Chapter-I

Introduction
1. Introduction

*Spectroscopy* is a branch of Physics which involves the study of the radiation absorbed, or reflected, transmitted or emitted, or scattered by a substance. Although, the term ‘radiation’ deals with photons (electromagnetic radiation), *spectroscopy* also addresses the interactions of other types of particles, such as neutrons, electrons, and protons, *alpha, beta* particles or high energy radiations such as gamma ray, x-ray and UV rays have also been in use to characterize materials [1].

In recent years, spectroscopic studies of trivalent lanthanide (Ln$^{3+}$) ions or rare earth(RE$^{3+}$) ions based materials are attracting special attention due to their potential technological applications in a wide variety of applications like solid state lasers, optical fibre amplifiers, light converters, optical storage materials, phosphors and sensors [2-6].

The spectroscopic properties of Ln$^{3+}$ ions in crystalline and glassy natured hosts have been a subject of significant importance and interest in the morning day advancements made in the progress of newer optical materials. The absorption and emission spectra of Ln$^{3+}$ ions in glasses are characterized by inhomogeneous broadening resulting from the distribution of several crystal-fields at the Ln$^{3+}$ ion sites in the amorphous solids. Longer fluorescence lifetime and a narrow absorption and emission bands are the critical requirements of a luminescent material, which can be determined through spectroscopic investigations. Optical spectroscopic techniques are employed to evaluate the quenching of excited state lifetimes due to non-radiative relaxation, resonant and non-resonant and large phonon energy of the host materials [7].

Glass science and technology development have gained more importance in recent years. Compared to crystals and ceramics, the optical performance of glasses, has been found to be more encouraging and more progressive towards the development of a wide variety of glasses for different applications.

*Glass* is defined in ASTM (American Society of Testing Materials) [8] as an inorganic product of fusion which has been cooled to a rigid condition without crystallization. Glass is defined as “an amorphous solid completely lacking in long
range, periodic atomic structure and exhibiting a region of "glass transformation behaviour". According to this definition, a glass is a noncrystalline material obtained by a melt-quenching process. Nowadays, noncrystalline materials that can not be distinguished from melt-quenched glasses of the same composition are obtainable by using various techniques such as chemical vapour deposition, sol-gel process, etc.

The atomic arrangement of a glass could significantly differ from those of crystalline materials due to the absence of long-range regularity, as is shown in Fig. 1.1.

![Fig. 1.1: A Schematic diagram showing a two-dimensional illustration of atomic arrangement in (a) crystal and (b) glass.](image)

Glass atomic arrangement environment is more closer to that of a solution. Therefore there exists neither a crystal lattice nor a lattice point in a glass structure and hence diffraction peaks of an amorphous glassy material could display halo or broad bands from its X-ray diffraction patterns unlike in crystals where the peaks are sharp and distinctive with a well defined structure.

Substances which can form noncrystalline solids with the atomic arrangement shown in Fig. 1.1(b) and at an appreciable size are found in oxide, halide, and chalcogenide systems. The three-dimensional random network of strong bonds is developed by the constituent called the 'network former'. Some components called network modifiers can also participate in glass formation by acting to modify the glass properties.
These components do not form networks but occupy thermodynamically stable sites as illustrated in Fig. 1.2 or those could be replacing a part of 'network former'. Glass formation is possible, in principle, for a system of any composition provided that it contains a sufficient quantity of the glass forming component called 'network former'. Thus, a wide variety of multi-component glasses can be prepared to attain the desired properties by adjusting the chemical composition at a level below 1%. Glass materials have several advantages over crystals as are listed out here:

i. Flexibility in choosing a suitable glass composition in a wide range,

ii. A disordered ion environment that can broaden emission bands bandwidths,

iii. Uniform (isotropic) optical properties over a wide range of composition,

iv. Convenient to fabricate optical materials in different shapes and dimensions and also it is easy to development optical fibres in desired lengths and required qualities for their specific applications.

v. Low cost fabrication and supportive viabilities could significantly encourage in undertaking a large scale production of such optical materials to meet certain specific applications.
vi. Physical properties, optical quality and other required factors could also be tailored in an ease by choosing the appropriate chemical combinations in the glass systems.

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.

1.1 Classification of Glasses

There are different types of glasses which include oxide, semi conducting, metallic and other related glasses. The most important glasses are formed by oxides. Several oxides such as SiO$_2$, GeO$_2$, B$_2$O$_3$, P$_2$O$_5$ etc., readily form glasses and are called network formers (NWF). These oxides could singly provide glassy phase materials which are called silicate, germinate, borate, phosphate, etc. Conditional glass formers like TeO$_2$, Al$_2$O$_3$, WO$_3$ etc., require the presence of one or more additional compounds to form a glass. Alkali oxides (M$_2$O, M=Li,Na, K, Rb and Cs), alkaline-earth oxides (MO, M=Mg, Ca, Ba and Sr) and other oxides like SeO$_2$,MoO$_3$,PbO,Bi$_2$O$_3$,V$_2$O$_5$ etc., when added to a glass forming chemical, which could modify the glass network properties to the desired extent etc., and therefore those are known as network intermediates (NWM).

1.2. Properties of the glasses

The physical properties of a given specimen of glass may depend upon the previous history of the specimen. This is particularly the case for the mechanical strength under tension; the surface pre-treatment of the specimen is of decisive importance [9,10].

Following are some of the properties of glasses:

i. Glass is transparent but non-crystalline, a major paradox in the physics of condensed matter.

ii. Glass, in general, has a very high resistance to the water and atmospheric agencies.

iii. Glass is hard and yet brittle. When it cracks, it shatters at the speed of sound.
iv. Glass usually breaks in a direction at right angles to the direction of maximum tensile stress.

v. Due to its brittle condition there is no plastic deformation in glass which will break suddenly when subjected to a stress exceeding its elastic limit. Glass obeys Hooke’s law accurately until the stress is great enough to cause fracture.

vi. The coefficient of linear thermal expansion is almost constant, for most types of glasses for temperature up to 400-600 °C. The actual value depends on the chemical constitution of the glass.

vii. Glass is electrically insulating at normal temperatures but becomes conducting at elevated temperatures.

All the above and other properties of glasses are infinitely variable and can be tailored according to the particular technological requirement by choosing proper glass composition.

1.3 Glass transition

The transition from a viscous liquid to a solid glass is called “glass transition” and the corresponding temperature is known as the glass transition temperature, \( T_g \). The reversible transformation from a glass to a viscous liquid takes place if the glass is heated to a temperature above \( T_g \). Since the glass transition occurs as a result of the increase of viscosity and the rate of viscosity increase is dependent on cooling rate, the glass transition temperature, \( T_g \), is not always the same. If the chemical composition is the same, \( T_g \) usually depends on the cooling rate of the glassy liquid. A specific volume-temperature diagram showing the cooling behaviour of a typical glass-forming melt is illustrated in Fig. 1.3 along with the variation of specific heat as a function of temperature. A slow cooling allows enough time for a viscous liquid to alter its local atomic arrangement to attain the minimum free energy at the corresponding temperature, whereas a rapid cooling causes an increase of viscosity that is too quick for the local atomic arrangement to follow and results in a transition into a glass at a higher temperature. The structure of a rapidly cooled glass is more open than that of a slowly cooled one because the ‘freezing-in’ of the atomic arrangement occurs at a higher temperature. The
properties of a glass are therefore different from glass to glass, depending on the thermal history, even if the chemical composition is the same [11].

![Diagram](image)

**Fig 1.3:** Dependence of specific volume on temperature for liquid crystals and glass

### 1.4 Optical absorption spectroscopy

Optical absorption spectroscopy is a powerful technique by means of which optical absorption analysis of the materials and the nature of the surroundings around the dopant transition metal or rare-earth ions could be studied. Transition metal ions absorb light at well-defined wavelengths based on the structures of crystals or natural glassy materials. It is necessary to know the free ion and the free ion terms, of the 3d elements characterized for optical properties.

#### 1.4.1 The free ion and the free ion terms

In the absence of the ligands, the central ion in solid sample is known as a free ion. Basic definitions are given below concerning to energy levels. *Configuration:* Which is the assignment of a given number of electrons to a certain set of orbitals and

(a) *Term:* Which is an energy level, which arises from a configuration. It is degenerate and characterized by

i. Its total *orbital angular momentum*, \( L \), which is zero or a positive integer equivalent to '1' for a single electron, and
ii. Its total spin angular momentum, \( S \), which is zero or a positive integer, or an half-integer equivalent to 's' for a single electron.

A term is labeled with the following nomenclature: \( (2S+1)L_\text{i} \)

For \( L=0,1,2,3,4 \), the terms are \( S,P,D,F,G \), respectively.

For \( S=0,\frac{1}{2},1 \), the terms are called as singlet, doublet, triplet, respectively.

The quantity \( (M=2S+1) \) is called 'spin multiplicity' of the term. The different terms that arise out of a given electron configuration have different energies on account of the force of repulsion acting between the electrons. Different terms arising from the different configurations \( (d^n) \) are presented in Table.1.1.

**Table.1.1: Various terms those arise from different \( d^n \) configurations.**

<table>
<thead>
<tr>
<th>Electronic Configuration</th>
<th>Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d^1, d^9 )</td>
<td>( ^2D )</td>
</tr>
<tr>
<td>( d^2, d^8 )</td>
<td>( ^3F, ^3P, ^1G, ^1D, ^1S )</td>
</tr>
<tr>
<td>( d^3, d^7 )</td>
<td>( ^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), \ P )</td>
</tr>
<tr>
<td>( d^4, d^6 )</td>
<td>( ^5D, ^3H, ^3G, ^3F(2), ^3D, ^3P(2), ^1I, ^1G(2), ^1F, ^1D(2), ^1S(2) )</td>
</tr>
<tr>
<td>( d^5 )</td>
<td>( ^6S, ^4G, ^4F, ^4P, ^2I, ^2H )</td>
</tr>
<tr>
<td>( d^{10} )</td>
<td>( ^2G(2), ^2F(2), ^2D(3), ^2P, ^2S )</td>
</tr>
</tbody>
</table>

The number of times a term that occurs has been given in parenthesis. The first term could be the ground term. According to Hund's rule, the term with a highest spin multiplicity and a largest orbital angular momentum, would lie lowest for any configuration. However, the ordering of the other terms and their separation from each other and from the ground term could be determined through the perturbation theory. The ground states for transition metal ions with different electronic configurations are presented in Table.1.2.
Table 1.2: The ground states for some transition metal ions.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Ions</th>
<th>Ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>d¹</td>
<td>Ti³⁺, VO²⁺(V⁴⁺)</td>
<td>²D₃/₂</td>
</tr>
<tr>
<td>d²</td>
<td>Ti²⁺, V³⁺, Cr⁴⁺</td>
<td>³F₂</td>
</tr>
<tr>
<td>d³</td>
<td>V²⁺, Cr³⁺, Mn⁴⁺</td>
<td>⁴F₃/₂</td>
</tr>
<tr>
<td>d⁴</td>
<td>Cr²⁺, Mn³⁺, Fe⁴⁺</td>
<td>⁵D₀</td>
</tr>
<tr>
<td>d⁵</td>
<td>Mn²⁺, Fe³⁺, Co⁴⁺</td>
<td>⁶S₅/₂</td>
</tr>
<tr>
<td>d⁶</td>
<td>Fe²⁺, Co³⁺, Ni⁴⁺</td>
<td>⁵D₄</td>
</tr>
<tr>
<td>d⁷</td>
<td>Co²⁺, Ni³⁺</td>
<td>⁴F₉/₄</td>
</tr>
<tr>
<td>d⁸</td>
<td>Ni²⁺, Cu³⁺</td>
<td>³F₄</td>
</tr>
<tr>
<td>d⁹</td>
<td>Cu²⁺</td>
<td>²D₅/₂</td>
</tr>
</tbody>
</table>

For partially filled in n-shell containing q electrons, the number of states is given by

$$\left[ \frac{2q}{4l+1} \right] = \frac{(4l+2)!}{q!(4l+2-q)!}$$

For example the number of micro states that rise out of a d³ configuration is

$$\left[ \frac{2}{10} \right] = \frac{10!}{2!8!} = 45$$

The energy level diagram for 3d² configuration is given in Fig.1.4, where all these 45 microstates are shown. Similarly for d¹, d⁴, d⁵ configurations, one can get 120, 210, 250 microstates, respectively. The transitions between energy states of an ion are governed by the following selection rules [12]

$$\Delta S = 0 \text{ and } \Delta L = \pm 1$$

where $\Delta S$ and $\Delta L$ are the differences in the respective quantum numbers of ground and excited states. By developing the theory of the interelectronic repulsions within a configuration to give the energies of the term for d electron, we will get two
interelectronic repulsion parameters or Racah parameters namely B and C [13]. The energies are the functions of these two parameters.

Fig. 1.4: Splitting of electronic energy levels for d^2 configuration with 45 microstates
1.4.2 Ligand field theory

In the crystal field approach, according to Bethe [14] and Van Vleck [15], the bonds are assumed ionic and the separations of the levels are calculated from the symmetry of the electric fields acting on the ion. Another approach starts from the molecular orbitals and covalent bond effects. The two treatments form a clear basis for the ligand field theory. The immediate neighbors of an ion are called ligands. In case of oxide glasses, the ligands are oxide ions.

By considering a simple case of an ion with a single electron in the d level, we can understand the basic idea of the 'ligand field theory'. This electron can occupy one of five 'd' orbitals corresponding to the five possible values of the magnetic quantum number. The first three are $d_{xy}$, $d_{xz}$ and $d_{yz}$ and these three orbitals are designated as 't$_2$ orbitals where 't' refers to three fold degeneracy and the last two are $d_{(x^2-y^2)}$ and $d_z^2$, follow the axes. For a free ion, these five orbitals belong to the same degenerate level. However, when the ion is placed in an electric field, the orbitals no longer have the same energy but separate into distinct groups.

![Diagram](image.png)

Fig.1.5: Diagrammatic representation of regular octahedron and regular tetrahedron
Thus, for an ion placed in an octahedral environment, the six oxygen ligands placed along the axes direct negative charges toward the central ion. The electron of the ion will tend to avoid the $d_{x^2-y^2}$ orbital and would preferably occupy the orbitals $d_{xy}$, $d_{xz}$ and $d_{yz}$ (calculation shows that $d_{x^2-y^2}$ is degenerate with $d_{x^2-y^2}$). These two orbitals are designated as 'e' orbitals where 'e' refers to a two fold degeneracy. The octahedral crystal field removes the degeneracy and separates the five levels into two groups, $t_{2g}$ and $e_g$. The energy difference between levels is designated by $\Delta$ (or $10D_q$) and constitutes an empirical parameter, which is the characteristic of the ligand strength. In tetrahedral crystal field, the situation becomes reversed. The electronic transitions between these two energy levels correspond to a band situated in the visible or near-IR region of the spectrum and measurement of the band position allows the determination of $10D_q$.

Two different notations were introduced by Bethe [14] and Mulliken [16] to represent electronic energy levels in the presence of crystal fields. The energy levels are represented by $A_1$, $A_2$, $B_1$, $B_2$, $E$, $T_1$ and $T_2$ where $A_1$, $A_2$, $B_1$ and $B_2$, are non-degenerate, $E$ is doubly degenerate and $T_1$ and $T_2$ are triply degenerate. In ligand field theory, octahedral ($O_h$) and tetrahedral ($T_d$) are the two most important cubic groups. The molecular structures of octahedral and tetrahedral symmetries are represented diagrammatically in Fig. 1.5. The different notations of the energy levels in different cubic symmetries ($O_h$ and $T_d$) are given in Table.1.3 and the splittings of various free ion terms in cubic field are given in Table.1.4.

Table 1.3: Notations of the energy levels

<table>
<thead>
<tr>
<th>Bethe[16]</th>
<th>Mulliken [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_1 )</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>( \Gamma_2 )</td>
<td>$A_{2g}$</td>
</tr>
<tr>
<td>( \Gamma_3 )</td>
<td>$E_g$</td>
</tr>
<tr>
<td>( \Gamma_4 )</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>( \Gamma_5 )</td>
<td>$T_{2g}$</td>
</tr>
</tbody>
</table>
For a transition metal ion in an octahedral crystal field, which possesses center of symmetry, the subscript 'g', is used. For tetrahedral symmetry, no subscripts are used, as this crystal field possesses no center of symmetry.

**Table 1.4:** Splitting of various free ion terms in a cubic field

<table>
<thead>
<tr>
<th>$f$</th>
<th>Free ion terms</th>
<th>Crystal field terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>S</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_1$</td>
</tr>
<tr>
<td>1</td>
<td>P</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>2</td>
<td>D</td>
<td>$E_g+T_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E+T_2$</td>
</tr>
<tr>
<td>3</td>
<td>F</td>
<td>$A_{2g}+T_{1g}+T_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_2+T_1+T_2$</td>
</tr>
<tr>
<td>4</td>
<td>G</td>
<td>$A_{1g}+E_g+T_{1g}+T_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_1+E+T_1+T_2$</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>$E_g+2T_{1g}+T_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E+2T_1+T_2$</td>
</tr>
<tr>
<td>6</td>
<td>I</td>
<td>$A_{1g}+A_{2g}+E_g+T_{1g}+2T_{2g}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A_1+A_2+E+T_1+2T_2$</td>
</tr>
</tbody>
</table>

The use of subscripts g (or u) is governed by the following rules. If the crystal has no center of symmetry, no subscripts are used, but when it has a center of symmetry the subscript g or u is used. The subscripts g and u depend upon the atomic orbitals: g is used for s, d and g orbitals while u is used for p, f and h orbitals. Thus in octahedral symmetry where there is a center of symmetry, the subscript g is used while no subscript is used in tetrahedral symmetry because of the absence of center of symmetry.

A free d-electron has five fold orbital degeneracy with all the five d orbitals, namely $d_{xz}$, $d_{yz}$, $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ possessing the same energy. Each of the five d-orbitals have four lobes at right angles. The $d_{z^2}$ orbital represents a linear combination of two other orbitals $d_{x^2-y^2}$ and $d_{x^2-x^2}$. The sign of the wave function for lobes in opposite quadrants is identical, but opposite to that of lobes in adjacent quadrants. This is shown in Fig. 1.8. The five d-orbitals may be divided into two groups on the basis of their angular distributions. Three of the orbitals $d_{xy}$, $d_{yz}$, $d_{xz}$ have lobes projecting between the Cartesian axes. This group is designated as $t_{2g}$ where t refers the three fold degeneracy; the subscript 2 indicates that the sign of the
wave function does not change on rotation about the axes diagonal to the Cartesian axes and the subscript $g$ again refers to the fact that the wavefunction does not change sign on inversion. The other two orbitals, $d_{x^2}$ and $d_{y^2}$ have lobes directed along the Cartesian axes[17-18]. They are designated as $e_g$ where $e$ stands for the two fold degeneracy. All the $d$ orbitals have symmetric wave functions.

When the $d$-electron is subjected to a crystal field, its five fold degeneracy will be lifted. In the case of octahedral crystal field, the $d$ orbitals would be split into triply degenerate $t_{2g}$ and $e_g$ orbitals, the former lower than the latter. In the case of tetrahedral crystal field, $e$ orbitals lie lower than $t_2$ orbitals. The energy separation between $t_{2g}$ and $e_g$ orbitals is designated as $10\,Dq$ which is a measure of the strength of the crystal field. The relative energies of $t_2$ and $e$ orbitals in case of $O_h$ and $T_d$ symmetries are schematically represented in Fig. 1.8. The triply degenerate $t_{2g}$ orbital can accommodate a maximum of six electrons while the $e_g$ orbital can accommodate a maximum of four electrons[19-20].

![Diagram of d orbitals](image)

**Fig. 1.6:** Five d orbitals (a) $t_{2g}$ orbitals (b) $e_g$ orbitals
The Hamiltonian of a free ion, which describes the optical absorption spectra, is given by [18]

\[ H = H_0 + H_{\text{ee}} + H_{\text{LS}} \]

where \( H_0 \) is the kinetic energy of the electron and Coulomb interaction of each electron with nucleus; \( H_{\text{ee}} \) is interelectronic interaction \( (e^2/r_{ij}) \) and \( H_{\text{LS}} \) is the spin-orbit interaction. If \( H_{\text{CF}} \) represents the crystal field at the central metal ion, based on the relative strengths of the above three terms \( (H_{\text{ee}}, H_{\text{LS}} \text{ and } H_{\text{CF}}) \), three types of crystal fields can be defined as follows.

(a) **Weak crystal field**: \( H_{\text{ee}} + H_{\text{LS}} > H_{\text{CF}} \)

It is normally observed in lanthanides and actinides. Here, crystal field splitting is of the order of \( 50-400 \text{ cm}^{-1} \).

(b) **Medium crystal field**: \( H_{\text{ee}} > H_{\text{CF}} > H_{\text{LS}} \)

Generally, iron group transition metal ions will experience this medium crystal field. The splitting is of the order of \( 10,000 - 20,000 \text{ cm}^{-1} \).

(c) **Strong crystal field**: \( H_{\text{CF}} > H_{\text{ee}} > H_{\text{LS}} \)

Tanabe and Sugano [21] have calculated the electrostatic energy values for different states of transition metal ions and they have plotted energy level diagrams which are known as 'Tanabe-Sugano Diagrams'. These diagrams are useful in evaluating crystal field parameter (Dq), interelectronic repulsion parameters B and C (Racah parameters) and also in assigning the observed absorption transitions.

Jahn - Teller theorem could be stated in a simplified form: If a molecule is seen to give rise to an orbitally degenerate ground term, it could be found to have a distorted situation so as to remove that degeneracy. The fact that orbitally degenerate terms are split by the Jahn-Teller effect, by energies of some hundreds of \( \text{cm}^{-1} \), provides another mechanism whereby the widths of bands involving transitions to T and E terms are expected to be of the order of \( 1000 \text{ cm}^{-1} \).
1.5 Luminescence Spectra

The word luminescence which comes from the Latin (lumen=light) was first used in 1888 by a German physicist namely Eilhardt Wiedeman for the emission of light by certain materials upon excitation from high energy radiations (X-rays or UV) or electrons. Such an emitted light would normally be pleasant and hence, it has been popularly known as 'cold light' or fluorescence light. Luminescent materials are mostly solid inorganic materials consisting of a host lattice, usually intentionally doped with impurities (activators).

When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations are created. Eventually, the electrons return to the ground state: if this relaxation is radiative, the emitted light is the photoluminescence signal. The intensity of this signal gives a measure of the relative rates of radiative and nonradiative recombinations.

Often one can also refer to fluorescence or phosphorence: the latter is a type of luminescence that occurs naturally in many minerals and metallic compounds, in some organic compounds, and in some living organisms such as marine fauna and insects (the most familiar one being the firefly, whose light flashes are produced by biochemiluminescence).

Phosphorescence is distinguished from fluorescence for two main reasons: a) in phosphorence there is a longer time period between the excitation and the emission of light; b) phosphorescence may continue for some time (even hours) after the exciting source has been removed, while Photoluminescence (PL) is the emission of light from a material under optical excitation. It is one of the kinds of the more general phenomenon of luminescence, namely the emission of optical radiation resulting from various types of excitation: chemical or biochemical changes, electrical energy, subatomic motions, reactions in crystals, or stimulation of an atomic system. Accordingly, one can speak about bio-, chemi-, electro-, thermo-, radio-luminescence, and so on. Indeed, the first object of scientific study of luminescent phenomena was a natural stone, subsequently referred to as the "Bolognian Phosphorus" or "Bolognian Stone" or "Litheophosphorus", which had been discovered in 1602 on Monte Paderno, just outside of Bologna, Italy, by Vincenzo Casciarolo, an amateur alchemist [22]. The beginning of luminescence can
be dated to 1852, when George Stokes interpreted the light-emitting phenomenon and formulated the law (the Stokes Law or the Stokes Shift) that the fluorescent light is of longer wavelength than the exciting light. It was Stokes who coined, in 1853, the term "fluorescence" from flurospar (calcium fluoride), the name of the mineral where he first noticed the phenomenon, and the ending -escence analogous to opalescence, phosphorescence, etc.

1.6 Classification of Luminescence based upon the excitation source

Luminescence can be classified to several types depending on the source of excitation as tabulated below (Table 1.5):

<table>
<thead>
<tr>
<th>Luminescence Type</th>
<th>Excitation Source</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoluminescence</td>
<td>Ultraviolet light</td>
<td>Fluorescent Lamps, Plasma Displays</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Electrons</td>
<td>Televisions, Colour Monitor</td>
</tr>
<tr>
<td>X-Ray Luminescence</td>
<td>X-Ray</td>
<td>X-Ray Amplifier</td>
</tr>
<tr>
<td>Electroluminescence</td>
<td>Electric Field</td>
<td>Light Emitting Diodes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electroluminescent Displays</td>
</tr>
<tr>
<td>Thermoluminescence</td>
<td>Heat</td>
<td>Thermoluminescent Dosimeters used in satellites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for nuclear explosion detection</td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>Chemical Reaction Energy</td>
<td>Analytical Chemistry</td>
</tr>
<tr>
<td>Triboluminescence</td>
<td>Mechanical Energy</td>
<td>Remote sensing of signal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mechanical failure, automobiles crashes</td>
</tr>
<tr>
<td>Sonoluminescence</td>
<td>Ultrasound</td>
<td>High speed laser and to destroy toxic chemicals</td>
</tr>
<tr>
<td>Solvatoluminescence</td>
<td>Photons</td>
<td>Detectors, Analytical Devices</td>
</tr>
<tr>
<td>Bioluminescence</td>
<td>Bio-Chemical Reaction Energy</td>
<td>Analytical Chemistry</td>
</tr>
</tbody>
</table>

16
1.7 Photoluminescence

A luminescence stimulated by light absorption in UV-Vis-NIR spectral region, represents any process in which material absorbs electromagnetic energy at a certain wavelength and then emits part of it at a different (usually longer) wavelength. Therefore, only a part of the absorbed energy is transformed into luminescent light. The rest of it ends up as molecular vibrations, or simply as a heat. Photoluminescence is the most popular type of luminescence because a large selection of reliable and inexpensive excitation sources are available and also because the effect can often be observed with the eyes. Photoluminescence can be classified as either intrinsic or extrinsic luminescence.

Nowadays, photoluminescence is mostly exploited for materials' characterization: from the analysis of the PL signal one can derive much information on the emitting material, and PL may be particularly useful in surface diagnostic, because the phenomenon often originates from the surface layers of the material. A noticeable advantage of PL analysis is that it is a simple, versatile, and non-destructive technique. Obviously, PL depends much on the nature of the optical excitation, as the excitation energy selects the initial photoexcited state and governs the penetration depth of the incident light.

The luminescence properties of glasses are important in a variety of industrial and research applications as windows, glass containers, display panels and opto-electronic applications etc. studies pertaining to the interaction of electromagnetic radiation with glasses are considered to be of great significance towards the development of optical glasses for their potential uses in the fields of glass laser technology and optical fibers[23-25].

In lanthanides, the intra ionic electronic transitions of f-f transitions are influenced by the local crystal fields. However, unlike d electrons in transition metals, the 4f electrons in the lanthanides are shielded by the outer 5s and 5p electrons and hence f-level splittings are much less dependent on the environment (such as co-ordination and type of ligands) than in the case of the transition metal ions.
According to the International Union of Pure and Applied Chemistry (IUPAC) recommendations (1968), lanthanides include elements 58 (Ce) to 71 (Lu), while the whole series from La (57) to Lu (71) should be called lanthanoids; when Sc (21) and Y (39) are added to the latter, then the resulting 17 elements should be termed rare earths. In practice, however, lanthanoids is rarely used, to the benefit of lanthanides.

The fascinating story of lanthanide elements started at the end of the 18th century when Carl Axel Arrhenius, an artillery lieutenant of the Swedish army, found a curious black mineral in a feldspar quarry near Ytterby in 1787. The mineral was called “Ytterby’s tungsten” because in Swedish “tungsten” means “heavy stone” and its analysis in 1788 by Geier B R, a mineralogist located in Stockholm. Due to vacancies at the chemistry department of Stockholm University, chemical analysis was only carried out in 1794 by Johan Gadolin, a professor at Abo (today Turku, Finland) University, who identified a new element which he named “yttrium”. The next 15 rare earth elements were discovered between 1803 (Ce) and 1907 (Lu) by outstanding scientists (Berzelius J J, Mosander C C, Galissard de Marignac J C, Cleve P T, Lecoq de Boisbaudran P E, DemarGay E A, Urbain G among others) while the last one, artificial Pm, had to wait its synthesis until 1947[26-28].

![Rare Earth Elements](image-url)

---

Fig.1.7 Position of rare-earth elements in the periodic table of elements
The first industrial application of a lanthanide element was proposed in 1891 by the extraordinary scientist and entrepreneur Carl Auer von Welsbach, who studied chemistry in Vienna and then in Heidelberg with Bunsen R W.

Table 1.6 Origin for the names of Rare Earth Ions

<table>
<thead>
<tr>
<th>Lanthanide</th>
<th>Discoverer</th>
<th>Year</th>
<th>Origin of its name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttrium</td>
<td>Gadolin</td>
<td>1794</td>
<td>named after the village of Ytterby, Sweden</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>Mosander</td>
<td>1839</td>
<td>From the Greek word “lanthanon” meaning I am hidden</td>
</tr>
<tr>
<td>Cerium</td>
<td>Berzelius, Hisinger</td>
<td>1804</td>
<td>After Greek deity of fertility, Ceres</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>Von Welsbach</td>
<td>1885</td>
<td>From the Greek words prasios (green) and didymos (twin)</td>
</tr>
<tr>
<td>Neodymium</td>
<td>Von Welsbach</td>
<td>1885</td>
<td>From the Greek word “neo” which means new one</td>
</tr>
<tr>
<td>Promethium</td>
<td>Marinsky, Coryell</td>
<td>1948</td>
<td>After Prometheus who brought fire to mortals</td>
</tr>
<tr>
<td>Samarium</td>
<td>De Boisbaudrau</td>
<td>1879</td>
<td>Vasili Samarsky-Bykhovets discovered the rare earth ore called samarskite</td>
</tr>
<tr>
<td>Europium</td>
<td>Demarcaty</td>
<td>1901</td>
<td>named after the continent Europe</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>De Boisbaudrau</td>
<td>1886</td>
<td>After Johan Gadolin (1760-1852) to honor his investigation of rare earths</td>
</tr>
<tr>
<td>Terbium</td>
<td>Mosander</td>
<td>1843</td>
<td>named after the village of Ytterby, Sweden</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>De Boisbaudrau</td>
<td>1886</td>
<td>from the Greek “dysprositos” meaning hard to get</td>
</tr>
<tr>
<td>Holmium</td>
<td>J.L. Soret</td>
<td>1878</td>
<td>From the Latin word Holmia (Stockholm)</td>
</tr>
<tr>
<td>Erbium</td>
<td>Mosander</td>
<td>1843</td>
<td>named after the village of Ytterby, Sweden</td>
</tr>
<tr>
<td>Thulium</td>
<td>Cleve</td>
<td>1879</td>
<td>refers to the mythological land of Thule</td>
</tr>
<tr>
<td>Ytterbium</td>
<td>De Marignac</td>
<td>1878</td>
<td>named after the village of Ytterby, Sweden, where the first rare earth ore was discovered</td>
</tr>
<tr>
<td>Lutetium</td>
<td>Georges Urbain</td>
<td>1907</td>
<td>From Lutetia (ancient name of Paris)</td>
</tr>
</tbody>
</table>
Just after completing his PhD degree, he discovered two lanthanide elements in 1885, Pr and Nd. The same year he filed a patent for electric bulbs containing Os and W filaments. But electricity was not readily available in those times and, as an alternative, Auer von Welsbach proposed the so-called Auer mantle for gas lighting in 1891. The mantle is made up of 99% thorium oxide and 1% cerium oxide; more than five billions were sold until 1935 and the company founded by Auer von Welsbach, Treibacher Chemische Werke, which also manufactured flint stones and Mishmetal (an alloy of 30% iron and 70% of a mixture of La, Ce, Nd, and Sm), is still producing rare earth materials nowadays. The other company founded in 1906 by Auer von Welsbach for the production of light bulbs, Osram, developed into a large multinational business which presently employs over 38000 collaborators [29-30].

The lanthanides are unique among the elements, except for the actinides, in resembling each other so markedly. This is easily explained by the electronic configuration of the atoms and their derived ions, which essentially exist in the trivalent state \( \text{Ln}^{3+} \) ([Xe] 4F, n - 0 - 14) in aqueous solutions. The shielding of the 4f orbitals by the filled 5p\(^6\)6s\(^2\) sub-shells results in special spectroscopic properties with parity forbidden 4f-4f transitions having very low molar absorption coefficients (\(< 10 \text{ M}^{-1} \text{ cm}^{-1}\), but very often \(1 \text{ M}^{-1}\)) and characteristic narrow-line emission, mostly in the visible and near infrared ranges. Luminescence has been instrumental in the discovery of several lanthanide elements and in turn, these elements have always played a prominent role in lighting and light conversion technologies (Auer mantles, incandescent lamps, lasers) and more recently in cathode-ray and plasma displays, and light-emitting diodes. The table 1.6 presented below gives the information about the discovery of the rare earth elements [7].

In the 1980's, it was realized that the peculiar luminescent properties of the lanthanide ions could be of great help in the analysis of environmental and biological samples and this led to most interesting developments which have stirred a vast interest for the coordination chemistry of these ions. Presently, attention focuses on several applications of luminescent lanthanide ions:

1. Their continuing use in lighting industry for the engineering of lamp and display phosphors
(2) Their ability to provide electroluminescent materials for organic light-emitting diodes as well as optical fibers and amplifiers for telecommunication

(3) Their potential in the design of luminescent liquid crystals

(4) Their capacity to yield functional complexes for biological assays and medical imaging purposes.

1.9 Characteristics of the Lanthanides

The lanthanides 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, akin to the Group II metals.

Table 1.7 Physical properties of Rare Earth metals

<table>
<thead>
<tr>
<th>Element</th>
<th>At. No</th>
<th>At. Wt</th>
<th>M.P (°C)</th>
<th>B.P (°C)</th>
<th>Density (g/cm³)</th>
<th>Colour of Ln³⁺ in Aqueous Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>39</td>
<td>88.90</td>
<td>1522</td>
<td>3338</td>
<td>4.469</td>
<td>Colourless</td>
</tr>
<tr>
<td>La</td>
<td>57</td>
<td>139.91</td>
<td>918</td>
<td>3464</td>
<td>6.145</td>
<td>Colourless</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
<td>140.12</td>
<td>798</td>
<td>3433</td>
<td>6.770</td>
<td>Green</td>
</tr>
<tr>
<td>Pr</td>
<td>59</td>
<td>140.90</td>
<td>931</td>
<td>3520</td>
<td>6.773</td>
<td>Violet</td>
</tr>
<tr>
<td>Nd</td>
<td>60</td>
<td>144.24</td>
<td>1021</td>
<td>3074</td>
<td>7.007</td>
<td>Pink</td>
</tr>
<tr>
<td>Pm</td>
<td>61</td>
<td>147.00</td>
<td>1042</td>
<td>3000</td>
<td>7.260</td>
<td>Pink</td>
</tr>
<tr>
<td>Sm</td>
<td>62</td>
<td>150.35</td>
<td>1074</td>
<td>1794</td>
<td>7.520</td>
<td>Pale Yellow</td>
</tr>
<tr>
<td>Eu</td>
<td>63</td>
<td>151.96</td>
<td>822</td>
<td>1529</td>
<td>5.243</td>
<td>Colourless</td>
</tr>
<tr>
<td>Gd</td>
<td>64</td>
<td>157.25</td>
<td>1313</td>
<td>3273</td>
<td>7.900</td>
<td>Colourless</td>
</tr>
<tr>
<td>Tb</td>
<td>65</td>
<td>158.92</td>
<td>1356</td>
<td>3230</td>
<td>8.229</td>
<td>Pale Pink</td>
</tr>
<tr>
<td>Dy</td>
<td>66</td>
<td>162.50</td>
<td>1412</td>
<td>2567</td>
<td>8.550</td>
<td>Pale Yellow</td>
</tr>
<tr>
<td>Ho</td>
<td>67</td>
<td>164.93</td>
<td>1474</td>
<td>2700</td>
<td>8.755</td>
<td>Yellow</td>
</tr>
<tr>
<td>Er</td>
<td>68</td>
<td>167.26</td>
<td>1529</td>
<td>2868</td>
<td>9.066</td>
<td>Rose</td>
</tr>
<tr>
<td>Tm</td>
<td>69</td>
<td>168.93</td>
<td>1545</td>
<td>1950</td>
<td>9.321</td>
<td>Pale Green</td>
</tr>
<tr>
<td>Yb</td>
<td>70</td>
<td>173.04</td>
<td>819</td>
<td>1196</td>
<td>6.965</td>
<td>Colourless</td>
</tr>
<tr>
<td>Lu</td>
<td>71</td>
<td>174.97</td>
<td>1663</td>
<td>3402</td>
<td>9.840</td>
<td>Colourless</td>
</tr>
</tbody>
</table>

hcp: hexagonal close packed; dhcp: double C hexagonal close packed; rohmb: rohmbedral; fcc: face centered cubic; bcc: body centered cubic.
Some of the Characteristics of the Lanthanides

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

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

iii. Moving from left to right across the period (increasing atomic number), the radius of each trivalent lanthanide ion steadily decreases. This is referred to as 'lanthanide contraction'.

_Cause of lanthanide contraction:_ The configuration of lanthanides show that the additional electron enters the $4f$-subshell. The shielding of one $4f$ electron by another from the increasing nuclear charge is very little, being even smaller than that encountered in case of d-electrons. The imperfect shielding of $f$-electrons is due to the shape (very much diffused) of $f$-orbitals. Thus as atomic number increases, the nuclear charge increases by unity at each step, while no comparable increase in the mutual shielding effect of $4f$ electrons occurs. This causes a contraction in the size of the $4f$-subshell. Consequently the atomic and ionic size go on decreasing as we move from La to Lu; thus the ionic radius changes from $1.06 \text{ Å (La}^{3+})$ to $0.85 \text{ Å (Lu}^{3+})$.

iv. Lanthanides possess high melting and boiling points.

v. Lanthanides react with water to liberate hydrogen ($H_2$), slowly in cold and quickly upon heating. Lanthanides commonly bind to water.

vi. Lanthanides can burn easily in air.

vii. They are strong reducing agents.

viii. Their compounds are generally ionic.

ix. Lanthanide compounds are strongly paramagnetic (except $\text{La}^{3+}$ and $\text{Lu}^{3+}$).
x. The magnetic moments of the lanthanide and iron ions oppose each other.

xi. The coordination numbers of lanthanides are high (greater than 6; usually 8 or 9 or as high as 12).

xii. The 4f orbitals in the Ln$^{3+}$ ion do not participate directly in bonding, being well shielded by the 5s$^2$ and 5p$^6$ orbitals. Their spectroscopic and magnetic properties are thus largely uninfluenced by the ligand.

The optical properties which make the lanthanide ions as favourable candidates for the luminescent device fabrication are:

i. They emit narrow line, almost monochromatic light and they have long emission lifetimes.

ii. They possess high refraction with relatively low dispersion.

iii. Luminescence of Ln$^{3+}$ ion spreads in the various spectral ranges.

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

v. The electronic states of the ground 4$f^*$ configuration provide complex optical energy level structure, thus there are many possible three and four level lasing schemes.

vi. There are several excited states suitable for optical pumping. These excited states decay non-radiatively to metastable states having high radiative quantum efficiencies.

vii. The availability of well developed theoretical models for accurate energy level analysis and transition intensities to predict/understand excited state dynamics.
1.10 Luminescence of Rare Earth Ions

Rare earths are seventeen elements consisting of the fifteen lanthanides from La (Z=57) to Lu (Z=71) and also two more elements namely Sc (Z=21) and Y(Z=39) [31]. The electronic configurations of trivalent rare earth ions in the ground states are shown in Table 1.8.

Table 1.8 Electronic configurations of trivalent Rare – Earths

<table>
<thead>
<tr>
<th>Atomic number (Z)</th>
<th>Ions</th>
<th>Corresponding elements</th>
<th>4f electrons</th>
<th>( \sum S )</th>
<th>( \sum L )</th>
<th>( J = \Sigma(L+\Sigma) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Sc(^{3+})</td>
<td>Ar</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>39</td>
<td>Y(^{3+})</td>
<td>Kr</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>57</td>
<td>La(^{3+})</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>58</td>
<td>Ce(^{3+})</td>
<td>Xe (\uparrow)</td>
<td></td>
<td>(\frac{1}{2})</td>
<td>3</td>
<td>5/2</td>
</tr>
<tr>
<td>59</td>
<td>Pr(^{3+})</td>
<td>Xe (\uparrow \uparrow)</td>
<td></td>
<td>1</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>Nd(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow)</td>
<td></td>
<td>3/2</td>
<td>6</td>
<td>9/2</td>
</tr>
<tr>
<td>61</td>
<td>Pm(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>2</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>62</td>
<td>Sm(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>5/2</td>
<td>5</td>
<td>5/2</td>
</tr>
<tr>
<td>63</td>
<td>Eu(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>64</td>
<td>Gd(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>7/2</td>
<td>0</td>
<td>7/2</td>
</tr>
<tr>
<td>65</td>
<td>Tb(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>66</td>
<td>Dy(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>5/2</td>
<td>5</td>
<td>15/2</td>
</tr>
<tr>
<td>67</td>
<td>Ho(^ {3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>2</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>68</td>
<td>Er(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>3/2</td>
<td>6</td>
<td>15/2</td>
</tr>
<tr>
<td>69</td>
<td>Tm(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>1</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>70</td>
<td>Yb(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>(\frac{1}{2})</td>
<td>3</td>
<td>7/2</td>
</tr>
<tr>
<td>71</td>
<td>Lu(^{3+})</td>
<td>Xe (\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow)</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
As shown in this table, Sc$^{3+}$ is equivalent to Ar, Y$^{3+}$ to Kr and La$^{3+}$ to Xe in electronic configuration. The lanthanides from Ce$^{3+}$ to Lu$^{3+}$ have one to fourteen 4f electrons added to their inner shell configurations, which is equivalent to Xe. Ions with no 4f electrons, i.e., Sc$^{3+}$, Y$^{3+}$ and Lu$^{3+}$ have no electronic energy levels that can induce excitation and reveal luminescence process in or near the visible region. In contrast, the ions from Ce$^{3+}$ to Yb$^{3+}$, which have partially filled 4f orbitals, have energy levels characteristic of each ion and show a variety of luminescence properties in the visible region. Many of these ions could be used as luminescent materials, mostly by replacing Y$^{3+}$, Gd$^{3+}$, La$^{3+}$ and Lu$^{3+}$ in different optical materials. The azimuthal quantum number (L) of 4f orbital is 3, giving rise to 7 ($=2L+1$) orbital, each of which can accommodate two electrons. In the ground state, electrons are distributed so as to provide a maximum combined spin angular momentum (S). The spin angular momentum (S) is further combined with an orbital angular momentum (L) to give rise to the total angular momentum (J) as given below [32].

\[
J = L - S, \text{ when the number of 4f electrons is smaller than 7}
\]

\[
J = L + S, \text{ when the number of 4f electrons is larger than 7}
\]

Electronic state is indicated by notation $^{2S+1}L_J$, where L represents S, P, D, F, G, H, I, J, K, L, M,... corresponding to $L = 0,1,2,3,4,5,6,7,8,9,10,...$, respectively. More accurately, an actual electronic state is expressed as an immediate coupling state, which can be written as $^{2S+1}L_J$, states combined by a spin orbit interaction. The mixing due to spin orbit interaction is small for the levels near the ground states, while it is considerable for excited states that have neighboring states with similar J numbers. The effect of mixing is relatively small on the energy of the energy levels, but can be large on their optical transition probabilities. The 4f electronic energy levels of lanthanide ions are shielded from the external electric fields by the outer 5s$^2$ and 5p$^6$ electrons. This feature is strong in rare earths compared with the transition metal ions, whose 3d electrons, located in an outer orbit, are heavily affected by the environmental or crystal electric fields. The characteristic energy levels of 4f electrons of trivalent lanthanides ions have precisely been reported by Dieke and several others [33-41].
Fig. 1.8 The Energy Levels of the 4f$^n$ Configuration of the Trivalent Lanthanides

Fig. 1.10 is known as the Dieke diagram, showing the energy levels of individual ions incorporated in lanthanum chloride crystalline matrices, this diagram is applicable to different rare earth ions doped in other matrices as well, for their analysis, because the shift in energy level position will be very insignificant with the change in the host matrices for the dopant rare earth ions.

The mechanism for the interpretation of the observed transitions of lanthanide ions can be classified into magnetic dipole transitions, the induced electronic dipole transitions and the electric quadrupole transitions. Though only a few magnetic dipole transitions exist for the trivalent lanthanide ions, magnetic dipole transitions are of interest, because their intensities are in a first approximation independent of the ligand environment and can be used as intensity standard. Induced electric dipole transitions occur much more frequently than magnetic dipole transitions. The major of the observed optical transitions in lanthanide ions are mostly due to the induced electric dipole transitions.
A magnetic dipole transition is caused by an interaction of the spectroscopic active ion (i.e. lanthanide ion) with the magnetic field component of the electromagnetic radiation through a magnetic dipole. An electric dipole transition is due to the consequence of the interaction of the lanthanide ion with the electric field vector through an electric dipole. The electric quadrupole transition arises from the displacement of a charge which is quadrupole in nature. Electronic quadrupole transitions are much weaker than magnetic dipole and induced electric dipole transitions. However, the so-called hypersensitive transitions are considered as pseudo quadrupole transitions because these transitions obey the selection rules of quadrupole transitions. The selection rules for both magnetic dipole and electric dipole transitions are summarized in Table 1.9 [42, 43].

The selection rules on ΔS and ΔL are not very strict and are only valid in the Russel-Saunders (LS) coupling scheme. In the Russel-Saunders coupling scheme, magnetic dipole transitions will be limited to the J-levels within a single term $^{2S+1}L$ (i.e. the ground term for transitions observed in the absorption spectrum). These selection rules can be relaxed in the intermediate coupling scheme, where only J remains as a good quantum number. The intensity of a magnetic dipole transition is relatively independent of the surroundings of the lanthanide. So, the kind of ligands or the symmetry of the coordination polyhedron around the lanthanide ion does not influence the magnetic dipole intensity that significantly.

Table 1.9: Selection rules

<table>
<thead>
<tr>
<th>Induced electric dipole transitions (ED)</th>
<th>Magnetic dipole transitions (MD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Δl = ± 1$</td>
<td>$Δτ = ΔS = ΔL = 0$</td>
</tr>
<tr>
<td>$Δτ = 0$</td>
<td>$ΔJ = 0, ±1$, but 0-0 is forbidden;</td>
</tr>
<tr>
<td>$ΔS = 0$</td>
<td>$-M + ρ + M^1 = 0$, where $ρ = 0, ±1$;</td>
</tr>
<tr>
<td>$</td>
<td>ΔL</td>
</tr>
<tr>
<td>$</td>
<td>ΔJ</td>
</tr>
<tr>
<td>$M^1 - M = - (q+p)$</td>
<td></td>
</tr>
</tbody>
</table>

τ = additional quantum number of discriminate between levels with same S and L quantum number, ρ = Polarization number.
Typical examples of this mechanism are demonstrated by the luminescence from the $^4D_J$ states of Eu$^{3+}$, the intensity of these transitions depends strongly on the site symmetry in the host matrices. The spectroscopic technique involves a transition, between two states and gives information about the difference between them. Since the absorption and emission transitions could occur between the ground and some excited states, the spectroscopic technique in general gives information on how the excited state differs from the ground state. The electronic state of an ion is different after the transition, and the way in which the ion interacts with its environment might also be different. This latter determines the band shape of the transition concerned and which strongly influences the process of non-radioactive relaxation out of the excited state.

1.11 Hypersensitive Transitions:

The intensities of the induced electric dipole transitions in lanthanide ions are not much affected by the environment. The dipole strength of a particular transition of a lanthanide ion in different matrices will not vary more than a factor two or three. However, a few transitions are very sensitive to the host environment and around the rare earth. Such transitions are called hypersensitive transitions [44, 45]. All hypersensitive transitions obey the selection rules

$$|\Delta S| = 0, |\Delta L| \leq 2 \text{ and } |\Delta J| \leq 2$$

These selection rules are the same as the selections rules of a pure quadrupole transition, but calculations have revealed that the intensities of hypersensitive transitions are several orders of magnitude larger for these transitions to have a quadrupole character. Therefore, hypersensitive transitions have been also called pseudo-quadrupole transitions. Magnetic Dipole and Hypersensitive transitions of different earth ions are given in Table.1.10.
Henrie et al. have [46] found a direct relationship between the hypersensitive transitions and the nephelauxetic effect. The nephelauxetic effect could be observed as a red shift of the f-f transitions and which increase with an increasing degree of covalency. Hypersensitive has been used for the study of the coordination polyhedron (coordination number and site symmetry) around the rare-earth ion.
1.12 Transition Metal Ions

The elements ranging from 3d<sup>2</sup>4s<sup>2</sup> (Ti) to 3d<sup>10</sup>4s (Cu) are considered transition metals. They share similar chemical properties. Many crystals/glasses containing transition metal ions in various valence states exhibit broad and intense 3d → 3d emission bands.

1.12.1 Properties of Transition Metals

The transition metal elements are quite similar in their physical and chemical properties. This is due to the fact, that for the elements in this series the inner 3d shell is being filled with electrons, whereas the outer filled 4s shell remains unchanged. Common properties include high tensile strength, density, hardness, high melting and boiling points. The transition metals show variable oxidation states, increasing in number towards the middle, and decreasing again towards the end of the series. All oxidation states can be exhibited in Mn<sup>N+</sup> ranging from N = 1 . . . 7. In general, the lower oxidation states are found in ionic compounds, whereas the higher ones preferentially occur in covalent compounds. The filling of the 3d orbitals, however, is irregular, since for chromium (3d<sup>5</sup>4s) and copper (3d<sup>10</sup>4s) an electron from the 4s shell is promoted to a 3d orbital. In chromium the 3d and 4s levels are fully occupied by unpaired electrons due to electron repulsion interaction.

Table 1.11 gives the details about most common transition metal ions and their corresponding numbers (n) of 3d valence electrons.

<table>
<thead>
<tr>
<th>Ions</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti&lt;sup&gt;3+&lt;/sup&gt;, V&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>1</td>
</tr>
<tr>
<td>V&lt;sup&gt;3+&lt;/sup&gt;, Cr&lt;sup&gt;4+&lt;/sup&gt;, Mn&lt;sup&gt;5+&lt;/sup&gt;</td>
<td>2</td>
</tr>
<tr>
<td>V&lt;sup&gt;2+&lt;/sup&gt;, Cr&lt;sup&gt;3+&lt;/sup&gt;, Mn&lt;sup&gt;4+&lt;/sup&gt;</td>
<td>3</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;2+&lt;/sup&gt;, Mn&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>4</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;2+&lt;/sup&gt;, Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>5</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;, Co&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>6</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;+&lt;/sup&gt;, Co&lt;sup&gt;2+&lt;/sup&gt;, Ni&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>7</td>
</tr>
<tr>
<td>Co&lt;sup&gt;+&lt;/sup&gt;, Ni&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>8</td>
</tr>
<tr>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;, Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>9</td>
</tr>
</tbody>
</table>
Optical glass doped with transition metal (TM) ions and rare-earth (RE) ions are an important class of luminescent material with applications in solid-state lasers, display and other field of technology. Moreover, in applications ranging from new optical material research to optoelectronic and integrated optical devices, there has been increasing interest in glasses due to their lower production costs with respect to single crystals. Among all the transition metal ions the most investigated ions are Cu\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\) and Cr\(^{3+}\) and the large number of review articles and papers are evidence for it. Hence in the present study we have chosen those five transition metal ions as the dopant ions to explore its spectral properties in the selected host glass. Some of its significant features have been given below for each ion to state its importance [47-49].

1.12.2 Manganese

Torben Olof Bergman (1735-1784), professor of chemistry at Uppsala, separated pyrolusite (MnO\(_2\)) from lime and magnesia alba, but failed to reduce the ore. In 1774 a friend of Bergman, Carl Wilhelm Scheele, completed a three years investigation, called it Manganese, and described it as "the calx of a metal different from any then known". Manganese is the 12th most abundant element and 3rd most abundant transition metal, exceeded only by iron and titanium, reaching an overall abundance of 0.106% in the earth's crust. Several silicates, oxides and carbonates containing Manganese are of economical importance, such as hausmannite (Mn\(_2\)O\(_4\)), rhodochrosite (MnCO\(_3\)), manganite (Mn\(_3\)O\(_7\) \cdot H\(_2\)O), and pyrolusite (MnO\(_2\)), while the latter probably has been used for glass fabrication already since the ancient times of the Pharaohs. Generally, Manganese is moderately reactive. At higher temperature, it reacts vigorously with oxygen, nitrogen, chlorine and fluorine, and combines directly with B, C, Si, P, As, and S. Due to its formidable range of oxidation states, oxides are known based on Mn\(^{2+}\) to Mn\(^{7+}\).

The Mn\(^{2+}\) ion has an emission which consists of a broad band, the position of which depends strongly on the host lattice. The emission can vary from green to deep red. The decay time of this emission is of the order of ms. From the Tanabe-Sugano diagram it is derived that the emission corresponds to the \(^4T_1\rightarrow^6A_1\) transition. This explains all the spectral properties: a broad band due to different slopes of the energy levels, a long decay time due to the spin selection rule, and a
dependence of the emission color on the host lattice due to the dependence on crystal field. Tetrahedrally co-ordinant Mn$^{2+}$ (weak crystal-field) usually gives a green emission, octahedrally coordinated Mn$^{2+}$ (stronger crystal field) give an orange to red emission. Mn$^{2+}$ is an efficient green phosphor widely used in plasma display panels (PDPs), cathode ray tube (CRT), tri-color lamps, color television and thin film electroluminescent devices because of its high luminescence efficiency, the purity of color, chemical stability and large color gamut. Mn$^{2+}$ doped luminescent materials have been known to have wide-range emissions from 500 to 700 nm depending on the crystal field of the host materials.

1.12.3 Copper

Copper is a chemical element with the symbol Cu and atomic number 29. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is rather soft and malleable and a freshly-exposed surface has a pinkish or peachy color.

Copper compounds are known in several oxidation states, usually 2+, where they often impart blue or green colors to natural minerals such as turquoise and have been used historically widely as pigments. Copper as both metal and pigmented salt, has a significant presence in decorative art. Copper 2+ ions are soluble in water, where they function at low concentration as bacteriostatic substances and fungicides. It is used as a thermal conductor, an electrical conductor, a building material, and a constituent of various metal alloys.

Common oxidation states of copper include the less stable copper (I) state, Cu$^+$; and the more stable copper (II) state, Cu$^{2+}$, which forms blue or blue-green salts and solutions. Under unusual conditions, a 3+ state and even an extremely rare 4+ state can be obtained. Using old nomenclature for the naming of salts, copper (I) is called cuprous, and copper (II) is cupric. In oxidation copper is mildly basic. There are two stable copper oxides, copper (II) oxide (CuO) and copper (I) oxide (Cu$_2$O). Copper oxides are used to make yttrium barium copper oxide (YBa$_2$Cu$_3$O$_{7-\delta}$) or YBCO which forms the basis of many unconventional superconductors. Copper ion is a common transition metal activator for many commercial phosphors. Also, Copper ions doped waveguides are successfully fabricated for exhibiting blue-green luminescence.
1.12.4 Cobalt

Cobalt is a hard, lustrous, grey metal, a chemical element with symbol Co and atomic number 27. Although cobalt-based colors and pigments have been used since ancient times for making jewelry and paints, and miners have long used the name kobold ore for some minerals, the free metallic cobalt was not prepared and discovered until 1735 by Georg Brandt. Cobalt is used in the preparation of magnetic, wear-resistant, and high-strength alloys. Cobalt blue (cobalt (II) aluminate, CoAl₂O₄) gives a distinctive deep blue color to glass, ceramics, inks, paints, and varnishes. Cobalt-60 is a commercially important radioisotope, used as a tracer and in the production of gamma rays for industrial use. Common oxidation states of cobalt include +2 and +3, although compounds with oxidation state +1 are also known. The most stable oxidation state for simple compounds is +2. Cobalt (II) salts form the red-pink \([\text{Co(H}_2\text{O)}_6]^{2+}\) complex in aqueous solution. Adding excess chloride will change the color from pink to blue, due to the formation of \([\text{CoCl}_4]^{2-}\).

Tetrahedral Co²⁺ ions in dielectric crystals such as MgAl₂O₄, ZnGa₂O₄ are characterized by strong and broad luminescence bands. Such materials are considered as possible candidates for tunable solid-state lasers in the visible and near infrared (NIR). On the other hand, a number of crystals (Y₃Al₅O₁₂, LaMgAl₁₁O₁₉, and MgAl₂O₄) doped with tetrahedral Co²⁺ ions have been reported to be useful saturable absorber Q-switches for 1.54 μm Er: glass lasers.

1.12.5 Chromium

Chromium is a chemical element which has the symbol Cr and atomic number 24. It is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odourless, tasteless, and malleable. The name of the element is derived from the Greek word "chôma" meaning color, because many of its compounds are intensely colored. It was discovered by Louis Nicolas Vauquelin in the mineral crocoite (lead chromate) in 1797. Crocoite was used as a pigment, and after the discovery that the mineral chromite also contains chromium this latter mineral was used to produce pigments as well. Chromium was regarded with great interest because of its high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium and nickel to form stainless steel.
The luminescence of \( \text{Cr}^{3+} \) in \( \text{Al}_2\text{O}_3 \) (ruby) has been known since 1960. The emission consists of two sharp lines (the so called R lines) in the far red. Since it is a line, it must be due to the transition \( ^2\text{E} \rightarrow ^4\text{A}_2 \), generally speaking, the emission of transition metal ions originates from the lowest excited state. The lifetime of the excited state amounts to some ms, because the parity selection rule as well as the spin selection rule applies. The emission line is followed by some well as the spin selection rule applies. The emission line is followed by some weak vibronic transitions: obviously this emission transition belongs to the weak-coupling case.

Among various transition metal ions, the paramagnetic chromium ion is found to be very sensitive to its chemical environment. Extensive investigations on the optical absorption, luminescence and electron spin resonance (ESR) spectroscopy of the \( \text{Cr}^{3+} \) ion in inorganic systems have been made in recent years in view of their importance in the development of tunable solid-state lasers and new luminescence materials. Divalent transition metals, particularly chromium, can be used in II–VI materials such as ZnSe and ZnS to produce broadly tunable continuous wave middle-infrared (mid-IR) lasers.

1.12.6 Nickel

Nickel is a chemical element, with the chemical symbol Ni and atomic number 28. It is a silvery-white lustrous metal with a slight golden tinge. It is one of the four ferromagnetic elements at about room temperature. Its use has been traced as far back as 3500 BC, but it was first isolated and classified as a chemical element in 1751 by Axel Fredrik Cronstedt, who initially mistook its ore for a copper mineral.

Nickel is a silvery-white metal with a slight golden tinge that takes a high polish. It is one of only four elements that are magnetic at or near room temperature. The most common oxidation state of nickel is +2 with several Ni complexes known. It is also thought that a +6 oxidation state may exist; however, this has not been demonstrated conclusively.

The \( \text{Ni}^{2+} \) ion (3d\(^1\)) gives a broad band emission in the near infrared due to the appearance of emission transitions from more than one level. Luminescence from \( \text{KMgF}_3:\text{Ni}^{2+} \) appears in the near infrared \(^3\text{T}_2 \rightarrow ^3\text{A}_2 \), the red \(^1\text{T}_2 \rightarrow ^3\text{T}_2 \) and the green \(^1\text{T}_2 \rightarrow ^3\text{A}_2 \). \( \text{Ni}^{2+} \) ion has become one of the most investigated ions of the TM and has complicated optical spectra when present in different transparent materials.
1.13 Objective of the Present Thesis

In the present thesis, we have undertaken to prepare and analyze the spectral properties of two new series fluoro borate (B₂O₃-BaO-AlF₃ and B₂O₃-BaO-LiF) glasses. These fluoro borate glasses will be characterized based on the measurement and analysis of structural, thermal, absorption and photoluminescence spectral features.

Table 1.12 Role of each chemical in the glass matrices studied

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Role of each chemical in the glass matrices studied</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂O₃</td>
<td>Glass Network Formers (NWF)</td>
</tr>
<tr>
<td>BaO</td>
<td>Glass Network Intermediates (NWI)</td>
</tr>
<tr>
<td>(AlF₃, LiF)</td>
<td>Glass Network Modifiers (NWM)</td>
</tr>
<tr>
<td>(Cu²⁺, Mn²⁺, Ni²⁺, Co²⁺, Cr³⁺)</td>
<td>Luminescent Transition Metal Ions</td>
</tr>
<tr>
<td>(Pr³⁺, Tm³⁺, Sm³⁺, Dy³⁺, Eu³⁺, Tb³⁺, Ho³⁺) and (Nd³⁺, Er³⁺)</td>
<td>Visible Color Luminescent Rare-Earth Ions NIR Luminescent Rare Earth Ions</td>
</tr>
</tbody>
</table>

Firstly, the author took up host glasses (undoped) to understand their structural and thermal properties. Since those results are quite encouraging and we have chosen them as potential hosts to dope certain significant transition metal ions (Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ & Cr³⁺) and some rare earth ions (Pr³⁺, Tm³⁺, Sm³⁺, Dy³⁺, Eu³⁺, Tb³⁺, Ho³⁺, Nd³⁺ & Er³⁺), to evaluate their optical characteristics, in order to validate their suitability as optical materials of significant importance[50-61]. These results that are obtained were explained appropriately in Chapter-III and chapter-IV of this thesis.
References

1. J. García Sole, L.E. Bausa and D.Jaque,
   An Introduction to the Optical Spectroscopy of Inorganic Solids,

2. A. A. Kaminskii,

3. J. H. Campbell, T. I. Suratwala,

4. R. Reisfeld, C. K. Jorgensen,
   Laser and Excited States of Rare-Earths (Springer, New York, 1997).

5. S. Tanabe, S. Yoshii, K. Hirao, N. Soga,

6. S. Schweizer, L.W. Hobbs, M. Secn, J. Spaeth, A. Edger, G. V. M. Williams,

7. Simon Cotton
   Lanthanide and Actinide Chemistry, John Wiley & Sons Ltd, UK, 2006

8. ASTM Standards on Glass and Glass Products, prepared by ASTM Committee C14,

9. A. E. Dale, J. E. Stanworth,


11. J. Hlavac,
    The Technology of Glass and Ceramics. (Elsevier Scientific Publishing Co.,
    Oxford, 1983), 1-376

12. P. Giri Prakash

13. B.N. Figgis

14. Bethe H
    Ann Physik, 3 (1929) 133.

15. Van Vleck J.H.

16. Mulliken R.S.
17. Carl J. Ballhausen
   Introduction to Ligand Field Theory

18. Brian N. Figgis, Michael A. Hitchman
   Ligand Field Theory and Its Applications
   John Wiley Publicatons, New York 1999

19. B. N. Figgis
   Introduction to ligand fields
   Interscience Publishers, 1966

20. Donald L. Pavia Gary M. Lampman George S. Kriz
    Introduction to Spectroscopy
    Publisher: Harcourt College Pub Date Published: 1996

21. Y. Tanabe, and S. Sugano

22. Newton Harvey N,

23. James F. A. J. L.,

24. E. Desurvire,
    Erbium-Doped Fiber Amplifiers, Principles and Applications

25. Digonnet M. J. F.,
    Rare-Earth Doped Lasers and Fiber Amplifiers (Marcel Dekker, Inc.) 2001

26. F. Auzel and F. Pelle
    Bottleneck in multiphonon nonradiative transitions

27. Stefan Hufner
    Optical spectra of transparent rare earth compounds
    Academic Press, 1978

28. M. J. Weber
    CRC, Boca Raton, FL vol 2 (1988)

29. Fu Xi Gan, Lei Xu
    Photonic Glasses
30. J. Lucas and J. L. Adam
   Halide Glasses and Their optical properties

31. W. T. Carnall
   Handbook on the Physics and Chemistry of Rare Earths,
   North Holland, Amsterdam (1979).

32. R P Rao
   Luminescence: phenomena, materials, and devices, Nova Science Publishers

33. G. H. Dieke
   Spectra and Energy levels of rare earth ions in crystals

34. B. G. Wybourne

35. L. A. Riseberg and H. W. Moos

36. W. T. Carnall, H. M. Crosswhite and H. Crosswhite
   Energy level structure and Transition Probabilities of the Trivalent
   Lanthanides in LaF.
   Laboratory Review Article, Argonne National Laboratory, Illinois, USA (1978).

37. G. Blasse
   Handbook on the Physics and Chemistry of Rare Earths
   Editors Jr. K. A. Gschneidner and L. Eyring, Vol. 4 North Holland

38. G. Adachi
   Rare Earths – Their Properties and Applications,

39. K. H. Butler
   Fluorescent lamp phosphors, Technology and Theory

40. F. C. Pallila

41. J. L. Somerdijk, A. Bril and F. M. J. H. Hoex–Strik

42. A. K. Gschneidner Jr. and L. Eyring
   Handbook on the Physics and Chemistry of Rare Earths, Vol. 25.

38
43. L.J. F. Broer, C.J. Gorter and J. Hoogschagen
    Phys. 11 (1945) 231.

44. C.K. Jorgensen and B.R. Judd

45. R.D. Peacock
    Structure and Bonding 22 (1975) 83.


47. D.S. McClure
    Solid State Physics, Vol. 9,

48. T.M. Dunn
    Modern Coordination Chemistry

49. Leslie E. Orgel
    Introduction to Transition-Metal Chemistry
    Ligand-Field Theory
    Wiley Publications, New York

50. Xia Haiping, Zhang Jianli, Wang Jinhao, Zhang Yuepin

51. L.R.P. Kassab, W.G. Horas, M. Piasecki, P. Brgiel, I.V. Kityk

52. M. Nikl, J. Pejchal, R. Jinhau, J. Zhang, G. Chen, A. Bejteleva, A. Yoshikawa,
    T. Fakuda,


54. Qiuhai Nie, Cheng Jiang, Xunsi Wang, Tiefeng Xu, Haoquan Li

55. L.R.P. Kassab, W.G. Horas, M. Piasecki, P. Brgiel, I.V. Kityk

56. T.F. Belliveau, D.J. Simkin

57. B.J. Ainslie, S.P. Craig, S.T. Davey, B. Wakefield
    Mater. Lett. 6 (1988) 139.
58. J.Dexpert-Ghys, B.Piriou, N.J.Fracillon, C. Sombret

59. J.E.Shelby, L.K.Downie

60. R.Staske, P.Frobel, M.V.Dirke, S.Muller, K. Barner

61. M.A.Saltberg, Yung-Haw Hu