

Chapter 2

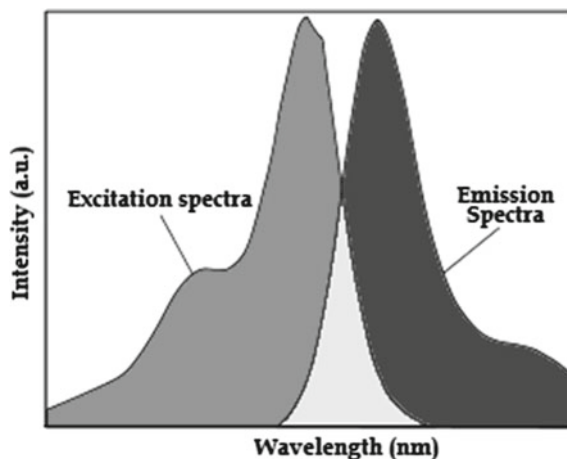
Basic Mechanisms of Photoluminescence

The phenomena which involve absorption of energy and subsequent emission of light are classified generically under the term luminescence. Phosphors are luminescent materials that emit light when excited by radiation, and are usually microcrystalline powders or thin-films designed to provide visible color emission. After decades of research and development, thousands of phosphors have been prepared and some of them are widely used in many areas. Excitation by absorbance of a photon leads to a major class of technically important luminescent species which fluoresce or phosphoresce. In general, fluorescence is “fast” (ns time scale) while phosphorescence is “slow” (longer time scale, up to hours or even days). For convenience, the topic of photoluminescence (PL) will be broadly divided into that based on relatively large-scale inorganic materials, mainly exhibiting phosphorescence, and that of smaller dye molecules and small-particle inorganic (“nanomaterials”), which can either fluoresce or phosphoresce. Their applications differ. For many of the derived technical applications, it is irrelevant whether the luminescence is fluorescence or phosphorescence. Either way the current range of applications is extensive, and in one case has been recognized by the award of a Nobel Prize, in 2008.

2.1 Excitation and Emission Spectra

Figure 2.1 shows a typical spectrum of the excitation and emission of a fluorochrome. These spectra are generated by an instrument called a *spectrofluorimeter*, which comprised two spectrometers: an illuminating spectrometer and an analyzing spectrometer. First, the dye sample is strongly illuminated by a color of light that is found to cause some fluorescence. A spectrum of the fluorescent emission is obtained by scanning with the analyzing spectrometer using this fixed illumination color. The analyzer is then fixed at the brightest emission color, and a spectrum of the excitation is obtained by scanning with the illuminating spectrometer and measuring the variation in emission intensity at this fixed wavelength. For the purpose of designing filters, these spectra are normalized to a scale of relative intensity.

Fig. 2.1 Generic excitation and emission spectra for a fluorescent dye



These color spectra are described quantitatively by wavelength of light. The most common wavelength unit for describing fluorescence spectra is the *nanometer* (nm). The colors of the visible spectrum can be broken up into the approximate wavelength values [1]:

<i>Violet and indigo</i>	400–450 nm
<i>Blue and aqua</i>	450–500 nm
<i>Green</i>	500–570 nm
<i>Yellow and orange</i>	570–610 nm
<i>Red</i>	610 to approximately 750 nm

On the short-wavelength end of the visible spectrum is the near-ultraviolet (near-UV) band from 320 to 400 nm, and on the long-wavelength end is the near-infrared (*near-IR*) band from 750 to approximately 2,500 nm. The broad band of light from 320 to 2,500 nm marks the limits of transparency of crown glass and window glass, and this is the band most often used in fluorescence microscopy. Some applications, especially in organic chemistry, utilize excitation light in the mid-ultraviolet band (190–320 nm), but special UV-transparent illumination optics must be used. There are several general characteristics of fluorescence spectra that pertain to fluorescence microscopy and filter design. First, although some substances have very broad spectra of excitation and emission, most fluorochromes have well-defined bands of excitation and emission. The spectra of Fig. 2.1 are a typical example. The difference in wavelength between the peaks of these bands is referred to as the *Stokes shift* [1].

In practical applications, phosphors are often excited by cathode rays, X-rays, or UV emission of a gas discharge, which correspond to applications in displays, medical imaging and lighting, respectively, such as cathode-ray-tube (CRT) color TV, X-ray fluorescent screens, and fluorescent lamps. Energy transfer mechanism

from one dopant (sensitizer) to another (luminescent center) is sometimes used to enhance the sensitivity of a phosphor. Earlier, several researchers have tried to sensitize this phosphor by co-doping with different rare earth metals. Energy transfer between pairs of rare earth ions at dilution level below the self quenching limits has been known to take place generally through multipolar interaction like dipole–dipole interactions or dipole–quadrupole interactions [2–4]. The use of energy transfer or metal enhancement effects has been applied in assays and in sensing with molecular fluorophores for sometime. These effects are also observed in nanoparticles and such approaches might lead to even more robust and flexible analytical methods for nanoscale inorganic phosphors. 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 LEDs. 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.

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. Generally, luminescence of phosphors involves two processes: excitation and emission. Many types of energy can excite the phosphors. Excitation by means of energetic electrons is cathodoluminescence (CL). PL occurs when excited by photon (often ultra-violet), electroluminescence (EL) is excited by an electric voltage, chemiluminescence is excited by the energy of a chemical reaction, and so on. The process of emission is a release of energy in the form of photon. The basic luminescence mechanisms in luminescent centers are illustrated in Fig. 2.2. In the host lattice with activator, the activator is directly excited by incoming energy; the electron on it absorbs energy and is raised to an excited state. The excited state returns to the ground state by emission of radiation [5].

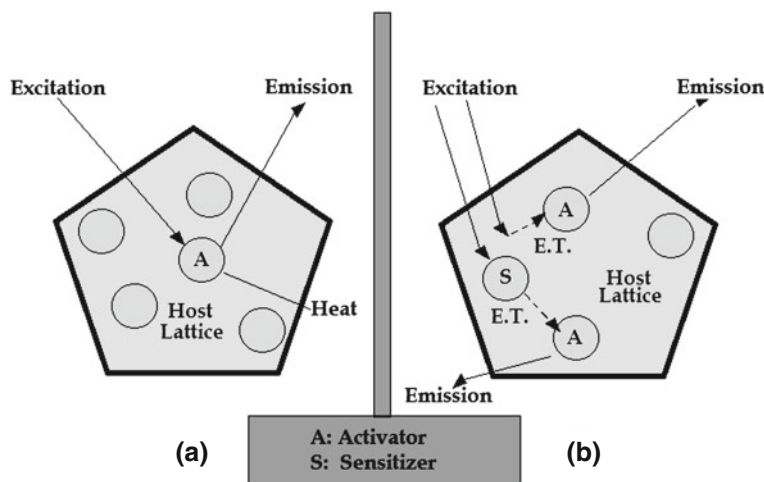
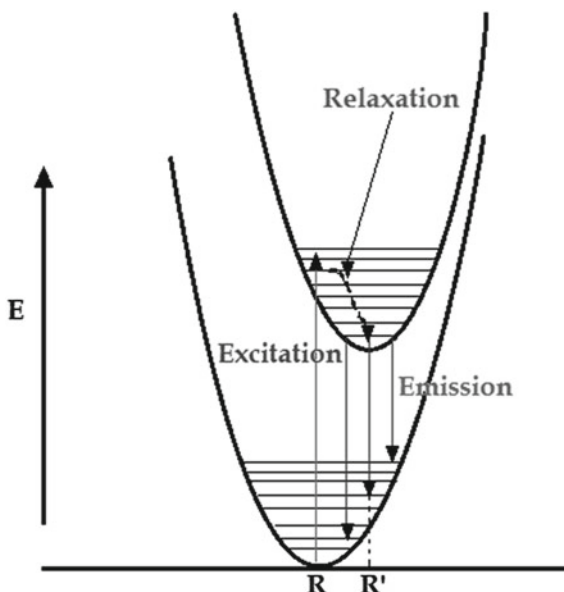


Fig. 2.2 Schematic diagram showing (a) direct excitation of the activator and (b) indirect excitation followed by energy transfer from the sensitizer or host to the activator [2]

2.1.1 Radiative Transition

There are several possibilities of returning to the ground state. The observed emission from a luminescent center is a process of returning to the ground state radiatively. The luminescence quantum efficiency is defined as the number of photons emitted divided by the number of photons absorbed, and in most cases is equal to the ratio of the measured lifetime to the radiative lifetime of a given level. The processes competing with luminescence are radiative transfer to another ion and nonradiative transfers such as multiphonon relaxation and energy transfer between different ions or ions of a similar nature. The last transfer is also named cross-relaxation. Figure 2.3 shows the configurational coordinate diagram in a broad band emission. Assumption is made on an offset between the parabolas of the ground state and the excited state. Upon excitation, the electron is excited in a broad optical band and brought in a high vibrational level of the excited state. The center thereafter relaxes to the lowest vibrational level of the excited state and give up the excess energy to the surroundings. This relaxation usually occurs nonradiatively. From the lowest vibrational level of the excited state, the electron returns to the ground state by means of photon emission. Therefore, the difference in energy between the maximum of the excitation band and that of the emission band is found. This difference is called the Stokes shift [6]. The radiative transfer consists of absorption of the emitted light from a donor molecule or ion by the acceptor species. In order to that such transfer takes place, the emission of the donor has to coincide with the absorption of the acceptor. The radiative transfer can be increased considerably by designing a proper geometry.

Fig. 2.3 Configurational coordinate diagram in a luminescent center



2.1.2 Nonradiative Transition

The energy absorbed by the luminescent materials which is not emitted as radiation is dissipated to the crystal lattice. It is crucial to suppress those radiationless processes which compete with the radiation process. In order to understand the physical processes of nonradiative transitions in an isolated luminescent center, the configurational coordinate diagrams are presented in Fig. 2.4. In Fig. 2.4a, there is a Stokes shift between the ground state and the excited state. The relaxed-excited-state may reach the crossing of the parabolas if the temperature is high enough. Via the crossing, it is possible for electrons to return to the ground state in a nonradiative manner. The energy is given up as heat to the lattice during the process [7]. In Fig. 2.4b, the parabolas of ground state and excited state are parallel. If the energy difference is equal to or less than four to five times the higher vibrational frequency of the surrounding, it can simultaneously excite a few high-energy vibrations, and therefore is lost for the radiation of phonons. This is called multiphonon emission. In a three-parabola diagram as shown in Fig. 2.4c, both radiative and nonradiative processes are possible. The parallel parabolas (solid lines) from the same configuration are crossed by a third parabola originated from a different configuration. The transition from the ground state to the lower excited state (solid line) is optically forbidden, but it is allowed to transit to the upper excited state (dash line). Excitation to the transition allowed parabola then relaxes to the relaxed excited state of the second excited parabola. Thereafter, emission occurs from it.

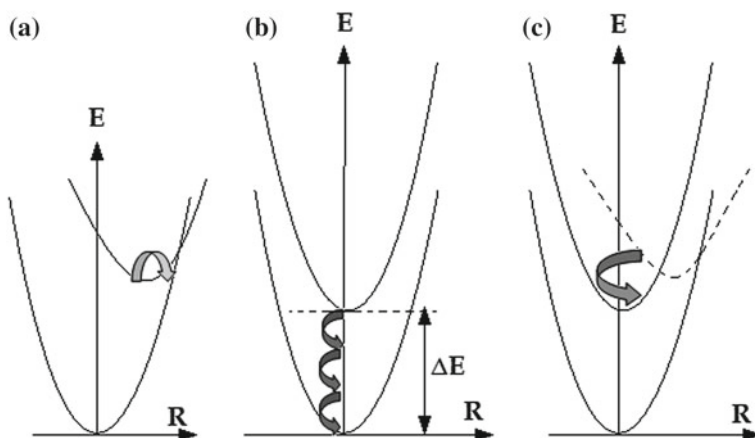


Fig. 2.4 Configurational coordinate diagram representing nonradiative transitions

The nonradiative processes competing with luminescence are energy loss to the local vibrations of surrounding atoms (called phonons in solids) and to electronic states of atoms in the vicinity, such as *energy transfer*, which may be resonant (including as a special case energy migration between identical systems, which may ultimately emit radiation) or phonon assisted [the excess energy being dissipated as heat, or, to a much smaller extent, the thermal reservoir supplying low-energy phonons ($kT = 210 \text{ cm}^{-1}$ at 300 K) to a slightly higher level of an adjacent system]. Special cases of energy transfer are cross-relaxation, where the original system loses the energy ($E_2 - E_1$) by obtaining the lower state E_1 (which may also be the ground state E_0) and another system acquires the energy by going to a higher state. Cross-relaxation may take place between the same lanthanide (being a major mechanism for quenching at higher concentration in a given material) or between two differing elements which happen to have two pairs of energy levels separated by the same amount [7].

2.1.3 Multiphonon Relaxation [8]

Today, multiphonon relaxation in lanthanide ions is a well-understood process, contrary to other transition metal ions, which still require additional understanding. Excited electronic levels of rare earths in solids decay nonradiatively by exciting lattice vibrations (phonons). When the energy gap between the excited level and the next lower electronic level is larger than the phonon energy, several lattice phonons are emitted in order to bridge the energy gap. It was recognized that the most energetic vibrations are responsible for the nonradiative decay since such a process can conserve energy in the lowest order. The most energetic vibrations are the stretching

vibrations of the glass network polyhedra; it was shown that these distinct vibrations are active in the multiphonon process, rather than the less energetic vibrations of the bond between the R and its surrounding ligands. It was demonstrated that these less energetic vibrations may participate in cases when the energy gap is not bridged totally by the high-energy vibrations. The experimental results reveal that the logarithm of the multiphonon decay rate decreases linearly with the energy gap, and hence with the number of phonons bridging the gap, when the number of phonons is larger than two [8].

2.1.4 Cross-Relaxations [8]

A special case of energy transfer is cross-relaxation, where the original system loses the energy ($E_3 - E_2$) by obtaining the lower state E_2 (which may also be the ground state E_1) and another system acquires the energy by going to a higher state E'_2 . Cross-relaxation may take place between the same lanthanide (being a major mechanism for quenching at higher concentration in a given material) or between two differing elements, which happen to have two pairs of energy levels separated by the same amount. The cross-relaxation between a pair of R ions is graphically presented in Fig. 2.5. The two energy gaps may be equal or can be matched by one or two phonons. Cross-relaxation has been measured in a variety of ions and it is a dominating factor in nonradiative relaxations at high concentration. The nonradiative relaxation rates can be obtained by analysis of the decay curves of R fluorescence using the formula of the general form where the population number of state i , N_i , is proportional to the intensity of emitted light, I_i :

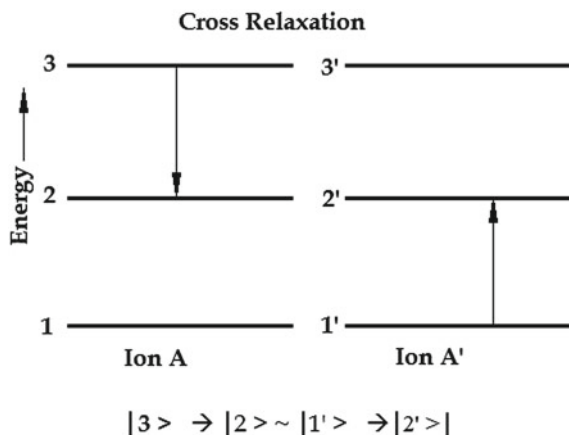
$$\frac{dN_i(t)}{dt} = -\left(\gamma_R + X_i + \sum_{i \neq j} W_{ij}\right)N_i(t) + \sum_{i \neq j} W_{ji}N_j(t)$$

$dN/(t)/dt$ is the decrease of intensity after pulse excitation, γ_R is the reciprocal of the lifetime of the excited state in the absence of a cross-relaxation process. $\sum W_{ij}$ is the probability for cross-relaxation, W_{ji} is the probability of the inversed process, and W_{ij} is the rate of cross-relaxation. Theoretically, the cross-relaxation rate for a dipole–dipole transfer can be obtained from the formula [9].

$$P_{SA}^{(DD)} = \frac{1}{(2J_s + 1)(2J_A + 1)} \frac{2}{3} \left(\frac{2\pi}{h}\right) \left(\frac{e^2}{R^3}\right)^2 \left[\sum_t \Omega_{is} \langle J_s || U^{(t)} || J'_s \rangle^2 \right] \\ \times \left[\sum_t \Omega_{iA} \langle J_A || U^{(t)} || J'_A \rangle^2 \right]_s$$

Here Ωt are the Judd–Ofelt intensity parameters, $\langle J || U^{(t)} || J' \rangle$ is the matrix element of the transition between the ground and excited state of the sensitizer and activator, respectively. The calculation of these matrix elements in the intermediate-coupling

Fig. 2.5 Scheme for cross-relaxation between two ions of the same, or of different nature [8]



scheme is now a well-known procedure and may be found in [9]. S is the overlap integral and R is the interionic distance.

2.1.5 Up-Conversion [8]

Up-conversion in its most general sense is the phenomenon whereby one or more photons of lower energy are absorbed by a material, and re-emitted as a higher energy photon. Materials able to cause this effect are known as up-converters. A main attraction is that they can be tuned to respond to near IR energy near 980 nm from commonly available and cheap diode lasers, and emit a range of photon energies at visible wavelengths. A major type of up-converter is based on rare earth-(RE)-doped salts of various metals, usually fluorides, in solid crystal or glass matrices. Up-conversion in such materials can occur by several different mechanisms whose full description goes beyond the scope of this book [10]. They rely on the multitude of accessible excited states within the different RE cations. Besides the RE materials there are others which bring about an up-conversion effect on photoirradiation, and which will be the subject of more detailed description later. They are introduced now for convenience. They in turn follow different mechanisms for up-conversion. Figure 2.6 summarizes diagrammatically some of the absorption–emission processes which lead to up-conversion. The vertical arrows represent absorption or emission of a photon, while the curved arrows represent energy transfer between species (usually ions).

- Mechanism (a) is the most common in RE systems. Here, two photoexcited RE ions (same species or different) each transfers its energy to a third ion which emits from the higher energy state. Ytterbium as Yb^{3+} is commonly used as a primary absorber of input photoradiation, and this transfers energy to emitter ions,

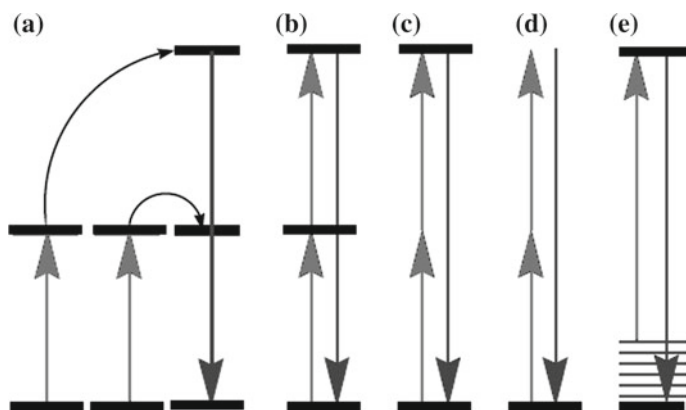


Fig. 2.6 Simplified representations of some up conversion processes

commonly Er^{3+} and Tm^{3+} . The efficiency of this energy transfer up-conversion (ETU) is surprisingly high and, of the five mechanisms shown in Fig. 2.6, this is the most efficient. Three-photon ETU is also well-known.

- In (b), initial absorption leads to an intermediate excited state, which lives long enough to allow ready absorption of a second photon to give a higher excited state, hence its name of 2-step absorption. Emission from this clearly gives a higher energy, up-converted, photon. This process is about two orders of magnitude less efficient than (a). Mechanisms related to (a) and (b) can involve subsequent absorption steps to reach yet higher excited states, prior to luminescence. Furthermore, there are not only several other distinct processes for RE up-conversion, but there are also combination processes, some including conventional down-conversion steps, so it must be accepted that an overview presented here for RE up-converters is very limited [1].
- Mechanism (c) is two-photon absorption, this time without a real intermediate excited state. This implies simultaneous absorption of two photons, which inevitably has a lower probability and the mechanism is thus much less efficient. However, by means of intense laser irradiation, two (or even multi) photon absorption (2PA, 3PA, etc.) has become well characterized for some organic dyes and specially modified derivatives. CaF_2 doped with Eu^{2+} is a 2PA example from RE chemistry. However, up-conversion from this material is about 10^{10} times less efficient than for an ETU material such as YF_3 doped with Er^{3+} and Yb^{3+} .
- Second harmonic generation (SHG) (d), under nonlinear optics (although mechanisms (a)–(c) are also nonlinear in character). Here, the interaction of two photons in the SHG material does not proceed by way of any excited energy state. The efficiency of up-conversion for the traditional SHG material KDP (potassium dihydrogen phosphate) is about eight orders of magnitude less efficient than that for ETU (a).

- Finally, the mechanism of up-conversion represented by (e) is sometimes called hot-band absorption. An electron in a vibrationally excited level of the ground state of a species is preferentially excited. Emission then proceeds back to a lower vibrational level within the ground state, and up-conversion by only a few units of thermal energy is observed.

2.2 Features of Rare Earth (RE) Ions with Respect to Luminescence

In display application of luminescence mostly inorganic solids doped with rare earth impurities are used. It is necessary to understand the mechanism of these display materials. Basically, there are four important parameters, viz. excitation type and spectrum, relaxation to emitting state and the decay time, and emission intensity and emission spectrum. RE spectra were observed extremely sharp (line-spectra). The above-mentioned four factors vary from one-host materials to another.

The characteristic properties of the RE ions are attributable to the presence in the ion of a deep-lying $4f$ shell, which is not entirely filled. The electrons of this shell are screened by those in the outer shells (except for La^{3+} and Lu^{3+}), and as a result they give rise to number of discrete energy levels. Since the presence of crystal lattice scarcely affects the position of these levels, there is a resemblance between the energy level diagram of a free ion and that of the incorporated ion. In case of the latter, usually the terms are shifted to lower wave numbers. Some empirical laws have been formulated regarding the magnitude of this effect [11–14].

In spite of the resemblance of the energy levels of free RE ions and the RE ions in solids, there is an important difference in the emission properties. In solids, the emission of RE ions is observed at different spectral position than the absorption. The difference between the absorption and emission wavelength is described as ‘Stokes Shift’. The shift for the transition within $4f$ shell results from the fact that the absorption and emission takes place between different levels. Usually, absorption corresponds to the transition from ground state to higher excited states. Electron in the higher excited state then loses energy to lattice till the states lying just below the previous excited states are available. When the difference between the adjacent states is large, then the energy corresponding to this transition cannot be transferred to lattice and it is given out in the form of emission. The emission thus corresponds to the transition from the intermediate state to the ground state.

RE ions are usually trivalent. Ions corresponding to configurations $4f^0(\text{La}^{3+})$, $4f^7(\text{Gd}^{3+})$ and $4f^{14}(\text{Lu}^{3+})$ are stable. The RE element next to these three tends to exchange electron and acquire this stable configuration. For understanding the luminescent properties of rare earth ions, it is necessary to know their key energy levels. The energy level may be divided into three categories, those corresponding to $4f^n$ configuration, $4f^{n-1}5d$ configuration, and those corresponding to charge transfer involving the neighboring ions.

2.2.1 Discrete f - f Transition

Except for Ce^{3+} and Yb^{3+} , number of discrete $4f$ energy levels is large. For Gd^{3+} , there are as many as 327 levels of $4f$ configuration. These levels further increase in number due to crystal field splitting. Most often the levels relevant to photoluminescence that can be excited by UV light and other levels are ignored.

The transitions within $4f$ shells are strictly forbidden, because the parity does not change. The forbidden transitions are observed due to the fact that the interaction of RE ion with crystal field or with the lattice vibrations can mix state of different parities into $4f$ states.

Coupling of $4f$ electrons with transient dipoles induced in the ligands by the radiation field leads to an amplification of the even parity multipolar transition amplitudes for transitions within $4f$ shell. These transitions are called as induced electric dipole transition. Quite often, the transition corresponding to selection rules ($\Delta S = 0, L \leq \pm 2$ and $J \leq \pm 2$) shows large variations in oscillator strengths depending upon the surround environment. These have been termed as the *hypersensitive transitions*. Table 2.1 lists the various hypersensitive transitions for different RE^{3+} ions.

The transitions that are not allowed as electric dipole may take place as magnetic dipole. The magnetic dipole transitions obey the selection rules $\Delta L = 0, \Delta S = 0, \Delta I = 0$ and $\Delta J = 1$ ($0 \rightarrow 0$ excluded). Spin orbit coupling weakens the selection rule on ΔL and ΔS .

Interaction of RE ions with lattice vibrations also can mix the state of different parities into $4f$ states. Vibronic transitions of RE ions are due to coupling of $4f^n$ state with the vibrational mode of the lattice.

Table 2.1 Hypersensitive transitions of rare earths

Rare earth	Excited state	Ground state
Ce	—	—
Pr	$^3\text{H}_5, ^3\text{F}_2$	$^3\text{H}_4$
Nd	$^4\text{G}_{5/2}, ^2\text{G}_{7/2}, ^4\text{G}_{7/2}$	$^4\text{I}_{9/2}$
Pm	$^5\text{G}_{12}, ^5\text{G}_3$	$^5\text{I}_4$
Sm	$^4\text{H}_{7/2}, ^6\text{F}_{1/2}, ^6\text{F}_{3/2}$	$^6\text{H}_{5/2}$
Eu	$^7\text{F}_2$	$^7\text{F}_1, ^7\text{F}_0$
Gd	—	—
Tb	$^7\text{F}_5$	$^7\text{F}_6$
Dy	$^6\text{F}_{11/2}, ^6\text{H}_{13/2}, ^6\text{H}_{11/2}$	$^6\text{H}_{15/2}$
Ho	$^5\text{G}_6, ^3\text{H}_6$	$^5\text{I}_8$
Er	$^2\text{H}_{11/2}, ^4\text{G}_{11/2}$	$^4\text{I}_{15/2}$
Tm	$^3\text{F}_4, ^3\text{H}_4, ^3\text{H}_5$	$^3\text{H}_6$
Yb	—	—

2.2.2 Broad Energy Bands

In addition to the discrete $4f$ levels there are other levels present. These are usually in the form of broad bands and play vital role in excitation. For Ce^{3+} and Eu^{2+} , these are vital for emission as well.

The bands referred to fall into two groups. In the first group, one of the $4f$ electrons is raised to the higher $5d$ levels. Transitions from configuration $4f^n$ to $4f^{n-1}$ are allowed. The second group of bands corresponds to the promotion of an electron from one of the surrounding ions to $4f$ orbit of the central ion. This is referred to as the charge transfer state and written as $4f^n 2p^{-1}$.

2.2.3 f - d Transition

$4f^{n-1}5d$ levels may be understood as formed by the electron in the $5d$ orbital interacting with $4f^{n-1}$ core. As a consequence of this strong crystal field effect on the $5d$ electron, $4f^{n-1}5d$ configurations of RE ions in solids are very different from those of free ions. $4f^n \rightarrow 4f^{n-1}5d$ absorption of most of the RE^{3+} and RE^{2+} ions exhibit two features. First, they consist of strong bands corresponding to the components of $5d$ orbital split in the crystal field. Consequently, their spectra are similar when ions are embedded in same type of host. Second, the structures of $5d$ bands can be fitted to energy differences in the ground multiplets of the $4f^{n-1}$ configurations.

For most of the trivalent RE ions, transitions from configuration $4f^n$ to $4f^{n-1}5d$ correspond to wavenumbers exceeding $50,000\text{ cm}^{-1}$, and thus not accessible to UV excitation. In case of Ce and Tb, they are usually accessible to UV excitation the position of these bands shifts to higher wavenumbers as one moves along the RE series from Ce to Gd. For Tb, the position is suddenly lowered and again the increasing trend is observed up to Yb^{3+} . Table 2.2 compares the characteristics of f - f and f - d transitions.

Table 2.2 Comparison of f - f and f - d transition of rare earths

	f - f	f - d
Electric dipole oscillator strength	10^{-6}	10^{-1} – 10^{-2}
Ion lattice coupling	Weak	Strong
Emission wavelength	200–500 nm	150–1,000 nm
Line width	10 cm^{-1}	$>1,000\text{ cm}^{-1}$
Life time	10^{-2} – 10^{-5} s	10^{-8} – 10^{-6} s

2.2.4 CT Bands

CT bands will depend on the ligand. It has been observed that the energy will decrease with the electronegativity of the ligand ion. Tetravalent ions often show absorption in the visible region of the spectrum, which corresponds to the CT state. In case of Eu^{3+} , the CT band provides strong excitation. No other RE ion is as much investigated for the CT bands as Eu^{3+} .

2.3 Excitation by Energy Transfer

Apart from the $f-d$ allowed transitions and the CT bands, strong excitation can often be achieved by the energy transfer. A RE ion or other species may absorb the energy and transfer to another RE ion which may lose the energy radiatively. When the energy transfer results in the increase in RE emission it is termed as the sensitization. The RE ion from which the emission results is called as the activator and the one which absorbs energy as the sensitizer.

An unwanted feature of the energy transfer is the reduction in emission. Indeed, there are many more examples of energy transfers resulting into reduction of the desired emission than the one in which sensitization has been achieved. The concentration quenching of RE emission most often takes place through the energy transfer. One may expect that the RE luminescence will increase with increase in the concentration of luminescent ions. In practice, this is valid only up to certain limiting concentration above which a RE ion in excited state loses energy to a nearby ion in the ground state. The excitation energy, thus hops from one ion to the other and ultimately it may reach a killer site (e.g., an impurity ion which absorbs the energy and dissipates it nonradiatively). The concentration quenching may take place through cross-relaxation also. In this process, the excitation ion comes to a less excited state. When the transition from this less excited state to the ground state is nonradiative, luminescence is completely quenched. Otherwise one observes emission at the longer wavelengths taking place at the cost of the short wavelength emission.

Since the interaction with lattice will be temperature dependent, it is quite understandable that the position, splitting, and lifetimes of various levels can be temperature dependent. It is quite common to find that at lower temperatures the host lattice offers conditions conducive for luminescence while at high temperatures, the nonradiative processes become dominant. This has been termed as thermal quenching. For many applications it assumes prime importance. It determines the operating temperature of the device based on the luminescent materials. In some cases (e.g. $\text{Y}_2\text{O}_3:\text{Eu}$), increase in luminescence efficiency at which high temperatures has been observed. This occurs due to the thermal quenching of the processes which compete with the desired emission.

2.4 Rare Earths Energy Levels and Transitions

There are 14 rare earth elements and they lie between lanthanum (^{57}La) and hafnium (^{72}Hf). Their atomic configurations consist of partially filled $4f$ shells. It is important to note that ions with either filled $4f$ levels such as Lu^{3+} or ions that have no $4f$ electrons such as La^{3+} , will have no electronic energy levels to induce excitation in/or near the visible region. The azimuthal quantum number (l) of $4f$ orbitals is 3, which gives $2l + 1 = 7$ orbital state (7 orbital orientation) and allows 14 electrons to stay. In the nonexcited state, these electrons will be distributed in such a way that they will have the maximum combined spin angular momentum (S). According to Hund's rule, the spin angular momentum S is added to the orbital angular momentum L to give the total angular momentum J . For the lowest ground state, $J = L - S$, when the number of $4f$ electrons is less or equal to 7, and $J = L + S$, when the number of $4f$ electrons is larger than 7.

2.4.1 Electronic Transitions

An electronic state is indicated by notation $^{2S+1}L_J$, where L represents the letters S, P, D, F, G, H, I, K, L, M, N... corresponding to the resultant orbital quantum number of $4f$ electrons $L = 0, 1, 2, 3, 4, 5, 6, 7, 8, \dots$, respectively [15]. An electronic state is actually expressed as an intermediate coupling state and can be described as a mixed state of several $^{2S+1}L_J$ states and a spin-orbit interaction. This mixing due to spin-orbit is actually small for the levels near the ground states, and it is larger for the states that are neighbors with the same J numbers. The effect of the mixing is very large in the optical transition probabilities, although it is relatively small on the energy levels. Rare earth ions (doubly or triply charged) can be present in ionic solids. For the case of the triply charged, all $5d$ and $6s$ orbitals are empty and the $4f$ is partially occupied. The optically active $4f$ electrons are shielded from the crystalline electric field by the outer $5s$ and $5p$ shells. The resulting effect is that the neighboring ligands have very little affection on the $4f$ electrons. The energy levels of the $4f$ electrons are very similar to the free ion levels characterized by the L , S , and J values with allowance made for some term mixing [15] and this is because of the weak interaction with the lattice environment. The spectral lines (either of emission or absorption) are sharp and the energy positions are not (usually) crystalline host dependent.

For the case of divalent rare earth ions, the energy separation between the $4f^n$ and $4f^{n-1}5d$ configurations will be large and the transitions between these two may be observed by normal spectroscopy. These transitions are dipole-allowed and are about 10^6 times stronger than the very frequently observed $4f \rightarrow 4f$ transitions in trivalent (rare-earth) ions. The emission and excitation spectra of the divalent europium ion are mainly composed of two types of electronic transitions: a strong $4f \rightarrow 5d$ transition with a high energy and a weak $4f \rightarrow 4f$ transition at low energies. The gross feature

of the spectra of this type of rare earth ions is considered to arise from the T_{2g} and E_g components of the $5d$ electron in the cubic crystalline field. The strongest lines were actually assigned to pure electronic transitions from $4f^n$ to $4f^{n-1}5d$ which was assumed to be caused by the interaction between the $4f^{n-1}$ core and the $5d$ electron, the $4f^{n-1}5d$ level being spaced with the energy gaps in the $4f^{n-1}$ ground multiplets [16].

Optical absorption of $4f$ electrons transitions is strongly forbidden by the parity selection rule [17]. However, this rule can be relaxed. When an ion occupies a crystalline site there are uneven components of the crystal field. These components mix a small amount of opposite parity wavefunctions into the $4f$ wavefunctions, and this causes intra-configurational $4f$ transitions to gain some intensity.

The allowed optical inter-configurational transitions for rare earth ions are divided into two types: $4f^n \rightarrow 4f^{n+1}L^{-1}$, L = ligand (charge-transfer transitions) and $4f^n \rightarrow 4f^{n-1}5d$ transitions. And both are allowed and have broad absorption band. The first type of charge transfer is found in rare earth elements that like to be reduced and is commonly observed in tetravalent rare earth ions. The second ($5d$ transition) on the other hand is found for the ones which like to be oxidized and is commonly observed in divalent rare earth ions.

2.4.2 Stark Splitting

As mentioned above, $4f$ electrons of rare earth are shielded from crystal environment by $5s$ and $5p$ shells. However, in a crystal field, the J degeneracy of spin-orbit state $^{2S+1}L_J$ can be shifted and split. This is called Stark splitting. In other words, this effect is the splitting of the spectral line into several components in the presence of an electric field. This effect is the analogous to the Zeeman effect in a magnetic field, but in this case the splitting is not symmetric. This splitting only occurs when the ion is polarized by the electric field resulting in a dipole moment. This dipole moment only depends upon magnitude (M_J), not direction, so the energy levels will be split into $J + 1$ or $J + 1/2$ levels.

This splitting is usually much less than the separation of the spin-orbit levels. Because of this, the main features of the energy levels diagrams remain almost unchanged for the rare earth ions in different host materials. On the other hand, the crystal-field splitting will vary for different host, and it will show the different symmetries and strengths of the crystal fields.

2.4.3 Multiphonon Process

Most $4f$ emitting levels are separated from the next lower level in a distance of at least $2 \times 10^3 \text{ cm}^{-1}$. Excited states of this kind release their energy via either of two competitive ways: light emission or by phonon emission. The rate of phonon emission is dependent on the number of phonons emitted at the same time to bridge the energy

gap. The probability of multiple phonon transitions is given by the relation:

$$w \propto \exp^{-kE} / h\nu_{\max}$$

where w is the phonon transition rate, E is the energy gap closest to the lower level and $h\nu_{\max}$ is the maximum energy of phonons (coupled to the emitting states). When E increases the phonon emission rate decreases rapidly; therefore, the competitive light emission process (radiative) becomes the dominant one. On the contrary, if the phonon energy is large or E is small, the phonon transition probability can be very high, and the radiative transition of the upper excited level can be seriously quenched.

2.4.4 Crystal Field Splitting

Wavefunctions of $5d$ of rare earth such as Eu^{2+} and $3d$ electrons of transition ions such as Mn^{2+} are quite extended. They will strongly interact with ligand ions in crystals. As a result, the resultant orbital states of d electrons will be split. The splitting is usually much larger than the splitting by $L-S$ coupling. Crystal-field splitting depends on several factors:

- (1) number of electrons in the d orbitals
- (2) oxidation state of the crystal (a high oxidation state will lead to a high-energy splitting)
- (3) the arrangement of the ligands around the crystal
- (4) the nature of the ligands

The most common type of complex is the octahedral. In this case, six ligands form an octahedral field around the metal ion and the ligands point directly into the d -orbitals and cause high-energy splitting. The second most common type of complex is the tetrahedral, for this case four ligands form a tetrahedral field around the metal ion, for this case the electrons are not oriented directly against the orbitals; therefore, the energy splitting level is lower than the previous case. The physics of this phenomenon is the following: as we know the transition metals have ions with partially filled orbitals (five of them) and they are degenerate. When a ligand approaches the metal ion, the electrons from the ligand are at different distances to the d -orbitals, and the electrons in the d -orbitals and the ones in the ligand have an acting repulsive force, because the d -orbitals are repulsed unequally by the ligand, and obviously the d -orbitals will split into energy.

In some cases, there are more than one d -electron and in these cases we observe a strong crystal field. These electrons affect each other electrostatically through a potential of the form:

$$\frac{\sum e^2 r}{r}$$

2.5 Energy Transfer

The process in which the excitation of a certain ion migrates to another ion is called energy transfer. It is very important to understand this effect in order to develop efficient luminescent materials. The luminescent materials had several types of energy transfer [18]:

- i. **Resonant energy transfer between ions of same energy level**—for this case, the excitation energy of a certain ion migrates to another one of the same species that is in the ground state. This type of transfer is also divided into three categories: First, multipolar interaction, and this is both transitions are of electric dipole character; the second is the exchange interaction, and this is when the donor and the acceptor are both located so close that their electronic wave functions overlap and the transfer is due to a quantum mechanical interaction; and lastly, the phonon-assisted energy transfer, which occurs when there is a difference E between the transition energies of the donor and the acceptor, and is compensated by either a phonon emission or absorption.
- ii. **Spectral diffusion**—in this case, the excited ion can give its energy to other ions that are at different sites and/or lattice environment, due to the fact that the doping ions stay at a slightly different lattice environment. This will translate to a shift in the emission spectrum to longer wavelengths and an increment on the width of the emission peak.
- iii. **Energy donation**—in this case, the energy transfer can occur between different ions, one of them is called a donor and the other an acceptor. An ion at an excited higher energy level can transfer most of its energy to other ions. The other ions stay at a lower energy levels and release the differential energy in the form of phonons.
- iv. **Sensitizer's transfer**—a donor that usually has a strong absorption of external radiation and transfers it very efficiently to an acceptor is called a sensitizer; the caused emission is greatly enhanced. This process is also known as sensitization of the luminescence.
- v. **Quenching centers transfer**—in this case, the acceptor kills the emission of the active center or the donating ions, and these ions neither emit at the required wavelength nor emit at all. Mostly, the phosphors that exhibit this type of luminescence are activated by sensitizers or co-activators (i.e. Mn^{2+}).

It is important to determine the optimum concentration of dopant to be used, in order to obtain efficient luminescence with a minimum energy loss. For display application, the purity of color is the most important issue. For many ions emissions can be from different upper excited states. The way to keep this emission from the upper states from occurring, and to purify the luminescence is to quench the emission via cross relaxation [19]. In this process, the excited ions from the upper states prefer to release part of their energy to the neighboring ions at the ground state, and then move to the lowest metastable state. Then these ions will return to the ground state and release the remaining energy at the desire wavelength. In order

to be able to do this, the doping concentration should be sufficiently high, but it is important to note that in a heavily doped system the average distance between the ions becomes smaller, and therefore the excited ions can move around in the host causing resonant energy transfer. Such transfer gives more chance to send the excitation to a quenching center, which will release the energy through a nonradiative process. This phenomenon is called concentration quenching, as we briefly described earlier. A compromise concentration should then be determined and this will give an efficient sensitization (efficient upper-state quenching) and a maximization of the number of activators to participate in the luminescence process. However, the concentration should not lead to any concentration quenching. These centers also can produce an undesired afterglow [20]. The sensitization is used to enhance the energy excitation efficiency.

In rare earth phosphors, when UV or VUV radiations populate optically a $5d$ -state, radiative and/or nonradiative channels are available for energy relaxation in the solid state. Energy transfer to the emitting $4f$ -level occurs through lattice phonon relaxation and intra-system energy crossing when the energies match. The efficiency of the latter process depends upon the magnitude of the square overlap integrals between absorption and emission. Following the well-known configuration coordinate model, coordinate displacement between the equilibrium positions of the ground and $5d$ excited states, called the Franck–Condon shift, can be adjusted in phosphor design by choosing suitable host anionic groupings in order to fix the emission frequency or to increase the phosphor efficiency. It is worthwhile considering that the variation of the energy of the lowest $4f$ – $5d$ level versus the number of f -electrons in the shell follows the variation of $3+/4+$ redox potential along the lanthanide series. It is related to the ability of the trivalent rare earth ion to lose one electron, and consequently to the stabilization energy of the $4+$ state. In large band gap materials, the energy levels of the impurity center are sparsely distributed between the valence and conduction bands. This is especially true for trivalent rare earth ions

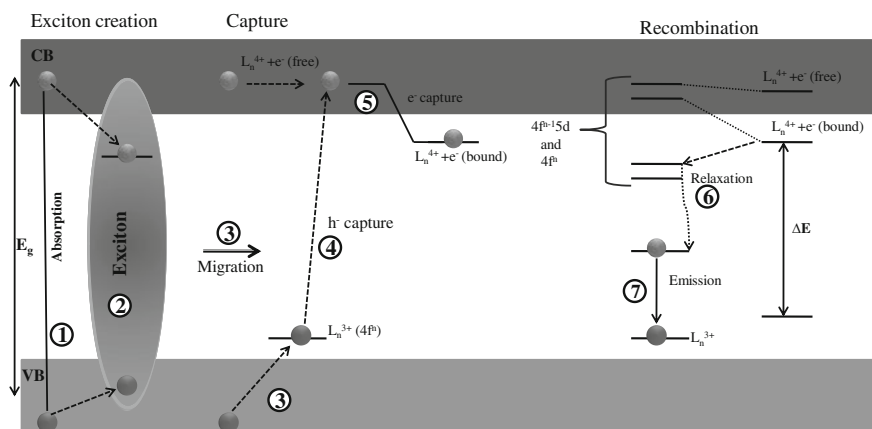


Fig. 2.7 Energy scheme of exciton and free charge carriers recombination on rare earth impurity involving the autoionization states

with discrete quasi-atomic states displayed within the large forbidden band gap of insulators (Fig. 2.7). In the combined host + rare earth impurity system, the VUV absorption can promote one electron from the ground state of the rare earth ion to excited $5d$ -states that overlap energetically the conduction band of the host. In the case of a strong coupling between these $5d$ -states and the continuum of the solid, the electron can be completely delocalized in the conduction band and the autoionization process of the rare earth ion occurs, giving rise to the $(\text{Ln}^{3+} + h^+) + e^-$ (free) state. The capture of the free-electron interpreted in the frame of the model of the exciton trapped on the impurity center as $(\text{Ln}^{3+} + h^+) + e^-$ (bounded) state, results in energy emission that corresponds to the excess of the exciton recombination energy. Part of this energy can be transferred to the $4f$ emitting level through; for example, dipole–dipole interaction in the case of allowed transitions or higher order multipole interactions for the quasi-forbidden ones.

The propensity of the rare earth ion to give up one electron should be regarded as its hole acceptor capability. It means that these ions embedded in a solid will develop a more or less intense short range potential for hole attraction depending upon the stabilization energy of the $4+$ state. This is the case for Ce^{3+} and Tb^{3+} with one more f -electron than respectively the empty and half shell.

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