Chapter 1

GENERAL INTRODUCTION
1.1 Objective and scope of research

Spectroscopy mainly concerns the study of interaction between electromagnetic radiation and matter. In fact, historically, spectroscopy deals with the use of visible light dispersed according to its wavelengths. Later the concept was expanded greatly to comprise any measurement of a quantity as function of either wavelength or frequency. The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules. This technique is one of the most powerful tools to investigate various physical and chemical properties of the matter in the modern science and technology.

The applications of spectroscopy not only confined to physics and chemistry but it also stretches to entire fields like astronomy [1, 2], biology [3, 4], communication [5], defence [6, 7], forensic [8, 9], geology [10, 11], industry [12-13] and medicine [14], etc. Optical spectroscopy has been instrumental in the discovery of many lanthanide (Ln) elements. In return, these elements have always played a prominent role in lighting devices and light conversion technology (incandescent lamps, lasers, cathode ray and plasma displays), highly sensitive luminescent bio-analyses and cell imaging. This is also useful to fabricate/analyse optical devices such as solid state lasers [15-19], light converters [20-24], optical fiber amplifiers [25-27], optical storage materials [28, 29], spectral hole burning high density memories [29], sensors [30-32], phosphors [33-35], acousto-optic modifiers [36-38], planar wave guides [39, 40] and so on.

One of today’s major challenges is the study of lanthanide (Ln)-doped materials for photonic applications with low cost and high efficiency for a wide range of fields such as Chemical, Biological, Industrial, Medicinal, Agricultural, etc. When entering into the 21st century, the pace of industrial internationalization and economical globalization is being speeded up. Even though it gives nightmares but the developments in various scientific fields are appreciable. Along with that, the growth of Ln spectroscopy is fast and significant. The increasing demand in its applications makes the finger print investigations worthy and interesting.
The unsaturated $4f$ electronic structures of Ln elements make them to have special properties in luminescence, magnetism and electronics. Now-a-days, Ln-doped materials are finding new areas of applications. Particular attention has been focused mainly on the synthesis and characterization of Ln-doped (glasses and nanocrystals) materials. Different synthesis methods may have different internal structures that affect the luminescence properties of materials consolidated from them. Optical materials doped with Ln elements are of great relevance in Science and Technology. Modern Optics and Laser Technology are mainly based on Ln-doped materials, with applications ranging from solid state lasers for industry, medicine and environmental monitoring; optical fibers for telecommunication and sensors and phosphors for display devices.

Moreover, from the scientific point of view, Ln-doped materials attract increasing interest due to their particular physical properties. Indeed the electron configuration involving $f$-electrons and the exceptional time and space coherence properties lead to the observation of new and fascinating phenomena. Among the materials, the attention was focused on amorphous (glasses) materials modified with different alkali and alkaline earth elements and metal oxide nanocrystals. These materials are distinguished by good transmission properties in the visible (Vis) part of the electromagnetic spectrum and by relatively low phonon energies. They can be efficiently doped with Ln ions, due to the similarity between the ionic radii of the alkali, alkaline earth and Ln ions. Therefore, these materials are prospective high efficiency luminophors and are attracting increasing interest for photonic and optoelectronic applications. Indeed alkali and alkaline earth doped materials are resistant to many chemicals and atmosphere and can also be grown with low-cost techniques.

The present thesis has two major aims. The first one is to develop optimized Ln$^{3+}$-doped materials and investigate their absorption and luminescence properties and energy transfer processes among Ln ions in those host materials. The opted dopant ions are Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Dy$^{3+}$, Ho$^{3+}$ and Er$^{3+}$ in the lithium-fluoro-borate glass materials. The second aim is the proper assessment of various spectroscopic properties which allow these materials for the development of photonic devices such as lasers, display devices, optical sensors, etc.
1.2 General introduction

1.2.1 Classification of solids

Solids can be classified into two categories, namely crystalline and amorphous. The X-ray diffraction technique is used to distinguish crystalline and amorphous nature of solids.

1.2.2. Crystalline solids

The crystalline solids have clear cut geometric structure and the atoms are arranged in regular long-range order with permissible rotational symmetry [41]. The X-ray diffraction spectrum of crystalline solid exhibits a series of sharp Bragg peaks each corresponding to a different periodicity in the crystalline lattice characterized by the long-range order as well as the anisotropic nature (property will be different in different directions). Examples are sugar, quartz, calcite etc.

1.2.3. Amorphous solids

The amorphous solids have no clear cut geometric structure and there is no order of arrangement of atoms. Even if order exists, it is a short range order. The X-ray diffraction spectrum of amorphous solid exhibits a series of broad peaks at small scattering angles indicating the short-range order. They are isotropic in nature (property is same in all directions). Examples are rubber, glass, plastic etc.

1.3 Introduction-Glasses

Amorphous materials are not new; the iron-rich siliceous glassy materials recovered from the moon by the Apollo missions are some billions of years old and man has been manufacturing glassy materials (principally from silica) for thousands of years. However, the “Scientific study” of amorphous materials and also there has been an explosion of interest recently as more new materials are developed in an amorphous form and some of which have potential technological applications.
Definition

This is concerned with non-crystalline (or amorphous) materials which possess randomness to some degree. Randomness can occur in several forms, of which topological, spin, substitutional, or vibrational disorder are the most important. Disorder is not a unique property, it must be compared to some standard, and that standard is the perfect crystal. This can be defined in the following way:

“A perfect crystal is that in which the atoms (or group of atoms or ‘motifs’) are arranged in a pattern that repeats periodically in three dimensions to an infinite extent”.

Nevertheless, there are ‘degree’ of topological disorder: certain amorphous materials have considerable short-range (or local) order while others have little; both have no long-range order, however, all amorphous or glassy solids are therefore distinguished by their lack of periodicity. There is a considerable amount of confusion in the literature concerning the terms ‘amorphous’, ‘non-crystalline’ and ‘glassy’ and there are as yet no universally accepted definitions.

“Amorphous materials do not possess the long-range order (periodicity) characteristic of a crystal”

The terms amorphous and non-crystalline are synonyms under this definition, and can be used interchangeably. The term ‘glass’ is more restricted and as a consequence varies most in its definition.

“A glass is an amorphous solid which exhibits a glass transition”

The glass transition (T_g), a more or less abrupt change in derivative thermodynamic properties (eg. heat capacity or thermal expansivity) from crystal-like to liquid-like values with change of temperature. It is to be noted that this definition differs from a commonly accepted version in which glass is defined simply as the amorphous product produced by the rapid quenching of a melt. The definition offered here has the advantage that the term glassy is confined to those materials which can be obtained in a
reproducible state (even after temperature cycling) since the material can be in a state of internal equilibrium above the glass transition. ‘Glassy’ materials, therefore, need not be prepared solely by quenching from the melt. Note that glassy (or equivalently, vitreous) solids are a special sub-set of amorphous materials or, to express it in a different way, all glasses are amorphous but not all amorphous solids are necessarily glasses.

The versatility of glass probably begins with transparent decorative windows and opens many technological challenges in the fields such as energy conversion, optical fiber communication, bioactivity, etc. Chemically, glass is actually more like a liquid, but at room temperature it is so viscous or ‘sticky’ it looks and feels like a solid. At higher temperatures glass gradually becomes softer and looks like a liquid. It is this latter property which allows glass to be poured, blown, pressed and moulded into such a variety of shapes.

Glass materials have advantages over crystals in many optical device applications. These advantages include

1. Flexibility of choosing glass composition over a wide range,
2. A disordered ion environment that can broaden fluorescence bandwidth,
3. Uniform (isotropic) optical properties over a wide range of composition,
4. Ease of fabrication into complex shapes including fibers,
5. Low fabrication cost, which lends itself to mass production and
6. Possibility of producing large active lasers with good optical quality.

The quest for glasses that combine desirable optical properties and environmental suitability has led to the development of many oxide glasses, in particular silicates, phosphates and tellurites.

The X-ray diffraction (XRD) technique is useful to study the atomic structure of materials to distinguish the crystalline and non-crystalline solids. Amorphous materials show pronounced structure in XRD at small scattering angles, which reflects correlation in the positions of neighboring atoms. In contrast, the scattering from a crystalline solid
exhibit a series of sharp Bragg peaks, each one corresponding to a different periodicity in the crystal lattice which is characterized by the long-range order in atomic arrangement.

Glasses differ from crystals with lack of long range spatial order and have many advantages over crystalline materials. They can be cast in variety of forms and sizes, from small hairy fibre to meter sized pieces. Glasses are also relatively inexpensive along with chemical homogeneity and low birefringence. The only major drawback of glass is its low thermal conductivity, which limits its applicability in high power systems.

In recent years, inorganic glasses doped with RE ions have found technological importance in the development of new solid state lasers, optical devices, opto-electronics and fibre amplifiers. Glasses can be manufactured with excellent homogeneity without grain boundaries, thereby minimizing the optical losses and can be also easily prepared in desired forms, e.g. prisms, flats, lenses and more importantly as optical fibers, needed for optical communications. At present glass is versatile material that is commercially available over a wide range of compositions and can be fabricated by several techniques to produce variety of products. The science of glass is going through a revolution, paving way for the next generation condensed matter physics. In general, glasses are categorized into two types, natural and artificial glasses.

1.3.1. Natural glasses

Natural glasses such as obsidians, pechsteins, pumice etc., can be formed when molten lava reaches the surface of the earth’s crust and cooled rapidly. They can also be formed by the sudden increase in temperature following strong shock waves e.g. tectites [42]. In some rare cases, biological process can lead to glass formation. The skeleton of some deep water sponges (monoharpis) consists a large rod of vitreous SiO$_2$ [43].

1.3.2. Artificial glasses

The artificial formation of glasses occurs in various classes of materials. Although many substances are used to form glasses, only some of them are of practical value.
(a) Oxide glasses-borate

Among inorganic glasses, the oxide glasses, for example silicate (SiO$_2$), borate (B$_2$O$_3$), phosphate (P$_2$O$_5$), tellurite (TeO$_2$) and germanate (GeO$_2$) are most important.

Boron trioxide is a significant component of glasses, enamels and glazes. It is very rarely added to the raw material mixtures in the form of oxide, more frequent use being made of H$_3$BO$_3$ or Na$_2$B$_4$O$_7$. Boron oxide (B$_2$O$_3$) usually occurs in the glassy form which is virtually incapable of direct crystallization. The crystalline forms of B$_2$O$_3$ can only be prepared by special procedure. Although borate glasses are of little commercial importance because they are water soluble, B$_2$O$_3$ is an important constituent of borosilicate glasses such as Pyrex. In contrast to SiO$_2$ and silicate glasses in which the silicon is present as SiO$_4$ tetrahedra, B$_2$O$_3$ glasses contain BO$_3$ triangular units and BO$_4$ tetrahedra depending on the composition. Addition of alkali oxide to glassy B$_2$O$_3$ gives rather different results from those obtained in the corresponding alkali silicates. The structure of borate glasses are explained in detail in section 1.1.7.

(b) Halide glasses:

BeF$_2$ is a glass-network former, which may be considered as weakened model of SiO$_2$ and its structure is based on BeF$_4$ tetrahedra. Fluoro-zirconate, fluoro-borate and fluoro-phosphate glasses are the best candidates for high power lasers and thermonuclear fusion applications.

(c) Chalcogenide glasses:

These glasses are prepared using the elements of group VI (S, Se and Te) combined with elements of group IV (Si and Ge) and group V (P, As, Sb and Bi), which do not contain oxygen. Vitreous Se possesses photoconductive properties which is used in photocopiers (xerography). The Ge-As-Si glasses possessing opto-acoustic properties are used as modulators and deflectors in the IR region.
(d) Metallic glasses:

Metallic glasses are the materials of the present century. They may be subdivided into two classes, metal-metalloid and metal-metal alloys. These glasses have extremely low magnetic losses, zero magnetostriction, high mechanical strength, hardness, radiation resistance and high chemical corrosion resistance. These materials are used as cores in moving magnets, recording cartridges, amorphous heads for audio, computer tape recording and high-frequency power transformers.

1.3.3 Constituents of glass

In general, glasses are either produced from high quality, chemically pure components, or from a mixture of far less pure minerals. Regardless of the source of the components used to produce a specific glass, the batch materials can be classified into four categories on the basis of their role in the process, namely,

i. glass former,

ii. property modifier,

iii. colorant and

iv. fining agent.

The same compound may be classified into different categories when used for different purposes. Alumina, for example, serves as a glass former in aluminate glasses, but it is considered as a property modifier in most silicate glasses [44]. The most essential component of any glass batch is always the glass former. Every glass contains one or more components which serve as the primary source of the structure. While these components are commonly designated as glass formers, they are also called network formers or glass forming oxides in many oxide glasses. The primary glass formers in commercial oxide glasses are silica (SiO$_4$), boric oxide (B$_2$O$_3$) and phosphorous oxide (P$_2$O$_5$), which are readily form single component glasses. A large number of other compounds may also act as glass formers under certain circumstances, including GeO$_2$, Bi$_2$O$_3$, As$_2$O$_3$, Sb$_2$O$_3$, TeO$_2$, Al$_2$O$_3$, Ga$_2$O$_3$ and V$_2$O$_5$. The identity of these components usually serves as the basis for the generic name.
used for the glass. If the glass former present in a specific sample is silica, for example, that glass is called a silicate glass. If a significant amount of $P_2O_5$ is also present, in addition to silica, the sample is termed phospho-silicate glass.

There are some oxides like alkali ($K_2O$, $Na_2O$, $Li_2O$, etc.) and alkaline earth ($CaO$, $MgO$, $BaO$, etc.) oxides which when added in small quantities (10 mol % to 15 mol %) to the glass network forming oxides produce drastic changes (melting point, conductivity, etc.) in their physical and chemical properties. Such oxides also modify the network structure of the glass and hence they are termed as property modifiers.

Colorants are used to control the color of the final glass. In most cases, colorants are oxides of either the $3d$ transition metals or the $4f$ Ln ions. Colorants are only used if control of the color of the glass is desired and are usually present in small quantities. When colorants are used to counteract the effect of other colorants to produce a slightly gray glass, they are referred to as decolorants. Finally, fining agents are added to glass forming batches to promote the removal of bubbles from the melt. Fining agents include the arsenic and antimony oxides, potassium and sodium nitrates, $NaCl$, fluorides such as $CaF_2$, $NaF$, $KF$ and $Na_3AlF_6$ and a number of sulfates. These materials are usually present in a very small quantities (< 1 wt %) and are usually treated as if they have only minor effects on the properties of commercial glasses, which would be prohibitively expensive to produce without the aid of fining agents in reducing the content of unwanted bubbles in the final product. Different types of compounds are categorized into glass formers, modifiers and intermediates and are presented in the Table 1.1.

1.3.4 Structure of borate glasses substituting with alkaline and transition metal ions

$B_2O_3$ is never used alone to form glass because of its hygroscopic nature. But it is incorporated in several industrial glasses. In spite of their ability to absorb moisture, borate glasses are being used for technological applications such as high refractive index rare earth borates and lead borate glasses in plasma soldering. The behavior of $ZnO$ in borate systems generates special interest owing to their applications in different fields of
<table>
<thead>
<tr>
<th>Glass formers</th>
<th>Modifiers</th>
<th>Intermediates</th>
</tr>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>Li$_2$O</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>GeO$_2$</td>
<td>Na$_2$O</td>
<td>PbO</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>K$_2$O</td>
<td>ZnO</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>MgO</td>
<td>CdO</td>
</tr>
<tr>
<td>TeO$_2$</td>
<td>CaO</td>
<td>TiO$_2$</td>
</tr>
<tr>
<td>As$_2$O$_3$</td>
<td>BaO</td>
<td></td>
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<tr>
<td>As$_2$O$_5$</td>
<td></td>
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</tbody>
</table>

**Table 1.1.**
Glass formers, modifiers and intermediates.
electronic products. The addition of alkali \([\text{M}^+]\) or the alkaline earth \([\text{M}^{2+}]\) cations act as network modifiers in the glass structure, breaking bridging oxygen bonds to form non-bridging oxygens (NBO) \([45, 46]\) and extends their scope of applications to radiation dosimetry, vacuum ultraviolet (VUV) optics, phosphors and solar energy converters, etc. \([47-49]\). Borate glass contains a mixture of BO\(_3\) triangles and BO\(_4\) tetrahedra depending on composition. An important constituent of vitreous B\(_2\)O\(_3\) is boroxol group and is shown in Fig. 1.1. It is a planar, six-membered ring of alternate boron and oxygen atoms which are randomly connected in a three-dimensional network by sharing all the three oxygen atoms with adjacent BO\(_3\) units. However, with the planar coordination of boron, in comparison with the tetrahedral coordination of silicon in SiO\(_2\), glassy B\(_2\)O\(_3\) has a rather open structure. Molten B\(_2\)O\(_3\) is also more fluid than molten SiO\(_2\). Using X-ray diffraction and various spectroscopic studies, the triangular coordination of boron in B\(_2\)O\(_3\) glass can be deduced.

The addition of alkali oxide to glassy B\(_2\)O\(_3\) gives rather different results than those obtained in the corresponding alkali silicates and an effect known as the boron oxide anomaly is observed. It was shown that a gradual change in the coordination number of boron from three to four occurs as alkali oxide is added. By combining Raman scattering studies and the NMR investigations with the available crystallographic data, structural groups present in these glasses have been clearly identified. Fig. 1.2 shows the several structural groups present in various borate compounds. Pure B\(_2\)O\(_3\) consists of planar BO\(_3\) units which are randomly distributed in a three-dimensional network by sharing all the three oxygen atoms with adjacent BO\(_3\) units and are shown by the Fig. 1.3. The planar BO\(_3\) unit presumably involved in sp\(^2\) hybridization, with the third orbital being vacant and extending in direction, perpendicular to the BO\(_3\) plane. This vacant orbital accepts an electron from the unpaired electrons from the oxygen atoms, forming a partial double bond.

The following modifications in the network can be enhanced by the addition of network modifying oxides. (a) Boron-oxygen-boron bonds may be broken by oxygen anions (as in the case of the breakdown of silica network) to form non-bridging atoms. (b) a filled orbital of an oxygen anion may overlap with an empty p-orbital
Figure 1.1. Schematic model of boroxyl group which is linked by shared oxygen in $B_2O_3$ glass
Figure 1.2. Structural groupings in borate glass
Figure 1.3. 3D structure of boron trioxide
of a boron atom resulting in a change of hybridization of the boron atom to the sp\(^3\) tetrahedra arrangement leading to BO\(_4\) tetrahedron with three bridging and one non-bridging oxygen, (c) an oxygen atom may contribute an electron pair to two BO\(_3\) units changing the coordination of the two borons from sp\(^2\) to sp\(^3\) hybridization and with no nonbridging oxygen.

Several attempts [50] were made to explain the structure of borate glasses on the basis of a number of imaginative structural models, all of which were built around the relatively unique ability of boron to exist in two distinct coordination states. However NMR studies [51, 52] showed that the four coordinated boron varies smoothly as x/(l-x) where x varied from 0 to 30 mol% modifier oxide without any unusual behavior in the critical range 15-20 mol% of modifier oxide. The BO\(_4\) groups are bonded to the rest of the structure in four directions and the structure is therefore tied together in three dimensions rather than two. This will produce a marked increase in the strength and tightness of the structure.

Bray [53, 54] has shown using B\(^{11}\) NMR spectroscopy that a gradual change in the coordination number of boron from three fold to four occurs as alkali oxide is added to B\(_2\)O\(_3\). By the time about 30 mol% has been added, approximately 40 percent of the borons would have changed to tetrahedral coordination and this is independent of the nature of the alkali. In triangular coordination, the B\(^{11}\) nucleus shows strong quadrupole coupling with a broad resonance line whereas in tetrahedral coordination, the quadrupole coupling is weak and the resonance is narrow. Extensive investigations have been carried out on crystalline and glassy borates by Krough-Moe [55] who proposed a new model for the structure of borate glass. Krough-Moe suggested that borate glasses are not merely a random network of BO\(_3\) triangles and BO\(_4\) tetrahedra joined at the corners, but, they actually contain well-defined and stable groups as segments of the disordered framework. These borate groups which are included in the glass structure should be identical with the groupings which occur in crystalline borates. From the experimental results of thermodynamic [56] and infrared [57] studies, the structural groupings in borate glasses can be classified into four different groupings. viz., boroxol, pentaborate, triborate and
diborate groups. The pentaborate and triborate groups will always occur in pairs and these pairs are referred to as tetraborate groups.

Fig. 1.4 shows the structure of borate glass with different bonding locations. The three dimensional random network of strong bonds in glass is formed by the constituents of the so called network former. To incorporate a foreign ion (RE$^{3+}$ ion) into such a structure, one often needs the addition of certain other compounds like alkali oxides, alkali fluoride, lead oxide, lead fluoride etc., called as network modifiers. The modified structure becomes loose and therefore, even permits ion migration. Melt-derived glasses are prepared by rapid cooling from the liquid state so that crystallisation does not occur and the material becomes rigid by virtue of its increased viscosity. Such glasses are composed of an interconnected near-random distribution of covalently-bonded 'network formers', for example borate chains, whose negative charges are balanced by coordination with Group I and/or II cations or 'network modifiers'.

1.3.5 Thermodynamic features of glass

In general a glass has a higher configuration entropy and higher free energy as compared to crystalline structure with the same composition. Thus, a glass is in a thermodynamically metastable state whose non-transformation to its most stable state is due to the freezing of the atomic arrangement in the process of glass formation. The transformation of a glassy state to a crystalline state is driven by the difference of free energy between the two states and is limited by the viscosity of the melt (behaves as a supercooled liquid). The enthalpy graph of glass and crystal formation is shown in Fig. 1.5. This thermodynamic phase transition graph (temperature versus enthalpy) shows the formation of the glass according to the definitions and the experimental evidence [44].

In materials that form crystalline compounds the enthalpy, H, decreases abruptly down the red path (BCD) and at temperature $T_x$ (called crystallization temperature) they instantaneously form long periodic range crystals. In the case of compounds that form glassy structures crystallization does not happen at $T_x$ and a
Figure 1.4. Structure of borate glass with different bonding locations
Figure 1.5. Enthalpy graph of glass and crystal formation. The red line highlights the crystalline phase while the blue line the path followed by the glassy compounds.
supercooled liquid is generated on the blue path (BE). Reducing the temperature gradually increases the viscosity of the melt and glass starts to form arranging ions in the typical glassy disorder. The process is gradual and at some point the viscosity is so elevated that ions cannot move and the liquid is frozen becoming a glass. The temperature range over which this takes place is called the glass transformation range and $T_g$ is called temperature of glass transition. The effect of rate of crystallization of an undercooled liquid on temperature is shown in Fig. 1.6. Heating dynamics have also to be tailored to the composition as the enthalpy graph is strongly composition dependent. The quenching has to be rapid enough to avoid the crystallization of the composition and slow enough not to generate strains and internal stresses in the glass compound.

Crystals, in fact, form in a glass with a two step process during the supercooled liquid phase, the growth process and the nucleation process. Decreasing the temperature from $T_x$, the material passes the grow process first and then the nucleation one, if the passage is quick, nucleation happens when very little crystals have formed thereby favoring the glassy state. The higher the difference $T_x-T_g$, the more stable the glass against crystallization [58]. The principal techniques used for the forming of glass and the consequent doping of it with active ions are the melt-quenching and the sol-gel methods, the latter provides great results for the dopant distribution but the process is long and difficult to repeat. All the research glasses in the present study have been prepared by melt-quenching method, which is described in section 2.2 of chapter 2 in detail.

**1.4 Rare earth ions as active elements**

**1.4.1 Lanthanide ions**

In IUPAC terminology, the Lns or lanthanoids are series of elements which are situated at the top row in the ‘f - block’ of the periodic table and the abundance of Lns are shown in Fig. 1.7. The word ‘lanthanide’ is a very appropriate name since it took more than a century to discover all the Lns. These are also called as ‘rare-earth’ elements due to the etymology of the term ‘lanthanide’ (derived from the Greek lanthanein, meaning
Figure 1.6. Effect of rate of crystallization of an undercooled liquid on temperature.
Figure 1.7. Abundance (fraction of atoms) of the chemical elements in Earth’s upper continental crust as a function of atomic number.
‘to lie hidden’) and the uncommon oxides from which they were first isolated, Lns are actually neither ‘rare’ nor ‘earths’, an old term used to describe certain metal oxides such as lime and magnesia [59].

The Ln series comprises fifteen elements with atomic number increasing from 57 (lanthanum, La) to 71 (lutetium, Lu). All the Lns are $f$-block elements, corresponding to the filling of the $4f$ electron shell. Lutetium, which is a $d$-block element, is also generally considered to be Ln. The trivalent state is the most stable and therefore predominant oxidation state for all Ln ions. Going from La$^{3+}$ to Lu$^{3+}$ the $4f$-shell, which is situated inside the $5s$ and $5p$ orbitals, is being filled from 0 to 14 electrons. Since the $4f$-shell is efficiently shielded by the closed $5s$ and $5p$ shells, the ligand environment has only a weak influence on the electronic cloud of the Ln$^{3+}$ ions and also they do not play a role in chemical bonding. The chemical properties of the Lns are therefore much alike. Some selected physico-chemical properties such as atomic number (Z), density ($\rho$, g/cm$^3$), melting ($T_{\text{melt}}$, K) and boiling ($T_{\text{boil}}$, K) points and physical appearance of the Ln elements are shown in Table 1.2 [60]. The $4f^0$ (empty $f$-shell), $4f^7$ (half-filled $f$-shell) and $4f^{14}$ (filled $f$-shell) configurations are most stable. Therefore, besides the trivalent state some ions also occur in divalent and tetravalent states. Examples are Ce$^{4+}$ ($4f^0$), Eu$^{2+}$ and Tb$^{4+}$ ($4f^7$) and Yb$^{2+}$ ($4f^{14}$).

1.4.2 Importance of lanthanides

The series of Ln elements are used in a multitude of applications which include chemical, metallurgical, ceramic, optical, magnetic and high temperature superconductivity. However, their role in optics is one of the most extensive, varied and significant. Optical applications of Lns span the spectral range from the ultraviolet (UV) to infrared (IR). Their role may be as a constituent of transmitting glasses and crystals, as a colorant, decolorant or antisolarant, as a luminescent ion in spectroscopy. In some applications, the use of Lns is overwhelming compared to most other transition group elements; in other applications the Lns play only a minor or negligible role. Ln-doped materials for optics also encompass an impressive range in sizes: from diameters measured in microns for Ln-doped optical fibers to dimensions of tens of centimeters for...
Table 1.2.

Selected physico-chemical properties of the lanthanide elements. \( Z \) = atomic number; \( \rho \) = density \((\text{g/cm}^3)\); \( T_{\text{melt}} \) and \( T_{\text{boil}} \) = melting and boiling points \((\text{K})\), respectively.

<table>
<thead>
<tr>
<th>Ln</th>
<th>( Z )</th>
<th>( \rho )</th>
<th>( T_{\text{melt}} )</th>
<th>( T_{\text{boil}} )</th>
<th>Physical appearance</th>
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<tbody>
<tr>
<td>Lanthanum (La)</td>
<td>57</td>
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<td>3743</td>
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<tr>
<td>Cerium (Ce)</td>
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<td>6.689</td>
<td>1068</td>
<td>3633</td>
<td>Colorless</td>
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<tr>
<td>Praseodymium (Pr)</td>
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<td>3563</td>
<td>Yellow green</td>
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<tr>
<td>Neodymium (Nd)</td>
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<td>3373</td>
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<tr>
<td>Europium (Eu)</td>
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<td>5.244</td>
<td>1099</td>
<td>1800</td>
<td>Essentially colorless</td>
</tr>
<tr>
<td>Gadolinium (Gd)</td>
<td>64</td>
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<td>3523</td>
<td>Colorless</td>
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<tr>
<td>Terbium (Tb)</td>
<td>65</td>
<td>8.219</td>
<td>1629</td>
<td>3503</td>
<td>Essentially colorless</td>
</tr>
<tr>
<td>Dysprosium (Dy)</td>
<td>66</td>
<td>8.551</td>
<td>1680</td>
<td>2840</td>
<td>Light yellow green</td>
</tr>
<tr>
<td>Holmium (Ho)</td>
<td>67</td>
<td>8.795</td>
<td>1734</td>
<td>2993</td>
<td>Brownish yellow</td>
</tr>
<tr>
<td>Erbium (Er)</td>
<td>68</td>
<td>9.066</td>
<td>1770</td>
<td>3141</td>
<td>Pink</td>
</tr>
<tr>
<td>Thulium (Tm)</td>
<td>69</td>
<td>9.321</td>
<td>1818</td>
<td>2223</td>
<td>Light green</td>
</tr>
<tr>
<td>Ytterbium (Yb)</td>
<td>70</td>
<td>6.570</td>
<td>1097</td>
<td>1469</td>
<td>Colorless</td>
</tr>
<tr>
<td>Lutetium (Lu)</td>
<td>71</td>
<td>9.841</td>
<td>1925</td>
<td>3675</td>
<td>-</td>
</tr>
</tbody>
</table>
laser amplifier disks, rods and scintillators.

**1.4.3 Spectroscopy of lanthanide ions**

The energy levels of 4f-orbitals are not degenerate because of electronic repulsion, spin-orbit coupling and the coordination environment of the ligand field. The strong interaction and the electronic repulsion between the electrons disrupt the degeneracy of the 4f energy levels and yields terms with separations in the order of $10^4$ cm$^{-1}$. Spin-orbit coupling is the interaction between the magnetic moments of the electrons due to their spin (spin angular momentum) and the magnetic moments due to their movement around the nucleus (orbital angular momentum). This causes further splitting of the energy levels into so called $J$-states. The splitting of these energy levels is in the order of $10^3$ cm$^{-1}$. The $J$ degeneracy is partially removed in a coordination environment by the ligand field, which results in crystal-field (CF) splitting being in the order of $10^2$ cm$^{-1}$, are not very pronounced since the 4f electrons are shielded effectively by the filled 5s and 5p orbitals. This weak CF splitting can be treated as a perturbation to the free-ion level. The thermal motion of the ligands has very little effect upon the CF splitting and as a consequence the 4f - 4f optical transitions of Ln ions have narrow homogeneous line widths.

The electronic states of Ln ions can be determined using the Russell-Saunders coupling scheme [61]. In this scheme, the electron spins are coupled through the pairing of the orbital angular moments of the electron, which are then unquenched. The coupling of the spins ($s$) of the individual electrons gives the total spin quantum number for the ion ($S$). For an $f$-electron, the orbital angular moment ($l$) = 3 and thus the magnetic quantum number $m_l$ can have any integral value between +3 and –3. The vector addition of the values of the $f$-electrons for the muti-electron ion provides the total orbital angular momentum quantum number ($L$) [62].

The term of the state is then derived from the following relation.

<table>
<thead>
<tr>
<th>$L$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Term symbol</td>
<td>S</td>
<td>P</td>
<td>D</td>
<td>F</td>
<td>G</td>
<td>H</td>
<td>I</td>
<td>K</td>
<td>L</td>
</tr>
</tbody>
</table>
The resulting quantum number $J$ can be obtained by the vector addition of $L$ and $S$. $J$ can have values of \( |L+S|, |L+S-1|, \ldots, |L-S| \).

The ground state of the ion \(^{(2S+1)L_J}\) is determined by Hund’s rule which predicts that

i. The term with highest spin multiplicity \((2S+I)\) has the lowest energy.

ii. If there is more than one term with the same spin multiplicity, then the term with the highest $L$ value is the ground state.

iii. For a shell less than half filled, $J$ for the ground state takes the lowest possible value; for a shell more than half filled, $J$ for the ground state takes the highest possible value.

The characteristic \(^{(2S+1)L_J}\) energy levels of Ln\(^{3+}\) ions doped into LaCl\(_3\) were measured by Dieke and coworkers in 1960’s [63, 64]. The energy level diagrams of Ln\(^{3+}\) ions along with possible emission channels are shown in Fig. 1.8 (generally termed as Dieke diagram).

### 1.4.4 Characteristics of lanthanide ions

The Lns exhibit a number of features in their chemistry that differentiate them from the $d$-block metals. The reactivity of the elements is greater than that of the transition metals, similar to the Group II metals:

i. Lns are silvery-white metals that tarnish when exposed to air, forming their oxides.

ii. These are relatively soft metals. Their hardness slightly increases with higher atomic number.

iii. They possess very wide range of co-ordination numbers (generally 6–12, but numbers of 2, 3 or 4 are also known).

iv. Insoluble hydroxides precipitate at neutral pH unless complexing agents are present.

v. Lns react with water to liberate hydrogen (H\(_2\)), slowly in cold/quickly upon heating. These are commonly bind to water.

vi. They do not form Ln=O or Ln= N multiple bonds of the type known for many transition metals and certain actinides.

vii. They possess high melting and boiling points and act as strong reducing agents.

viii. Ln compounds are generally ionic in nature and strongly paramagnetic (except La\(^{3+}\)}
Figure 1.8. Partial energy level diagram of Ln$^{3+}$ ions derived from Ln$^{3+}$:LaCl$_3$ system.
and Lu$^{3+}$).

ix. The magnetic moments of the Ln and iron ions oppose each other.

x. Their spectroscopic and magnetic properties are largely uninfluenced by the ligand field due to well shielding of 5s$^2$ and 5p$^6$ orbitals.

xi. Small CF splitting and very sharp electronic spectra in comparison with the $d$-block metals.

xii. Ln ions tend to be pale colors, resulting from weak, narrow, forbidden $f$-f optical transitions.

### 1.4.5 Optical properties of lanthanide ions

The Ln$^{3+}$ ions are the most widely used ions in solid state lasers. The wide applicability and versatility of Ln$^{3+}$ ions give rise to several attractive optical properties favourable for achieving low threshold, efficient laser action, etc. The following are some of the optical properties of Ln$^{3+}$ ions: The electronic states of the ground 4$f$$^n$ configuration provides complex and varied optical energy level structure, thus there are many possible three and four level lasing schemes.

i. These excited states decay non-radiatively to metastable states having high radiative quantum efficiencies.

ii. There are several excited states suitable for optical pumping.

iii. They possess high refraction with relatively low dispersion.

iv. The $f-f$ transitions have small homogeneous linewidths.

v. Many Ln compounds fluoresce strongly under UV light.

vi. The availability of well developed models for accurate energy level analysis and transition intensities to predict/understand the excited state dynamics.

### 1.4.6 Host materials for lanthanide ions

The luminescence of Ln ions has a large technological importance in a variety of photonic device applications like phosphor lamps, displays, lasers, sensors and optical amplifiers. A significant proportion of research on Ln-doped optical materials has been investigated the effect of host on the luminescence properties of the dopant ions. The
interest has stemmed from the knowledge that variations in the host material can be used to enhance various properties of optical devices in which the doped material is being used.

One of the main contributions to the host dependent effects lie in the structural organization of the material. In crystal structures, for example, the ions lie in well defined positions, with the Ln dopant ions occupying a specific structural site. Glasses on the other hand tend to have disorganized structures which allow the Ln ions to be positioned in a range of locations in the host material structure. The majority of the Ln ions in crystals are therefore subjected to a CF of the same magnitude, while in glasses Ln ions in different structural locations experiences different CFs from the surrounding ions. This results in the majority of Ln ions in a crystalline host having very similar energy levels, while in glasses the positions of the energy levels (in particular Stark levels) can vary depending on the local field in which the Ln ions are situated. This tends to broaden the linewidths of transitions of Ln ions in glass hosts in comparison to crystalline materials [65, 66].

The composition of Ln ion host materials has also been found to affect the upper limit of the useful doping concentration of Ln ions. In many cases the practical dopant concentration limit can be determined by reductions in the quantum efficiency or the lifetime of an energy level due to ion-ion interactions such as energy transfer, cross-relaxation and upconversion (all these phenomena are discussed in subsequent sections of this chapter). The extent of these interactions depend upon the distance between neighbouring Ln ions in the host and increases with reduced average separation. The present thesis has been focused on concentration dependent luminescence properties of Ln$^{3+}$ ions in glasses and nanocrystalline material since these inorganic materials are best hosts for Ln ions as they show high quantum yields in these hosts.
1.5 Theory

1.5.1 Theory of IR absorption spectroscopy

The atoms constituting a molecule are not stationary and are continuously rotating and vibrating in a number of ways. Two atoms joined by a covalent bond may undergo a stretching vibration. In this type of vibration the two atoms move back and forth as if joined by a spring.

(a) Stretching vibration

This type of vibrations arises because of stretching and contracting bonds without producing any change in bond angles. Two types of stretching vibrations are (i) Symmetric stretching (ii) Asymmetric stretching.

(i) Symmetric stretching

In this type of stretching, the movement of atoms with respect to a particular atom in a molecule is in the same direction. The Fig. 1.9 a shows the symmetric stretching vibrations of molecules.

(ii) Asymmetric stretching

In this type of stretching one atom approaches the central atom whereas the other atoms move away from it. The Fig. 1.9 b shows the asymmetric stretching vibrations of molecules.

(b) Bending vibrations or Deformations

In case of bending vibrations there is a deformation of bond angles and there is no change in bond lengths. Once again these vibrations are classified as (i) Scissoring (ii) Rocking (iii) Wagging and (iv) Twisting. Fig. 1.10 shows the four types bending vibrations of molecules.

(i) Scissoring: In this type of vibration, the two atoms approach each other in the same plane.

(ii) Rocking: In this type of vibration, the movement of atoms occur in the same direction as also in the same plane.
Figure 1.9. Stretching vibrations of molecules

Figure 1.10. Bending vibrations of molecules
(iii) **Wagging**: The two atoms move up and down the plane with respect to the central atom.

(iv) **Twisting**: One of the atoms moves up the plane and other moves down the plane with respect to the central atom.

### 1.5.2 Energy level calculations

The 4f\(^n\) electron state configuration of the rare-earth ions is not sensitive to the surrounding ions but the transition probability between these electron states is sensitive to the surrounding ions. For this reason, the rare earth ion energy levels are calculated taking into account only the interaction among the 4f electrons. The energy level structure of 4f electrons is evaluated by a Hamiltonian operator \(H\) that can be factorized in a part containing the angular dependence which holds information regarding the number of levels, their arrangement and the selection rules, the remaining part can be written as follows (neglecting the exchange-correlation terms)

\[
H = T + H_{en} + H_{ee} + H_{so} \quad \text{(or)}
\]

\[
H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} \frac{Z^* e^2}{r_i} + \sum_{i,j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \xi(r_i) S_i l_i
\]

(1.5.1)

where \(e\) and \(m\) are the electron charge and mass respectively, \(\hbar\) is the reduced Planck constant, \(N\) is the total number of electrons in the incomplete shell \((N = 1, 2, \ldots, 14)\), \(z^*e\) is the screened charge of the nucleus, \(r_i\) is the radial coordinate of the \(i\)-th electron, \(r_{ij}\) is the relative position of the electron \(i\) respect to the electron \(j\), \(S_i\) and \(l_i\) are the spin and the orbital momentum for the \(i\)-th electron and \(\xi\) is the spin-orbit interaction constant. The first two terms in Eq. (1.5.1) represents the kinetic energy \((T)\) and the electrostatic interaction between the electrons and the nucleus \((H_{en})\), which is purely radial and contributes energy shifts that are the same for all the levels belonging to a configuration without affecting the energy level structure of the configuration. The third term \((H_{ee})\) represents the inter-electron Coulomb repulsion between a pair of electrons at a distance of \(r_{ij}\), which varies for different states of the same configuration. The fourth term \((H_{so})\)
describes the spin-orbit interaction, which can be understood as magnetic dipole-dipole interactions between the spin and angular moment of the electrons. The spin-orbit coupling constant $\xi(r_i)$ is defined as function of $r_i$. In terms of the central field approximation, each electron is considered to be moving independently in the field of the nucleons and spherically averaged potential of all the other electrons. The Coulomb interaction produces different SL and thus is depend on the local angular momentum. In terms of quantum mechanics, the spin-orbit operator does not commute with $L^2$ and $S^2$, but it does commute with $J^2$ and $J_z$. In simple terms this means that the Coulomb interaction removes degeneracy in S and L, while the spin orbit interaction removes degeneracy in J. The $M_J$ degeneracy remains. This is only removed by the crystal field. Hence the energy levels of the free-ion states are independent of $M$, so they are $(2J + 1)$ fold degenerate and the intermediate coupling scheme describes the energy states of the Hamiltonian including Coulomb and spin-orbit interactions and is obtained from mixing all $LS$ terms with the same $J$ in a given $4f^n$ configuration. The rare earth ion interactions and energy level splitting are depicted in Fig. 1.11.

The observed spectra of rare earth ions in solutions and in crystal lattices arise from forbidden transitions within the ground $4f^N$ configuration [67]. According to a first approximation, the energy level structure of the $4f^N$ configuration arises from electrostatic and magnetic interactions between the $4f$ electrons. These interactions may be represented by the Hamiltonian.

$$ H = H_e + H_{so} $$

where $H_e$ involves the Coulomb interaction between pair of $f$ electrons and $H_{so}$ represents the coupling of spin and orbital angular momenta which is the most important magnetic interaction for $f$ electrons.

The electrostatic energy arising from the electrostatic repulsion between electrons in the $f^N$ configuration is expressed in terms of products of Slater radial integrals ($F_k$) and angular coefficients $f^k$ [68]. The spin-orbit radial interaction energy is expressed in terms of the product of spin-orbit radial integral ($\xi_{4f}$) and angular part of the spin-orbit interaction ($A_{so}$). The Slater radial integrals and the spin-orbit radial
Figure 1.11. Schematic diagram of the splitting of rare earth energy levels due to the electrostatic, spin-orbit and crystal field interactions.
integrals are treated as parameters to be determined from the experimental data. The initial estimated parameters, $F_k$ and $\xi_{4f}$ for all lanthanides are reported in Ref. [67, 69]. The methods of Racah [70] are used to calculate the electrostatic interaction matrix elements. Neilson and Koster [71] provided complete tabulation of these matrices. The spin-orbit matrix elements for all the $f^N$ configurations can be calculated using the method of Wybourne [67] and the tables of Nielson and Koster [71] and Appel [72]. The electrostatic matrix elements are the same for $4f^N$ (N electrons) and $4f^{14-N}$ (N holes) configurations because a two particle interaction is present [73].

The electrostatic and spin-orbit interactions give the right order for the energy level splitting of the $f^N$ configurations. However, these primary terms of the free ion Hamiltonian does not accurately reproduce the experimentally measured energy level structures. This is because, the parameters $F^k$ and $\xi_{4f}$ cannot absorb all the effects of additional mechanisms such as relativistic effects and configuration interactions. Hence, introduction of new terms to the effective operator Hamiltonian is required to get better interpretation of the experimental data.

The effective operator Hamiltonian of free ion interaction that was used to study the energy level structure of rare earth ions may be written as [73]

$$H_{fI} = \sum_k F^k f^k + \xi_{4f}A_{so} + \alpha L(L+1) + \beta G(G_z) + \gamma G(R_z)$$

$$+ \sum_i T^i t_i + \sum_k p^k p_k + \sum_j M^j m_j \rightarrow (1.5.2)$$

where $k=2, 4, 6, i=2, 3, 4, 7, 8$ and $j=0, 2, 4$. The operators ($f_k, A_{so}, L, G, i, p_k$ and $m_j$) and their associated parameters such as two body electrostatic parameters, $F^k$; spin-orbit coupling, $\xi_{4f}$; two body configurations $\alpha$, $\beta$ and $\gamma$; three body configuration, $T^k$; spin-other-orbit, $M^j$; electro-statically correlated spin-orbit, $p^k$ are written according to conventional notation and meaning. The $\alpha$, $\beta$ and $\gamma$ are the linear combinations of radial integrals $E^k$ and $\xi_{4f}$ and are treated as adjustable parameters. The RMS deviations of the energy levels can be reduced by considering these parameters into account. The terms
G(G₂) and G(R₇) are the eigen values of Casimer’s operator for the groups G₂ and R₇ used to classify the states of fⁿ configuration and L is the orbital angular momentum.

Racah [74] noticed that the Coulomb interaction is primarily responsible for the free ion structure of the rare earth ions and are described by the electrostatic interaction matrix elements. If the crystal field effects are taken into account one has to rediagonalize the matrix for the same rare earth ion substituted in different host materials. Wong [75] observed that the effect of the crystalline field on these parameters is small and hence a Taylor series expansion of the intermediate coupling energy levels for rare earth ion is valid. Thus, new energy levels for rare earth ions in any matrix can be calculated without having to rediagonalise the matrix. The Taylor series expansion is of the form [75]

\[
E_J = E_{0J} + \left[ \frac{\partial E_J}{\partial E^1} \right] \Delta E^1 + \left[ \frac{\partial E_J}{\partial E^2} \right] \Delta E^2 + \left[ \frac{\partial E_J}{\partial E^3} \right] \Delta E^3 + \left[ \frac{\partial E_J}{\partial \xi_{4f}} \right] \Delta \xi_{4f} + \left[ \frac{\partial E_J}{\partial \alpha} \right] \Delta \alpha + \left[ \frac{\partial E_J}{\partial \beta} \right] \Delta \beta + \left[ \frac{\partial E_J}{\partial \gamma} \right] \Delta \gamma \rightarrow (1.5.3)
\]

where \( E_{0J} \) is the zero-order energy of the Jth level and \( \Delta E^k, \Delta \xi_{4f}, \Delta \alpha, \Delta \beta \) and \( \Delta \gamma \) are the variations in the \( E^k, \xi_{4f}, \alpha, \beta \) and \( \gamma \) parameters due to the interactions with the matrix environments. Using the experimental energy levels for \( E_J \) and numerical values of zero-order energies [73] and partial derivatives [75], a number of linear equations, equal to observed energy levels, can be formed. The delta values can be calculated using a least squares method. The calculated delta values are then added to zero order parameters to obtain the free ion parameters. Thus

\[
E^k = E^0_k + \Delta E^k; \ (k= 1, 2 \text{ and } 3)
\]

\[
\xi_{4f} = \xi_{4f}^0 + \Delta \xi_{4f}
\]

\[
\alpha = \alpha^0 + \Delta \alpha
\]

\[
\beta = \beta^0 + \Delta \beta
\]
In the present work, the energy level calculations have been made for Pr$^{3+}$, Er$^{3+}$, Nd$^{3+}$, Ho$^{3+}$ doped different phosphate glasses. The fitting procedure between experimental and calculated energy levels involves the standard least square fit method to get the free-ion parameters given in Eq. (1.5.3) along with the minimum values of rms deviation ($\sigma_{rms}$) as a figure of merit in describing the quality of the fit. The $\sigma_{rms}$ is defined as [76, 77]

$$
\sigma_{rms} = \sqrt{\frac{\sum_{i=1}^{p}(E_i^{exp} - E_i^{cal})^2}{P}}
$$

where $E_i^{exp}$ and $E_i^{cal}$ are the experimental and calculated energies for level i and $P$ denotes the total number of experimental levels included in the energy level fit.

### 1.5.3 Spectral intensities of absorption bands

The intensity of an absorption band is expressed in terms of a quantity called the “oscillator strength or spectral intensity”. Experimentally, the spectral intensity (f) is a measure of the intensity of an absorption band and is proportional to the area under the absorption peak. The area under an absorption peak is a better measure of the intensity than the molar absorptivity at the peak maximum, because the area is the same for both the resolved and unresolved band. The oscillator strength (f) of each absorption band is expressed in terms of absorption coefficient $\alpha(\lambda)$ at a particular wavelength $\lambda$ and is given by [78]

$$
f_{exp} = \frac{mc^2\nu^2}{Ne^2} \int \varepsilon(\nu)d\nu \quad \text{or} \quad f_{exp} = 4.32 \times 10^{-9} \int \varepsilon(\nu)d\nu \quad (1.5.4)
$$

where $m$ and $e$ are the mass and charge of the electron, $c$ is the velocity of light, $N$ is the density of the absorbing ions obtained from the rare earth ion concentration and glass density values, respectively. $\int \varepsilon(\nu)d\nu$ represent the area under the absorption curve. The molar absorptivity $\varepsilon(\nu)$ of an absorption band at energy $\nu$ (cm$^{-1}$) is given by
\[ \varepsilon(\nu) = (CI)^{-1} \log\left( \frac{I_0}{I} \right) \]

where \( C \) concentration of rare earth ions per unit volume, \( l \) optical path length and \( \log\left( \frac{I_0}{I} \right) \) is the optical density.

### 1.5.4 Application of Judd-Ofelt theory

Optical spectroscopy often used to measure optical absorption of trivalent rare earth ions in UV-VIS-NIR regions, from which the effect of a host matrix on the local environment of a given rare earth cation with its first neighbor anions such as oxygen can be elucidated using the theory proposed by Judd [79] and Ofelt [80]. Each observed transition corresponds to a transition between two spin-orbit coupling levels. The Judd-Ofelt theory has been applied for the interpretation of these transitions by the three mechanisms: 1. magnetic dipole transitions, 2. induced electric dipole transitions and 3. electric quadrupole transitions. The quantitative analysis of the intensities of these f-f transitions in the rare earth ions has been provided independently by Judd [79] and Ofelt [80]. The basic idea of Judd and Ofelt is that the intensity of f-f electric dipole transitions can arise from the admixture into the \( 4f^N \) configuration of opposite parity (e.g., \( 4f^{N-1}n^1d^1 \) and \( 4f^{N-1}n^1g^1 \)). According to Judd-Ofelt theory, the intensity of magnetic and electric dipole transition is represented as

\[ f_{\text{cal}} = f_{\text{ed}} + f_{\text{md}} \]

This means that experimentally measured oscillator strengths could be expressed to a good approximation in terms of absorption of light by electric dipole and magnetic dipole mechanisms. But, the order of magnitude of magnetic dipole oscillator strengths \( (f_{\text{md}}) \) are found to be very low for the observed intensities of rare earth ions and thus will not be considered further. The experimental oscillator strengths are therefore approximately equal to electric dipole oscillator strengths i.e.
\[ f_{\text{cal}} = f_{\text{ed}} = \sum_{\lambda=2,4,6} T_{\lambda} v \left\langle (S, L) J \left\| U^J \right\| (S', L') J' \right\rangle^2 \]  

\rightarrow (1.5.7)

where \( v \) is the mean energy of the transition \( \psi J \rightarrow \psi' J' \), \( \left\| U^J \right\|^2 \) are the squared reduced matrix elements of the unit tensor operator of the rank, \( \lambda (= 2, 4 \text{ and } 6) \). \( T_2, T_4 \text{ and } T_6 \) are related to the radial part of \( 4f^N \) wavefunctions, the refractive index of the medium, and the ligand-field parameters that characterize the environment of the ion. These quantities are treated as parameters and are determined from the spectral intensities. In the above equation, the reduced matrix elements of the unit tensor operator, \( U^J \) were calculated using the equation [81].

\[ \left\langle (S, L) J \left\| U^J \right\| (S', L') J' \right\rangle = \left(-1\right)^{S+L+J+\lambda} \left[(2J+1)(2J'+1)\right]^{1/2} \begin{bmatrix} J & J' \lambda \\ L' & L & S \end{bmatrix} \begin{bmatrix} J' \lambda \\ L' & L & S \end{bmatrix} \left(f^{N \alpha S L} \right) \left(U^J \right) \left(f^{N \alpha ' S' L'} \right) \]  

\rightarrow (1.5.8)

The matrix elements of unit tensor operators within the LS terms have taken from the tables of Nielson and Koster [71]. The reduced matrix elements are not dependent on the ligand species surrounding the rare earth ions and thus approximately unchanged from host to host [82]. In the present work, the author has used the squared reduced matrix elements reported by Carnall et al [83] for LaF\(_3\) crystal. The squared reduced matrix elements of different absorption transitions of Pr\(^{3+}\), Er\(^{3+}\), Nd\(^{3+}\), Dy\(^{3+}\), Sm\(^{3+}\), Ho\(^{3+}\) and Eu\(^{3+}\) ions which are used in the calculations of lifetimes of excited states are taken from literature [84]. Using the squared reduced matrix elements, \( \left\| U^J \right\|^2 \) and using \( f_{\text{exp}} \) for \( f_{\text{ed}} \), the \( T_{\lambda} (\lambda=2, 4, 6) \) parameters are calculated by applying least squares fit method using equ. 1.5.1. The magnitude of these parameters (introduced by Judd) depends on the intensities of transitions between \( 2s+1L \) levels. The goodness of the fit is determined by the root mean square (\( \delta_{\text{rms}} \)) deviation between the measured and calculated oscillator strengths by the relation

\[ \delta_{\text{rms}} = \left[ \frac{\sum(f_{\text{exp}} - f_{\text{cal}})^2}{P} \right]^{1/2} \]
The Judd-Ofelt intensity parameters $\Omega_{\lambda}$ ($\lambda = 2, 4, 6$) are calculated by using the formula,

$$
\Omega_{\lambda} \left( \text{cm}^2 \right) = \frac{3h}{8\Pi mc} \times \frac{9n}{(n^2+2)^2} (2J+1) T ; \quad (\lambda = 2, 4 \text{ and } 6) \tag{1.5.9}
$$

where $n$ is the refractive index of the medium, $J$ is the ground term and remaining symbols have their usual meaning. The Judd-Ofelt intensity parameters represent the square of the charge displacement due to the induced electric dipole transition. The advantage of $\Omega_{\lambda}$ parameters is that a set of parameters is needed for describing both the absorption and emission processes. The $\Omega_{\lambda}$ parameters are important for the investigation of the local structure and bonding in the vicinity of rare earth ions. Reisfeld [84] indicated that $\Omega_2$ parameter is sensitive to both asymmetry and covalency at rare earth sites. Oomen and van Dongen [85] pointed out that the rigidity or long range effects of glass hosts were responsible for changes in $\Omega_6$. The $\Omega_4$ parameter is affected by the factors causing changes in both $\Omega_4$ and $\Omega_6$. $\Omega_{\lambda}$ can also be written as [86]

$$
\Omega_{\lambda} = (2\lambda+1) \sum_{t,p} \left| A_{t,p} \right|^2 \Xi^2(t, \lambda) (2t+1)^{-1} ; \quad \lambda = 2, 4, 6 \tag{1.5.10}
$$

where $A_{t,p}$ are the components of the crystal field operator and depend on the symmetry of the crystal field around rare earth ions. $\Xi(t, \lambda)$ is a function of radial integral and depends reciprocally on the energy separations of the 4f level and admixing levels e.g. 5d, 5g. The sum over $\lambda$ includes only the even values 2, 4 and 6 whereas the sum over $t$ includes only the odd values 1, 3 and 5. It has been suggested by Reisfeld [84] that $\Xi$ is related to the nephelauxetic parameter $\beta$ which indicates the degree of covalency of RE-O bond.

**1.5.5 Hypersensitive transitions**

The amount of covalency between the rare earth ion and the surrounding oxygens in the glass increases the intensity of hypersensitive transitions. It has been suggested by
Reisfeld and co-worker \[86, 87\]. Equ. 1.5.10 indicates that both A_{t,p} and Ξ(t,λ) are responsible for the increase of covalency (Ω_2 parameter). Judd \[88\] suggested that the appearance (position and intensity) of the hypersensitive transition is strongly affected by changes in the symmetry of the crystal field acting on the rare earth ions. According to Gruen and Dekock \[89\] and Gruen et al \[90\], the intensity of the hypersensitive transitions increases up to a factor 200. Jorgensen and Judd \[91\] have called such transitions as hypersensitive transitions. These hypersensitive transitions obey the selection rules ΔJ≤2, ΔL≤2 and ΔS=0. These are associated with a very large value of the reduced matrix element <∥ U ∥^2>; hence hypersensitivity is much related with the Ω_2 parameter. Table 1.3 shows <∥ U ∥^2> values along with the transition energies (cm⁻¹) of the hypersensitive transitions in Pr^{3+}, Er^{3+}, Nd^{3+}, Dy^{3+}, Sm^{3+}, Ho^{3+} and Eu^{3+} ions (aqua ions). Several authors discussed the hypersensitivity in the review articles \[92-95\].

Hypersensitive transitions have been observed for all the lanthanide ions. Karraker \[96\] studied the hypersensitive transitions of certain rare earth ions in detail and concluded that the hypersensitive transitions show differences that are characteristic for the co-ordination and the symmetry of the lanthanide ion. Choppin et al \[97\] suggested that the band shape intensity of hypersensitive transitions could be used as a qualitative indication of the site symmetry. Normally peak splitting were observed by the stark splitting and the relative peak varied with the glass composition. Nageno \[98\] suggested that an increase of the intensity ratio I_L/I_S indicates a shift of the centre of the gravity of the transitions to lower energies (longer wavelengths) indicates an increase in the covalency of RE-O bond. In the present work, the shapes, positions of peak wavelengths and peak splitting of the hypersensitive transitions of Pr^{3+}, Er^{3+}, Nd^{3+}, Dy^{3+}, Sm^{3+}, Ho^{3+} and Eu^{3+} ions are investigated in different phosphate glass to study the nature of RE-O bond.

1.5.6 Radiative properties

The computed Judd-Ofelt intensity parameters (Ω_λ) are used to study certain radiative properties for the principal fluorescence transitions of rare earth ions in host matrix. We can estimate (a) radiative transition probabilities or radiative lifetimes of
Table 1.3.
Energies and squared reduced matrix elements of hypersensitive transitions of Pr$^{3+}$, Er$^{3+}$, Nd$^{3+}$, Dy$^{3+}$, Sm$^{3+}$, Ho$^{3+}$ and Eu$^{3+}$ (aquo ions) [Ref. 100].

| Ion   | Transition                      | Energy (cm$^{-1}$) | $<||U||^2>$ | $<||U||^2>$ | $<||U||^2>$ |
|-------|---------------------------------|-------------------|-------------|-------------|-------------|
| Pr$^{3+}$ | $^3\text{H}_4 \rightarrow ^3\text{F}_2$ | 5200              | 0.509       | 0.403       | 0.117       |
| Er$^{3+}$ | $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$ | 19200             | 0.716       | 0.414       | 0.093       |
|        | $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$ | 26400             | 0.916       | 0.526       | 0.117       |
| Nd$^{3+}$ | $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$ | 17300             | 0.968       | 0.585       | 0.062       |
| Dy$^{3+}$ | $^6\text{H}_{15/2} \rightarrow ^6\text{F}_{11/2}$ | 7700              | 0.939       | 0.846       | 0.408       |
| Sm$^{3+}$ | $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{1/2} + ^4\text{F}_{3/2}$ | 6400              | 0.194       | 0.000       | 0.000       |
| Ho$^{3+}$ | $^5\text{I}_8 \rightarrow ^5\text{G}_6$ | 22100             | 1.483       | 0.820       | 0.140       |
| Eu$^{3+}$ | $^5\text{I}_8 \rightarrow ^5\text{H}_6$ | 27700             | 0.254       | 0.234       | 0.161       |
|        | $^7\text{F}_1 \rightarrow ^5\text{D}_1$ | 18700             | 0.002       | 0.000       | 0.000       |
|        | $^7\text{F}_0 \rightarrow ^5\text{D}_2$ | 21500             | 0.001       | 0.000       | 0.000       |
|        | $^7\text{F}_2 \rightarrow ^5\text{D}_0$ | 16300             |             |             |             |
excited states (b) branching ratios of all the transitions from the excited states to ground state and (c) integrated absorption cross-sections. The radiative transition probability

$$A_{\text{rad}}(\psi J, \psi J')$$ for emission from an initial excited state $\psi J$ to a final ground state $\psi J'$ is given in [99]

$$A_{\text{rad}}(J \rightarrow J') = \frac{64\pi^4e^2}{3h(2J+1)\lambda^3} \left[ \frac{n(n^2+n)^2}{9} S_{ed} + n^3 S_{md} \right]$$  \hfill (1.5.11)

where

$$S_{ed}(J \rightarrow J') = \sum_{\lambda=2,4,6} \Omega_{\lambda} \left\langle (S, L) J \mid \left( J^2 \right) \left( S', L' J' \right) \right\rangle^2$$

and

$$S_{md}(J \rightarrow J') = \left( \frac{\hbar^2}{16\pi^2m^2c^2} \right) \left\langle (S, L) J \mid L + 2s \left( S', L' J' \right) \right\rangle^2$$

In case of electric dipole transition, the radiative transition probability is

$$A_{\text{rad}}(J \rightarrow J') = \frac{64\pi^4e^2}{3h(2J+1)\lambda^3} \left[ \frac{n(n^2+n)^2}{9} S_{ed} \right]$$  \hfill (1.5.12)

The factor $\frac{n(n^2+2)^2}{9}$ represents the local field correction term for the ion in a medium, $\nu$ is the energy of transition and $n$ is the refractive index of the glass.

The total radiative transition probability, $A_T(\psi J)$ involving all the intermediate terms between $\psi J$ and $\psi J'$ is given by

$$A_T(J) = \sum_{J'} A(J \rightarrow J')$$  \hfill (1.5.13)

The radiative lifetime ($\tau_R$) of an excited state $\psi J'$ is calculated from

$$\tau_R(J) = \frac{1}{\sum_{J'} A(J \rightarrow J')}$$  \hfill (1.5.14)

The fluorescence branching ratio, $\beta_R$, predicts the relative intensity of lines from a given excited states and characterizes the lasing potency of that particular transition. In order to choose suitable lasing transition, one has to select the transition having branching ratio
>0.5 and the energy difference of about 3000 cm\(^{-1}\) between the emitting level and the
next lower level. The fluorescence branching ratio (\(\beta_R\)) is given by

\[
\beta_R(J \rightarrow J') = \frac{A(J \rightarrow J')}{\sum_{J'} A(J \rightarrow J')} \quad (1.5.15)
\]

The experimental branching ratios can be computed from the relative areas encompassed
by the emission lines. The integrated absorption cross-section (\(\Sigma\)) for a particular
transition can be found from the relation [101]

\[
\Sigma = \frac{1}{v^2} \frac{A}{8\pi cn^2} \quad (1.5.16)
\]

### 1.5.7 Stimulated emission cross-section

The stimulated emission cross-section is an important parameter and its value signifies that the rate of energy extraction from the optical material. The Judd-Ofelt
theory can be applied to laser glasses and can successfully account for the induced
emission cross-sections that are observed.

The efficiency of a laser transition is evaluated by considering the stimulated
emission cross-section and it is related to the radiative transition probability. It was
obtained from the emission spectra using Fuchtbauer-Ladenburg method [102]

\[
\sigma_p = \frac{\lambda_p^4}{8\pi cn^2 \Delta \lambda_{\text{eff}}} A_{\text{rad}}(J \rightarrow J') \quad (1.5.17)
\]

where \(\lambda_p\) is peak wavelength and \(\Delta \lambda_{\text{eff}}\) is the effective linewidth. The effective linewidth
\(\Delta \lambda_{\text{eff}}\) is obtained from

\[
\Delta \lambda_{\text{eff}} = \int \frac{I(\lambda)}{I_{\text{max}}} \, d\lambda \quad (1.5.18)
\]

where \(I(\lambda)\) is the integrated fluorescence intensity and \(I_{\text{max}}\) is the peak fluorescence intensity.
Eqn. (1.5.19) implies that $\sigma_p$ depends on the intensity parameters $\Omega_\lambda$, the bandwidth, $\Delta\lambda_{\text{eff}}$ and refractive index $n$. The bandwidth is a measure of the overall extent of the Stark splitting of the J-manifold and inhomogeneous broadening due to site-to-site variation in the local field seen by the rare earth ions. Both $\Omega_\lambda$ and $\Delta\lambda_{\text{eff}}$ are affected by the compositional change in the glass matrix. The stimulated emission cross-section may also be written in terms of frequency as

$$\sigma_p = \frac{\lambda_p^2}{8\pi cn^2 \Delta\lambda_{\text{eff}}} A_{\text{rad}} (J \rightarrow J') \quad (1.5.19)$$

In the present work, the author has evaluated the peak stimulated emission cross-sections ($\sigma_p$) for various observed emission bands of Pr$^{3+}$, Er$^{3+}$, Nd$^{3+}$, Dy$^{3+}$, Sm$^{3+}$, Ho$^{3+}$ and Eu$^{3+}$ ions by measuring the areas under the emission peaks.

High emission probabilities and more transitions from an excited level lead to faster decay and shorter lifetimes. The discrepancy between the theoretical radiative lifetime ($\tau_R$) calculated from J-O intensity parameters and the experimental lifetimes is mainly due to the manifestation of non-radiative processes by multi phonon relaxation rate, which is estimated according to the formula

$$W_{NR} = \frac{1}{\tau_{\text{exp}}} - \frac{1}{\tau_R} \quad (1.5.20)$$

where $W_{NR}$ is the non-radiative relaxation rate (s$^{-1}$), $\tau_{\text{exp}}$ is the experimental lifetime and $\tau_R$ is calculated lifetime. From the measured and calculated lifetimes, the quantum efficiency ($\eta$) of an excited level can be estimated by the expression

$$\eta = \frac{\tau_{\text{exp}}}{\tau_R} \quad (1.5.21)$$

Equations (1.5.11) - (1.5.23) are useful to evaluate various optical parameters, which are necessary to characterize the materials for the design and development of lasers and other optical devices. Good laser transitions are characterized by large cross-
sections for stimulated emission. Therefore, the experimental results obtained can be coupled with the available theoretical models in terms of interaction parameters which give lanthanide-ligand, ion-ion and ion-ligand interaction mechanisms. Hence, an attempt has been made in the present investigation to understand and estimate the contributions of these interactions to develop optical devices for specific applications.

### 1.6.3 McCumber theory

The stimulated emission cross-sections ($\sigma_e$) can also be calculated from the absorption data by using the McCumber’s theory [103]. According to this theory, $\sigma_e$ is given by

$$\sigma_e = \sigma_a \exp \left( \frac{\varepsilon - h\nu}{kT} \right)$$

where $\nu$ be the frequency of photon and $k (=0.695 \text{ cm}^{-1}/\text{K})$ be the Boltzmann’s constant. The factor $\varepsilon$ is the net-free energy required to excite the ions from the ground state to the excited state at absolute temperature $T$. The absorption cross-sections ($\sigma_a$) can be calculated from the absorption spectra by the relation [104]:

$$\sigma_a = \frac{2.303}{C l} \varepsilon(\nu)$$

where $C$ represents the concentration of RE$^{3+}$ ions (in cm$^{-3}$), $l$ is the thickness of the sample and $\varepsilon(\nu)$ is the wavenumber dependent absorbance.
References


Chapter 1

General Introduction


