) is into the ${}^3\text{H}_4$ band, centered at $12\,450\text{ cm}^{-1}$ (at 880 nm). This extremely high efficiency suggests that even lasing might be achievable on this transition if one were able to grow an optical-quality macroscopic single crystal of this phosphor (at present, only micrometer-sized powders exist).

To end this section, a brief discussion of upconversion lasers is included, as such lasers always use rare earth ions for the actual upconversion. Early upconversion lasers were demonstrated with bulk crystals, which often had to be cooled to very low temperatures, making the systems impractical. Nowadays, most upconversion lasers are based on fibers, where high pump intensities can be maintained over long lengths, so that the laser threshold can be reached even under otherwise difficult conditions. In most cases, silica glass is unsuitable because of its high phonon energies, which causes strong multi-phonon transitions and thus do not allow one to obtain large enough metastable level lifetimes. Instead, one frequently uses heavy-metal fluoride glasses (e.g., ZBLAN), which are typically quite fragile and expensive. Three specific examples of upconversion fiber lasers will be sketched here.

1. First, Tm^{3+} -doped blue upconversion lasers. These ZBLAN upconversion fibers are pumped at around 1120 nm (into the $^3\text{H}_5$) and show, after two sequential excited-state absorption steps, lasing around 480 nm (from the $^1\text{G}_4$). A laser diode pumped fiber laser has been demonstrated with blue output power levels up to 106 mW. Differential optical-to-optical conversion efficiencies up to 30 % are measured with respect to pump power coupled into the upconversion fiber. High quality (single spatial mode) blue output beams have been demonstrated.
2. Room-temperature continuous-wave upconversion laser emission was achieved on the green transition ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) in $\text{LiYF}_4:\text{Er}^{3+}, \text{Yb}^{3+}$ at 551 nm. Green laser operation was obtained for titanium sapphire pump wavelengths between 955 and 974.5 nm. Codoping with Yb^{3+} results in a more efficient excitation of the upper laser level by a sensitized energy transfer upconversion process. A maximum green laser output power of 37 mW at an incident titanium sapphire pump power level of 1.58 W (at 966 nm) has been achieved, but there is no reason to assume that this is the limit, and higher powers are expected for the future.
3. Praseodymium-doped upconversion lasers are pumped at around 850 nm (into the $^1\text{G}_4$ state) and have emission from the $^3\text{P}_0$ at various visible wavelengths, depending on the final state: in the red (to the $^3\text{F}_3$ at 635 nm), orange ($^3\text{F}_2$ at 605 nm), green ($^3\text{H}_5$ at 520 nm), or blue ($^3\text{H}_4$ at 491 nm) spectral region. The mismatch in excitation wavelengths required for the two excitation steps (1035 nm for the ground state absorption and 850 nm for the excited state absorption) can be solved using a second pump wavelength (two-color excitation, as discussed briefly in Section 6.2.1) or by use of a suitable codopant to transform 850-nm pump photons into 1035-nm photons. Codoping with Yb^{3+} results in the upconversion occurring via an avalanche process (as described in Section 6.2.4) to the $^3\text{P}_{0,1}$.

As a typical example, 1.6 W of pump power generates 165 mW of avalanche upconversion lasing in the blue, with a threshold of 0.14 W.

Finally, it should be mentioned that in certain other devices (such as erbium-doped fiber amplifiers), upconversion can cause highly unwanted parasitic losses. In fact, the fundamental upper limit for the efficiency of such devices is often related to the onset of upconversion. It is for this very reason that the very efficient (quantum efficiency $\approx 98\%$) phosphors used in fluorescent tubes and television screens cannot be made to lase.

6.3.2

Transition Metal Upconverters

Since the spectroscopically active d orbitals in transition metals are the valence orbitals, any environmental perturbation is expected to be more influential in these ions than in the more commonly studied trivalent rare earth metal ions. As discussed in the previous section, the spectroscopically active f orbitals are strongly shielded from their environment, resulting in nearly host-lattice-insensitive energy level positions for the spectroscopic states of the rare earth ions. However, it is the accessibility of the frontier d orbitals that make transition metal ions extremely attractive in the search for new upconversion materials. The reason for the attraction lies in the fact that the environmental sensitivity of transition metal ions suggests mechanisms by which their photophysical properties may be modified or even controlled using external chemical, redox, or magnetic perturbations. Furthermore, such d metals have spectroscopically active states that are strongly influenced by the local crystal field, allowing for chemical variation of the photophysical characteristics such as the energy levels, excited state dynamics and lifetimes, multiphonon relaxation rates, and electron-phonon interaction strengths.

One of the first examples of an upconversion phosphor containing a transition metal as the active ion was discovered by Auzel and coworkers, in the form of single-crystalline $\text{MgF}_2:\text{Ni}^{2+}$ [21]. This phosphor also doubles as a laser material that is tunable because of the broad band characteristics of the d-d emission of the Ni^{2+} ion. The green emission centered at 500 nm, attributed to the ${}^1\text{T}_2({}^1\text{D}) \rightarrow {}^3\text{A}_2({}^3\text{F})$ transition, is excited in the near-infrared at 752.5 nm via a ${}^3\text{T}_1({}^3\text{F}) \rightarrow {}^3\text{T}_1({}^3\text{P})$ excited-state absorption step. The upconversion is mainly efficient at low temperatures ($T < 100$ K). At higher temperatures, the self-quenching of the emission through a $|{}^1\text{T}_2, {}^3\text{A}_2\rangle \rightarrow |{}^3\text{T}_2, {}^3\text{T}_1\rangle$ cross-relaxation step becomes dominant.

Subsequently, the majority of all the research on transition metal-doped upconversion phosphors has occurred since the late 1990s in the group of Güdel. Their systematic investigation has focused on the ions Ni^{2+} and Mn^{2+} , but they have also ventured in the direction of Cr^{3+} , Ti^{2+} , Re^{4+} , Os^{4+} , and Mo^{3+} doped materials. Most of the crystals that were synthesized by this group were low-phonon energy halides (bromides, chlorides, and fluorides), which often had to be studied in an inert (e.g., helium) atmosphere because of the hygroscopic nature of these materials. The

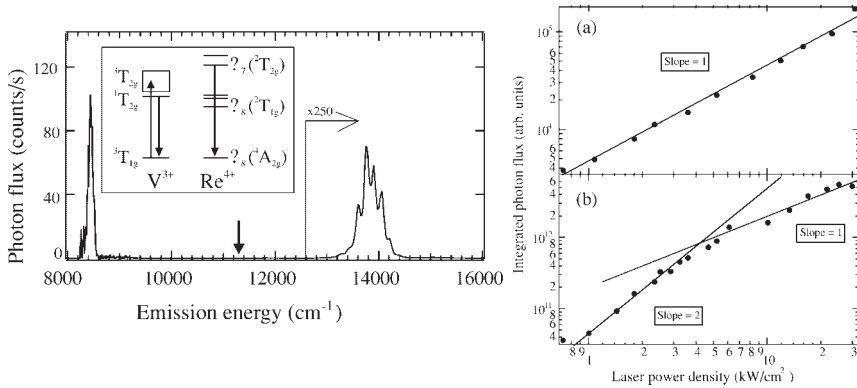


Fig. 6.15 (Left) Room temperature emission spectrum of $\text{Cs}_2\text{NaYCl}_6:\text{V}^{3+},\text{Re}^{4+}$. Excitation (indicated by the arrow) was at $11\,350\text{ cm}^{-1}$, and the measurement was recorded in the high-power limit (25 kW cm^{-2}). Note the vertical scaling for the upconversion emission part of the spectrum. The inset shows the relevant V^{3+}

and Re^{4+} energy levels as well as the excitation (upward arrow) and emissions (downward arrows) that are observed in this sample. (Right) Laser power dependence of the integral of the following transitions in the sample: (a) $\text{V}^{3+} \text{}^1\text{T}_{2g} \rightarrow \text{}^3\text{T}_{1g}$ at 8500 cm^{-1} and (b) $\text{Re}^{4+} \text{}^1\Gamma_7(\text{}^2\text{T}_{2g}) \rightarrow \text{}^1\Gamma_8(\text{}^4\text{A}_{2g})$ at $13\,800\text{ cm}^{-1}$.

combination of two different d metal ions has also led to new and interesting materials. An interesting example can be seen in Fig. 6.15 (left), where the room temperature emission spectrum of a $\text{Cs}_2\text{NaYCl}_6$ crystal doped with V^{3+} and Re^{4+} is shown [22].

The energy level schemes of V^{3+} and Re^{4+} are shown in the inset of Fig. 6.15 (left). From the emission spectrum, both V^{3+} and Re^{4+} related emissions are readily identified. Clearly, the V^{3+} emission is the dominant spectral feature, but, because of the broad-band nature of the Re^{4+} emission, the upconversion efficiency is still in the 1% range at room temperature. At lower temperatures, a higher value for the upconversion efficiency is found, relating to a decreased nonradiative multiphonon relaxation in rhenium at low temperatures.

The excitation of the phosphor is into the $\text{}^3\text{T}_{2g}$ absorption band of V^{3+} , which acts as a sensitizer in this system. From the energy level scheme, it is immediately clear that the Re^{4+} related emission $\text{}^1\Gamma_7(\text{}^2\text{T}_{2g}) \rightarrow \text{}^1\Gamma_8(\text{}^4\text{A}_{2g})$ at $13\,800\text{ cm}^{-1}$ must be sensitized by V^{3+} . The right hand panel of Fig. 6.15 shows the influence of the laser power density on the sensitizer and acceptor emissions in $\text{Cs}_2\text{NaYCl}_6:\text{V}^{3+},\text{Re}^{4+}$. Clearly, the V^{3+} (sensitizer) emission retains a slope of 1 irrespective of the power density, in accordance with the theory discussed in Section 6.2.3. The Re^{4+} (acceptor) emission, on the other hand, has a slope of 2 in the low-power regime, which gradually decreases to a slope of 1 in the high-power limit, which agrees well with the sensitized nature of this upconversion emission.

A totally different upconversion mechanism in the same $\text{Cs}_2\text{NaYCl}_6$ host lattice can be found when it is codoped with Mo^{3+} and V^{3+} [23]. The energy level schemes of Mo^{3+} and V^{3+} are shown in Fig. 6.16, together with a schematic representation of the

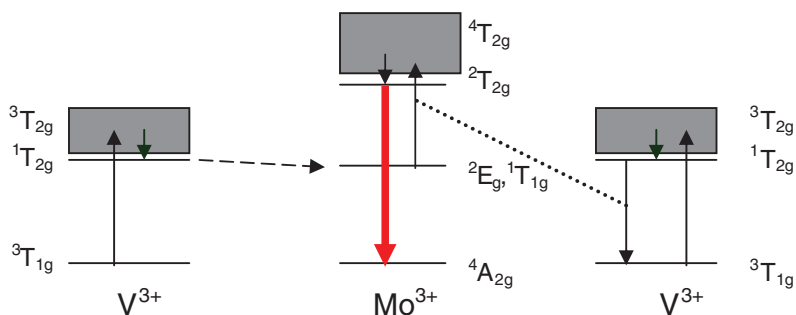


Fig. 6.16 Schematic energy level schemes of trivalent vanadium and molybdenum. The two excitations are into V³⁺, from which there is an energy transfer upconversion step to Mo³⁺ as indicated by the arrows connected by the dotted line. The emission occurs from Mo³⁺, and the processes are described in detail in the text.

relevant energy transfer processes that are described here. At low temperature, the upconversion luminescence in the red spectral range ($14\,300\text{ cm}^{-1}$) is assigned to the ${}^2\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$ transition in Mo³⁺. The red emission is observed after direct excitation into the Mo³⁺ ${}^2\text{E}_g$ and ${}^2\text{T}_{1g}$ states ($\sim 9700\text{ cm}^{-1}$), which are weak and narrow spectral features. However, excitation into the broad V³⁺ ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}$ absorption band (spanning the range from $10\,000$ to $12\,500\text{ cm}^{-1}$) also results in the observation of this Mo³⁺-related emission. This is because the excitation energy is transferred from the ${}^1\text{T}_{2g}$ state of V³⁺ to the Mo³⁺ ${}^2\text{E}_g$ state. Interestingly, this process is dependent on the relative V³⁺ and Mo³⁺ concentrations. The Mo³⁺ ${}^2\text{T}_{2g}$ luminescence is at higher energy and is not affected by the presence of V³⁺ because of a lack of spectral overlap. The most interesting mechanism explaining the 2-photon excitation pathway of the red upconversion emission is a nonradiative energy transfer upconversion process between Mn³⁺ and V³⁺. The first excitation in the broad $10\,000$ – $12\,500\text{ cm}^{-1}$ band brings V³⁺ into its ${}^3\text{T}_{2g}$ excited state, from which rapid multiphonon relaxation occurs to the ${}^1\text{T}_{2g}$ state. From this state there is an energy transfer process to the Mo³⁺ ${}^2\text{E}_g$ state. Next, the second excitation in the broad $10\,000$ – $12\,500\text{ cm}^{-1}$ band brings another V³⁺ into its ${}^3\text{T}_{2g}$ excited state, from which again rapid multiphonon relaxation occurs to the ${}^1\text{T}_{2g}$ state. Subsequently, a Mo³⁺-V³⁺ two-ion energy transfer upconversion process takes place, whereby the V³⁺ ${}^1\text{T}_{2g}$ energy is transferred to the Mo³⁺ ion in its ${}^2\text{E}_g$ state, resulting in the upconversion to the Mo³⁺ ${}^4\text{T}_{2g}$. Finally, multiphonon relaxation occurs, and the red-emitting Mo³⁺ ${}^2\text{T}_{2g}$ state is reached. This particular phosphor is interesting mainly because of its broad excitation band. As a result, one can use excitation with the broad-band near-infrared output of a tungsten lamp. At low temperatures, this excitation pathway induces more than an order of magnitude more red upconversion luminescence in Mo³⁺ and V³⁺ doped Cs₂NaYCl₆ compared to purely Mo³⁺ doped Cs₂NaYCl₆, clearly demonstrating the sensitization function of V³⁺.

Finally, a particularly nice example of transition metal upconversion can be found in chloro- and bromo-elpasolites doped with Mo^{3+} [24]. In these materials, no fewer than three competing upconversion processes are active. Two of these involve the sequential absorption of two near-infrared photons of the same color. However, in the third process, the sequential absorption of two near-infrared photons of different colors is involved. The two one-color upconversion mechanisms are distinguishable on the basis of time-dependence measurements. Of the three mechanisms, the two-color sequential two-photon absorption process is found to be much more efficient than the corresponding one-color mechanism (roughly by a factor of 100), which is in agreement with the relatively small effective spin-orbital coupling magnitude in this ion. The distinction between these processes can be made based on the time evolution (e.g., lifetimes, decay dynamics, and transients under square-wave excitation blocks) of the upconversion and downconversion emission intensities. The significant difference in efficiency clearly demonstrates the added value of two-color excitation over single-color spectroscopy, as mentioned in Section 6.2.1 .

6.3.3

Mixed Rare Earth/Transition Metal Upconverters

The combination of trivalent rare earth (Ln^{3+}) and transition metal (TM) ions in the same host lattice introduces new cooperative upconversion mechanisms involving both ions. Mixed Ln^{3+} /TM compounds are particularly interesting, as the absorption and luminescence properties of transition metal ions are susceptible to changes in the ligand environment and the coordination geometry. In contrast, the Ln^{3+} f-f transitions are almost independent of the local environment. Thus, the choice of the host lattice allows one (to some extent) to selectively optimize the energetic positions of the absorption and luminescence of the transition metal ion. Furthermore, it paves the way toward upconversion materials where sharp line excitation in the near-infrared leads to broadband emission in the visible spectral region and vice versa. Such features are potentially interesting for new visible laser sources as well as for lighting and display devices.

Two fundamentally different upconversion schemes in mixed Ln^{3+} /TM compounds are possible: lanthanide-sensitized transition metal upconversion luminescence, or transition metal-sensitized lanthanide upconversion luminescence. In the remainder of this section, upconversion mechanisms in different Yb^{3+} -sensitized TM upconversion systems and various TM-sensitized Ln^{3+} upconversion systems are described.

Figure 6.17 shows the excitation pathways for several representative upconversion phosphors that have a mixed rare earth/transition metal ion couple as the chromophoric unit. As indicated, these particular phosphors have very different excitation mechanisms: (a) and (b): excited-state absorption, (c): cooperative sensitization, and (d): energy transfer upconversion, respectively. This may seem surprising considering that the excitation energies are always (roughly) the same ($\sim 10\,000\text{ cm}^{-1}$), and the initial excitation starts in Yb^{3+} in each case. However, the presence of different transition metal ions, in combination with changes in the host lattice properties

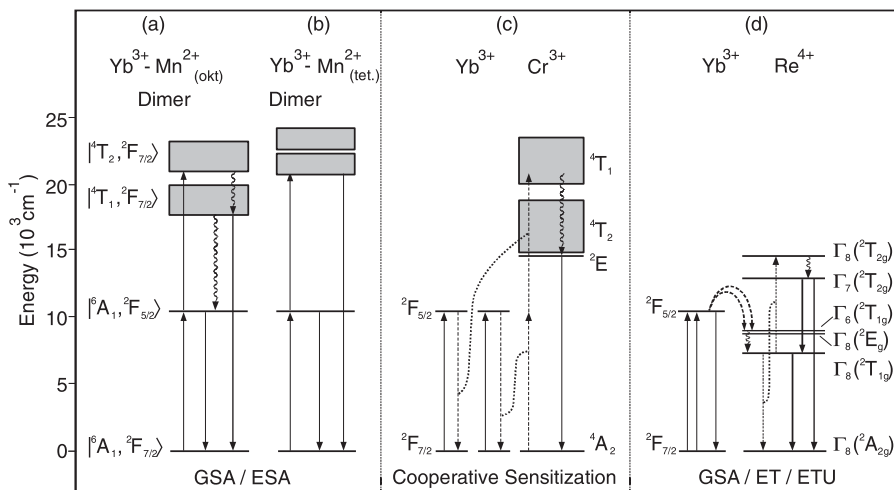


Fig. 6.17 The underlying mechanisms for several mixed rare earth/transition metal upconversion examples. The energy level schemes relevant for (a) $\text{CsMnBr}_3:\text{Yb}^{3+}$ and (b) $\text{Zn}_2\text{SiO}_4:\text{Yb}^{3+},\text{Mn}^{2+}$ are schematically shown. The chromophoric unit is an exchange-coupled $\text{Yb}^{3+}-\text{Mn}^{2+}$ dimer, and thus the energy levels are assigned in dimer notation. (c) Cooperative sensitization leading to upconversion

luminescence in $\text{Y}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+},\text{Cr}^{3+}$. (d) The upconversion mechanism active in $\text{Cs}_2\text{NaYbBr}_6:\text{Re}^{4+}$, where Yb^{3+} acts as a sensitizer for Re^{4+} . Full arrows up and down represent absorption and luminescence transitions, dashed arrows represent energy transfer processes, and curly arrows represent multiphonon relaxation.

(mainly the crystal field strength and local site symmetry), ensures these large differences in photophysical processes.

The example of the $\text{Mn}^{2+}-\text{Yb}^{3+}$ dimer, as shown in Fig. 6.17(a) and (b), nicely illustrates the importance of the crystal field strength. After the first excitation, the phosphor is in the Yb^{3+} -dominated ${}^6\text{A}_{1,2}({}^2\text{F}_{5/2})$ excited state. The second excitation allows for an excited-state absorption into the Mn^{2+} -dominated ${}^4\text{T}_{1,2}({}^2\text{F}_{7/2})$ state, from which fast multiphonon relaxation to the ${}^4\text{T}_{1,2}({}^2\text{F}_{7/2})$ state occurs. If the crystal field is strong, the energy gap will be sufficiently small as to allow for strong ${}^4\text{T}_{1,2}({}^2\text{F}_{7/2}) \rightarrow {}^6\text{A}_{1,2}({}^2\text{F}_{5/2})$ nonradiative multiphonon relaxation, as is the case in an octahedral $\text{CsMnBr}_3:\text{Yb}^{3+}$ crystal. This is demonstrated in Fig. 6.17(a) and implies that although this phosphor may have an efficient upconversion process, it will nevertheless have a poor upconversion efficiency because of the loss of the majority of the ${}^4\text{T}_{1,2}({}^2\text{F}_{7/2})$ population. When the crystal field strength is reduced, as in the $\text{Zn}_2\text{SiO}_4:\text{Yb}^{3+},\text{Mn}^{2+}$ example shown in Fig. 6.17(b), the Mn^{2+} -dominated ${}^4\text{T}_{1,2}({}^2\text{F}_{7/2})$ state shifts to higher energy. This quenches the multiphonon relaxation, and a much more efficient upconverter is the result. This way, an impressive two orders of magnitude in upconversion efficiency can be gained through the careful choice of the most suitable host lattice for the chromophoric unit in the phosphor.

The Yb^{3+} and Cr^{3+} ion couple also shows a cooperative upconversion process, which leads, amongst other spectral features, to sharp-line $\text{Cr}^{3+} {}^2\text{E}$ luminescence after near-infrared Yb^{3+} excitation. In the emission spectrum, two further features can be observed: the Yb^{3+} -related downconversion (at $\sim 10\,000\text{ cm}^{-1}$) and the very weak Yb^{3+} - Yb^{3+} two-ion cooperative luminescence, as shown in Fig. 6.1(d). Clearly, the most interesting emission is the $\text{Cr}^{3+} {}^2\text{E}$ upconversion luminescence. At 15 K and a laser power of 4.5 kW cm^{-2} , the $\text{Cr}^{3+} {}^2\text{E}$ emission accounts for 10.5% of all excitation photons absorbed. Figure 6.17(c) shows the underlying energy transfer process that governs the upconversion excitation. When two excited Yb^{3+} ions are located close to a Cr^{3+} ion, they can simultaneously transfer their energy to a single Cr^{3+} ion. Such a transfer can occur because there is overlap between twice the $\text{Yb}^{3+} {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ luminescence energy and the $\text{Cr}^{3+} {}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ absorption band. The system rapidly relaxes to the ${}^2\text{E}$ state by multiphonon processes, from where the emission is observed. On going from low temperature to 250 K, the emission is quenched by roughly six orders of magnitude. At low temperatures, the $\text{Cr}^{3+} {}^2\text{E}$ state is the emitting state. However, at elevated temperatures, the ${}^4\text{T}_2$ state of Cr^{3+} becomes increasingly thermally populated. As a result, the emission spectrum gradually changes from a sharp-line $\text{Cr}^{3+} {}^2\text{E} \rightarrow {}^4\text{A}_2$ luminescence to a very weak broad emission, which is assigned to the $\text{Cr}^{3+} {}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ transition [25]. Because of the large Stokes shift of this high-temperature transition, the energy difference between the maximum of this broad band and the $\text{Yb}^{3+} {}^2\text{F}_{5/2}$ excited state reduces to only 2300 cm^{-1} at 200 K. Therefore, the strong thermal quenching of the $\text{Cr}^{3+} {}^2\text{E} \rightarrow {}^4\text{A}_2$ luminescence can be attributed to energy transfer from the thermally activated $\text{Cr}^{3+} {}^4\text{T}_2$ state to the $\text{Yb}^{3+} {}^2\text{F}_{5/2}$ state.

Figure 6.17(d) shows the Re^{4+} and Yb^{3+} energy level schemes such as can be found in the elpasolite $\text{Cs}_2\text{NaYbBr}_6:\text{Re}^{4+}$. In this upconversion phosphor, Yb^{3+} acts as a sensitizer for the energy transfer upconversion on Re^{4+} . Because the full f-f oscillator strength of Yb^{3+} is located in the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition, the addition of Yb^{3+} can significantly enhance the Re^{4+} -related upconversion efficiency. The reason that Re^{4+} , even though it is a d metal that does upconversion on its own, has a rather small absorption cross-section in the near-infrared is related to the fact that the relevant excitation transition is spin forbidden. The Re^{4+} upconversion luminescence is in the red spectral region, around $13\,000\text{ cm}^{-1}$, and is attributed to a transition from the $\text{Re}^{4+} \Gamma_7({}^2\text{T}_{2g})$ state to its ground state. The excitation mechanism, shown in Fig. 6.17(d), requires sequential injection of two $\text{Yb}^{3+} {}^2\text{F}_{5/2}$ excitations into nearby Re^{4+} ions, leaving them (after multiphonon relaxation) in their $\Gamma_8({}^2\text{T}_{1g})$ intermediate excited states. An energy transfer upconversion step between two excited Re^{4+} ions promotes one to its $\Gamma_7({}^2\text{T}_{2g})$ excited state, from which emission is observed.

For the second part of this section, we turn to materials where a transition metal ion is used as the sensitizer, while a lanthanide ion is used as the upconversion emitter. This particular avenue of research is of great interest for future applications to sensitize upconversion via efficient broad-band near-infrared absorbers. Clearly, materials which show broad-band near-infrared absorption and are able to convert this energy into visible output radiation through upconversion are very interesting from an application point of view. Efficient materials of this type could be used in

lighting devices, for example, by converting near-infrared “waste-light” of an incandescent lamp into useful visible emission. Choosing a suitable ion couple requires one to keep several stringent criteria in mind: First, the d metal sensitizer must have a sufficient absorption cross-section in the near-infrared. Second, it must have an emission that overlaps with an absorption band of the upconverting f metal ion. Third, the sensitizer must not absorb in the visible, and specifically not at energies where the upconversion luminescence is expected. These constraints rule out many ion couples. Fortunately, the ligand field dependence of the excited states of the transition metal ion allows one to tune the energy levels of the sensitizer ion to match the required acceptor-ion conditions, by chemically varying the host lattice.

Figure 6.18 shows three examples of low-temperature emission spectra of upconversion phosphors, where the excitation is in the broad-band feature of a transition metal ion, while the upconversion emission is assigned to the rare earth ion. The fact

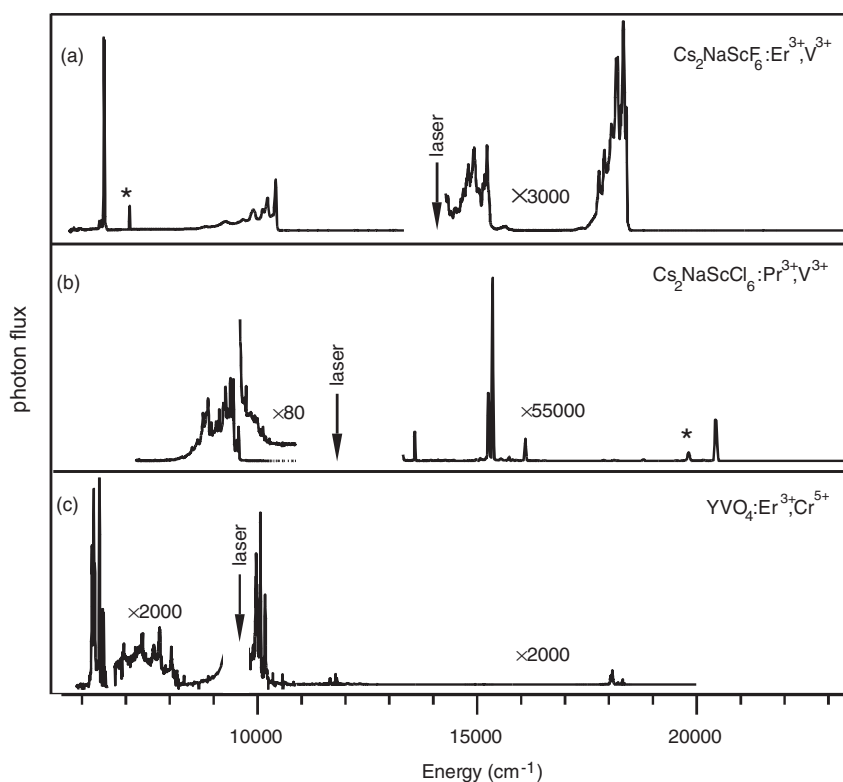


Fig. 6.18 Low-temperature spectra of (a) $\text{K}_2\text{NaScF}_6:\text{Er}^{3+},\text{V}^{3+}$; (b) $\text{Cs}_2\text{NaScCl}_6:\text{Pr}^{3+},\text{V}^{3+}$; and (c) $\text{YVO}_4:\text{Er}^{3+},\text{Cr}^{5+}$. The excitations are into $\text{V}^{3+} {}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}$ or $\text{Cr}^{5+} {}^2\text{A}_1 \rightarrow {}^2\text{B}_2$ absorptions. The relevant upconversion luminescence bands are: (a) $\text{Er}^{3+} {}^4\text{F}_{9/2}$ at $15\,000\text{ cm}^{-1}$ and $\text{Er}^{3+} {}^4\text{S}_{3/2}$

at $18\,200\text{ cm}^{-1}$; (b) $\text{Pr}^{3+} {}^3\text{P}_0 \rightarrow {}^3\text{F}_2$ at $15\,400\text{ cm}^{-1}$ and $\text{Pr}^{3+} {}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ at $20\,500\text{ cm}^{-1}$; and (c) ${}^4\text{I}_{11/2}$ at $10\,000\text{ cm}^{-1}$ and ${}^4\text{S}_{3/2}$ at $18\,200\text{ cm}^{-1}$. Asterisks (*) denote peaks to laser stray light and second order of the pump laser, respectively. Note the scaling factors.

that these examples are based on V^{3+} in elpasolite host lattices or Cr in the exotic 5+ state as sensitizer illustrates how difficult it is to realize such upconversion materials. The detailed excitation mechanisms for these phosphors have all been elucidated through a combination of spectroscopic techniques, using the theory described in Section 6.2.

In the $K_2NaScF_6:Er^{3+},V^{3+}$ example shown in Fig. 6.18(a), at least three distinctly different mechanisms contribute to the Er^{3+} upconversion. The dominant mechanism under $14\,175\text{ cm}^{-1}$ illumination involves a $V^{3+} \ ^3T_{1g} \rightarrow \ ^3T_{2g}$ excitation followed by an excited-state absorption step to the $Er^{3+} \ ^2H_{9/2}$ upper excited state. The upconversion luminescence is observed from the $Er^{3+} \ ^4S_{3/2}$ and $^4F_{9/2}$ states. This unusual mechanism is best understood by viewing a $V^{3+}-Er^{3+}$ dimer as the chromophoric unit. It is the same type of cooperative UC mechanism as was discussed for $Yb^{3+}-Mn^{2+}$ containing materials earlier in this section.

Figure 6.18(b) shows the emission spectrum of $Cs_2NaYCl_6:Pr^{3+},V^{3+}$. The mechanism begins with $^3T_{1g} \rightarrow \ ^3T_{2g}$ absorption on V^{3+} , and this is followed by energy transfer from the $V^{3+} \ ^3T_{2g}$ state to 1G_4 of Pr^{3+} . Subsequent $Pr^{3+} \ ^1G_4 \rightarrow \ ^3P_{1,0}$ excited state absorption promotes the system into the blue-emitting level from which the emission is observed. The overall efficiency of this process is very low, because the long-living $V^{3+} \ ^1T_{2g}$ level lies about 250 cm^{-1} below the $Pr^{3+} \ ^1G_4$ level. As a consequence, the upconversion in this system is only observed because the competition with multiphonon relaxation ($V^{3+} \ ^3T_{2g} \rightarrow \ ^1T_{2g}$) does not fully quench the 1G_4 population. A small fraction of the $V^{3+} \ ^3T_{2g}$ population decays radiatively, corresponding to the very weak shoulder on the high-energy side of the $V^{3+} \ ^1T_{2g} \rightarrow \ ^3T_{1g}$ transition shown in Fig. 6.18(b). Only in this small overlap region between V^{3+} emission and Pr^{3+} absorption is the necessary energy transfer condition required for upconversion fulfilled.

The upconversion to $YVO_4:Er^{3+},Cr^{5+}$, shown in Fig. 6.18(c), is based on three consecutive energy transfer steps from the 2B_2 level of Cr^{5+} to the $Er^{3+} \ ^4I_{13/2}$, $^4I_{9/2}$, and $^4S_{3/2}$ levels, respectively. As the 2B_2 lifetime is orders of magnitude shorter than the lifetimes of the Er^{3+} energy levels involved, all three energy transfer steps can originate from the same Cr^{5+} ion. The $^2B_2 \rightarrow \ ^4I_{13/2}$ energy transfer is highly efficient, more than 99% of the total number of emitted photons after Cr^{5+} excitation originating from Er^{3+} . The green $^4S_{3/2} \rightarrow \ ^4I_{15/2}$ emission is clearly visible by eye at 15 K, but is strongly quenched at room temperature. Unfortunately, even at 15 K the upconversion efficiency is very low because of the three-photon upconversion excitation process and the high phonon energy of the host lattice (leading to extensive multiphonon relaxation in Er^{3+}).

6.3.4

Organic Upconverters

In contrast to the inorganic and ionic phosphors that have been discussed so far, there is not a large variety of mechanisms available when one wishes to investigate the upconversion properties of organic molecules. Because almost all excited state \rightarrow ground state transitions are considerably more allowed in organic phosphors than in

inorganic ones, the associated lifetimes of the excited states in organic phosphors are extremely short (typically in the nanosecond range). This very fast decay time means that an organic upconverter cannot be long enough in its excited state to allow for energy transfer upconversion. As a result, the few organic upconversion phosphors that have been identified in the literature all require the excited-state absorption mechanism to populate the emitting state.

One of the best documented organic upconversion phosphors is the organic dye, *trans*-4-[*p*-(pyrrolidinyl)styryl]-*N*-methylpyridinium iodide (abbreviated as PSPI) [26]. This dye is capable of normal (downconversion) laser action and has a significant two-photon absorption cross-section (under 930 nm excitation). The absorption spectrum shows a strong absorption band with a peak wavelength of 482 nm, corresponding to the first excited singlet state S_1 . Another absorption band at wavelengths shorter than 350 nm corresponds to the second excited singlet state S_2 . As the lifetime of the S_1 state is ~ 100 ps, there can be enough population in this state for excited-state absorption via the allowed $S_1 \rightarrow S_2$ transition, after which emission from the S_2 state is observed to the ground state. It remains doubtful if one can achieve upconversion laser action on the $S_2 \rightarrow S_0$ transition, but in principle this may be possible.

Apart from the example of PSPI, not many organic upconverters exist and none are anywhere close to efficient. Solutions of triphenylmethane dyes, such as crystal violet and malachite green, have been studied. Their fluorescence quantum yield is very small (< 0.1) in fluid solvents, but increases to about 30 % in extremely viscous media. Both fluorescence yield studies and picosecond spectroscopic kinetic measurements of the decay of excited-state absorption and of the rates of ground state repopulation show that increased solvent viscosity leads to reduced rates of electronic relaxation. From time-resolved emission studies of crystal violet fluorescence (through picosecond kinetic studies), the solvent-dependent relaxation of these materials has been studied by laser upconversion of the fluorescence emission. It is concluded that excited-state absorption occurs and that upconversion emission can be observed.

Some results on excited-state absorption cross-sections have been recorded for the phenylene-vinylene oligomer 1,4-bis-(α -cyanostyryl)-2,5-dimethoxybenzene dissolved in toluene [27]. For different probe wavelengths, the excited-state cross-section has been recorded, but to date no emission has been observed. The reason for the investigation was to determine if the excited-state absorption cross-section is larger than the stimulated emission cross-section (because then lasing cannot be obtained in such a medium), and no measurement of possible upconversion emission has been made. However, it can be speculated that, although this is a rather efficient downconversion phosphor, the upconversion efficiency will be very low.

The only exception to the rule that organic upconversion must have an intrinsically low efficiency is through studying reverse-saturable absorber (RSA) dyes such as metallo-phthalocyanin and metallo-porphyrin derivatives, both of which have strong absorption bands in the red/near-infrared (Q-band) and the blue/ultraviolet (B-band) spectral regions. With picosecond pulses, strong excited-state absorption (ESA) is observed from the bottom of this manifold. The strong RSA exhibited by these

materials at 532 nm prompted researchers to study the excited-state absorption and refraction at other wavelengths throughout the visible spectral region. It should, however, be noted that such organometallic upconverting phosphors are, in essence, very close to the normal d metal upconverters that have been discussed in Sections 6.3.2 and 6.3.3.

6.3.5

Nanocrystalline Upconverters

The research in the field of photon upconversion has been devoted almost exclusively to bulk materials in the solid state. Therefore, the idea of inducing upconversion in a nanocrystalline material (perhaps even while suspended in the fluid state) is interesting by itself. If it is possible to prepare sufficiently small and efficient upconversion units, one could use them as new luminescent markers for the detection of biomolecules or as security labels. Compared to conventional luminescent markers, which are excited in the ultraviolet or blue spectral region, excitation in the near-infrared obviously has the great advantage that the emission in which one is interested is spectrally well separated from the normal downconversion of the material. As a result, the commonly observed autofluorescence that presents a large background in, e.g., biological systems is not present when using upconversion phosphors. In addition, photo-degradation is strongly reduced, and many materials such as biological tissue are much more transparent to near-infrared light than to ultraviolet or blue wavelengths.

A large number of studies on nanocrystalline materials capable of converting photons of a certain wavelength into shorter-wavelength ones have all focused on two-photon absorption to the conduction band of a semiconductor nanocrystal. Often the subsequent emission is simply band-band emission, although sometimes incorporation of dopants of luminescent defect states results in specific emission characteristics. Typical examples of such nanocrystals are ZnO, GaAs, and CdS, where the band gap of the material is strongly size-dependent because of the quantum-size effects. However, these materials are not upconverters in the sense of the definitions given at the beginning of this chapter, and therefore they will not be discussed here.

The first example of photon upconversion in a nanocrystal was obtained using Y_2O_3 nanocrystals doped with Er^{3+} [28]. The nanocrystals can be prepared via a standard combustion synthesis, and one usually ends up with a powder of (agglomerated) nanocrystals. A major problem of such a synthesis route is that the dopant concentration tends to vary from nanocrystal to nanocrystal (differences as large as 10–20% are not uncommon), and there is no clear relationship between the amount of dopant precursor used in the synthesis and the dopant concentration incorporated into the nanocrystals themselves. When using continuous-wave excitation light (815 nm, resonant with the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$ transition in Er^{3+}) to illuminate the nanocrystals, significant emission bands can be observed in the visible spectral region. These red and green emissions are straightforwardly assigned to the transitions, $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ at 525 nm, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ at 550 nm, and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ at

660 nm. The fact that the spectral band shapes and positions of these three emissions are identical to those obtained upon 488 nm excitation suggests that the Er^{3+} responsible for the upconversion emission does not form a different species (e.g., as a result of a different crystallographic site symmetry) compared to the majority species responsible for the downconversion. A major problem with these nanocrystals is that their surfaces are poorly passivated, resulting in the presence of large amounts of CO_3^{2-} ions remaining on the surface. As these ions have high-energy phonon modes available, the upconversion luminescence is strongly quenched, and the efficiency is obviously very low. As the passivation problem cannot be easily solved because of the combustion synthesis underlying the fabrication of the nanocrystals, these nanocrystals are not expected to be very suitable for application.

More recently, detailed investigations of nanocrystalline $\text{Y}_2\text{O}_2\text{S}:\text{Er}^{3+}$ upconversion phosphors have shown that with 2–4 at.% $\text{Er}^{3+} - \text{Yb}^{3+}$ codoping, the nanocrystals (with typical diameters of 20–50 nm) have upconversion efficiencies that are ~20–25 % higher than that of their bulk counterparts. Furthermore, a clear dependence of the upconversion efficiency on the nanocrystal size has been documented [29]. It is known that in these nanocrystals, the Er^{3+} upconversion emission (green 550 nm emission under 880 nm near-infrared excitation) is predominantly induced by phonon-assisted energy transfer upconversion processes. Therefore, the experimental finding can be understood to be due to the lack of the low-frequency phonon modes that are needed to match the energy difference between the donor and acceptor in nanocrystals [30]. It can be concluded that the size confinement effects on phonon-assisted energy transfer may significantly reduce the upconversion efficiency because of the lack of low-frequency phonon modes in nanocrystals, while resonant energy transfer is significantly reduced in nanoparticles with radii less than 20 nm. In addition to size restrictions on phonon relaxation, phonon-assisted energy transfer processes strongly influence the dynamics of luminescence centers in nanocrystals.

A third example of nanocrystalline upconverters can be found in erbium-doped vitroceraic materials, which are in the class of (doped) $\text{PbGeO}_3\text{-PbF}_2\text{-CdF}_2$ -based transparent glass ceramics in which the $\beta\text{-PbF}_2$ nanocrystals contain the trivalent rare earth dopant [31]. The nanocrystals are typically 5–10 nm in size. In such materials, blue (410 nm), green (530 and 550 nm) and red (660 nm) emission signals are observed under 980 nm infrared excitation. These emissions are all related to transitions in Er^{3+} (from the $^2\text{H}_{9/2}$, $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ states to the ground state, respectively), and the excitation is into the $^4\text{I}_{11/2}$ state of Er^{3+} . When similar vitroceraic samples are doped with Ho^{3+} rather than Er^{3+} , intense red (650 nm) as well as rather weak blue (490 nm) and green (540 nm) upconversion emissions are observed under 980 nm infrared excitation. These emissions are assigned to the $^5\text{F}_5 \rightarrow ^5\text{I}_8$; $^5\text{F}_{2,3} \rightarrow ^5\text{I}_8$; and $^4\text{S}_2, ^5\text{F}_4 \rightarrow ^5\text{I}_8$ transitions, respectively. Interestingly, when the excitation wavelength is shortened to 850 nm, the green 540-nm upconversion emission becomes the dominant spectral feature. The reason for this lies in the fact that after 850 nm excitation ($^5\text{I}_8 \rightarrow ^5\text{I}_5$), subsequent excited state absorption to the $^5\text{F}_1, ^5\text{G}_6$ can take place. After fast multiphonon relaxation, predominantly green emission will be observed from the $^4\text{S}_2$. If the excitation is at 980 nm, on the other

hand, the two excitation photons only have enough energy to reach the 5F_5 state (${}^3I_8 \rightarrow {}^5I_6 \rightarrow {}^5I_7$ followed by ${}^5I_7 \rightarrow {}^5F_5$), and an energy transfer upconversion step is required to reach the ${}^5F_1, {}^5G_6$ band. As mentioned above, the phonon spectrum of nanocrystals becomes strongly size dependent below a critical radius. Therefore, in these small $\beta\text{-PbF}_2\text{:Ho}^{3+}$ nanocrystals there will be a strong dependence of the upconversion characteristics and the efficiency on the crystal size.

A new and highly interesting direction in the field of nanocrystalline upconverters was recently started with the investigation of upconversion visible by the naked eye in a transparent solution using nanocrystals as active upconversion units. One promising way to induce efficient upconversion in solution is to use a dispersion of individual nanocrystals of well-defined quality. There are several requirements on the nanocrystals that have to be fulfilled for this purpose. The diameter should be below ~ 30 nm to effectively eliminate light scattering in the solution. Furthermore, the material should have reasonably low phonon energies and offer the possibility to introduce lanthanide ions. It is a challenging task to synthesize nanocrystals with these properties.

The first systems in which upconversion in solution was successfully achieved were the Er^{3+} - and Tm^{3+} -doped phosphates YbPO_4 and LuPO_4 [32]. These materials showed characteristic red and green Er^{3+} - or blue Tm^{3+} -related upconversion emissions under near-infrared (10230 cm^{-1}) excitation. The spectroscopically straightforward assignments of these emissions have been confirmed by the experimental power dependencies of the respective upconversion emission intensities. However, because of the strong coupling to high-energy phonon modes of the phosphate groups, only very inefficient upconversion was observed. In order to improve the efficiency, one obvious direction is the reduction of the phonon energies of the host lattice to reduce the importance of multiphonon relaxation processes and thus increase the lifetimes of the metastable states involved in the upconversion. Another direction is the protection of the nanocrystals from high-energy vibrational oscillators by growing a crystal layer of an inert material around the nanocrystal core. Given the extraordinarily high upconversion efficiency of the bulk upconversion phosphor $\text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ (as described and discussed in Section 6.3.1), this material is a logical choice to attempt to “nano-size” in order to improve the upconversion efficiency.

The synthesis and very intense multicolor upconversion emission of nanocrystalline NaYF_4 codoped with Yb^{3+} and Er^{3+} transparently dispersed in solution has recently been described [33]. Figure 6.19(a) and (b) show the TEM characterization results obtained on such NaYF_4 nanocrystals. Clearly, crystalline particles of roughly spherical shape and with a reasonably homogeneous size distribution were obtained in the synthesis. A histogram of the particle size distribution, deduced from several overview TEM images [see Fig. 6.19(c)] shows particle sizes ranging from 5 to 30 nm, the main particle fraction being in the size range 10–17 nm. The high crystallinity of the material is confirmed by the observation of clear lattice fringes in the high-resolution TEM image, as shown in Fig. 6.19(b). Furthermore, X-ray diffraction data agrees well with the expected pattern for phase-pure cubic $\alpha\text{-NaYF}_4$ crystals with a mean particle size of 15 nm. This value is in very good agreement with the TEM result shown above.

Figure 6.20(a)–(c) show color photographs of the visible upconversion luminescence in transparent 1 wt % colloidal solution of $\text{NaYF}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ nanocrystals

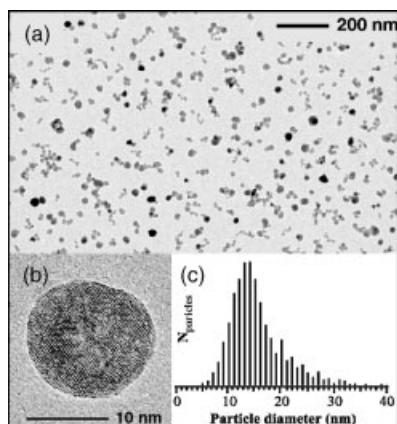


Fig. 6.19 Characterization of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanocrystals. (a) Transmission electron microscopy (TEM) micrograph. (b) High-resolution image of a single nanocrystal. (c) Histogram derived from the TEM diameter of 1000 nanocrystals.

under near-infrared excitation. By eye, the emission looks yellow, as can be seen in Fig. 6.20(a). However, when using green and red band pass filters, as shown in Figures 6.20(b) and (c), it becomes clear that the emission actually consists of two spectrally separated emission bands: a red and a green band centered at roughly 660 and 550 nm, respectively. Similar measurements on colloidal solutions of $\text{NaYF}_4:20\% \text{Yb}^{3+}, 2\% \text{Tm}^{3+}$ nanocrystals are shown in Fig. 6.20(d) and reveal a strong blue emission centered at roughly 470 nm. The corresponding emission spectra for both materials are similar to their bulk counterparts, and therefore the assignment of the emission bands to Yb^{3+} , Er^{3+} , and Tm^{3+} transitions is straightfor-

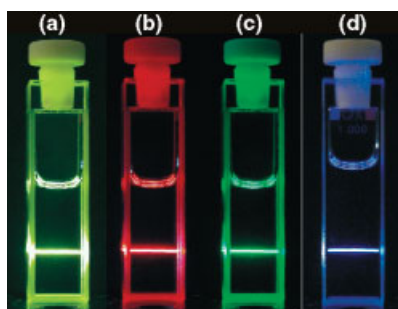


Fig. 6.20 Photographs of the upconversion luminescence in 1 wt% colloidal solutions of nanocrystals in dimethyl sulfoxide excited at $10\,270\text{ cm}^{-1}$ (invisible) with a laser power density of 5.9 kW cm^{-2} . (a) Total upconversion

luminescence of a $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ sample. (b) and (c) show the same luminescence through green and red color filters, respectively. (d) Total upconversion luminescence of an $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}$ sample.

ward and goes parallel to the bulk upconversion phosphor $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ (as described and discussed in Section 6.3.1). However, in the Er^{3+} -doped sample, the relative red to green emission ratios are very different in the nanocrystalline materials compared to the bulk ones. This effect is related to the fact that the bulk phosphor is in the hexagonal β -phase, while the nanocrystalline phosphor is in the cubic α -phase. In these nanocrystals, Yb^{3+} acts as the sensitizer for the upconversion in both samples. This is proven by means of the upconversion excitation spectra, which shows the $\text{Yb}^{3+} {}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ excitation characteristics.

In comparison with the most efficient bulk upconversion phosphors (the β -phased $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ discussed earlier, for which the upconversion efficiencies are known), these nanocrystals show a factor 10^2 – 10^3 lower visible emission under comparable experimental conditions. Two reasons for this reduction in upconversion efficiency can be identified. First, the nanocrystals crystallize in the cubic α -phase, and the α -phase of bulk NaYF_4 is known to be about an order of magnitude less efficient than the corresponding hexagonal β -phase. Second, OH^- impurities are present in the nanocrystals, and many Er^{3+} and Tm^{3+} ions are very close to the surface. Organic ligands with high-energy C–H and C–C vibrational oscillations are efficient luminescence quenchers for nearby lanthanide ions. However, regardless of these possible avenues for further improvement, it remains a most significant result that such bright visible light output from transparent colloidal solutions using moderate intensity near-infrared excitation can be achieved. When compared to colloidal solutions of doped YbPO_4 and LuPO_4 nanocrystals, about eight orders of magnitude more visible emission is observed for the $\text{NaYF}_4:\text{Er}^{3+},\text{Yb}^{3+}$ colloidal nanocrystals shown in Fig. 6.20. This enormous improvement is ascribed to reduced nonradiative multiphonon relaxation in NaYF_4 compared to YbPO_4 (due to the lower phonon energies), the fact that fluoride particles are significantly larger than the phosphate particles (implying that the fraction of lanthanide ions near the surface is smaller), and the very high Yb^{3+} concentration in the phosphate samples, which is likely to lead to concentration quenching of the luminescence.

6.4

Conclusions and Outlook

An overview of the main theory underlying photon upconversion is presented. After an introductory section dealing with the possible processes involved with the conversion of long-wavelength photons to shorter-wavelength ones, two main chapters follow. The first (theoretical) section deals with the fundamentals of the field of upconversion. Starting with a general introduction into the field of upconversion spectroscopy, some of the main physical points that are required for a thorough understanding of the field are visited. The goal is for the reader to appreciate the physical processes involved with photon upconversion. Here, the following topics are treated in considerable detail: absorption, excitation, time evolution, power dependence, photon avalanche, optical bistability, and the determination of the upconversion efficiency.

The second main section describes some of the most typical results on upconversion spectroscopy obtained in recent years. Note that it is not the intention here to give a detailed overview of the photon upconversion literature, as there are several excellent review papers dedicated to this goal (e.g., Refs. [1,16,17]). Here, five different types of upconversion materials currently under investigation are presented: rare earth ions, transition metals, mixed rare earth/transition metal systems, organic upconverters, and nanocrystalline upconverters.

It is mainly the intention of this chapter to demonstrate that photon upconversion is a fully mature and active research field with a well-developed theoretical foundation. Even though serendipity remains an important factor in the discovery of new and efficient upconverting materials, it is clear that it is becoming increasingly possible to predict the upconverting behavior of new materials, enabling one to effectively design materials tailored to specific applications. A case in point with respect to this design strategy is that of mixed transition metal ion/rare earth ion systems, where the upconversion emission energy as well as its efficiency can be predicted based on microscopic physical and chemical arguments. However, due to the vast number of design choices available for such upconversion systems, further fundamental research in this interesting field remains more than ever warranted.

6.5

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Professor Hans-Ulrich Güdel and all his coworkers at the University of Bern are gladly acknowledged for all they have taught me about upconversion research. Naturally, any errors in this chapter should only reflect on the author. Dr. Marieke van Veen is gratefully acknowledged for a critical proof reading of this chapter. Some parts of Section 6.3 have been taken from Ref. [17]. Philips Research is acknowledged for allowing me to work on this chapter while in their employ.

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Please note that only the literature referred to specifically in this chapter is listed here. For a much more detailed list of references in this field, please see the references listed in Refs.[1] [16], and [17].

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7

Luminescent Materials for Phosphor-Converted LEDs

Thomas Jüstel

7.1

Inorganic Light-Emitting Diodes (LEDs)

The first practical inorganic semiconductor LEDs were conceived at Texas Instruments in 1961 by Baird and Pitman. These devices emitted in the near infrared because the material used was InGaP with a band gap of 1.37 eV. One year later, the first LED in the visible was built by Holonyak et al. They used a different composition, viz. GaAsP, to fabricate a device emitting red light. From that time on, the use of more refined processing and other materials (e.g., AlGaAs) led to the development of the common LED, mainly used in indicator lights.

For several decades, LEDs were not attractive for illumination purposes, mainly for two reasons. Firstly, the optical output power (i.e. the lumen package, defining the amount of light emitted from a single LED) was fairly limited, since the packaging and the materials in use did not allow high current densities in the small chips. Since the efficiency was far less than 100 %, a great deal of heat would have been generated, destroying the semiconductor chip. Secondly and more importantly, no efficient blue-emitting semiconductor material was available. For several years semiconductors containing group II and group VI elements, e.g., ZnSSe/ZnTe were researched as possible candidates for blue LEDs with limited success. However, in 1993 Nakamura et al. achieved the breakthrough for solid-state lighting by proving the successful use of InGaN as a material in LEDs [1]. Since the material is chemically very stable, it is difficult to achieve high-quality epitaxial layers for high-efficiency LED operation, but, on the other hand, the high stability allows very high current densities without disintegration of the LED material. Therefore the lumen package can be increased to values relevant for lighting applications (Fig. 7.1). More important, however, is the insensitivity of InGaN to defects. Although the defect density in common InGaN LEDs is much higher than would be acceptable in other material combinations, e.g., AlGaAs (10^9 cm^{-3} vs. 10^6 cm^{-3}), the low surface recombination velocity of InGaN allows efficient LEDs to be built from defect-rich layers. Additionally, with the advent of bright and stable blue and UV LEDs it became possible to generate white light from solid-state devices, either by color conversion of blue LEDs using phosphors or by externally mixing the light from blue, green, and red LEDs.

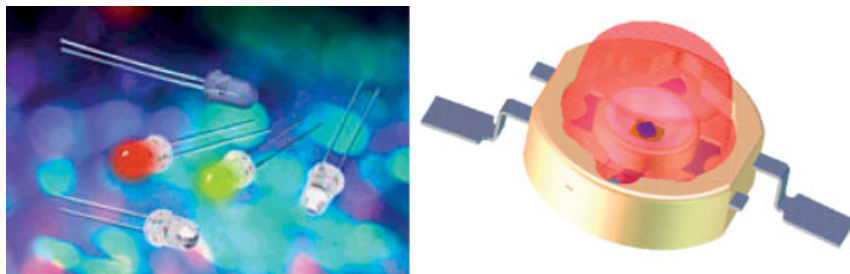


Fig. 7.1 Classical 5-mm LEDs (left) and a high-power-illumination LED (right).

The principle of LEDs is explained in much detail in semiconductor device literature [1–3]. Here the use of LEDs for white light generation and the respective relevant aspects concerning luminescent materials will be discussed. Because of the importance of color conversion in generating white light from LEDs, the nature of the phosphors used is discussed in more detail.

7.2

White and Colored LEDs

White light is, generally speaking, always a mixture of several pure colors. The simplest way to achieve a light source with a white appearance is to combine blue with yellow/orange primary light sources (Fig. 7.2). However, only a very low color-rendering index (CRI) is obtained, i.e. many colors are poorly reproduced under illumination by such a light source. Increasing the number of primary colors by combining, e.g., a red, a green, and a blue (RGB) LED immediately enables much higher CRI values to be achieved and hence a high-quality white light source. In the limit of using many different visible LEDs, the black-body radiation spectrum of 5500 K (essentially the visible spectrum of sunlight) is generated, which has, by definition, a CRI of 100. However, because of the finite size of the LED dies and their package, it is rather difficult to achieve homogeneous mixing of the discrete LEDs, at least in a small package.

The major application of colored LEDs as light sources is thus not in the area of general lighting, but in areas where pure colors, e.g., as depicted by the spectra in Fig. 7.3, have to be reproduced, as in traffic signals and automotive brake or indicator lights. In these application areas, InGaN and AlGaInP LEDs have largely replaced filtered white incandescent light bulbs because of their higher efficiency and longer lifetime.

Two major materials are used in colored LEDs: AlGaInP for red, orange, and yellow and InGaN for green and blue. The quaternary mixture of AlGaInP is the prime candidate for a red to yellow emission color. It is typically grown on GaAs wafers, since the lattice matching of substrate and epilayer guarantees a small number of defects, essential for high efficiency and long lifetime. After deposition

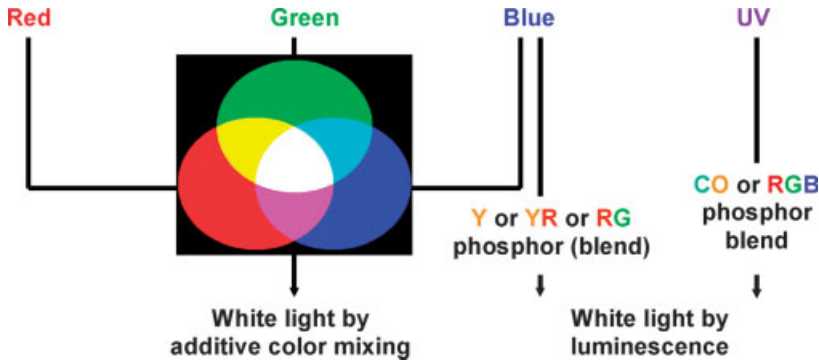


Fig. 7.2 Summary of different concepts to generate white light by primary light sources.

of the various layers, the wafer is bonded to a GaP substrate, and the original GaAs substrate, which absorbs in the spectral region of the LED emission, is removed. This increases the efficiency, since, if the substrate was absorbing, half of the light would be lost, i.e. all the light emitted toward the substrate. Still, a lot of light is trapped inside the die by total internal reflection. Since the refractive index of the material is greater than one, all light emitted at an angle greater than the Brewster angle is reflected back into the crystal. Because of some residual absorption, e.g., at the metal contacts or the charge transporting layers, multiple internal reflections still diminish the efficiency. By shaping the semiconductor chip in form of a truncated inverted pyramid (Fig. 7.4), the highest efficiency of a red light source was achieved by an LED some years ago [4].

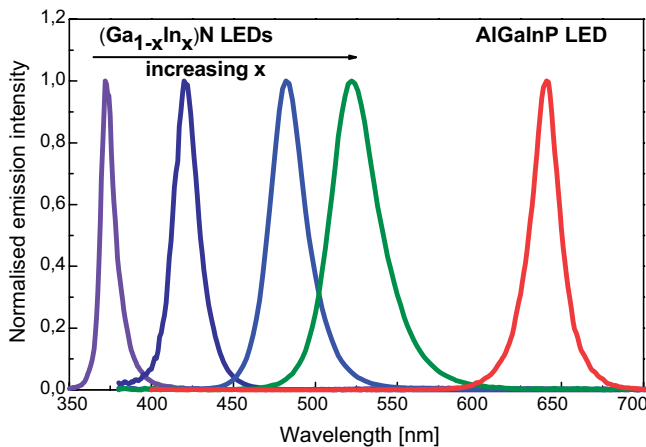


Fig. 7.3 Typical spectra of blue and green InGaN LEDs and of a red AlGaInP LED ($x=0.0$ to ca. 0.45).

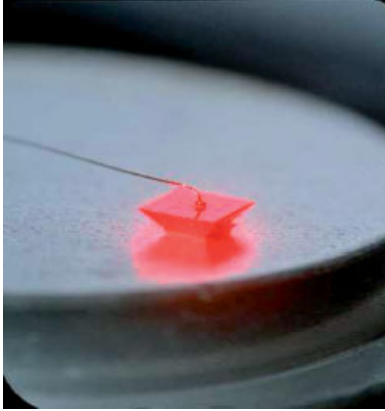


Fig. 7.4 InGaP LED shaped as truncated inverted pyramid for efficient light extraction (Source: Lumileds).

This LED is estimated to have close to 100% internal efficiency and an external efficiency of about 55%, resulting in a luminous efficiency of 102 lm W^{-1} . This value demonstrates the potential of LED technology as the future light source of first choice, since this is the most efficient red-light source available to date.

The lumen package of AlGaInP LEDs is, however, limited because of thermal quenching of the emission. For power densities beyond 0.1 W cm^{-2} , the efficiency and also the lifetime of AlGaInP LEDs drops significantly, since the chip temperature increases. Moreover, the efficiency drops tremendously with increasing energy of the emission band (Fig. 7.5).

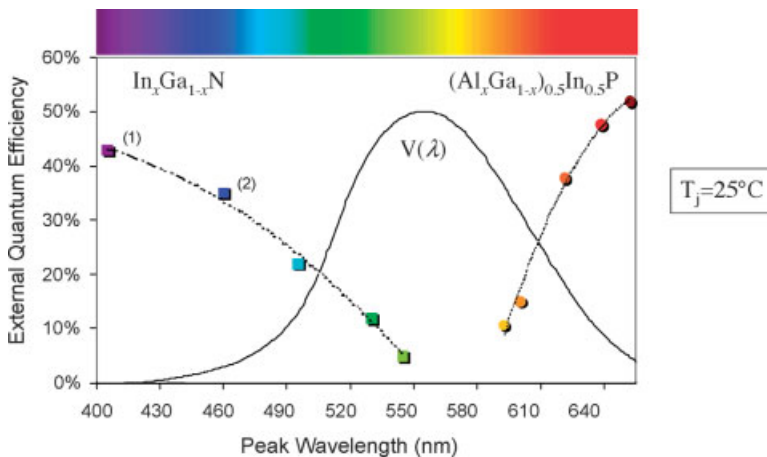


Fig. 7.5 Efficiency of InGaN- and AlGaInP-based LEDs as a function of emission wavelength at room temperature. $V(\lambda)$ gives the eye-sensitivity as a function of the wavelength (Source: Lumileds).

For the higher-energy emission from green to blue and beyond, InGaN has become the material of choice. After several years of intensive research, it has become possible to create working LEDs in the InGaN material system. The major difficulty to overcome was the problem of p-doping GaN. This is achieved by doping Mg into the InGaN lattice, which happens at temperatures above 1100 °C in the deposition process. By varying the amount of In in the composition of the LED, the emission can be tuned from UV to green. However, because of segregation effects and subsequent development of lattice defects, the efficiency drops with increasing wavelength, i.e. for high In contents. Comparing the different classes of materials, it turns out that the defect density of InGaN LEDs is much higher than would be tolerable in more conventional III-V compound semiconductors. This is mainly because of the lack of a lattice-matched substrate material. At the present time, mostly Al₂O₃ (sapphire), with a lattice mismatch of approx. 15 %, is being used. Current external efficiencies range from 40 % for blue to 10 % for green wavelengths, with efficiency figures tending to increase continuously – new values being published literally week by week. As a summary, efficiency as a function of wavelength for the two-material systems is plotted in Fig. 7.5 together with the eye-sensitivity curve.

7.3

Phosphor-Converted LEDs

As mentioned above, combining the light of several colored LEDs can create white light. The use of separate RGB LEDs promises high efficiencies and flexible, user-controlled color but requires complicated electronics, because the amounts of red, green, and blue light must be carefully controlled since the LED light output (intensity and color) varies with drive current, temperature, and time (device ageing). Homogeneous optical mixing of the light is also rather difficult. Because of the high saturation of the primary LED colors, displays with a large color gamut can be made. This can be exploited for the improvement of LCDs, since standard backlights for LCDs are based on fluorescent lamps yielding a smaller color gamut.

However, the most common method to achieve white emission from LEDs to date is by partially converting blue light from the InGaN semiconductor to lower-energy emission by means of phosphors, which are deposited onto the LED chip as a thin layer (Fig. 7.6).

These phosphor-converted LEDs (pcLEDs) display a color point which is heavily dependent on the type, thickness, and packaging density of the phosphor layer. The applied phosphor(s) must show strong absorption of the blue light and a high photochemical stability due to the high excitation density, e.g., 30 W cm⁻² for 1 W InGaN LED (chip area 1 mm², ext. efficiency ca. 30 %). This value is almost three orders of magnitude higher than the excitation density experienced by phosphors in fluorescent lamps, with many consequences for the chemical and physical properties of applicable phosphors. Consequently, LED phosphors can only be activated by those ions which show a high quantum efficiency, even at elevated temperatures (up to 150–200 °C). The host lattice must show high chemical and thermal stability in order

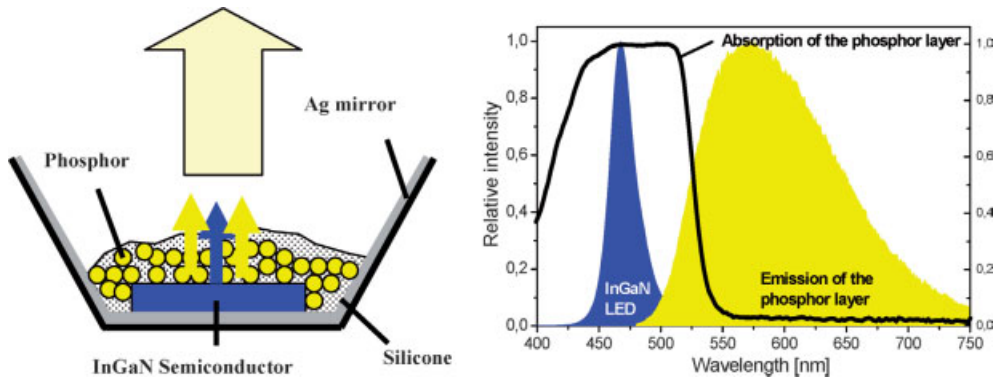


Fig. 7.6 Principle of color conversion in a phosphor-converted pcLED.

to survive the LED lifetime of more than 10 000 h [10]. Moreover, the phosphor should have a short decay time to avoid saturation at high drive levels, since this will result in a change, i.e. a blue-shift, of the LED spectrum with driving conditions. Most prominent LED converter materials are thus activated by those ions relying on allowed 4f-5d transitions, i.e. Eu^{2+} and Ce^{3+} , which are doped into rigid host lattices (oxides, nitrides, and sulfides).

Today, the white LED market is dominated by pcLEDs comprising a blue-emitting InGaN semiconductor (420–480 nm) coated with a Ce^{3+} -activated phosphor derived from the mineral grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) crystallizing in the garnet structure [2]. The replacement of Ca^{2+} by Y^{3+} and of Si^{4+} by Al^{3+} yields $\text{Y}_3\text{Al}_5\text{O}_{12}$ (Yttrium-Aluminum-Garnet YAG), which can easily be doped by Ce^{3+} and other trivalent rare-earth ions, e.g. Gd^{3+} or Tb^{3+} . The most widely applied phosphor is $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (YAG:Ce) [1], where the effective color temperature of the emitted light from a pcLED depends on the optical thickness of the phosphor layer. By increasing the layer thickness the color shifts from bluish white (cool white) to yellowish white (warm white) (Fig. 7.7).

The first cool white LEDs including YAG:Ce as a phosphor showed a luminous efficiency of about 10 lm W^{-1} [8]. This corresponds to a light output of 0.7 lm at a power consumption of 70 mW. Presently, cool white LEDs already show an efficiency of 30 lm W^{-1} , i.e. a high-power 5-W LED yields up to 150 lm [9].

A disadvantage of the application of a single yellow phosphor is that low color temperatures (warm white light) cannot be achieved with a high color rendering because of the lack of red light in the LED spectrum [7]. In addition, the color rendering of cool white LEDs depends on the driving conditions. These problems are solved by trichromatic white LEDs comprising two phosphors, the first emitting between 520 and 570 nm and the second emitting between 590 and 660 nm.

The first trichromatic LED introduced into the market was based on a YAG:Ce pcLED, which comprises an additional red phosphor to achieve illumination grade warm white LEDs with a high color rendering. Red luminescent materials used in combination with the yellow YAG:Ce are $(\text{Sr}_{1-x}\text{Ca}_x)\text{S}:\text{Eu}$ [5] and $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Si}_5\text{N}_8:\text{Eu}$

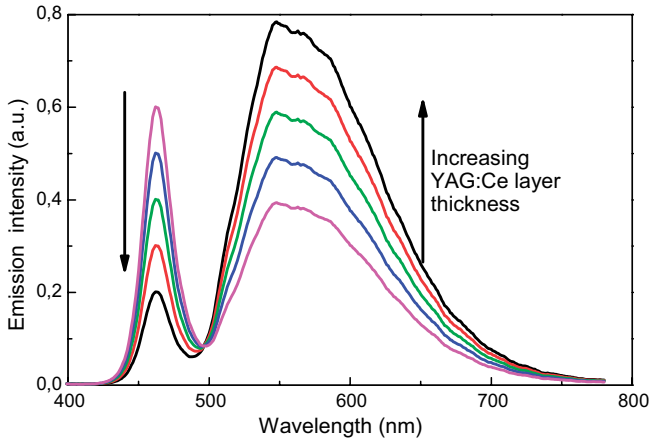


Fig. 7.7 Emission spectra of a white LED comprising a 460 nm-emitting blue InGaN chip and a phosphor as a function of the optical thickness of the YAG:Ce layer.

[6]. These red-enhanced LEDs show high CRIs (above 90) for low color temperatures (between 2500 and 4000 K).

An even more advanced approach for a trichromatic light source, however, is the application of a green- and a red-emitting phosphor. This concept has the advantage of enabling a high color rendering at all relevant lighting color temperatures, i.e. between 2500 and 8000 K. It was demonstrated by Opstelten and Koedam for fluorescent lamps in the 1970s, after the theoretical treatment by Thornton, that an RGB light source can simultaneously yield high color rendering and high luminous efficiency [9].

A two-component phosphor blend for application in trichromatic RGB LEDs was first proposed by Müller and comprises $\text{SrGa}_2\text{S}_4:\text{Eu}$ (535 nm) and $\text{SrS}:\text{Eu}$ (610 nm) [7], yielding pcLEDs with a very high color quality at an arbitrary color temperature between 2500 and 8000 K (Fig. 7.8).

The main drawback of the above-mentioned phosphor blend is the sensitivity of sulfides to water, resulting in the production of H_2S . This volatile and reactive product diffuses to other LED components, e.g. to the Ag mirror, where it converts Ag into black Ag_2S . However, this problem can be circumvented by the application of a dense particle coating preventing the diffusion of water toward the phosphor surface [11]. Although this measure is sufficient to obtain usable LED phosphors with the composition $(\text{Sr}_{1-x}\text{Ca}_x)\text{S}:\text{Eu}$, the thiogallates such as $\text{SrGa}_2\text{S}_4:\text{Eu}$ are still not applied in LEDs, since they exhibit pronounced thermal quenching. The luminescence of the green-emitting thiogallate is strongly quenched with increasing temperature, i.e. its quantum efficiency is reduced by 50 % at 170 °C.

Alternative green phosphors are Eu^{2+} -doped orthosilicates of the formula $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{SiO}_4:\text{Eu}$, which were invented by Barry about 40 years ago [12]. Their color point shows a tremendous red shift due to the replacement of Ba^{2+} by Sr^{2+} . A further red-shift of the color point can be achieved by the incorporation of Ca^{2+} into the lattice.

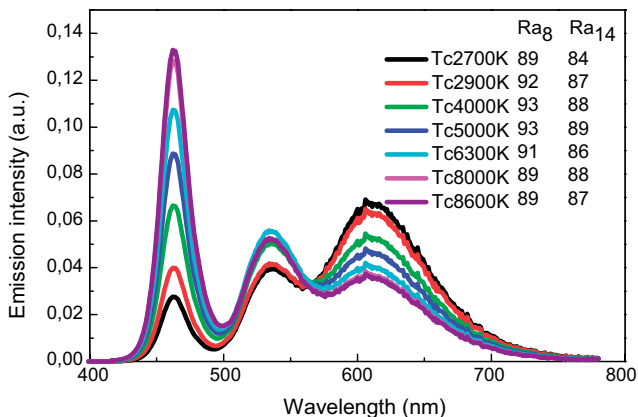


Fig. 7.8 Emission spectra of white trichromatic LEDs comprising $\text{SrGa}_2\text{S}_4:\text{Eu}$ and $\text{SrS}:\text{Eu}$. The R_a values mentioned are the CRIs for 8 and 14 reference colors, respectively (the maximum CRI is 100 in both cases).

These alkaline earth orthosilicates have been claimed recently to convert blue InGaN LEDs into white pcLEDs at different color temperatures [13]. The main problem with orthosilicates is their strong alkaline character and thus reactivity towards electrophilic attack, e.g. by CO_2 or H^+ , as a result of the rather high electron density on the oxygen atoms of the SiO_4^{4-} groups. Therefore, a stability improvement measure, e.g. a particle coating, is still necessary.

While $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}$ is considered as a potential green-emitting LED phosphor, Park described the application of the composition $(\text{Ba,Sr,Ca})_2\text{SiO}_4:\text{Eu}$, which emits at 570 nm (Fig. 7.9), to obtain a white pcLED based on just a single phosphor, i.e. similar

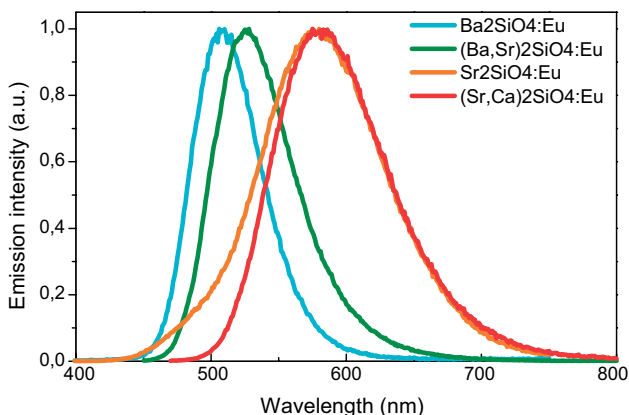


Fig. 7.9 Emission spectra of selected compositions of the solid solution $(\text{Ba}_{1-x-y}\text{Sr}_x\text{Ca}_y)_2\text{SiO}_4:\text{Eu}$.

to the YAG:Ce LEDs. Another possibility to achieve a white pcLED with a single phosphor is the application of $\text{SrLi}_2\text{SiO}_4:\text{Eu}$ or $\text{Tb}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (TAG:Ce), which were claimed as LED phosphors a few years ago [14,15].

In view of the chemical reactivity of $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{SiO}_4:\text{Eu}$, the search for further green-emitting phosphors applicable in pcLEDs is ongoing. Some interesting candidates are $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (LuAG:Ce) and the oxynitrides $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ and $\text{CaSi}_2\text{N}_2\text{O}_2:\text{Eu}$ [16], which were quite recently mentioned as LED phosphors. From a chemist's point of view, the oxynitride is a very interesting compound, since this material formally includes trivalent N^{3-} anions. On the one hand, the nitride anion can undergo three or four covalent bonds resulting in materials with a higher hardness, stability, and density than observed for similar oxides. On the other hand, the strongly covalent character of the nitride-metal bonds results in a strong reduction of the energy separation between the ground state ($4f^n$) and the excited state configuration ($4f^{n-1}5d^1$) of Ce^{3+} and Eu^{2+} . A rather small separation yields phosphors with absorption bands in the near UV to green and emission bands in the green, yellow, or even red spectral range. As expected, the composition $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}$, solely comprising nitride as an anion, is an orange powder with a broad emission band around 610 nm [17].

A trichromatic LED on the basis of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}$ and $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ shows high color rendering at all relevant color temperatures (Fig. 7.10), as already shown for the sulfide LED, but with the advantage of a higher lifetime and less dependence of the light output and color point on the drive conditions [18].

Even though this phosphor composition is a powerful and promising blend for pcLEDs, there are more potential LED phosphors, mainly based on nitrides, SiONes, or SiAlONes as a host lattice. One of the recently developed materials is $\text{CaAlSiN}_3:\text{Eu}$ [19], which can be applied as a deep red emitter to further improve color rendering at low color temperatures.

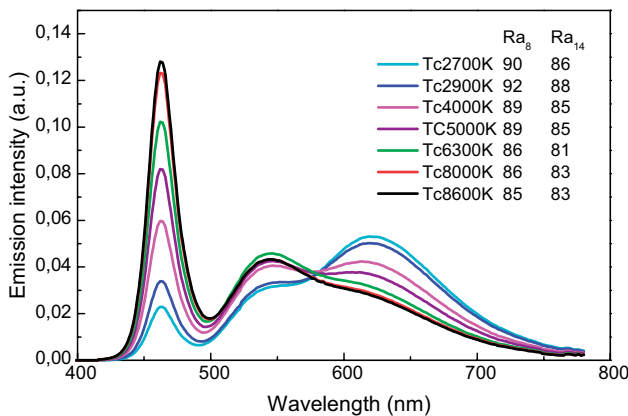


Fig. 7.10 Emission spectra of white trichromatic LEDs comprising $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ and $\text{S}_2\text{Si}_5\text{N}_8:\text{Eu}$.

7.4

Future Trends

A practical efficiency target for a phosphor-converted LED light source is about 100 lm W^{-1} , which is comparable to high-end white fluorescent lamps. Improving the external phosphor quantum efficiency, stability, linearity, and temperature performance are the most important issues to meet this target.

The improvement of the internal quantum efficiency of the presently applied materials can itself hardly contribute to this goal, since LED phosphors, such as YAG:Ce, (Ca,Sr)S:Eu, or (Ca,Sr)₂Si₅N₈:Eu, are already operating at the physical limit as far as the internal quantum efficiency is concerned. More important is the improvement of the so-called LED package gain, which describes the overall efficiency of the conversion of photons emitted by the InGaN semiconductor into the desired LED spectrum. Since light out-coupling from the phosphor grains and light scattering in the conversion layer significantly contribute to the package gain, the optimization of the particle size distribution and the surface morphology of LED phosphors will be in the focus of future R&D activities.

A recent development, for instance, is the enhancement of the light out-coupling efficiency by the application of a grainy coating to gradually match the refractive index of the highly refractive sulfide and nitride phosphors to the package material [20]. Further measures are the reduction of the decay time [21], the enhancement of the absorption of LED phosphors to improve their linearity with excitation density [21], and the application of red line emitters instead of red broad-band emitters to enhance the lumen equivalent [22].

Even though cool and warm white LEDs with a rather high color rendering are already on the market, the final goal is to produce LED light sources with a color quality close to that of a black-body radiator at a temperature of 2500 to 6000 K. This means that upcoming LEDs have to match the spectrum of incandescent and halogen lamps more closely. This requires novel LED phosphors to fill up the spectral gaps in the emission spectrum of current white pcLEDs. To this end, many novel nitride and oxynitride host lattices doped by Eu^{2+} and Ce^{3+} are presently under development, since the spectra of Eu^{2+} and Ce^{3+} can easily be tuned by the host lattice, and many of the luminescent materials activated by these ions exhibit high efficiency, strong absorption, short decay time, and broad emission bands.

Despite the success of white pcLEDs operating on the basis of blue InGaN dies, the conversion of near-UV LEDs (370–420 nm) is another approach of broad interest. The main reason is that near-UV LEDs would allow the application of many more types of luminescent materials than those mentioned in Table 7.1.

In particular, Eu^{3+} doped phosphors are of strong interest for the application in near-UV LEDs, since they exhibit a high lumen equivalent, quantum efficiency, and photostability at the same time. Moreover, from a practical point of view a fluorescent light source comprising a red line emitter emitting at 610–615 nm is the best compromise between luminous efficacy and color rendering [9].

A drawback is, however, the weak absorption of Eu^{3+} in the blue and even in the near UV. The main strategy to solve this problem has focused on materials that have

Tab. 7.1 Overview of the spectral properties and problem areas of the most important LED phosphors.

Chemical composition	Emission color	Emission peak at [nm]	Lumen equivalent (LE) [$\text{lm}/\text{W}_{\text{opt}}$]	Problem areas
(Ba,Sr) ₂ SiO ₄ :Eu ²⁺	Green	525	530	Stability
Lu ₃ Al ₅ O ₁₂ :Ce ³⁺	Green	530	465	Narrow absorption band
SrSi ₂ N ₂ O ₂ :Eu ²⁺	Green	540	530	Synthesis
SrGa ₂ S ₄ :Eu ²⁺	Green	535	575	Thermal quenching
Y ₃ Al ₅ O ₁₂ :Ce ³⁺	Yellow	540	450	Narrow absorption band
Tb ₃ Al ₅ O ₁₂ :Ce ³⁺	Yellow	560	410	Narrow absorption band
CaSi ₂ N ₂ O ₂ :Eu ²⁺	Yellow	565	485	Synthesis
(Y,Gd) ₃ Al ₅ O ₁₂ :Ce ³⁺	Yellow	570	400	Narrow absorption band
SrLi ₂ SiO ₄ :Eu ²⁺	Yellow/orange	580	415	Stability
Ca ₂ Si ₅ N ₈ :Eu ²⁺	Red	610	270	Synthesis
Sr ₂ Si ₅ N ₈ :Eu ²⁺	Red	620	240	Synthesis
CaAlSiN ₃ :Eu ²⁺	Red	650	150	Synthesis, LE
CaS:Eu ²⁺	Red	650	85	Stability, LE

broad and intense charge-transfer (CT) absorption bands in the near UV and are therefore capable of efficiently absorbing the emission from InGaN based LEDs. Such materials include oxysulfides, vanadates, molybdates, tungstates, etc., where the oxygen to Eu³⁺ charge-transfer band are very intense and broad and the position is at rather low energy, as for e.g. in Y₂O₂S:Eu or Gd₂O₂S:Eu [23].

A recent idea is to convert near-UV or blue light via the 4f-4f transitions of Eu³⁺ located at 394 (⁷F₀-⁵L₆) and 465 nm (⁷F₀-⁵D₂), which are rather intense in tungstates and molybdates. Following the excitation process, Eu³⁺ relaxes nonradiatively to the ⁵D₀ state, which is the emitting energy level. For instance, the composition NaY_{0.95}Eu_{0.05}(WO₄)(MoO₄) shows a much higher light output than Y₂O₂S:Eu for 394 nm excitation. These results feed the hope that an Eu³⁺ phosphor, which is sufficiently strongly luminescent under 394- and/or 465-nm excitation, can be found in the future. The higher lumen equivalent of Eu³⁺ (260–300 lm W^{-1}) compared to Eu²⁺ phosphors (Table 7.1) will contribute to a further enhancement of the luminous efficacy of LEDs.

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8

Organic Electroluminescence

Joseph J. Shiang and Anil R. Duggal

8.1

Introduction

Organic electroluminescence is an exciting field that exists at the intersection between many scientific disciplines including synthetic and physical chemistry and semiconductor and optical physics. Organic light-emitting devices (OLEDs) are the practical manifestation of the tremendous progress that has been achieved in this field, highly efficient devices having been developed [1,2] and successfully employed in commercial products [3]. The basic scientific area is now extremely active, with many new publications outlining new device and material architectures appearing each month. Most of the progress to date has been fueled both by advances in the basic knowledge of electronic processes in organic materials [4,5] and an applied interest in developing flat panel displays. More recently, researchers have set their sights on applying this technology for general lighting, arguably the most demanding luminescence application [6,7]. Achieving this goal will require substantial improvements to materials and device architectures to increase efficiency, and the simultaneous development of a high throughput manufacturing infrastructure to enable high performance at low cost.

In this chapter, the basic mechanisms behind organic electroluminescence will be described, and then the promise, challenges, and some unique approaches to developing this technology for the ultimate application of general lighting will be outlined. The chapter begins with a description of the fundamental physics of OLED devices and materials. Following this, Section 8.2 provides more detail by presenting a somewhat historical overview of the major trends and innovations in device and material design that have enabled the impressive progress to date. Section 8.3 outlines an example of how these different elements: physics, device design, and materials can be combined to make a practical, large-area illumination source. This example demonstrates both the possibilities inherent in this technology and the areas where effort needs to be focused in order for progress to continue. Conclusions are presented in the final section.

8.2 OLED Fundamentals

An organic light-emitting device consists of one or more semiconducting organic thin films sandwiched between two electrodes, one of which must be transparent. A simplified schematic of an OLED is shown in Fig. 8.1. In a typical device, indium tin oxide (ITO) is utilized as a transparent anode electrode and an evaporated metal is utilized as the cathode. The OLED shown in Fig. 8.1 represents the most common “down-emitting” device structure and is typically fabricated by sequentially depositing layers onto the transparent substrate. Typically, the substrate is glass or plastic that has been pre-coated with ITO. The organic layers consist of materials that transport charge and emit light. These are applied via either a solution-based or a vapor-based coating process. The number and type of layers depends upon the chosen materials and fabrication methodology. These layers, which determine fundamental OLED properties, form the focus of this chapter. An electron-injecting cathode is applied on top of the organic layers via thermal evaporation. Typically this electrode consists of a low work function metal such as calcium or a magnesium silver alloy. Finally, the entire package is sealed to prevent ingress of water or oxygen. When voltage is applied between the two electrodes, diode-like rectification is observed with appreciable current flow occurring when the ITO anode is biased positively. Under this forward bias, light is generated and emitted into the surroundings through the transparent substrate. On the right side of Fig. 8.1 is a commonly used form of energy level diagram for the device. The vertical axis is energy with the energy of a free electron in the vacuum located at the top of the axis and set to a value of zero by convention.

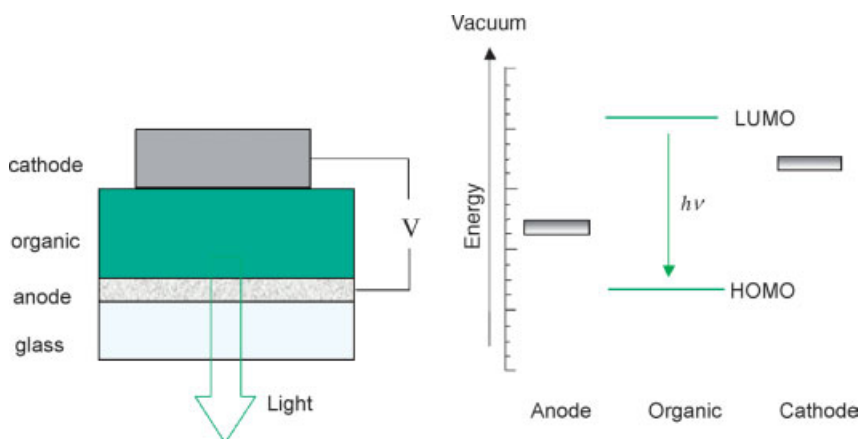


Fig. 8.1 A schematic drawing of the layer structure of a simple OLED (left) and the corresponding energy level diagram (right). The energy scale indicates binding energy relative to the vacuum level. For this scale, the free electron in vacuum has the highest energy of 0 and corresponds to the top of the scale.

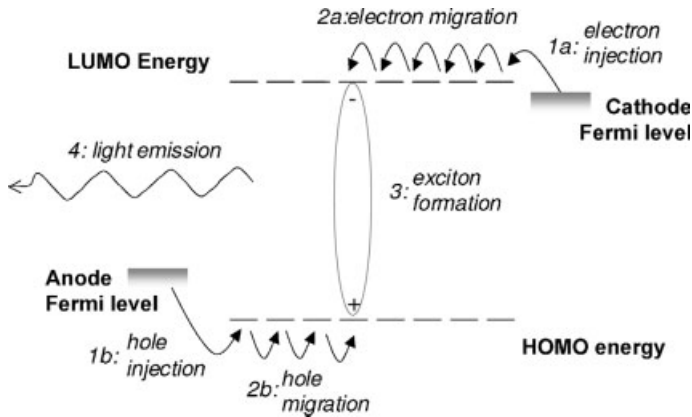


Fig. 8.2 Diagram illustrating the physical processes involved in electroluminescence from organic materials.

Electronic states that weakly bind electrons are high on this axis, states that have very high affinity for electrons being lower down on the axis. Typically, the negative sign is not included, so that a state that is denoted as having an energy of 6 eV is actually *lower* in energy relative to the vacuum by 6 eV. Metal work functions are denoted by a single broad line to represent their Fermi level. The organic materials are typically described using two lines, the upper one corresponding to the lowest unoccupied molecular orbital (LUMO) and the lower one the highest occupied molecular orbital (HOMO). These levels correspond to the conduction and valence bands of a covalent semiconductor material.

Qualitatively, the device physics of an OLED is best illustrated by examining the simplest type of device structure – one which uses only a single organic layer. The operating principles of this single-layer device are shown in Fig. 8.2. When a forward bias is applied, electrons are injected from the cathode into the LUMO of the organic material and holes are injected from the anode into the HOMO of the material. Thus, the electrons must overcome the barrier between the Fermi level of the top electrode and the LUMO level of the polymer, while the holes must overcome the energy barrier between the ITO Fermi level and the HOMO of the polymer. After the carriers are injected, they drift in the presence of the externally applied electric field by hopping from molecule to molecule to the opposite electrode. If an electron and a hole happen to meet, they may combine to form a molecular excited state known as an exciton that may then radiatively recombine to generate a photon.

There are five distinct steps in the light emission process: (1) charge injection, (2) charge migration, (3) exciton formation, (4) light emission, and (5) light extraction. To achieve optimal OLED performance, each step must operate at its maximal efficiency. The first four of these steps are illustrated in Fig. 8.2. While these steps occur in traditional semiconductor based LEDs (e.g., GaAs, GaN), each step is

significantly different in organic materials because the electronic states in organic materials are highly localized and the mobility of the charge carriers is orders of magnitude lower [4]. Devices based upon organic semiconductors require a special description of the physics of operation which utilizes both the language of solid state physics, originally developed to describe plane wave-like transport states, and the language of molecular physics, developed to describe electronic processes in localized states [5].

For an electroluminescent device, the radiant “wall-plug” efficiency of the light source (radiant power out divided by electrical power in) is given by the following equation:

$$\eta = \frac{eV_{\text{photon}}}{V_{\text{device}}} \cdot \text{EQE} \quad (1)$$

The ratio is the average energy of the emitted photons in electron volts (typically 2.4 eV for a white-light emitter) divided by the applied device voltage. Because of the intrinsically low conductivities of these materials, the injection and drift of carriers require high electric fields ($\sim 0.1 \text{ MV cm}^{-1}$), and achieving low-voltage operation thus limits the thickness of the organic layers to a few hundred nm. The electron (hole) injection and transport processes are illustrated as steps 1a (1b) and 2a (2b) in Fig. 8.2. The second term, the external quantum efficiency (EQE), is the ratio of the number of photons emitted into the ambient divided by the number of electrons injected into the device. We can further decompose the device EQE into several terms:

$$\text{EQE} = \eta_{\text{recombination}} \eta_{\text{PL}} \eta_{\text{extract}} \quad (2)$$

The first two efficiency terms correspond to the remaining processes depicted in Fig. 8.2. Thus, $\eta_{\text{recombination}}$, is the fraction of electrons and holes that meet at a particular site within the device to form a potentially emissive state or exciton. Electrons or holes that do not meet but rather migrate to the opposite electrode are lost and reduce this term below unity. The next term η_{PL} is the photoluminescent efficiency of the exciton state. It reflects the fact that the exciton may relax thermally to produce heat rather than radiatively to produce light. To avoid losses due to this term, the rate of radiative processes, k_{rad} , must be much higher than the rate of the nonradiative process, k_{nr} , so that the ratio:

$$\eta_{\text{PL}} = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{nr}}} \quad (3)$$

is nearly unity. In organic materials, this term is typically “spin dependent”, as an electron and a hole, each with spin $\frac{1}{2}$, can form two types of excitons – “singlet” with a spin-state of 0 or “triplet” with a spin state of 1. In general, these states have different radiative and nonradiative rates. Fig. 8.3 illustrates the different pathways that can occur in the presence of multiple spin states. A more complete equation for η_{PL} is

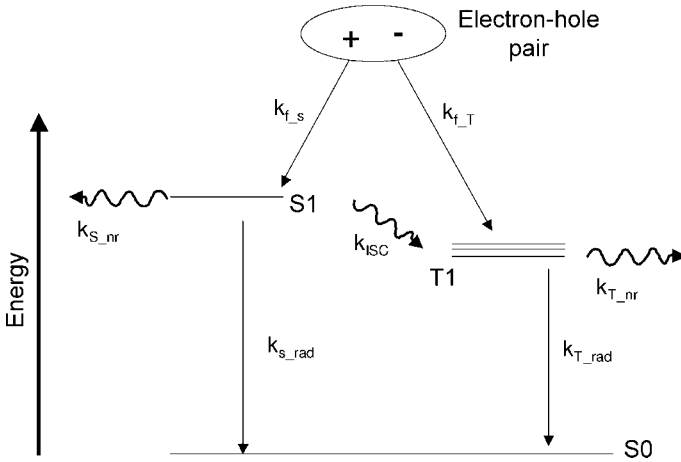


Fig. 8.3 Energy level and kinetic diagram of the charge recombination process.

thus:

$$\eta_{\text{PL}} = f_s \frac{k_{\text{S,rad}}}{k_{\text{S,rad}} + k_{\text{S,nr}}} + (1 - f_s) \frac{k_{\text{T,rad}}}{k_{\text{T,rad}} + k_{\text{T,nr}}} \quad (4)$$

The first term on the right hand side corresponds to singlet emission; the second term corresponds to triplet emission. Here, f_s is the fraction of singlets formed and is given by a similar type of rate expression:

$$f_s = \frac{k_{f,S}}{k_{f,S} + 3k_{f,T}} (1 - \Phi_{\text{ISC}}) \quad (5)$$

Here we have defined $k_{f,S}$ and $k_{f,T}$ as the rate of formation of singlet (S1) and triplet (T1) excitons from an initially separated electron hole pair; these rates are sensitive to the details of the charge recombination process. Φ_{ISC} , “the intersystem crossing quantum yield” [8] refers to the fraction of the initially formed S1 states that non-radiatively convert to T1 states and is determined by the associated rate constant k_{ISC} as follows:

$$\Phi_{\text{ISC}} = \frac{k_{\text{ISC}}}{k_{\text{S,rad}} + k_{\text{S,nr}} + k_{\text{ISC}}} \quad (6)$$

In most highly fluorescent organic materials, the coupling between the spin and spatial degrees of freedom is small, and Φ_{ISC} is near zero. In theory, we should also consider a reverse process, i.e. triplets that later form singlets, but in almost all organic materials the T1 state is 0.25–1.0 eV lower in energy than the S1 state. As this is significantly greater than the ambient thermal energy (kT), once the triplet

state is formed on a particular molecule, it will not later form an excited singlet state without additional energy input. This differs from the case of inorganic electroluminescent emitters, which have much smaller exciton binding energies for both singlet and triplet excitons. The factor of 3 in the denominator comes from spin statistics: there are 3 combinations of two spins of $1/2$ that can yield a triplet and only one that can yield a singlet. Thus, assuming that $k_{f,S}$ and $k_{f,T}$ are equal, then the “statistical” limit of singlets and triplets is obtained, and 25 % of the excitons that are formed are singlet and 75 % of the excitons that are formed are triplets.

Whether the statistical limit ($f_s = 0.25$) is obeyed in all organic electroluminescent materials is the subject of some controversy, as the details of the charge recombination mechanism under electrical injection conditions are hard to probe. In the simplest mechanism, an electron and hole collide and form a highly excited exciton that is either singlet (25 % of the time) or triplet (75 % of the time). These highly excited states then rapidly relax to the either S1 or T1 before any intersystem crossing can occur. This mechanism leads to singlet and triplet formation rates that are solely governed by initial charge recombination rates, i.e. the “statistical limit”. In an alternative mechanism, charge recombination occurs through multiple intermediate states following formation of the initial charge pair, and thus $k_{f,S}$ and $k_{f,T}$ are actually the product of several rate constants [9]. Here, $k_{f,S}$ and $k_{f,T}$ can be nonequal when two conditions are met: (a) there are different energy barriers to the formation of S1 and T1 from one or more of these intermediate states and (b) there is a process whereby the charge pairs can interchange their spin orientation while in these intermediate states [10]. In this case, the fraction of singlets formed can differ greatly from the statistical limit. Note that this alternative mechanism is but one of several other processes that also may be occurring in the device, such as triplet-triplet annihilation, that can lead to values of $f_s \neq 0.25$ [11]. Each of these mechanisms, however, depends upon the exact details of intermolecular charge transfer processes, which are hard to describe theoretically, even when the microstructure is well known [12]. Thus, careful experimental measurements are necessary to determine which mechanisms are operative.

Experimentally, most measurements of the singlet triplet ratio are somewhat indirect and usually require additional modeling. Currently, however, there appears to be consensus that for small molecules (<1000 amu) the statistical limit seems to hold, but that in polymer materials it may or may not. For polymers, some theoretical calculations [13] and indirect experimental results [14,15] suggest that, depending on material, k_s can be greater than 0.25, while other results suggest that f_s is the same for polymers and small molecules.

The distinction between singlets and triplets is important because the ground state of most organic emissive molecules has singlet spin, and thus radiative emission from singlet excited states is spin allowed while emission from triplet excited states is formally spin forbidden. In most organic materials, singlet transitions have typical values for k_{S_rad} on the order of 10^9 s $^{-1}$. In contrast, k_{T_rad} is on the order of 10^{-1} s, which is only competitive with nonradiative relaxation at low temperatures (<100 K). Hence, for these materials, only singlet emission is observed at room temperature,

and the second term in Eq. (4) makes only a negligible contribution to the total photoluminescence.

The final term, η_{extract} , is the efficiency of coupling the light generated in the high index polymer layers (refractive index, $n = 1.5\text{--}2.0$) out of the device and into the ambient ($n = 1$). Typically, internal reflection limits this term to between 0.2 and 0.4 [16]. A number of schemes exist for increasing this output coupling efficiency. One method relies on modification of the emission layers to adjust the physical optics of the optical microcavity formed between the two electrodes. This approach modifies the angular dependence of the emission profile of the light-emitting layers so that most of it is not internally reflected. The optical microcavity is designed to ensure that light is emitted in the forward direction at angles below the critical angle of the interface [17]. A variant of this solution is to place a very low-index aerogel ($n \approx 1.01$) next to the thin cavity. In a complementary approach, the OLED substrate is modified so as to outcouple light that would normally be trapped via internal reflection. For example, one solution, most applicable to point sources, is to use a shaped substrate, and it has been demonstrated that certain lens-like shapes will result in almost complete light extraction [18,19]. In addition, the substrate itself can be physically textured [20] or modified to scatter light volumetrically [21]. Both microcavity and substrate modification effects can be modeled, and it is possible to obtain a complete description of light extraction from the device. These calculations indicated that under the correct conditions the overall extraction efficiency can be quite high, and values for η_{ex} are potentially >0.6 [21].

8.3

Key OLED Trends and Innovations

In order to achieve optimal performance, each of the physical processes described above must operate at maximal efficiency. Historically, there have been two schools of thought on how to achieve this goal. One is to utilize multiple organic layers, each of which is optimized for a distinct function. This approach has typically utilized “small-molecule” materials that are applied as thin films by means of thermal evaporation. The second school of thought has been to minimize the number of organic layers necessary by building as much functionality as possible into a single or at most a few materials. This approach has typically utilized polymeric materials that are applied as thin films via solution processing methods such as spin coating. In the following sections, the historical trends and current materials and device structures for these two approaches are described in more detail.

8.3.1

Electroluminescence from Vapor-deposited Organic Films

Electroluminescence from organic material was first observed in the 1960s using anthracene crystals [22,23] (see structural formulae in Fig. 8.4). However, the efficiency of light generation was low ($\eta < 0.01$) [24]. Improvements in efficiency

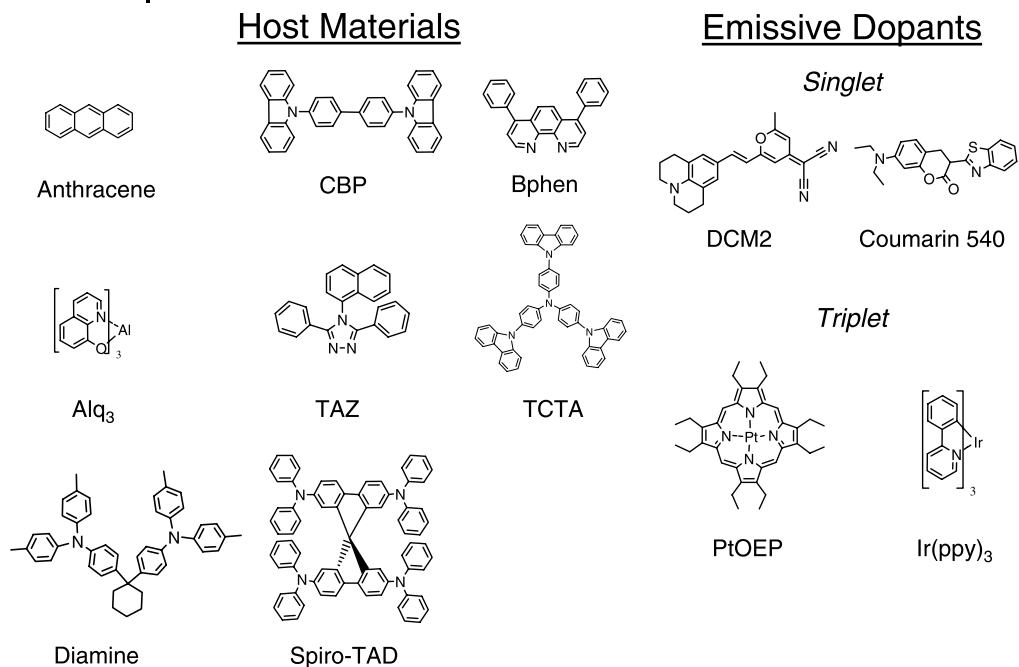


Fig. 8.4 Some of the materials used in vapor-processed devices, including materials that are commonly used as host materials (left) and typical singlet fluorescent and triplet phosphorescent emissive dopants (right).

were made when thin films of amorphous organic materials were utilized rather than single crystals [24,25], but the most dramatic breakthrough occurred when devices containing two different stacked organic layers were utilized [24]. The two layers in this case consisted of a di-triphenyl amine into which holes are injected and aluminum tris-quinolate (Alq₃) into which electrons are injected. The device structure for this OLED and the relevant energy levels for each device layer are shown in Fig. 8.5. The important feature is that the energy levels of the two organic layers are offset so that neither electrons nor holes can easily transit from one side of the device to the other. Thus, exciton formation and emission are forced to occur at the interface between the hole-transporting layer (HTL, diamine) and the electron-transporting layer (ETL, Alq₃). These devices exhibited EQE values of 1 % and a luminous efficacy of 1.5 lumens/watt (LPW), which is substantially higher than that of the previous single-layer devices. The relative ease by which two highly dissimilar materials are layered atop one another illustrates an additional characteristic of organic materials: the lack of dangling bonds and interface surface states. In general, there is no covalent chemical bond between adjacent molecules, and thus no chemical bonds are disrupted at the interface between one material and another. In contrast to inorganic semiconductor materials, it is relatively easy to form many layers of dissimilar materials – there is no “lattice matching” problem.

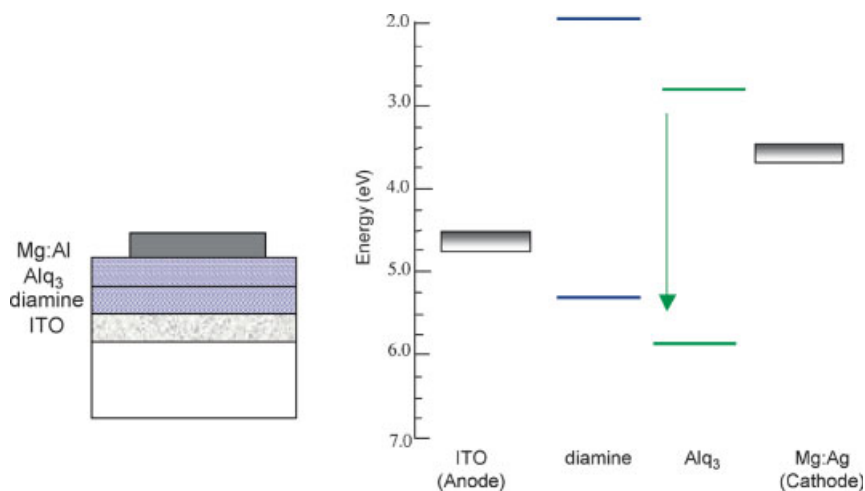


Fig. 8.5 Device structure (left) and energy level diagram (right) of a bilayer OLED device prepared by vapor deposition. The energy levels for the diagrams were taken from information obtained from Refs. [26] and [36].

The emission efficiency of the device structure depicted in Fig. 8.5 is limited by the low photoluminescence efficiency of Alq₃. However, it was later shown that this limitation could be overcome through co-deposition of small quantities of very high-PL efficiency materials in the transport layers near the HTL/ETL interface [26]. By co-deposition of a highly fluorescent dopant at low concentrations ($\sim 1\%$), such as Coumarin 540 (blue-green emission) or DCM1 (red emission) into an ETL host, the device efficiency could be greatly increased (by a factor of >2.5) and the emission color tuned. In these dilute guest-host systems, if the dopant is chosen correctly, all energy is transferred from the host to dopant. Once on the dopant, it does not return to the host. Thus, the only restriction on this method is that the energy of the emissive dopant (usually a singlet) must be lower than the singlet level of the host to prevent back energy transfer from the dopant to the host.

In these two-layer devices, 6 V–8 V is required to reach significant brightness ($\sim 100\text{--}1000\text{ cd m}^{-2}$). These high operating voltages reflect the difficulty in charge injection from the electrodes. These difficulties are caused by the negligible intrinsic charge concentration in the organic material and an energy level mismatch with the electrode Fermi level. The voltage characteristics of the device can be improved by creating more charge carriers near the electrode by doping the HTL (or ETL) with dopants that act to p-dope (n-dope) or partially oxidize (reduce) the region of the OLED layer near the anode (cathode). There are now several vapor phase routes to charge doping that result in desirable charge injection characteristics and reduced operational voltage [27–29].

A further refinement to the two-layer device structure is to insert between the ETL and HTL a third distinct emission layer that further confines charge carriers and excitons [30]. This approach can be extended and multiple emission layers deposited, each of which possesses a different emission color. Using this idea, a “white light” OLED that combined a blue, green, and red emitter in a single, many-layer device was demonstrated [31]. Numerous variants of the general design of multilayers to force charge confinement and favorable luminescent efficiency have been made, and currently a large variety of dopants and charge-transporting host materials are in existence [32]. However, while the use of highly fluorescent dyes and sophisticated device architectures increases EL efficiency for small-molecule OLEDs, only those excitons that lead to the formation of an emissive state with a high room temperature quantum yield are harvested. Excluded are most triplet excitons, as their slow radiative rates lead to very small room temperature quantum yields. Since in the “statistical” limit described earlier, these triplet excitons comprise 75 % of all excitons formed, this would potentially limit devices based upon organic electroluminescence to low power efficiencies.

Some organic materials, however, exhibit bright emission at room temperature from triplet excitons. In these materials, the singlet and triplet states are mixed, and hence the excited triplet states share some singlet character and have much faster rates of radiative decay to the ground state than a pure triplet state. For instance, incorporating a heavy metal atom, such as iridium, in an organo-metallic molecule increases the spin-orbit coupling that mixes singlet and triplet excited states [8]. For some Ir-containing molecules, this mixture of singlet and triplet states increases the rate of radiative emission to 10^6 s^{-1} , and allows for efficient, phosphorescent, radiative decay of triplet excitons [33].

An early demonstration of a phosphorescent OLED was made by Baldo et al. and involved doping a platinum porphyrin (PtOEP) phosphorescent emitter into a standard Alq₃ host material [34]. In this work they showed that the simultaneous use of both a fluorescent (DCM2) and a phosphorescent emitter resulted in a device that exhibited emission from both the fluorescent and phosphorescent dopants. When compared to a similar device that was not doped with PtOEP, the intensity of the fluorescent emission was unchanged. This result indicates that the phosphorescent emitter is able to make use of a different set of excited states in the host material (i.e. the triplet states) than the fluorescent emitter. Once again, energy transfer must be favorable from the host to emissive dopant, and in this case this requires that the triplet energy of the dopant be lower than the triplet energy of the host. The low triplet energy of the Alq₃ host ($\sim 1.9 \text{ eV}$) prevents any other color than deep red from being obtained using triplet emission, but the same group very quickly used a different set of host materials and dopants to obtain both blue [35] and green [36] emission. For example, the host material CBP has a higher triplet energy level (2.6 eV) and can be used to make efficient green (2.4 eV) emitting devices based upon the phosphorescent iridium complex Ir(ppy)₃ [37].

Much work has focused on developing and employing phosphorescent iridium complexes, and now green-emitting OLEDs have been demonstrated which exhibit a “wall-plug” efficiency of 17 % at a practical display brightness of 100 cd m^{-2} [38]. The

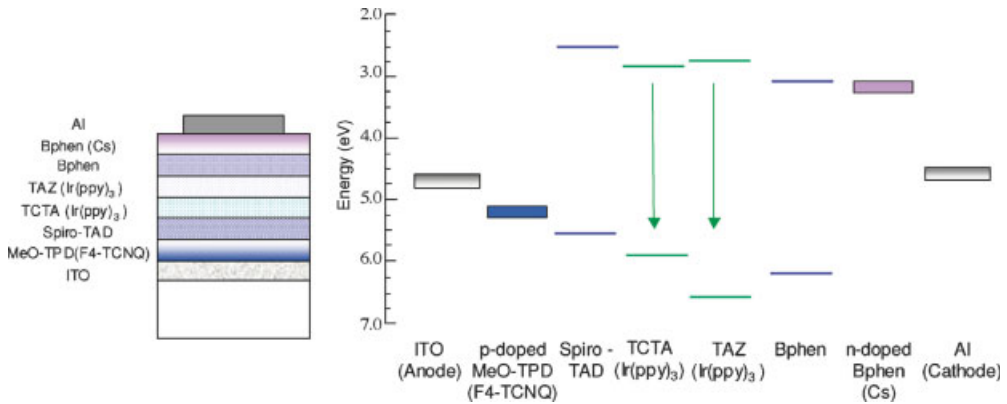


Fig. 8.6 Device structure (left) and energy level diagram (right) of an OLED device with six active organic layers prepared by vapor deposition. The green arrows indicate the layers

from which emission is expected to take place. The primary components of each layer are given beneath the diagram. Key dopants are also shown enclosed by parentheses.

device structure for the most efficient of these devices to date is depicted in Fig. 8.6 and represents perhaps the ultimate development of the technology enabled by organic vapor deposition. It consists of no fewer than 6 organic layers, each of which having a specific function. Thus, adjacent to the ITO structure, there is a p-doped organic layer that promotes hole injection. Since doping sometimes quenches luminescent efficiency, the doped layer is then followed by a “buffer” layer, which transports charge away from the doped layer to the emission zone. This layer also prevents electrons from reaching the anode. The next two layers constitute the desired emission zone for this device structure and consist of two different host materials doped with the phosphorescent emitter $\text{Ir}(\text{ppy})_3$. The first host material, TCTA, is a hole transport material, while the next host, TAZ, is an electron transport material with a deep HOMO level. This design ensures that holes build up at the TCTA/TAZ interface, which forces charges to meet and form excitons within the desired zone. The next two layers are an electron-transporting buffer layer and an “n-doped” layer that promotes the injection of electrons into the device. In addition, the materials are arranged so that triplets, when formed on the emission zone, do not migrate to the electrode, but are rather forced to recombine at the green emission site.

Detailed calculations of the light outcoupling efficiency for the green-emitting phosphorescent OLED shown in Fig. 8.6 indicate that nearly 100% internal quantum efficiency was achieved. Achieving this level of performance in the blue spectral range has proven more challenging [35,39]. A key issue has been the difficulty in finding host materials with good injection and charge transport properties that also satisfy the requirement of having triplet levels above those of blue phosphorescent dopants. Additionally, in contrast to green or red emitters, it has been difficult to find pure blue phosphorescent emitters with adequate stability under operating conditions [40,41].

8.3.2

Electroluminescence from Solution-Deposited Organic Films

In general, vapor deposition processes, while offering exquisite control over the film thickness, composition, and multilayer ordering, require relatively sophisticated high-vacuum processing techniques. In addition, there are limits on the molecular weight of a material that may be processed using vapor deposition methods. These molecular weight restrictions limit the degree of conjugation and chemical functionality that can be built into a single molecule. While this limitation can be overcome through the use of complicated multilayer architectures, use of these architectures tends to increase processing costs. The use of solution-processable materials holds promise for overcoming these issues. Controlled printing of organic layers from a solution of electro-active material can be extremely fast – potentially at a throughput and cost structure akin to that of newspaper production. Solution processing also allows some control over the final morphology of the layer through judicious choice of processing conditions [42–44]. In addition, solution processing allows the use of high-molecular-weight oligomers or polymers that incorporate multiple types of functional groups, thereby expanding the available material design options.

The advantages of solution processing are offset by the difficulty in forming complicated multilayer structures, and thus solution-processed OLEDs require materials that are able to perform well in simple structures. In addition, the synthesis and isolation of highly pure polymer materials is an art form in itself and requires more demanding synthesis than the isolation of a molecular species. For example, a chemical reaction that leads to the formation of an undesirable byproduct 1 % of the time can usually be purified quite easily at the molecular level, but can be impossible to separate if the byproduct is incorporated into a long-chain polymer. Thus, considerable material design and development effort is required to engineer the properties of an OLED device made using solution-based processing. As a consequence, solution-processed OLEDs have mostly improved as a result of materials development, and not through increasing device architecture sophistication. The discussion in this section will mirror this trend, and will primarily focus on some of the different strands of materials development that have enabled these performance increases.

Some of the first solution-deposited OLEDs were based upon the well-known polymer polyvinyl carbazole [25], PVK (note: structures for this section are given in Figs. 8.8 and 8.9). This polymer, which exhibits a near-UV/blue luminescence, also has considerable charge mobility, particularly for holes [5]. In a series of papers, published in the early 1980s, Partridge demonstrated that through chemical oxidation or reduction, both electrons and holes could be injected into the polymer material. In addition, Partridge showed that by doping the PVK with a luminescent dopant, the emission color could be readily tuned. While these devices were quite thick by today's standards (ranging from 0.5 μm to several μm in thickness) and operated at high voltage, they anticipated many features that characterize present day vapor-deposited OLEDs, i.e. separate hole and electron injection layers and a color-tunable dopant in an emissive layer. These elements are all illustrated in Fig. 8.7.

Key:

- 10 Glass with transparent conductor (+ contact)
- 12 PVK+
- 14 PVK with luminescent dopant
- 16 PVK-
- 18 Cs
- 20 Metal ring (- contact)
- 22 Encapsulant

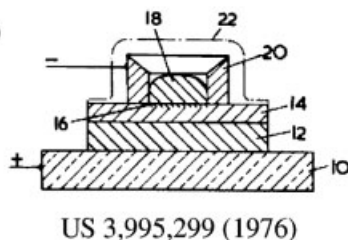


Fig. 8.7 Schematic illustration of a solution-processed OLED made using PVK as the primary electroactive component (figure taken from the United States Patent [45]).

As with vapor-deposited OLEDs, these polymer-based devices were fabricated starting with a glass plate coated with a transparent conductor. The next layer that was deposited was a solution of PVK and SbCl_5 . Here the SbCl_5 acts as both an oxidizing agent to p-dope the PVK and, since PVK tends to cross-link when oxidized, as a crosslinking agent. The next layer that was deposited (again from solution) was a mixture of PVK and a luminescent dopant such as perylene or acridine orange. Finally, a layer of cesium metal was deposited on top. Following cesium deposition,

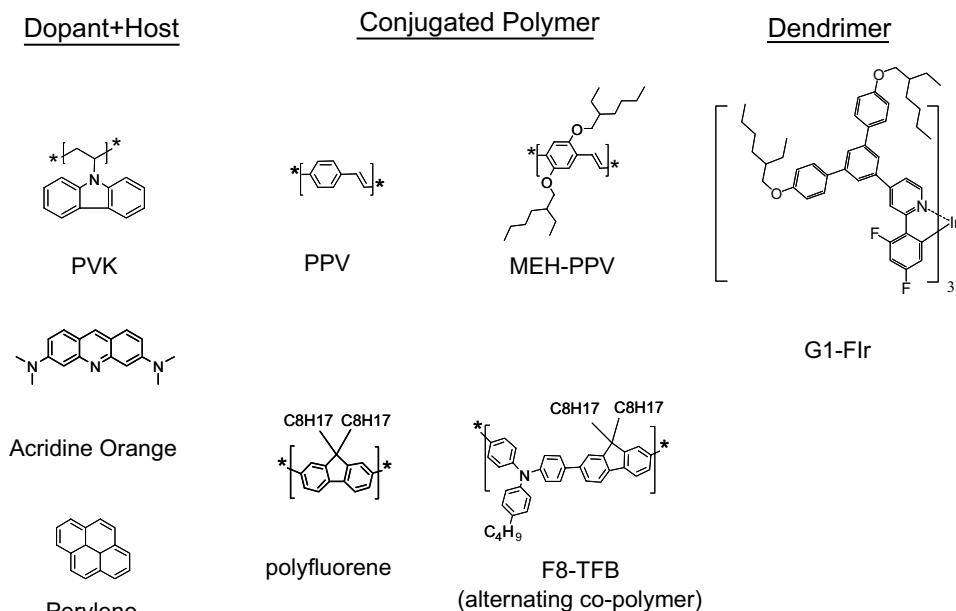


Fig. 8.8 Some of the materials used in solution-processed devices. Linear polymers are denoted by the brackets and asterisks on each side of the repeat unit.

the PVK film was observed to darken, suggesting n-doping through the formation of carbazole anions. Instead of directly reducing the polymer, it was also demonstrated that electron transport could be facilitated by inclusion of a dopant molecule (typically a di- or tri-cyanobenzene derivative) that acts as an electron acceptor in PVK at sufficient concentration to provide a low-energy hopping pathway. Thus, instead of having to inject electrons directly into PVK, the electrons could be injected into the more easily reduced dopant molecules, eliminating the need for highly reactive cathodes such as cesium.

Partridge's work, which was actually patented in the 1970s [45], demonstrated an important advantage of solution-processing for OLEDs – the ability to mix a variety of relatively complex molecular structures together in solution to form a thin film designed for multiple functions. However, further work in this area did not pick up until the two-layer breakthrough in vapor-deposited OLEDs was reported in the late 1980s. Researchers then improved Partridge's original PVK system by applying more effective dopants for electron transport and luminescence [46]. More recently, after the introduction of phosphorescent OLEDs, the use of PVK has accelerated, since its relatively high triplet level makes it an attractive solution-processable host system. Recent results utilizing PVK co-doped with both triplet emitters and charge-transporting small molecules demonstrated that very high performance can be obtained using this basic design and host material [47,48].

Research in solution-processable OLEDs accelerated greatly in the early 1990s, when it was discovered that relatively efficient single-layer devices could be made using conjugated polymers. Conjugated polymers are unique in that they have alternating single and double bonds along the polymer backbone that result in extended electronic states over multiple polymer repeat units [49]. In devices, thin films of conjugated polymers behave similarly to thin films of small molecules in that charge injection is limited by the energy level mismatch with the electrodes and is improved by charge doping, and in that charge transport is limited by charge hopping between polymer chain segments. However, in addition, the extended states enable more effective charge motion along the chain axis and, as discussed earlier, according to some theoretical models, the potential for a higher ratio of singlet to triplet formation under device-operating conditions.

The first demonstration of a conjugated polymer in an OLED utilized phenylene vinylene (PPV), which is highly luminescent in thin-film form even in the absence of additional dopants [50]. The first device had a very simple structure consisting of a plate of ITO-coated glass as transparent anode, the polymer layer (70-nm thickness), and a top vapor-deposited aluminum layer. Pure PPV does not dissolve in most solvents, so the thin film was formed by first depositing polymer precursors from solution and then polymerizing the resulting film *in situ* via heat treatment. Soon after this demonstration, soluble variants of PPV, such as MEH-PPV, were utilized, so that the final materials could be solution deposited into a thin film in one step [51]. Also soon thereafter, it was found that the repeatability and stability of PPV-based devices could be enhanced by depositing a highly p-doped conjugated polymer such as PEDOT:PSS (a poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) blend) or polyaniline between the ITO and the light-emitting polymer [52,53]. At present, this

basic configuration of a highly doped conjugated polymer layer followed by an undoped light-emitting polymer layer is still the most popular solution-processable device configuration.

Various modifications of the basic PPV structure have been made to enable tuning of the emission color from green to red – but not blue [54]. On the other hand, light-emitting polymers were developed based on the basic polyfluorene structure which are tunable in color over the whole visible range. The polyfluorene system has enabled increasing material design sophistication through the use of the Suzuki reaction [55]. This reaction permits a wide variety of AB-type regular alternating polymers to be readily prepared in high molecular weight. This provides an additional degree of structural control and polymer design flexibility and has led to some materials that can be tuned to have excellent specific properties. Examples include the fluorene-tri-aryl amine co-polymers which were engineered to have very high hole mobilities. This polyfluorene system was aggressively examined by the Dow Chemical company in the late 1990s and has resulted in a suite of full-color-emissive materials [56] (red, blue, green) and a series of hole transport materials [57]. These materials have been shown to yield very high performance, with EQEs greater than 8% at very low operating voltages [58].

One of the design philosophies that has pervaded the light-emitting polymer field has been the desire to produce highly efficient devices using only a single organic thin film layer. Part of the reason for this philosophy has been the desire for simple, low-cost fabrication processes. However, another reason has been the practical consideration that it is difficult to make multilayer devices via solution processing, because the solvent required to deposit a top layer often dissolves an underlying layer. As the design sophistication of polymers has increased, it has now become possible to design polymers that are not dissolved by common solvents, this being achieved either through a crosslinking strategy [59] or through judicious functionalization. Thus, efforts are under way to apply some of the lessons learned from multilayer vapor-deposited OLED technology to improve solution-processed devices. An example is the use of a layer of a tri-arylamine-fluorene copolymer under an emissive fluorene copolymer [60]. This multilayer approach led to an increase in both efficiency and life relative to a single layer device with the same emissive copolymer.

The PPV and polyfluorene conjugated polymer systems exhibit relatively low energy triplet states. This characteristic makes them unsuitable for use as host materials for green- and blue-emitting phosphorescent materials. Thus, while materials based upon polyfluorene (triplet energy of 2.15 eV [61]) have been used to prepare polymers and oligomers with red triplet emissive dopants [62], there are no examples which successfully use polyfluorene or other conjugated linear polymers as hosts for green or blue phosphorescent materials. Seemingly, the only way to achieve very high efficiencies with such linear conjugated polymers is to design a structure which forces all recombination events to lead to singlet states, which is a daunting task from both a theoretical and a chemical synthesis point of view.

An alternative approach to efficient light generation is to design other classes of solution-processable materials that will support emission from blue or green

triplet states. One example is the use of highly structured non-linear molecules such as dendrimers [63]. These molecules are intermediate in molecular weight between polymers and vapor-deposited molecules and feature an emissive core chemically bonded to a charge-transporting dendrimer structure. Since the central emitting species is fully surrounded, these molecules are fully three-dimensional structures, in contrast to more commonly used ‘one-dimensional’ polymers. The thickness of the layer that surrounds the emissive core is determined by the ‘generation’ of the dendrimer and can be also tuned. The dendrimer molecule can be thought of as either a phosphorescent molecule with a very large ligand, as shown by the ‘first-generation’ blue-emitting species shown in Fig. 8.8 (G1-Fir) or as very large charge transporting materials with a luminescent core as shown in Fig. 8.9. Thus, these materials can be used either neat or co-deposited as a dopant in another layer. Recent studies have shown that OLED devices incorporating phosphorescent Ir cores can be made in a variety of colors and have EQE efficiencies comparable to vapor-deposited OLED structures [64]. These systems provide for an even larger degree of molecular engineering than modification of linear polymers while still retaining the ease of processing that is achieved via solution processing.

It should be noted that this treatment has only touched on some of the major material classes. Many more types of solution-processable materials have been

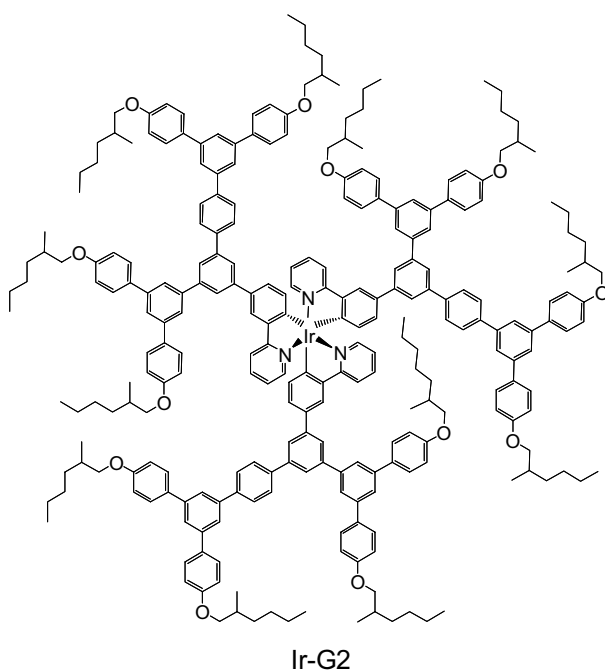


Fig. 8.9 Structural formula of a second-generation green-emitting dendrimer.

synthesized, and new materials are appearing daily. Material development in this field is still in its infancy, and there are an infinite variety of chemically accessible structures that can be prepared in sufficient purity and quantity. One should thus expect that these materials will continue to mature and lead to solution-processed devices with ever greater performance.

8.4 Prospects for General Illumination

Most of the effort expended to date on developing OLED technology has been aimed at developing an OLED-based display. Progress in this endeavor has been considerable. OLED displays for small-format applications are now commercially available. It is generally agreed that OLED displays have superior display characteristics, e.g., viewing angle, brightness, and efficiency, to those of conventional liquid-crystal display (LCD) technology [3]. However, OLEDs still represent only a small fraction of the total available flat-panel display market. Further adoption of OLED displays requires continued technology development to enable integration with high-performance and large-area active matrix backplanes, and many companies are pursuing these goals.

Starting in ca. 2000, technology organizations around the world have started to explore the possibility of developing OLEDs for lighting, rather than display, applications. One reason for this interest is the tremendous rate of increase in efficiency that has been achieved over the last decade. As described in the last section, green-emitting OLEDs have progressed from ~ 1 LPW to ~ 100 LPW at brightness levels adequate for displays. A similar rate of progress in making illumination-quality light would imply that OLEDs have the potential to not only surpass incandescent lighting sources, which have an efficacy of 15 LPW and a lifetime of ~ 1000 h, but even fluorescent lighting sources, which have an efficacy of 100 LPW and a lifetime of 20 000 h.

An equally important attribute of OLED technology is the potential for low cost. Electric lighting technology has existed for ca. 100 years and, in this time, optimization of mass production methods has led to a highly affordable technology that is, at least in the developed world, taken for granted as a low cost necessity. These perceptions impose cost constraints on any new lighting technology. OLEDs are potentially consistent with these constraints fundamentally because the electro-active organic materials do not need to be fabricated into a single crystal form for proper device operation. For example, the active layers of the polymer-based technologies can be deposited with high throughput roll-to-roll techniques such as gravure or flexographic printing.

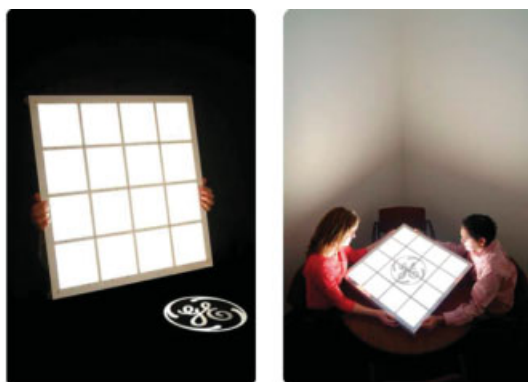
Another important feature of OLED technology is the potential for new device form factors. Early on, it was demonstrated that OLEDs can be fabricated on flexible plastic substrates [65]. This first demonstration was not practical because the plastic substrate was not hermetic enough to protect the OLED from moisture and oxygen-induced degradation. However, more recently, transparent, flexible, plastic substrates have been demonstrated which provide the required hermeticity, and

these have been successfully utilized as substrates for OLEDs [66,67]. A mechanically flexible OLED that enables new form factors is not necessarily required for general illumination applications. However, this feature will likely be important in enabling the early commercialization of OLED lighting products. In particular, since it provides a function that is not possible today, it will enable the early adoption of OLED lighting even before the technology is competitive with conventional lighting technology on a cost or efficiency basis.

8.4.1

A First OLED Lighting Demonstration

In 2003, a key milestone was achieved when an OLED was demonstrated that could provide light with a quality, quantity, and efficiency on a par with what can be achieved with traditional light sources. The actual 2 ft × 2 ft demonstration device and some key performance metrics are shown in Fig. 8.10. The demonstration device was made by tiling together 16 separate 6 in × 6 in blue-emitting OLEDs, each of which was made on a glass substrate. Note that the efficiency, total lumen output, and lifetime are the same as would be achieved with an 80-W incandescent bulb. For lighting, the appropriate white color is determined by the correlated color temperature (CCT) of the source and should be in a range between 2800 K and 6000 K. The illumination quality of a given light source is typically measured in terms of the color rendering index (CRI), which has a maximum possible quality value of 100 and is typically around 80 for the standard fluorescent lamps used in most modern commercial



Luminous Efficacy:	15 LPW
Total luminous output:	1200 Lumens
Correlated Color Temperature:	4400 K
CRI	88

Fig. 8.10 2 ft × 2 ft OLED demonstration device and some key performance figures. The active layers of the device were prepared using solution processing. All the light utilized for these pictures is generated by the OLED.

buildings. Both the CCT and CRI can easily be calculated from the output spectrum of the light source [7,70]. One can see that the color temperature for the demonstration device is appropriate for lighting and that the color rendering index is slightly better than that of standard fluorescent lamps.

The device depicted in Fig. 8.10 employed solution-processed OLEDs and introduced three technology strategies developed specifically for OLED lighting – down-conversion for white light generation [68], scattering for outcoupling efficiency enhancement [21], and a scalable monolithic series architecture to enable large-area devices to be produced [69]. In the following, a brief description of these technology strategies is provided along with the motivation for their adoption.

8.4.1.1 Downconversion for White Light Generation

The downconversion approach consists of optically coupling a blue-emitting OLED to a phosphor downconversion layer [68]. The downconversion layers are chosen to absorb the blue OLED emission and then re-emit at longer wavelengths. The layers are designed such that the unabsorbed blue emission and the longer wavelength re-emission combine to make white light. This approach is attractive for lighting applications because only a single color OLED with a single emitting species is required. Fig. 8.11 depicts an implementation of this device architecture, consisting of a polymer-based blue-emitting OLED and three downconversion layers. Two of the downconversion layers utilize perylene-based dyes from BASF AG of Germany with high quantum efficiency (>98%), and one of the layers consists of inorganic

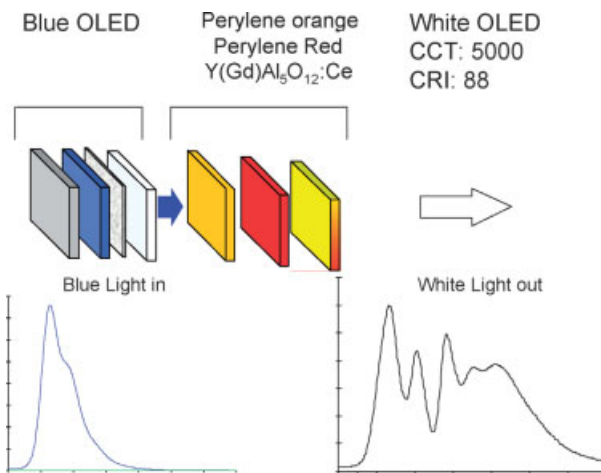


Fig. 8.11 Schematic of a white-light OLED made using a downconversion architecture. The source consists of a blue OLED and three phosphor layers. At the lower left is shown an actual measured electroluminescence spectrum from a blue device. The calculated white-light emission spectrum following transmission, absorption, and emission of the light through each layer is shown on the right.

phosphor particles [Y(Gd)AG:Ce] with a quantum efficiency of $\sim 85\%$. By independently varying the thickness of these downconversion layers, the composite emission spectrum can be varied to maximize performance for lighting (e.g., black-body temperature and color rendering) while keeping the properties of the underlying blue OLED constant. An example spectrum optimized for general lighting is shown on the right hand side of Fig. 8.11.

The downconversion architecture has several features that make it attractive for lighting. To a first approximation, there should be no color change as the luminance or current density is varied. Similarly, color shifts due to differential aging of different color components are avoided if one ensures that the lifetime of the down-conversion layers is substantially greater than that of the underlying blue OLED. This requirement is not particularly onerous, as inorganic phosphor materials are already designed to be stable over the lifetime of fluorescent lamps, and there are a number of long-lived organic dyes that were originally designed for applications such as solar collection. An added benefit of this approach is that a single blue OLED device can be utilized for a wide variety of applications requiring different color temperatures and/or color rendering capabilities by simply varying the applied downconversion layers. Finally, this architecture is relatively simple, requiring the manufacture of a single-color OLED followed by the application of a set of phosphor layers by means of a printing or lamination technique. OLED production costs are thus minimized, and a wide variety of final white colors can be achieved while only having to maintain one set of materials for the blue OLED “engine” and one production line.

There are two losses associated with any downconversion approach. One is the Stokes loss associated with the fact that higher-energy photons are converted to lower-energy photons and the other is simply the fact that the quantum efficiency for downconversion is typically less than 100%. It is important to realize that the Stokes loss is not unique to the downconversion approach. Although not explicitly defined as a Stokes loss, any white OLED that runs off of a single voltage has this type of loss because the voltage needs to be high enough to allow the highest energy (blue) emission. This is a loss because, in principle, the lower energy emission colors would require lower voltages if operated alone. For our phosphor system we calculate that there is a about a 20% loss in energy efficiency due to this term.

8.4.1.2 Scattering for Outcoupling Efficiency Enhancement

As described in Section 8.1, electroluminescent devices are limited by the optical extraction efficiency, η_{extract} , which is the ratio of the light generated within the device to the light emitted into the ambient. The demonstration lighting device utilized light scattering to increase this ratio. The light-scattering function was provided by the Y(Gd)AG:Ce downconversion layer at the top surface of the device. In fact, this layer increased the light extraction to the point where the energy efficiency of the device with all the downconversion layers was actually higher than the energy efficiency of the device without them. To confirm this assignment, a tape of non-absorbing scattering particles in silicone was made and applied to a blue OLED device. Care was

taken to use particles with similar size and loading as those used in the YAG:Ce layer of a white device. The resulting blue device showed a 27% enhancement in the measured external quantum efficiency relative to the device without the scattering tape. This 27% increase overcomes the 20% loss introduced by downconversion and leads to a net increase in energy efficiency.

Light scattering enhances outcoupling efficiency by scattering a percentage of the light modes that are normally trapped in the device to modes that can escape from the device. The potential achievable enhancement can be accurately calculated using a radiative transport methodology [21]. Such calculations suggest that one can utilize volume scattering to increase the light output by up to a factor of 2. Since scattering can be accomplished simply by applying ultra-low-cost materials such as titanium dioxide particles, this approach to increasing output coupling efficiency is uniquely suited to the cost requirements of general lighting applications.

8.4.1.3 A Scalable Monolithic Series Architecture

OLEDs are current-driven devices and, because of their thin active layers, are extremely sensitive to defects that cause electrical shorts. These two characteristics are the key limitations to fabricating large-area OLEDs, particularly non-pixelated devices such as general lighting devices. Current driving implies that, for large-area devices, there will be a large efficiency loss and nonuniformity in emission due to the spreading resistance of the relatively resistive transparent conductor. Similarly, as device area increases, there will be an increased chance of an electrical short, which will cause efficiency loss and nonuniformity. In an effort to overcome these issues for the demonstration device, the series architecture depicted schematically in Fig. 8.12 was utilized [69].

The architecture works by dividing the desired large-area device into separate smaller emitting elements connected monolithically in series. With this approach, the required current is controlled by the individual element area rather than by the total emitting area of the device. The individual element area can always be chosen to minimize current-spreading effects. Similarly, the series connection addresses the electrical short issue. Shorts still occur but their deleterious effect becomes isolated to

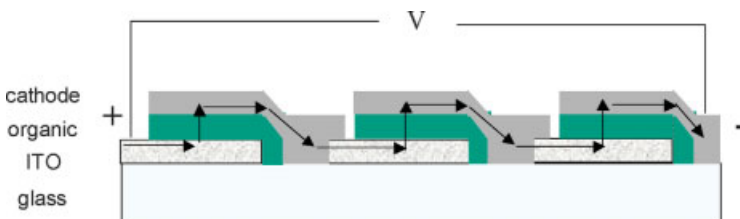


Fig. 8.12 Schematic side view representation of the series-connected architecture used in the demonstration device shown in Fig. 8.10.

the particular element affected, while the required current continues to flow through the rest of the device. This minimizes the efficiency loss that occurs due to shorts without requiring any active control elements.

The demonstration device shown in Fig. 8.10 was made by tiling together 16 separate 6 in \times 6 in blue-emitting OLEDs, each of which was made on a glass substrate using the monolithic series architecture. The total area of each 6 in \times 6 in device was divided into 144 1.2-cm² emitting elements consisting of 12 rows connected electrically in parallel, where each row contained 12 elements connected in series, as depicted in Fig. 8.12. In order to make white devices, downconversion layers were optically coupled to the output side of the 6-in blue OLEDs, as depicted in Fig. 8.11.

8.4.2

Efficiency Challenge for General Illumination

The first OLED lighting demonstration described above nicely illustrates what the ultimate goal must be in order to enable general illumination applications. The key point to note is that, in order to generate a lumen output relevant for lighting, a relatively large (4 ft²) surface area was employed. This is in contrast to an incandescent bulb, which generates the same lumen output from a much smaller area. The required OLED area could be decreased by increasing the input power and hence output brightness, but there is a tradeoff between brightness and operating life which makes it unlikely that the area could shrink to that of an incandescent bulb. This illustrates the fact that OLEDs are by nature a diffuse light source. Currently, the premier diffuse light source is the fluorescent bulb. Hence, in order to become a competitive light source for general illumination, OLED technology must match the performance and cost that is achievable with fluorescent technology.

The efficiency of a high-performance fluorescent bulb of 100 LPW corresponds to a wall-plug efficiency of 28 %. This is more than 6 times higher than that attained in the demonstration device. OLEDs must be able to match or exceed this value in order to displace fluorescent technology on the market. The efficiency of the OLED lighting demonstration was limited by the performance of the underlying blue-emitting OLED, since downconversion was employed to generate the red and green color components of the white light. However, it is in fact generally true that the efficiency of a white-emitting OLED is limited by the generation efficiency of the blue component of the spectrum regardless of the device design utilized. This stems from the fact that illumination-quality white light requires no less than a 25 % contribution or weighting of each primary color component (red, green, or blue) [70]. When white light is generated by a non-downconversion method, e.g., by mixing the light from separate red, green, and blue OLEDs, one might expect that the maximum achievable efficiency would be limited by the color component which is generated least efficiently. However, because the red and green color components can alternatively be made by coupling the appropriate downconversion layer to a blue OLED with reasonable efficiency, one can always compensate for an inefficient red or green

Tab. 8.1 External quantum efficiencies for various methods of blue-device fabrication.

System	% EQE	Ref.
PVK + blue phosphorescent dopant	9	[47]
Blue conjugated polymer	9	[58]
Blue phosphorescent dendrimer	10.4	[64]
Vapor-deposited blue	11.6	[39]

device. Thus, to improve the performance of white-emitting OLEDs for lighting, it is critical to concentrate on ensuring that the blue component of the final spectrum is generated as efficiently as possible.

For blue fluorescent devices like those used to make the demonstration device shown in Fig. 8.10, it is possible to operate OLEDs with 1000 cd m^{-2} brightness at 3.2–3.3 V. Thus, the primary limitation of these devices is their external quantum efficiency, which is currently 8–9 % for blue-polymer OLED devices. At the present time, each of the approaches to blue-device fabrication described in Section 8.2 (doped host, co-polymers, dendrimer, and vapor deposition) yield very similar values of external quantum efficiency for blue devices. These efficiencies are listed in Table 8.1.

All of these devices were measured without the use of additional scattering or other optical enhancement techniques. Even using light enhancement techniques, in order to overtake the 28 % wall-plug efficiency fluorescent lamp, substantial technical progress is required.

In addition to efficiency, there are two other key challenges that must be overcome to enable OLEDs to displace fluorescent technology for general lighting. These are to achieve an operating lifetime of $\sim 20\,000 \text{ h}$ at a brightness of $\geq 1000 \text{ cd m}^{-2}$ and to achieve a cost of less than \$10 for a device that produces 1000 lumens of light. A detailed explanation for these targets has been given elsewhere [7]. For the purposes of this chapter, the key point to emphasize is that these parallel challenges must be taken into consideration when designing strategies to increase OLED efficiency for lighting.

8.5 Conclusions

Organic materials, which have been traditionally viewed as “soft”, malleable insulators, are now being successfully utilized for electroluminescent applications requiring thousands of hours of life, traditionally the domain of “hard” inorganic semiconductor materials. While the fundamental physical operation of these organic light-emitting devices can be described using the traditional tools of semiconductor physics, there are several notable differences in how charges move

and recombine, and these differences introduce new challenges but also new design opportunities.

There are two basic OLED design paradigms. One utilizes relatively simple molecular organic materials that are vapor processed into relatively sophisticated multilayer device architectures. The other paradigm utilizes higher-molecular-weight and more complex organic materials but much simpler device architectures. These higher-molecular-weight materials cannot be evaporated, and so they are instead processed from solution using printing techniques that should be scalable to high throughput and low cost. To date, the first paradigm, vapor processing, has always led in device performance. This is in part because of the relative ease in creating and testing new device architectures in the laboratory. It is harder to build complex device architectures at whim using solution processing, but the extra molecular design flexibility that is possible with high-molecular-weight chemical structures has to a large extent compensated for this disadvantage. Thus, the performance of solution-processed OLEDs has never lagged far behind that of vapor-deposited OLEDs. Both paradigms rely upon the capabilities of modern organic chemistry to create a large variety of different organic molecules, and both offer the potential for devices with increased efficiency and lifetime.

Researchers are putting increasing effort into developing OLEDs for the ultimate luminescent application – general lighting. Overall, there is good reason to be optimistic that OLED-based general lighting will become a reality. The field of organic electroluminescence has demonstrated incredible progress in the last decade – progressing from very primitive devices to large, efficient demonstration devices. Furthermore, the field is really still in its infancy with regard to understanding what types of molecules should be made. While the device physics of an OLED is largely understood, the relationship between molecular structure and the detailed physics of charge transport, exciton spin formation, and energy transfer in amorphous organic materials is not. As basic research into the fundamental physics and chemistry of organic materials continues and focused research on developing OLEDs for general lighting accelerates, it is likely that the exponential rate of progress seen in the last decade will continue into the next. If so, then by the end of the next decade the only factor that could possibly prevent the large-scale adaptation of an OLED-based lighting technology would be cost. Given the fact that, even today, OLEDs are able to leverage low-cost, high-throughput technologies from the printing industry, it would be surprising if this hurdle could not be overcome as well.

8.6

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9

Experimental Techniques

Peter Vergeer

9.1

Introduction

Interaction of electromagnetic radiation with matter causes absorption, emission, and scattering of radiation [1]. As a result of this interaction, one is able to characterize the optical properties of materials by measuring the properties of electromagnetic radiation. This chapter is concerned with the spectroscopic techniques used to control and measure different properties of electromagnetic radiation, such as its wavelength, intensity, and coherence.

In the last two centuries, spectroscopy has developed from being a tool for studying solar radiation to a versatile technique to study electric and magnetic properties on the molecular and atomic scale. This development started in the early 19th century when W.H. Wollaston and J. Fraunhofer independently observed numerous dark lines in the solar spectrum. Some of these lines could be reproduced when light from an electric arc was passed through a flame tinted yellow by sodium salt. Soon after this it was discovered that each element had characteristic emission and absorption lines. This discovery led to the use of spectroscopy as a powerful technique for the qualitative analysis of elements.

The success of spectroscopy would not have been possible without major technological developments. For spectroscopy, three basic components are needed: an excitation source, a light-dispersing element, and a detector.

During the 19th century, the sun as an excitation source was replaced by an arc or spark lamp or a gas discharge tube filled with one of the noble gases. The first mercury tube was built in 1892 by Arons. These light sources are the predecessors of the lamp light sources that we use at present. The laser was invented in 1960 by T.H. Maiman [2]. During the last decades, laser excitation sources have become available for operation at an increasing number of wavelengths. The intense, monochromatic, pulsed, and coherent laser radiation offers many new possibilities.

Up to the 18th century, light was dispersed with prisms. In the 1820s, gratings were introduced as dispersing elements, providing equal or better resolution than the prism. In the late 19th century, Michelson, Fabri and Perot, introduced the interferometer, which led to another major improvement in resolution.

For light detection, good alternatives for the eye were developed. In the 18th and 19th century photographic film was mainly used. During the 1930s the photomultiplier tube (PMT) was introduced. By combining a photoemissive cell with a number of electron multiplier steps a sensitive detector for the ultraviolet, visible, and infrared was obtained. At present, PMTs are used alongside other detectors. Photodiodes are mainly used for the infrared region. As a wide-angle detector, the CCD detector has become popular.

In the organization of this chapter, the spectroscopic techniques that are used to measure a specific optical property of an ion are grouped together in one section. Every section starts with an introduction of the property of the optical material and the corresponding properties of the electromagnetic radiation. The various techniques used to measure these are introduced and discussed.

Section 9.2 describes the most basic form of spectroscopy: the detection of the energy of optical transitions. This is done by detecting the energy (or an equivalent quantity) of photons. Techniques such as absorption spectroscopy, diffuse reflection spectroscopy, emission spectroscopy, and excitation spectroscopy are introduced, and basic spectroscopic components such as broadband excitation sources, dispersing elements, and detectors are discussed. Section 9.3 is concerned with the strength of optical transitions, determined from absorption, excitation or emission spectra and luminescence decay curves. Also, an overview of lasers as excitation sources is given. Section 9.4 deals with the energy efficiency and the quantum efficiency of luminescent materials, which are both related to nonradiative processes. Methods are discussed to detect the amount of heat generated by nonradiative relaxation. Section 9.5 deals with detection of homogeneous line widths and dephasing times with the use of monochromatic laser sources and pulse sequencing. The topics of Section 9.6 are optical properties on a single-particle level.

9.2

Energy of Optical Transitions: Absorption, Excitation, and Emission Spectroscopy

The most classic (and persistently the most popular) experiments in spectroscopy are concerned with the determination of the transition energies of the optical center. Transition “energies” are commonly expressed in terms of energy (eV), frequency ν (s^{-1}) or ω (rad s^{-1}), wavelength λ (nm), or wavenumbers $\hat{\nu}$ ($=$ in cm^{-1}). In such an experiment one measures the intensity of electromagnetic radiation as a function of photon energy. A graph that plots the intensity versus photon energy is called a spectrum (see Fig. 9.1). Peaks (or dips) in the spectrum reveal the locations of optical transitions.

To perform an experiment, a (broadband) excitation source, light-dispersing elements, and a detector are needed. The sample is irradiated with radiation from the excitation source. When this radiation induces a transition to an excited state in the material (usually from the ground state) this may lead to emission of light from the sample. The detector is used to measure either the intensity of the emitted light or the intensity of the residual light from the excitation source.

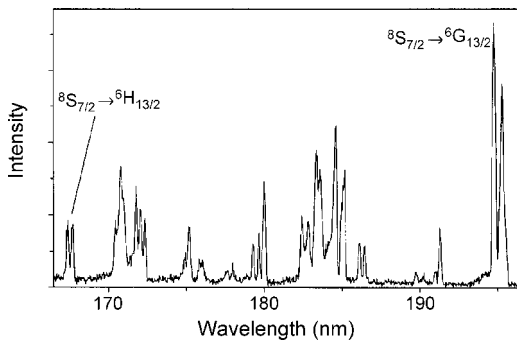


Fig. 9.1 VUV excitation spectrum (9 K) of $\text{LiYF}_4:\text{Gd}^{3+}$ 5% monitoring the ${}^6\text{P}_{7/2} \rightarrow {}^8\text{S}_{7/2}$ emission. Only the part starting from 165 nm is shown (reproduced from Ref. [4] with permission from the American Physical Society).

Four techniques are commonly used for this kind of experiment: absorption spectroscopy, diffuse reflection spectroscopy, excitation spectroscopy, and emission spectroscopy. In absorption spectroscopy the photon energy of the radiation incident on the sample is selected by a scanning monochromator. A typical set-up for absorption spectroscopy is shown in Fig. 9.2a. The radiation selected by the monochromator is passed through a chopper that alternately directs the radiation along a reference beam path (going through compartment R) and through a path containing

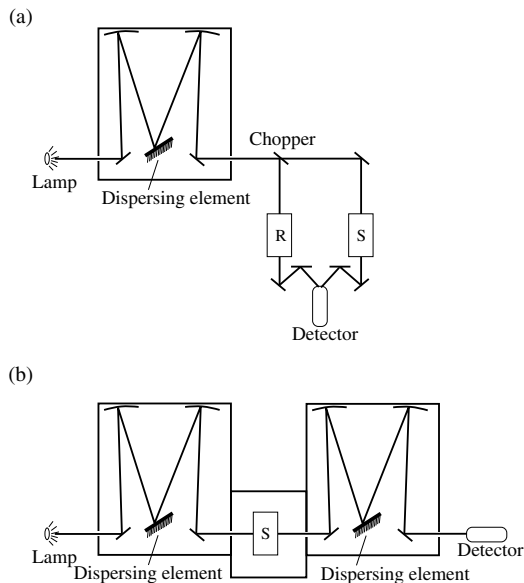


Fig. 9.2 Schematic set-up for (a) absorption spectroscopy (dual beam) and (b) emission and excitation spectroscopy.

the sample (compartment S). One detector alternately records the signals from both beam paths. The transmittance $T(\lambda)$ is defined as the ratio of the intensity of the light passed through the sample $I(\lambda)$ to the intensity of the reference signal $I(\lambda)_0$. In a transmission spectrum, T is plotted as a function of wavelength (or an equivalent quantity, see above). Instead of transmittance, the absorbance or optical density, A , is often the quantity plotted on the y-axis. It is related to the transmittance by $A = -\log_{10}(T)$.

Absorption spectroscopy is used to measure the transmitted signal for transparent (non-scattering) samples such as single crystals or solutions. An alternative for strongly scattering materials, such as polycrystalline powders, is diffuse reflection spectroscopy. The difference in set-ups for absorption and reflection spectroscopy is in the detection compartment. When diffuse reflection spectroscopy is used, the backscattered signal is detected and compared to the backscattered signal from a reference material. Polycrystalline powders of MgO or BaSO_4 can be used as a reference. These materials scatter all the light in the wavelength range 200–3000 nm. The reflectance, R , defined as $\frac{I}{I_0}(\lambda)$, is plotted on the y axis.

The two other techniques, emission and excitation spectroscopy, use the phenomenon that after excitation of the sample to an excited state the transition to the ground state results in the emission of light. Usually, emission and excitation spectroscopy are both performed in one set-up (see Fig. 9.2b), which contains a broadband excitation source, a light-dispersing element for the excitation radiation, a sample compartment S , a light-dispersing element for the radiation emitted, and a sensitive detector for measuring the intensity of the radiation emitted. In emission spectroscopy, the emitted light is spectrally resolved by scanning the emission-dispersing element. The dispersing element for the excitation source remains fixed during scanning of the emitted light. An emission spectrum yields information on the energetic positions of the optical transitions that are involved in the emission of light. In excitation spectroscopy, the emission monochromator is set at a wavelength corresponding to a (strong) emission line and the excitation light is scanned. In contrast to an absorption spectrum, an excitation spectrum yields information on the energetic position of absorption bands *that lead to emission of the chosen wavelength*. Therefore, the last technique can prove very valuable in studying specific absorption transitions, e.g., in the case that more than one optical absorbing species is present in the material.

The different experimental set-ups for absorption/reflection and emission/excitation spectroscopy lead to a different performance. Excitation and emission spectroscopy have very low background levels and a much higher sensitivity. They are used in combination with samples containing very small quantities of luminescent species. Absorption and diffuse reflection spectroscopy have much larger background and noise levels and are used for more concentrated samples. Both types of techniques also show different requirements for the equipment used. For absorption and diffuse reflection spectroscopy the requirements for the output powers of lamps and the sensitivity of the detector are less demanding than for emission and excitation spectroscopy. Collimated radiation from the excitation

source is measured in the former two techniques, while in the latter diffuse (and spectrally resolved) emission radiation of much lower intensity has to be detected. Properties of the equipment that is generally used will be discussed below.

9.2.1

Broadband Light Sources

Broadband light sources are excitation sources that emit radiation with a continuum spectrum in a broad spectral range. For the ultraviolet (UV) and visible (VIS) spectral region, common broadband light sources are arc or halogen lamps. Arc lamps are based on high-pressure gas discharges. Halogen lamps are incandescent lamps that can be operated at higher temperatures than “classic” incandescent lamps because they are filled with a halogen gas.

Typically, a 20–30 W tungsten halogen lamp is used in absorption/reflection spectroscopy to cover the VIS and infrared (IR) wavelength region from 350 to 3000 nm. At wavelengths of 350–190 nm a D₂ lamp (also typically 20–30 W) is used. For emission and excitation spectroscopy, stronger light sources are common, such as a 150–450 W Xe lamp (air cooled) for the UV/VIS region (250–800 nm) or a 150 W D₂ lamp (water cooled) for shorter wavelengths down to 140 nm. For excitation sources with wavelengths shorter than 200 nm, oxygen strongly absorbs the radiation, and nitrogen purging or vacuum conditions are needed for spectroscopic experiments. The spectral output curves of the lamps discussed are shown in Fig. 9.3.

Because of low energy-to-light efficiencies, the radiated power of a D₂ lamp is relatively weak. Intense radiation with wavelengths shorter than 200 nm is generated in a synchrotron facility. In such a facility, intense electromagnetic radiation is created by charged particles with relativistic velocities that traverse a curved path. The curvature in the path is achieved by letting the particles pass through bending

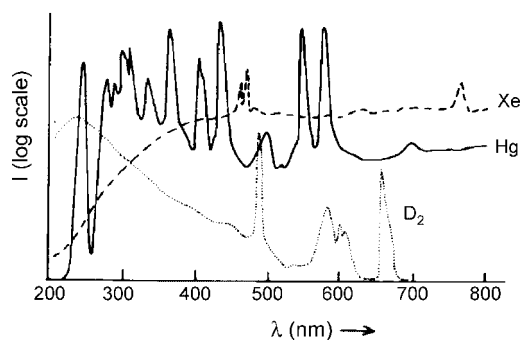


Fig. 9.3 Typical spectral distribution curves for three widely used arc lamps: high-pressure xenon, mercury, and deuterium (reproduced from Ref. [21] with permission from Plenum Press).

magnets. The oscillations of the charges cause emission of so-called synchrotron radiation. Compared to the broadband radiation sources discussed above, synchrotron radiation is of extreme brightness and covers a shorter-wavelength spectral range, from the UV to the X-ray region (0.01 nm). Apart from this, it has other remarkable properties that suit spectroscopic experiments: synchrotron radiation is pulsed (frequencies around 1 MHz, pulse widths shorter than 0.1 ns), strongly linearly polarized (depending on the angle of incidence 80% or more [3]), and strongly collimated; the dimensions of the beam spot for vacuum ultraviolet (VUV, $10 > \lambda > 200$ nm) light are typically 1 mm horizontally by 0.1 mm vertically and become even smaller at shorter wavelengths. These properties allow not only for the experiments discussed above but also for additional spectroscopic measurements such as polarization-dependent and time-resolved spectroscopy, discussed in Section 9.3.

An example of an excitation spectrum obtained with synchrotron radiation is shown in Fig. 9.1. Because of the brightness of the excitation radiation, a monochromator with a large dispersion can be used. This results in a resolution for this spectrum of up to 0.03 nm [4]. A typical resolution for spectrometers for VUV excitation is 0.5 nm [4]. Compared to this, the improvement by using the intense synchrotron radiation is remarkable. Even higher resolution can be obtained using wavelength-tunable lasers as the excitation source [5]. Lasers can be used as extremely monochromatic, pulsed light sources. They are discussed in Section 9.3.

9.2.2

Dispersing Elements

Dispersing elements are able to separate radiation spectrally. In combination with a broadband light source they are used to produce and select monochromatic excitation light. In order to obtain an emission spectrum, the radiation emitted from a sample is dispersed. Gratings and interferometers are nowadays commonly used as dispersing elements, while the use of prisms is restricted to photon energies for which the prism material is transparent. In this section the characteristics of gratings and interferometers are discussed.

9.2.2.1 Gratings

Figure 9.4 shows a schematic diagram of a grating. A grating is a reflecting surface with a periodic arrangement of grooves with distance d at blaze angle φ to the grating's back surface. The inset shows a spectrometer with a Czerny-Turner arrangement, which is a common arrangement in commercial apparatus. An incoming light beam is passed through a lens with diameter l and focal length f , which focuses the light on the entrance slit of the monochromator. The f -number of the monochromator is defined as F/L . The focal length F is the distance from the entrance slit to the concave mirror while L is the diameter of the mirror. The f -number of the lens is defined as f/l . When the f -number of the lens matches the f -number of the spectrophotometer, the grating surface is completely covered by the light beam and maximum performance is obtained. The wavelength of the light is scanned by slowly rotating the grating. A second mirror focuses the selected light on an exit slit.

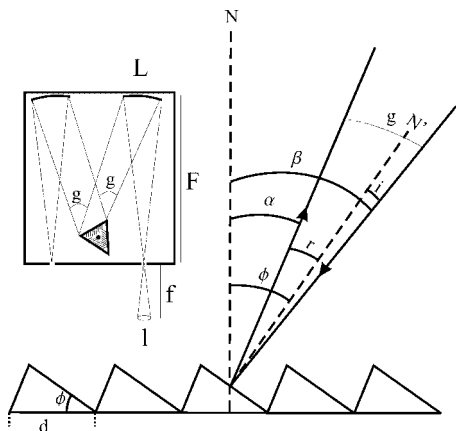


Fig. 9.4 Schematic of a grating with incident and diffracted light beams. The inset shows a spectrometer with a grating turret in a Czerny-Turner arrangement.

The principle of a grating is spectral separation of light by constructive and destructive interference of the diffracted light beam from the grating surface. For constructive interference the difference in path length for the light diffracted from two neighboring grooves has to be a multiple of the wavelength λ (see also Fig. 9.4).

$$m\lambda = d(\sin \alpha \pm \sin \beta), \quad (1)$$

where m is the order of diffraction and d is the spacing between two grooves. The angles α and β are defined in Fig. 9.4. In Eq. (1) a plus sign means that the incident and diffracted beams are on the same side of the grating normal N . Equation (1) shows that, for the same order m , light with different wavelengths λ will show constructive interference at different angles α , resulting in spectral separation. However, for different orders m and m' , wavelengths λ and λ' that are related by $m\lambda = m'\lambda'$ show constructive interference at the same angle α . This means that when radiation with a spread in wavelengths is dispersed by a grating, some wavelengths show constructive interference in the same direction and cannot be detected separately with the use of a grating only. The spread in wavelengths that can be detected uniquely is given by the free spectral range $\Delta\lambda_{\text{spec}}$,

$$\frac{m\lambda}{m+1} < \Delta\lambda_{\text{spec}} < \frac{m\lambda}{m-1}. \quad (2)$$

Equation (2) shows that for unique detection of light with wavelength λ in order m , light of wavelengths $\frac{m\lambda}{m+1}$ and $\frac{m\lambda}{m-1}$ should be absent.

When the grating is used in first order ($m=1$), cut-off filters are often used to prevent the presence of second-order diffractions of shorter-wavelength radiation.

Another important property that can be derived from Eq. (1) is the angular dispersion. For a constant angle β (when the grating is not rotating), the angular dispersion is obtained by the inverse of the derivative of Eq. (1),

$$\frac{d\alpha}{d\lambda} = \frac{m}{d \cos \alpha}. \quad (3)$$

In practice it is not the angular distribution of the light that is important but the linear distance between two diffracted wavelengths at the exit slit. This is given by the linear dispersion. The linear dispersion at the exit slit is the product of the focal length p of the grating and the angular dispersion,

$$p \frac{d\alpha}{d\lambda} = \frac{pm}{d \cos \alpha}. \quad (4)$$

From Eq. (4) it can be understood that long focal lengths, high orders of diffraction, and small groove spacing lead to a higher resolution.

The theoretical maximum resolution, or resolving power, that can be achieved is determined by the value $\Delta\lambda$ for which there is constructive interference for λ and destructive interference for $\lambda + \Delta\lambda$. The difference between the two wavelengths $\Delta\lambda$ depends on the total number of grooves in the grating. It can be derived that

$$\frac{\lambda}{\Delta\lambda} = mN_g, \quad (5)$$

where N_g is the number of grooves on the grating.

Another important characteristic of the grating is the throughput: the amount of light that reaches the exit slit under reference conditions. From the discussion above it can be concluded that there is a trade-off between resolution and throughput, since the larger the linear dispersion, the lower is the throughput. Additionally, the blaze angle φ influences the throughput. For any grating, the light yield is maximal if the grating works as a reflecting mirror. This is achieved when constructive interference occurs at an angle r (with respect to the grating normal N') which is equal to the angle of incidence i . When this condition is applied to Eq. (1) it can be derived that

$$2d \sin \varphi \cos i = m\lambda. \quad (6)$$

Since in general the angle i is very small, the blaze angle φ determines the blaze wavelength λ for which the throughput is maximal. In practice, the throughput is relatively high for some 100 nm on both sides around the blaze wavelength.

To improve the flexibility of spectrometers with respect to resolution and throughput, a grating turret arrangement (as depicted in Fig. 9.4) has become popular nowadays. On a grating turret three different gratings can be mounted, giving the user the possibility to choose a particular grating for his experiments.

For a certain grating, the throughput is not only a function of wavelength but also of the polarization of the radiation. With respect to the direction of the grooves (and the

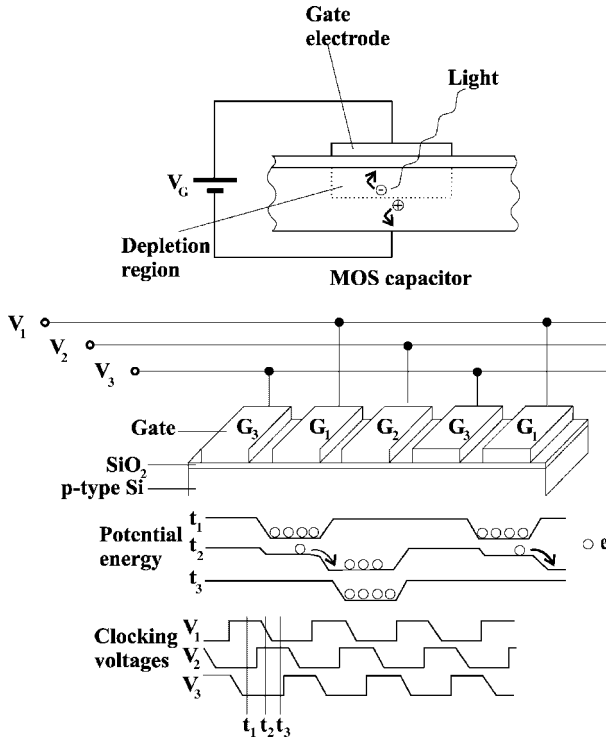


Fig. 9.5 Schematic of a MOS capacitor inside a CCD detector and a CCD array with a three-phase clocking sequence (adapted from Ref. [7]).

slits) two types of orthogonal polarization directions are possible: with the plane of polarization parallel to the grooves (P-polarization) or perpendicular (S-polarization). Of the two types of polarization, P-polarized radiation usually gives the smoothest throughput curve [3]. When using powders or solutions, completely unpolarized light is emitted, and the throughput curve will be intermediate between the curves for S- and P-polarization.

9.2.2.2 Interferometers

For higher wavelength selectivity a Fabry-Perot interferometer, also known as an etalon, can be used for wavelength dispersion. These interferometers (see Fig. 9.5) are based on multiple reflection of light between two parallel plates. The reflection coefficients of the inner surfaces are typically greater than 95%. The optical path length difference determines the condition for constructive interference of light reflected between the two plates,

$$\nu = \frac{mc}{\Delta S} \quad (7)$$

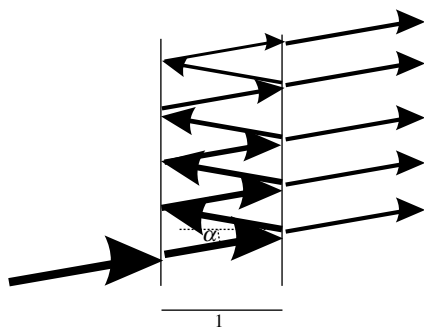


Fig. 9.6 Schematic of a Fabry-Perot interferometer. The optical path length difference is given by $\Delta S = n2l \cos \alpha$.

where ν is the frequency of light that shows constructive interference, m the order of the reflected light, c the speed of light, and ΔS the optical path length difference. $\Delta S = n\lambda$, where n is the refractive index and λ the geometrical path length of the light reflected once between the two plates.

The resonance frequency ν can be scanned by changing the optical path length difference ΔS . In practice, this is done by filling the space between the plates with a gas, which gradually changes n , or by changing the distance between the plates with high precision.

Typically, ΔS is between 0.1 and 10 cm, so that for optical frequencies m is on the order of 10^5 .

When radiation with a frequency of $\frac{m\nu}{\Delta S}$ shows constructive interference, radiation with frequencies corresponding to $m \pm 1$ will also interfere constructively. This leads to a free spectral range $\Delta\nu_{\text{spec}}$ of

$$\Delta\nu_{\text{spec}} = \frac{c}{\Delta S} \quad (8)$$

which is typically on the order of 10^{10} Hz. Note that, compared to a typical frequency for visible radiation of 10^{14} to 10^{15} Hz, the free spectral range of an etalon is small.

In order to avoid detection of radiation of unwanted orders it is common to disperse emissions broader than the free spectral range of the etalon by a grating before the light enters the Fabry-Perot interferometer.

The resolving power of a Fabry-Perot interferometer is given by

$$\frac{\nu}{\Delta\nu_{1/2}} = \frac{F\nu}{\Delta\nu_{\text{spec}}} \quad (9)$$

where the intensity at frequency $\nu + \Delta\nu_{1/2}$ is half of the intensity at the resonance frequency ν and F is the finesse of the etalon. Typical numbers for the finesse of etalons with high resolving power are 50 to 70. Although the finesse is determined by many factors [6], F is typically limited by surface roughness of the two plates. The

spread in optical path lengths due to surface roughness leads to a spread in the resonance frequency $\Delta\nu_r$, which can be estimated by

$$\Delta\nu_r = \nu \frac{\sqrt{2}\Delta r}{\Delta S} \quad (10)$$

where Δr is the average surface roughness of one plate.

This limits the finesse to

$$F_r = \frac{\Delta\nu_{\text{spec}}}{\Delta\nu_r} = \frac{\lambda}{2\sqrt{2}\Delta r}, \quad (11)$$

where F_r is the finesse due to surface roughness. A relatively small surface roughness of $\Delta r = \frac{\lambda}{200}$ yields a finesse of 70.

Care should be taken in handling etalons: parallelism of the plates is extremely important since relatively small misalignments result in a considerable reduction of the finesse. Also, etalons should be isolated from any vibrational interference, and the separation between the plates should not be allowed to drift.

9.2.3

Detectors

In spectroscopy, detectors of radiation are used for two purposes. Firstly, they are used as power meters to measure output powers of excitation sources. Secondly, more sensitive detectors are used to measure the intensity of the wavelength-resolved emission light from luminescent samples.

Most power meters are thermal detectors. In a thermal detector the absorption of photons leads to an increase in temperature of the detector material. This results in a change of a temperature-dependent property of the material, which is used to measure the temperature. In principle, thermal detectors respond uniformly to radiation of all wavelengths. The range of powers that can be detected is broad, from $10 \mu\text{W}$ to 10kW , depending on the detector material. For lower powers, photodiodes are commonly used, and these are discussed below.

For the detection of low-intensity emission light, several types of detectors are used. As a first classification, these detectors can be divided into devices which require scanning of the dispersing element to obtain a spectrum and detectors that can measure intensity with a high spatial resolution so that a spectrum can be measured directly from spectrally dispersed light. Among the latter type, the CCD (Charge Coupled Device) detector has gained popularity owing to major improvement of its performance in the past 15 years [7]. CCD detectors find application not only in scientific apparatus but also in digital photo cameras and camcorders.

The principle of a CCD detector is electron storage after charge separation by absorption of photons. Each pixel in a CCD array contains a Metal-Oxide-Silicon (MOS) capacitor (see Fig. 9.6). When a photon is absorbed, an electron-hole pair is generated and the electron is captured under the gate electrode. The quantum

efficiency of this process is high, typically between 10 and 80 % depending on the geometry of the CCD array. During exposure to light, a positive voltage is applied at the gate electrode, which depletes the p-type Si under the gate from positive charge carriers and creates a potential well for the electrons of the electron-hole pairs generated by the absorption of light. Electrons are gathered at the potential well during the exposure time, which typically varies from 0.1 s to 1 min. After exposure, the number of electrons is read out pixel-by-pixel by a sequence of electron transfer steps, called clocking. Clocking transfers the electrons through adjacent pixels to a read-out array.

A common clocking sequence is three-phase clocking, which is shown in Fig. 9.6. In this case, electrons are collected at gates 1 by setting clocking voltage V_1 during exposure to light. After this, electrons are moved from gates 1 to 2 by raising the voltage of gates 2 and subsequently lowering the voltage of gates 1. They are moved to gates 3 by a similar procedure of raising and lowering gate voltages. This sequence is repeated until all electrons are transferred to the read-out array.

CCD detectors can be used to measure radiation of very low intensity because of the possibility of long exposure times, high quantum efficiencies, and effective noise reduction by cooling with liquid nitrogen. The wavelength range for CCD detectors is limited by the band gap of crystalline Si, which results in an upper limit for the wavelength of 1.1 μm .

A special type of CCD detector can be used for single-photon detection [8,9]. This type is an intensified CCD (ICCD), and the signal is intensified by preamplification of the number of photons before the light is guided to the CCD array. Preamplification is done by letting the radiation impinge on a micro channel plate (MCP). An MCP is an electron-multiplying device consisting of an array of small channels of about 10 μm diameter and roughly 2 mm deep, present in an insulating material with a strong electric-field gradient in the direction of the channels. The same principle of electron multiplication is also applied in a photomultiplier tube, as will be explained below. At the entrance of a channel, a photon generates a primary electron. The electron is accelerated and creates secondary electrons due to inelastic scattering with the walls of the channel. In this way the number of electrons increases by a few orders of magnitude. At the end of the channel, the electrons are converted back into photons by letting them impinge on a phosphor screen. The photons generated at the exit of the channels are subsequently guided to the CCD array.

In contrast to CCD detectors, detectors that rely on scanning of the dispersing element are generally able to measure with shorter time windows ($\Delta t < \text{ms}$). Also, the wavelength range of these detectors is broader. For the detection of UV/VIS radiation, photomultiplier tubes (PMTs) are most popular. Photodiodes are commonly used for detection of near-infrared (NIR) radiation.

Photomultiplier tubes (see Fig. 9.7a) are based on the photo-emissive effect. If an incident photon has a higher energy than the work function of the photo-emissive material, a free electron is created when the photon is absorbed by the photo-emissive surface. The surface consists of either a material with a low work function, such as an alkali metal, or a material with low electron affinity in combination with a low-band-gap semiconductor, for example CsO/GaAs [6]. A number of popular PMTs with some typical performance values are listed in Table 9.1.

Tab. 9.1 Typical characteristics of selected photomultiplier tubes.

Cathode material	Range (nm)	λ_{peak} (nm) for M.R.S. ^a	M.R.S. at λ_{peak} (mA W^{-1})	QE (%) at λ_{peak}	Dark current (nA cm^{-2} cathode surface)	Typical transit time (ns)	Rise time ^b (ns)
Low-noise bialkali	165–680	410	90	25	0.1	15	1.4
GaAs:Cs	185–930	300–800	90	14 ^c	1	25	2.5
Multialkali	190–900	400	70	22	3	22	2.2
Sb-Cs	200–660	340	18	20	0.5	15	1.4
Ag-O-Cs	400–1200	800	2.5	0.4	100	17	1.1

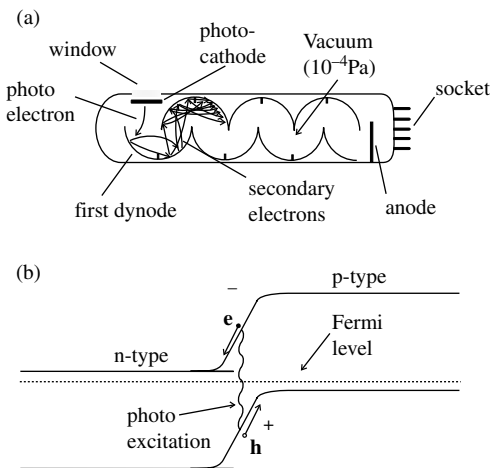
^aM.R.S. denotes maximum radiant sensitivity.

^bThe rise time is defined as the time difference between a signal at 10% of the maximum peak height and 90% of the maximum peak height.

^cAt a wavelength of 800 nm.

If the free electron is directed to an anode directly, a very small current is the result. The ingenuity of the PMT is that the single charge at the cathode is multiplied to roughly 10^6 charges at the anode by letting the electron strike a series of secondary electron-emitting surfaces, called dynodes. Each dynode multiplies the number of electrons so that the number of charges increases exponentially with the number of dynodes. The multiplication factor is known as the gain of the PMT. Higher gain leads to higher signal-to-noise ratios but also leads to higher response times, since the electrons travel longer pathways. Moreover, a high gain results in poor time resolution, since electrons can travel through various pathways, which results in a spread of arrival times at the anode.

Suppliers give figures of merit for PMTs (see Table 9.1). These are the wavelength-dependent radiant sensitivity at the photocathode, the dark current and other noise


Fig. 9.7 (a) Schematic of a photomultiplier tube; (b) principle of a photodiode detector.

characteristics, the typical electron transit time, and the rise time [10,11]. The radiant sensitivity S_c at the photocathode is the current generated at the photocathode per watt of incident light (mA W^{-1}). It is a function of the quantum efficiency (QE) of the photocathode. The quantum efficiency is the number of electrons generated at the cathode divided by the number of incident photons. In general, S_c is a strong function of wavelength. For the various kinds of PMTs, manufacturers provide curves for selection and reference. On the long-wavelength side, a sharp drop in S_c is observed, since photon energies become smaller than the work function of the photocathode material. On the short-wavelength side, the window material often determines the cut-off wavelength. Curves showing the radiant sensitivity should be interpreted as typical curves, since S_c varies from tube to tube. The wavelength range for PMTs is typically from 120 to 800 nm. IR-sensitive PMTs can go up to 1700 nm but have poorer signal-to-noise characteristics.

The dark current is a measure of the noise level of the PMT. For a good signal-to-noise level a small dark current is required. For low-work-function photocathodes, the main source of noise contributing to the dark current is thermionic emission of electrons. Its intensity depends exponentially on temperature, so that cooling to -30°C by dry ice or a thermoelectric cooler suppresses this phenomenon. Cooling a PMT may lead to condensed water at the contacts in the PMT socket, which could result in leakage currents. Other sources of noise are ionization of residual gases in the tube, cosmic rays, and radioactive materials in the tube envelope. For low-intensity measurements, these noise contributions can be greatly reduced when a discriminator is used. A discriminator counts signals only when they are within a window set by a minimum and a maximum signal. Compared to the peak current from photons incident on the photocathode, noise sources originating from dynodes lead to a lower signal since they experience less gain, and noise originating from cosmic rays typically leads to a much larger signal. Discrimination of noise is achieved when the values for the minimum and maximum signal are well chosen. Detection with the use of a discriminator is known as single-photon counting.

Quantities that characterize the signal-to-noise properties of PMTs are the noise-equivalent-power (NEP) and the detectivity (D). The NEP ($\text{W Hz}^{-1/2}$) is the amount of light in watts needed to produce a signal-to-noise ratio of unity for a system with a detection bandwidth Δf (in which the noise spectrum is constant). The usual value for Δf is 1 Hz. The NEP can be calculated from the dark current at the anode (adc), the cathode radiant sensitivity and the gain (g) from the equation

$$NEP = \frac{\sqrt{2q \times adc}}{S_c \times \sqrt{g}} \quad (12)$$

where q is the electron charge. A small NEP means a high signal-to-noise ratio of the PMT. From Eq. (12) it can be seen that high cathode radiant sensitivity, large gain, and small dark currents lead to a small NEP .

Typical electron transit times for PMTs are in the 0.1 to 10 ns regime, depending on the amount and the configuration of dynodes. Also the rise time, which is indicative of the spread in arrival times, depends on the geometry of the dynode sequence. Rise

Tab. 9.2 Typical characteristics (at room temperature) of selected photodiode materials (adapted from Ref. [6]).

Photodiode	Range (nm)	D_{\max} (cm Hz ^{1/2} W ⁻¹)	τ (ns)
Si	200–1100	2×10^{13}	>0.006
Ge	400–1800	10^{11}	0.3
InAs	1000–3800	4×10^9	5
InSb	1000–7000	1.5×10^8	100

times are typically 10 % of the electron transit time. For a fast response (100 ps), very small PMTs are used.

Photodiode detectors are more sensitive than other detectors in the NIR region. They are based on the generation and separation of an electron-hole pair when a p-n junction is illuminated (see Fig. 9.7b). The electron and the hole can be registered as a small current or as a small change in voltage. Typical photodiode materials are Si for the wavelengths up to 1.1 μm and InAs for 1 to 3.8 μm . Table 9.2 shows characteristics of several photodiode materials.

Instead of *NEP*, the common quantity to characterize the signal-to-noise performance of photodiodes is the detectivity D (cm Hz^{1/2} W⁻¹). It is defined as,

$$D = \frac{\sqrt{A}}{NEP} \quad (13)$$

where A is the surface area of the photodiode. With Eq. (13), the *NEP* of a PMT can be converted to D (both as a function of wavelength), so that a comparison between the performance of the different type of detectors is possible. A typical PMT has an *NEP* of 5×10^{-16} W Hz^{-1/2} at the wavelength of maximum radiant sensitivity and a cathode surface area of 1 cm², which leads to $D = 2 \times 10^{15}$ cm Hz^{1/2} W⁻¹. Typical detectivities for photodiodes (for wavelengths in the NIR) vary from 10^8 to 10^{13} cm Hz^{1/2} W⁻¹ (see Table 9.2).

A dramatic increase in the sensitivity of photodiodes is achieved when they are operated under strong reverse bias so that a strong electric field over the junction region is created. When an electron-hole pair is photogenerated, they experience such strong accelerations that they generate new electron-hole pairs by inelastic scattering. This effect is known as an avalanche cascade, and the gain of this effect can be as high as 10^5 to 10^6 . As a consequence, the sensitivity of avalanche photodiodes (APDs) is comparable to the sensitivity of PMTs, so that they can be used for single-photon counting experiments [8,9].

9.3

The Transition Dipole Moment: Absorption Strengths and Luminescence Lifetimes

The physical property that describes the strength of an optical transition is the transition dipole moment μ . Two experimental observables are related to the transition dipole moment: the absorption cross-section and the luminescence lifetime. In this

section, different spectroscopic techniques are discussed to obtain these two properties. The section starts with the determination of the absorption cross-section from absorption and excitation spectroscopy. After this, the laser as an excitation source is introduced, and the determination of luminescence lifetimes is then discussed. The section ends by discussing the relationship between the absorption cross-section and the luminescence lifetime.

From absorption, emission, and excitation spectroscopy, not only can the energetic position of optical transitions be obtained but also information on the strength of the optical transition.

The absorbance A is related to the integrated absorption cross-section σ ($\text{m}^2 \text{ Hz}$) by [3]

$$\int A(\nu) d\nu = \frac{1}{\log e} N \sigma l \quad (14)$$

where N is the number density (m^{-3}) of optical centers and l the path length (m) of light through the sample. Often, the integral $d\nu$ is chosen over the line shape for a specific transition. In this case, σ is defined for a specific transition from level a to b and is related to the oscillator strength f_{ab} , which is a number quantity, via [12]

$$\sigma = \frac{e^2}{4\pi\epsilon_0 m c n} \left[\frac{E_{loc}}{E} \right] f_{ab}(ED) \quad (15)$$

for electric dipole transitions and

$$\sigma = \frac{e^2 n}{4\epsilon_0 m c} f_{ab}(MD) \quad (16)$$

for magnetic dipole transitions. In the equations above e , ϵ_0 , m , c and n have their usual meanings and $\left[\frac{E_{loc}}{E} \right]$ is the local field correction factor [13], which depends on n and differs for different symmetries of the optical center. Often it is neglected and replaced by unity. Table 9.3 gives typical characteristics of common optical impurities in the solid state (F-centers, transition metals, and rare earth ions). These are rough estimates since the actual figures depend strongly on the host lattice.

Tab. 9.3 Typical values for oscillator strengths f_{ab} , integrated absorption cross-sections σ , and transitions probabilities Γ_{ba} for various types of transitions on common optical impurities (adapted from Ref. [21], with permission).

Center	Transition type	Transition	f_{ab}	$\sigma(\text{m}^2 \text{ Hz})$	$\Gamma_{ba}(\text{s}^{-1})$
F-center	ED allowed	$s \rightarrow p$	1	5.6×10^{-7}	10^7
Cr^{3+}	forced ED, spin allowed	${}^4A_2 \rightarrow {}^4T_2$	10^{-2}	5.6×10^{-9}	10^5
Mn^{2+}	forced ED, spin forbidden	${}^6A_1 \rightarrow {}^4T_2$	10^{-8}	5.6×10^{-15}	10^1
Eu^{3+}	forced ED	${}^7F_0 \rightarrow {}^5D_2$	10^{-6}	5.6×10^{-13}	10^3
Eu^{3+}	MD	${}^7F_0 \rightarrow {}^5D_1$	10^{-8}	5.9×10^{-14}	10^1

From an excitation spectrum no absolute values for the strengths of optical transitions can be obtained, but in some cases it makes sense to compare the measured intensities for absorption transitions at different wavelengths. The signal $I_{em}(\lambda)$ in an excitation spectrum is proportional to,

$$I_{em}(\lambda) \propto I_0 \times q \times (1 - R) \quad (17)$$

where $I_{em}(\lambda)$ is the measured intensity and I_0 the intensity of the light incident on the sample. The materials' properties are q , the quantum efficiency of the sample and R , the reflectance of the powder sample in the absence of transmission through the sample (in case of a transparent sample one can replace R by transmittance T).

In general, all three quantities on the right hand side of Eq. (17) are a function of λ , which complicates the interpretation of the relative intensities. To correct for the obscuring influence of $I_0(\lambda)$, a reference spectrum can be obtained from a compound for which q and R are independent of wavelength [14]. Examples of such compounds are a concentrated Rhodamine B dye solution for the UV/VIS spectral range or sodium salicylate powder for the VUV/UV spectral range [15,16]. After correction, the intensities in the excitation spectra are proportional to $q \times (1 - R)$. Note that for the intensity to become proportional to $q \times A$ two more conditions need to be fulfilled. First, R needs to be 0.9 or larger at all wavelengths so that saturation effects are minimal. Second, R needs to be independent of wavelength in the spectral area of interest.

From emission spectra, no information about the absolute value of the transition strengths can be obtained, but comparison of relative intensities (after correction for instrumental response) is straightforward for transitions originating from the same level. In this case, the observed intensities $I_{em}(\lambda)$ for transitions to various levels are proportional to the corresponding radiative transition rates.

For spectroscopic purposes, lasers provide an extremely useful excitation source. They emit radiation with high power, small divergence, and a high degree of coherence and polarization. Moreover, lasers can generate very short pulses or extremely monochromatic radiation. It is therefore not surprising that a wide selection of lasers find application in a variety of spectroscopic techniques. Below, a short overview of gas, solid-state, diode, and dye lasers is given.

9.3.1

Lasers

In a gas laser, electric current is discharged through a gas to produce laser light. Depending on the constituents of the gas, laser radiation with different (simultaneous) wavelengths is created. Table 9.4 lists several gas media and their lasing wavelengths. A low-power helium-neon (He-Ne) laser is often used for optical alignment purposes and, because of its extreme monochromaticity, as a frequency standard. Ar, Kr, and XeCl lasers can be used to pump dye lasers, which will be treated below. Argon/fluorine or fluorine gas lasers yield wavelengths of 193 and 157 nm respectively, which are among the shortest wavelengths available for laser radiation.

In solid-state lasers, the lasing material is either an optical impurity in a solid-state medium, or a semiconductor diode. The Nd-YAG ($Y_3Al_5O_{12}$ doped with Nd^{3+}) laser is

Tab. 9.4 Overview of different laser gases, laser wavelengths, pulse widths, and typical output powers.

Laser gas	Wavelength (nm)	Typical pulse width	Typical output power
He-Cd	442, 325	CW ^a to ps	100 mW
He-Ne	632.8 ^b	CW to ps	20 mW
He-Ne	543, 1150, 3390	CW to ps	2 mW
Ar	514.5 ^b , 528.7, 488.0, 457.9, 351, 300	CW to ps	500 mW
Kr	647.1	CW to ps	30 mW
Xe-F ₂	351	10 ns	1.5 W
Xe-Cl ₂	308	10 ns	1.5 W
Kr-F ₂	248	10 ns	3 W
Ar-F ₂	193	10 ns	1.5 W
F ₂	157	10 ns	400 mW

^aCW denotes continuous wave.

^bStrongest lines.

an example of the first type [17]. This laser can be operated in pulsed mode with a typical pulse width for Q-switching of 20 ns, down to ps for mode-locked lasers [12]. Because of the high output power, its wavelength can be varied over several harmonics, from the fundamental ($\text{Nd}^{3+} \ ^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{11/2}$, 1064 nm) up to the fourth order (266 nm).

Ti:sapphire lasers are pumped by frequency-doubled AlGaAs diode lasers at 530 nm. Compared to other lasers, Ti:sapphire lasers have two distinctive features that make them popular. Firstly, because of the broadband emission of the $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transition of Ti^{3+} in sapphire, the wavelength of the laser emission is tuneable, typically in the 700 to 1000 nm region. In combination with higher harmonic generation (up to fourth order is commercially available), a wide spectral range is provided. Secondly, pulses of extremely short time width can be created with Ti:sapphire lasers, up to a few fs, which allows the study of comparatively fast relaxation processes. The frequency spectrum of an fs pulse laser has a Fourier-transform-limited distribution. The frequency width $\Delta\nu$ of the pulse and the time width Δt of the laser pulse are related by $\Delta\nu\Delta t \geq 1$.

The field of semiconductor diode lasers is developing rapidly because of their ease of handling and low cost. Depending on the semiconductor material, available laser wavelengths vary from the IR to the violet spectral region. Diode lasers consist of a semiconductor diode that is driven in forward bias. Light generated at the junction is only amplified in a certain direction since the diode material is welded in between lower-refractive index material, and the ends act as mirrors to form a laser cavity. Because of their fast response to the driving current, the output power of a diode laser can be modified from continuous wave to oscillatory up to some 100 MHz. When fast electrical switching is used, pulse widths of only tens of ps can be achieved. The drawback of diode lasers is their wavelength stability, which is within some 5 nm. Currently, the smallest wavelengths can be achieved by GaN diode lasers, which operate at a wavelength around 400 nm. For GaN diode lasers, output powers under continuous wave (CW) operation can range up to 200 mW [18].

Dye lasers use a solution of an organic dye as the laser medium [19]. The dyes are excited by a high-intensity pump laser, for example an XeCl excimer, Ar gas, frequency-doubled Nd-YAG or GaN diode laser. Because of the broad emission band of dyes and the availability of dyes with a range of emission wavelengths, dye lasers are versatile instruments. The typical wavelength range for dye lasers is from 360 to 900 nm, excluding second-harmonic generation, and pulse widths can vary from around 10 ns to continuous wave. The spectral width of a dye laser can be minimized with the use of an etalon.

9.3.2

Luminescence Lifetimes

The strength of optical transitions is not only manifest in the absorption properties but also in the emissive properties of luminescent materials. The rate of spontaneous emission, also known as the luminescence lifetime, is proportional to the square of the transition dipole moment. Its experimental determination is discussed below.

Experimentally, there are two ways to determine the luminescence lifetime [20]. One is by a sinusoidal modulation of the excitation intensity and measuring the time-dependent response of the optical species. The other is by using a pulsed excitation source and measuring a histogram of photon arrival times. Because of the wide availability of pulsed sources, the most popular way to measure luminescence lifetimes is the histogram method. The line connecting all points in the histogram is known as a decay curve.

In the simplest case all the excited optical species luminescence with the same decay rate. Then, a decay curve $I(t)$ is obtained according to,

$$I(t) = C \times \Gamma_{rad} \exp[-(\Gamma_{rad} + \Gamma_{nr})t] \quad (18)$$

The measured intensity is proportional to the radiative decay rate, Γ_{rad} . The constant C is determined by the collection efficiency of the detection system and the amount of excited species at $t = 0$. The nonradiative decay rate is given by Γ_{nr} and t denotes time. To extract the lifetime, $\ln(I)$ versus t is plotted. The slope of this curve yields the experimentally determined decay rate, $\Gamma_{rad} + \Gamma_{nr}$.

Note that the signal at $t = 0$ is proportional to Γ_{rad} . Therefore, sets of decay curves with different Γ_{nr} but (presumably) the same radiative decay rate may be plotted with equal intensities at $t = 0$. In the case of single exponential decay, the fall-off of the excitation pulse should be much smaller than the life time.

In general, the optical species may luminesce with different decay rates and the decay curve becomes non-exponential. In this case, a distribution of lifetimes is obtained. The pulse width of the excitation source should be much smaller than the lifetime.

Apart from pulsed laser sources, sometimes flash lamps are used as pulsed light sources. Flash lamps are available with pulse widths of less than 1 ns and repetition rates up to 50 kHz. Also synchrotron radiation can be used to measure lifetimes. A typical pulse width for synchrotron radiation is 0.2 ns [3]. The repetition rate (typically MHz) limits the detection of lifetimes to a maximum of $\sim 1 \mu\text{s}$.

Depending on the range of decay times expected, different detection systems may be used. For detection of lifetimes down to the 100-ps regime, a PMT or photodiode can be connected to an oscilloscope or a pulse-height analyzer. An oscilloscope registers the current from the photodetector as a function of time after a single excitation pulse. The signal after one excitation pulse has a poor signal-to-noise ratio, so that averaging of multiple (typically 1000 or more) decay curves is required. Decay times up to ~ 100 ns can be measured with the use of an oscilloscope.

Faster decay times (from 100 ns up to ~ 100 ps) can be measured by pulse-height analysis. This relies on the measurement of 1 (or 0) photons per excitation pulse. The time it takes to detect a photon after an excitation pulse is registered by increasing a voltage linearly in time after the excitation pulse until a photon is detected (or the next excitation pulse is given). The distribution of arrival times obtained from multiple measurements gives the decay curve. For good statistical accuracy, the fraction of detected photons per excitation pulse is typically smaller than 0.2 [21]. The limiting factor in the short-time limit is the detector. The fastest PMTs have a rise time of about 200 ps. Si photodiodes have a much shorter response time, up to 6 ps.

To detect events on even shorter time scales, femtosecond lasers can be used as excitation sources. On the detection side, no electronic equipment is fast enough to register events on this timescale. To overcome this limitation, a pump-probe method is used. The laser output is split by a semi-transparent mirror in a pump and a probe beam. The pump pulse excites the system and the delayed probe pulse probes the material as a function of delay time.

Since both the integrated absorption cross-section and the luminescence lifetime are proportional to the square of the transition dipole moment, one can be derived from the other.

For optical transitions between the same pair of (degenerate) energy levels, the following relationship is used to convert one into the other [22]:

$$\sigma = \Gamma_{ba} \frac{g_b}{g_a} \frac{c^2}{8\pi n^2} \frac{\nu_{\text{abs}}}{\nu_{\text{em}}^3} \quad (19)$$

In Eq. (19), g denotes the degeneracy of the state (b is ground, a is excited), ν_{abs} the mean absorption frequency of the absorption line, and ν_{em} the mean emission frequency of the emission line. This relationship can be used to validate the accuracy of complementary measurements of lifetimes and absorption cross-sections. When using this relationship, note that changes in the transition dipole moment between absorption and emission transitions are ignored [23]. When a large Stokes shift is observed between absorption and emission transitions, the different transitions involved in absorption and emission may have different transition dipole moments.

9.4 Quantum Efficiency and Nonradiative Relaxation

Relaxation processes in luminescent materials can proceed via emission of radiation or via nonradiative relaxation through vibrational modes [24]. The split between the

Tab. 9.5 Quantum efficiencies for some commercially applied phosphors. Excitation at 254 nm (reproduced from Ref. [25] with permission from Wiley-VCH).

Phosphor	$\lambda_{\text{max, em}}$ (nm)	QE (%)
BaMgAl ₁₀ O ₁₇ :Eu ²⁺	450	90
LaPO ₄ :Ce ³⁺ , Tb ³⁺	545	93
Y ₂ O ₃ :Eu ³⁺	611	90

two processes determines the energy efficiency of a luminescent material. Because of the Stokes shift observed in luminescent processes, energy efficiencies are always less than the theoretical maximum of 100 %. An energy efficiency of around 50 % is typical for luminescent phosphors used in commercial lighting applications. For these phosphors, the 50 % contribution of nonradiative decay is even desirable to provide the necessary red shift to downconvert the UV excitation photons to visible photons. In relation to this, the quantum efficiency q of a phosphor is defined as

$$q = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}} [\%]. \quad (20)$$

The present generation of commercial phosphors has quantum efficiencies close to 100 % [25]. The quantum efficiencies of some well-known standard phosphors are listed in Table 9.5.

Generally, quantum efficiencies are a function of excitation wavelength. However, some materials have a uniform quantum efficiency over a sizeable wavelength region. For example, Rhodamine 6G has a uniform quantum efficiency close to 100 % in the UV/VIS region in several solvents [14,26]. Therefore, such solutions of Rhodamine 6G can be used as a reference to measure quantum efficiencies of other materials. This leads to a good indication of the quantum efficiency.

Absolute determination of quantum efficiencies is difficult. An integrating sphere has to be used to collect all photons with a PMT positioned at the focal point. The techniques involved are laborious and there are many pitfalls [3].

Other methods are based on determination of the energy efficiency and correcting for the excitation and emission photon energies afterwards. First, the intensity of absorbed photons is determined from diffuse reflection or absorption spectra. The energy efficiency is then determined by measuring the energy dissipated by non-radiative relaxation processes by photothermal detection techniques [27], e.g., calorimetric absorption spectroscopy (CAS) [28], compensation photocalorimetry (CPC) [29], and photothermal deflection spectroscopy (PDS) [30].

For CAS measurements, the increase in temperature of the sample is measured upon excitation. In order to do this the sample should be kept at low temperatures in a ³He or ⁴He cryostat. The temperature of the sample can be related to the power dissipated by calibrating the set-up with a small heater that is in thermal contact with the sample.

Compensation calorimetry can be performed with samples at room temperature. The sample is connected to a thermal bath at a lower temperature via a weak thermal link. A feedback-regulated heater that keeps the sample at constant temperature compensates the heat flow from the sample to the bath. During illumination,

nonradiative relaxation produces heat, which results in a smaller heat flow from the heater. The difference between the steady-state heating power when the light is turned on and when it is turned off gives a measure of the nonradiative losses.

In photothermal deflection spectroscopy, a pump-probe set-up is used to measure time-dependent changes in the macroscopic refractive index in the area illuminated by the pump beam. Changes in the refractive index can be caused by heating (nonradiative processes) or expansion of ions in the excited state. The probe beam is incident at a slant angle to the surface of the sample, so that changes in the refractive index become apparent by the deflection of the probe beam. For a Gaussian pump beam, changes in the angle of deflection are proportional to the refractive-index change [30]. When nonradiative processes and radiative decay (leading to expansion or contraction of ionic radii) occur on different time scales, these two contributions can be separated, and quantum efficiencies or values for the expansion of ions in the excited state can be obtained.

An alternative method to get an indication of the quantum efficiency is to measure the temperature dependence of the light output or the luminescence decay of a luminescent material. For a single-exponential decay curve, the decay time τ can be expressed by

$$\frac{1}{\tau} = \Gamma_{\text{rad}} + \Gamma_{\text{nr}}, \quad (21)$$

where Γ_{rad} is the radiative decay rate and Γ_{nr} is the nonradiative relaxation rate. In many cases Γ_{nr} shows a strong temperature dependence while Γ_{rad} is relatively independent of temperature. If at low temperatures the contribution from Γ_{nr} is assumed to be small, the quantum efficiency at higher temperatures is given by

$$\eta(T) = \frac{I(T)}{I_{\text{low}T}} = \frac{\tau(T)}{\tau_{\text{low}T}}, \quad (22)$$

where $I(T)$ stands for the measured intensity and $\tau(T)$ for the lifetime at temperature T .

9.5 Homogeneous Broadening and Dephasing

Emissions from optically active centers show homogeneous and inhomogeneous broadening. In solids, inhomogeneous broadening is due to differences in the local environment. An emission spectrum is said to be inhomogeneously broadened when different parts of the spectrum can be assigned to transitions from distinct optical centers (see Fig. 9.8). In contrast, homogeneous broadening is a collective property of the oscillating dipoles and is due to the finite lifetime of the states involved in the optical transition. Typically, line widths due to inhomogeneous broadening from optical centers in solids are of the order of $0.1\text{--}50\text{ cm}^{-1}$. Homogeneous line widths can be much smaller, up to 10^{-6} cm^{-1} (tens of kHz), depending on the type of

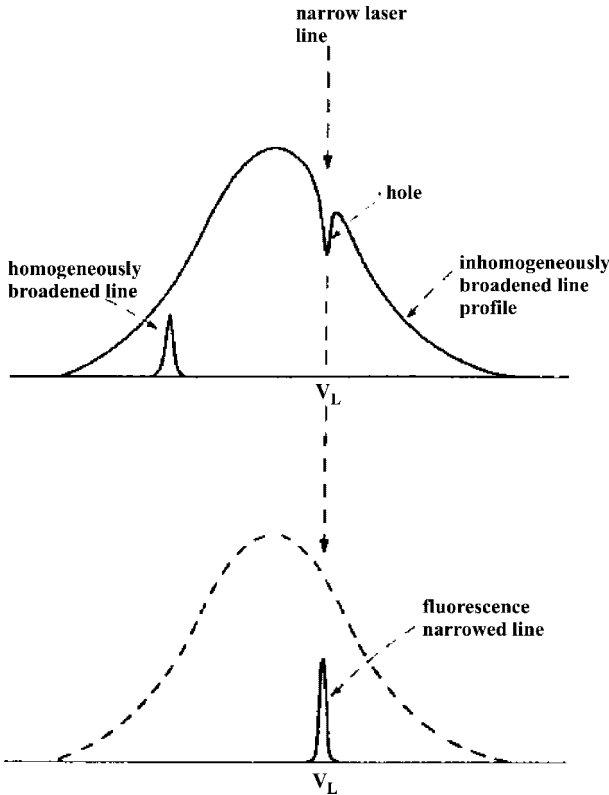


Fig. 9.8 OHB (top) and FLN (bottom) of an inhomogeneously broadened spectroscopic line (reproduced from Ref. [12] with permission from the Oxford University Press).

transition [12]. The homogeneous line width Γ_{hom} and the relaxation time T are related due to the Heisenberg uncertainty by

$$\Gamma_{\text{hom}} = \frac{1}{2\pi T}. \quad (23)$$

For relaxation of optical centers, a distinction between two contributions can be made. The first contribution leads to depopulation of the excited state, while the second contribution changes the phase properties of the wave function without changing the population of the excited state. The former processes were treated in relation to the experiments discussed in Section 9.3. The latter kind of interactions causes decoherence of the wave functions and usually occurs on much faster time scales. Therefore, homogeneous line widths are commonly determined by dephasing interactions. Techniques that use the frequency domain to measure homogeneous line widths, which are fluorescence line narrowing and optical hole burning, will be

discussed. For techniques that use the time domain, such as optical free induction decay, optical nutation, and photon echo, the common principles will be discussed. For more details the reader is referred to Refs. [31–33].

In the case of optical hole burning (OHB, see Fig. 9.8), a narrow-band CW laser, with a spectral width Γ_1 much smaller than the expected homogeneous line width Γ_{hom} of the optical center, is used to excite a subset of optical centers at laser frequency $\nu \pm \Gamma_1$. This results in a depletion of the ground state for this subset of optical centers. When scanning the absorption spectrum with a second laser (of 10–1000 times lower intensity), a dip will be recorded at the position of the second laser beam. In principle, the width of this dip represents the homogeneous line width as long as $\Gamma_1 < \Gamma_{\text{hom}}$, but care has to be taken to avoid unwanted contributions such as power broadening, dynamic inhomogeneous broadening, or broadening owing to local heating [21].

Furthermore, a distinction between the types of holes burnt can be made, based on the flexibility in scanning with the second laser beam. First, holes that last a very long time after excitation with the intense laser pulse can be created, which can be scanned after they are burnt. These permanent holes can be created when the first laser beam induces a photochemical reaction, leading to a large change in the absorption frequency, or by inducing a reorientation of the close environment of the optical center, causing a small shift in the absorption frequency. The experiment is performed at low temperatures, since for permanent holes relaxation back to the ground state is often prevented by a small energy barrier. The second type of holes are transient holes, where decay to the ground state occurs in typically microseconds to milliseconds. In this case, simultaneous pumping with the first laser beam and scanning with the second laser beam is required. The change in absorption spectrum around the transition frequency is determined by the competition between absorption and spontaneous relaxation to the ground state. Typically, the first laser has an intensity of 5–100 mW cm⁻²[21].

Fluorescence line narrowing (FLN, see Fig. 9.8) is closely related to optical hole burning. Instead of measuring absorption spectra, in this case, after excitation by a

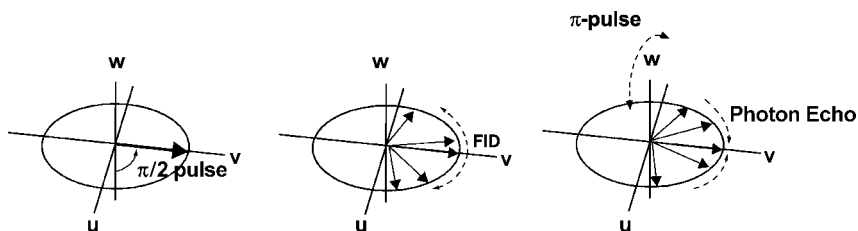


Fig. 9.9 Bloch diagrams showing a photon echo experiment of an inhomogeneously broadened line. The w axis represents the population difference between the excited and the ground state. The v axis represents the in-phase component of the oscillators with the laser radiation, and the u axis represents the out-of-phase component. Left: A $\pi/2$ pulse

equals the populations of the ground and excited states, bringing the population difference to zero. Middle: After the $\pi/2$ pulse, the different oscillators become out of phase, leading to FID. Right: After a time interval T the π pulse shifts the out-of-phase components by 180° . After another time interval T a photon echo is observed.

narrow-band laser, an emission spectrum is detected. When one is interested in homogeneous line widths, an emission line that is resonant to the excitation line should be measured [31]. Additionally, transfer of excitation energy between optical centers should be minimized. If this is the case, the recorded emission line width Γ_{obs} is given by,

$$\Gamma_{\text{obs}} = \Gamma_1 + 2\Gamma_{\text{hom}}. \quad (24)$$

The advantage over OHB is that the emission properties can be monitored as a function of time. This allows for not only the observation of homogeneous line widths, but also for the detection of time-dependent changes in the spectra (spectral diffusion), e.g., those due to transfer of excitation energy among inhomogeneously broadened optical centers. However, as well as a narrow-band excitation source, FLN requires detection of the emission spectrum with high resolution. For this purpose, interferometers with high finesse have to be used. The best narrow-beam lasers, i.e. continuous-wave ring dye lasers, can produce line widths down to 1 MHz. This imposes a lower limit on the line widths that can be determined by techniques that probe the frequency domain and excludes determination of line widths in the 1 MHz–10 kHz range.

In order to overcome this limitation, complementary techniques that measure dephasing times can be used. Time domain techniques rely on the coherent properties of the laser beam. They use the time-dependent phase of the laser radiation to generate a coherent state in the system. In a classical picture, the coherent, monochromatic laser beam excites one subset of oscillators that all become in phase with the excitation light. Because of the high intensity of the laser radiation, transitions which are slightly out-of-phase with the laser frequency are also excited. If the laser is suddenly switched off, the excited oscillators continue to oscillate, but now at their “natural” frequencies. The amplitude of the emitted radiation wave due to these oscillations is dependent on the coherence (in-phase component) of the oscillators. As time proceeds, the oscillations grow out of phase because of different oscillator frequencies (inhomogeneous broadening) and dephasing interactions (homogeneous broadening). In analogy to nuclear magnetic resonance (NMR) spectroscopy, this process is called free induction decay (FID). The measured intensity of the radiation (which is proportional to the square of the field amplitude) quickly decays to zero because of loss of coherence. When the signal is only homogeneously broadened, the dephasing time T_2 can be extracted from the FID signal by an exponential fit (yielding a relaxation time $T = T_2/2$). In many cases, however, inhomogeneous broadening is the dominant process. This obscures the detection of T_2 via the FID.

To circumvent the contribution from inhomogeneous broadening to the FID, the photon echo technique can be used. In relation to the photon echo experiment, the phenomenon of optical nutation will first be introduced.

During continuous stimulation with a coherent laser beam, optical nutation occurs; a set of oscillators is switched back and forth from the ground state to the excited state (by absorption of radiation and stimulated emission of radiation).

Note that the time-dependent behavior of the optical centers is now described by two frequencies. One is the transition frequency, which determines the energy of emitted photons, and the next is the “population frequency”, which determines the time-dependent probability of finding an optical center in the ground or excited state. Cycling the population between ground and excited state typically occurs at a frequency many orders of magnitude lower than the transition frequency. During one cycle between ground and excited state, complete population inversion occurs. The frequency of such an oscillation is inversely proportional to the square of the laser intensity, and is known as the Rabi frequency. A laser pulse (of a typical time-duration) that induces one Rabi oscillation is known as a 2π pulse. When the transmitted intensity is measured during continuous laser stimulation, an oscillatory intensity is obtained due to alternating absorption and stimulated emission.

In a photon echo experiment, optical nutation is used twice to obtain the FID signal due to homogeneous broadening. First, the system is prepared in such a way that the ground and excited state populations are equal. This is done by stimulating the system for an appropriate time so that it ends up with half-complete population inversion (see Fig. 9.9). In conjugation with a 2π pulse for one Rabi oscillation, this pulse is known as a $\pi/2$ pulse. Then the laser radiation is switched off and the system is left to decay by FID (see Fig. 9.9). After the $\pi/2$ pulse, the relative phase of oscillators that have a different transition frequency from that of the driving frequency will deviate according to $2\pi\Delta\nu t$, where $\Delta\nu$ is the frequency difference between different oscillators, while dephasing interactions cause random phase fluctuations.

The second pulse is used to circumvent the influence of inhomogeneous broadening on the FID. After a time interval T , the second pulse reverses the time evolution of the relative phases. This is done by applying a π pulse, which shifts the out-of-phase components by 180° (see Fig. 9.9). Oscillators that were $\Delta\nu$ ahead in phase will now be $\Delta\nu$ behind in phase. As a result, after another time T , inhomogeneously broadened oscillators will be in phase again and an “echo” radiation wave can be measured. Ideally, only dephasing interactions reduce the intensity of this echo wave. A plot of the intensity of the echo signal versus time interval T between the $\pi/2$ and π pulse allows for extraction of the dephasing time T_2 by $I_{\text{echo}} = I_0 \exp(-4T/T_2)$. For detailed information on photon echo experiments the reader is referred to Refs. [31–33].

9.6

Detection of Luminescence from Individual Optical Centers

In the foregoing sections, techniques to measure properties from an ensemble of optical centers have been discussed. The properties obtained, however, are interpreted with models based on the behavior of individual optical centers. Translation from the theoretical individual particle level to the experimental level of ensemble averages leads to a considerable loss of information; only ensemble statistics can be

obtained, and as a consequence the statistical fluctuations on the single-particle level remain hidden. Moreover, experimental techniques often try to circumvent obscuring ensemble effects, for example FLN and OHB for the determination of the homogenous line width and photon echo experiments to determine dephasing times from an inhomogeneously broadened ensemble.

The most elegant way to overcome the limitations mentioned above is to measure optical properties on a single-particle level, a research field known as single-molecule spectroscopy. This requires the capability to measure optical properties with high spatial resolution, which is nowadays generally achieved by narrowing down the excitation volumes. Detectors capable of efficient single-photon counting, such as APD, sensitive PMT, or (I)CCD detectors are used (see Section 9.3).

Single-molecule spectroscopy not only enables properties that are already apparent from ensemble measurements to be elegantly detected. Phenomena that are a manifestation of optics on a single-particle level have also been discovered. Most noticeable among these are photon antibunching [34], spectral diffusion [35,36], and blinking [37,38].

Photon antibunching is the phenomenon that photons have a tendency to arrive separated in time. It is inherent in spectroscopy of single optical centers that when one center is excited it typically takes a finite time T (where T is the radiative decay time) before a photon is emitted and a second excitation-emission cycle is possible. Therefore, under conditions of continuous excitation, photons have a tendency to arrive after a typical time interval T . Photon antibunching experiments are often used to prove that spectroscopy is being done on single optical centers. These experiments are commonly performed using a pulsed excitation source in which the pulse width is much smaller than the expected decay time. On the detection side, the beam path is split in a 1:1 fashion by a dichroic mirror, and each path is led to a single-photon detector (see Fig. 9.10). The two detectors are connected by a specialized computer

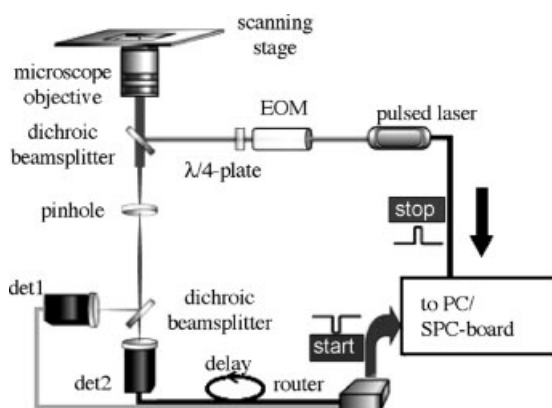


Fig. 9.10 Set-up for dual-beam antibunching experiments (reproduced from Ref [8] with permission from Wiley-VCH).

plug-in card for time-correlated single-photon counting (TCSPC). The dead time for signal processing is adjusted so that only one photon can be detected per pulse per detector. Thus, at most, two photons can be detected per excitation pulse. When a single optical center is present, the number of photons per pulse is limited to one, and the TCSPC signal will show antibunching peaks with correlation times determined by the repetition frequency of the laser pulse. When more than one optical center is present in the volume of the excitation pulse, an additional photon-bunching signal will be detected with very small correlation times, peaking at zero time interval. Thus, an absence of a peak at zero time interval is a fingerprint for the detection of a single molecule.

Spectral diffusion is observed when the emission (or excitation) spectrum of a single optical center changes as a function of time, where time typically ranges from 1 s to 1 h. It is a probe of the influence of the dynamics of the local surroundings on the optical center. This causes time-dependent spectral shifts on the single-particle level and cannot be monitored by ensemble measurements.

Blinking is the alternation of periods where the optical center shows high quantum efficiency (the “on” state) with periods where the optical center shows no luminescence (the “off” state). It is observed in organic dyes, where the “on” state is the excited singlet state and the “off” state is the excited triplet state, which has a small probability to be populated by intersystem crossing from the excited singlet state. Semiconductor colloidal quantum dots also exhibit blinking [39], where the “off” state can be manifest for minutes. Here, the “off” state is generated when the electron of the exciton is trapped by oxidative species in the local environment.

Since detectors capable of single-photon registration are commercially available, the key experimental challenges for single-molecule spectroscopy are the reduction of the excitation volume and the optimization of the photon collection efficiency. Excitation volumes should be small, so that on average only one optical center is present within the excitation volume. Additionally, small excitation volumes lead to minimization of background signals.

For far-field microscopy, the smallest size for the detection volume available is given by the diffraction limit, which yields an approximate minimal dimension of $\lambda/2$, where λ is the excitation wavelength used. The excitation volume for confocal microscopy approaches this diffraction limit by focusing the excitation laser beam to a near diffraction-limited focus by using an oil- or water-immersion, high-numerical-aperture (NA) objective (see Fig. 9.11). Furthermore, only the fluorescence originating from this volume is detected. Out-of-focus fluorescence light is rejected by the use of a small pinhole (50 to 100 μm in diameter [8]), which is positioned in the confocal plane. In this way, excitation volumes as small as 0.2 femtoliters [40,41] can be obtained, which leads to required concentrations of optical centers on the order of nanomolar.

To narrow down the excitation volume, the optical near field can be used. The accompanying techniques are called near-field scanning optical microscopy (NSOM) or spectroscopy (NSOS). These techniques are the optical variants of STM or AFM. By bringing a sample to within 5–10 nm of a subwavelength-sized optical aperture,

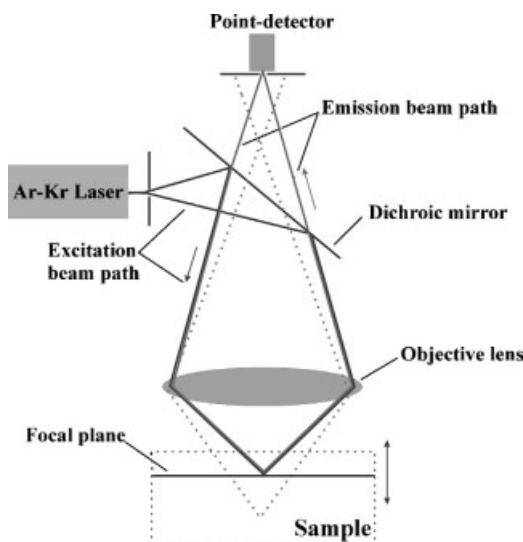


Fig. 9.11 Schematic set-up of a confocal fluorescence microscope. A pinhole in front of the detector selects light from a focal point (solid lines) to be detected. Out-of-focus light is rejected (dotted lines). In this way a volume with a size close to the diffraction limit is imaged. With a confocal microscope, scanning in three dimensions is possible (reproduced from Ref. [49]).

photons from the aperture do not cover enough distance to experience diffraction (see Fig. 9.12a). A typical resolution of 100–50 nm can be obtained in this way [8]. The element that critically determines the resolution is the optical tip. Tips can be “passive” wave guides or “active” exciton/light sources [42]. Passive tips are often made of aluminum-coated tapered optical fibers, where active tips contain fluorescent molecules that can transport excitation energy to the tip front by Förster-Dexter energy transfer [43,44]. The optical center can either be excited by nonradiative energy transfer or by a radiative emission-absorption process. One of the major issues is attenuation of the light beam when it traverses the narrow tip-region before it illuminates the sample, leading to a reduction of excitation intensity to roughly 0.1 % [9].

When NSOM (or NSOS) is used on solutions, inversion of the geometry may overcome this problem. Illumination of arrays of subwavelength holes made in a conducting material can yield evanescent fields in the holes [45]. When the holes are filled with the sample solution, higher intensities for the attenuated fields can be obtained than by ordinary near-field techniques. Moreover, reducing the size of the hole diameters leads to extremely small detection volumes of 10^{-21} L for a hole diameter of ~50 nm. Such a small excitation volume allows for higher concentrations of optical centers, up to the μM range.

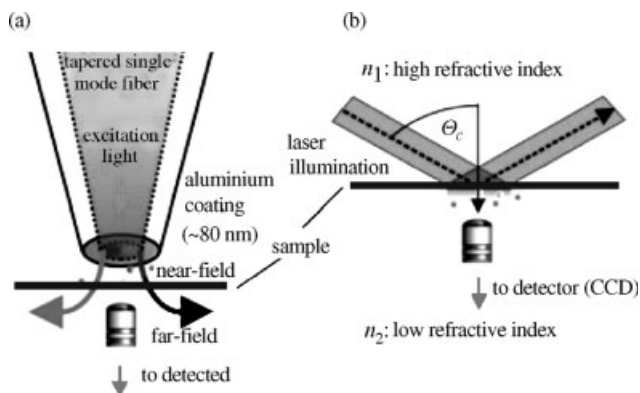


Fig. 9.12 Schematic set-up of (a) near-field scanning optical microscopy (NSOM), and (b) total internal reflection fluorescence microscopy (TIRFM) (reproduced from Ref. [8] with permission from Wiley-VCH).

Another method which probes the surface is total internal reflection (TIR) spectroscopy. This uses the evanescent wave of laser light that undergoes total internal reflection (see Fig. 9.12b) [46,47]. The evanescent wave, present on the low-refractive-index side, probes the sample immediately next to the surface to a depth of approximately 200 nm [8]. This excitation technique has the advantage that the laser beam can cover a relatively large surface area. In combination with a wide-field multichannel detector such as an (I)CCD detector, this advantage can be exploited, and multiple single molecules can be monitored in parallel.

Another means to narrow the excitation volume is the use of two-photon excitation. Since the excitation probability depends on the square of the intensity of the excitation light, only the small part where the overlap of the laser beams is strongest leads to a fluorescence signal [48].

The techniques involved in single-molecule spectroscopy are relatively new, and rapid development is expected in the near future. The field itself is developing toward smaller detection volumes and larger collection efficiencies. Also, the object of study will become more various since many areas can benefit from techniques that probe optical properties on a local scale, from the study of doped semiconductors to high-resolution imaging of living cells.

9.7

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Index

a

- absorber
 - broad-band 18
 - line 18
 - reverse-saturable (RSA) 170
- absorption 1, 3ff.
 - cross-section 140, 150, 234, 238
 - excited-state 159f., 162
 - parasitic 96
 - self- 117
 - single-photon 134
 - spectrum 14, 50ff.
 - steps 140, 157
 - strength 233
 - two-photon (TPA) 134
- AC surface discharge 61f.
- acceptor 8f., 15
- ACTFEL process 25
- activation energy 116f.
- activator
 - concentration 108, 113
 - ions 3, 12ff.
- afterglow 111, 116, 120ff.
- amplification experiments 160
- angle of incidence 226
- annihilation 106, 133
 - positron-electron 106
 - process 106f.
- anti-Stokes emission 133f.
 - bands 133
- attenuation 112, 120
 - length 112
- Auger process 21, 99
- avalanche
 - effect 151f.
 - photodiodes (APDs) 233
 - quantum counting 137
 - threshold 152

b

- backscatter coefficient 22
 - band
 - absorption 4, 97
 - broad 4f., 8, 82
 - conduction 9, 26, 45, 117
 - edge emission 127
 - emission 4ff.
 - gap 2, 22, 68, 109, 113
 - parabolic 4
 - structure 99
 - valence 9, 26, 45, 99
 - barrier ribs 62f.
 - barycenter 27, 79, 114
 - Bessel function 40, 47
 - BGO ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) 115f., 127
 - bleaching 151
 - blinking 245f.
 - Bohr radius 42, 45f.
 - branching ratio 151
 - Brewster angle 181
 - Bridgman technique 119
 - broadband light sources 223f.
 - broadening
 - homogeneous 240f., 243
 - inhomogeneous 240ff.
 - buffer layer 201
- ### c
- calorimetry 239
 - calorimetric absorption spectroscopy (CAS) 239
 - cathode
 - ray excitation 25
 - ray tubes (CRT) 1ff.
 - surface material 63, 231, 233
 - CaWO_4 8, 123f.
 - CCD (charge coupled device) 105

- CdS:Te 128
 - CdWO₄ 120f.
 - center for nonradiative recombination,
 - see killing centers
 - center of gravity, *see* barycenter
 - centroid shift 27, 78f.
 - charge
 - carriers 11, 22
 - coupled devices (CCDs) 105
 - transfer 189
 - transport 13
 - trapping 111
 - chemical
 - bonding 4f., 8
 - reaction 14
 - CIE diagram 68
 - coating densities 123
 - coherent 134f.
 - coincidence 106, 112
 - color
 - gamut 68, 183
 - mixing 181
 - point 68, 70, 183, 187
 - quality 185
 - rendering index (CRI) 180, 184f., 187
 - rendition 55
 - television 68
 - temperature 13, 186f., 208
 - Computed Tomography (CT) 12, 105ff.
 - applications 107, 120
 - configuration coordinate diagram 4
 - confinement 46, 48
 - axis 46
 - quantum 49, 56
 - strong 47
 - weak 46
 - confocal fluorescence microscope 247
 - continuous wave (CW) 236
 - conversion
 - color 179f.
 - down 94, 96
 - efficiency 100, 111, 161
 - optical-to-optical 161
 - mechanism 133
 - multi-photon process 133
 - single-photon process 133
 - coordination
 - number 83
 - polyhedra 83, 85
 - twelve-fold 83
 - Coulomb
 - energy 48f.
 - interaction 15ff.
 - potential 40f.
 - term 9f.
 - covalent 5, 27, 58, 78
 - bonds 187
 - lattices 113
 - critical power 151
 - cross relaxation 19f., 76, 81, 94f., 97, 138, 159
 - path 95
 - process 151
 - rate 151f.
 - step 162
 - cross-valence luminescens (CVL) 128,130
 - crystal
 - field splitting 78
 - field strength 27f., 79, 83
 - lattice 6, 10
 - one-dimensional 43
 - CsI:TI 118, 121f., 124, 126
 - CsMnBr₃:Yb 166
 - Cs₂NaScCl₆:Pr,V 168
 - Cs₂NaYbBr₆:Re 166
 - Cs₂NaYCl₆ 163
 - Cs₂NaYCl₆:V,Re 163
 - CW (continues wave) 236
 - Czerny-Turner arrangement 224f.
 - Czochralski technique 116ff.
- d**
- DC discharge 61f.
 - decay
 - constant 122, 128, 130
 - curve 21, 80, 237f.
 - free induction (FID) 243f.
 - intrinsic 17
 - lifetime 129
 - non-radiative 21, 159, 239
 - radiative 21, 78, 90f., 152
 - rate 16f., 146, 237
 - time 6, 10f., 17, 31, 53f., 65, 79, 108, 110ff.
 - defect
 - centers 79, 97
 - density 183
 - lattice 111
 - states 3, 11, 85
 - deflection 240
 - degradation processes 29, 31, 33f., 70
 - dendrimer structure 206
 - density-functional theory 120
 - density of states (DOS) 43f.
 - depopulation processes 142f., 148, 159
 - detectivity 232
 - detector 106f., 220ff.
 - Charge Coupled Device (CCD) 228ff.

- gamma 111
- Intensified Charge Coupled Device (ICCD) 230
- photodiode 233
- ring 106
- single-photon 245
- size 108
- thermal 229
- time-correlated
 - single-photon counting (TCSPC) 245f.
- dichroic
 - beamsplitter 245
 - mirror 247
- Dieke diagram 155, 157, 160
- dielectric constant 45f.
 - optical 23
 - static 23
- dielectric layer 62f.
- diffraction 225f., 246
 - second-order 225
- diode-pumped 136
- dipole 15f., 18
 - electric 114
 - oscillation 15f.
- direct-gap material 128
- discharge 26
 - cell 62
 - efficiency 100
 - electrodes 62
 - emission 71
 - gas 63, 70
 - low-pressure 64
 - PDP 63
 - plasma 61
 - self-sustaining 63
 - xenon 100
- discriminator 232
- dispersing element 220f., 224
- dispersion
 - angular 226
 - curve 38, 48
 - linear 226
 - relation 39
- display
 - color plasma flat-panel 100
- donor 8f., 15
- donor-acceptor pair 8ff.
- dopant 203f.
- downconversion 153, 239
 - architecture 209f.
 - emission photon 153
 - layers 207
- dynodes 231f.

e

efficiency

- conversion 2
- discharge 2
- external quantum (EQE) 194, 205
- extraction 197
- index 23
- light generation 2
- transfer 109f.
- wall-plug 194

electric field 25, 63

- strength 25

electrode

- address 63
- bus 63
- display 62f.

electroluminescence (EL) 24, 26, 197, 202

- high-voltage 24
- low-voltage 26

electroluminescent structure

- organic 26

electron

- secondary 63, 231
- storage 229

electron transporting layer (ETL) 198f.

electronegativity 79, 129

electron-electron scattering 21

electron-hole pair 22f., 43, 48, 81, 84, 109, 233

- primary 99
- secondary 99

electron-phonon coupling 6, 11

electron substitution reaction 15

electronic

- charge distributions 15
- configuration 5f., 113f.
- states 4ff.

electrophilic attack 186

emission 1, 3ff.

- band 4ff.
- color 1, 3, 27
- cooperative 135, 152
- intensity 28, 81, 95f., 115, 127, 157
- layer 200
- line 1, 28
- mechanism 10
- parity allowed 112
- pathway 157
- recombination 56
- spectrum 3, 5f., 8ff.
- spin-allowed 112
- time-delayed 11

emitter

- broad-band 18
- line 18

energy

- band gap 21f.
- barrier 114
- conservation 14
- efficiency 2f., 14, 17, 21ff.
- gap 2, 9, 23, 47, 86, 113
- gap law 138
- ionization 42
- kinetic 26, 39, 45ff.
- level diagram 75ff.
- loss 2, 29, 100
- migration 21
- separation 27, 92
- threshold 99
- transfer 6, 14, 19, 85, 143
- mechanism 12ff.
- nonradiative 134
- rate 15, 18
- two-step 96

epitaxial

- layer 179
- techniques 49

equation

- single-particle 43
- two-particle 42f.

etalon 237

excitation 1, 12

- cross-sections 143f., 153f.
- delta-type 144
- density 149, 158, 183
- elementary 45
- energy 3, 11, 156f.
- excimer laser 82
- excited state 93
- high energy 98
- intensity 144
- laser power 147
- mechanisms 1ff.
- near-infrared 143, 157, 160
- one-color 143
- one-photon 93
- optical 11f.
- pathway 160
- photon 153f.
- power 148f., 152ff.
- pulse 144f.
- radiation 150
- radiative 150
- second color 143
- sources 223
- spectrum 12f., 158
- square-wave 146
- synchrotron 82
- two-color 142f., 161

- two-photon 93
- volume 65
- wavelength 143

excited state dynamics 144

excitons 26, 45ff.

- radii 49
- self-trapped (STE) 81f., 113
- singlet 194
- triplet 194

eye-sensitivity curve 182f.

f

fan beam 107

Field Emission Displays (FEDs) 65

Flat Dynamic X-ray Detector (FDXD) 124, 126

fluorescence

- labels 56
- dopant 199

fluorescent lamp phosphors 1ff.

- compact 2
- high-quality 5f., 13, 20
- low-pressure 100

fluoride materials 76, 83, 92f.

- rare earth ion-activated 91

Forster-Dexter

- energy transfer 247
- theory 53

free induction decay (FID) 243f.

gGOS ($\text{Gd}_2\text{O}_3\text{:Pr}$) 122

grating 224ff.

- turret arrangement 226

grooves 226f.

growth axis 108

GSO ($\text{Gd}_2\text{SiO}_5\text{:Ce}$) 119**h**

Hamiltonian 45, 48

heavy-metal fluoride glasses, see ZBLAN

Heisenberg uncertainty relation 39, 241

Hg

- atoms 2
- discharge lamps 1f., 55
- plasma 83
- radiation 2

histogram method 237

hole transporting layer (HTL) 198f.

holes 9, 21f., 45

- trapped 85

host lattice 3f., 6, 12, 23, 85f.

- physical density 108
- sensitization 12
- stopping power 108

Huang-Rhys factors 4
 hydrogen atom 42f., 45
 hygroscopic 118, 155, 162

i

illumination 127
 impurity 3, 12
 –concentration 3
 incident
 –light 235
 –photons 99, 232
 incongruent melting 108
 inhomogeneities 108
 inorganic solids 105
 InP 52
 ionization 21, 63
 –impact 23, 63
 –threshold 21, 23
 Indium-Tin-Oxide (ITO) 62f., 192,
 204
 –coated glass 204
 –Fermi level 193
 InGaN 182
 inorganic materials 3, 26
 interaction
 –crystal field 27
 –dephasing 240, 243f.
 –dipolar 18f.
 –dipole-dipole 18
 –dipole-quadrupole 18, 21
 –electron-optical
 phonon 21
 –electrostatic 9, 14f., 139
 –energy 16
 –exchange 14ff.
 –higher-order 18
 –ligand field 12
 –quadrupole-quadrupole 18
 –physical 14
 –repulsive electrostatic 15
 –sensitizer-activator 76
 –spin-orbit coupling
 113f., 139
 interference
 –constructive 225ff.
 –destructive 226
 interferometers 224, 227
 –Fabri-Perot 228
 intersystem crossing 195
 intrinsic traps 122
 IR-light 12, 64
 isoelectronic
 –hole traps 129
 –impurity 128

j

Judd-Ofelt
 –intensity parameters 90f.
 –theory 28, 79, 89, 139f., 143

k

killing centers 33
 $K_2NaScF_6:Er,V$ 168

l

LaBr₃:Ce 118
 lamp
 –arc 223
 –halogen 223
 laser 235ff.
 –ablation techniques 49
 –fiber 161
 –gas 235f.
 –helium-neon (He-Ne) 235
 –mode-locked 236
 –narrow-band 243
 –pulsed 236f.
 –pump dye 235, 237
 –radiation 235
 –semiconductor diode 236f.
 –solid state 235
 –threshold 161
 –wavelength 236
 lattice
 –defects 50, 91
 –mismatch 49, 183
 –relaxation 5, 91
 –vibrational modes 113
 –vibrations 6
 LGSO ((Lu_{0.4}Gd_{1.6})SiO₅) 120
 lifetime 135f.
 –metastable level 161
 –quenching 90f.
 ligand field theory 5
 light
 –extraction 182
 –indicator 179
 –output (LO) 66
 –scattering 210
 –trapping effects 25
 –trichromatic 185
 –visible 1ff.
 –imaging 107f.

m

MgF₂:Ni 163
 MgWO₄ 8
 metal-ligand 4
 –bond distance 33, 91

Metal-Oxide-Silicon (MOS) 228f.
 –capacitor 229
 metastable
 –atoms 63f.
 –state 64
 micro channel plate (MCP) 230
 microscopy
 –fluorescence 58
 –near-field scanning optical (NSOM) 246ff.
 –total internal reflection fluorescence (TIRFM) 248
 monochromaticity 235
 monochromator 221f., 224
 monochrome display 62
 monomers 100
 multiphonon
 –emission 76
 –relaxation (MPR) 55, 79, 86, 91, 94, 97, 138
 multiphoton
 –emission 98f.

n

Nal:TI 116, 118f.
 nanocrystals
 – β -PbF₂ 171
 –Y₂O₃ 171
 –Y₂O₃:Er³⁺ 172
 nanophosphors 35
 nanoscale materials 49
 NaYF₄ 159
 NaYF₄:Er,Yb 157
 NaYF₄:Tm,Yb 160, 174
 NaYF₄:Yb, Er 173
 Near-Field Scanning Optical Microscopy (NSOM) 246ff.
 Near-Field Scanning Optical Spectroscopy (NSOS) 246f.
 Near-Infrared Radiation (NIR) 230, 233
 neon glow discharge 61f.
 nephelauxetic effect 27, 79, 83
 nitride-metal bonds 187
 noise-equivalent power (NEP) 232f.
 nonradiative
 –channels 31
 –rate constant 139
 normalization constant 37
 Nuclear Magnetic Resonance (NMR) 243
 number of states 42ff.

o

optical
 –bistability 152
 –centers 4, 8, 12, 14, 87, 242ff.
 –cycle 75
 –excitation 11f.
 –frequency 228
 –hole burning (OHB) 241 ff.
 –line shape function 15
 –mutation 242ff.
 –output power 179
 –path length 228f.
 –process 5
 –properties 35
 –selection rules 39
 –transitions 4ff.

orbitals 8, 19
 –highest occupied molecular (HOMO) 193, 201
 –lowest unoccupied molecular (LUMO) 193
 –valence 162

organic
 –chromophores 56
 –electroluminescence 191
 –fluorescent compounds 56f.
 –fluorophores 57

Organic Light Emitting Devices (OLED) 191ff.
 –applications 207
 –innovations 197
 –large area 211f.
 –layer 199
 –lighting demonstration 208, 212
 –performance 193
 –phosphorescent 200f.
 –production costs 210
 –single color 209
 –solution processed 202ff.
 –technology 207, 212
 –trends 197

ortho-phosphates 55
 ortho-silicates 185
 oscillator strength 16f., 19, 139, 156, 234
 outcoupling efficiency enhancement 210
 oxide materials 83
 oxynitride 187

p

parity
 –selection rule 50
 –forbidden 97

particle 37ff.
 –coating 185
 –high-energy 21f.

- morphology 123
- nano 43, 46, 49ff.
- non-interacting 45
- primary 22
- quasi 45
- size distribution 49, 123
- pcLED (phosphor-converted LEDs) 184ff.
- penning ionization process 63f.
- periodic boundary condition 43
- perturbation 124, 155
 - environmental 162
 - external chemical 162
 - magnetic 162
 - redox 162
- phenylene vinylene (PPV) 204f.
- phonon
 - emission 19, 25
 - energy 2, 4, 155
 - frequency 4, 23, 112f.
 - high-energy 19, 56
 - lines 10, 84
 - longitudinal optical 10
 - modes 134, 157
 - optical 23
 - state 4
- phosphor 1ff.
 - applications 29f., 65
 - blend 181, 185
 - coatings 75
 - converted LEDs 179, 183ff.
 - emission 3, 92
 - energy loss factor 29
 - green 5f, 11, 13f., 28
 - high-density 105
 - inorganic 1
 - layer 62, 183f.
 - lifetime 31, 184
 - long afterglow 11f.
 - multi photon-emitting 75
 - quantum-splitting (QSPs) 75ff.
 - storage 124, 127
 - upconversion 133ff.
 - white 13
- photocathodes 115, 231f.
- photochemical stability 183
- photoconductivity 110, 117
- photodiodes 105, 107, 111, 121, 124, 220, 233
 - avalanche (APDs) 233
- photo fraction 118
- photographic film 123
- photoionization 32, 110, 113
- photoluminescence 52f., 66
 - efficiency 194
- photomultiplier tubes (PMTs) 105, 115, 118, 220, 230ff.
 - signal-noise properties 232
- photon
 - absorption 45
 - antibunching 245
 - avalanche effects 150ff.
 - cascade process 75
 - echo 242, 244f.
 - emission 76, 79, 90, 153
 - energy 9ff.
 - flux 154
 - γ - 106, 111f.
 - high-energy 21, 76, 99, 111
 - infrared 64, 89, 154
 - upconversion 133, 157
 - yield 112
- photophysical
 - characteristics 162
 - properties 162
- photosensitive devices 105
- Plasma Display Panels (PDPs) 1, 5, 29, 61 ff.
 - AC- 62, 64
 - application 66
 - operation 61
 - problem areas 65
- plasma firing voltage 64
- plastic substrates 207
- polarization 227, 235
- polyfluorene 205
- polymer 193, 202f.
 - conjugated 203f.
- polyvinyl carbazole (PVK) 202ff.
- population
 - density 146ff.
 - frequency 244
- Positron Emission Tomography (PET) 105ff.
 - application 107, 117f.
 - modality 118
 - physical principles 106
 - time-of-flight (TOF) 111, 113, 118
- potential
 - barrier 88
 - one-dimensional 35
 - symmetric 40
 - three-dimensional 40
 - well 36, 39ff.
- PtOEP (platinum porphyrin) 200
- pulse-height analyzer 237
- pulse widths 236f.
- pulsed mode 235

q

- quadruples 18
- quantum
 - dots 35, 43, 46ff.
 - cutters 28
 - efficiency (QE) 17f., 28ff.
 - number 37, 40f., 47, 139
 - angular momentum 139
 - magnetic 40
 - orbital 40, 48, 139
 - principal 40
 - size effects 49
 - splitting systems 75ff.
 - well 41, 46
 - wire 46
 - yield processes 29, 32, 55, 89ff.
- quenching 182
 - processes 29, 87f.

r

- Rabi
 - frequency 244
 - oscillation 244
- radiant sensitivity 231ff.
- radiation 64
 - collimated 223
 - damage 120f.
 - dimer 64
 - electromagnetic 219f., 223
 - excitation 134
 - harmful 108
 - incident 97
 - intra-ionic 113
 - ionizing 111
 - laser 219
 - monochromatic 235
 - synchrotron 84, 99, 224, 237
- radiative
 - lifetime 16, 79, 87
 - recombination rate 10
 - relaxation 93
- rare-earth ions 3, 5f., 8, 112, 155
 - mixed 165
- rare-earth phosphors 55
- rate equations 144
- recombination 26, 81f., 99, 127
 - center 128
 - donor-acceptor 127
- reflectance 67, 97
- reflection
 - coefficients 227
 - multiple internal 181, 227
 - spectroscopy 34
 - total internal (TIR) 181, 247

- reflectivity 66
- refractive index 112f., 139, 154, 181, 228
- relaxation
 - energy 4
 - multiphonon 154ff.
 - nonradiative 96ff.
 - process 86, 94
 - rate constant 147
- resolution 226
 - energy 108, 111, 117f.
 - spatial 106, 108, 123f., 127
 - timing 108, 110, 113, 116ff.
- resonance frequency 228f.
- Robbins equation 109
- Rydberg
 - constant 42
 - energy 48

s

- scanning
 - laser beam 127
 - monochromator 221
- Schrödinger equation 36, 42
- scintillating
 - composition 114, 120ff.
 - crystals 114
 - emission efficiency 110
 - materials 105ff.
- scintillation
 - decay 120
 - process 108, 110
- scintillator 1f., 12, 105ff.
 - application 105f.
 - band gap 109
 - ceramic 107f., 121f.
 - commercial 129
 - crystals 106
 - density 115f., 120
 - Hi-Light 121
 - physics 22
 - properties 116f., 121
 - semiconductor 127
- second harmonic generation (SHG) 134ff.
- self-absorption 33
- self-activated 8
- self-quenching 162
- self-trapped excitons (STE) 81f., 113
- semi-conducting 8, 24, 46
- semiconductors 2f., 128, 179, 183
- sensitization
 - cooperative 134f.
 - direct 98
- sensitizer ions 3, 12ff.
- series architecture 211

- sharpness 123
 - silicon 134
 - diodes 105
 - single crystal 107, 112, 114
 - growth 108
 - singlet-triplet ratio 196
 - sol-gel chemistry 56
 - solid state 40
 - solution-deposited organic films 202
 - solvothermal synthesis 56
 - space group 85
 - spectral
 - diffusion 245
 - distribution curves 223
 - match 112
 - overlap 14f., 17, 19, 81, 92
 - positions 3, 28
 - range 28, 156f.
 - sensitivity 115
 - width 4
 - spectrum 4f.
 - discrete 48
 - reflection 31
 - spectroscopic properties 43, 82f
 - spectroscopic techniques 220ff.
 - absorption 139, 220ff.
 - calorimetric absorption (CAS) 239
 - diffuse reflection 220f.
 - emission 220ff.
 - excitation 139f., 142, 220ff.
 - diffuse reflection 222
 - near-field scanning optical (NSOS) 246f.
 - photothermal deflection 240
 - polarization-dependent 224
 - Raman 133
 - single-molecule 245f.
 - time-resolved 224
 - total internal reflection (TIR) 247
 - spin 5f., 18
 - forbidden 97
 - selection rule 65
 - state
 - electronic 27f.
 - excited 4f., 10, 31f., 75
 - excimer 65
 - final 112
 - ground 4f., 10, 31f., 75
 - host lattice 24f.
 - initial 112
 - localized 24
 - multiplet 158
 - statistical limit 196
 - Stokes shift 5, 21, 25f., 29, 32, 88, 115f., 119, 238
 - emission 129
 - Stranski-Krastanow 49
 - structures
 - energy level 155
 - low-dimensional 43, 46
 - sum-frequency mixing 135
 - surface
 - quenching 56
 - recombination velocity 179
 - surfactant-templated-assisted 85
 - symmetry 5, 28, 87
 - inversion 28, 69
 - properties 90
 - site 85
 - system
 - zero-dimensional 44, 46
- t**
- TAG:Ce (Tb₃Al₅O₁₂:Ce) 187
 - thermal
 - activated trapping 128
 - excitation 11
 - expansion 5
 - quenching 5, 32, 128, 185, 189
 - stability 183
 - throughput 226f.
 - time-of-flight (TOF) 111, 113, 118
 - Positron Emission Tomography 105ff.
 - total internal reflection(TIR) 181, 247
 - transition 4ff.
 - absorption 81, 94, 139, 234
 - charge transfer 123
 - d → d 5f.
 - d → f 5f., 8, 27
 - dipole moment 233
 - electric dipole 28, 68, 121
 - electronic 68
 - emission 92
 - excitonic 48
 - f → f 5
 - interband Auger 99
 - interconfigurational 82, 87, 97
 - intra-band 21
 - intra-excited state 154, 160
 - magnetic dipole 28, 68, 234
 - metal ions 162
 - multiphonon 161
 - nonradiative 31, 33, 55, 79, 153
 - parity 114
 - probabilities 78f.
 - radiative 16, 31, 69, 78f., 89

- rate 31
- spin-allowed 18, 114
- spin-flip 6
- spin-forbidden 65
- vertical 45
- transition metal ions 5, 27
- transmittance 152, 235
- transparency 107, 121
- two-photon absorption (TPA) 134

u

- ultraviolet (UV) 1, 12, 14, 27f.
 - converter 55
 - excitation 3
 - LEDs 12
 - photon 2, 76f.
 - spectrum range 136
 - vacuum (VUV) 62, 64ff.
- upconversion (UC) 136ff.
 - avalanche effects 138, 151f., 162
 - compounds 155
 - efficiency 153, 160
 - emission 140ff.
 - energy transfer 136ff.
 - excitation schemes 137
 - fiber lasers 161
 - laser 137, 161
 - laser emission 161
 - luminescence 155
 - material 136, 162
 - mechanism 142f., 160
 - nanocrystalline 171
 - organic 169
 - power dependence 146
 - properties 155
 - rate constant 147
 - sensitized 158
 - spectroscopy 155
 - state 151f.
 - theory 137
 - time evolution 143
 - transition metal-doped 162, 165
 - two-photon 136
- upconverters
 - nanoscale 136
 - rare-earth 155
 - transition metal 162

v

- van-der-Waals radii 19

- vanadates 55
- vapor-deposited organic films 197, 202, 214
- vapor-processed devices 198
- vibrational mode 10, 139, 238
- vibronic lattice states 11
- Volmer Weber 49

w

- wall losses 2
- wave functions 36f., 41, 43
 - final state 15
 - initial state 15
- wave number 69, 139
- wave vector 36
- wavelength
 - blaze 226
 - dispersion 227
 - emission 69, 111f., 117, 119, 160, 182
 - excitation 66, 70f., 161, 246
 - resolved emission 29
 - second pump 161
 - selectivity 227
- weak coupling case 138
- wet chemical precipitation method 49, 52
- white light generation 209

x

- X-ray 8, 21, 105, 107, 123f.
 - absorption 123
 - detectors 124
 - image 123
 - intensifying screens 123, 125
 - irradiation 124, 127
 - photons 2f.
 - secondary 21
 - tube 107

y

- YAG: Ce LEDs 184, 187f., 210
- YbPO₄ 173
- (Y,Gd)₃Al₅O₁₂:Ce(YAG:Ce) 184, 210
- (Y,Gd)₂O₃:Eu 121
- Y₃Gd₅O₁₂:Yb,Cr 166
- YVO₄:Er,Cr 168

z

- ZBLAN 161
- zero phonon line 4, 10
- ZnO 50
- Zn₂SiO₄:Yb,Mn 166