# Luminescence of Phosphors

Robert Withnall and Jack Silver

## Contents

**Abstract**

This chapter introduces the subject of luminescence in inorganic materials and the physical mechanisms that are responsible for the light-emitting behavior of fluorescent and phosphorescent phosphors, including Stokes (and anti-Stokes) emission, spontaneous emission, electric dipole transitions, oscillator strength, and emission lifetimes.

**List of Abbreviations**

| | |
|---|---|
| CL | Cathodoluminescence |
| CRT | Cathode ray tube |
| EL | Electroluminescence |
| LED | Light-emitting diode |
| OLED | Organic light-emitting diode |
| PL | Photoluminescence |

---

R. Withnall (✉) • J. Silver
Wolfson Centre for Materials Processing, Brunel University London, Uxbridge, Middlesex, UK
e-mail: jack.silver@brunel.ac.uk

J. Chen et al. (eds.), *Handbook of Visual Display Technology*,
DOI 10.1007/978-3-319-14346-0_67

## Introduction

Luminescence can be defined as the conversion of energy into visible (or near-visible) light by nonincandescent sources. It can be induced by electron impact, electromagnetic radiation, chemical, electrical, or physiological excitation, as well as friction and thermal stimulation, and it is distinct from incandescence, which is broadband light emission from thermally excited blackbodies.

The emitted light arises from electronic transitions between discrete stationary states of luminescent centers or, in the case of extended electronic state solids having delocalized electrons, between electronic bands. In this section, we discuss the physics of luminescence in phosphors and how this relates to display applications. The specific case of rare-earth phosphors is discussed in detail in the chapter "▶ Physics of Light Emission from Rare Earth-Doped Phosphors".

## Phosphors

A phosphor can be defined as a solid material that manifests luminescence following the absorption of energy from an external source. Light emission from a material during the time it is exposed to exciting radiation (or other energy source) is referred to as fluorescence, in contrast to where the emission (afterglow) is detectable after the end of the excitation, which is called phosphorescence (which could be up to several hours).

It is important to highlight that these are definitions as used for inorganic materials, whereas the terminology has specific meaning related to organic molecules in organic light-emitting diode (OLED) technology. For organic compounds, fluorescence is used to describe light emission from a singlet state, and phosphorescence refers to emission from a triplet state (chapter "▶ Organic Light-Emitting Diodes (OLEDs)"). In display technology, the constraints on energy provision for phosphors are as follows:

- Photons – Photoluminescence
- An electric field – Electroluminescence
- Cathode rays – Cathodoluminescence

Other kinds of luminescence include chemiluminescence, thermoluminescence, and triboluminescence.

Electroluminescence is the phenomenon of light emission as a result of the application of an external electric field to a special kind of phosphor (i.e., an electroluminescent (EL) phosphor). EL phosphors are specially designed to respond to such a field. The term *EL* is also used to describe the light emission produced by low-field, injection, or recombination luminescence, which is covered in the chapter "▶ Light-Emitting Diodes: Fundamentals" on light-emitting diodes.

**Table 1** Example ZnS phosphors

| | Co-activator ion | | |
|---|---|---|---|
| Activator ion | (Donor) | (Acceptor) | Quencher ion (Luminescence killer) |
| Ag | Cl | Al | Fe |
| Cu | Br | Sc | Co |
| Au | I | Ga | Ni |
| Mn | | In | |

*Cathodoluminescence* is the term used to describe emission from a solid phosphor that is excited by electron beams. In cathode ray tubes (CRTs), the electrons can be focused into a beam that can be raster scanned across the screen. The application of cathodoluminescence to CRTs is discussed in the chapter "▶ Cathode Ray Tubes (CRTs)."

Phosphors essentially consist of very pure inorganic materials doped with suitable ions called activators. The activator is usually present in concentration levels varying from a few parts per million to 1–5 % of the host lattice. Often, additional ions act as charge compensators or donors in the lattice. These are termed coactivators. An example of the combination of activator, coactivator, and quenching ions that determine the properties of a ZnS host lattice phosphor is given in Table 1.

## Stokes and Anti-Stokes Luminescence

To understand all the processes that are usually included under the general heading of Luminescence, it is first necessary to appreciate how photons interact with solid-state lattices.

Thus, in Stokes luminescence, higher energy (could be a photon or energetic electron) is absorbed in some form, and then there is an emission at lower energy of a photon. The emission is due to an electronic transition from an upper excited state to the ground state or lower-energy excited state. The excitation may be due to the absorption of energy from an external source (examples of such sources include high-energy particles, other electrons, photons, or even external electric fields), or else it could be due to energy transfer within the phosphor sample. This process takes place in the solid often on a dopant atom (cation), and this atom is referred to as the activator and its location as an active center. In such a case, the excess energy that was absorbed by the solid is converted to lattice vibrational energy (heat).

If instead of Stokes luminescence, two or more photons excite the same activator center, then the emission can occur at higher energy than that of the exciting photons; this is referred to as upconversion, which is an anti-Stokes process. The kinetics of the latter process exhibit a nonlinear dependence of the emission intensity on the exciting power density.

## Spontaneous Emission of a Two-Level System

We consider two levels coupled by an electric dipole-allowed transition. In addition to stimulated emission, which occurs at a rate that is proportional to the density of radiation at the transition frequency, Einstein found that a spontaneous emission process must occur at the transition frequency in order to obtain thermal equilibrium in the radiation field (Einstein 1917). The spontaneous radiative decay rate coefficient, $A_{21}$, is the inverse of the natural radiative lifetime (i.e., the 1/e emission lifetime, $\tau$), and it can be deduced that the emission lifetime can be determined from the absorption coefficient, $B_{12}$, according to Eq. 1 (Steinfeld 1986):

$$A_{21} = \frac{1}{\tau} = \frac{8\pi h v_{21}^{3}}{c^{3}} \frac{g_1}{g_2} B_{12} \tag{1}$$

where $h$ is Planck's constant, $c$ is the velocity of light, $\nu_{21}$ is the transition frequency, and $g_1$ and $g_2$ are the degeneracies of the lower and upper levels.

Thus, it can be seen from (Eq. 1) that the spontaneous emission rate increases as the transition frequency, $\nu_{21}$, increases. It should be noted that spontaneous emission is a random process and obeys first-order kinetics.

## Electric Dipole Transitions

Strong absorption and emission are due to electronic transitions that are electric dipole in type. For the case of absorption, the oscillating electric field of the incident light beam induces an oscillating dipole in the molecule, and when this corresponds to a natural frequency of the molecule, resonance occurs and the molecule gains energy from the light wave. For the case of spontaneous emission, it can be viewed that the emission is stimulated by zero-point fluctuations in the vacuum electromagnetic field, which induce an oscillating dipole in the molecule causing it to lose energy to the surrounding field. For both the aforementioned absorption and emission cases, the processes are electric dipole allowed. Such electric dipole-allowed transitions occur for s-p, p-d, and d-f transitions, but s-d, p-p, d-d, and f-f transitions are electric dipole forbidden according to the so-called parity or orbital selection rule.

## Oscillator Strength

The oscillator strength, $f_{21}$, is useful for specifying the intensity of a transition and is directly proportional to the spontaneous radiative decay rate coefficient, $A_{21}$, as can be seen from Eq. 2 (Steinfeld 1986):

$$\mathrm{f}_{21} = \frac{mc^3}{8\pi^2\nu_{21}^2 e^2}\frac{\mathrm{g}_2}{\mathrm{g}_1}\mathrm{A}_{21} \tag{2}$$

where $m$ is the mass of an electron, $e$ is the electronic charge, $c$ is the velocity of light, and $\mathrm{g}_2$ and $\mathrm{g}_1$ are the degeneracies of the upper and lower levels.

The oscillator strength links the quantum theory of emission and absorption of radiation to the classical theory, and it is observed that f is close to unity for electric dipole-allowed transitions and f is very much less than unity for forbidden transitions.

## Emission Lifetimes

For the aforementioned two-level system, the emission rate is given by Eq. 3:

$$I_{\mathrm{em}} = -\frac{\mathrm{d}N_2}{\mathrm{d}t} = \mathrm{A}_{21}N_2 \tag{3}$$

where $\mathrm{N}_2$ is the number of emitters populating level 2 at time $t$ and $\mathrm{A}_{21}$ is the spontaneous emission rate coefficient.

Integration gives

$$N(t) = N(0)\exp(-\mathrm{A}_{21}t)$$

and since the emission intensity is proportional to the number of emitters at any given time,

$$I(t) = I(0)\exp(-\mathrm{A}_{21}t)$$

Substituting the emission lifetime $\tau = 1/\mathrm{A}_{21}$ gives

$$I(t) = I(0)\exp(-t/\tau)$$

Thus, after a time $t$ equal to $\tau$, the emission intensity has decreased to 1/e (=0.368) of its value at $t = 0$ (see Fig. 1). Consequently, $\tau$ is referred to as the 1/e emission lifetime.

*Luminescence* is a general term for an emission process that does not distinguish the magnitude of the emission lifetime, but *fluorescence* and *phosphorescence* are more specific terms.

Fluorescence is a spin-allowed ($\Delta\mathrm{S} = 0$) emission process that occurs on a relatively fast timescale (1/e emission lifetime < ca. 1 μs) due to the relatively high oscillator strength of the electronic transition that gives rise to the emission.

Conversely, phosphorescence is a spin-forbidden ($\Delta\mathrm{S} \neq 0$) emission process that occurs on a relatively slow timescale (1/e emission lifetime > ca. 1 μs) due to the

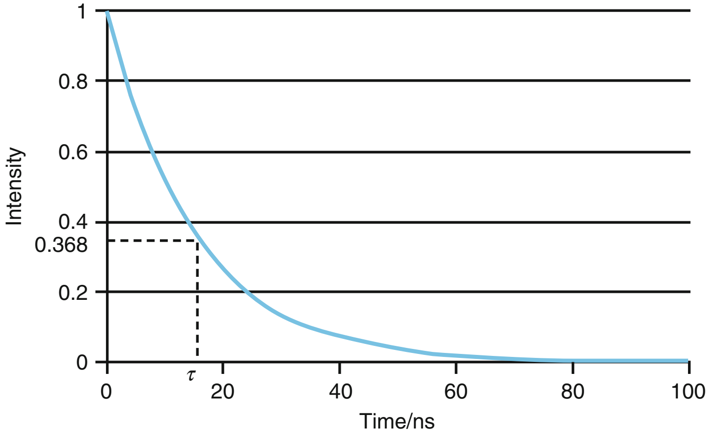

**Fig. 1** A plot of spontaneous emission intensity versus time showing the 1/e emission lifetime, τ

relatively low oscillator strength of the electronic transition that gives rise to the emission.

Typical 1/e emission lifetimes of activator ions in seconds are as follows:

- $$Mn^{2+}(3d \rightarrow 3d) \sim 10^{-2}$$
- $$Cu^{+}(4s \rightarrow 3d) \sim 10^{-3} - 10^{-4}$$
- $$Ag^{+}(5s \rightarrow 4d) \sim 10^{-6} - 10^{-5}$$
- $$Eu^{3+}(4f \rightarrow 4f) \sim 10^{-4} - 10^{-2}$$
- $$Tb^{3+}(4f \rightarrow 4f) \sim 10^{-4} - 10^{-2}$$
- $$Ce^{3+}(5d \rightarrow 4f) \sim 3 \times 10^{-8}$$
- $$Eu^{2+}(5d \rightarrow 4f) \sim 8 \times 10^{-7}$$

## Conclusion/Summary

The principles of luminescence in inorganic materials have been discussed, outlining the primary mechanisms that affect the energy conversion and light-emitting properties of phosphors for use in displays and other visible light-emitting applications. A more detailed discussion of the physics of rare-earth phosphors is given in the chapter "▶ Physics of Light Emission from Rare Earth-Doped Phosphors", with an outline of the chemistry and synthesis of phosphor materials provided in the chapter "▶ Chemistry and Synthesis of Inorganic Light-Emitting Phosphors".

## Further Reading

Blasse G, Grabmeier BC (1994) Luminescent materials. Springer, Berlin
Einstein A (1917) Zur Quantentheorie der Strahlung. Phys Z 18:121
Kitai AH (ed) (1993) Solid state luminescence. Chapman & Hall, London
Kitai AH (ed) (2008) Luminescent materials. Wiley, Chichester
Nakazawa E (2007) Fundamentals of luminescence, Chapter 2. In: Phosphor handbook, 2nd edn. CRC Press, Boca Raton
Ronda C (ed) (2008) Luminescence. Wiley VCH, Weinheim
Steinfeld JI (1986) An introduction to modern molecular spectroscopy, 2nd edn. MIT Press, Cambridge