Chapter I

INTRODUCTION
1. INTRODUCTION

1.1 SPECTROSCOPY OF LANTHANIDES

Spectroscopy is a branch of physics which deals with the study of interaction of electromagnetic radiation with matter. The interaction of electromagnetic 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 tool 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 also it stretches to entire fields like biology, communication, defence, forensic, geology, industry and medicine [1-14]. In recent years, spectroscopic studies of trivalent lanthanide (Ln³⁺) ion based materials are attracting much attention due to their potential technological applications in optical devices such as solid state lasers, optical fiber amplifiers, light converters, optical storage materials, phosphors and sensors, spectral hole burning high density memories, acousto-optic modifiers and planar wave guides [15-20] and so on.

The design and development of these optical devices require a detailed spectroscopic study of the optical properties such as peak wavelengths, line widths, lifetimes, emission cross-sections and quantum efficiencies which inturn depend on the nature and type of the surrounding Ln³⁺ ion and on the phonon energies of the host matrix. Hence, there is a need of rigorous search for a low phonon energy and high quantum efficiency host. In order to
develop/design the new optical devices that possess high performance, the fluorescence properties of Ln$^{3+}$ ions doped into different host matrices are being investigated through evaluating the interaction mechanism between the Ln$^{3+}$ ion and ligand. The rich electronic structure of lanthanide ions in any host is due to the weak perturbation of the shielded 4f shells by the surrounding environment, the analysis of which provides a detailed knowledge about the arrangement of atoms and their interactions with the 4f electrons.

Glasses are particularly attractive hosts because they can be fabricated in the form of bulk devices and also foreign ions can be incorporated over a long interaction length unlike in crystals. The absorption and emission spectra of lanthanide ions in glasses are characterized by inhomogeneous broadening resulting from the distribution of several crystal-fields at the lanthanide ion sites in the amorphous solids. Hence there is an increasing demand for the lanthanide doped glasses for the development of various optical devices. Also good literature is available on fundamentals of physics and chemistry of lanthanides [21-26]. The present work deals with composition dependent optical absorption and photoluminescence studies of Pr$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ doped different chlorophosphate glasses.

Group of elements having atomic number Z=57 to 71 are usually classified as lanthanides and very often referred to as ‘rare earths’ (RE’s). They are situated at the bottom of the periodic table, one row above the actinides as Group IIIA elements. The word “Lanthanide” is a Greek origin which means ‘to lie hidden’. This is a very appropriate name, since it took more than a
century to discover all the lanthanides. Table 1.1 represents the lanthanides which are arranged in ascending order of $Z$ along with its color. According to this arbitrary classification, elements with $Z = 57$ to 63 are 'light lanthanides' and those with $Z = 64$ to 71 are 'heavy lanthanides'. Promethium is the only lanthanide that does not occur in nature in a stable form.

1.2 PROPERTIES OF LANTHANIDE IONS

Almost all the lanthanide elements appear to be bright silver in color. Among various lanthanides, lanthanum, cerium, praseodymium, neodymium and europium are very reactive, they will form oxide coating and tarnish the surface when exposed to air. The remaining lanthanides are not so reactive and gadolinium and lutetium retain their silvery metallic appearance for a long time. The lanthanides become brittle when they react with non metals such as oxygen or nitrogen. All the lanthanide elements possess high melting and boiling points. Their melting points are in the range 820° C-1660° C.

The lanthanide elements form alloys with many other metals and these alloys exhibit a wide range of physical properties. The lanthanides react slowly with cold water and more rapidly with hot water to form hydrogen gas. Neutral lanthanides possess the electronic configuration $[\text{Xe}]4f^n5d^m6s^2$, where $[\text{Xe}]$ denotes the neutral electronic configuration of xenon and the number of $4f$ electrons '$n$' ranges from 2 to 14. For all lanthanide ions, trivalent state is common and the electronic configuration for trivalent lanthanide ion is $4f^n5s^25p^6$, where '$n$' increases from 0 ($\text{La}^{3+}$) to 14 ($\text{Lu}^{3+}$).
Table 1.1 The rare earth elements and their features.

<table>
<thead>
<tr>
<th>Atomic No. (Z)</th>
<th>Element</th>
<th>Symbol</th>
<th>Physical appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>Lanthanum</td>
<td>La$^{3+}$ [Xe] 4f$^0$</td>
<td>Colorless</td>
</tr>
<tr>
<td>58</td>
<td>Cerium</td>
<td>Ce$^{3+}$ [Xe] 4f$^3$</td>
<td>Colorless</td>
</tr>
<tr>
<td>59</td>
<td>Praseodymium</td>
<td>Pr$^{3+}$ [Xe] 4f$^2$</td>
<td>Yellow green</td>
</tr>
<tr>
<td>60</td>
<td>Neodymium</td>
<td>Nd$^{3+}$ [Xe] 4f$^0$</td>
<td>Red violet</td>
</tr>
<tr>
<td>61</td>
<td>Promethium</td>
<td>Pm$^{3+}$ [Xe] 4f$^0$</td>
<td>Unknown</td>
</tr>
<tr>
<td>62</td>
<td>Samarium</td>
<td>Sm$^{3+}$ [Xe] 4f$^6$</td>
<td>Yellow</td>
</tr>
<tr>
<td>63</td>
<td>Europium</td>
<td>Eu$^{3+}$ [Xe] 4f$^6$</td>
<td>Essentially colorless</td>
</tr>
<tr>
<td>64</td>
<td>Gadolinium</td>
<td>Gd$^{3+}$ [Xe] 4f$^7$</td>
<td>Colorless</td>
</tr>
<tr>
<td>65</td>
<td>Terbium</td>
<td>Tb$^{3+}$ [Xe] 4f$^8$</td>
<td>Essentially colorless</td>
</tr>
<tr>
<td>66</td>
<td>Dysprosium</td>
<td>Dy$^{3+}$ [Xe] 4f$^9$</td>
<td>Light yellow green</td>
</tr>
<tr>
<td>67</td>
<td>Holmium</td>
<td>Ho$^{3+}$ [Xe] 4f$^{10}$</td>
<td>Brownish yellow</td>
</tr>
<tr>
<td>68</td>
<td>Erbium</td>
<td>Er$^{3+}$ [Xe] 4f$^{11}$</td>
<td>Pink</td>
</tr>
<tr>
<td>69</td>
<td>Thulium</td>
<td>Tm$^{3+}$ [Xe] 4f$^{12}$</td>
<td>Light green</td>
</tr>
<tr>
<td>70</td>
<td>Ytterbium</td>
<td>Yb$^{3+}$ [Xe] 4f$^{13}$</td>
<td>Colorless</td>
</tr>
<tr>
<td>71</td>
<td>Lutetium</td>
<td>Lu$^{3+}$ [Xe] 4f$^{14}$</td>
<td>-</td>
</tr>
</tbody>
</table>
Some of the general properties that are commonly observed by the lanthanides are (1) Lanthanides are relatively soft metals. Their hardness increases with increasing atomic number (2) Lanthanides possess high melting and boiling points (3) They are strong reducing agents (4) Lanthanide compounds are strongly paramagnetic and (5) The coordination numbers of lanthanides are high. The optical properties that are making the Ln$^{3+}$ ions as favorable candidates for the development of luminescent devices are (a) They emit narrow line, almost monochromatic light and they have long emission lifetimes (b) They possess high refraction with relatively low dispersion (c) Luminescence of Ln$^{3+}$ ion spreads in various spectral ranges (d) There are several excited states suitable for optical pumping (e) The f-f transitions have small homogeneous linewidths and (f) The availability of well developed theoretical models for intensities and accurate energy level transitions. Energy level diagram of trivalent lanthanides is shown in Fig. 1.1.

1.3 THE AMORPHOUS MATERIAL

One of the most active fields of solid-state research in recent years is the study of solids that are not crystals, in which the arrangement of atoms lacks long-range order. The advances that have been made in physics and chemistry of these materials are amorphous solids or glasses. Glasses have been widely appreciated within the research community. In the practical sphere, amorphous solids are beginning to find applications in areas such as solar energy conversion, electromagnetic machinery and data recording. The amorphous materials are not new; the iron-rich siliceous glassy materials recovered from
Fig 1.1: Energy level diagram of trivalent lanthanide ions
the moon by the Apollo missions some billions of years old. However, the "scientific study" of amorphous materials 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. The non-crystalline or amorphous materials possess randomness to some degree. Randomness can occur in several forms, of which topological, spin, substitutional or vibrational disorders are the most important. 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. Amorphous materials do not possess the long-range order characteristic of a crystal.

1.3.1 Glass

Glass is the best example for amorphous solid. Any liquid or supercooled liquid whose viscosity is greater than about $10^{13}$ Poise is called a glass. The term glass is commonly used to mean the fusion product of inorganic materials which have been cooled to a rigid condition without crystallizing. Various definitions of glassy materials are (1) A glass is an amorphous solid which exhibits a glass transition (2) A glass is an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region at glass transformation behavior. The glass transition is the phenomena in which a solid amorphous phase exhibits more or less abrupt change in derivative thermodynamic properties from crystal-like to liquid-like values with change of temperature (3) An inorganic product of fusion which has been cooled to rigid condition without crystallization. According to this definition, a glass is a non-
crystalline material that can not be distinguished from melt-quenched states of the same composition. The atomic arrangement of a glass is different from that of crystalline material and lacks long-range regularity as shown in Fig. 1.2. This is quite close to the atomic arrangement in a liquid. These are neither crystal lattice nor lattice point in the glass structure and therefore instead of diffraction peaks a halo is seen in the diffraction patterns of a glass.

The classical explanation for the formation of a glass is that, when a liquid is cooled, its fluidity (reciprocal viscosity) decreases and at certain temperature below the freezing point, becomes melting zero [27]. The relation between crystal, liquid and gas can easily be explained by means of a volume-temperature diagram as shown in Figure 1.3. On cooling a liquid from the initial state A, the volume will decrease steadily along AB. If the rate of cooling is slow, and nuclei are present, crystallization will take place at the freezing temperature (T_f). The volume will decrease sharply from B to C. Therefore, the solid will contract with falling temperature along CD. The volume of the super cooled liquid decreases along BE, which is smooth continuation of AB. At certain temperature T_g, the volume-temperature graph undergoes a significant change in slope and continues almost parallel to the contraction graph CD of the crystalline form. T_g is called transformation or glass transition temperature. Glass formation takes place only below T_g. The location of E, the point corresponding to T_g, varies with the rate than a fixed point. At which T_g below, the volume G will continue to decrease slowly. The
Fig. 1.2 Representation of the structure of (a) crystalline compound and (b) glassy matrix.
Fig. 1.3. The effect of temperature on the enthalpy (or volume) of a glass forming melt.
glasses also change with time in the vicinity of Tg. Then the glass reaches a more stable condition and is known as "stabilization".

Glass materials have advantages over crystals in many optical device applications. These advantages include a) flexibility of choosing glass composition over a wide range. b) A disordered ion environment that can broaden fluorescence bandwidth. c) Uniform (isotropic) optical properties over a wide range of composition. d) Ease of fabrication into complex shapes including fibers. e) Low fabrication cost, which leads itself to mass production, and f) Possibility of producing large active lasers with good optical quality.

The amorphous phase is less thermodynamically stable than the corresponding crystalline form and hence possess a high free energy. Hence the preparation of amorphous materials can be considered as the addition of excess of free energy to the crystalline polymorph. Among various methods of preparation of amorphous materials such as thermal evaporation, melt quenching, gel desication, sputtering, chemical vapor deposition etc., in the present work, the author has used melt quenching technique.

1.3.2 Melt quenching method

The oldest method of producing amorphous solid is to cool the melt at sufficiently faster rates. In this process, the amorphous solid is formed by the continuous hardening of the melt. Hence the formation of glass is strongly dependent on the cooling rate of the melt. The cooling rate should be high enough to bypass the crystal nucleation and growth. The crystallization phase is
more thermodynamically stable than the amorphous phase, it allowed to take place slowly. The crystal nucleation and growth kinetics were discussed by Turnbull [28]. The cooling rate required for glass formation depends on the constituents of the melt. For certain easy glass formers such as P₂O₅, the cooling rate 1Ks⁻¹ is sufficient to form glass while certain other materials such as metallic glasses, the required cooling rate is ~10⁵ Ks⁻¹.

In preparing glasses with easy glass formers, a batch of finely powdered chemicals (~5-10 g) taken in a porcelain crucible is placed in a furnace maintained at high temperatures. Homogeneous liquid is obtained by stirring the melt uniformly. After sometime, the crucible is taken out of the furnace and melt is poured on a plate having high thermal conductivity (e.g. Brass or copper) and pressed with another plate so that the heat will be removed quickly from the melt. A cooling rate of order of 10 Ks⁻¹ can be achieved by this method and is sufficient for the preparation of most of the glasses. In this work, the melt quenching is employed and the phosphate glasses of good quality are prepared, which are used for spectroscopic investigations.

1.3.3 Glass formation and its optical properties:

There are different types of glasses which include oxide, semiconducting, metallic and complex type of glasses. The most important glasses are formed by oxides such as SiO₂, GeO₂, B₂O₃, P₂O₅ etc., these are called glass formers. These oxides exist in glassy phase singly and constitute simple glass formers. Based on the network former, the formed glasses are called silicate, germinate, borate, phosphate etc., Conditional glass formers like
TeO₂, Al₂O₃, WO₃ etc., require the presence of one or more additional compounds to form a glass. Alkali oxides (M₂O, M=Li, Na, K, Rb and Cs), alkaline-earth oxides (MO, M=Mg, Ca, Ba and Sr) and other oxides like SeO₂, MoO₃, PbO, Bi₂O₃, V₂O₅, Gd₂O₃ modify the network when added to glass. These oxides are called network modifiers. The nature and structure of oxide glasses have remained as an important topic since the introduction of the “random network theory” by Zachariasen [29]. Several analytical methods are available which provide information about the local environment in the oxide glasses [30, 27]. The optical properties of glasses are based on the interaction electromagnetic waves with the material. The interest in glasses in optics is related to certain intrinsic characteristics such as isotropy, high degree of homogeneity, possibility to extend and continuous variation of their properties by variation in composition. There has been a great deal of interest shown on the preparation and characterization of a wide variety of inorganic glasses such as silicates, borates, phosphates and fluorides for their possible applications in the laser glass technology. For practical applications of glasses, the wavelength range studied is 240-2400 nm with visible range lying between 400-750 nm.

1.4 PHOSPHATE GLASSES

Phosphates are in general good glass formers. The basic building block in phosphate glasses is the phosphorous oxygen tetrahedron. The glass former component in phosphate glass is P₂O₅. It has a melting point of 560°C and boiling point of 605°C. Some of the properties of pure P₂O₅ glass are
extraordinary refractive index, $n_e=1.493$ ($\lambda=546.1$ nm) and thermal expansion coefficient $\alpha=13.7\times10^{-6}/^\circ C$. $P_2O_5$ generally contains water and this shifts the edge towards longer wavelengths. Phosphate glasses are technologically and biologically important materials as they generally have a higher thermal expansion coefficient, $\alpha$ and a lower glass transition temperature $T_g$ than silicate and borate glasses [31]. Many alkali, alkaline earth, transition metal and rare earth oxides can be added to modify these properties. There is also great interest in alkaline earth phosphate glasses due to their high transparency for ultra violet (UV) light. However, phosphate glasses have poor chemical durability which often limits their practical applications that generally overcome by adding certain oxides to the phosphate glasses such as $PbO$, $Al_2O_3$ and $Fe_2O_3$ [32].

The chemical durability and low processing temperature of iron phosphate glasses have led to their development as nuclear waste hosts [33]. Bio-compatible phosphate glass and glass-ceramics have medical applications and amorphous lithium phosphate and phosphorus oxynitride glasses have fast ion conductivity that make them useful as solid state electrolytes [34]. Glasses of NaCaPO$_4$–SiO$_2$ systems belong to a group of bioactive glasses are capable of forming bonds with tissue [35].

Optical properties of phosphate glasses show may favorable features for their use in optical devices because of their excellent transparency and good mechanical and thermal stability. They act as good hosts for large concentrations of dopant rare earth ions with good homogeneity. These glasses
find applications in ultrafast switches and laser-induced gratings as well. Phosphate glasses are attractive host materials for rare earth lasers and amplifiers because of their transmittence from ultraviolet to infrared spectral region, their fluorescence properties and their low non-linear refractive indices. Phosphate glasses have unique properties such as low softening temperatures and they have been studied widely for practical applications. Their low softening temperatures allows them to be used to develop Pb-free sealing materials. Now a days phosphate glasses are finding applications in many emerging technologies e.g vetrification of radioactive waste, photonics, fast ion conductors, glass to-metal seals and biomedical engineering [36-39]. Hence in the present work the author selected phosphate glasses and studied various spectroscopic properties of different rare earth ions in these glass matrices.

1.5 OPTICAL ABSORPTION AND EMISSION SPECTRA

When an electromagnetic radiation interacts with matter, a different phenomenon takes place. If the photons of radiation possess sufficient energies, they may be absorbed by the matter. Due to this vibrational changes or rotational changes may takes place. Atoms and molecules become excited by the absorption of radiation. Then they release energy quickly either by loosing energy in the form of heat or re-emitting electromagnetic radiation. In some cases, the portion of electromagnetic radiation which passes into matter, they may undergo scattering or reflection or may be re-emitted with same energy or different energies. In another case, when the molecules absorb radiation and become excited, they do not loose energy very quickly but with some delay.
This phenomenon is termed as fluorescence. If the re-emission takes place with some time delay, the phenomenon is termed as phosphorescence.

Due to interaction of electromagnetic radiation with matter, after interaction there may occur variation in intensity of electromagnetic radiation absorbed with frequency or wavelength. There are two ways in which the interactions are observed, in the first, the sample itself emits radiation and in the second, the sample absorbs radiation from a continuous source. The spectrum obtained in the former case is known as emission spectrum whereas in the latter case it is termed as absorption spectrum.

The absorption of electromagnetic radiation in the visible region can be classified into distinct classes of electronic transitions. Interionic transitions are those in which an electron leaves an orbital located largely on another ion or atom to occupy an orbital located largely on another ion or atom. Such transitions are referred to as charge transfer transitions and they are allowed transitions. Intra-ionic transitions are the second type which involves the excitation of the ligand electrons to higher level localized on the same ligand. In another type, the transitions occur between non-degenerate energy levels of ions with unfilled inner electron shells. These transitions are spin forbidden and the associated absorption bands are having lower intensities. The above two types of transitions are having higher intensities. The optical absorption spectra of triply ionized rare earth ions emanate from intraionic transitions. They exhibit very sharp absorption and fluorescent lines compared to transition metal ions, as the 4f electrons are shielded by the outermost electrons.
In the emission spectra, if the photons of visible or ultraviolet light are used for excitation, the emission of light is called photoluminescence. Photoluminescence is further classified fluorescence or phosphorescence depending on the time delay in re-emission. Fluorescent emission involves optical transitions between electronic states characteristic of the radiating substance. Fluorescent emissions occur in the spectral region where the crystal or glass is non-absorbing. The radiative de-excitation is affected by the symmetry of the surrounding binding forces in glass matrix. These forces are determined by the immediate neighbourhood of the fluorescing ion. Therefore, the potential fluorescent centres may find themselves in different environments within a given glass. Hence the structure of the glass matrix affects the position and intensity of the fluorescent lines. Therefore it is of interest to study fluorescence spectra of rare earth ions in different host glass matrices.

In the present work, optical absorption and emission properties of Pr$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Dy$^{3+}$ and Er$^{3+}$ ions in sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), sodium-potassium (Na-K), sodium-magnesium (Na-Mg) and sodium-calcium (Na-Ca) chlorophosphate glass matrices are studied in detail.
REFERENCES


