

Lanthanide Luminescence and Its Applications in Modern Engineering: A Review

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Abstract: The luminescence of trivalent lanthanide ions has been studied intensively and has found applications in lasers, lighting, optical telecommunications, drug delivery, cancer therapy and various other fields. In the last decades, lanthanide-doped phosphors and crystals as well as complexes with organic and inorganic ligands have received more attention with respect to their preparation and applications. This review presents the basics of lanthanide photophysics as well as the numerous applications of lanthanide doped luminescent materials.

Keywords: lanthanides, luminescence, antenna effect, energy transfer, sensitization, imaging technique.

1. INTRODUCTION

Lanthanides occupy a special place in the periodic table because of their unique photophysical properties, especially with respect to the generation and amplification of light. In the last decades, it has been observed that lanthanide luminescence have a major role in several scientific domains, ranging from molecular biology to laser physics [1-5]. Several reviews on luminescence properties of lanthanides have been reported including the applications of lanthanide luminescence in biomedical imaging [6], light-emitting diodes [7] and two photon microscopy[8].

Lanthanide ions also have the ability to form soluble complexes with organic ligands. This becomes beneficial for low-cost alternatives to inorganic materials. Lanthanide complexes can easily be doped with polymers which are used for optical amplification [9, 10]. Currently, lanthanide complexes become active elements for Organic Light Emitting Diodes.

Recently, one of the most significant uses of luminescent lanthanide complexes is in medical diagnostics. For medical purposes, designing of luminescent lanthanide complexes in aqueous medium becomes very important. In aqueous medium, the safety of lanthanide ion from the O-H oscillator is very important for better emission. For efficient sensitization, the co-ordinating ligands of lanthanide ion needs a high absorbing $\pi\pi^*$ singlet state (S_1). The lowest $\pi\pi^*$ triplet state (T_1) of the ligand playing the vital role as donor state. Thus T_1 state must be suitably placed in comparison to the emissive state of lanthanide ion for better energy transfer. Whereas, the existence of a charge transfer (CT) state either between the S_1 and T_1 state of the ligand or between the T_1 state and the emissive state of lanthanide ion can deactivate the sensitization process.

Another advantage of lanthanide complexes in the field of detection is that they put forward high detection sensitivity, with very low background signals. In this review, some of the characteristics of the lanthanide ions and their sensitization pathways will be described. Furthermore, an overview on applications of lanthanide luminescence will be given.

2. Spectral Features of Lanthanide Ions:

Lanthanides are characterized by the progressive filling of the 4f orbitals with an electronic configuration $[Xe]4f^{1-14} 5d^{0-1} 6s^2$ [11, 12]. The oxidation states are included between 2^+ (Yb) and 4^+ (Sm and Eu), but 3^+ is by far the most stable one. The luminescence properties of the trivalent lanthanide cations (Ln^{III}) in solution and in the solid state are characterized by narrow emission bands and relatively long luminescence lifetimes of up to milliseconds [13]. Except lanthanum (La^{III}) and lutetium (Lu^{III}), each lanthanide ion has its specific emission bands: for example, the lanthanide ion terbium (Tb^{III}) emits green light, europium (Eu^{III}) red light, samarium (Sm^{III}) pink light, dysprosium (Dy^{III}) yellow light, thulium (Tm^{III}) blue light and neodymium (Nd^{III}), holmium (Ho^{III}), ytterbium (Yb^{III}), erbium (Er^{III}) emit near-infrared light. Ce^{III} , being one electron system has the lowest oxidation potential of the lanthanide ions making the allowed 4f-5d transitions possible in the UV region. Gd^{III} emits in the ultraviolet region, but its luminescence can only be observed in the absence of organic ligands with low-lying singlet and triplet levels. All trivalent lanthanide ions have unpaired electrons except lutetium. The Gd^{III} ion has maximum number of unpaired f-electrons i.e. seven (overall spin = 7/2). That is why gadolinium complexes are used as good contrast agents for magnetic resonance imaging.

The interesting and useful photophysical properties of the lanthanide ions are due to their partially filled 4f orbital. The 4f electrons of a lanthanide ion (Ln^{III}) are well shielded from the crystal field by the energetically higher lying s, p and d orbitals. Therefore, 4f-4f transitions do not contribute to chemical bonding and the sharp lines positions in the luminescence spectra of Ln^{III} ions remain unaffected in crystals and solutions like free ions. However, the crystal field could still have an effect on the 4f-4f transition probability [14]. Ce^{III} is a special case because this ion emits intense broadband emission due to allowed f-d transitions. The position of the emission maximum strongly depends on the ligand environment of the Ce^{III} ion [15].

The first energy level diagram in which the allowed optical transitions are plotted as energies for several lanthanide ions in the infra-red (IR), visible and ultra-violet (UV) region of the spectrum was presented by Dieke in 1963 [16]. The Russell-Saunders coupling allows the representation of the electronic states as function of total orbital angular momentum (L), spin multiplicity (2S+1) and total angular quantum number (J) by the following expression: $^{2S+1}L_J$ [11]. La^{III} and Lu^{III} have a completely empty and a completely filled 4f shell, respectively, and therefore have no optical transitions.

2.1. Radiative Transitions:

Ln^{III} ions can be excited both by electric dipole and magnetic dipole radiations. Electric dipole transitions are much weaker in lanthanides ($\epsilon \sim 0.1 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) since these are Laporte forbidden [17, 18]. In 1937 Van Vleck suggested [19] that f-f transitions become partially allowed as electronic dipole transitions due to admixture of configurations of opposite parity, such as the $4f^{n-1}5d^1$ configuration. The uneven components of the crystal field mix a small called "intensity stealing"[20-22]. However, magnetic dipole transitions are Laporte (parity) allowed and can often be seen, but generally their intensity is weak. The selection rule for the magnetically allowed transitions are $\Delta J = 0$, and $\Delta J = \pm 1$ (but $J = 0 \rightarrow J = 0$ is forbidden). Their probability is practically independent of the surrounding matrix. One example of a purely MD transition is the $^5D_0 \rightarrow ^7F_1$ emission line of Eu^{III} . Quadrupolar transitions are also parity allowed, but they are much weaker than magnetic dipole transitions so

that they are usually not observed. The nature of the transitions varies from pure magnetic dipole transitions to pure electric dipole transitions and mixtures of the two. Most of the lanthanide ions have emission spectrums that are usually induced by mixed electric and magnetic dipole transitions and the effects of the symmetry are less pronounced. Some induced electric dipole transitions are highly sensitive to minute changes in the Ln^{III} environment and are called hypersensitive or sometimes pseudo-quadrupolar transitions, since they apparently follow the selection rules of electric quadrupolar transitions. Though theoretically absorption of radiation can promote the lanthanide ion to any energetically excited state, emission generally takes place from the lowest lying spectroscopic level of the first excited term due to rapid internal conversion. The electronic configuration of lanthanides is split due to a variety of interactions (Figure 1). The initial configuration is split into spectroscopic terms by the Coulombic interaction, which represents the electron-electron repulsions within the 4f orbitals, is the largest among the 4f electronic interactions and yields terms with a separation in the order of 10^4 cm^{-1} [13]. These terms can be further split into several J-levels by spin-orbit coupling in lanthanide ions because of their heavy nuclei. The energy differences between split J states lie in the range of (10^3 cm^{-1}) [23]. These levels, in turn, can be split again into Stark sublevels due to ligand field effects from the coordination sphere around the lanthanide ion. These splitting are usually small in the order of (10^2 cm^{-1}) [24]. Depending on the spectral resolution of the spectrometer the Stark sublevels are appeared as fine structure on the individual bands. These fine structures may be used to gather information about the symmetry of the coordination environment [25]. This result in the overall emission peak position remaining largely unchanged as the f-electrons remain shielded, but the relative intensity and degree of splitting of emission peaks can vary greatly depending on modulation of these influences [26, 27].

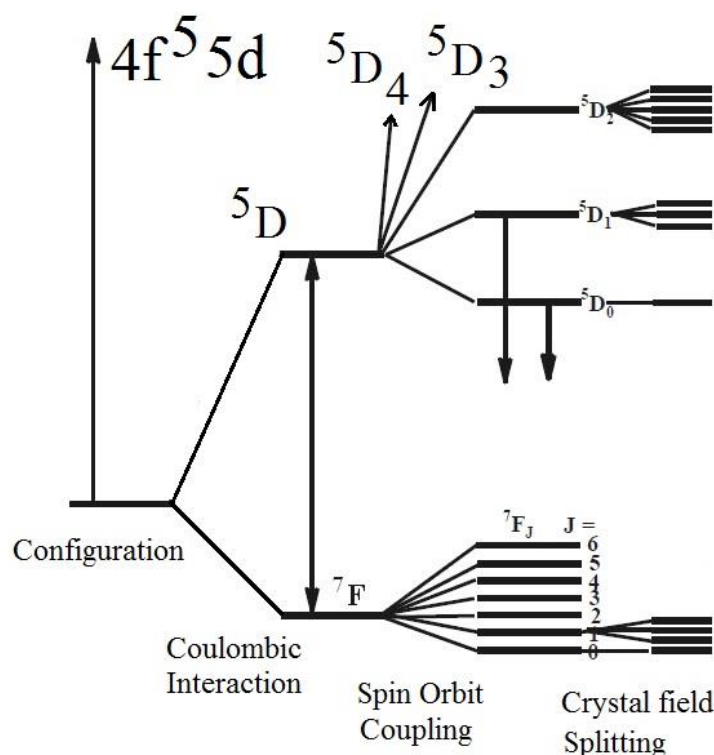


Figure 1 : Splitting of Eu^{III} electronic configuration.

2.2. General Mechanism of Lanthanide Sensitization:

In the previous section, we have seen that the lanthanide ions have unique luminescence properties, but that they possess low absorption coefficient. Consequently, direct excitation of the lanthanide ions is unfavorable. This problem can be overcome by sensitization or 'antenna' effect. In that case, light is first absorbed by an organic antenna chromophore which acts as sensitizer. Upon excitation of the antenna chromophore, the excitation energy is transferred to the lanthanide ion and populates the lanthanide luminescent state. For efficient energy transfer i) the sensitizer needs to be in close proximity of the ion, ii) the matching of the energy levels of sensitizer and lanthanide ion. In general this process takes place via the antenna triplet state with an electron exchange (Dexter) mechanism [28]. This requires a spectral overlap between the orbitals of donor and acceptor, and is therefore strongly distance dependent. In fact, the energy transfer rate diminishes rapidly at distances larger than 5 \AA .

The sensitization pathway in luminescent lanthanide complexes consists of excitation of the antenna chromophore into its singlet excited state, subsequent intersystem crossing of the antenna to its triplet state, and energy transfer from the lowest triplet state to the lanthanide ion [29- 32]. There are several competing processes such as fluorescence of the antenna, which is competing with intersystem crossing, and quenching of the triplet state by dissolved molecular oxygen, which is competing with the energy transfer to the lanthanide ion. The architecture of 'antenna effect' is shown in Figure 2.

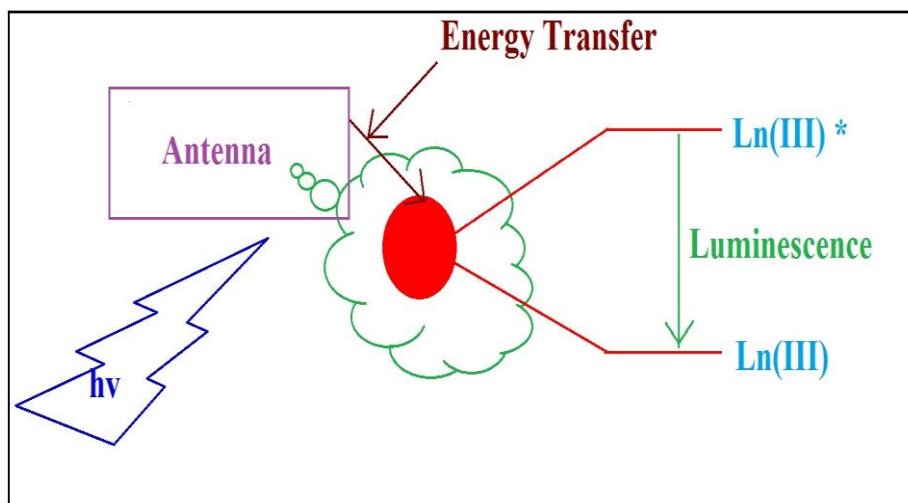


Figure 2: Mechanism of antenna effect.

3. Applications:

High-technology and environmental applications of rare earth elements have grown interest dramatically over the past four decades. Nowadays, lanthanide elements have been extensively studied and are used as numerous high technological applications. Many of these applications are highly specific and have acquired a level of great technological significance. In many applications, rare-earth elements (REE) are advantageous because of their relatively low toxicity. For example, the most common types of rechargeable batteries contain either cadmium (Cd) or lead (Pb). Rechargeable lanthanum-nickel-hydride (La-Ni-H) batteries are gradually replacing Ni-Cd batteries in computer and communicative applications and could eventually replace lead-acid batteries in automobiles. Lanthanide luminescence device in lighting and displays include phosphor, organic light-emitting diode, laser and magnetic sensitive device.

3.1. Lighting:

Interest on lighting has increased in the last decades because of growing demand and related consumption of electricity. Extensive adoption of more efficient light sources, such as light emitting diodes (LED), organic light emitting diodes (OLED) and efficient fluorescent lamps, reduce the energy demand/waste. Furthermore, old fashioned Cathode Ray Tubes (CRT, consisting of a screen with red, green, and blue phosphor pixels excited by fast electrons), commonly used in computer monitors and television devices, being gradually replaced by much more high quality and efficient Liquid Crystal Displays (LCD) and Plasma Display Panels (PDP), which may bring significant electricity savings. Color cathode-ray tubes and liquid-crystal displays used in computer monitors and televisions employ europium as the red phosphor.

3.2. Analytical Probe:

Analytical applications of lanthanide probes also have grown much attention in the field of science and technology. For the determination of tetracycline and its derivatives, the luminescence of Eu^{III} , complexed with the relevant antibiotic was used [33]. This method was later combined with chromatographic separation of tetracyclines and improved by introducing a surfactant (Triton X-100) and a synergistic agent (tri-n-octyl phosphine oxide (TOPO)) into the system [34, 35]. The emission of Tb^{III} , complexed with ciprofloxacin was used for the determination of this antibiotic (fluoroquinolone group) in biological fluids, in combination with liquid chromatography [36]. Intramolecular energy transfer from bleomycins and nalidixic acid to Tb^{III} allowed the fluorometric determination of these antibiotics on separation by liquid chromatography with reversed phases [37]. Another interesting application of the specific lanthanide properties involves the determination of steroids in biological fluids, based on sensitized Tb^{III} emission in the Tb^{III} -steroids-sodium dodecylsulphate system [38]. Sensitized emission of Tb^{III} ions complexed with erotic acid and reversed phase ion-pair chromatography were used for the determination of orotates in urine [39]. One more important specific application of ytterbium complexes with porphyrins is worth mentioning. These complexes can be used as fluorescent labels of malignant tumors in mice (in vivo) [40]. The use of ytterbium complexes (emitting in the range 900-1050 nm), instead of free porphyrins, eliminates the background luminescence from biological probes.

3.3. Biomedical Field:

In the areas of life science, biotechnology and clinical diagnostics, several bio-labelling reagents, including radio-isotopes, enzymes, fluorescence dyes, and chemiluminescent compounds, have been developed and widely used for the detection of biological molecules [41, 42]. Among these reagents, due to its high sensitivity, fluorescent dyes have occupied the most important position in fluoroimmunoassay and medical-imaging [43, 44]. However, the conventional fluorescence bioassay has the problem that the fluorescence detection is easily affected by the background noises caused by biological sample and analysis instrument. The use of Ln^{III} complexes remarkably improves the sensibility of such diagnostic techniques. Since the lanthanide ions have much longer luminescence lifetimes than conventional fluorescent probes the signals arising from the lanthanide ions can be separated from background biological fluorescence using time-gated techniques. To this purpose, the near infrared luminescent Nd^{III} and Yb^{III} complexes are the promising probes since near-infrared (NIR) light offer high photon penetration, reduced scattering and minimal auto fluorescence from living tissues [43, 45, 46].

Nowadays, DELFIA (Dissociation Enhanced Lanthanide Fluorescence Immunoassay) is a well-known medical diagnostic detection system [47] that is used to detect small amounts of biomolecules. DELFIA, a robust, high-performance immunodetection platform, provides a superior medical diagnostic technology, is used for testing newborn babies (for cystic fibrosis, hypothyroidism and congenital adrenal hyperplasia) and in the diagnosis of many diseases [48, 49]. In DELFIA, the luminescence of the lanthanide ion is detected after adding reagents that optimise the lanthanide luminescence.

There has another important use of lanthanide ion in the field of magnetic resonance imaging. The contrast in a magnetic resonance image (MRI) is due to the different relaxation times of water protons in different environments within the body. Protons with short relaxation times give rise to brighter images. To enhance the contrast in a magnetic resonance image it is sometimes necessary to administer a contrast agent that

localizes in a particular region of the body [50, 51]. Complexes of Gd^{III} are widely used as contrast agents because of its high magnetic moment and long electronic relaxation times. Gd^{III} complexes that are used as MRI contrast agents must be stable in aqueous solution at physiological pH so that no free Gd^{III} ions are present. They must have at least one free site for the coordination of H_2O [52, 53].

3.4. Telecommunications:

Telecommunication plays a vital role in modern society. In optical telecommunication networks data are transported as optical pulses through silica fibers. Since copper wires cannot satisfy the required data-transfer due to low transmission speed and small signal bandwidth, data transport with fiber-optics is very much useful. It has higher information capacity and allows transport over longer distances. Since silica is transparent to near-infrared light, two wavelength regions are used for the optical pulses: around 1330 nm (second communication window) and around 1550 nm (third communication window). For long distance communication it is necessary to compensate the losses in the fibre by regenerating the signal typically every 50–150 km (depending on the data rate). This is currently done by optical amplifiers. An amplifying medium contains a material capable of luminescence at the signal beam wavelength. The luminescent material needs to be pumped with a laser, a signal beam travelling through the amplifying medium will stimulate the emission of light, which is of the same wavelength and phase. For amplification of an 1.55 μm –signal, erbium doped fibre amplifiers [54] (EDFA's) are used due to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition.

3.5. Lasers:

Rare earth ions doped into various crystals are well-known to exhibit laser operation as active elements. Recently, a comprehensive overview of transition metal and rare earth ion doped crystals for application as tunable solid-state lasers has been reported [55]. Neodymium is the most common lanthanide used as laser source because of its emission line at 1064 nm [56]. Yttrium Aluminium Garnet doped with Nd^{III} (Nd:YAG) is, by far, the most commonly used type of solid-state laser medium, because of the combination of properties uniquely favorable for lasing [57]. In Nd:YAG the lowest laser threshold occurs at 1064 nm, but laser effect is obtainable also at 946, 1319 and 1839 nm [57]. Tm^{III} doped $YAlO_3$, $Y_3Al_5O_{12}$ (YAG) is a well known laser crystal [58]. An orange and red upconversion laser has been developed, based on an avalanche pumping mechanism of Pr^{III} , Yb^{III} in BaY_2F_8 (BYF) [59-61]. Solid state lasers based on Tm^{III} and Ho^{III} have many applications in remote sensing, medical, and military technologies. Tm^{III} , Ho^{III} and Er^{III} in $Y_3Al_5O_{12}$ (YAG) have been demonstrated to lase at room temperature [62]. A high-power laser based on Cr^{III} , Tm^{III} , Ho^{III} (CTH) in YAG has been conceived soon afterwards. Q-switched Cr,Tm:YAG and CTH:YAG laser operation emitting at 2 μm wavelength has been achieved with maximum pulse energy of 0.7 and 0.5 J, respectively, and corresponding pulse widths of 140 ns and 165 ns. The extraordinary high efficiency is responsible due to the Cr^{III} to Tm^{III} energy transfer having high quantum efficiency. Recently, improved laser operation of $LiCAF:Ce^{III}$ and $LiLuF_4:Ce^{III}$ was observed at output energies of 60 mJ and 27 mJ, respectively [63].

4. Conclusion:

The unique luminescence properties of lanthanide ions have been discussed. Some promising applications especially in biomedical assay of lanthanide luminescence have also been demonstrated. The aim of this review is to provide some inspiration of novelty research and to the development of new lanthanide complexes especially with biological applications.

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