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**Review Article** 

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## Spectral Properties and Applications of Ln (III) Ion and Their Complexes

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Abstract In lanthanides transitions involve only a redistribution of electrons within the 4f-orbitals (f $\leftrightarrow$ f transition) are orbitally forbidden by the selection rule. Crystal field effects in lanthanides are virtually insignificant due to 4f-electrons are well shielded from external charge by 5s<sup>2</sup> and 5p<sup>6</sup> sub-shells. Their (f $\leftrightarrow$ f transition) absorption bands are very sharp. Their optical spectra are virtually independent of environment they show similar spectra in gas/solution/solid (sharp lines like typical gas atom spectra). Analysis of the UV-Visible spectra for rare earth ions in aqueous solutions are complex.

#### Keywords Lanthanide, sharp-spectra, transition

#### 1. Introduction

The electronic configurations of the lanthanides are described by using the Russell-Saunders coupling scheme. Values of the quantum numbers S and L corresponding to the lowest energy are obtained in the conventional manner [1-3]. Effectively shielded from their chemical environment .Because of lanthanides 4f electrons, ions are largely burried in the inner core, they an -orbit coupling is much larger than the crystal field (2000 cm<sup>-1</sup> compared to 100 cm<sup>-1</sup>) and must be considered first Electronic absorption spectra are produced when electromagnetic radiation promotes the ions from their ground state to excited states. For the lanthanides the most common of such transition involve the excited states which are either components of the ground term or else belong to excited states, which arise from the same 4f<sup>n</sup> configuration as the ground term. In either case, the transitions therefore involve only a redistribution of electrons within the 4f orbitals (i.e.  $f \rightarrow f$  transitions) and so are orbitally forbidden, just like  $d \rightarrow d$ transitions. In the case of the latter, the rule is partially relaxed by a mechanism which depends on the effect of the crystal field in distorting the symmetry of the metal ion. However, it has already been pointed out that crystal field effects are very much smaller in the case of Ln<sup>III</sup> ions and they cannot therefore produce the same relaxation of the selection rule. Consequently, the colours of Ln<sup>III</sup> compounds are usually less intense. A further consequence of the relatively small effect of the crystal field is that the energies of the electronic states are only slightly affected by the nature of the ligands or by thermal vibrations, and so the absorption bands are very much sharper than those for  $d \rightarrow d$  transitions. Because of this, they provide an useful means of characterizing, and quantitatively estimating, Ln<sup>III</sup> ions [4-5]. Nevertheless, crystal fields cannot be completely ignored. The intensities of a number of bands ("hypersensitive" bands) show a distinct dependence on the actual coordinated ligands. Also, in the same way that crystal fields lift some of the orbital degeneracy (2L + 1) of the terms of d<sup>n</sup> ions, so they lift some of the 2J + 1degeneracy of the states of  $f^n$  ions, though in this case only by the order of 100cm<sup>-1</sup>. This produces a fine structure in



some bands of Ln<sup>III</sup> spectra. Ce<sup>III</sup> and Tb<sup>III</sup> are exceptional in providing (in the ultraviolet) bands of appreciably higher intensity than usual. The reason is that the particular transitions involved are of the type  $4f^n \rightarrow 4f^{n-1}5d^1$ , and so are not orbitally forbidden. These 2 ions have 1 electron more than an empty f shell and 1 electron more than a halffull f shell, respectively, and the promotion of this extra electron is thereby easier than for other ions. Sm, Dy but more specifically Eu and Tb has excited states which are only slightly lower in energy than the excited states of typical ligands. If the electrons on the ligand are excited, the possibility therefore exists that, instead of falling back to the ground state of the ligand, they might pass first to the excited state of the Ln<sup>III</sup> and then fall to the metal ground state, emitting radiation of characteristic frequency in doing so (fluorescence or, more generally, luminescence). Excitation by UV light produces luminescence spectra, which gives information about the donor atoms and co-ordination symmetry. In lanthanides transitions involve only a redistribution of electrons within the 4forbitals (f $\leftrightarrow$ f transition) are orbitally forbidden by the selection rule. Crystal field effects in lanthanides are virtually insignificant due to 4f-electrons are well shielded from external charge by  $5s^2$  and  $5p^6$  sub-shells. Their (f \leftrightarrow f transition) absorption bands are very sharp. Their optical spectra are virtually independent of environment they show similar spectra in gas/solution/solid (sharp lines like typical gas atom spectra). Ce<sup>3+</sup> (empty sub-shell) and Tb<sup>3+</sup> (half-filled sub-shell) have high intensity bands in the UV, due to  $4f^n \rightarrow 4f^{n-1}5d^1$  transitions i.e.,  $f \rightarrow d$  and therefore not orbitally forbidden. The intensity of the absorption band in Ln (III) spectra has been studied both theoretically and experimentally. The theory proposed independently by Judd [6] and by Ofelt [7] has been reasonably successful in accounting for the intensity for most transitions on the basis of crystal-field induced electric dipole transitions between individual Stark components [8]. The correlation between structure and absorption spectra for complexes of the transition metals is rather well understood in terms of the ligand field theory. Regrettably, the same situation is not true for complexes of the lanthanide and actinide metals. It is well known that the visible and near-infrared absorption spectra, consisting of narrow bands due to electronic transitions (Laporte forbidden) within the f  $^{n}$ configuration, are affected only slightly by changes in the environment of the metal ion. This is attributed to the shielding effect on the f-electrons by the outer electrons of the ion.

Interpretation of the spectra of rare earth ions in aqueous solutions is often greatly complicated by the simultaneous occurrence of several complex species. Only in the case of well defined complexes can certain conclusion be drawn from the absorption spectra concerning structure [9]. Most of the sharp lines like  $4f \leftrightarrow 4f$  transitions originating within the 4f-configuration of the lanthanide (III) ions are little affected by the environment of the lanthanide ions. Such transitions have been called hypersensitive transitions by Jorgensen and Judd [10]. The oscillator strengths and shapes of the hypersensitive transitions can be used to probe complex formation, coordination geometry, and ligand structure and chelate solvent interactions [11]. The spectra of their complexes show much narrower and more distinct absorption bands which is associated with weak f-f transition. The 4f orbital are deeply embedded inside the atom and well shielded by 5s and 5p electrons. The f electrons are practically unaffected by complex formation; hence colour remains almost constant for a particular ion regardless of the ligands. The bands due to f-f transition are sharp compared to the broad bands for d-d transition. Absorption bands due to 4f-5d transitions are broad and are affected by ligand environment All lanthanide ions (except La<sup>3+</sup> (f <sup>o</sup>) and Lu<sup>3+</sup> (f <sup>14</sup>) show luminescence Eu<sup>3+</sup> (f <sup>6</sup>) and Tb<sup>3+</sup> (f<sup>8</sup>) showing particularly strong emissions. This has being attributed to the large number of excited states that exist which decays to the ground state with either emission of energy (fluorecence) or non-radiative pathways. The origin of this is f-f transition. The luminescence of lanthanoid complexes is the reason they are used as phosphors on TV screens and fluorescent lighting.

#### 2. Application of Lanthanide Complexes

The established applications are in the field of metallurgy, ceramic, optical, semi-conducting and in electrical field like superconductivity etc. Applications of lanthanides and actinides in ionic liquids have been reported [12].

(a) Ceramics:  $BaTiO_3$  is the most extensively used ceramic material in the electronic industries. Large ions such as La (III) and Nd (III) give exclusive substitution at the Ba site as their size is incompatible with that of Ti (IV) [13].

(b) MRI (Magnetic Resonace Imaging): The Coordination chemistry of lanthanide ions with functionalized macrocyclic ligands has been widely investigated over the last two decades because of the importance of their



medicinal and biochemical applications. For example, Gd (III) complexes have been studied as contrast agents in magnetic resonance imaging (MRI) [14-15], Yttrium complexes in radio-immunotherapy and Eu and Tb complexes as luminescent probes.

(c) Luminescence: Many lanthanide complexes are noted for their interesting photophysical properties arising from  $f \leftrightarrow f$  transitions and are used as candidates for a number of applications, such as electro- luminescence devices and photo-luminescence devices and labels in a variety of biological and chemical applications.

(d) Fluorescence / Phosphorescence: Luminescence is emission of light by material as a consequence of its absorbing energy and fluorescence is short time lapse ( $\sim 10^{-8}$  s) between excitation and emission. Lanthanides have many applications in the field of fluorescence / Phosphorescence [16-17].

(e) Chemiluminescence: The lanthanide compound accepts the energy of excited products of chemi-luminescent reaction and re-emits chemi-luminescence (CL), but does not alter the rate / pathway of reaction. Highly luminescent lanthanide chelates are used to enhance the light intensity in those CL reactions where the primary excited product formed is non-luminescent but can transfer its energy to the Ln(III) chelate, e.g. in the case of triplet excited species [18].

**Laser:** Studies of spectral properties and the coordination chemistry of lanthanide chelates have been widely carried out because of their possible use as laser materials. Considerable research interest has been exhibited in these materials and the complexity of their coordination chemistry is now becoming more fully understood.

**Paramagnetic:** Ln (III) ions shows paramagnetism due to the presence of unpaired electrons in 4f-orbitals. According to modern view, the paramagnetism is contributed to both spin motion and orbital motion of electron. Thus Russell-Saunders coupling scheme is considered in which spin magnetic moment and orbital magnetic moment both are included [19].

(h) Other Applications: Lanthanides have also been used in superconductors, heterogeneous catalysts, nuclear power production, waste water analysis, reagents and catalysts in organic synthesis [20-24].

Tumor targeting with radioisotope labelled antibodies is being used for (a) cancer radio-immunotherapy [with  ${}^{90}$ Y(III)as a  $\beta$ -emitter], (b) cancer diagnosis [with<sup>111</sup> In(III) and  ${}^{67}$ Ga(III) as or with  ${}^{64}$ Cu(II) as a positron emitter and (c) *in vivo* magnetic resonance imaging (MRI) [with Gd(III) as a paramagnetic contrast agent] [25]. The application of lanthanides molecular compounds in organic synthesis, with a particular emphasis in the field of enantio-selective catalysis by lanthanides co-ordination complexes [26-28].

#### 3. Existing Problems with Lanthanide Studies

It is known that complexes of lanthanides are less stable than transition metal complexes. The formation of a coloured complex between the metal and coloured or colourless ligand is the basis for the development of spectrophotometric studies. Electronic spectral characterisation of complexes of lanthanides is essential in order to calculate various parameters such as intensity, energy or interaction and bonding parameters. The intensity parameters are Oscillator Strength (Px10<sup>6</sup>) and Judd - Ofelt parameters (T<sub> $\lambda$ </sub>), Energy or Interaction perameters are Slater-Condon Parameters (F<sub>2</sub>, F<sub>4</sub> and F<sub>6</sub>)Lande Parameters or spin-orbit interaction parameters ( $\zeta_{4f}$ ) Racah Parameters or Energy parameters (E<sup>1</sup>, E<sup>2</sup> and E<sup>3</sup>). The bonding parameters include nephelauxetic ratio( $\beta$ ) and bonding parameter (b<sup>1/2</sup>), Sinha's covalency parameter ( $\delta_{\%}$ ), Covalency angular overlap parameter ( $\eta$ ). These investigations involving the use of chemical, physical, mathematical and biological sciences provide fundamental basis for the development of interdisciplinary science and essential for the discovery and invention of novel and potential photoluminescence systems which are useful in many fields such as photoluminescence, medical and nuclear chemical technology. In addition to above, another problem is the selection of suitable solvent systems where lanthanide complexes can easily be solubilised forming a stable system and the solvent systems should not be toxic. Most of the time solubility of lanthanide system is also a major problem.

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