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Long Afterglow Phosphorescent Materials

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Contents

Chapter 1
Fundamentals of Luminescent Materials

1.1 Fundamentals of Luminescence

Luminescent materials have attracted tremendous research interest due to their widespread applications, ranging from lamps for home use to radars in civil defense. Inorganic luminescent materials usually feature a crystalline host and encapsulated dopants serving as light-emitting centers. Taking the commercialized white-light-emitting diodes (WLEDs) for instance [1], $Y_3Al_5O_{12}$ is generally used as the host while a small amount of Ce^{3+} dopants serves as the luminescent centers. These luminescent materials can be utilized for frequency conversion, as evidenced in $Y_3Al_5O_{12}:Ce^{3+}$ phosphors capable of turning blue irradiation into yellow emission.

A recent development in the luminescent materials field is the emergence of lanthanide-doped luminescent inorganic nanoparticles (NPs) as a new generation of bioprobes, relative to conventional molecular probes (i.e., organic dyes and lanthanide chelates). Particularly, significant progress has recently been achieved for up-conversion nanoparticles (UCNPs) in tumor biomarker detection and imaging, due to their superior physicochemical features such as long lifetime luminescence, large anti-Stokes shifts, narrow emission bands, high resistance to photobleaching, and low toxicity [2, 3]. Herein, up-conversion (UC) describes a nonlinear optical process, in which low-energy photons (usually NIR radiation, i.e., 980 nm) are used to generate high-energy photons (visible and UV light). Remarkably, UCNPs possess further inherent merits, i.e., NIR light penetrates deeper in tissues, and avoids the problem of autofluorescence and a light scattering background [3]. However, up-conversion luminescence relies strictly on high power coherent excitation, e.g., laser sources, and the NIR laser may create a heating effect at high input laser power.

Persistent luminescent materials or phosphors feature long-lasting emission up to several days after the removal of the excitation sources (usually UV and X-rays). Over the past 20 years, persistent phosphors have been widely used in commercial products, including luminous paints, watch dials, fire safety signs, and glow-in-the-dark toys [4]. Recently, there is a growing interest in developing persistent

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nanophosphors with near-infrared (NIR) emission for optical imaging in vivo [5]. The persistent luminescence nature of these nanomaterials allows us to achieve real-time imaging without external excitation, rendering low autofluorescence and subsequently high signal-to-noise ratio (SNR). More importantly, the emission range from red to NIR is particularly suitable for bioimaging application because it falls within the well-known “optical transparency window” (700–1100 nm), thus resulting in a significant reduction in the photodamage [6].

In this chapter, the underlying mechanism of luminescence involving photon absorption and emission processes is first described. We then place our emphasis on the discussion of emission features of inorganic persistent phosphors. The influence of defects and impurities on the properties of persistent luminescence is subsequently followed.

When an optical material is irradiated under a light source, five types of optical process could occur, namely light reflection, refraction, scattering, absorption, and emission. In this section, the excitation and emission processes governing the luminescence phenomenon and the transfer of excitation energy within a given phosphor system will be introduced.

1.1.1 Absorption

The event of absorption occurs when the energy of incident light matches well with the energy gap of two energy states of the optical materials. During this process, the intensity of incident light will be attenuated, and a fraction of the photons with lower energy could be emitted, giving rise to the occurrence of luminescence. Concurrently, the other portion of the absorbed photons is dissipated through non-radiative processes.

For a simple system with two energy levels, the electron could be excited from the ground state (E_1) to an excited state (E_2) after absorbing incident photons with appropriate energy. The photon energy and the energy difference between E_2 and E_1 states must obey the following equation:

$$h\nu = E_2 - E_1 \tag{1.1}$$

where h is the Planck’s constant, and ν is the frequency of the photon.

1.1.2 Emission

Luminescence is a photodynamic process where the excited electrons return to their ground state along with a spontaneous emission of photons. It can be considered as an inversed process of absorption, despite not being always occurring upon excitation. Luminescence is a kind of cold body radiation that differs from incandescence arising from a heat-mediated process. Based on the types of excitation source, luminescence can be divided into several categories such as photoluminescence upon an electromagnetic radiation (usually ultraviolet), cathodoluminescence excited by a beam of energetic electrons, and electroluminescence after stimulation of an electric voltage. It should be noted that thermoluminescence is a re-emission phenomenon, characterized by the release of accumulated energies upon heating, irrespective of the excitation source [7].

Photoluminescence is a light-emitting process from a given luminescent material after the absorption of electromagnetic radiation. Such a photodynamic process is associated with optical transitions of electrons between different electronic energy states. For example, electrons are pumped into higher electronic energy states (excited states) after photon absorption, followed by an emission of photons when the electrons return to lower energy states. Note that the optical transition probability largely depends on the selection rules of quantum mechanics such as Laporte rule. Given the existence of non-radiative decay channels, not all materials have radiative emission on excitation. Specifically, the electrons in the excited electronic states can relax back to their ground states through non-radiative channels where the excitation energy is dissipated by thermal processes instead of being converted into photons. Apparently, to enhance the luminescence efficiency of a given material, the most straightforward strategy is to effectively suppress those non-radiative processes.

1.1.2.1 Pure Electronic Transitions

In a given phosphor containing a single emitting center (activator), the photoluminescence efficiency is mainly determined by the distance between two neighboring activators and the absorption cross-section of the activators. Moreover, non-radiative relaxation between electronic states is another important factor that determines the efficiency of the photoluminescence process. In addition to the general factors as described above, there are specific conditions that need to be taken into account. For instance, a minimized energy difference between each excited state and its lower-lying intermediate state could largely facilitate photon absorption and energy transfer during up-conversion photoluminescence processes. However, such singly doped activator usually cannot meet all the requirements, thus leading to the development of multiply doped strategy. The typical photoluminescence processes in the framework of sensitizer–activator pairs can also be depicted schematically in terms of photon absorption, energy transfer, radiative emission, and non-radiative relaxation, as shown in Fig. 1.1. Instead of being excited directly, the activators usually receive the pumping energy transferred from the sensitizers which should have a sufficient absorption cross-section for achieving enhanced photoluminescence efficiency. As an additional benefit, multiply doped approach can also be utilized as an effective tool for the discovery of new types of emitting ions by taking the advantages in the optical transition resonance between the sensitizers and the activators. Förster and Dexter energy transfers are the two main mechanisms underlying the

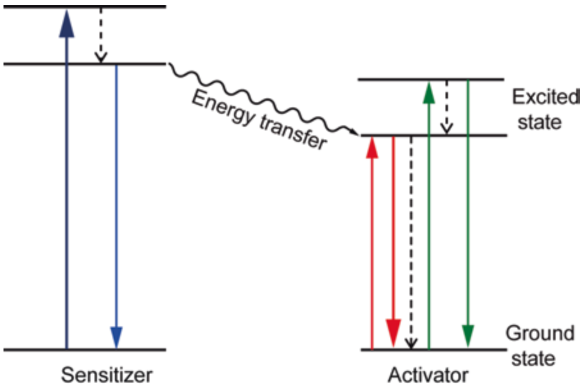

Fig. 1.1 Photoluminescence process in a given system containing sensitizer–activator pairs. The *upward-solid*, *downward-solid*, *downward-dotted*, and *curved solid arrows* represent photon excitation, radiative emission, non-radiative relaxation, and energy transfer processes, respectively

energy transfer process in doped systems. Note that the sensitizers may emit photons upon excitation in some particular cases.

1.1.2.2 Franck–Condon Principle

Vibronic transitions involving simultaneous changes in electronic energy states and vibrational energy states of a given molecule can occur when the molecule absorbs or emits photons with appropriate energies. The intensities of the vibronic transitions can be depicted by Franck–Condon principle under which the nuclear configuration of molecule seldom changes during an electronic transition. Given the large mass of the nucleus relative to the electron, it is a general consensus that the electronic transition occurs much faster than the time required for the nucleus to rearrange into a new configuration. The principle also states that the nucleus must vibrate to adopt the new electronic configuration. According to the quantum mechanical perspective of this principle, one can approximately estimate the intensity of a vibronic transition by correlating the square of the overlap integral of vibrational wavefunctions between the two states involved in the transition.

As illustrated in Fig. 1.2, the Franck–Condon principle for vibronic transitions in a molecule can be best described using Morse-like potential energy functions in both the ground and excited electronic states. This diagram shows a correlation between the energy of two electronic states of a vibronic system and the configuration coordinate q. When the system reaches a particular excited state upon irradiation, the newly formed electron configuration would result in a shift in the equilibrium position of the ground state (q_{01} as shown in Fig. 1.2). Given the extremely fast electronic transition processes, the molecule could move to a new vibrational state only when it was placed in close proximity to the nuclear and the momentum of the vibrational state is in the original electronic state. The vibronic transition is represented by a vertical arrow because nuclear coordinates are assumed as constant during the transition. Here, the probability of finding the molecule at any particular vibrational energy level is proportional to the square of the vibrational

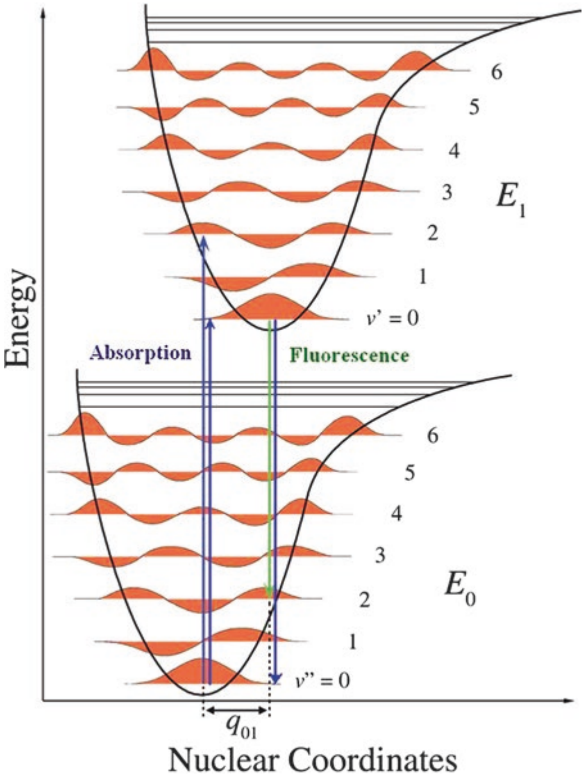

Fig. 1.2 Franck–Condon principle energy diagram. E_0 and E_1 correspond to the ground-state and excited-state energy, respectively. ν'' and ν' represent vibrational levels at the ground and excited states, respectively. The diagram indicates favored vibronic transitions between $\nu = 0$ and $\nu = 2$. Adapted from https://en.wikipedia.org/wiki/Franck%E2%80%93Condon_principle

wavefunctions overlap between the original and final states. According to Kasha's rule, molecules at the excited state can quickly relax to the lowest vibrational energy level, followed by radiative decay to the lowest electronic level via photon emission. Therefore, the emission generally occurs at a lower energy (longer wavelength) than absorption, and such an energy mismatch is recognized as Stokes shift. Note that electronic transitions to and from the lowest vibrational energy levels are often defined as 0–0 transitions (zero phonon line), featuring the same energies in absorption and emission processes.

For a doped solid phosphor consisting of luminescent centers and an inorganic crystalline host material, a strong coupling between the electrons and the phonons may occur, resulting in continuous vibronic bands. In such situation, optical transitions to higher electronic states can take place by absorbing the pure energies originating from the electronic transition or from the combination of the electronic transition and the phonon-based vibrational transition. In principle, the absorption and emission bands for a particular vibrational mode of the solid lattice are composed of a series of discrete lines, which are similar to those observed in molecules. Each line corresponds to the generation of a specific number of phonons. However, in practice, the electronic states can couple to many different phonon modes covering a whole range of frequencies, thus giving rise to the spectra in the form of continuous bands [8].

1.1.3 Afterglow

Persistent luminescence, also known as long-lasting phosphorescence or afterglow, is a special optical phenomenon characterized by the ability of some materials to emit light even after the end of external light stimulation. This phenomenon could be traced back to ancient Chinese paintings [9] and it was firstly documented for Bologna Stone at the beginning of the seventeenth century [10]. Copper-doped zinc sulfide ($ZnS:Cu^{2+}$) has dominated the market as the first commercially available persistent phosphor, including luminous paints and watch dials alongside with glow-in-the-dark toys [4]. Inspired by the pioneering work of Matsuzawa et al. on $SrAl_2O_4:Eu^{2+},Dy^{3+}$, research interest on long afterglow phosphors has been placed on lanthanide-activated inorganic materials since the end of the twentieth century [11]. In the past few years, NIR-emitting persistent phosphors doped with transition metals have attracted much attention because these materials in the form of nanoparticles have proven effective as luminescent probes for real-time, high sensitivity optical imaging in living animals [5].

Despite the complex mechanisms, it is well known that the process of persistent luminescence involves three key steps, namely ionization, transportation, and liberation (Fig. 1.3). Ionization refers to the process where charge carriers (electrons and holes) are generated upon photon irradiation. The charge carriers can be subsequently trapped at impurity levels, which can be considered as energy reservoirs. Note that the impurity levels could trap free charge carriers either by quantum tunneling or through conduction band-mediated channels. Upon appropriate stimulations, those trapped charge carriers can be gradually released as photons responsible for the observed persistent luminescence.

It is generally accepted that electrons are the main charge carriers. To effectively trap electrons, the most efficient way is to transport the electrons to the trapping center through the conduction band of a host. In principle, the electrons can be transported to the host's conduction band through any of the following channels: (1) directly excited to the conduction band from their ground state upon irradiation, (2) pumped to the emitter's excited states above the conduction band, and (3) energy jumping from the gap states to the conduction band with the assistance of thermal fluctuation [12]. For ultra-long persistent luminescence, the electron trapping is likely due to quantum tunneling. The trapping centers could be in various forms, including codopant, cation or anion vacancy, and antisite defect.

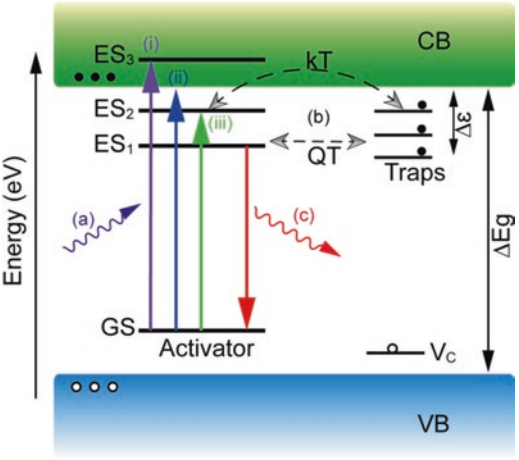

Fig. 1.3 Schematic diagram of the process of persistent luminescence. CB and VB stand for the conduction band and the valence band of the host, respectively. GS and ES indicate the ground state and excited state of the luminescent system, respectively. ΔE_g is the bandgap of the host material, $\Delta\varepsilon$ is the trapping depth of the impurity level, T is the temperature, k is the Boltzmann constant, and QT is the abbreviation of Quantum Tunnelling. Steps (*a*), (*b*), and (*c*) represent the absorption, electron trapping, and emission processes. The *upward* and *downward arrows* represent photon excitation and emission processes, respectively

1.2 Inorganic Afterglow Phosphors

As mentioned in Sect. 1.1.3, the influence of both host lattices and activators plays an important role in determining the persistent luminescence mechanism or regulating luminescence features. In this section, the band structure of inorganic hosts and the energy levels of typical afterglow emitters as well as the influence of defects and impurities on the persistent luminescence are presented.

1.2.1 Band Structure of Inorganic Host

The landscape of main energy levels in a solid is the band structure. Similar to insulators, semiconductors have few electrons that are able to gain enough thermal energy to leap across the bandgap at room temperature. The smaller bandgap of the semiconductors, however, allows for their electrical properties to be tuned by many other means in addition to temperature. When a radiation strikes a piece of semiconductor, it may excite an electron out of its valence band to the conduction band and consequently leave a hole in the valence band. This process is called electron–hole pair generation. Electron–hole pairs are also subject to recombination. The event of recombination is accompanied either by photon radiation or thermal emission in the form of phonons [8].

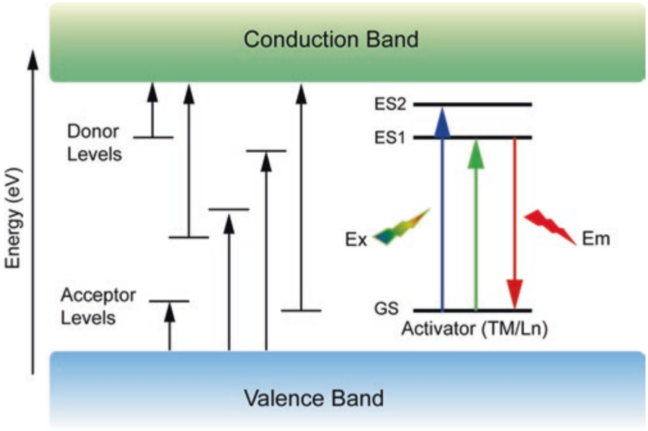

Fig. 1.4 Proposed electronic transitions in a solid containing defects. The transitions involving transition metal (TM) ions occur within d orbitals, while the optical transitions based on lanthanide (Ln) dopants proceed within *f* orbitals

In practice, the band architecture is rather complex due to the existence of defects. The probability of recombination may be increased by defect-induced carrier traps. Such carrier traps are often purposely added by introducing impurities, in a process known as doping. The amount of the dopant added to an intrinsic semiconductor can modulate the electronic structure of the semiconductor. The defect levels in relation to the dopants within the bandgap could be referred to electron acceptors or donors (Fig. 1.4). A donor atom contributes its weakly bound valence electrons to the material, producing excess carriers with negative charge. The donor atom introduces energy levels under, but very close to the conduction band minimum. Conversely, an acceptor creates a hole, which results in energy states near the valence band maximum. Those energy levels close to the band edges are defined as shallow levels, while those levels located at the center of the bandgap are deep levels.

The electronic transitions may take place directly between the valence and conduction bands, without the involvement of defect levels in the generation and recombination of electron–hole pairs. In addition, the electron may transit between the host band and defect levels, depending on the nature of the levels being deep or shallow. Transitions from shallow energy levels to a nearby host band tend to emit infrared radiation, while transitions involving deep defect levels are likely to generate high-energy emission in the ultraviolet region. Furthermore, transitions can also occur within defect levels without the participation of the valence or conduction bands (Fig. 1.4). For instance, when transition metal ions or lanthanide ions are doped into oxide crystals, they can provide a new set of energy states within the wide bandgap of the oxides (Fig. 1.4). Electron transitions may occur within the *d*-manifolds (*d*-*d* transitions) for transition metal dopants or the f-manifolds (f-f transitions) for lanthanide dopants.