This chapter presents the general introduction, scope, contents and aim of the present work. In this chapter, the basic theory related to dielectric and spectroscopic properties of Li$_2$O–PbO–P$_2$O$_5$ glasses doped with tin oxide and rare earth ions are presented systematically.
**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. These materials have potential applications as laser materials, IR domes, optical fibers, modulators, memory devices, photonic devices for communication and advanced computer applications and as semi conducting devices. Applications of these materials can also be found in nuclear waste management, optical fibers, 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.

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 ionic radius ratio of the cation, $R$, to the oxygen 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., SiO$_2$, GeO$_2$, B$_2$O$_3$, As$_2$O$_3$ and P$_2$O$_5$; 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.

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 coordination 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.

Basing on these rules, a continuous random network for a glass can be constructed as shown in Figs. 1.1.

![Crystalline A$_2$O$_3$ and Glassy A$_2$O$_3$](image-url)

Fig. 1.1 Two dimensional schematic of crystalline and non-crystalline (glass) materials.
As per these rules, the oxides of the type $A_2O$ (alkali oxides like $Li_2O$, $Na_2O$, $K_2O$), $AO$ (alkaline earth oxides like $CaO$, $BaO$, $SrO$ etc.,) should not form glasses and these are called modifying oxides. The rules are satisfied only for oxides of the type $A_2O_3$ ($B_2O_3$, $As_2O_3$), $AO_2$ ($SiO_2$, $GeO_2$) and $A_2O_5$ ($P_2O_5$). The first group of oxides is known as modifier oxides, whereas the latter group belongs to network forming oxides. Normally, most of the modifier oxides break-up the continuous network by introducing non-bridging oxygens. 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 $Sb_2O_3$, $Bi_2O_3$, $Al_2O_3$, $Ga_2O_3$, $In_2O_3$, $TeO_2$, $Ta_2O_5$, $Nb_2O_5$ etc.

Excellent reviews and articles on the topology of the glass by Vogel [2], Elliott [3], Doremus [4], Shackelford [5], Varshneya [6] and Shelby [7] give useful information.

Glasses are traditionally formed by cooling the molten liquid. However, there are a number other non-conventional methods like chemical vapour deposition, solgel process techniques, etc. 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/enthalpy at $T_m$. Continued cooling of the crystal will result in a further decrease in the volume/enthalpy due to the heat capacity of the crystal. If the liquid is cooled
below the melting temperature without crystallization, a super cooled liquid is obtained. In this region, the structure of the liquid continues to rearrange as the temperature decreases, but there is no abrupt decrease in volume/enthalpy due to discontinuous structural rearrangement.

As the liquid is cooled further, the viscosity increases. This increase in viscosity eventually becomes so great that the atoms can no longer completely rearrange to the equilibrium liquid structure, during the time allowed by the experiment. The structure begins to lag behind that which would be present if sufficient time were allowed to reach equilibrium. The enthalpy begins to deviate from the equilibrium line, following a curve of gradually decreasing slope, until it eventually becomes determined by the heat capacity of the frozen liquid, \textit{i.e.}, the viscosity becomes so great that the structure of the liquid becomes fixed and is no longer temperature-dependent. The temperature region lying between the limits where the enthalpy is that of the equilibrium liquid and that of the frozen solid, is known as the glass transformation region. The frozen liquid is now a glass. The glass transition temperature lies in between these two temperatures, as such it is a fictitious temperature and depends on the heating rate and previous thermal history of the sample.

This process of changes in volume/enthalpy with temperature as a super cooled liquid is cooled through the glass transition region is illustrated in Fig. 1.2.
During the last few decades a 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/rare earth metal ions for their use in solid-state devices. Work along these lines was carried out on a number of glasses giving valuable information [8-15].

1.2 Scope of the present work

Interest in amorphous phosphates was stimulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing [16].
The melting point and boiling point of P₂O₅ glasses are 560 °C and 605 °C respectively. Some other properties of pure P₂O₅ glass are (refractive index = 1.4930 at λ = 546.1 nm; thermal expansion coefficient = 13.7 x 10⁻⁶ / °C [17]. Hypothetically P₂O₅ glass has a UV edge less than 150 nm (~ 8.27 eV). However, P₂O₅ glass generally contains water and shifts the edge towards longer wavelength. A comparative diagram of the UV edges of various glass formers is shown in Fig. 1.3.

![Diagram](image)

**Fig. 1.3** Comparative diagram of the UV edges of various glass formers.

P₂O₅ glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficients, low melting and softening temperatures and high ultraviolet transmission [18]. The advent of solid state lasers in 1960’s heralded a new era of phosphate glass research. Certain compositions of these glasses have large rare-earth stimulated emission cross-sections and low thermo optical coefficients (compared with silicate glasses) and are the materials of choice
particularly for high power laser applications [19]. During the last two decades phosphate glasses have been investigated intensively, but there is still a great interest in developing new glasses related to the demands of both industry and technology. Many phosphate glasses are prone to crystallization or devitrification either during processing or in applications where they may be held at high temperatures for long periods. Therefore it would seem that a detailed study of the thermal behaviour of such glasses is of some importance.

In the particular field of thermoluminescence (TL) dosimetry, much recent work is concentrated on optimizing the glass compositions to give the best TL characteristics. However the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in this field [20, 21].

Normally, with the addition of modifier oxides like Li$_2$O or PbO to P$_2$O$_5$, the structural species gradually change from Q$^3$ to Q$^0$ (ultra $\rightarrow$ meta $\rightarrow$ pyro $\rightarrow$ ortho) phosphate glasses. Metaphosphates consist of long chains in the structure while pyrophosphates consist of discrete di-tetrahedral units (Figs. 1.4 (a and b). But in the glass structure it would be more appropriate to treat pyrophosphate as [POO$_{1/2}$O$_2$]$^{2-}$ units, which behave as chain terminators (they attach singly to other groups). Therefore their presence and concentration in the structure lead to a distribution of chain lengths. It is important to note that the formation of glasses is easier in metaphosphates than in pyrophosphates. In fact, pyrophosphates appear to undergo structural disproportionation. This step
can be visualized as involving the formation of \([\text{POO}_2\text{O}]^-\) and \([\text{POO}_3]^{3-}\) as the first step.

The metaphosphate unit is like a 'synthon' which adds on to any chain and expands the chain length. When the metaphosphate disproportionates, it forms ultra- and pyrophosphates. In \(Q^2\) (metaphosphate) units, the P-O\(^-\) and P=O establish resonance and as a consequence become indistinguishable. This indistinguishability manifests in the gradual disappearance of the P=O absorption in vibrational spectra in the region of 1200-1300 cm\(^{-1}\).

Network glasses such as phosphates can often be prepared with addition of substantial quantities of salts such as alkali oxides. The purpose of adding such salts is to increase the concentration of charge carrier ions. In such glasses, the matrix is provided by the phosphate network, which generally lies in the composition regime of ultra to meta phosphates are randomly distributed between chains and sheet-like islands of ultra-phosphates.
Alkali phosphate glasses containing heavy metal oxides like PbO are being rigorously pursued in recent years because the presence of lead oxide makes the glass more denser and also increase their refractive index [22-25]. Such glasses may offer more suitable environment for hosting rare earth ions to give high luminescence output. Earlier X–ray absorption fine structure (EXAFS) investigations on the structure of lead–silicate glasses indicated that lead ions participate in the glass network predominantly due to PbO$_4$ structural units when the concentration of PbO is higher, whereas in low content PbO glasses co–existence of the PbO$_6$, PbO$_4$ and PbO$_3$ groups were detected [26, 27]. PbO$_4$ structural units occupy network forming positions, whereas PbO$_6$ units act as modifiers and induce bonding defects as shown in Fig. 1.5. The creation of non-bridging oxygens (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.

![Fig.1.5 Entry of Pb$^{2+}$ ions as modifiers into a glass network](image-url)
Addition of SnO\(_2\) to lithium phosphate glass brings interesting changes in its electrical characteristics. To be more specific SnO\(_2\) improves \(n\)-type conductivity [28–32] of the glass to a large extent. Further, tin oxide containing lithium phosphate glasses are more advantageous as electrolytes in high energy density rechargeable batteries [33, 34], storage materials of solar energy [35]. Tin oxide containing phosphate glasses have also been developed successfully as anode materials for Li-batteries, transparent coatings, heterojunction solar cells and chemical sensors [36, 37]. This oxide is a versatile intermediate to metallic Sn, SnO, SnO\(_2\) and Sn\(_3\)O\(_4\) [28]. Since the electrical properties and performance of glasses containing such metal oxide are influenced by oxidation states and the environment of tin ions, it is necessary to have an understanding over the morphologies of Sn ion for the practical applications of these glasses.

In case if these ions exists in Sn\(^{2+}\) state, they possess an electron lone pair and form the apex of trigonal SnO\(_3\) pyramids in phosphate glasses [38, 39]. As a result there will be a lack of strong bonding cross links through this corner of the Sn-polyhedron and brings substantial changes in electrical characteristics. Szirtes et. al. have investigated on the oxidations states of tin ion in phosphate composites using Mössbauer studies [40] and illustrated more on different oxidation states of Sn ions. In general the tin ions participate in glass network in octahedral positions as shown in Fig. 1.6.
Fig. 1.6 Tin ions in octahedral positions in the glass network.

Thus the presence of tin ions in various oxidation states with different coordination numbers with oxygen in lithium phosphate glasses influence electrical properties of host glasses to a large extent. In view of this a part of the thesis is devoted to investigate the influence of tin ions on dielectric properties and ac conductivity of the titled glasses.

Further, Sn$^{4+}$ ions are expected to exhibit luminescence in UVB (due to $S_2 \rightarrow S_0$ transition) and broad yellow-orange (due to $S_1 \rightarrow S_0$ transitions) regions in the glass materials [41]. Hence these ions are predicted to act as an energy transfer bridging ions for blue and orange emission of rare earth ions like Gd$^{3+}$ and Er$^{3+}$ ions, respectively. Hence the codoping of Sn$^{4+}$ with Gd$^{3+}$ ions is expected to give strong UVB emission and similarly, co-doping with Er$^{3+}$ ions is predicted to enrich the orange emission of Er$^{3+}$ ions. With these views, a part of the thesis is devoted to the studies of luminescence properties of titled glasses codoped with Gd$^{3+}$ and Er$^{3+}$ ions.
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-PbO-P$_2$O$_5$: SnO$_2$/Gd$_2$O$_3$/Er$_2$O$_3$ glasses is given below:

### 1.2.1 Physical parameters

Some physical parameters useful for characterization ZnF$_2$–As$_2$O$_3$/WO$_3$–TeO$_2$ glasses doped with transition metal oxides and rare earth oxides are estimated from the measured value of density (d) and the average molecular weight $\bar{M}$, using the following equations [42–45]:

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

$$N_i = \frac{N_A M (\text{mol}%)}{\bar{M}}$$  \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:

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

Polaron radius (Å), $$r_p = \frac{1}{2} \left[ \frac{\pi}{6N_i} \right]^{1/3}$$  \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 ($r_p$) of the transition metal ions by:
Field strength (cm$^{-2}$), $F_i = \frac{z}{r_p^2}$ \hspace{1cm} (1.4)

1.2.2 Dielectric properties

When an insulating glass (a dielectric) like ZnF$_2$–As$_2$O$_3$–TeO$_3$ glass is placed in external electric field two types of polarizations – the electronic and the ionic – are expected to develop in the glass. 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 exist 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) [46].

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 [47].

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:

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

(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:

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

(1.8)

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

\[
\tan \delta = \frac{4 \pi \sigma}{\omega \varepsilon'(\omega)} + \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{\varepsilon_s + \varepsilon_\infty \omega^2 \tau^2}
\]  

(1.9)
By plotting \( \log(\tan\delta) \) as a function of \( \log(\omega) \), information regarding ac conductivity as well as the behaviour of the dipoles present if any can be obtained.

1.2.3 Electron spin resonance

Among various rare earth ions the Gd\(^{3+}\) ion is the only rare earth ion that exhibit Electron spin resonance (ESR) signal at about 2.0 at room temperature. The information on environment of Gd\(^{3+}\) ions in the titled glasses can be obtained from these studies. Such studies help in interpreting the luminescence properties of Sn\(^{4+}\) ions and its contribution to the enrichment of luminescence emission of rare earth ions. With this view we have studied the ESR spectra of Gd\(^{3+}\) doped glasses. Hence, a preliminary information regarding ESR spectra is given below.

Electron spin resonance 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 neighbors. 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
\[ \mathbf{J} = \mathbf{L} + \mathbf{S}. \]  \hspace{2cm} (1.10)

Associated with the total angular momentum \( \mathbf{J} \), the magnetic dipole moment \( \mu \) given by
\[ \mathbf{\mu} = -g\beta \mathbf{J} \]  \hspace{2cm} (1.11)

where
\[ g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \]  \hspace{2cm} (1.12)

which is known as the Lande splitting factor for free ion and
\[ \beta = \frac{e\hbar}{2mc} = 9.274096 \times 10^{-27} \text{ erg/ gauss} \]  \hspace{2cm} (1.13)

which is known as the Bohr magneton. When a magnetic dipole is placed in a uniform magnetic field \( B \), it precesses about the direction of \( B \) with the Larmor angular frequency \( \omega_L \) which is given by \([48]\)
\[ \omega_L = \gamma B \]  \hspace{2cm} (1.14)

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
\[ \hbar \nu = g \beta B. \]  \hspace{2cm} (1.15)

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. 1.7, if \( g \) is constant.

\[
\Delta E = h \nu = g \beta B
\]

Fig. 1.7  Zeeman energy for a single unpaired electron as function of magnetic field \( B \). A magnetic dipole aligned parallel to \( B \) has lower energy while a magnetic dipole aligned antiparallel to \( B \) has higher energy.
The energies of these levels are

\[ E_{±1/2} = ±(1/2) g \beta B, \]  

and the energy difference between the two levels for a given value of \( B \) is

\[ \Delta E = g \beta B \]  

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 (1.15) and \( \Delta M_s = ±1 \) 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. (1.15) and \( \Delta M_J = ±1 \). Such a situation will give rise to multiple absorption lines. The resonance condition (1.15) 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 [49–53].

1.2.4 Infrared spectra

Infrared absorption spectra of glasses 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 glasses enables the assignment of characteristic frequencies to molecular groups in the glasses and hence correlation of IR absorption bands with different units of vitreous structure. In the case of phosphate glasses, the basic glass contains several structural units in the glass network and when cations such as Li$^+$ and Pb$^{2+}$ are added, it may reside 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 glasses are independent [54–56], unlike the vibrations of complex ions in a glass 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 Li₂O–PbO–P₂O₅ 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 [55] for some of the vibrational frequencies assigned to phosphate groups.

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

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

(1.18)
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 [55, 56].

1.2.5 Rare earth ions and optical properties

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, Nd$^{3+}$, Sm$^{3+}$ and Eu$^{3+}$ are incorporated into the Li$_2$O–PbO–P$_2$O$_5$ 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–PbO–P$_2$O$_5$ glasses. These ions exhibit sharp absorption and luminescence transitions. Since, these 4f ions are weakly perturbed by the surrounding ligands [57]. The spectral intensities have been carried out with the
help of Judd-Ofelt theory [58]. The spectral intensities are often expressed in terms of oscillator strength (\( f \)). Experimentally, this can be calculated from the following expression:

\[
\exp f = 2.303 \left( \frac{mc^2}{N_A} \right) \pi e^2 \int \varepsilon(v) dv
\]  

(1.19)

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

\[
\varepsilon(v) = \frac{1}{LC} \log(\frac{I_0}{I})
\]  

(1.20)

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. (1.19) reduces to:

\[
\exp f = 4.319 \times 10^{-9} \int \varepsilon(v) dv
\]  

(1.21)

According to the conventional Judd–Ofelt (JO) theory [58, 59], the calculated OS of the electric dipole transition between two states can be expressed as follows:

\[
f_{cal} = \frac{8\pi^2 mc^2 \chi}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_\lambda \left( f^N_\gamma S L J \right) \left\| U^A \right\| f^N_\gamma S' L' J \right\|^2 
\]  

(1.22)

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

$$\Delta l = +1; \Delta S = 0, \Delta L < 2, \Delta J < 2$$  \hspace{1cm} (1.23)

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 [60]:

$$A_{J''} = \frac{64\pi^4 e^\lambda^3}{3h(2J+1)} \frac{n(n^2 + 2)^2}{9} \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle f^{J',S',L'} | U^{\lambda} | f^{J,S,L} \rangle^2$$  \hspace{1cm} (1.24)

where $e$ is the charge of electron, and all other quantities are the same as in Eq. (1.21). The values of $\|U^{\lambda}\|^2$ taken from the literature for various absorption transitions of Gd$^{3+}$ and Er$^{3+}$ are presented in Tables 1.2 (a & b) [61, 62].

Summing up the $A_{J''}$ quantities over all possible final states, one can get the radiative life time $\tau$ of an excited energy level as,

$$\tau = \frac{1}{\sum_{J''} A_{J''}}$$  \hspace{1cm} (1.25)

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

$$\beta_{J''} = \frac{A_{J''}}{\sum_{J''} A_{J''}}.$$  \hspace{1cm} (1.26)
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 1.1(a)**

Values of reduced matrix elements for the absorption transitions of $\text{Gd}^{3+}$ in phosphate glasses.

| Transition | $(\leftarrow^{8}S_{7/2})^6$ | $|\langle \hat{J} | U^{(2)} | J^{-}\rangle|^2$ | $|\langle \hat{J} | U^{(4)} | J^{-}\rangle|^2$ | $|\langle \hat{J} | U^{(2)} | J^{-}\rangle|^2$ |
|------------|-------------------|-----------------|-----------------|-----------------|
| $P_{7/2}$  | 0.0010            | 0               | 0               | 0               |
| $^6P_{5/2}$| 0.0004            | 0               | 0               | 0               |
| $^6I_{7/2}$| 0                | 0               | 0.0041          | 0               |
| $^6I_{9/2}$, $^6I_{17/2}$ | 0 | 0 | 0.0318 | 0 |
| $^6I_{11/2}$ | 0 | 0 | 0.0177 | 0 |
| $^6I_{15/2}$, $^6I_{13/2}$ | 0 | 0 | 0.0511 | 0 |
| $^6D_{9/2}$ | 0.0057 | 0.0001 | 0 | 0 |
| $^6D_{7/2}$ | 0.0044 | 0 | 0 | 0 |
| $^6D_{5/2}$, $^6D_{3/2}$ | 0.0033 | 0 | 0 | 0 |
Table 1.1(b)

Values of reduced matrix elements for the absorption transitions of Er$^{3+}$ in phosphate glass

| Transition (from $^4I_{15/2}$) | $|U|^2$ | $|U^4|^2$ | $|U^6|^2$ |
|-------------------------------|-------|----------|----------|
| $^4I_{15/2}$                   | 0.0195 | 0.1173   | 1.4316   |
| $^4I_{9/2}$                    | 0      | 0.1733   | 0.0099   |
| $^4F_{9/2}$                    | 0      | 0.5354   | 0.4618   |
| $^4S_{3/2}$                    | 0      | 0        | 0.2211   |
| $^2H_{11/2}$                   | 0.7125 | 0.4125   | 0.0925   |
| $^4F_{7/2}$                    | 0      | 0.1469   | 0.6266   |
| $^4F_{5/2}$                    | 0      | 0        | 0.2232   |
| $^4F_{3/2}$                    | 0      | 0        | 0.1272   |
| $^2G_{9/2}$                    | 0      | 0.0189   | 0.2256   |
| $^4G_{11/2}$                   | 0.9183 | 0.5262   | 0.1172   |
| $^4G_{9/2}$                    | 0      | 0.2416   | 0.1235   |
1.3 Brief review of recent studies on phosphate glasses

Abo-Naf et al. [63] have investigated in vitro bioactivity evaluation, mechanical properties and microstructural characterization of Na$_2$O–CaO–B$_2$O$_3$–P$_2$O$_5$ glasses. Their experimental results revealed the formation of a bioactive hydroxyapatite (HA) layer, composed of nano-crystallites, on the surface of glass grains after the in vitro assays. From these results they have concluded that the formation of HA as a function of glass composition and soaking time in the SBF and also reported that increasing B$_2$O$_3$ content in glass composition enhanced the bioactivity of glasses. Sun et al. [64] have studied the role of P$_2$O$_5$ on the structure of CaO–SiO$_2$–P$_2$O$_5$ and CaO–SiO$_2$–TiO$_2$–P$_2$O$_5$ glasses was identified using Fourier transformation infrared (FTIR), Raman and Magic Angular Spinning Nuclear Magnetic Resonance (MAS NMR) spectra. Sdiri et al. [65] investigated the effects of substituting P$_2$O$_5$ for B$_2$O$_3$ on the thermal and optical properties of sodium borophosphate glasses doped with Er and reported that the PL intensity, the PL life time and the quantum efficiency relative to the $^4$I$_{13/2} \rightarrow ^4$I$_{15/2}$ (1530 nm) transition of Er$^{3+}$ were all found to decrease with the addition of B$_2$O$_3$.

Li et al. [66] have studied the structure of three ZnO–Fe$_2$O$_3$–P$_2$O$_5$ glass series. They have investigated Raman and IR spectral changes with increasing O/P ratio from 2.8 to 3.7 and reported a gradual depolymerization of phosphate network and the variation of dominant structural units from Q$^2$ to Q$^1$ species with increasing O/P ratio from 2.8 to 3.7. Lakshmana Rao et al. [67] have
studied the spectroscopic and EPR studies on PbO–Y_2O_3–P_2O_5 glasses doped with molybdenum ion and reported from EPR signals that the molybdenum ions exist in Mo^{5+} state with Mo^{6+} act as modifiers with MoO_4 and MoO_6 structural groups in these glasses. Winegar et al. [68] have studied X-ray photoelectron spectroscopy and Raman microscopy of 50SnF_2–20SnO–30P_2O_5 glass. Their investigations resulted that the O 1s X-ray photoelectron spectra indicate a high non-bridging to bridging oxygen ratio, a sign of relatively high durability needed for this glass to be applied to solar energy.

Ravi Kumar et al. [69] have studied the dielectric dispersion and spectroscopic investigations on Na_2SO_4–B_2O_3–P_2O_5 glasses mixed with low concentrations of TiO_2. They have reported that the values of dielectric parameters viz., dielectric constant, loss and ac conductivity at any frequency and temperature are observed to increase with the concentration of TiO_2. Raguenet et al. [70] have prepared a series of lithium boro-phosphate glasses of composition 45 Li_2O–55 [x B_2O_3–(1 – x) P_2O_5], 0 ≤ x ≤ 1. These glasses exhibit a mixed glass former effect with non linear increase in both glass transition temperature and conductivity when phosphorous is replaced by boron. A fairly good conductivity (∼ 2 × 10^{-7} \Omega^{-1}.cm^{-1} at room temperature) coupled to a high T_g (∼ 450 °C) makes these glasses interesting as solid electrolytes for the development of thin-film batteries. On the whole it was shown that while the T_g evolution relied upon the presence of mixed boro-phosphate entities, the
conductivity was directly linked to the presence of BO\textsubscript{4} entities alone irrespective of their specific environment.

Kiran et al. [71] have studied the electron paramagnetic resonance (EPR), optical absorption and emission spectra of Cr\textsuperscript{3+} ions doped in (30−x) (NaPO\textsubscript{3})\textsubscript{6}+30PbO+40B\textsubscript{2}O\textsubscript{3}+xCr\textsubscript{2}O\textsubscript{3} (x=0.5, 2.0, 3.0, 4.0 and 5.0 mol\%) glasses. The EPR spectra exhibit resonance signals with effective g values at g≈4.55 and g≈1.97. The intensity of the resonance signals increases with decrease in temperature. The optical absorption spectrum exhibits four bands characteristic of Cr\textsuperscript{3+} ions in octahedral symmetry. From the analysis of the bands, the crystal-field parameter Dq and the Racah interelectronic repulsion parameters B and C have been evaluated. The emission spectrum exhibit one broad band characteristic of Cr\textsuperscript{3+} ions in octahedral symmetry. This band has been assigned to the transition \( ^4\text{T}_{2g} (F) \rightarrow ^4\text{A}_{2g} (F) \).

Chanshetti et al. [72] prepared Sodium borophosphate glasses doped with copper ions using conventional melt-quench method having general composition 20Na\textsubscript{2}O–20ZnO–25B\textsubscript{2}O\textsubscript{3}–(35−x) P\textsubscript{2}O\textsubscript{5}–x CuO (x=1–8 mol \%) and characterized by density, UV–visible optical absorption, photoluminescence and conductivity measurements. Network modifying action of CuO with the glass network has been confirmed from the UV–visible optical absorption studies. Presence of Copper in the form of Cu\textsuperscript{+} species has been confirmed from photoluminescence measurements. The electrical conductivity (\( \sigma \)) increases with increase in copper oxide content in the
glass and temperature dependence of electrical conductivity confirmed the semi conducting nature of the samples.

Liu et al. [73] has synthesized a novel cobalt borophosphate \((\text{NH}_4)_2(\text{C}_4\text{H}_{12}\text{N}_2)\) \([\text{Co}_2\text{B}_4\text{P}_8\text{O}_{24}(\text{OH})_2]\cdot\text{H}_2\text{O}\) with the mixed cations under mild hydrothermal conditions. The crystal structure consists of a new type of three-dimensional borophosphatic anionic partial framework, which is built from the condensation of the fundamental building unit (FBU) \([\text{B}_2\text{P}_3\text{O}_{14}(\text{OH})]\). The \(\text{CoO}_6\) octahedra are enchased in such borophosphate network to form a complex open framework with a three-dimensional intersecting channel system, the voids of which are occupied by ammonium, dipronated piperazine ions and water molecules, respectively. The magnetic measurement of the title compound has also been investigated. Liang et al. [74] has prepared a borophosphate glass with the mol\% composition \(25\text{Na}_2\text{O}-25\text{CaO}-5\text{P}_2\text{O}_3-45\text{B}_2\text{O}_5\). The conversion of the binding scaffolds to hydroxyapatite (HA) was investigated by measuring the weight loss after soaking the sample in a solution of 0.25 M \(\text{K}_2\text{HPO}_4\) with a pH value of 9.0 at 37 °C as a function of time.

Zhi-wei Luo et al. [75] prepared and studied the UV-transmitting borophospho-silicate glasses series, \(2\text{Al}_2\text{O}_3-x\text{SrO}-(18-x)\text{ZnO}-33.3\text{P}_2\text{O}_5-16.7\text{B}_2\text{O}_3-30\text{SiO}_2\) glasses with \(x=0-18\) mol\%. The substitution of SrO for ZnO increases the density and the thermal expansion coefficient \((\alpha)\), but decreases the molar volume \((V_m)\). The glass transition temperatures \((T_g)\) and softening points \((T_d)\)
vary within a small range. The structural changes with the glass compositions were examined by FT-IR and Raman spectra. Mascaraque et al. [76] have studied the structure of glasses within the system Li₂O–Al₂O₃–B₂O₃–P₂O₅ through 31P, 11B and 27Al Nuclear Magnetic Resonance, and the effect of Al₂O₃ substitution by B₂O₃ and P₂O₅ network formers on the structure and properties investigated for a constant Li₂O content. The behavior of the glass transition temperature and electrical conductivity of the glasses has been interpreted as a function of the structural changes induced in the glass network when alumina is substituted for B₂O₃, P₂O₅ or both. Small additions of alumina produce a drastic increase in glass transition temperature, while it does not change for [Al₂O₃] greater than 3 mol%.

Lim et al. [77] studied the effects of B₂O₃-additions on the properties and structures of two series of Sn(II)-borophosphate glasses were determined. The addition of up to 28 mol% B₂O₃ to a 66.7SnO–33.3P₂O₅ base glass (series I), and the substitution of up to 13 mol% B₂O₃ for P₂O₅ in the same base glass (series II) increase Tg from 265 °C to 357 °C and 306 °C, respectively. Raman spectroscopy reveals that borate additions to both series reduce the number of P–O–P linkages by converting pyrophosphate anions to orthophosphate anions. ¹¹B NMR spectra indicate that tetrahedral borophosphate units, B(OP)₄, are initially formed when B₂O₃ is added to the Sn-pyrophosphate base glass. More complex tetrahedral and trigonal borate sites form when B₂O₃ contents exceed about 10 mol%. Muralidhara et al. [78] have carried out investigations of the
electron paramagnetic resonance (EPR) and optical absorption spectral on Fe$^{3+}$ ions doped sodium borophosphate glasses (NaH$_2$PO$_4$–B$_2$O$_3$–Fe$_2$O$_3$). The EPR spectra exhibit resonance signals with effective g values at g=2.02, g=4.2 and g=6.4. The resonance signal at g=4.2 is due to isolated Fe$^{3+}$ ions in site with rhombic symmetry whereas the g=2.02 resonance is due to Fe$^{3+}$ ions coupled by exchange interaction in a distorted octahedral environment. The intensity of the resonance signals decreases with increase in temperature whereas line width is found to be independent of temperature. The optical absorption spectrum exhibits bands characteristic of Fe$^{3+}$ ions in octahedral symmetry. The crystal field parameter (Dq) and the Racah interelectronic repulsion parameters (B and C) have also been evaluated and discussed.

Mošner et al. [79] studied the Zinc boro-phosphate glasses doped with TeO$_2$ in the compositional series (100 – x)[0.5ZnO–0.1B$_2$O$_3$–0.4P$_2$O$_5$]–xTeO$_2$ in a broad concentration range of x = 0–80 mol% TeO$_2$. The structure of the glasses was studied by Raman and IR spectroscopy and by 31P and 11B MAS NMR spectroscopy. The incorporation of TeO$_2$ modifies also the coordination of boron atoms, where B(OP)$_4$ structural units are gradually replaced by B(OP)$_4$–n(OTe)$_n$ units. The addition of TeO$_2$ to the parent zinc borophosphate glass results in a decrease of glass transition temperature associated with the replacement of stronger P–O and B–O bonds by weaker Te–O bonds. Bingham et al. [80] have studied the effects of modifier additions on the thermal properties, chemical durability, oxidation state and structure of P$_2$O$_5$–Fe$_2$O$_3$–
FeO–BaO glasses. The analysis of the results of their studies has indicated that these glasses are ultra-durable, thermally stable, low-melting glasses with a large glass-forming compositional range.

Gaylord et al. [81] studied the viscosity behavior of (1–
\(x\))NaPO\(_3\)–\(x\)Na\(_2\)B\(_4\)O\(_7\) glasses (\(x = 0.05–0.20\)) have been measured as a function of temperature using beam-bending and parallel-plate viscometry. The viscosity was found to shift to higher temperatures with increasing sodium borate content. The decrease in fragility with increasing \(x\) is due to the progressive depolymerization of the phosphate network by the preferred four-coordinated boron atoms present in the low alkali borate glasses. As confirmed by Raman spectroscopy increasing alkali borate leads to enhanced B–O–P linkages realized with the accompanying transition from solely four-coordinated boron (in BO\(_4\) units) to mixed BO\(_4\)/BO\(_3\) structures. Vijaya Kumar et al. [82] have investigated dielectric properties of novel set of glasses of the type (B\(_2\)O\(_3\))\(_{0.10}–(P_2O_5)_{0.40}–(CuO)_{0.50–x}–(MoO_3)x, 0.05\leq x\geq0.50\), in the frequency range 100 Hz–100 kHz and temperature range 300–575 K. From the total conductivity derived from the dielectric spectrum the frequency exponent, \(s\), and dc and ac components of the conductivity were determined. Neel et al. [83] have investigated the effect of doping a high calcium oxide in metaphosphate glass series (CaO)\(_{40}(\text{Na}_2\text{O})_{10}(\text{P}_2\text{O}_5)_{50}\) with TiO\(_2\) (1, 3, and 5 mol\%). They have found that TiO\(_2\) incorporation increased the density and glass transition temperature
while reduced the degradation rate (5 mol% in particular) by twofold compared with (CaO)_{30} system.

Florian et al. [84] have reported structure and properties of high Li_{2}O-containing aluminophosphate glasses. In this study they investigated the influence of the alumina content on the properties of lithium phosphate glasses, and the room temperature ionic conductivity in particular, with potential application as solid electrolytes in lithium secondary batteries. Kord et al. [85] have studied the effect of ZrO_{2} addition on crystallization behaviour, porosity and chemical–mechanical properties of a CaO–TiO_{2}–P_{2}O_{5} microporous glass ceramic. From this study they have concluded that the ZrO_{2} addition improved the chemical durability and bending strength of porous glass ceramics. Gabriel et al. [86] have reported the structural studies of La-based metaphosphate glasses modified with aliovalent alkaline earth elements (M = Ba, Ca, Sr), with P:(M + La) ratio kept approximately at 3, were analyzed using Raman and IR spectroscopy. In this study it was found that the replacement of divalent elements for trivalent La in a metaphosphate glass structure was partially accommodated by incorporation of protons as charge compensating defects. The protons were found to be in close proximity to the divalent cations. Shapaan et al. [87] have studied the hyperfine structure, thermal stability and electric–dielectric properties of vanadium iron phosphate glasses. From the dielectric data the authors have concluded that iron ions in this glassy system exist only in the ferric (Fe^{3+}) state located on the tetra hedral and octahedral sites. The
number of ferric ions which located on the octahedral sites (network modifier)
increased with increasing $\text{V}_2\text{O}_5$ contents and contributed to the electrical
conductivity.

Bingham et al. [88] studied the coordination and stability under electron
irradiation of boron in glasses with nominal molar composition $60\text{P}_2\text{O}_5 \text{−} (40 – x)\text{Fe}_2\text{O}_3 \text{−} x\text{B}_2\text{O}_3$, for which $x = 0, 5, 10, 15$ and 20, have been investigated for
the first time by electron energy loss spectroscopy (EELS) with transmission
electron microscopy (TEM). Analysis confirms that boron is present in un-
irradiated samples as tetrahedral $\text{BO}_4$ units; there is no evidence of any trigonal
$\text{BO}_3$ units. TEM analysis reveals no tendency for sub-micron phase separation
of the as-annealed glass. Iron borophosphate glasses exhibit high resistance to
structural damage by electron beam irradiation by comparison with literature
values for a range of other silicate and phosphate glasses. Agathopoulos et al.
[89] have reported the results of their study on the structural analysis and
devitrification of calcium silicate glasses with $\text{P}_2\text{O}_5$ as additive. Karan et al. [90]
have investigated the lithium ion transport process and glass network
modification upon the variation of network modifier (M) to former (F) ratio
(M/F) in 30% $\text{LiBO}_2$–70% [(M $\text{Li}_2\text{O}$–F $\text{P}_2\text{O}_5$)] glasses. The glasses with
different M/F ratios (0.42–1.0) were prepared by melt quenching technique and
characterized by X-ray diffraction (XRD), differential scanning calorimetry
(DSC), Raman and impedance spectroscopy techniques. The glass transition
temperature, Tg increased with increasing M/F ratio suggesting an increase in
overall connectivity of the network structure. Dc conductivity showed an enhancement of three orders of magnitude with increasing M/F. The observed increase in Tg and dc conductivity with modifier concentration has been explained on the basis of the competition between network breaking/forming events, leading to an increase in overall connectivity of the network and the formation of continuous channels for ion migration. Furthermore, the scaling of both ac conductivity and electrical modulus data showed an excellent collapse on to a single master curve indicating that there is a good time–temperature superposition and that conduction mechanism remains unchanged in this glass system.

Takebe et al. [91] have carried out the studies on the dissolution behaviour of zinc phosphate glasses in water. Dutta et al. [92] have reported the influence of manganese and vanadium ions on the physical properties of phosphate glasses. Krishna Mohan et al. [93] have recently reported the dielectric and spectroscopic properties of lead niobium phosphate glasses mixed with small concentrations of V\(_2\)O\(_5\). Saranti et al. [94] have reported preparation structural study and vitro evaluation of calcium borophosphate bioactive glass system. Garbarczyk and Wasiucionek [95] have investigated the electrical properties and crystallization process of silver phosphate glasses. Malakho et al. [96] studied the crystallization of glasses with compositions \((1-x)(0.95\ NaPO_3+0.05\ Na_2B_4O_7)+x\ Nb_2O_5\), \(x = 0.43\), 0.45, 0.48 was investigated by differential scanning calorimetry and X-ray powder diffraction. The results of
Raman spectroscopy show the formation of three-dimensional (3D) niobium oxide framework in the glasses with increase of niobium concentration. This framework is supposed to have tetragonal tungsten bronze structure and to be responsible for nonlinear optical properties of the glass. Second harmonic generation signals of as prepared and crystallized glass after thermal poling are compared. The nucleation and crystallization do not improve the NLO properties of the glasses under study.

Lee et al. [97] have synthesized series of sodium borophosphate glasses of the composition \((1-x)\) NaPO₃− x B₂O₃ and their optical and thermal properties investigated. The results show that refractive index (n) and glass transition temperature (Tg) show a maximum at about B/(B+P)=0.6 while thermal expansion coefficient (α) and thermo-optic coefficient (dn/dT) change monotonically with the B/(B+P) ratio. These observations can be interpreted based on the incorporation of BO₃ and BO₄ units into the glass structural network. Jozwiak and Garbarczyk [98] have reported the mixed electronic–ionic conductivity in the lithium phosphate glasses mixed with V₂O₅. Nogami et al. [99] have reported the results of their studies on proton conductivity in sol-gel-derived P₂O₅-TiO₂-SiO₂ glass system. Sundeep Kumar et al. [100] have prepared the glasses in the system xLi₂O·(1−x)[0.5B₂O₃·0.5P₂O₅] and xAg₂O·(1−x)[0.5B₂O₃·0.5P₂O₅] from melt quenching method. Structural studies have been done using infrared and high resolution magic angle spinning nuclear magnetic resonance. Boron is present only in tetrahedral coordination
except in Li$_2$O-rich glasses. Transport properties have been investigated over a wide range of frequency and temperature. Silver containing glasses are found to possess higher conductivities and lower barriers than lithium containing glasses. A structural model has been proposed in which pure B$_2$O$_3$–P$_2$O$_5$ compositions are assumed to be constituted of BPO$_4$ units and modification occurs selectively on the phosphate moiety. Tetrahedral boron units are thus expected to be retained in the glass structure. Ahmed et al. [101] have reported the processing and characterization of ternary based sodium calcium phosphate glass system.

Rajendran et al. [102] have studied the effect of thermal treatment on elastic properties of SiO$_2$–Na$_2$O–CaO–P$_2$O$_5$ glasses that are useful for biomedical applications. Salgram et al. [103] have reported about the optical band gap studies on Pb$_3$O$_4$–P$_2$O$_5$ lead (II,IV) phosphate glasses. Ilieva et al. [104] have studied infrared and Raman spectra of Ga$_2$O$_3$–P$_2$O$_5$ glasses and concluded that the structure of these glasses is highly polymerized network. R.K. Brow [105] has reviewed the spectroscopic and diffraction studies of simple phosphate glasses and structures of anhydrous ultra phosphate glasses. Na$_2$O–Ga$_2$O$_3$–P$_2$O$_5$ glasses are structurally characterized as a function of Na/Ga molar ratio by Belkabir et al. [106].

Koudelka et al. [107] prepared twenty-eight samples of the ZnO–B$_2$O$_3$–P$_2$O$_5$ system by cooling the melt from 1230°C in the compositional series containing 30, 40, 50 and 60 mol.% of ZnO. A large glass-forming region was
found at the phosphate side of the ternary system with homogeneous glasses containing up to 20–40 mol.% of B$_2$O$_3$. The values of $V_M$ and $\alpha$ decrease with increasing B$_2$O$_3$ content, while $T_g$ and $T_d$ increase. The reason for the observed changes is the incorporation of trigonal BO$_3$ and tetrahedral BO$_4$ units into the chain-like structural network of phosphates increasing thus its dimensionality. Raman and infrared (IR) spectra confirm these structural changes. Suzuya et al. [108] have studied the structures of lead indium phosphate and lead scandium phosphate and reported about the coordination numbers. Krishna et al. [109] reported the electron paramagnetic resonance (EPR) and optical absorption structural investigations of Mn$^{2+}$ ions in alkali barium boro-phosphate glasses at room temperature. The Mn$^{2+}$ EPR hyperfine sextet centered at $g = 2$ was observed in all the glasses for 1 mol% Mn$_2$O$_3$. The absorption spectra of Mn$^{2+}$ ions in these glasses showed broad absorption bands characteristic of Mn$^{2+}$ ions in octahedral symmetry. From the EPR and optical results, it is concluded that the site symmetry around Mn$^{2+}$ ions is octahedral, and the nature of the bonding character is dominantly ionic. Zhao et al. [110] have reported that most of the glasses in the PbO-PbBr$_2$-PbF$_2$-P$_2$O$_5$ system show strong stabilities against crystallization.

Sidek and Senin [111] have investigated elastic and inelastic and non-linear acoustic properties of ZnCl$_2$-P$_2$O$_5$ glasses. Liu et al. [112] have concluded that the length of phosphate chains decreases with increase in PbO and or ZnO contents in the glass matrix. Zhao et al. [113] have reported the synthesis of
three Eu$^{3+}$ doped in B$_2$O$_3$-P$_2$O$_5$-R$_2$SO$_4$ (R=Li, Na, K) glass system; on excitation with 395 nm (Xe-arc lamp) these Eu$^{3+}$ glasses are found to be red fluorescent and the richness of the red colour is high in Li$^+$ glass than the rest of the glasses. Meyer [114] has analysed the characterization of the structure of binary zinc ultra phosphate glasses by IR and Raman spectroscopy. Aruna and Buddhudu [115] have studied the spectral properties of Tb$^{3+}$: B$_2$O$_3$-P$_2$O$_5$-R$_2$SO$_4$ glasses (R=Li, Na, K) and they have found that this glass system to be green fluorescent ($\lambda_{exc} = 487$ nm). Hattori et al. [116] studied optical and structural properties of Er$^{3+}$doped P$_2$O$_5$-SiO$_2$ and Al$_2$O$_3$-SiO$_2$ planar wave-guides. Miklos and Doupovec [117] have studied the dielectric properties of V$_2$O$_5$-P$_2$O$_5$ glasses and reported that the conductivity and dielectric properties of the glasses could be described by mechanism of electron hopping between energy states of the chain of molecules or by a tunneling effect. Rao et al. [118] have studied elastic properties of binary and ternary P$_2$O$_5$ glasses using ultrasonic measurements and reported that the variations in the moduli are consistent with the nature of the structural units formed at various compositions.

Brow et al. [119] examined the polyhedral arrangements in ZnO-P$_2$O$_5$ glasses using MAS-NMR spectroscopy and Raman spectroscopy. Sakai et al. [120] studied the properties and origin of fine Na$_2$SO$_4$ blisters have been studied experimentally. They are 0.1–1.0 mm in size and contain crystalline Na$_2$SO$_4$ with a small amount of CaO and K$_2$O. Most of them are formed in molten glass during decomposition of the batch mixture. The blisters are formed by
condensation of Na$_2$SO$_4$ from Na$_2$O and SO$_3$ selectively absorbed into dolomite at an early stage of batch melting. They remain immiscibly in molten glass, after MgO and CaO in the dolomite have been dissolved into the glass. Quinn, et al. [121] have concluded from their studies that zinc phosphate glasses are chemically durable and have processing temperatures under 400 °C and can be co-formed with high temperature polymers to produce unusual organic/inorganic composites. Marotta et al. [122] have studied the thermal properties and devitrification behaviour of sodium, lithium and barium borophosphate glasses by differential thermal analysis. The results are in good agreement with the hypothesis that BO$_4$ groups form when a network modifier oxide (Na$_2$O or Li$_2$O or BaO) is added to B$_2$O$_3$. The excess of negative charge is compensated by metallic cations or positively charged PO$_4$ groups. Activation energy for crystal growth and devitrification mechanism under non-isothermal condition in sodium, lithium and barium metaphosphate glasses were also evaluated.

Angell [123] has reported that the transition from cross-linked ultra phosphate structures to polymer like metaphosphate structures, affects the temperature dependence of viscosities of alkali phosphate liquids. Average chain lengths of typical metaphosphate glasses, with $n_{av}$ ranging from 40-100 P-Tetrahedra and terminated by hydroxyl groups, have been reported by Bunker et al. [124]. Ray [125] has studied the Raman spectra of K-ultra phosphate glasses and Gresch, et al. [126] have analyzed the spectral studies of Na-ultra phosphate
glasses. Kordes and coworkers [127, 128] showed a compositional dependence for the coordination number of metal cations like Zn$^{2+}$. Ingram [129] has reviewed the ionic conductivity in these glasses and suggested that it is related to the structural disorder in the form of the amorphous cluster theory.

1.4 Motivation and objective of the present work

Lithium–phosphate glasses are found to be suitable candidates for the potential applications in integrated microbatteries, solid electrolytes (ionic conducting glasses), or mixed electronic–ionic cathode materials and low loss optical waveguides. Further, the addition of Sn$^{4+}$ ions is expected to bring interesting changes in electrical characteristics of the titled glasses. Especially, these ions improve the n-type conductivity of lithium phosphate glasses. The electrical conductivity of Li$_2$O–PbO–P$_2$O$_5$ glasses doped with SnO$_4$ consists of both ionic and electronic conduction. Ionic conduction in these glasses occurs via the motion of Li$^+$ ions mainly while electronic transport takes place by electron (polaron) hopping between Sn$^{2+}$ and Sn$^{4+}$ centers. As such the studies available on electrical properties of lithium lead phosphate glasses mixed tin ions are very rare. The studies on dielectric properties such as dielectric constant, dielectric loss, ac conductivity, electric moduli, impedance values of Li$_2$O–PbO–P$_2$O$_5$: SnO$_2$ glasses over a wide range of frequency and temperature are expected not only to reveal comprehensive knowledge about the conduction mechanism in these materials but also provide information on the structural aspects of the glasses to a large extent. Hence the initial part of the thesis is
devoted to have a broad understanding over the influence of tin ions on dielectric properties. The results of optical absorption, luminescence and IR spectral studies that are helpful in analyzing the data on dielectric properties are also reported.

Detailed studies on $^4G_{11/2} \rightarrow ^4I_{11/2}$ orange emission transition of Er$^{3+}$ ions were less focused even though such laser sources are being widely used in medical field. However, erbium has only weak pumping bands hence it is necessary to assist the pumping by resonant transfer donors like tin ions. Incidentally, the Sn$^{4+}$ ions also give rich emission in the orange region and hence these ions contribute to the enrichment of orange emission of Er$^{3+}$ ions in the host glass. Similarly, the emission properties of another rare earth ion viz., Gd$^{3+}$ which is well known due to its strong narrow UVB $^6P_{7/2} \rightarrow ^8S_{7/2}$ emission transition at 311 nm has been less investigated among all the other rare earth ions. UVB 311 nm emission has got important applications especially in the treatment of vitiligo vulgaris. Sn$^{4+}$ ions also give blue emission at about the same wavelength region and hence the codoping of Sn$^{4+}$ ions with Gd$^{3+}$ ions is an added advantage for enhancement of this important UVB 311nm emission band. With these views a part of the thesis is devoted to the studies on spectroscopic properties of Er$^{3+}$ and Gd$^{3+}$ ions doped Li$_2$O–PbO–P$_2$O$_5$: SnO$_2$ glasses.
Thus the clear objectives of the present investigation are to study

- ac conductivity and dielectric dispersion over a wide frequency range from 100 Hz to 1 MHz and in the low temperature range viz., 200 to 370 K of Li$_2$O–PbO–P$_2$O$_5$: SnO$_2$ glasses.
- the influence of Sn$^{4+}$ ions on the emission features of Er$^{3+}$ ions (especially the orange emission band) in Li$_2$O–PbO–P$_2$O$_5$ glass system.
- to throw some light on the influence of tin ions on the enrichment of UVB 311 emission of Gd$^{3+}$ ions in Li$_2$O–PbO–P$_2$O$_5$ glass system.

1.5 Contents of the present work

The glasses used for the present studies are:

1. 20 Li$_2$O–20PbO–(60-x)P$_2$O$_5$: x SnO$_2$,
2. 20 Li$_2$O–20PbO–(59-x)P$_2$O$_5$–1.0Er$_2$O$_3$: x SnO$_2$,
3. 20 Li$_2$O–20PbO–(59-x)P$_2$O$_5$–1.0Gd$_2$O$_3$: x SnO$_2$

with x=0, 1.0, 3.0, 5.0, 7.0

The studies carried out are:

(v) infrared spectral studies in the wavenumber range 400–2000 cm$^{-1}$ and the study of the effect of concentration of tin ions on the position and intensity of various vibrational bands;

(vi) electron spin resonance measurements of Gd$^{3+}$ doped glasses at room temperature;
(vii) dielectric properties viz., dielectric constant $\varepsilon'$, dielectric loss tan $\delta$ and ac conductivity $\sigma_{ac}$, electric moduli and the impedance parameter in the frequency range $10^2$–$10^6$ Hz and in the temperature range 200–370 K;

(viii) optical absorption, photoluminescence and luminescence decay studies of $\text{Er}^{3+}\text{Sn}^{4+}$ and $\text{Gd}^{3+}\text{Sn}^{4+}$ ions doped $\text{Li}_2\text{O-PbO-P}_2\text{O}_5$ glasses.
References


