Chapter 1

General Introduction, Scope and Contents of Present Work

This chapter presents the general introduction, scope, contents and aim of the present work. The basic theory related to spectroscopic and electrical properties of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass system mixed with Fe and spectroscopic features of Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$ ion Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass systems is presented.
General introduction, Scope and Contents of present work

1.1 Introduction

Glass is an inorganic solid material that is usually clear or translucent with different colors. It is hard, brittle and stands up to the effects of wind, rain or Sun. In more precise terminology, glass is an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior. Any material inorganic, organic or metallic, formed by any technique, which exhibits glass transformation behavior, is a glass. The exceptionally rapid development of technological research in all fields of knowledge is accompanied by intense work by scientists and technologists on glass materials.

A study of the physical properties including spectroscopic, dielectric properties etc., of the glasses is of considerable importance because of the insight it gives into the fundamental process-taking place in them. In fact, the physical properties of the glasses are to a large extent controlled by the structure, composition, and the nature of the bonds of the glasses. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition, doping etc., is of considerable interest in the application point of view.

These materials have potential applications as laser materials, IR domes, optical fibers, modulators, memory devices, photonic devices for
communication, advanced computer applications and as semi conducting devices. Applications of these materials can also be found in nuclear waste management, solid electrolytes, electronic displays, biocompatible implants, dental posterior materials, high performance composites etc. In view of such vast and diversified applications, the investigation on the development and characterization of different glass materials has gained momentum in the recent years.

Materials prepared from a melt quenching are often referred to as glasses. Unlike crystals, these materials do not possess the long-range periodicity of the arrangement of the atoms. However the building block, \((\text{AO}_3)^{-3}\) triangle, where A stands for metal) or tetrahedra which is known as short-range order, is retained in the glass. These materials possess ionic as well as covalent bonding interaction.

When a liquid is cooled from high temperature, crystallization may take place at the melting point \(T_m\). If the crystallization takes place, there will be an abrupt change in the volume at \(T_m\) and if the glass formation takes place, there will be a gradual break in slope. The region over which the change of slope occurs is known as glass transition temperature \(T_g\). This process of changes in volume with temperature as a super cooled liquid is cooled through the glass transition temperature \(T_g\) is illustrated Fig. 1.1.
Fig. 1.1 Schematic illustration of the change in volume with temperature as super cooled liquid is cooled through the glass transition temperature $T_g$. 
The literature survey on the formation of glass theories indicates that it was the Goldschmidt who proposed the theory of glass formation based on the examination of various glass systems that glasses of the general formula $R_nO_m$ form most easily when the ratio of the ionic radius of the cation (R) to the oxygen (O) ion lies in the range 0.2 to 0.4. Since radius ratios in this range tend to produce cations surrounded by four oxygen ions in the form of tetrahedra, Goldschmidt believed that only melts containing tetrahedrally-coordinated cations form glasses during cooling. This contention was purely empirical, with no attempt to explain why tetrahedral coordination should be so favorable to glass formation. A few years later, Zachariasen extended the ideas of Goldschmidt and attempted to explain why certain coordination numbers might favor glass formation.

According to Zachariasen [1] there are only five oxide materials which form the glass by themselves viz., $P_2O_5$, $B_2O_3$, SiO$_2$, GeO$_2$ and As$_2$O$_3$; two more non-oxide compounds viz., As$_2$S$_3$ and BeF$_2$ are also added to this list recently [2]. Though, the glass materials do not possess the long-range periodicity but they retain short range order with AO$_3$ and AO$_4$ basic building blocks and follow certain rules proposed by Zachariasen. Basing on these rules, a continuous random network for a glass can be constructed (Fig.1.2).
Crystalline A$_2$O$_3$  Glassy A$_2$O$_3$

**Fig. 1.2** Two dimensional schematic of crystalline and non-crystalline (glass) materials.
As per these rules, the oxides of the type AO (CaO, BaO etc.), \(\text{A}_2\text{O}\) (\(\text{Li}_2\text{O}, \text{Na}_2\text{O}\) etc.) cannot form glasses on their own and the rules are satisfied only for oxides of the type\(\text{A}_2\text{O}_3, \text{AO}_2\) and \(\text{A}_2\text{O}_5\) and for non-oxide compounds \(\text{As}_2\text{S}_3\) and \(\text{BeF}_2\). The cations such as \(\text{A}^+\) (example \(\text{Li}^+, \text{Na}^+, \text{K}^+\) etc.,) \(\text{A}^{2+}\) (example \(\text{Ca}^{2+}, \text{Pb}^{2+}, \text{Cd}^{2+}\) etc.,) other than \(\text{A}^{3+}\) and \(\text{A}^{4+}\) are known as network modifiers. Alkali oxides/fluorides, alkali earth oxides/fluorides, \(\text{ZnO}, \text{PbO}, \text{CdO}\) etc., are some of the basic examples of modifiers in glass network. These modifiers break-up the continuous network by introducing non-bridging oxygens (Fig.1.3).

![Fig. 1.3 Structure of a general glass with modifier oxides](image)

Fig. 1.3 Structure of a general glass with modifier oxides
A third group of oxides known as intermediate class of oxides also exist which
by themselves not readily form glasses but do so when mixed with other
oxides; such oxides are known as intermediate glass formers. The examples of
this group include Sb$_2$O$_3$, Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$, TeO$_2$, WO$_3$, MoO$_3$, V$_2$O$_5$ etc.
The summary of the rules for glass formation proposed by Zachariasen is as
follows:

a) A high proportion of glass network forming cations (Si, B, P, Ge, As,
etc..) is surrounded by oxygen tetrahedra or triangles.
b) The polyhedra, share should not more than one corner with each other
c) The number of corners of polyhedra is less than 6
d) Anions (O$^{2-}$, S$^{2-}$, F$^-$) should not be linked with more than two cations
   and do not form additional bonds with any other cations.
e) At least three corners of polyhedra must connect with the neighboring
   polyhedra.
f) The network modifiers participate in the glass network with the co-
   ordination number generally greater than 6.
g) Intermediate glass formers (do not form the glass on their own) but
   either reinforce network or loosen the network with co-ordination
   number 6 to 8 and may participate in the network with coordination
   number 3 or 4 in the presence of modifiers.
Excellent reviews and articles on the topology of the glass by Doremus [3], Hlavac [4], Elliott [5], Rao [6], Shelby [7] and Ingram [8] give useful information.

Vitreous silica (SiO$_2$) serves as the prototype of a glass. Its structure is the simplest of all glass structures [9, 10]. The structural unit consists of slightly distorted SiO$_4$ tetrahedra with all bridging oxygens (BOs). Hence a strongly connected three-dimensional network is established. The disorder in the structure is caused mainly by variations in the bond angles $\beta$ and the torsion angles (Fig. 1.4) and only to a minor extent by the distortion of the tetrahedra.
Fig. 1.4 Structure elements in pure silica glass: a) SiO$_4$ tetrahedron (range I), b) definition of the bond angle $\beta$ (range II), c) definition of the torsion angle (range II), d) SiO$_2$ glass network showing different ring structures (range III).

The Fig. 1.4 also serves to introduce the concepts of short-range order (range I) extending to about 250 pm from an arbitrary Si or O atom (local coordination sphere). The range II order from 250 to 500 pm which is determined by the bond and torsion angles. The intermediate range (range III) order which is essentially determined by the shortest-path ring size of the glassy network and finally the long-range structure which describes density and phase composition fluctuations.
There is a wide glass forming range in the binary alkali silicate system (alkali ions M = Li, Na, K, Rb, Cs). The network modifiers (alkali ions) enter the glass as singly charged cations and occupy interstitial sites. Their charge is compensated by NBOs created by breaking bridges between adjacent SiO$_4$ tetrahedra. This reaction may be written as

\[
\begin{array}{c}
\text{--Si--O--Si--} + \text{M}_2\text{O} = 2 \text{--Si--O}^{(-)}\text{M}^{(+)}
\end{array}
\]

and is depicted in the Fig. 1.5. Every alkali ion creates one NBO. The creation of NBOs reduces the connectivity of the glass network, and hence the thermal expansion coefficient, the fluidity (inverse of viscosity), diffusion, electrical conduction and chemical corrosion all increase with increasing modifier content.

During the last few decades a large variety of inorganic glasses have been developed with an attempt to achieve suitable optical, electrical and mechanical characteristics. These characteristics are associated with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, IR transmission performance and their ability to accept rare earth and transition metal ions for their use in solid-state devices. Work along these lines was carried out on a number of glasses giving valuable information [11-20].
Investigations on dielectric properties of transition metal ion doped glasses help to throw some light on insulating/conducting character of the material. Investigations on the spectroscopic properties such as infrared spectra and electron spin resonance help to throw some light on the structural aspects of these glasses. Investigations on luminescence properties of different rare earth singly and co-doped glasses with different modifiers/intermediates give an idea to what extent the materials can be exploited as laser hosts and how
best the high luminescence efficiency can be achieved by varying the environment of rare earth ions in the glass network.

1.2 Scope of the present work

Discovery and study of different amorphous glass materials, whose properties can be tailored, constitute the base of development of the solid state technology. One of these materials is lithium yttrium silicate (LYS) glasses which are known due to their high transparency in the near infrared region (NIR) and for their relatively moderate density and refractive index. Lithium silicate glasses mixed with sesquioxides like Y$_2$O$_3$ were considered as excellent materials for integrated optics, photonic and biomedical applications because of their high thermo-physical, chemical and mechanical stability [21–25]. The presence of yttrium ions in silicate glasses is proved to diminish the phonon energies, to broaden the spectral range of transparency and to enhance the refractive indices [26–28]. Further, solid-state laser materials containing Y$_2$O$_3$ are proved to have the efficient operation both in continuous wave operation and in pulsed regimes [29, 30].

The transition metal ions are very interesting ions to probe in the glass networks because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent.
Three series of elements are formed by filling the 3d, 4d and 5d shells of electrons. Together these comprise the d-block elements. They are often called ‘transition elements’ because their position in the periodic table is between s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of the s-block, which typically form ionic compounds and the elements of p-block, which are largely covalent. In s- and p-blocks, electrons are added to the outer shell of the atom, whereas in d-block they are added to the penultimate shell. Typically transition elements have an incompletely filled d level.

In the d-block elements, the penultimate shell of electrons is expanding. Thus they have many physical and chemical properties in common and hence all the transition elements are metals. They are therefore good conductors of electricity and heat have a metallic luster and are hard, strong and ductile. They also form alloys with other metals.

One of the most striking features of the transition metal elements is that they usually exist in several different oxidation states (Table 1.1). Furthermore, the oxidation states change in units of one, e.g. Fe$^{3+}$ and Fe$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$.
Among the first five transition metal elements, the correlation between the electronic structures and minimum and maximum oxidation states in simple compounds is complete. In the highest oxidation states of these first five elements, all of the s and d electrons are used for bonding. Thus the properties depend only on size and valency; consequently show some similarities with elements of the main groups in similar oxidation states. Once the d⁵ configuration is exceeded, i.e., in the last five elements, the tendency for all the d electrons to participate in bonding decreases. Thus Fe has a maximum oxidation state of (+VI).

Table 1.1
Oxidation states of transition metal elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
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<tr>
<td>Electronic structure</td>
<td>d¹s²</td>
<td>d²s²</td>
<td>d³s²</td>
<td>d⁴s²</td>
<td>d⁵s²</td>
<td>d⁶s²</td>
<td>d⁷s²</td>
<td>d⁸s²</td>
<td>d⁹s²</td>
<td>d¹⁰s²</td>
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<tr>
<td>Oxidation numbers</td>
<td>7</td>
<td>6</td>
<td>6</td>
<td>5</td>
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</table>
The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (d electrons shield less efficiently than p electrons, which in turn shield less effectively than s electrons). Because of this poor screening by d electrons, the nuclear charge attracts all of the electrons more strongly; hence a contraction in size occurs.

Though, a quite good number of studies on dielectric properties of silicate glasses mixed with several transition metal ions are available [31–35], the studies especially at low temperatures on alkali yttrium silicate glass system containing small concentrations of iron ions are very rare. Such studies are helpful for considering these materials as electrolytes in low temperature region. In the present work, we have measured electrical properties (dielectric constant, loss, electric moduli, impedance spectra, ac conductivity and dc conductivity) of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses doped with different concentrations of Fe$_2$O$_3$ over a wide continuous frequency range (viz., 40 Hz to 2 MHz) and also dc conductivity in the low temperature region (100 K to 360 K). Using these data we have attempted to have a comprehensive understanding over the topology and valence states of iron ions and their influence on a.c. conduction phenomenon.
As mentioned earlier, the presence of Y$_2$O$_3$ in lithium silicate glass network is observed to decrease the phonon energies and to pave the way for high luminescence efficiency if the glasses are doped with rare earth ions [36]. The variation in the concentration of Y$_2$O$_3$ in lithium silicate glasses may cause the structural modifications and local field variations around Ln$^{3+}$ ion embedded in the glass network; such changes may have strong bearing on various luminescence transitions of lanthanide ions. In view of this, a part of the thesis is devoted to characterize the optical absorption and the fluorescence spectra of three important lanthanide ions, viz., Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$ firstly by singly doping and secondly Ce$^{3+}$-Yb$^{3+}$ and Tm$^{3+}$-Yb$^{3+}$ co doping in lithium silicate glasses mixed with different concentrations of Y$_2$O$_3$.

A preliminary description of the above mentioned properties along with their relation to some of the investigations on Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses is given below.

1.2.1 Physical parameters

Some physical parameters useful for characterization of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses doped with different transition metal ions and rare earth ions are estimated from the measured value of density ($d$) and the average molecular weight $\bar{M}$, using the following Eqs. [1.1-1.4]:
The transition metal ion concentration ($N_i$) could be obtained from:

(i) $N_i \ (10^{22} \text{ ions/cm}^3) = \frac{N_A M \ (\text{mol}%) d}{M}$ \hspace{1cm} (1.1)

From the $N_i$ values obtained, the polaron radius ($r_p$) and inter–ionic distance ($r_i$) of transition metal ions could be evaluated:

(ii) Inter–ionic distance $r_i (\text{Å}) = \left[ \frac{1}{N_i} \right]^{1/3}$ \hspace{1cm} (1.2)

(iii) Polaron radius $r_p (\text{Å}) = \frac{1}{2} \left[ \frac{\pi}{6N_i} \right]^{1/3}$ \hspace{1cm} (1.3)

The field strength ($F_i$) of transition metal ion in the glass matrix is described through the oxidation number ($z$) and the ionic radii ($r_i$) of the transition metal ions by:

(iv) Field strength $F_i (\text{cm}^{-2}) = \frac{z}{r_i^2}$ \hspace{1cm} (1.4)

\textbf{1.2.2 Dielectric properties}

When an insulating glass (a dielectric) like Li$_2$O–Y$_2$O$_3$–SiO$_2$ is placed in external electric field two types of polarizations – the electronic and the ionic – are expected to develop in the glass system. If the dielectric contains permanent dipoles, they experience a torque in an applied field that tends to orient them in the field direction. Consequently, an orientational (or dipolar)
polarization can arise. These three polarizations are due to charges locally bound in atoms, molecules or in the structures of solids. Additionally to all these, generally there exists charge carriers that can migrate for some distance through the dielectric. Such charge carriers during their motion may be trapped in the material or on interfaces (because they cannot be freely discharged or replaced at the electrodes); due to these causes, space charges and a microscopic field distortion result. Such a distortion appears as an increase in the capacitance of the sample and may be indistinguishable from a real rise of the dielectric constant. Thus a fourth polarization, called the space charge polarization comes into play. The total polarization is sum of these four polarizations (assuming that they act independently) [37].

When the dielectric is placed in alternating fields, these polarizations are set up and the dielectric constant is a consequence of them; also a temporal phase shift is found to occur between the applied field and the resulting polarization and a loss current component appears, giving rise to the dielectric loss of the sample [38].

The complex dielectric constant, according to Debye for a material having permanent dipoles characterized by single relaxation time \( \tau \), given by:

\[
\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + i \omega \tau}
\]  \hspace{1cm} (1.5)
where $\varepsilon_s$ is the static dielectric constant and $\varepsilon'$ is the dielectric constant value of the material corresponding to its electronic and atomic polarization. Separating this equation into its real and imaginary parts, one obtains:

$$
\varepsilon'(\omega) = \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2}
$$

(1.6)

and

$$
\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2 \tau^2}
$$

(1.7)

The dielectric loss of the material (generally expressed by $\tan \delta$) is given by the expression:

$$
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon'_s - \varepsilon'_\infty)\omega\tau}{\varepsilon'_s + \varepsilon'_\infty \omega^2 \tau^2}
$$

(1.8)

If the conductivity ($\sigma_{ac}$) of the sample is also taken into account, it can be shown that

$$
\tan \delta = \frac{4\pi\sigma}{\omega\varepsilon'} + \frac{(\varepsilon'_s - \varepsilon'_\infty)\omega\tau}{\varepsilon'_s + \varepsilon'_\infty \omega^2 \tau^2}
$$

(1.9)

By plotting log ($\tan \delta$) as a function of log ($\omega$), information regarding d.c conductivity as well as the behaviour of the dipoles present if any can be obtained.

**1.2.3 D.C. conductivity**

Glasses of various chemical compositions offer a considerable interest from the viewpoint of their electrical conduction. The resistivity of these glasses is known to vary from $10^{-2}$ to $10^{-10}$ $\Omega^{-1}m^{-1}$. In the glasses, the
conductivity is due to both ions and electrons and sometimes mixed conduction is also possible. From the conductivity data, information such as the density of charge carriers, the mobility of each carrier can be obtained.

The d.c. resistivity, which is independent of the geometry of the sample is defined as

$$\rho = \frac{RA}{d} (\Omega - m) \quad (1.10)$$

And the reciprocal of the resistivity known as conductivity is given as

$$\sigma = \frac{1}{\rho} (\Omega - m)^{-1} \quad (1.11)$$

When the direct current is passed through glass while it is being heated, reduces viscosity and increases conductance’s or decreases with increasing temperature, the variation can be approximated to the form

$$\sigma = \sigma_0 e^{-\frac{\sigma_d}{kT}} \quad (1.12)$$

where $W_{dc}$ is the activation energy, i.e. energy needed for the charge carriers to conduct. The conductivity of glasses depends on many factors; chemical composition, glass transition temperature, annealing temperature, the structure of the glass, applied electric field etc.

1.2.4 Optical absorption

Optical radiation interacts with materials in a variety of ways depending upon the material and the wavelength of the optical radiation-giving rise to the
optical spectra, which could be either emission or absorption spectra in solids, normally it is the absorption spectra, which is observed. This is nothing but the variation of the radiation intensity as a function of wavelength. Study of the absorption spectra of transition metal ions embedded in solids had been extensively used to obtain information about the local symmetry in which the ion sits, its valence state, its site preference and determination of the degree of covalency of the metal-ligand bond. When a transition metal ion is embedded in a glass it need not have a centre of symmetry. This leads to mixing of d- and p- orbitals of the ion and, therefore, an electronic transition involves some charge transfer from a d- to a p- orbital leading to weak absorption bands. If an ion is at the centre of symmetry, such a mixing does not occur but during the inevitable molecular vibrations make an ion spend part of the time away from the equilibrium position which enables mixing of d- and p-orbital and allow such transitions.

Most of the physical properties of the transition metal complexes are studied with the help of crystal field, ligand field and molecular orbital theories. The ligand field theory explains the optical levels by energy splitting of the states of the central ion in the field of the surrounding atoms. The theory of this splitting under the influence of fields produced by various symmetries was worked out by Bethe [39] and further developed by Schlapp and Penny [40], Van Vleck [41] and others. The principal symmetry of the transition
metal complexes is usually an octahedral one while in a few cases, tetrahedral, square planar and lower symmetries occur. In a complex the site symmetry of anions is always degraded from the extremely high spherical one to a lower symmetry. Two types of symmetries, known as octahedral (designated by $O_h$) and tetrahedral (designated by $T_d$) are important. The corresponding molecular structures having these symmetries are shown diagrammatically in Fig. 1.6.

![Diagram](image)

**Fig. 1.6** (a) Regular octahedron point group ($O_h$)  
(b) Regular Tetrahedron point group ($T_d$)

A free d-electron has five-fold degeneracy with all the five d-orbitals, namely $d_{xy}$, $d_{yz}$, $d_{zx}$, $d_{x^2-y^2}$ and $d_z^2$ possessing the same energy (Fig. 1.7 a). In a weak field approach, one tries to understand the effect of crystal fields on the free ion terms (Fig. 1.7 b).

In a weak field approach, one tries to understand the effect of crystal fields on the free ion terms. For d, the application of the group theory results in the
splitting of $^2\text{D}$ state into $e_g$ and $t_{2g}$ representations in octahedral crystal field. 

The crystal field potential acting on the ion is given by

$$V_{\text{oct}} = D(x^4 + y^4 + z^4 - (3/5)r^4)$$

(1.13)

**Fig. 1.7 (a)** Five d orbitals of $t_{2g}$ orbitals and $e_g$ orbitals.
Fig. 1.7 (b) Energy spectra of transition metal ions.
Where \( D = (Ze/4a^5) \). This potential has to be applied on the wave functions which transform as \( t_{2g} \) whereas \( d_{x^2-y^2} \) and \( d_{z^2} \) transform as \( e_g \), and

\[
\langle t_{2g}/V_{\text{oct}}/t_{2g} \rangle = -4D_q
\]

\[
\langle e_g/V_{\text{oct}}/e_g \rangle = 6D_q
\]

so that the separation to \( D_q \) between \( t_{2g} \) and \( e_g \) levels is a measure of the crystal field. The centre of gravity of the levels is preserved after application of the crystal field potential.

In \( T_d \) symmetry the nature of the splitting is the same but ordering of the levels is inverted as shown in Fig. 1.8. If the symmetry is lower than octahedral, say tetragonal or orthorhombic, then these levels will split into levels of lesser degeneracy. The above discussion is valid for single electron \( d \) orbitals. Similar procedure is adopted for multi electron system where the terms will be split into various irreducible representations.

In the case of strong octahedral crystal fields, the single electron \( t_{2g} \) and \( e_g \) functions become the basis. The various configurations of many electron systems are obtained by filling the \( t_{2g} \) shell first and then the \( e_g \) shell. Thus for example, the \( d^2 \) ion has \( t_{2g}^2 \), \( t_{2g}^1 \), \( e_g^1 \) and \( e_g^2 \) configurations with energies \(-8D_q, 2D_q \) and \( 12D_q\), respectively.
The electrostatic energy values for different states have been calculated by Tanabe and Sugano [42] and Griffith [43] and they have presented these energy values in the form of matrices. For convenient interpretation of the observed optical spectra, Tanabe and Sugano have drawn energy level diagrams between \( E/B \) and \( D_q/B \) for various \( d^n \) configurations popularly known as Tanabe-Sugano diagrams. Here, \( E \) corresponds to the energy level of a \( d^n \) system and \( B \) is the Racah inter-electronic repulsion parameter. These diagrams are mainly used in crystal field spectroscopy to evaluate the crystal field parameter \( D_q \) and parameters \( B \) and \( C \). From these diagrams, it is possible to obtain a quantitative measure of the ease of spin pairing. These diagrams also help in assigning the transitions correctly.
1.2.5 Electron spin resonance

Electron spin resonance (ESR) has been developed as an extremely sensitive and important spectroscopy technique, which is widely used to study systems having unpaired electrons. In condensed matter physics, ESR is used as a powerful technique to study the lowest energy levels, hence, the electronic state of the unpaired electrons of paramagnetic species in solids. This technique provides information on understanding of the symmetry of the surroundings of the paramagnetic ion and the nature of its bonding to the nearest diamagnetic neighbours. Following are a few examples of systems containing unpaired electrons.

1. Atoms having odd number of electrons, e.g., atomic hydrogen and lithium atom.
2. Molecules with odd number of electrons such as NO, and triplet state molecules like oxygen molecule.
3. Ions having partially filled inner electronic shells, e.g., iron, rare earth ions etc.
4. Defects produced in a solid by irradiation.
5. Free radicals, e.g., CH$_3$ and diphenyl-picrylhydrazyl.
6. Conduction electrons in metals, semiconductors and dilute alloys etc.

When a system having non zero angular momentum and magnetic moment is placed in an external magnetic field, each degenerate electronic
level splits into a number of levels depending upon the value of angular momentum (Zeeman splitting). The ESR technique, basically, is the observation of the transitions induced by an electromagnetic radiation of appropriate polarization and energy (frequency) between these Zeeman levels. The energy separation of these levels is typically of the order of 1 cm\(^{-1}\) (microwave frequency range) in atomic and molecular systems. Thus, a microwave spectrometer is normally required to observe ESR.

An electron possesses spin and associated with it is the spin angular momentum “S” in units of \(\hbar\). An electron in a system like an atom or ion will also have, in general, an angular momentum “L” in units of \(\hbar\). The total angular momentum “J” is then given by

\[
\vec{J} = \vec{L} + \vec{S}.
\]  

(1.16)

Associated with the total angular momentum \(J\), the magnetic dipole moment \(\mu\) given by

\[
\vec{\mu} = -g\beta \vec{J}
\]  

(1.17)

where

\[
g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}
\]  

(1.18)

which is known as the Lande splitting factor for free ion and
\[ \beta = \frac{e\hbar}{2mc} = 9.274096 \times 10^{-27} \text{erg/gauss} \] (1.19)

which is known as the Bohr magneton. When a magnetic dipole is placed in a uniform magnetic field \( H \), it precesses about the direction of \( H \) with the Larmor angular frequency \( \omega_L \), which is given by [44]

\[ \omega_L = \gamma B \] (1.20)

where \( \gamma = g \beta/\hbar \) is known as the gyromagnetic ratio. Thus, the resonance condition will be satisfied only when the frequency of the incident radiation is given by

\[ h\nu = g \beta B. \] (1.21)

When an electromagnetic radiation of a frequency \( \nu \) is applied to the sample, the resonant absorption of the energy by the unpaired electrons in the sample takes place whenever the resonance condition is satisfied.

The energy level of an electron with total angular momentum \( J \) has a degeneracy of \((2J + 1)\). The application of an external magnetic field removes this degeneracy and the energy level splits into \((2J + 1)\) levels. When angular momentum \( L \) is zero then \( J \) becomes equal to \( S \). The transitions between these levels are governed by the selection rules \( \Delta M_s = \pm 1 \), where \( M_s \) is the spin magnetic quantum number. An unpaired electron with \( S = \pm 1/2 \), when placed in a uniform magnetic field \( B \), will have two energy levels, as shown in Fig. 1.9, if \( g \) is constant.
The energies of these levels are \( E_{\pm1/2} = \pm (1/2) \ g \ \beta \ B \) \hspace{1cm} (1.22)

and the energy difference between the two levels for a given value of H is

\[ \Delta E = g \ \beta \ B \] \hspace{1cm} (1.23)

The above equation shows that the energy difference between the two levels increases linearly with B in the ESR technique. The magnetic dipole transitions between the levels are induced between the two levels in the presence of a uniform magnetic field B and an alternating magnetic field polarized
perpendicular to B by an incident radiation of frequency \( \nu \), if the quantum condition (1.18) and \( \Delta M_s = \pm 1 \) are satisfied. This will give rise to only one absorption line. When the orbital angular momentum is not zero then the degenerate energy level will split into \((2J+1)\) levels and the conditions for the transitions by absorption of energy is given by Eq. (1.18) and \( \Delta M_J = \pm 1 \). Such a situation will give rise to multiple absorption lines. The resonance condition (1.18) can be satisfied either by changing the magnetic field or the frequency of the radiation incident on the magnetic dipole. Practically, it is more convenient to vary the uniform magnetic field rather than the frequency of the incident radiation since the frequency variation of a microwave source is possible within a very small range only.

Thus, from an ESR spectrum recording one can get information about the resonance field at a fixed frequency of the electromagnetic radiation, hence, the ‘g’ value, the shape, amplitude and width of the absorption line. The ‘g’ value may be modified by the crystal field surrounding the free ion from the value of the “free ion value”. All of these parameters, when interpreted properly and in conjunction with the appropriate theoretical ideas, provide valuable information on the system studied. In addition, one may vary certain other external parameters like temperature, composition etc., which would possibly change ESR parameters leading to additional information on the
system under study. A vast discussion on ESR technique and its applications is available in a number of pioneering books written by many authors [45-49].

(a) General Spin–Hamiltonian

In ESR spectroscopy, the transitions can be observed between the energy levels of ground state. In order to get the eigen values and eigen functions, we need to solve the Schrödinger’s time-dependent equation applied on Hamiltonian operator. For a Hamiltonian consisting of more than one term, the easier way to solve the equation is by perturbation theory. Here the eigen value is found by taking the strongest interaction and then the next interaction will be treated as a perturbation of the levels obtained in the first case. This procedure is repeated until the weakest interaction is included. This method suffers with a draw back that various interactions should differ from one another by at least one or two orders of magnitude. Incidentally, this condition is satisfied in EPR spectroscopy.

The Hamiltonian, which describes various interactions of unpaired electrons with the static magnetic field and that of the surrounding environment, can be formalized in terms of spin operators. The coefficient of spin operators is called spin-Hamiltonian parameters.

The concept of Hamiltonian was originally developed by Pryce [50] and Abragam and Pryce [51] to interpret the observed resonance of ions in the first transition series. The concept was subsequently extended by Elliott and
Stevens [52] to interpret the paramagnetic behaviour observed for the rare earth ions. The terms in the general Hamiltonian for an ion in a crystalline environment can be written as [53].

\[ H = H_E + H_{LS} + H_{SI} + H_Q + H_V + H_{SH} + H_{iH} \]  \hspace{1cm} (1.24)

Where the symbols indicate the type of interaction to which Hamiltonian applies and have the following meaning.

i. \( H_E \) is a composite term expressing the total energy of electrons, the columbic attractions of the electrons and the nuclei and the repulsion among the electrons

\[ H_E = \sum_i \left( \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right) + \sum_{ij} \frac{e^2}{r_{ij}} \]  \hspace{1cm} (1.25)

Where \( P_i \) is the momentum of \( i^{th} \) electron, \( r_i \) is the distance of the electron from the nucleus, \( r_{ij} \) is the distance between the \( i^{th} \) electron and \( j^{th} \) electron and \( Ze \) is the nuclear charge.

These terms are summed over all the electrons and yield the unperturbed electronic levels before considering the interaction between spin and orbital angular momenta. The separations will be of the order \( 10^5 \text{ cm}^{-1} \).

ii. \( H_{LS} \) represents the spin-orbit coupling and may be written in the form.

\[ H_{LS} = \sum \lambda_{ij} \cdot l_i \cdot s \]  \hspace{1cm} (1.26)
where $l_i$ is the orbital angular momentum of the individual electron, ‘s’ is the spin angular momentum of the individual electron and $\lambda_{ij}$ is the spin–orbit coupling constant. This can be written in a simple form as

$$H_{ls} = \lambda \ L \cdot S$$  \hspace{1cm} (1.27)

where L and S are the total orbital angular momentum and the spin angular momentum of free ion respectively. The magnitude of this interaction lies between $10^2$ to $10^3$ cm$^{-1}$.

**iii.** $H_{SI}$ describes the magnetic interaction between each electron and the nucleus

$$H_{si} = \sum a_i \cdot J_i \cdot I_i$$  \hspace{1cm} (1.28)

Where $J_i$ is the total angular momentum of the $i^{th}$ electron and $I_i$ is the nuclear spin. The magnitude of this interaction will be of the order of $10^{-2}$ cm$^{-1}$.

**iv.** $H_Q$ represents the nuclear quadrupole interactions, which are even smaller than $H_{SI}$ (\(-10^{-4}\) cm$^{-1}$) and may be neglected. For nuclei with spin $I > \frac{1}{2}$, these interactions shift the hyperfine levels by a small amount.

$$H_Q = \sum I_i \cdot Q_i \cdot I_i$$  \hspace{1cm} (1.29)

**v.** $H_v$ represents the effect of crystal field, which can be written as

$$H_v = \sum e_i \ V(r_i)$$  \hspace{1cm} (1.30)

where $V(r_i)$ is the electrostatic potential at the ion with which each electron interacts.
In an external magnetic field $B$, the terms $H_{SH}$ and $H_{IH}$ must be added to represent the interaction of the angular momentum of electrons and nuclei respectively with the magnetic field.

$$H_{SH} = \beta \left( L + g_e S \right) \cdot B$$

$$H_{IH} = \hbar / 2 \pi \sum_i -\gamma_i \cdot I_i \cdot B$$

Where $\gamma_i$ is the gyrometric ratio of the $i^{th}$ nucleus and the latter terms (about $10^{-4}$ cm$^{-1}$) may be neglected expect in considering second order effects in the nuclear hyperfine interaction.

(b) Line shapes

The most commonly observed shape functions in EPR spectroscopy are Lorentzian and Gaussian, described by the functions given below.

$$I = I_0 \frac{1}{T_2^2 (B - B_i)^2 + 1}$$  \hspace{1cm} (1.33)

$$I = I_0 \exp [-b (B - B_i)^2 T_2^2]$$  \hspace{1cm} (1.34)

Where $I_0$ is the intensity of the absorption at its centre, $B_i$ is the resonant field at the line centre. The constants $T_2^2$ and $b$ are related to the half width at full maximum of each of the two types of curves.

The Lorentzian shape arises due to harmonically bound electron. If the harmonic motion of the electron is interrupted by some process, then the distribution of frequencies follows the Eq. [1.34] for an EPR spectrum, the interruption will be in the form of exchange. Since all the electrons are
equivalent, their interchanging between two molecules is quite possible if the molecules are close enough to each other. If this exchange is so rapid to affect the phase coherence of the spins, Lorentzian shape results.

On the other hand, Gaussian shape results from the paramagnetic ion separated from each other by molecules, which are having no unpaired electrons but possessing magnetic nuclei. Each unpaired electron will experience a local static magnetic field which will be dominated by how the nuclear spins are arranged in the near by host molecules. The observed EPR spectra will be a superposition of shapes from all the spins with their local fields. Since the local fields will be randomly distributed, the total line shape results in a Gaussian line shape according to Eq. (1.33). The characteristic Lorentzian and Gaussian line shape are shown in the Fig. 1.10.

(c) Line Width and Intensities

Generally the EPR signals are recorded as the first derivative of the absorption curve and hence the area under the EPR signal can be calculated by numerical double integration method. In this method, the EPR spectrum is divided in to ‘n’ small intervals having length’d’. The height $h_r$ of the EPR signal corresponding to the centre of $r^{th}$ interval is noted and the area under the curve can be calculated from the equation

$$ A = \frac{1}{2} d^2 \sum_{r=1}^{n} \left( n - 2r + 1 \right) h_r $$  \hspace{1cm} (1.35)
Fig. 1.10 The characteristic Lorentzian and Gaussian line shapes.

Fig. 1.11 shows the method of finding the area under the first derivative absorption curve by numerical double integration method. The accuracy of this method depends on the number of intervals and complexity of the spectrum. Using about 8 to 10 intervals per peak, the error in calculating the area will likely be within 2 to 3% in Gaussian curves. For Lorentzian curves, the error may be greater due to the presence of long tails.
For ESR signals, the line widths are measured from the maximum and minimum line positions at the first derivative curve. The ESR lines always have a finite width due to electrons interacting magnetically with the environment of the sample. Hence, from the line width and the rate of build up or decay of the line intensity, one can obtain information about spin environment.

The intensity of ESR signals depends on various factors (1) Concentration of the paramagnetic ion (2) the microwave frequency (3) the power of micro waves (4) the transition probability and (5) the temperature.

Fig. 1.11 The method of finding the area under the first derivative absorption curve by numerical double integration method.
1.2.6 Infrared spectra

Infrared absorption spectra of glasses and can provide significant and valuable information on the arrangement of atoms, nature of chemical bonding between them, the changes in the atomic configurations caused by increase or decrease of concentration of glass-forming systems and in general, facilitate the probing of the short-and intermediate range in glass networks.

In addition, the investigation of infrared spectra (IR) of these materials enables the assignment of characteristic frequencies to molecular groups in the glass and hence correlation of IR absorption bands with different units of vitreous structure. In the case of lithium yttrium silicate glasses, the basic glass contains SiO$_4$ and Y$^{3+}$ structural units in the silicate network and when a cation such as Li$^+$ is added, it resides interstitially. Such information about the changes in the basic glass structure that take place upon the addition of a cation can also be studied from the IR spectra.

The vibrations of structural units in a glass are independent [54-56], unlike the vibrations of complex ions in a crystalline matrix which are dependent of the vibrations of other groups. In probing the structural units and changes that take place in the network with composition of a ternary glass, infrared spectroscopy lends itself as an effective tool, because the technique is sensitive to short-range ordering and local interactions.
The assignment of the important IR bands observed in Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses of the present work is in general made by comparison of the data with the bands observed in literature, even though some bands attributions have their support from the theory. However, it is possible to provide quantitative justification from the theoretical calculation in the literature [57] for some of the vibrational frequencies assigned to silicate and other transitional ion groups. Such justification could have been offered even for the IR spectrum observed for Y$_2$O$_3$ provided the force constant corresponding to Y–O stretching is known.

When the characteristic group frequencies arise from the vibrations of pure stretching character or of pure bending nature the wavenumber- $\nu$ is to given by the equation

$$\nu = \frac{1}{2\pi c} \left( \frac{K}{\mu} \right)^{1/2}$$

(1.36)

where $c$ is the velocity of light, $\mu$ is the reduced mass of the diatomic or triatomic group, $K$ is the stretching or bending force constant. For certain diatomic and triatomic groups, the force constant was evaluated using various empirical formulae available in the literature [58, 59].

1.2.7 Rare earth ions and optical properties

As mentioned earlier Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses offer highly suitable environment for hosting rare earth ions and to give high luminescence output.
In view of this the later part of thesis is devoted to comprehensive spectroscopic studies on three interesting rare earth ions (viz., Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$) in Li$_2$O−Y$_2$O$_3$−SiO$_2$ glasses.

In the periodic Table, elements from lanthanum (Z=57) to lutetium (Z=71) are known as lanthanides. These are f-block elements with 4f$^n$ 5s$^2$ 5p$^6$ as the outermost electronic configuration of the trivalent states of these elements. As the 4f sub shell of these ions is filled there is shrinkage in the volume of these ions and this is known as lanthanide contraction. This contraction is due to imperfect shielding from the nuclear charge of one f electron followed by another electron. All the rare-earths exist in trivalent state and some occasionally in divalent and tetravalent states. These rare-earth ions are associated with the f−f and f−d transitions. In the present study three rare earth ions viz, Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$ are incorporated into the Li$_2$O−Y$_2$O$_3$−SiO$_2$ glasses.

The fact that the shielding of outermost electrons of these rare earth ions, makes them to serve as active centers in the solid state laser hosts like the present Li$_2$O−Y$_2$O$_3$−SiO$_2$ glasses. These ions exhibit sharp absorption and luminescence transitions. Since, these 4f ions are weakly perturbed by the surrounding ligands [60]. The spectral intensities have been carried out with the help of Judd-Ofelt theory [61]. The spectral intensities are often expressed
in terms of oscillator strength ($f$). Experimentally, this can be calculated from the following expression:

$$f_{\text{exp}} = 2.303 \left( \frac{mc^2}{N_A} \right) \pi e^2 \int \varepsilon(\nu) d\nu$$  \hspace{1cm} (1.37)

Where $N_A$ = Avagadro’s number, $c$ is the velocity of light and $\varepsilon(\nu) = \text{molar absorption coefficient}$, which is evaluated from Beer’s law:

$$\varepsilon(\nu) = \frac{1}{LC} \log\left( \frac{I_0}{I} \right)$$  \hspace{1cm} (1.38)

with $C$ being the rare earth ion concentration (mol %), $L$ the optical path length (thickness) and $\log(I_0/I)$ the optical density. After substituting the constants, Eq. (1.37) reduces to:

$$f_{\text{exp}} = 4.319 \times 10^{-9} \int \varepsilon(\nu) d\nu$$  \hspace{1cm} (1.39)

According to the conventional Judd-Ofelt (JO) theory [61, 62], the calculated OS of the electric dipole transition between two states can be expressed as follows:

$$f_{\text{cal}} = \frac{8 \pi^2 m c \nu \chi}{3h(2J + 1)} \sum_{\lambda = 2, 4, 6} \Omega_\lambda \left[ \left\langle f^N[S, L] J_J \right| \left| f^N[S', L'] J_J' \right\rangle \right]^2$$  \hspace{1cm} (1.40)

where $m$ is the electron mass, $c$ the speed of light, $h$ the Planck constant, \( \chi = \frac{(n^2 + 2)^2}{9n} \) the local field correction, $n$ is the refractive index, and the bra- and ket-vectors \( \left\langle f^N[S, L] J_J \right|, \left| f^N[S', L'] J_J' \right\rangle \) stand for the initial and final states, respectively, with all necessary sets of quantum numbers in square
brackets. \( \| U^4 \| \) are the reduced matrix elements of the unit tensor operators calculated between the states involved into a considered transition [63]. Admitting that the f-f transitions are mainly due to electric dipoles [64], the following selection rules are used:

\[
\Delta l = +1; \Delta S = 0, \Delta L < 2, \Delta J < 2
\]  

(1.41)

where \( l = 3 \) for the lanthanides. Using Judd–Ofelt parameters (\( \Omega_\lambda \)), the radiative properties of the fluorescence levels could be determined. The spontaneous emission probability for an electric dipole transition is obtained from [65];

\[
A_{jj'} = \frac{64\pi^3 e^2 \nu^3}{3h(2J + 1)} \frac{n(n^2 + 2)^2}{9} \sum_{\lambda=2,4,6} \Omega_\lambda \left( \left\langle f^N [\gamma, S, L] \right\rangle \right)^2 \| U^4 \| \left( \left\langle f^N [\gamma', S, L] \right\rangle \right)^2
\]  

(1.42)

where \( e \) is the charge of electron, and all other quantities are the same as in Eq. (1.40). The values of \( \| U^4 \|^2 \) taken from the literature for various absorption transitions of Tm\(^{3+} \) are presented in Tables 1.2 [63].
Table 1.2
Reduced matrix elements for different absorption levels of Tm$^{3+}$ ions

| Ground term $^3\text{H}_6$ | Transition $\Psi_J \rightarrow \Psi_{J'}$ | Energy (cm$^{-1}$) | $||U^2||^2$ | $||U^4||^2$ | $||U^6||^2$ |
|-----------------------------|---------------------------------|-----------------|------------|------------|------------|
| $^3\text{H}_6$              | $^3\text{H}_6$                  | 57              | 1.2509     | 0.6929     | 0.7767     |
| $^3\text{H}_4$              | $^3\text{H}_4$                  | 5942            | 0.5399     | 0.7261     | 0.2428     |
| $^3\text{H}_3$              | $^3\text{H}_3$                  | 8204            | 0.1075     | 0.2316     | 0.6388     |
| $^3\text{F}_4$              | $^3\text{F}_4$                  | 12637           | 0.2337     | 0.1067     | 0.589      |
| $^3\text{F}_3$              | $^3\text{F}_3$                  | 14630           | 0.0000     | 0.3166     | 0.8417     |
| $^3\text{F}_2$              | $^3\text{F}_2$                  | 15210           | 0.0000     | 0.0000     | 0.254      |
| $^1\text{G}_4$              | $^1\text{G}_4$                  | 21259           | 0.0497     | 0.0764     | 0.0134     |
| $^1\text{D}_2$              | $^1\text{D}_2$                  | 28142           | 0.0000     | 0.2806     | 0.0928     |
| $^1\text{I}_6$              | $^1\text{I}_6$                  | 35211           | 0.0098     | 0.0359     | 0.0124     |
| $^3\text{P}_0$              | $^3\text{P}_0$                  | 36578           | 0.0000     | 0.0000     | 0.0754     |
| $^3\text{P}_1$              | $^3\text{P}_1$                  | 37512           | 0.0000     | 0.0000     | 0.124      |
| $^3\text{P}_2$              | $^3\text{P}_2$                  | 38590           | 0.0000     | 0.2998     | 0.0254     |
| $^1\text{S}_0$              | $^1\text{S}_0$                  | 75873           | 0.0000     | 0.0000     | 0.0000     |
| $^3\text{P}_0$              | $^1\text{I}_6$                  | 1367            | 0.0000     | 0.0000     | 0.0267     |
| $^1\text{D}_2$              | $^1\text{D}_2$                  | 8436            | 0.024      | 0.0000     | 0.0000     |
| $^1\text{G}_4$              | $^1\text{G}_4$                  | 15319           | 0.0000     | 0.0397     | 0.0000     |
| $^3\text{F}_2$              | $^3\text{F}_2$                  | 21368           | 0.3609     | 0.0000     | 0.0000     |
| $^3\text{F}_3$              | $^3\text{F}_3$                  | 21948           | 0.0000     | 0.0000     | 0.0000     |
| $^3\text{F}_4$              | $^3\text{F}_4$                  | 23941           | 0.0000     | 0.0248     | 0.0000     |
| $^3\text{H}_3$              | $^3\text{H}_3$                  | 28374           | 0.0000     | 0.0000     | 0.0000     |
| $^3\text{H}_4$              | $^3\text{H}_4$                  | 30636           | 0.0000     | 0.2834     | 0.0000     |
| $^1\text{D}_2$              | $^3\text{H}_6$                  | 36521           | 0.0000     | 0.0000     | 0.0754     |
| $^1\text{G}_4$              | $^1\text{G}_4$                  | 6883            | 0.2263     | 0.1682     | 0.0000     |
| $^3\text{F}_2$              | $^3\text{F}_2$                  | 12932           | 0.0624     | 0.2966     | 0.0000     |
| $^3\text{F}_3$              | $^3\text{F}_3$                  | 13512           | 0.1471     | 0.0558     | 0.0000     |
| $^3\text{F}_4$              | $^3\text{F}_4$                  | 15505           | 0.1133     | 0.0155     | 0.2261     |
| $^3\text{H}_3$              | $^3\text{H}_3$                  | 19938           | 0.0000     | 0.0001     | 0.0262     |
| $^3\text{H}_4$              | $^3\text{H}_4$                  | 22200           | 0.5285     | 0.0885     | 0.0217     |
| $^3\text{H}_6$              | $^3\text{H}_6$                  | 28085           | 0.0000     | 0.2806     | 0.0928     |
| $^1\text{D}_2$              | $^3\text{F}_2$                  | 6049            | 0.0031     | 0.0659     | 0.0411     |
| $^3\text{F}_3$              | $^3\text{F}_3$                  | 6629            | 0.0094     | 0.0671     | 0.2891     |
| $^3\text{F}_4$              | $^3\text{F}_4$                  | 8622            | 0.1526     | 0.0034     | 0.3496     |
| $^3\text{H}_5$              | $^3\text{H}_5$                  | 13055           | 0.0708     | 0.0044     | 0.5243     |
| $^3\text{H}_4$              | $^3\text{H}_4$                  | 15317           | 0.0039     | 0.0204     | 0.074      |
| $^3\text{H}_6$              | $^3\text{H}_6$                  | 21202           | 0.0497     | 0.0764     | 0.0134     |
Summing up the $A_{jj'}$ quantities over all possible final states, one can get the radiative life time $\tau$ of an excited energy level as,

$$\tau = \frac{1}{\sum_{jj'} A_{jj'}} \quad (1.43)$$

Finally, the branching ratio $\beta_{jj'}$ is evaluated using

$$\beta_{jj'} = \frac{A_{jj'}}{\sum_{jj'} A_{jj'}} \quad (1.44)$$

This analysis on photoluminescence and optical absorption data, guide us to know to what extent the present glasses can be used as laser hosts.

### 1.3 Brief review of some recent studies on silicate glasses

Richet *et al.* [66] studied the composition dependence of glass formation and examined in a variety of silicate systems that include alkali and alkaline earth alumino-, titano-, ferro- and ferrisilicates. The close connection between glass formation and viscosity is reviewed in the light of the melt properties. Feller *et al.* [67] studied a series of lead silicate glasses, spanning the broadest reported range of lead contents (up to 83 mol% PbO), were prepared, and the spectroscopic observations viz., $^{29}$Si magic angle spinning nuclear magnetic resonance, time of flight mass spectroscopy, raman spectroscopy and fourier transform infrared spectroscopy were made. Kanunnikova *et al.* [68] studied the mechanisms of formation of the surface layer of lead silicate glasses during their interaction with hydrogen under heating by X-ray photoelectron
spectroscopy. De Sousa Meneses et al. [69] studied the polar lattices dynamics of seven binary lead silicate glasses by infrared spectroscopy. The analysis of the reflectivity spectra with a dielectric function model, based on a modified Gaussian profile, allows a quantitative evaluation of the presence of lead cations within different structural sites. Davis et al. [70] in their studies used the two-dimensional Magic Angle Flipping Nuclear Magnetic Resonance (2D MAF NMR) experiment on $^{29}\text{Si}$ nuclei to determine the distribution of $Q^{(n)}$ sites in two $^{29}\text{Si}$-enriched magnesium silicate glasses with compositions $2\text{MgO}\cdot\text{SiO}_2$ and $\text{MgO}\cdot\text{SiO}_2$. A significant degree of polymerization is observed in the $2\text{MgO}\cdot\text{SiO}_2$ glass, supporting previous studies using Raman and $^{29}\text{Si}$ NMR spectroscopy. Koide et al. [71] measured the viscosity of pre-annealed lead-silicate glass below the glass transition temperature using the fiber-bending method. Weigel et al. [72] in their studies, the short and medium range structure of a $\text{NaFeSi}_2\text{O}_6$ (NFS) glass has been investigated by high-resolution neutron diffraction with Fe isotopic substitution, combined with Empirical Potential Structure Refinement (EPSR) simulations.

A detailed analysis of the reflectance and transmittance spectra of a set of calcium silicate glasses was studied by De Sousa Meneses et al. [73] and shown that the calcium cations that exceeds the compositional threshold does not act as modifiers of the silicate network since they form Ca–O–Ca bonds in the glass structure. Obvious changes occurring at the threshold in the physical
or chemical properties can be understood in the light of the structural changes observed in the system. Duhan et al. [74] studied the frequency and temperature dependent conductivity measurements for heat treated titanium bismuth silicate glasses of composition $5\text{TiO}_2\cdot(95-x)\text{Bi}_2\text{O}_3\cdot x\text{SiO}_2$ ($x=30$, 40 and 50 mol%) by using impedance spectroscopy in the frequency range from 20 Hz to 1 MHz and temperature range from 210 to 360 °C. They reported that the absence of maxima in the dielectric permittivity ($\varepsilon'$) spectra indicates the non-ferroelectric behavior of the samples. The loss factor (tan $\delta$) is associated with the losses by conduction and it decreases with decrease in bismuth oxide. The effect of temperature on scaling of dielectric modulus indicates that the conductivity relaxation mechanism is temperature independent.

Villain et al. [75] studied the Cr$^{3+}$-containing alkali, alkaline earth and doped alkali–alkaline earth silicate glasses and have been investigated using Cr K-edge extended x-ray absorption fine structure (EXAFS) and optical absorption spectroscopy. They reported that, in doped alkali–alkaline earth glasses optical absorption parameters remain close to the values found in binary silicate glasses with the same alkali, which reveals a preference for alkalis in the surrounding of Cr$^{3+}$. Tordjeman et al. [76] measured the high temperature viscoelastic properties of two different silicate glass melts with a new high temperature rheometer between 700 and 900 °C. Their experiments demonstrate that the viscoelastic properties in the terminal zone, a low
frequency domain which has never been explored, are very sensitive to the chemical composition of the glass and to the thermal treatment applied during the preparation of the samples.

Ferraris et al. [77] have been studied the photosensitive, germanium-doped multicomponent silicate glasses with different amount of boron oxide and sodium oxide and investigated by means of electron paramagnetic resonance (EPR) and ultraviolet–visible (UV–Vis) spectroscopy in order to investigated by the structural changes occurring in the glasses under UV laser irradiation at 248 nm (KrF excimer UV laser). In their studies a clear correlation between the EPR signal and the UV–Vis absorption is observed only for the 240 nm band. It is also demonstrated that the sodium ions decrease the number of paramagnetic defects in these glasses and deeply change the germano-silicate glass structure. M. Waseem et al. [78] have been studied the synthesis and characterization of silica, iron hydroxide and their mixed oxides $M_1$ (0.25 M SiO$_2$:0.75 M Fe(OH)$_3$), $M_2$ (0.50 M SiO$_2$:0.50 M Fe(OH)$_3$), and $M_3$ (0.75 M SiO$_2$:0.25 M Fe(OH)$_3$) of various molar ratios. The surface charge and structure of the materials were investigated by X-ray diffraction (XRD), surface area analysis (SAA), thermal analysis (TG-DTG), scanning electron microscopy (SEM), electron dispersive X-ray (EDX) analysis, Fourier transform-infrared (FT-IR) spectroscopy and the point of zero charge (PZC)
was determined by the salt addition method and by measuring the $\zeta$-potential versus pH.

M. Gu et al. [79] synthesized the GeO$_2$-doped, Tb$_4$O$_7$-doped, and GeO$_2$ and Tb$_4$O$_7$ co-doped silicate glasses by high-temperature melting method, and their optical spectra were analyzed. It was found that the Ge$^{2+}$ centers could exist in the co-doped silicate glasses, and moreover, there was energy transfer from T$_1$ level of Ge$^{2+}$ centers to $^5$D$_3$ level of Tb$^{3+}$ ions under UV excitation. The way of the transfer was nonradiative energy resonance transfer, and its efficiency increased with increasing the concentration of GeO$_2$. Dogan et al. [80] prepared the Lead–alkali–silicate glass samples and were irradiated with 0.998–35.939 kGy dose levels using a $^{60}$Co gamma radioisotope source. The colour of the lead–alkali–silicate glass turned to brownish orange with absorbed dose. They can be used as radiation dosimeters, especially for medical dosimeters.

Sitarz et al. [81] studies concerns to silicate–phosphate glasses belonging to NaCaPO$_4$-SiO$_2$, NaCaPO$_4$-SiO$_2$-AlPO$_4$, KCaPO$_4$-SiO$_2$, KCaPO$_4$-SiO$_2$-AlPO$_4$, (Na, K)CaPO$_4$-SiO$_2$ and (Na, K)CaPO$_4$-SiO$_2$-AlPO$_4$ systems of systematically changed [SiO$_4$]$^{4-}$/[PO$_4$]$^{3-}$ proportion. It has been established that addition of aluminum dramatically changes the composition of the matrix and disperse phase. Significant influence of Al$^{3+}$ and modifying cation (Na$^+$ and K$^+$) on the glass structure has been established. The presence of aluminum
causes the elimination of $\text{P}═\text{O}$ bonds. This phenomenon can be observed easily when only one modifying cation is present. Lezzi et al. [82] determined the enthalpy of mixing of doped alkali ($\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$) silicate glasses containing various concentrations of alumina by using an ion-exchange equilibrium method. For glasses with a constant alkali concentration, the enthalpy of mixing was found to become less negative with alumina addition.

Nie et al. [83] prepared a series of glasses samples with the higher ZnO concentration from 30 mol% to 45 mol% and their optical absorption and photoluminescence properties were investigated. It is shown that the composition of glass strongly affects the position of the absorption edge and emission band where a fairly big red-shift was observed with increasing of ZnO concentration. It is most likely attributed to the reduced quantum confinement effect due to increased aggregation degree of ZnO in the glass matrix. Azooz et al. [84] prepared glasses by adding 0.1% of the oxides of any of 3d-transition metals (Ti $\rightarrow$ Cu) to a base binary high lead silicate glass PbO 60%-$\text{SiO}_2$ 40% (wt). UV–visible spectra of the undoped base glass and transition metals (TM)-doped glasses have been measured before and after successive gamma irradiation. The intensity and growth behaviour of the radiation-induced bands are seen to depend on the type of the 3d-transition metal. The host lead silicate glass reveals some shielding effect towards the successive gamma irradiation.
Jogad et al. [85] studied the synthesis of machinable quality magnesium aluminum silicate (MgO–Al₂O₃–SiO₂) for fabrication of insulators/spacers usable in high-voltage applications under high vacuum conditions has been carried out following two different routes, i.e., (a) sintering route and (b) glass route. The dielectric constant (\(\varepsilon'\)) and the dielectric loss (\(D=\tan\delta\)) have been measured in MAS glass–ceramics (GC) at different temperatures for frequencies up to 12 MHz. Parkinson et al. [86] studied the raman spectroscopy and has been used to measure the fraction of tetrahedral silicate units connected at three corners into the network (\(Q^3\)) in binary lithium silicate glasses and also in the more complex borosilicate glasses used for waste immobilization.

Ezz Eldin et al. [87] measured and studied the electrical conductivity and activation energy of some sodium-silicate glasses containing different substituted cations (Ca or Al) at different temperatures, with the view to throw some light on the mechanism of electrical conduction in relation to glass structure. The electrical conductivity of the studied glasses is correlated with the change in chemical composition which affects the change in chemical composition and the internal structure and hence the ability or the freedom of charge carriers to conduct electricity. Sharma et al. [88] studied the optical absorption and photoluminescence spectra of Er\(^{3+}\) doped soda lime silicate glasses of the composition (in wt.%) 68.94SiO₂–22.55Na₂O–1.91CaO–
4.96K₂O–0.85B₂O₃–0.29As₂O₃–xEr₂O₃ where x = 0.0, 0.2, 0.3 in the UV–VIS/NIR regions. Radiative properties of fluorescence band at ~1.54 µm suggest the suitability of this glass system for broadband amplifier in the third telecom window.

Rahimi et al. [89] prepared the high-temperature (1200–1350 °C) corrosion of fused-cast ZrO₂–Al₂O₃–SiO₂ (ZAS) refractory contacting lead silicate glass melt (LSG) containing 68.5 wt% PbO and was investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), differential scanning calorimetry (DSC), X-ray diffraction (XRD), thickness measurement and Archimedes density measurement. The elasticity and structure of lithium silicate glasses Li₂O–3SiO₂, Li₂O–2SiO₂, and Li₂O–2SiO₂–0.135ZrO₂ were studied by Lin et al. [90] at ambient conditions, using both Raman and Brillouin spectroscopies. The conventional nucleating agent, i.e., Zr⁴⁺ caused a more polymerized silicate network, amorphous phase separation before crystallization, and a significant drop in shear, Young's and bulk moduli, though Raman spectra have revealed that the partial substitution of Zr for Si occurred chiefly in the less polymerized Q² species.

Congshen et al. [91] have been successfully synthesized ZrO₂–TiO₂–SiO₂ systems by the sol-gel route. Detailed studies were carried out on the whole synthesis process including hydrolysis, polymerization, gelling and conversion from gel to glass. The information about the structural
variation of the gels during heat treatment has been obtained by means of X-ray diffraction, infrared spectroscopy and the results suggest the different function of $\text{Zr}^{4+}$ ions from $\text{Ti}^{4+}$ ions in this kind of glass, i.e. $\text{Ti}^{4+}$ ions act as network formers, while $\text{Zr}^{4+}$ ions act as network modifiers. Lin et al. [92] prepared the CaO–ZrO$_2$–TiO$_2$–Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glass, a potential glaze, solder and immobilizer of high-level radioactive wastes, with the additives of B$_2$O$_3$, SiO$_2$ and Al$_2$O$_3$ and at a firing temperature of $\approx 1200^\circ\text{C}$. When the glass-ceramics were subjected to prolonged annealing, the ZrO$_2$-derived phases always survived while borate, silicate and other phases appeared.

Banijamali et al. [93] studied the effects of different amounts of TiO$_2$, ZrO$_2$ and CaF$_2$ nucleating agents on sinterability, crystallization, mechanical properties and chemical resistance of glass–ceramics belonging to the CaO–Al$_2$O$_3$–SiO$_2$ systems and were investigated, using differential thermal analysis (DTA), X-ray diffractometry (XRD), scanning electron microscopy (SEM), mechanical and chemical resistance measurements. Addition of ZrO$_2$ and TiO$_2$ increases the firing temperature required for complete densification of specimens.

Mechnich et al. [94] reported that the presence of 3$^{rd}$ group transition metal oxides yttria and lanthana has a strong accelerating influence on the reaction bonding of mullite (RBM) from silicon and $\alpha$-alumina, even at temperatures below 1350 $^\circ\text{C}$. Sc$_2$O$_3$ does not form low viscous Sc–Al–Si–O
liquid phases which enhance reactivity. Instead, a direct formation of Sc-disilicate $\text{Sc}_2\text{Si}_2\text{O}_7$ is observed. At temperatures between 1350 and 1550 °C, a slightly enhanced mullite formation due to accelerated solid state diffusion, and the formation of a ternary Sc-rich aluminosilicate is evident. Kelsey et al. [95] examined aluminosilicate glasses containing a variety of network modifying to intermediate cations (Li, La, Sc, and Fe), quenched from melts at 1 atm to 8 GPa, to further investigate the role of cation field strength in Al coordination changes and densification. $^{27}\text{Al}$ Nuclear Magnetic Resonance Spectroscopy (NMR) reveals that the mean Al coordination increases with increasing pressure in the Li-containing glasses, which can be explained by a linear dependence of fractional change in Al coordination number on cation field strengths in similar K⁺, Na⁺, and Ca-containing aluminosilicate glasses ($K < Na < Li < Ca$). Inaba et al. [96] measured the heat capacities of vitreous silica, and some binary and ternary silicate, borate and phosphate glasses were measured in the temperature range from 300 to 840 K by ac calorimetry. The factor effecting heat capacity was investigated by use of the three-band theory which is composed of separate contributions from one- and three-dimensional Debye model and Einstein model. The heat capacity of oxide glass in the temperature range of measurements follows the one-dimensional Debye model and the compositional variations of heat capacity are evaluated in terms of the ionic packing ratio and the dissociation energy of oxide glass. Zou et al. [97]
we developed a glass in the Li₂O–MgO–Al₂O₃–Y₂O₃–TiO₂–SiO₂ system with elastic modulus value greater than 130 GPa and bending strength higher than 50 kg f/mm². This high modulus glass substrate is expected to provide a solution to the vibration problem of rapid rotation magnetic disk and allow higher track density per inch to be achieved for high performance hard-disk drives (HDDs).

Kadono et al. [98] we studied the influence of various additive ions incorporated into a soda-lime silicate glass on the optical density and stability of the color induced by X-ray irradiation. Additive ions were incorporated as metal oxides, namely TiO₂, V₂O₅, Fe₂O₃, ZnO, Ga₂O₃, GeO₂, ZrO₂, Nb₂O₃, MoO₃, Ag₂O, In₂O₃, SnO, SnO₂, CeO₂, Eu₂O₃, Ta₂O₅, WO₃ and Bi₂O₃. Among them, TiO₂, GeO₂, Nb₂O₃, MoO₃, Ag₂O, In₂O₃, Eu₂O₃, Ta₂O₅, WO₃ and Bi₂O₃ have a large effect on optical density. The optical densities in the visible region for glasses doped with these oxides were much stronger than for undoped soda-lime silicate glass.

The crystallization behavior of the ternary SiO₂–MgO–CaO system comprising different nucleating agents was studied by Alizadeh et al. [99] and investigated by using DTA and XRD techniques. It was found that the pairs of V₂O₅+MoO₃ and CaF₂+MoO₃ are more effective nucleants compared with that of Fe₂O₃+WO₃. The coarse fibrous morphology with directional surface crystallization was observed for some specimens containing Fe₂O₃+WO₃ as
nucleates. O'Neill et al. [100] studied the solubility of W in 18 melt compositions in the system CaO–MgO–Al₂O₃–SiO₂ in equilibrium with W metal and determined as a function of oxygen fugacity (fＯ₂) at 1400 °C and atmospheric pressure, using CO–CO₂ and H₂–CO₂ gas mixtures to control fＯ₂. The variation of W solubility with fＯ₂ establishes that W dissolves predominantly as W⁶⁺, with a possible contribution from W⁴⁺ only at the very lowest fＯ₂ accessible to the experimental method, in which regime experimental difficulties make the reliability of the results uncertain. X-ray absorption near edge structure (XANES) spectroscopy at the L3-edge of representative samples confirms the oxidation state of W as 6+, and suggests that W⁶⁺ occurs in tetrahedral coordination in silicate melts.

Muthupari et al. [101] prepared the glasses of the ternary MoO₃–SiO₂–P₂O₅ system by melt quenching in air and studied using Si K-edge X-ray absorption near-edge structure (XANES) spectroscopy to estimate proportion of sixfold co-ordinated silicon. Sixfold Si is detectable in most glasses prepared with molar (MoO₃ + SiO₂) > P₂O₅. In ternary MoO₃–SiO₂–P₂O₅ composition space, isopleths of proportion of sixfold Si trend parallel to the MoO₃–SiO₂ join and indicate that the ternary glass structure is comprised of separate molybdophosphate and silicophosphate entities. Mingsheng et al. [102] were carried out experiments on studying the effect of phase separation on nucleation and crystallization in the glass based on the system of CaO–
MgO–Al$_2$O$_3$–SiO$_2$–Na$_2$O. Three batches of 5, 8 and 10 wt% TiO$_2$ substitution were investigated by the techniques of DSC, XRD, FTIR and FESEM equipped with EDS. XRD and FTIR analysis indicated that the super cooled glasses were all amorphous, the heat treatment leading to nucleation would cause a disruption of silica network which followed phase separation. The phase separation followed the generation of crystal seeds Mg(Ti, Al)$_2$O$_6$. FESEM observation and EDS analysis revealed that the more TiO$_2$ content of glass, the more droplet separated phase and crystal seeds after nucleation heat treatment. The main crystal phase is clinopyroxene, Ca(Ti, Mg, Al)(Al, Si)O$_6$, of crystallized glass.

Berneschi et al. [103] prepared a set of soda-lime alumino silicate (SLAS) glasses doped with a fixed percentage of Er$^{3+}$ and different percentages of Yb$^{3+}$ ions was produced by conventional melting process. Planar and channel optical waveguides were produced in these glasses by ion-exchange, and their characterization is reported as well.

Gandhi et al. [104] studied the principal role of Al$_2$O$_3$ on the features of the photoluminescence spectra of Tm$^{3+}$ ion and upconversion phenomenon in Tm$^{3+}$ and Er$^{3+}$ co-doped CaF$_2$–Al$_2$O$_3$–P$_2$O$_5$–SiO$_2$ glass system. The reasons for enhancement in the intensity of various emission bands due to codoping have been identified and discussed with the help of rate equations for various emission transitions. Salavcova et al. [105] presented a new method of
fabrication of erbium containing thin optical layers that could be interesting for photonics active structures. A number of nuclear analytical methods (i.e., Rutherford backscattering spectroscopy—RBS, and neutron depth profiling—NDP), as well as scanning electron microscopy (SEM–EDAX) were used to confirm presence of erbium in the glass surface and to determine the chemical composition of the fabricated layers.

Murata et al. [106] have performed Extended X-ray absorption fine structure (EXAFS) measurements on Er\(^{3+}\) in silicate, borate, and phosphate glasses in order to investigate the local structure surrounding the Er\(^{3+}\). Er\(^{3+}\) ions coordinate to non-bridging oxygen ion sites, where alkali or alkaline earth ions terminate the network structure of silicate glasses. In borate glasses, the local structure surrounding Er\(^{3+}\) ions is altered by the structural change of the borate anion. Er\(^{3+}\) ions coordinate to non-bridging oxygen ion sites and BO\(_4\) structural units in the cases with and without the formation of non-bridging oxygen, respectively. The former is similar to the case in silicate glasses. Er\(^{3+}\) ions selectively coordinate to the P=O site regardless of the glass composition variation. Kholodkov et al. [107] studied the Er\(^{3+}\) luminescence in bulk silica samples with Ge, Al, K, N, F as additives. Doped glasses were synthesized by means of a reduced-pressure plasma chemical method in a microwave-induced discharge. Luminescence spectra and decay times at 0.98 and 1.53 \(\mu\)m
wavelengths were recorded from the samples with erbium concentration up to $4.2 \times 10^{20}$ cm$^{-3}$ pumped by Ar$^+$ laser at 514.5 nm wavelength.

L. Lin et al. [108] studied the fluorine losses during synthesis of Er$^{3+}$ doped transparent glasses in the SiO$_2$–PbO–PbF$_2$ system. The thermal and spectroscopic properties of the glasses and the corresponding glass ceramics were investigated through the analysis of the differential scanning calorimetry (DSC), absorption and upconversion luminescence spectra. The effects of fluorine contents show a decrease of the glass transition temperatures (Tg) of the glasses and an enhancement of upconversion intensity of the corresponding glass ceramics. Capek et al. [109], in order to design silicate glasses suitable as the host media for the Er$^{3+}$ ions they studied a role of divalent cations (magnesium, calcium and/or zinc) on the properties of the glasses. Fujita et al. [110] studied the persistent spectral hole-burning spectroscopy has been carried out for the $^3H_4 \rightarrow ^1D_2$ transition of Pr$^{3+}$ in (100–x)SiO$_2$·xNa$_2$O glasses with x=10, 20, 33.3 and 45 in order to examine the effect of Na$_2$O content on the homogeneous width and hole-burning efficiency. Both the homogeneous width and hole-burning efficiency increase with an increase in Na$_2$O content at 4.2 K. These observations are interpreted based on the coupling of the $^3H_4\rightarrow^1D_2$ transition of Pr$^{3+}$ to the low-energy excitation modes in sodium silicate glasses. Biswas et al. [111] prepared the Pr$^{3+}$-doped silica glasses by using acid hydrolyzed tetraethyl orthosilicate (TEOS). Thermal analysis and linear
shrinkage of the pure and doped gels indicate that the Pr\(^{3+}\) ion modifies the structure of the gel. The absorption peak positions of Pr\(^{3+}\) ions in silica change with Al co doping. Fluorescence of Pr-doped gels shows some interesting behavior and changed considerably with the addition of Al\(^{3+}\). Choi et al. [112] studied the Pr\(^{3+}\): \(^{1}D_2 \rightarrow ^{1}G_4\) transition in silica-based oxide glasses, which emits a strong luminescence centered at about 1530 nm with full-width at half-maximum wider than 200 nm, may reserve potential practicality owing to its fairly long fluorescence lifetime of \(\sim 270 \mu s\) corresponding to theoretical quantum efficiency approaching unity and its emission wavelengths matching up to the optical communication window of silica transmission fiber. Mekki et al. [113] have studied Sodium praseodymium silicate glasses of nominal composition 0.3Na\(_2\)O \(x\)Pr\(_2\)O\(_3\) \((0.7-x)\) SiO\(_2\), where 0\( \leq x \leq 0.10\) by magnetisation and X-ray photoelectron spectroscopy (XPS). It was found that most of the Pr ions are in Pr\(^{3+}\) valence state and only a small fraction (\(\leq 5\%\)) in the Pr\(^{4+}\) state. Analysis of the XPS line shape indicates only the presence of Pr\(^{3+}\) ions in these glasses.

1.4 Motivation and objective of the present work

The lithium yttrium silicate (LYS) glasses are well known due to their high transparency in the near infrared region and for their relatively moderate density and refractive index. In view of such features, these materials are expected to be potential candidates as gain media for ultra broadband optical
fiber amplifiers, tunable lasers and ultra short pulse lasers in telecommunication wavelength regions.

The transition metal ions in lithium yttrium silicate (LYS) glasses act as network modifying ions and produce structural modifications and local field variations in the glass network and will strongly influence electrical properties. Among various transition metal ions, iron ions exist in different valence states with different coordinations in glass matrices and have a strong bearing on electrical of lithium yttrium silicate glasses. In view of this a part of the thesis is devoted to explore the influence of Fe$_2$O$_3$ on electrical properties of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses and to analyze the results with the aid of the data on spectroscopic properties.

Study on the dielectric properties helps in assessing the insulating strength of these glasses and also give the information on the nature of a.c. conduction phenomenon. Detailed studies on spectroscopic properties (viz., optical absorption, luminescence, infrared and ESR spectra) of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses containing transition metal ions is expected to throw some light not only on structural aspects but also on the suitability of these materials in a variety of electrical and optical devices.

Further, Li$_2$O–SiO$_2$ glasses with higher refractive indices, high thermal stability, chemical durability and good optical transparency over a wide range of wavelengths are particularly useful in data busses which cover short
distances. Lithium silicate glasses containing Y$_2$O$_3$, offer suitable environment for hosting interesting rare earth ions (like Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$) and expected to give high luminescence output in view of the peculiar characteristics of these glasses possess. Further, we may expect the structural environment and local field strength around rare-earth ion when the concentration of Y$_2$O$_3$ is varied in the glass matrix. Such differences may have strong bearing on various luminescence transitions of rare earth ions.

In view of this, fluorescence characteristics of three interesting rare earth ions (Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$) that exhibit high luminescence efficiencies in visible and NIR regions in these glasses have also been investigated. Thus the clear objectives of the present study are to prepare, characterize and

- To have a comprehensive understanding over the influence of iron ions on electrical properties of Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses by investigating the dielectric properties coupled with the results on optical absorption, ESR and IR spectral studies.

- To study the fluorescence properties of Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$ ions, up-conversion fluorescence and the energy transfer from Ce$^{3+}$ to Yb$^{3+}$ and Yb$^{3+}$ to Tm$^{3+}$ in Li$_2$O–Y$_2$O$_3$–SiO$_2$ glass system with the gradual increase of Y$_2$O$_3$ content.

1.5 Contents of the present work

The compositions of the glasses used for the present study are:
The studies carried out are:

(vi) Dielectric properties viz., dielectric constant $\varepsilon'$, dielectric loss, $\tan \delta$ and ac conductivity, $\sigma_{ac}$ in the frequency range 40 Hz to 2 MHz and in the temperature range 100 K to 360 K and to evaluate the insulating character and the nature of the a.c conduction phenomenon.

(vii) optical absorption studies in the wavelength range 300–1800 nm, identification of various electronic transitions of iron ions and fluorescence studies of Ce$^{3+}$/Yb$^{3+}$ and Yb$^{3+}$/Tm$^{3+}$ ions doped Li$_2$O–Y$_2$O$_3$–SiO$_2$ glasses.

(viii) infrared spectral studies in the wavenumber range 400–1600 cm$^{-1}$ and the study of the effect of concentration of iron ions on the position and intensity of various vibrational bands;

(ix) electron spin resonance measurements and the identification of the positions and valence states of iron ions in the glass network.
References


