1.1 Introduction

1.1.1 Chemistry of lanthanide ions

The lanthanides are the elements following lanthanum in the periodic table. They are shiny and silvery-white, relatively soft, and reactive metals. Since the lighter elements in the series are chemically similar to lanthanum, they have been termed as lanthanides. They possess certain chemical features that differentiate them from the \( d \)-block elements. The lanthanide series is defined by the progressive filling of the \( 4f \) orbitals, namely, \( z, xz, yz, xyz, z(x-y), x(x-3y) \) and \( y(3x-y) \). Since there are seven such orbitals, each with a capacity of two electrons, a total of fourteen elements of this \( f \)-type series may result before the \( 5d \) orbitals start filling up again. These \( 4f \) electrons are shielded from the environment of the atom by the filled \( 5s \) and \( 5p \) shells.

Since the valence electrons are the same for all the ions, they all show very similar reactivity and coordination behaviour. Lanthanum (the \( d \)-block element preceding this series) has the electronic structure: xenon core \( 5d^16s^2 \). It might be expected that the 14 elements from cerium to lutetium would be formed by adding 1, 2, 3,.....14 electrons into the \( 4f \) level. However, it is energetically favourable to move the single \( 5d \) electron into the \( 4f \) level in most of the elements, but not in the cases of Ce, Gd and Lu. Ce has the electronic configuration \([\text{Xe}]\ 6s^2\ 5d^1\ 4f^1\); Pr having the arrangement \([\text{Xe}]\ 4f^3\ 6s^2\). This trend continues for the metals Nd to Eu having the arrangement \([\text{Xe}]\ 4f^n\ 6s^2\) where \( n = 4 \) to 7. After Eu, the next metal Gd has the arrangement \([\text{Xe}]\ 6s^25d^14f^7\). The reason why Gd has a \( 5d^1 \) arrangement is that this gives an increased stability due to half-filled \( 4f \) level. At Tb, the earlier pattern is resumed having the arrangement as \([\text{Xe}]\ 6s^24f^9\). This trend of electronic arrangement is also followed by the succeeding elements up to
GENERAL INTRODUCTION

Yb; their general arrangement being [Xe] 6s² 4fn (n= 10-14). The last lanthanide element, Lu has a 5d¹ arrangement as the f shell is already completely filled and has the arrangement as [Xe] 6s² 5d¹ 4f¹⁴[1]. Because of the nature of these 4f orbitals, the chemistry of lanthanides differs from the main group elements and transition elements. These orbitals are shielded from the atom’s environment by the 4d and 5p electrons. As a result, the chemistry of the lanthanides largely depend on the atomic size of the elements, which decreases gradually from La³⁺ (102 pm) to Lu³⁺ (86 pm). This decrease in atomic size is better known as the lanthanide contraction. As one goes through the series i.e. from La-Lu, there is a decrease in atomic radii as well as in the ionic radii of the Ln³⁺ ions, which is more prominent at the start of the series. The 4f electrons are ‘inside’ the 5s and 5p electrons and are core-like in their behaviour, which are shielded from the ligands, thus taking no part in bonding, and their spectroscopic and magnetic properties are independent of environment. The 5s and 5p orbitals penetrate the 4f subshell and are not shielded from increasing nuclear charge, and hence because of the increasing effective nuclear charge they contract as the atomic number increases [2]. The oxidation state (+ III) is ionic and Ln³⁺ dominates the chemistry of these elements. The Ln²⁺ and Ln⁴⁺ that do occur are always less stable than Ln³⁺ ions. Oxidation numbers (+II) and (+IV) occur particularly when they lead to: (a) a noble gas configuration e.g. Ce³⁺ can lose its single f electron to form Ce⁴⁺ and leads to the stable electronic configuration of xenon; (b) a half filled f orbital e.g. Eu³⁺ can gain an electron to form Eu²⁺ with the f⁰ configuration which has the extra stability of a half-filled shell. Similarly Tb³⁺ can lose an electron to form Tb⁴⁺ which has f⁰ configuration to gain the stability of a half-filled shell; (c) a completely filled f shell: Yb³⁺ can gain an
electron to form Yb\(^{2+}\) which has a completely filled \(f\) shell configuration which has the extra stability of a completely filled shell.

1.1.1 (i) History of discovery of lanthanides

It took more than 160 years until all of them were discovered, starting in 1787 when C.A. Arrhenius found a black stone in the vicinity of Ytterby (Sweden) from which several lanthanides could be isolated [3]. There are mainly two reasons why the discovery took so long: Though being abundant in nature, lanthanides can be found only in very small concentration in numerous rocks. In addition, they all behave similar in complex formation and solubility making it difficult to separate them. Their popularity in modern technology is due to the exceptional luminescence properties they possess.

In the early 19\(^{th}\) century, most of the lanthanide ions were discovered and the remaining ions were discovered in the 20\(^{th}\) century. These elements are also known as rare earth elements. The ions are abundant in earth’s crust but they do not form concentrated ore deposits [4]. Since the discovery of the lanthanides, the technological importance of the ions has been growing rapidly. A wide variety of minerals, which can be found on a few places in the world, do contain rare earth elements at relatively high concentration, in different compositions. The lighter elements are found more abundantly in these ores and consequently have lower prices.
1.1.1 (ii) Applications of lanthanide ions

The lanthanide ions have widespread applications in various fields such as in laser action, permanent magnet, catalysis, batteries and optics [5]. The luminescence of the ions is widely studied in many inorganic hosts, like crystals or glasses [6]. The optical properties of lanthanide ions became important due to its numerous applications in Cathode Ray Tubes of computers and colour television [7], in fibre optic telecommunication and also in laser amplifiers [8].

Recently, considerable attention has been paid on the development of lanthanide ion doped materials as phosphors, especially those with high intensity and efficiency, for their important applications in fluorescent lamps, plasma display panels and field emission display devices [9-11]. Lanthanide ions doped in inorganic host materials of YPO$_4$, LaPO$_4$, GdPO$_4$, LuPO$_4$, GdVO$_4$, CaWO$_4$, SrWO$_4$, CaMoO$_4$, Y$_2$O$_3$, SnO$_2$, ZrO$_2$ etc. have been extensively studied [12-22]. These inorganic host materials usually have very high thermal and chemical stability. The lanthanide ions which are doped in inorganic host materials have been extensively used in luminescent devices, solid state lasers, displays, LEDs, luminescent markers etc. [23-30].

1.1.2 Nanotechnology and Nanoparticles

Nanotechnology which is a quickly emerging field refers to technological study and application of nanoparticles. The wide variety of nanostructures such as nanorod, nanowire, nanotube, nanobelt, nanosheets etc. increases the applicability of nanotechnology to the welfare of mankind. Richard Feynman, the late preeminent physicist (Nobel Prize for Physics 1965), proposed employing “machine tools to make
smaller machine tools, these in turn to be used in making still smaller machine tools and so on all the way down to the atomic level.” This discussion was the earliest vision of nanotechnology.

Prior to Feynman, J. C. Maxwell in 1867 imagined in a thought experiment, a tiny entity that could manipulate individual molecules. The discovery of subatomic particles laid the foundation of nano science and nanotechnology. The works of G. J. Stoney, J. J. Thompson and Irving Langmuir led to the development in the field of particle physics and aroused interest in the research of substances of small particles. With the development of various scanning microscopes, the visualization and manipulation of nano-sized structures have been enabled. With the advent of scanning probe microscopes, which permit observation of individual atoms and molecules, it has become possible to manipulate and move atoms and molecules to form new structures and, thus design new materials that are built from simple atomic level constituents. This ability to carefully arrange atoms provides opportunities to develop mechanical, electrical, magnetic, and other properties that are not otherwise possible. This approach is known as ‘bottom-up’ approach and the study of the properties of these materials is termed as “nanotechnology”; the “nano” prefix denotes that the dimensions of these structural entities are in the order of a nanometer (10⁻⁹ m) and as a rule, less than 100 nm. The very term ‘nanotechnology’ was first coined by Norio Taniguchi and his co-workers in the year 1974 [31] to describe semiconductor processes such as thin film deposition and ion beam milling; and they defined this technology as the processing, separation, consolidation, and deformation of materials by one atom or by one molecule. It was Drexler who popularized the field of nanotechnology by publishing
two of the earliest books on the field: *Engines of Creation: The Coming Era of Nanotechnology and Nanosystems and Molecular Machinery, Manufacturing and Computation*. Later on, ‘nanoscience’ and ‘nanotechnologies’ have been defined by the Royal Society and Royal Academy of Engineering [32, 33] as follows: “Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where the properties differ significantly from those at a larger scale”; likewise, “Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale”. The most widely accepted definition of nanotechnology to date appears on the NASA website[34] as: the creation of functional materials, devices and systems through control of matter by on the nanometer length scale (1-100 nm) and exploitation of novel phenomena and properties (physical, chemical, biological) at that length scale.

Nanoparticles have been defined as a small particle with all three dimensions less than 100 nanometres. Nanoparticles have attracted great scientific interest as they serve as a bridge between the bulk materials and atomic or molecular structures. Usually a bulk material is expected to have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super paramagnetism in magnetic materials. At the nanoscale level, the known physical and chemical properties of substances are altered, providing new possibilities for using the same substances only in nano sizes rather than in micro-sized particles and this makes the nano-sized matter unique from its bulk counterparts. Hence
nanomaterials may be classified as those materials which have at least one of their dimensions in the nanometric range, below which there is significant variation in the property of interest compared to microcrystalline materials.

1.1.2 (i) Classification of nanomaterials

Nanoparticles have been classified into four kinds by Richard W. Siegel [35] according to their dimensionality as

<table>
<thead>
<tr>
<th>Type</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 D nanoclusters</td>
<td>They have unique properties due to quantum confinement and very high surface/volume ratio</td>
</tr>
<tr>
<td>1 D multilayers</td>
<td>The magnitudes of length and width of 1 D are much greater than the thickness (only a few nanometers in size)</td>
</tr>
<tr>
<td>2 D ultrafine-grained</td>
<td>The length is substantially larger than width or diameter, which are of nanometer dimensions</td>
</tr>
<tr>
<td>overlayers or buried layers</td>
<td></td>
</tr>
<tr>
<td>3 D equiaxed bulk solids</td>
<td>All the three dimensions are of nanometer size and are termed nanostructured crystallites</td>
</tr>
</tbody>
</table>

Fig 1.1 The different forms of nanomaterials as classified by Seigel.
Gleiter [36] further classified nanostructured materials according to the composition, morphology and distribution of the nanocrystalline component. This classification includes many possible permutations of materials and is quite broad. According to the shape of the crystallites, three categories of nanostructured materials are distinguished as (i) one dimension e.g. thin films whose thickness is less than 100 nm, (ii) two-dimension e.g. nanowires and (iii) three dimensions e.g. quantum dot. Nanoparticles or nanocrystals made of metals, semiconductors and oxides are of great interest due to their fascinating mechanical, electrical, magnetic, optical, chemical and other properties.

Nanostructured materials may occur in several geometric configurations including wires, tubes, rods, shells, pores, etc. they possess unique properties and are being developed for specific applications. Some of the emerging trends in nanostructures have explained below:

**Nanowires**: These can be defined as 1 D nanostructures with nanometric width dimensions and exhibiting aspect ratios (the ratio between length and width) of 1000 or more. Nanowires exhibit interesting properties that deviate from bulk behaviour due to their quantum confinement in the lateral dimensions. Nanowires are also, therefore, frequently referred to as ‘quantum wires’.

Nanowires made of several metals such as Au, Ni, Pt; semiconductors such as In, P, Si, GaN and insulators such as SiO$_2$, TiO$_2$ have been fabricated. These nanowires find interesting applications in the field of electronics, opto-electronic and nanoelectromechanical sensors and devices. They are also used as metallic interconnects in quantum devices and for toughening advanced composites.
Nanorods: They differ from nanowires in their aspect ratio, with their standard ratios being 3-5. This means that they have their dimensions in the range of 1-100 nm and hence are 3D nanostructures. They can find numerous applications in display technologies and in micromechanical switches.

Nanoshells: These are those structures where the nanocrystalline particles are coated with a thin layer of a different material with thickness in nanometric dimensions. Due to their nanometric width and size, nanoshells can exhibit interesting quantum confinement effects. These structures are useful in nano-drug delivery for in vivo therapeutic applications.

Nanotubes: These are tubes with diameters in the nanoscale. Various number of nanotubes of different materials have been reported, but till date carbon nanotubes are the most important group. Carbon nanotubes exhibit unique electronic, mechanical properties. They also show good nano-mechanical properties due to their high Young’s modulus.

Nanofluids: These are fluids (e.g. water, ethylene glycol, lubricants) with dispersions of nano-sized particles (e.g. carbon, metal oxides, etc.). Popular nanofluids are magnetic nanofluids and thermal nanofluids. They find wide applications in drug delivery, magnetic storage media, refrigerant chillers, electronic manufacturing, cosmetics, pharmaceuticals, power generation, air-conditioning, etc.

Due to the reduction in size, the proportion of atoms in the surface and near surface layers are increased and therefore properties like quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super paramagnetism in magnetic materials could be varied with change in size and shape[37-
The properties such as melting point, colour, ionization potential, hardness, catalytic activity and selectivity [58-61] or magnetic properties such as coercivity, permeability and saturation magnetization [62-64] changes with size and shape. Thus we can say that nanoparticles are promising materials for wide range of industrial and technological applications.

**Fig. 1.2** TEM images of (a) nanowire, (b) nanotubes, (c) nanoshells and (d) nanorods
1.1.3 Advances in Nanotechnology

Today's nanotechnology harnesses current progress in chemistry, physics, materials science, and biotechnology to create novel materials that have unique properties because their structures are determined on the nanometer scale. Some of these materials have already found their ways into consumer products, such as sunscreens and stain-resistant pants. Others are being intensively researched for solutions to humanity's greatest problems — diseases, clean energy, clean water, etc.

The technology has been used in diagnosis, therapeutics, prosthesis materials and tissue engineering. Nanomaterials have dimensions similar to those of biological molecules and hence they are useful in biomedical applications. Nanoparticles have been used in living subjects to target tissue-specific vascular biomarkers [65] and cancer cells[66-69] and in identification of sentinel lymph nodes in cancer[70-74]. Another most publicized use of nanotechnology is drug delivery to cancer cells. Particles are engineered so that they are attracted to diseased cells, which allow direct treatment of those cells. This technique reduces damage to healthy cells in the body. However, there are a number of other ways that nanotechnology can make the delivery of drugs more efficient and potentially less unpleasant for the patient. Some techniques are only imagined, while others are at various stages of testing, or actually being used today. Many researchers attach ethylene glycol molecules to nanoparticles that deliver therapeutic drugs to cancer tumours. The ethylene glycol molecules stop white blood cells from recognizing the nanoparticles as foreign materials, allowing them to circulate in the blood stream long enough to attach to cancer tumors. Some other researchers believe that they can increase the time nanoparticles can circulate in the blood stream. They are coating
nanoparticles containing therapeutic drugs with membranes from red blood cells and have shown that these nanoparticles will circulate in a mouse's bloodstream for almost two days, instead of the few hours observed for nanoparticles using ethylene glycol molecules.

1.1.4. Nanoparticles- Synthesis routes

There are different ways of classifying the synthesis routes for nanostructured materials. The most popular way of classifying the synthesis routes is based on how the nanostructures are built and such an approach leads to two routes, namely the ‘bottom-up’ and the ‘top-down’ approaches (shown in fig. 1.3). A top down involves division of a massive solid into smaller portions. This approach may involve milling or attrition, chemical methods and volatilization of a solid followed by condensation of the volatilized components. The bottom-up method of nanoparticles fabrication involves condensation of atoms or molecular entities in a gas phase or in solution.

![Fig.1.3 Schematic illustration of the preparative methods of nanoparticles](image-url)
1.1.5 Rare-earth doped nanoparticles

Till date, various techniques have been reported for the preparation of rare-earth doped nanoparticles. Some of the most effectively used methods for synthesis are layer-by-layer technique [75], hydrogen flame pyrolysis method [76], hydrothermal process [77], sol-gel process [78], co-precipitation technique [79], combustion technique [80] etc. Some commonly used reducing agents are ascorbic acid, potassium bitartarte, sodium borohydride, etc.. Capping agents and reaction media such as ethylene glycol, tributyl phosphate (TBP), polyethylene glycol (PEG), dimethyl sulphoxide (DMSO) etc. have also been employed in order to tune the particle size of the nanomaterials. In the process where capping agents are used, the metal solution and the reaction medium are mixed together at desired temperature by continuous stirring. The reducing agent is immediately added in order to hasten the reduction reaction. In this manner, small particles are obtained. High temperature synthesis of nanoparticles results in large sized nanoparticles due to agglomeration; they are insoluble in organic solvents due to lack of solubilizing surface groups. Thus a suitable capping agent needs to be used in preparation of nanoparticles.

1.1.6 Nucleation and growth from solutions

Solution-based processing routes used for the synthesis of nanoparticles include precipitation of solids from a supersaturated solution, homogeneous liquid phase chemical reduction and ultrasonic decomposition of chemical precursors. These processes are attractive due to their simplicity, versatility and availability of low cost precursors. In the precipitation technique, solid particles are obtained from a solution.
In general, soluble or suspended salts undergo reactions in solvent (aqueous or non-aqueous). Once the solution becomes supersaturated with the product, a precipitate is formed by either homogeneous or heterogeneous nucleation. Homogeneous and heterogeneous nucleation refers to the formation of stable nuclei with or without foreign species respectively. In order to form mono dispersed particles, all the nuclei must form at the same instant of time, and the growth must take place without further nucleation [81, 82].

There are certain factors which influence the rate of reactions such as temperature, pH of the solution, concentration and the order of reagents which are added to the solution. As a result, the rate of the reaction is affected by the particle size, particle-size distribution, amount of crystallinity, crystal structure and degree of dispersion of the prepared particles. Special care should be taken to avoid multiple precipitations at different pH levels in the solution.

1.1.7 Preventing agglomeration of nanoparticles

Nanoscale particles often agglomerate forming lumps and secondary particles. They agglomerate due to their large surface areas and their huge surface area is reduced by forming lumps. When the particles are held strongly forming hard agglomerates they are known as aggregates. Agglomeration of fine particles can occur at the synthesis stage or during drying and subsequent processing of the particles. Thus it is very important to stabilize the particles against adverse agglomeration at each step of particle production and powder processing. Surfactants are used to produce dispersed particles in the synthesis process or to disperse synthesized agglomerated fine particles.
Many technologies use surfactants [83,84] to prevent agglomeration of the particles. A surfactant is a surface-active agent that has an amphipathic structure in that solvent, i.e. a lyophobic (solvent repulsive) and lyophilic group (solvent attractive). At low concentrations, the surfactant molecules absorb on the surfaces or interface in the system, and can significantly alter the interfacial energies.

The attractive van der Waals force and/or the driving force which tends to minimize the total surface energy of the system is the cause of agglomeration of nanoparticles. Repulsive inter-particle forces are required to prevent the agglomeration of these particles. For this purpose, two methods are commonly used. The first method is stabilization method which causes dispersion using electrostatic repulsion. Repulsion results from the interactions between a particle’s surface and the solvent. Electrostatic stabilization of dispersion occurs when the electrostatic repulsive force overcomes the attractive van der Waals forces between particles. This stabilization method is generally effective in dilute systems of aqueous or polar organic media. The second method for stabilization is the one using steric forces. This method is used particularly in case of dispersing high concentrations of particles.

**1.1.8 Luminescence material**

In 1888, the German physicist Eilhardt Wiedemann coined the word ‘‘luminescence’’ for characterizing the light emission not conditioned by a rise in temperature [85]. Luminescence material which is commonly known as phosphor is a material that emits energy or radiation from an excited electron as light. The excitation of the electron is caused by absorption from an external source of energy such as an electron, a photon or
an electric field. A schematic energy level scheme of the luminescent ion A has been shown in Fig. 1.4.

The system consists of a host lattice and an activator which is the luminescent centre. The exciting radiation is absorbed by the activator, raising it to its excited state \( A^* \). The excited state returns to the ground state by emission of radiation \( R \). The ion or the material may not show luminescence if the excited state returns to the ground state by a non-radiative path. Instead, the energy of the excited state is used to heat the host lattice. The thesis reports the luminescence properties of \( \text{CaWO}_4 \), \( \text{CaMoO}_4 \) and \( \text{SrWO}_4 \) as host material with rare-earth ions such as \( \text{Eu}^{3+} \), \( \text{Tb}^{3+} \), \( \text{Dy}^{3+} \) and \( \text{Sm}^{3+} \) as the activator ion.

![Schematic energy level scheme of luminescent ion A. Asterisk indicates the excited state, R the radiative return to ground state and NR the non-radiative return.](image)

There are various kinds of luminescence having different modes of excitation of the activator ion. Some of them are:

(a) Photoluminescence (PL)  
(b) Electroluminescence (EL)  
(c) Cathodoluminescence (CL)  
(d) Mechanoluminescence  
(e) Chemiluminescence  
(f) Thermoluminescence
When an insulator or semiconductor absorbs electromagnetic radiation in the form of a photon, an electron may get excited to a higher energy quantum state, thereby radiating a photon, this process is called photoluminescence (PL). Electroluminescence (EL) is the emission by recombination of electrons and holes under the influence of an electric field; i.e. when a material emits radiation as a result of application of an electric field. When a material emits radiation when it is excited by energetic electrons, the process is known as cathodoluminescence (CL). Other kinds of luminescence are: chemiluminescence (non-thermal production of light by a chemical reaction), or triboluminescence (emission observed by applying mechanical stress to crystals or by fracture of crystals).

Photoluminescence of a material may be either fluorescence or phosphorescence. Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation of a different wavelength. The process of fluorescence takes place in a very short period of time. The time between initial absorption and return to the ground state takes place in the order of $10^{-8}$ s. fluorescence occurs between singlet states whereas phosphorescence is a transition between a triplet state in and singlet ground state. Phosphorescence takes longer time and continues emitting radiation for few microseconds, milliseconds, seconds, minutes or even hours.

1.1.9 Luminescence of trivalent lanthanide ions

In lanthanide elements, the 4f shell is successively filled. These 4f electrons are shielded from the environment by the filled 5s and 5p shells. Since the valence electrons are the same for all the ions, they all show almost same reactivity and coordination behaviour
[2]. Since luminescence of the trivalent lanthanide ions arises from transitions within the 4$f$ shell and because this shell is shielded by filled 5$s$ and 5$p$ shells, the absorption and emissions of the ions are only slightly affected by the environment. The transitions within the 4$f$ state are parity forbidden, but still $f$-$f$ transitions do occur. This is due to mixing with allowed transitions, like the 4$f$-5$d$ transitions. As a result of the forbidden character, absorption coefficients are low and luminescence lifetimes are long, ranging from micro-seconds up to several milli seconds. Since the 4$f$ orbital lies inside the ion and is shielded from the surroundings by the filled 5$s^2$ and 5$p^6$ orbitals, the influence of the surrounding (or host lattice) on the absorption and emission of the ions is small. One of the interesting features of these ions is their photoluminescence. Several lanthanide ions show luminescence in the visible or near-infrared spectral regions upon irradiation with ultraviolet radiation.

The colour of the emitted light depends on the lanthanide ion. For instance, Eu$^{3+}$ emits red light, Tb$^{3+}$ green light, Sm$^{3+}$ orange light, and Tm$^{3+}$ blue light. The electronic configuration of trivalent rare-earth ions in the ground state are shown in Table 1.1. In the ground state electrons are distributed so as to provide the maximum combined spin angular momentum (S). The spin momentum S is further combined with the orbital angular momentum (L) to give the total angular momentum (J) as follows $J= L-S$, when the number of 4$f$ electrons is smaller than 7, $J= L+S$, when the number of 4$f$ electrons is larger than 7.
Table 1.1. Electronic Configuration of trivalent lanthanide ions in ground state

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Corresponding element</th>
<th>4f electrons</th>
<th>( S \Sigma s )</th>
<th>( L \Sigma l )</th>
<th>( J \Sigma (L+S) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>58 Ce(^{3+})</td>
<td>Xe</td>
<td>↑</td>
<td>1/2</td>
<td>3</td>
<td>5/2</td>
</tr>
<tr>
<td>59 Pr(^{3+})</td>
<td>Xe</td>
<td>↑ ↑</td>
<td>1</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>60 Nd(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑</td>
<td>3/2</td>
<td>6</td>
<td>9/2</td>
</tr>
<tr>
<td>61 Pm(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑</td>
<td>2</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>62 Sm(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
</tr>
<tr>
<td>63 Eu(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>64 Gd(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>7/2</td>
<td>0</td>
<td>7/2</td>
</tr>
<tr>
<td>65 Tb(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>66 Dy(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>5/2</td>
<td>5</td>
<td>15/2</td>
</tr>
<tr>
<td>67 Ho(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑</td>
<td>2</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>68 Er(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>3/2</td>
<td>6</td>
<td>15/2</td>
</tr>
<tr>
<td>69 Tm(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>1</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>70 Yb(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>1/2</td>
<td>3</td>
<td>7/2</td>
</tr>
<tr>
<td>71 Lu(^{3+})</td>
<td>Xe</td>
<td>↑ ↑ ↑ ↑ ↑</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

An electronic state is indicated by the notation \( ^{2S+1}L_{J} \), (Russel- Saunders notation), where L represents S, P, D, F, G, H, I, K, L, M,……….., corresponding to L= 0, 1, 2, 3, ………., respectively. Fig. 1.4 shows the energy levels originating from the \( 4f^{n} \) configuration as a function of n for the trivalent ions. The width of the bars in figure gives the order of magnitude of the crystal field splitting which is seen to be very small in comparison to the metal ions. La\(^{3+}\) has completely empty and Lu\(^{3+}\) has a completely filled \( 4f \) shell and hence they do not have optical transitions. Ce\(^{3+}\) has one electron and
one 4f level just above the ground state (not shown here). Ce\textsuperscript{3+} has the lowest oxidation potential of the lanthanide ions making the allowed 4f-5d transitions possible in the UV region. The crystal field has almost no effect on the energy of the levels and therefore this energy level diagram could be used in all sorts of host materials. This may lead to very similar emission and absorption spectra for the same lanthanide ion in different host matrix, however, symmetry and quenching will have an effect on the optical properties which are discussed in the upcoming chapters.

\textbf{Figure 1.4} Energy level diagrams of the lanthanide ions

The selection rules for the different transitions are influenced by the symmetry of the environment. The nature of the transitions varies from pure magnetic dipole transitions
to pure electric dipole transitions and mixtures of the two. The emission spectrum of the Eu\(^{3+}\) ion is strongly influenced by the symmetry of the surroundings. The main emissions of this ion occur from the \(^5\text{D}_0\) to the \(^7\text{F}_J\) (\(J = 0-6\)) levels. The \(^5\text{D}_0\rightarrow^7\text{F}_1\) transition is a pure magnetic dipole transition, which is practically independent of the symmetry of the surroundings and the strength can be calculated theoretically. The transitions to the \(^7\text{F}_0, 3, 5\) levels are forbidden both in magnetic and electric dipole schemes and are usually very weak in the emission spectrum. The remaining transitions to the \(^7\text{F}_{2, 4, 6}\) levels are pure electric dipole transitions and they are strongly dependent on the symmetry of the environment. In a crystal site with inversion symmetry the electric dipole transitions are strictly forbidden and the \(^5\text{D}_0\rightarrow^7\text{F}_1\) transition is usually the dominant emission line. In a site without inversion symmetry the strength of the electric dipole transitions is higher. The \(^5\text{D}_0\rightarrow^7\text{F}_2\) transition is usually the strongest emission line in this case, because transitions with \(\Delta J = \pm 2\) are hypersensitive to small deviations from inversion symmetry [86]. The symmetry around the lanthanide ion can thus be obtained from the shape of the emission spectrum of the Eu\(^{3+}\) ion. The other lanthanide ions have transitions that are usually mixtures of electric and magnetic dipole transitions and the effects of the symmetry are less pronounced. In case of the Eu\(^{3+}\) ion, the symmetry around the lanthanide ion could be obtained from the shape of the emission spectrum. The other lanthanide ions which have mixtures of electric and magnetic dipole transitions, the effects of the symmetry are less pronounced. The symmetry also has an influence on the radiative lifetime of the \(^5\text{D}_0\) level. The radiative lifetime is the time for the luminescence to drop to 1/e in intensity in absence of quenching. In the case of a Eu\(^{3+}\) ion without inversion symmetry the rate of the forced
electric dipole transition is higher than in the case of a Eu$^{3+}$ ion with inversion symmetry. This automatically means that the radiative lifetime of a Eu$^{3+}$ ion in a site with inversion symmetry is longer. Radiative lifetimes of lanthanide ions have been calculated with several methods, of which the Judd-Ofelt theory is the most popular [87]. In this theory the strength of the electric dipole transitions are calculated from the absorption spectrum and these strengths can be related to the radiative lifetime.

### 1.1.10 Charge Transfer

Besides the absorption and emission lines which can be attributed exclusively to transitions inside the Ln electron configurations, the excitation and emission spectra of Ln-containing compounds sometimes show broad bands which can be explained assuming charge transfer (CT) transitions between the Ln dopant and a host ion or between the host ions themselves. Transitions between Ln$^{3+}$ ions and host ions can occur in both directions, either from the ligand to the Ln$^{3+}$ ion, usually referred to as an Ln$^{3+}$ CT or from the Ln$^{3+}$ to a host cation, a so-called inter valence charge transfer (IVCT). IVCT transitions have been observed so far only in the transition metal oxides [88].

### 1.1.11 Luminescence quenching

Quenching is any process that decreases the fluorescence intensity, and as such, may be the result of a variety of processes. Every luminescent material may not show proper luminescence intensity as there is a competition between the radiative and non-radiative path to return to the ground state. There are three common quenching mechanisms; they
are (i) Multi-phonon emission (ii) Cross-relaxation and (iii) energy transfer between lanthanide ions. Multi-phonon emission is the non-radiative return to the ground state and this is possible when the energy difference is equal to or less than 4-5 times the vibrational frequency of the surroundings. The energy of the excited state is taken in the form of phonon emission; and hence this emission may be understood as the energy taken up by the surrounding in the form of vibrational energy. The effectiveness of this process depends on the availability of high energy vibrations in the surrounding and the energy difference between the lanthanide ion. The fundamental vibration of the chemical bonds in the surrounding and the energy of the vibration are determined by the reduced mass of a bond. Therefore bonds with hydrogen have small reduced mass and high vibrational energies. These bonds can take up large amounts of energy and quench lanthanide ions with large separations between the energy levels.

Cross-relaxation process is associated with exchange interaction between two lanthanide ions which are closely together and have interaction. This type of luminescence quenching occurs when the concentration of lanthanide ions is large, i.e. when the Ln-Ln distance is very short. The donor and acceptor do not have to have overlap of their wave functions, but the process is strongly distance dependent. For dipole-dipole interactions the rate of quenching has a distance dependence of \( r^{-6} \) [89]. Energy transfer between the same or different lanthanide ions result in quenching of luminescence. Two different lanthanide ions can transfer energy when they have similar separations between the energy levels.
1.2 Thesis Outline

In this thesis, synthesis of some lanthanide ions (Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$ and Sm$^{3+}$) doped in the inorganic hosts such as CaWO$_4$, CaMoO$_4$ and SrWO$_4$ with detailed study on the luminescence properties is presented. Chapter 4 presents a study on CaWO$_4$ doped with rare earth ions. Of these materials, Photoluminescence (PL) excitation and emission spectra are recorded. For Eu$^{3+}$ doped in CaWO$_4$, the Thermoluminescence (TL) spectra are also recorded. The re-dispersible behaviour of the nanoparticles in some polar solvents are also discussed. Further, incorporation of the prepared nanoparticles in the polymer film such as poly vinyl alcohol (PVA) is also discussed.

Chapters 5 and 6 focus on the synthesis, characterization and PL studies of CaMoO$_4$ and SrWO$_4$ doped with the above lanthanide ions. The luminescence intensity is altered by varying the solvents used. This is due to the presence of high-energy vibrations of the organic bonds surrounding the lanthanide ion. The nano-sized lanthanide ion doped inorganic host materials have been prepared in water, ethylene glycol (EG), dimethyl sulfoxide (DMSO) and in mixed solvent system at comparatively low temperature (130°C). The white emission study has also been discussed in Chapter 4. The prepared nanoparticles have been characterized using X-ray diffraction (XRD), Transmission electron microscopy (TEM), FT-IR spectroscopy. Photoluminescence (PL) and their luminescence decay processes are discussed in detail in the thesis.
References


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