This chapter presents the general introduction, scope, contents and aim of the present work. In this chapter, the basic theory related to “microstructural, dielectric and spectroscopic properties of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass system crystallized with CuO and V$_2$O$_5$ & emission features of Nd$^{3+}$ and Ho$^{3+}$ ions in LiNb$_2$O$_5$/Ta$_2$O$_5$/La$_2$O$_3$–ZrO$_2$–SiO$_2$ glass systems”.
1.1 Introduction

a. Glasses

A study of the physical properties of the glasses is of considerable importance because of the insight it gives into the fundamental process-taking place in them. Such a study paved the way for the application of some of these glasses in technology. 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.

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 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 \( T_g \).
Why do certain materials readily form glasses on cooling a melt and why do only certain chemical compositions of materials have a greater glass-forming tendency? To the present day, the perfect knowledge on the answers of these questions is lacking. However, there are several factors which play a significant role in determining the ease of glass formation, for example, chemical or structural properties of the glass system, thermodynamic or free volume aspects of the materials, the average atomic coordination number etc.

The credit of first successful attempt to categorize the materials into glass formers and non-glass formers goes to Zachariasen [1]. He prepared the glasses with five oxide materials which are the only known glass formers by themselves: SiO$_2$, GeO$_2$, B$_2$O$_3$, As$_2$O$_3$ and P$_2$O$_5$. In addition, these oxides can also form glasses when doped up with other oxides (up to certain percentage), which were not by themselves glass formers. Basing on these glasses, Zachariasen proposed certain rules that an oxide should obey if it has to form a glass. The latest rules after Cooper [2] objections to original rules are

i) A high proportion of glass network forming cations is surrounded by oxygen tetrahedra or triangles.

ii) The oxygen polyhedra share only corners with each other.

iii) Some oxygen atoms are linked to only two cations, and do not form additional bonds with any other cations.
Basing on these rules, a continuous random network for a glass can be constructed as shown in Fig. 1.2.

![Crystalline $A_2O_3$ vs Glassy $A_2O_3$]

**Fig. 1.2** Two dimensional schematic of crystalline and non-crystalline (glass) materials.

As per these rules, the oxides of the type $AO$, $A_2O$ should not form glasses, and the rules are satisfied only for oxides of the type $A_2O_3$, $AO_2$ and $A_2O_5$. Oxides such as $A^+$ (example $Li^+$, $Na^+$, $K^+$ etc.,) $A^{2+}$ (example $Ca^{2+}$, $Pb^{2+}$, $Cd^{2+}$ etc.,) other than $A^{3+}$ and $A^{4+}$ are known as network modifiers. $Li_2O$, $Na_2O$, $K_2O$, $PbO$, $CaO$, $CdO$ 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). A third group of oxides known as intermediate class
of oxides also exist which by themselves not readily form glasses but do so when doped with other oxides; such oxides are known as intermediate glass formers. The examples of this group are TeO$_2$, WO$_3$, MoO$_3$, Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$, V$_2$O$_5$, etc. Excellent reviews and articles on the topology of the glass by, Elliott [3], Polk [4], Ingram [5], Rao [6] give useful information.

![Vitreous silica](image)

**Fig. 1.3** Structure of a general glass with modifier oxides. For the silica glass a fourth would be located above each cation.

Vitreous silica (SiO$_2$) serves as the prototype of a glass. Its structure is the simplest of all glass structures [7, 8]. 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.
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.

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).
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

$$\text{--Si--O--Si--} + M_2O \rightarrow 2 \text{--Si--O}^{(-)}M^{(+)}$$

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 electrical, mechanical and optical 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 more transition metal ions and rare earth ions for their use in solid-state ionic devices and lasing devices. Work along these lines was carried out on a number of glasses giving valuable information in the recent years [9-24]. Investigations on electrical properties such as dielectric properties of glasses help to have an idea over their insulating character. Investigations on the spectroscopic properties such as optical absorption, infrared, Raman spectra and electron spin resonance can be used as probes to throw some light on the structural aspects of the glasses. Luminescence studies on rare earth doped glasses will help to what extent the glasses can be used as laser materials.

b. Glass-ceramics

Glass-ceramic processing consists of melting together a mixture of compounds (usually oxides), to form a fluid of high viscosity, which when cooled at moderate rates gradually increase in viscosity until a vitreous (non-crystalline) solid (glass) is formed; as has been discussed above. The cooled glass body is then partially or completely crystallized (devitrified) by heat
treatment. A distinctive advantage of the glass-ceramic process is that crystallization may be accomplished at a temperature where the viscosity of the glass is still high, so that the glass body does not deform, but to a first approximation, passes from a solid glass shape to a solid crystal-line shape of the same dimensions. In these materials finely dispersed crystalline structures are stimulated to "grow" within the solidified glass matrix by a process of controlled devitrification.

There are two parts to the ceramming process; crystal nucleation and crystal growth. Each phase happens because the glass body is held at a specific temperature for a specific length of time.

Crystals have a tendency to develop in a mixture of glass when it is held at a specific temperature, called the crystal nucleation temperature. This means that when held at the crystal nucleation temperature, multiple seed crystals begin to grow throughout the glass body. The longer the glass is held at this temperature, the more seed crystals will form. Ideally, a glass ceramic will be strongest when there are a very large number of small crystals distributed evenly throughout its mass. Once a seed crystal forms, it will also begin growing larger at this temperature, but quite slowly. If the temperature of the glass body is held at the crystal nucleation temperature for a very long time, a very large number of crystals of widely varying size will form. The earliest to
the largest while the crystals that have recently just begun to grow will be the smallest.

In order to better control the esthetics of the finished product, the ideal glass ceramic will have crystals of a small, relatively uniform size. Any form of devitrification in a glass structure will produce one degree or another of opacity. Large crystals are more prone to making the glass opaque, while small crystals evenly scattered throughout the structure have less of an impact on the optical qualities of the finished product. Thus it is of benefit to hold the temperature at the point of maximum seeding for a finite length of time in order to allow numerous tiny seed crystals to nucleate, and then to stop the nucleation process and encourage the ones that have already formed to grow to suitable size.

The presence of native crystalline inclusions strengthens the glass and makes it more flexible, reducing the presence and severity of micro-cracks and acting as crack stoppers. Further glass-ceramics are stronger at high temperatures than glasses.

The advantages of the glass-ceramic process have been applied to a whole spectrum of compositions and applications. Their high mechanical strength and chemical inertness makes them suitable for prosthetic implants, for missile radomes. Yet, their low thermal expansion coefficients, makes these
materials suitable for gas tight electrical feed-throughs. These materials are very poor conductors of electricity.

Most glass-ceramic formulations contain small amounts of special additives, called nucleating agents that initiate the crystallization process and influence the particular mix of phases that develops. Platinum, V$_2$O$_5$, TiO$_2$, ZrO$_2$, NiO, CuO etc., from 0.01 to 10 percent are commonly used nucleating agents glass-ceramics.

Although the nucleation and growth process in glass ceramics has been extensively studied for the last 25 years since it was discovered, at present there is no general theory that explains how the nucleating agents operate. Most available models are specific to a given system, and they commonly postulate the formation of some sort of heterogeneity by the nucleating agent that catalyzes the subsequent crystallization [25].

Recently, the nucleation and crystal growth mechanism in a lithium zirconium silicate glass ceramic has been studied in detail [26]. Transmission electron microscopy, X-ray diffraction, and differential thermal analysis showed that at the nucleation temperature, SiO$_2$ reacts with the glass constituents to precipitate small Li$_2$Si$_2$O$_3$ crystallites throughout the molten glass. The size and degree of faceting of the Li$_2$Si$_2$O$_3$ crystallites was found to dependent on time at the nucleation temperature.
There are two parts to the ceramming process; crystal nucleation and crystal growth. Each phase happens because the glass body is held at a specific temperature for a specific length of time. Crystals have a tendency to develop in a mixture of glass when it is held at a specific temperature, called the crystal nucleation temperature. This means that when held at the crystal nucleation temperature, multiple seed crystals begin to grow throughout the glass body. The longer the glass is held at this temperature, the more seed crystals will form. Ideally, a glass ceramic will be strongest when there are a very large number of small crystals distributed evenly throughout its mass. Once a seed crystal forms, it will also begin growing larger at this temperature, but quite slowly. If the temperature of the glass body is held at the crystal nucleation temperature for a very long time, a very large number of crystals of widely varying size will form. The earliest to seed will be the largest while the crystals that have recently just begun to grow will be the smallest.

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temperature at the point of maximum seeding for a finite length of time in order to allow numerous tiny seed crystals to nucleate, and then to stop the nucleation process and encourage the ones that have already formed to grow to suitable size.

The characteristics of glass ceramic however depend on the kind and quantity of the crystal phase formed as well as on the residual glass composition. Hence, the selection of a suitable nucleating agent in the correct concentration and determination of the temperature and the time of nucleation and growth are important factors, in the formation of a glass-ceramic. The nucleating agents that are generally used for controlled crystallization processes, giving rise to enormous numbers of nucleation centres in the original glass are, gold, silver, platinum or the oxides of Ti, Cr, Mn, Ce, V, Ni and Zr or certain sulfides or fluorides. In the present study two interesting nucleating agents (viz., CuO and V$_2$O$_5$) are chosen for inducing crystallization in these glasses. Additionally, the transition metal ions are very interesting ions to probe in the glass ceramic 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.
1.2 Scope of the present work

Lithium silicate glasses and glass ceramics containing transition metal ions have been the subject of an increasing academic and technological interest. These glasses find a wide range of applications, such as glass fibers and optical lenses as electrodes for radioactive waste immobilization in hermetic sealing of metallic and ceramic materials and as glass planar optical waveguides fabricated by ion exchange. The addition of Nb$_2$O$_5$ bestows the base glass to possess electro chromic and electro-optical properties. The addition of ZrO$_2$ to niobium silicate glasses is expected to increase the electrical resistivity and chemical inertness.

The crystallization of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glasses with V$_2$O$_5$ is an added advantage for the simple reason that the presence of vanadium ions makes the material to exhibit semiconducting behavior with the electrical conductivity $>10^{-3}$ to $10^{-5}$ (ohm cm)$^{-1}$ due to electron hopping between V$^{4+}$ to V$^{5+}$ ions. Similarly the glasses or glass ceramics containing copper ions in different oxidation states are highly useful for consideration of the materials to use in electrical memory switching devices and as cathode material for an advanced lithium ion batteries.

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 where as 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.
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>
</tr>
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<tbody>
<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>
</tr>
<tr>
<td>Oxidation numbers</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>3</td>
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<td>3</td>
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</tr>
</tbody>
</table>

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).
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.

All these elements are found to be effective nucleating agents in glass materials. In many cases it has been found that the size of the crystal grains and the number of the crystallites and the orientation of granules in the residual glass is found to be strongly dependent on the valence state of these crystallizing agents. These transition metal ions in addition to acting as crystal stimulators, widen the range of technological applications (for example in the development of tunable solid state lasers, solar energy converters, fiber optic communication devices, in bio-technology as bio-active materials etc.) of the glass ceramic materials.

In view of these, the first part of the thesis is devoted to the studies on dielectric and spectroscopic properties of Li₂O–Nb₂O₅–ZrO₂–SiO₂ glasses crystallized with vanadium and copper ions. The studies on dielectric properties,
and the dependence of these properties on the composition, structure and on
various external factors such as humidity, radiation effect, mechanical action
etc., pave the way for estimating the insulating character of the glass ceramics.
Whereas the investigations on spectroscopic (viz., optical absorption, electron
spin resonance, infrared spectra and photoluminescence) give the information
on the environment and oxidation states of the transition metal ions (nucleating
agents) in the glass ceramic network and help to assess the suitability of these
materials for practical applications.

A preliminary description of the above mentioned properties along with
their relation to some of the investigations (similar to those of present work) on
Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramics is given below.

### 1.2.1 Physical parameters

Some physical parameters useful for characterization Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–
SiO$_2$ glasses crystallized with some transition metal oxides are estimated from
the measured value of density (d) and the average molecular weight $\bar{M}$, using
the following equations [27]:

The transition metal ion concentration ($N_i$) could be obtained from:

$$N_i \left(10^{22} \text{ions/cm}^3\right) = \frac{N_A M_{(\text{mol\%})} d}{\bar{M}}$$  \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:
The field strength \( F_i \) of transition metal ion in the glass matrix is described through the oxidation number \( z \) and the ionic radii \( r_p \) of the transition metal ions by:

\[
\text{(iv) Field strength } F_i \text{ (cm}^{-2}\text{)} = \frac{z}{r_p^2} 
\]

\[(1.4)\]

### 1.2.2 Dielectric properties

When an insulating glass ceramic (a dielectric) like Li\(_2\)O–Nb\(_2\)O\(_5\)–ZrO\(_2\)–SiO\(_2\) is placed in external electric field two types of polarizations – the electronic and the ionic – are expected to develop in the glass ceramic. 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) [28].

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 [29].

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

\[
\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i \omega \tau}
\]

(1.5)

where \( \varepsilon_s \) is the static dielectric constant and \( \varepsilon_\infty \) 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:
\begin{align*}
\varepsilon'(\omega) &= \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau^2} \quad \text{(1.6)}
\intertext{and}
\varepsilon''(\omega) &= \frac{(\varepsilon_s - \varepsilon_{\infty}) \omega \tau}{1 + \omega^2 \tau^2} \quad \text{(1.7)}
\end{align*}

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

\[\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon'_s - \varepsilon'_{\infty}) \omega \tau}{\varepsilon'_s + \varepsilon'_{\infty} \omega^2 \tau^2} \quad \text{(1.8)}\]

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

\[\tan \delta = \frac{4\pi \sigma}{\omega \varepsilon'} + \frac{(\varepsilon'_s - \varepsilon'_{\infty}) \omega \tau}{\varepsilon'_s + \varepsilon'_{\infty} \omega^2 \tau^2} \quad \text{(1.9)}\]

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 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-orbitals 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 [30] and further developed by Schlapp and Penny [31], Van Vleck [32] 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 \( \text{O}_h \)) and tetrahedral (designated by \( \text{T}_d \)) are important. The corresponding molecular structures having these symmetries are shown diagrammatically in Fig. 1.6.

![Diagrams of octahedral and tetrahedral symmetries](image)

**Fig. 1.6** (a) Regular octahedron point group (\( \text{O}_h \))
(b) Regular Tetrahedron point group (\( \text{T}_d \))

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, c, d).

![Diagrams of d orbitals](image)

**Fig. 1.7** (a) Five d orbitals of \( T_{2g} \) orbitals and \( e_g \)
Fig. 1.7 (b) Detailed spectral information on various transition metal (from $d^1$ to $d^4$) ions.
Fig. 1.7 (c) Detailed spectral information on various transition metal (from d$^6$ to d$^9$) ions.
Fig. 1.7 (d) Energy spectra of transition metal ions.

- $\text{Ti}^{3+}, \text{V}^{4+}$
- $\text{Ti}^{2+}, \text{V}^{3+}, \text{Cr}^{4+}$
- $\text{V}^{2+}, \text{Cr}^{3+}, \text{Mn}^{4+}$
- $\text{Cr}^{2+}, \text{Mn}^{3+}, \text{Fe}^{4+}$
- $\text{Mn}^{2+}, \text{Fe}^{3+}$
- $\text{Fe}^{2+}, \text{Co}^{3+}$
- $\text{Co}^{2+}, \text{Ni}^{3+}$
- $\text{Ni}^{2+}$
- $\text{Cu}^{2+}$
- $\text{Cu}^{+}, \text{Zn}^{2+}$
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

$$V_{\text{oct}} = D(x^4+y^4+z^4-(3/5)r^4)$$  \hspace{1cm} (1.10)

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

$$<t_{2g}/V_{\text{oct}}/t_{2g}> = -4D_q$$  \hspace{1cm} (1.11)

$$<e_g/V_{\text{oct}}/e_g> = 6D_q$$  \hspace{1cm} (1.12)

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 \( t_{2g}^2 \), \( t_{2g} \text{ } e_g \) and \( e_g^2 \) configurations with energies - 8Dq, 2Dq and 12Dq, respectively.

![Diagram showing relative energy of \( e_g \) and \( T_{2g} \) orbitals resulting from the splitting of d orbitals by octahedral environments.](image)

The electrostatic energy values for different states have been calculated by Tanabe and Sugano [33] and Griffith [34] 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 \( D_{eq}/B \) 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.

1.2.4  **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., CH₃ 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 ħ. An electron in a system like an atom or ion will also have, in general, an angular momentum “L” in units of ħ. The total angular momentum “J” is then given by

\[ \vec{J} = \vec{L} + \vec{S}. \]  \hspace{1cm} (1.13)

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

\[ \vec{\mu} = -g\beta \vec{J} \]  \hspace{1cm} (1.14)

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

(1.15)

which is known as the Lande splitting factor for free ion and

\[ \beta = \frac{e\hbar}{2mc} = 9.274096 \times 10^{-27} \text{erg/gauss} \]  

(1.16)

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 [35]

\[ \omega_L = \gamma B \]  

(1.17)

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

\[ h\nu = g \beta B. \]  

(1.18)

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

$$E_n = g \beta H$$

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

$$\Delta E = g \beta B$$  \hspace{1cm} (1.20)

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 eqn. (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 [36-40].
**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 drawback 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 [41] and Abragam and Pryce [42] to interpret the observed resonance of ions in the first transition series. The concept was subsequently extended by Elliott and Stevens [43] 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 [44].

\[
H = H_E + H_{LS} + H_{SI} + H_Q + H_V + H_{SH} + H_{IH}
\]  \hspace{1cm} (1.21)

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

\[
H_E = \sum_i \left[ \frac{P_i^2}{2m} - \frac{Z e^2}{r_i} \right] + \sum_{ij} \frac{e^2}{r_{ij}}
\]  \hspace{1cm} (1.22)

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 \( Z e \) 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} (1.23)
Where \( l \) 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

\[
H_{LS} = \lambda \ L \cdot S
\]  

(1.24)

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\(^{-1}\).

\textbf{iii.} \( H_{SI} \) describes the magnetic interaction between each electron and the nucleus

\[
H_{SI} = \sum a_i \cdot J_i \cdot I_i
\]  

(1.25)

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\(^{-1}\).

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

\[
H_Q = \sum I_i \cdot Q_i \cdot I_i
\]  

(1.26)

\textbf{v.} \( H_v \) represents the effect of crystal field, which can be written as

\[
H_v = \sum e_i \ V(r_i)
\]  

(1.27)

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.

\[
H_{SH} = \beta \left( \mathbf{L} + g_e \mathbf{S} \right) \cdot \mathbf{B} \tag{1.28}
\]

\[
H_{IH} = \hbar / 2\pi \sum_i -\gamma_i \cdot \mathbf{I}_i \cdot \mathbf{B} \tag{1.29}
\]

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

### Line shapes

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

\[
I = \frac{I_0}{T_2^2(B - B_r)^2 + 1} \tag{1.30}
\]

\[
I = I_0 \exp \left[ -b (B - B_r)^2 T_2^2 \right] \tag{1.31}
\]

Where \( I_0 \) is the intensity of the absorption at its centre, \( B_r \) is the resonant field at the line centre. The constants \( T_2^2 \) and \( b \) are related to the half width 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 follow the equation \([1.31]\) 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 equation (1.30). The characteristic Lorentzian and Gaussian line shape are shown in the Fig. 1.10.

**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 hr 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
Fig. 1.10 The characteristic Lorentzian and Gaussian line shapes.

\[
A = \frac{1}{2} d^2 \sum_{r=1}^{n} \left( n - 2r + 1 \right) h_r
\]  

(1.32)

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 microwave waves (4) the transition probability and (5) the temperature.

1.2.5 Infrared spectra

Infrared absorption spectra of glasses and glass ceramics 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 phosphate glasses, the basic glass contains PO_4 structural units in the phosphate network and when a cation such as Li^+ or Ca^{2+} 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 [45-47], 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_2O-CaF_2-P_2O_5 glasses and glass ceramics 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 [48] for some of the vibrational frequencies assigned to phosphate and other transitional ion groups. Such justification could have been offered even for the IR spectrum observed for TiO$_2$, Cr$_2$O$_3$, NiO provided the force constant corresponding to Ti-O, Cr-O and Ni-O stretchings are known.

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

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

where c is the velocity of light, m 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 [48, 49].

1.2.6 Raman spectra

Among variety of spectroscopic methods, Raman spectroscopy provides information about molecular symmetry of relatively small molecules and functional groups in large and complex molecules. Raman spectroscopy became
a useful technique with the introduction of lasers as a convenient monochromatic light source. It has become widely available only after the introduction of holographic filters to reject the light scattered without frequency change. In this method, the sample is illuminated with monochromatic light (a laser) and the light scattered by the material is analyzed by a conventional optical microscope coupled to a Raman spectrometer or a very sophisticated filter. Most of the scattered light has the same frequency as the laser, but a very tiny amount experiences a frequency shift, which is characteristic of the chemical bonds or molecules present in the material. This inelastic scattering of light is called the Raman effect. The analysis of the scattered frequencies (Raman spectroscopy) gives information on the material chemical composition, state, aggregation, and even factors like stress, orientation etc.,

The difference between incident photon and the scattered photon occurs as a result of the coupling between incident radiation and the quantized states of target material. The incident photon can lose (stokes) or gain (antistokes) the
energy by a vibrational quantum of the target molecule. The energy increase or decrease from the excitation is related to the vibrational energy spacing in the ground electronic state of the molecule and therefore the wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule. A schematic Raman spectrum may appear as:

In Raman spectrum, the Stokes and anti-Stokes lines are equally displaced from the Rayleigh line. This occurs because in either case one vibrational quantum of energy is gained or lost. Also, note that the anti-Stokes line is much less intense than the Stokes line. This occurs because only molecules that are vibrationally excited prior to irradiation can give rise to the anti-Stokes line. Hence, in Raman spectroscopy, only the more intense Stokes line is normally measured. For a vibrational motion to be IR active, the dipole moment of the molecule must change. For a transition to be Raman active there must be a change in polarizability of the molecule with the vibrational motion. Thus, Raman spectroscopy complements IR spectroscopy. For example, homonuclear diatomic molecules do not have an infrared absorption spectrum, because they have no dipole moment, but do have a Raman spectrum, because stretching and contraction of the bond changes the interactions between electrons and nuclei, thereby changing the molecular polarizability. For highly
symmetric polyatomic molecules possessing a center of inversion (such as benzene) it is observed that bands that are active in the IR spectrum are not active in the Raman spectrum (and vice-versa). In molecules with little or no symmetry, modes are likely to be active in both infrared and Raman spectroscopy [50].

In the present study the Raman spectroscopy has been used for identifying various structural units like PO$_4$, CrO$_4$, TiO$_4$ and TiO$_6$ in the glass matrix and the change in the concentration of these structural units with the varying concentration of the dopant ions. In certain cases, it could also be possible to identify whether the dopant ion occupy either tetrahedral or octahedral positions in the glass network.

1.2.7 Scanning electron microscopy (SEM) and Energy dispersive spectrum (EDS)

Scanning electron microscopy is used for inspecting topographies of specimens at very high magnifications using a piece of equipment called the scanning electron microscope.

SEM inspection is often used to identify whether the prepared material is amorphous or crystalline in nature. The formation of crystal grains, their size and some times their orientation and physical defects on the surface of the specimen can also be identified by the images of SEM. During SEM inspection, a beam of electrons is focused on a spot volume of the specimen,
resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal. To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analyzed, and translated into images of the topography being inspected. Finally, the image is recorded. The SEM pictures of an amorphous material and a glass ceramic material recorded are shown in Fig. 1.12

![Amorphous material](image1)
![Glass ceramic material](image2)

**Fig. 1.12** Scanning electron microscopic pictures.

A SEM may be equipped with an **EDX analysis** system to enable it to perform compositional analysis on specimens. EDX analysis is useful in identifying materials and contaminants, as well as estimating their relative
concentrations on the surface of the specimen. EDX Analysis stands for Energy Dispersive X-ray analysis. It is sometimes referred to also as EDS or EDAX analysis. The EDX analysis system works as an integrated feature of a SEM.

During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms’ own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

The output of an EDX analysis is an EDX spectrum (Fig. 1.13). The EDX spectrum is just a plot of how frequently an X-ray is received for each
energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks are unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.

![Example of an EDX Spectrum](image)

**Figure 1.13** Example of an EDX Spectrum.

### 1.2.8 Photoinduced second order susceptibility

When a dielectric medium like antimony borate glass ceramic is placed in an electric field and each constituent molecule acts as a dipole, with a dipole moment $P_i$. The dipole moment vector per unit volume $P$ is given by

$$P = \sum_i P_i = \chi E$$

(1.34)

The orienting effect of the external field on the molecular dipoles depends both on the properties of the medium and on the field strength. In the Eq. (1.34), $\chi$ is called polarizability or dielectric susceptibility of the medium. When the
material is subjected to high intensity laser radiation, the equn. does not hold good and has to be generalized to

\[
\vec{P}_i = \vec{P}_i^L + \vec{P}_i^{NL} = \alpha_{ij} E_j^{(\omega)} + \beta_{ijk} E_j^{(\omega)} E_k^{(\omega)} + \gamma_{ijkl} E_j^{(\omega)} E_k^{(\omega)} E_l^{(\omega)} + \ldots (1.35)
\]

where \( \alpha_{ij}, \beta_{ijk}, \gamma_{ijkl} \) etc., are microscopic susceptibilities in microscopic case (hyper polarizabilities) which are related with macroscopic susceptibility \( \chi_{ijk} \) by Eqs:

\[
\chi_{ij}^{(\omega)} = L_i^{(\omega)} L_j^{(\omega)} \alpha_{ij}; \quad \chi_{ijk}^{(\omega)} = L_i^{(\omega)} L_j^{(\omega)} L_k^{(\omega)} \beta_{ijk}; \quad \chi_{ijkl}^{(\omega)} = L_i^{(\omega)} L_j^{(\omega)} L_k^{(\omega)} L_l^{(\omega)} \gamma_{ijkl} (1.36)
\]

In these Eqs., \( \chi_{ij}, \chi_{ijk}, \chi_{ijkl} \) represent first, second and third order susceptibilities respectively and \( L_{ij,k} \) representing Lorenz field factors. \( \chi_{ijk} \) and \( \chi_{ijkl} \) define the degree of nonlinearity and are known as nonlinear susceptibilities.

A polarization, oscillating at frequency \( 2\omega \), radiates an electromagnetic wave of the same frequency. The wave thus produced has the same characteristics of directionality and the monochromacity as the incident wave and emitted in same direction. This phenomenon is known as second harmonic generation (SHG). This polarization is represented by

\[
P_i^{(2)} = \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k (1.37)
\]

For amorphous material as such this \( \chi_{ijk} \) is zero and it is non-zero when exposed to high intense laser beam. The development of Q-switched laser has made possible to generate third harmonic represented by
$p_i^{(3)} = \sum_{j,k} \chi_{ijkl}^{(3)} E_j E_k E_i \quad (1.38)$

even in amorphous materials by optical poling. But the energy conversion efficiency in such cases is very low. In case of the optical poling, the IR induced non-centro symmetry of the photo-induced vibrations begins to play a dominant role and it is necessary to consider a process of interaction of at least two photons and three phonons. Interactions of the one or two photons with one or two phonons do not give contribution to the non-zero polarization of the medium (Fig. 1.14)

Fig. 1.14 General scheme of the medium polarization for the pure electronic contribution

Fig. 1.15 Scheme Electronic + harmonic electron-phonon contribution
For getting birefringence, anharmonic electron-phonon interactions with at least three phonons as shown in Fig. (1.16) are required. Otherwise, we shall have harmonic electronic-phonon interactions which would not give non-centro symmetry as shown in Fig. (1.15).

![Figure 1.16](image)

**Fig. 1.16** Electronic + harmonic electron-phonon + anharmonic electron-phonon contribution

1.2.9 *Rare earth ions and optical properties*

As mentioned earlier Li$_2$O-ZrO$_2$-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 two interesting rare earth ions (viz., Nd$^{3+}$ and Ho$^{3+}$) in Li$_2$O-ZrO$_2$-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 $4f^n5s^25p^6$ as the outer most 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 two rare earth ions viz, Nd$^{3+}$ and Ho$^{3+}$ are incorporated into the Nb$_2$O$_5$, Ta$_2$O$_5$ and La$_2$O$_3$ doped lithium zirconium silicate 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–ZrO$_2$–SiO$_2$ glasses. These ions exhibit sharp absorption and luminescence transitions. Since, these 4f ions are weakly perturbed by the surrounding ligands [51]. The spectral intensities have been carried out with the help of Judd-Ofelt theory [52]. The spectral intensities are often expressed in terms of oscillator strength (f). Experimentally, this can be calculated from the following expression:

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

(1.35)
Where \( N_A = \) Avagadro’s number, \( c \) is the velocity of light and \( \varepsilon (\nu) = \) molar absorption coefficient, which is evaluated from Beer’s law:

\[
\varepsilon (\nu) = \frac{1}{LC} \log(I_0/I)
\] (1.36)

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. (1.35) reduces to:

\[
f_{\text{exp}} = 4.319 \times 10^{-9} \int \varepsilon (\nu) d\nu
\] (1.37)

According to the conventional Judd–Ofelt (JO) theory [52, 53], the calculated OS of the electric dipole transition between two states can be expressed as follows:

\[
f_{\text{cal}} = \frac{8\pi^2 mc \nu \chi}{3h(2J + 1)} \sum_{\kappa=2,4,6} \Omega_{\kappa} \left\langle f^N [\gamma, S, L] \right| \| U^2 \| f^N [\gamma', S', L'] \right\rangle^2
\] (1.38)

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 \( \left\langle f^N [\gamma, S, L] \right| \| f^N [\gamma', S', L'] \right\rangle \) stand for the initial and final states, respectively, with all necessary sets of quantum numbers in square brackets. \( \| U^2 \| \) are the reduced matrix elements of the unit tensor operators calculated between the states involved into a considered transition [54]. Admitting that the
f-f transitions are mainly due to electric dipoles [55], the following selection rules are used:

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

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 [56];

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

where $e$ is the charge of electron, and all other quantities are the same as in Eq. (1.38). The values of $||U||^2$ taken from the literature for various absorption transitions of Nd$^{3+}$ and Ho$^{3+}$ are presented in Tables 1.2 (a and b) [57, 58].

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,

$$\tau = \frac{1}{\sum_{jj'} A_{jj'}}$$

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

$$\beta_{jj'} = \frac{A_{jj'}}{\sum_{jj'} A_{jj'}}.$$  

This analysis on photoluminescence and optical absorption data, guide us to know to what extent the present glasses can be used as laser hosts.
Table 1.2 (a)
Reduced matrix elements for different absorption levels of Nd$^{3+}$ ions.
(Ground term: $^4I_{9/2}$)

<table>
<thead>
<tr>
<th>Transition ($\Psi_j \rightarrow \Psi_f$)</th>
<th>Energy (cm$^{-1}$)</th>
<th>$| U^2 | ^2$</th>
<th>$| U^4 | ^2$</th>
<th>$| U^6 | ^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4I_{11/2}$</td>
<td>2007</td>
<td>0.0194</td>
<td>0.1073</td>
<td>1.1652</td>
</tr>
<tr>
<td>$^4I_{13/2}$</td>
<td>4005</td>
<td>0.0001</td>
<td>0.0136</td>
<td>0.4557</td>
</tr>
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Table 1.2 (b)

Reduced matrix elements for different absorption levels of Ho\(^{3+}\) ions.

<table>
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<tr>
<th>Transition (\Psi_J \rightarrow \Psi_{J'})</th>
<th>Energy (cm(^{-1}))</th>
<th>(| U^2 |^2)</th>
<th>(| U^4 |^2)</th>
<th>(| U^6 |^2)</th>
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<tr>
<td>(5^I_7)</td>
<td>5130</td>
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<td>0.1344</td>
<td>1.5230</td>
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<td>(5^I_6)</td>
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1.3 Review of the previous work on silicate glasses and glass ceramics

The studies as such on silicate glass ceramics are relatively small in number when compared with silicate glasses. Brief review of some of the latest studies related to the present work on silicate glasses and glass ceramics is however, given below.

Richet et al. [59] studied the composition dependence of glass formation is 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 melt properties. Feller et al. [60] have investigated a series of lead silicate glasses, spanning the broadest reported range of lead contents (up to 83 mol% PbO). They have produced a quantitative distribution of PbO. Ananthanarayanan et al. [61] have made NMR studies on Lithium aluminum silicate (LAS) glasses. XRD and $^{29}$Si NMR showed that lithium metasilicate ($\text{Li}_2\text{SiO}_3$) is the first phase to form followed by cristobalite ($\text{SiO}_2$) and lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$). The $^{27}$Al MAS-NMR spectra indicate the presence of tetrahedrally coordinated Al species, which are only slightly perturbed by the crystallization. They have also studied MAS-NMR studies of lithium aluminum silicate (LAS) glasses and glass–ceramics having different Li$_2$O/Al$_2$O$_3$ ratio.
Meneses et al. [62] have investigated the structure and lattice dynamics of binary lead silicate glasses by infrared spectroscopy. They showed that the analysis of far infrared measurements combined with the knowledge of the UV edge optical response is very promising to characterize the local disorder around cations in glasses. Duhan et al. [63] have studied Dielectric properties and conductivity enhancement on heat treatment of bismuth silicate glasses containing TiO$_2$. In heat treated glass samples conductivity increased with the concentration of bismuth oxide. The absence of maxima in the dielectric permittivity ($\varepsilon'$) spectra indicated the non-ferroelectric behavior of the samples. The loss factor ($\tan \delta$) is associated with the losses by conduction and it decreased with decrease in bismuth oxide. The effect of temperature on scaling of dielectric modulus indicated that the conductivity relaxation mechanism is temperature independent. Stebbins et al. [64] have made Nuclear Magnetic Resonance (NMR) studies of $^{17}$O in silicate glasses. They have discussed two techniques viz., Dynamic Angle Spinning (DAS) and Triple Quantum Magic Angle Spinning (3QMAS), which have resolved and distinguished peaks for bridging oxygens linking Si, Al and B cations, as well as non-bridging oxygens.

Ferraris et al. [65] have investigated photosensitive, germanium-doped multicomponent silicate glasses with different amount of boron oxide and sodium oxide by means of EPR and UV–Vis spectroscopy. The main results
showed that the presence or the absence of boron and sodium and their amount play a role in the type and the number of defects, their time and thermal decay, under the same UV laser exposure conditions. The role of sodium and boron in order to increase the photosensitivity of germano-silicate glasses, for their interest in the field of ion-exchangeable glasses for photonic waveguides and Bragg-grating based devices was discussed. Wahab et al. [66] studied amorphous lithium aluminum silicate glass system (LAS) implanted with chromium ions. The ac and dc conductivities ($\sigma_{\text{ac}}$ and $\sigma_{\text{dc}}$) of as-prepared bulk samples are measured. The ac conductivity versus frequency plots were analyzed. A comparison between values of the index $s$ with those numerically calculated from different conduction models reveals that correlated barrier hopping (CBH) is a fairly good model to describe the dominant ac conduction mechanism. Sitarz [67] studied the influence of modifying cations on the structure and texture of silicate–phosphate glasses. The influence of Al$^{+3}$ and modifying cation (Na$^+$ and K$^+$) on the glass structure has been established.

Singh et al. [68] investigated electron spin resonance and magnetic studies on CaO-SiO$_2$-P$_2$O$_5$-Na$_2$O-Fe$_2$O$_3$ glasses. The ESR spectra of the glass exhibited the absorptions centered at $g \approx 2.1$ and $g \approx 4.3$. The variation of the intensity and linewidth of these absorption lines with composition has been interpreted in terms of variation in the concentration of the Fe$^{2+}$ and Fe$^{3+}$ in the
glass and the interaction between the iron ions. The magnetic susceptibility data were used to obtain information on the relative concentration and interaction between the iron ions in the glass. Xiao et al. [69] investigated thermal properties of $P_2O_5$ doped $Li_2O-Al_2O_3-SiO_2$ glass-ceramics. They have undertaken DSC to analyze the change of characteristic temperature $T_g$, $T_c$ and $T_p$. Thermal expansion coefficient (TEC) of matrix glass and glass-ceramic containing different $P_2O_5$ were measured. The results showed that introducing $P_2O_5$ effectively decreased the melting temperature and viscosity of LAS glasses. XRD analysis indicated that $\beta$-spodumene is the main crystalline phase in the $P_2O_5$ doped LAS glass-ceramics. Marzouk [70] measured longitudinal and shear ultrasonic wave velocities for different compositions of $SiO_2-Na_2O-CaO-P_2O_5$ glasses at room temperature (305 K) using a pulse-echo method at a frequency of 4 MHz. He has obtained elastic moduli, Poisson's ratio, microhardness, Debye temperature and other ultrasonic parameters from experimental data and analyzed using bond compression theory. He has also studied the structural changes after doping with $CeO_2$ were investigated by FTIR spectroscopy. Wang et al. [71] prepared lithium disilicate glass-ceramics derived from the $SiO_2-Li_2O-K_2O-Al_2O_3-ZrO_2-P_2O_5$ system with different $P_2O_5$ content for dental restorative application. They have measured flexural strength of final glass-ceramics and translucent characteristics expressed in term of
contrast ratio (CR). The interrelations between P$_2$O$_5$ content, microstructure and properties were discussed. Suárez et al. [72] studied glass and glass-ceramics of the Na$_2$O-CaO-K$_2$O-MgO·SiO$_2$·P$_2$O$_5$ system, modified with B$_2$O$_3$, Al$_2$O$_3$ or B$_2$O$_3$/Al$_2$O$_3$ up to 0.66. They have tested both, bioactivity using simulated body fluid (SBF) immersion and mineral nodule formation using calvaria derived osteoblasts. The composition containing B$_2$O$_3$/Al$_2$O$_3$ = 0.66 showed the best biocompatibility with hydroxyapatite nodule formation on its surface, especially on the glass-ceramics. Kumar Singh and Srinivasan [73] investigated EPR and magnetic susceptibility studies of iron ions in ZnO-Fe$_2$O$_3$-SiO$_2$-CaO-P$_2$O$_5$-Na$_2$O glasses. EPR and magnetic susceptibility data of the glasses revealed that both Fe$^{2+}$ and Fe$^{3+}$ ions are present in the glasses, with their relative concentration being dependent on the glass composition. Mozafari et al. [74] investigated the physico-chemical reactivity of a mesoporous bioactive SiO$_2$-CaO-P$_2$O$_5$ glass in simulated body fluid. They have used inductively coupled plasma-atomic emission spectrometry (ICP-AES), SEM, EDS, XRD and FTIR to characterize the MpBaG surfaces and the SBF compositional changes. From these studies, they have demonstrated that the synthesized MpBaG is a non-toxic and biocompatible material for ongoing osteogenic studies in segmental defects in the goat model in vivo.
1.4 Motivation and objective of the present work

The crystalline glass materials contain a fine-grained uniform structure, consisting of small crystals of irregular and distorted form, often aggregated into spherulites, with residual glass inter-layers, cementing the crystalline glass-ceramic concretion. These materials possess very small and strain free intertwined crystals that hinder the crack growth. As a result, glass ceramics are expected to possess outstanding properties like high mechanical, electrical and thermal properties, high chemical durability and very low coefficient of thermal expansion. 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. Glass-ceramic materials are better candidates over the glass materials for such application since the dominance of non-radiative losses over the relaxations of excited states of transition metal ions is low in these materials.

The characteristics of glass ceramic however depend on the kind and quantity of the crystal phase formed as well as on the residual glass composition. Hence, the selection of a suitable nucleating agent in the correct concentration and determination of the temperature and the time of nucleation and growth are important factors, in the formation of a glass-ceramic. Among various nucleating agents, the vanadium and copper ions are considered as
effective and useful nucleating agents owing to the fact that these ions may exist in different valence states with different environments simultaneously in the final glass-ceramic.

There are a considerable number of recent reports where transition metal ions have been used as nucleating agents and observed to induce phase separation in other glass systems like SiO$_2$, P$_2$O$_5$, GeO$_2$. Lithium zirconium silicate glasses, in particular, are well recognized due to their far infrared transmission and owing to their other technological applications like solid electrolytes in electrochemical devices. The crystallization of lithium zirconium silicate glasses with CuO and V$_2$O$_5$ as stimulators may improve the physical properties and widen the range of the applications. Addition of Nb$_2$O$_5$ further, in to lithium zirconium silicate glass matrices is predicted to be an effective mineralizer.

Though considerable number of studies is available on lithium zirconium silicate glass ceramics with the some transition metal oxides as nucleating agents, still there is a lot of scope to investigate on electrical and spectroscopic properties of these glass ceramics. Study on the dielectric properties including the dielectric breakdown strength 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, infrared, Raman and ESR spectra) and non linear optical properties of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramics containing transition metal ions are 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. The first part of the thesis is devoted to these studies.

Further, Li$_2$O–ZrO$_2$–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. When these glasses are doped with Nb$_2$O$_5$, La$_2$O$_3$ and Ta$_2$O$_5$ offer suitable environment for hosting interesting rare earth ions (like Nd$^{3+}$ and Ho$^{3+}$) 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 as different for Nb$_2$O$_5$, La$_2$O$_3$ and Ta$_2$O$_5$ doped Li$_2$O–ZrO$_2$–SiO$_2$ glasses. Such differences may have strong bearing on various luminescence transitions of rare earth ions. With this view the later part of the thesis is devoted to investigate the luminescence efficiency of two rare earth ions viz., Nd$^{3+}$ and Ho$^{3+}$ in Li$_2$O–ZrO$_2$–SiO$_2$ glasses doped with Nb$_2$O$_5$, La$_2$O$_3$ and Ta$_2$O$_5$ and to identify the better glass host for giving high efficient luminescence output.
Thus the clear objectives of the present study are to prepare Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glasses and

- To crystallize them with two different nucleating agents viz., CuO and V$_2$O$_5$.
- To characterize them by a variety of techniques those include XRD, SEM, EDS and DTA.
- To have a comprehensive understanding over the influence of Cu ions on structural aspects of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramics by investigating optical absorption, ESR, Raman, IR, photoluminescence, photo induced birefringence and dielectric properties.
- To investigate the role of vanadyl ions on the crystallization and structure of Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramics from a systematic study of various dielectric properties coupled with spectroscopic studies.
- To investigate the luminescence efficiencies of two rare earth ions (viz., Nd$^{3+}$ and Ho$^{3+}$) in Li$_2$O–ZrO$_2$–SiO$_2$ glasses doped with Nb$_2$O$_5$, Ta$_2$O$_5$ and La$_2$O$_3$ and to examine the possible uses of these glasses laser hosts.

1.5 Contents of the present work
The chemical compositions of the samples used for the present study are:

4. \((30-x) \text{Li}_2\text{O-10 Nb}_2\text{O}_5-5\text{ZrO}_2-55 \text{Si}_2\text{O}_2: x \text{CuO (0} \leq x \leq 0.3)\)

5. \((30-x) \text{Li}_2\text{O-10 Nb}_2\text{O}_5-5\text{ZrO}_2-55 \text{Si}_2\text{O}_2: x \text{V}_2\text{O}_5 (0 \leq x \leq 1.0)\)

6. \(30 \text{Li}_2\text{O-9 Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5/\text{La}_2\text{O}_5-5 \text{ZrO}_2-55 \text{SiO}_2: 1 \text{Nd}_2\text{O}_3/\text{Ho}_2\text{O}_3\)

The studies undertaken and their purpose are:

(i) differential thermal analysis, XRD, scanning electron microscopic and EDS studies to examine the nature of the crystallites formed and to identify the elements in the final product.

(ii) dielectric properties viz., dielectric constant \(\varepsilon_1\), dielectric loss tan \(\delta\) and ac conductivity \(\sigma_{ac}\) in the frequency range \(10^2-10^5\) Hz and in the temperature range 30-250 \(^\circ\)C and to assess the insulating character and the nature of the a.c conduction phenomenon.

(iii) infrared spectral studies in the wave number range 400-4000 cm\(^{-1}\) and Raman spectra in the region 100 to 2000 cm\(^{-1}\) at room temperature using argon laser 514 nm as the excitation source to study the effect of concentration of nucleating agents on the position and intensity of various vibrational bands.

(iv) electron spin resonance measurements at liquid nitrogen temperature and at room temperature and optical absorption
studies in the wavelength range 250-1000 nm to identify the valence states of the nucleating agents.

(v) Photo induced birefringence studies of copper ions doped Li$_2$O–Nb$_2$O$_5$–ZrO$_2$–SiO$_2$ glass ceramics

(vi) optical absorption and photoluminescence studies of Nd$^{3+}$ and Ho$^{3+}$ ions doped Li$_2$O–ZrO$_2$–SiO$_2$ glasses doped with Nb$_2$O$_5$, Ta$_2$O$_5$ and La$_2$O$_3$. 

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References


