General introduction scope and contents of present work

1.1 Introduction

In day to day language a glass is defined as a fragile and transparent material. Glasses are particularly non-crystalline substances obtained from melt quenching between two metallic plates [1-4]. Thus, glass is an amorphous material, completely lacking in long range order of periodic atomic structure and exhibiting a region of glass transformation nature.

Over the past several years, glass science has been accelerating with the development of many new glasses as novel optical materials [5-10]. From the literature it has been learnt that there is still a great deal of potential in finding several more new optical systems, to explore their uses in the development of some important electro chromic, laser materials and also in fiber optic materials.

An analysis of the physical properties of glasses is of considerable importance for gaining an insight into the fundamental process occurring in them. Such a study paved the way for the application of some of the glasses in technology. In fact, the physical properties of glasses to a large extent are controlled by the structure, composition, and the nature of the bonds of glasses. The investigation of the changes in the physical properties of glasses with controlled variation of factors such as chemical composition and doping is of considerable interest from the application point of view.

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

![Diagram of volume change with temperature](image.png)

**Fig. 1.1** Schematic illustration of the change in volume with temperature as super cooled liquid is cooled through the glass transition temperature \( T_g \).

When a liquid is cooled from high temperature, crystals may form at the melting point \( T_m \). If crystallization takes place, there will be sudden variation in the volume at \( T_m \) and, if 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 in Fig. 1.1.

Certain materials readily form glasses on cooling a melt and certain chemical compositions of materials have a greater glass forming tendency. Even today the reason for the above said phenomenon is not known. However, there are so many factors which play an important 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, and the average atomic coordination number.

The credit of categorizing the materials into glass formers and non-glass formers goes to Zachariasen [11]. He fabricated the glasses with five oxide materials which were 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 mixed up with other oxides (upto a 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 [12] 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.

Based on these rules, a continuous random network of a glass can be formed as depicted in Fig. 1.2. As per these rules, the oxides of the type AO, A$_2$O should not form glasses, and the rules are satisfied only for oxides of the type A$_2$O$_3$, AO$_2$ and A$_2$O$_5$. The presence of 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$_2$O, Na$_2$O, K$_2$O, PbO, CaO, CdO are some of the basic examples of modifiers in glass network. These modifiers break up the continuous network by introducing non-bridging oxygens, as demonstrated in Fig.1.3. A third group of oxides, known as intermediate class of oxides, also exist which by themselves do not readily form glasses but do so when
mixed with other oxides; such oxides are known as intermediate glass modifiers. The examples of this group are TeO$_2$, WO$_3$, MoO$_3$, Al$_2$O$_3$, Ga$_2$O$_3$ and V$_2$O$_5$. Excellent reviews and articles on the topology of the glass by Vanvotert [13], Elliott [14], Polk [15], Ingram [16], give useful information.

![Fig. 1.2](image1.png)

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

![Fig.1.3](image2.png)

**Fig.1.3** Structure of a glass with modifier oxide.
During the last few decades, different types of inorganic glasses have been produced with an attempt to accomplish suitable electrical, mechanical and optical characteristics. These characteristics are linked with 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 ionic devices. Work along these lines was carried out on a number of glasses giving valuable information [17-24]. Analysis on electrical properties such as dielectric properties and dielectric breakdown strength of glasses provide information about their insulating character. Studies on the optical properties like optical absorption, and FTIR can be used as probes to throw some light on the structural properties of these glasses.

1.2 Scope of the Present Work

When compared to the silicate glasses the structure of borate glasses is more complex due to the fact that both trigonal BO₃ and tetrahedral BO₄ polyhedra form the 3D network. The pure B₂O₃ glass is formed from BO₃ triangles (BO₃/2) ordered in six-membered boroxol rings. Due to the equilibria between the three- and four-coordinated boron, the compositional dependence of various physical properties of alkali-borate and alkaline earth-borate glasses is not monotonous. Borate-based glasses have been drawing attention for years because of the boron anomaly [25] and also B₂O₃ is one of the best glass formers. The borates with a modifier like PbO will form stable glasses. B₂O₃ glasses are found to be very interesting amorphous materials whenever the specific structure and physical properties of which taken into consideration. When P₂O₅ is added to borate glasses, it lowers the melting and softening temperatures and shifts
the optical edge towards lower wavelength. The phosphate ions may influence the physical properties of glasses very strongly because these ions participate in the glass network with different structural groups, viz. $\text{PO}_4$, $\text{PO}_4^{3-}$, $\text{P-}\text{O}^-$ and $\text{P=O}$, etc. In recent years much research work is going on in improving the physical properties and chemical durability of various glass systems containing $\text{P}_2\text{O}_5$. By the addition of transition metal ions to the borate glasses, they would exhibit specific physical properties [26,27]. The conductivity of borophosphate glasses can be improved by adding $\text{Li}_2\text{O}$ to the glass system. The mixed electronic and ionic conduction of these glasses depend on the glass composition. Alkali lead borophosphate glasses are well known due to several potential applications such as radiation dosimetry in view of the fact that their effective atomic number is very close to that of human tissue, phosphors, solar energy converters, vacuum ultraviolet (VUV) optics and semiconductors lithography and in a number of electronic devices [26-28].

Alkali lead borophosphate glasses are transparent from the near ultra-violet (UV) to the near infrared (IR) region. They are resistant to atmospheric moisture and are capable of accepting large concentrations of transition metal ions. Addition of $\text{Li}_2\text{O}$, $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$, into the glass matrix lowers the viscosity and decreases the melting temperature to a substantial extent and further it acts as an effective mineralizer, giving scope for the formation of large concentration of color centers when the glasses are exposed to ionizing radiations [29]. $\text{Li}_2\text{O}-\text{PbO-} \text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glass systems in particular are very stable against devitrification. The origin of the properties of lithium lead borophosphate glasses has been strongly correlated to the local order around boron atoms. The coordination geometry of boron atoms has been shown to be strongly
dependent on the composition of the glasses and on the chemical nature of the network modifier. For example the addition of alkali oxide in to the borate glass network changes the coordination of boron atom from $\text{BO}_4$ tetrahedral units to $\text{BO}_3$ trigonal units. Alkali oxides are expected to make the glasses more moisture resistant. The addition of alkali oxide, like $\text{Li}_2\text{O}$, $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$ to $\text{B}_2\text{O}_3$ glasses further makes them suitable for radiation dosimetry applications [30]. Modifier oxide like $\text{CaO}$, $\text{SrO}$, $\text{BaO}$ and $\text{PbO}$ enters the glass network by breaking up the random network. Normally the oxygens of such alkaline earth and lead oxide break the local symmetry while the cations ($\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$ and $\text{Pb}^{2+}$ions) occupy the interstitial positions in the glass system [31]. Glasses containing transition metal ions have attracted a great interest because of their uses as memory and photo conducting devices [32], cathode materials in batteries [33], magnetic materials [34] etc. They also find potential applications in the development of new tunable solid-state lasers, solar energy converters and fiber-optic communication devices [35].

A very little addition of borate and some modifiers (e.g., $\text{CaO}$, $\text{SrO}$, $\text{BaO}$, $\text{ZnO}$, $\text{PbO}$) promotes reasonably excellent glass formation. With large additions, widespread areas of glass formation are detected [2]. Besides, glasses mixed with transition metal ions are expected to be promising candidates as gain media for ultra-broadband optical fiber amplifiers, tunable lasers and ultra short pulse lasers in telecommunication wavelength regions over the glass materials. This is because of the dominance of non-radiative losses over the relaxations of the excited states of transition metal ions/lasing spices in the glass materials. Besides, the outer d-electron orbital functions of transition metal ions have large radial distribution. Hence, they are extensively used to probe into
the glass matrix since they are very sensitive to the changes in the surrounding actions. Moreover, transition metal ions are available in different oxidation states along with various coordinations and it leads to significant changes in the physical as well as chemical properties of glass matrix. And the redox ratio \((\text{TM}^{n+}/\text{TM}^{(n+1)+})\) of transition metal ions plays an important role, especially for electrical properties in semiconductor glasses.

Transition metal ions are highly interesting ions to explore the glass network due to their outer d-electron orbital functions have rather broad radial distributions and their response to surrounding atoms are very sensitive; as a result these ions influence the physical properties of the glasses to a greater extent.

Three series of elements are formed by filling the 3d, 4d and 5d shells of electrons. Together these comprise the d-block elements. They are often called ‘transition elements’ because their position in the periodic table is between s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of the s-block, which typically form ionic compounds, and the elements of p-block, which are largely covalent. In s-and p-blocks, electrons are added to the outer shell of the atom 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. \( V^{4+}, V^{5+}, Cr^{3+}, Cr^{4+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, \) and \( Fe^{3+} \).

### Table 1.1

**Oxidation states of transition metal elements**

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Among the first five transition metal elements, the correlation between the electronic structures and minimum and maximum oxidation states in simple compounds is complete. In the highest oxidation states of these first five elements, all of the s and d electrons are being used for bonding. Thus the properties depend only on size and valency, and consequently show some similarities with elements of the main groups in similar oxidation states. Once the d⁵ configuration is exceeded, i.e. in the first 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 moving 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.

Recently considerable attention has been paid to research in inorganic glasses alloyed with transition metal ions because of their technological importance in the development of tunable solid state lasers, new luminescence materials, solar energy converters and fiber optic communication devices.

In view of these, it is felt worth to have some understanding over the dielectric and spectroscopic properties of $K_2O$-$BaO$-$B_2O_3$-$Fe_2O_3$, $RO$-$Na_2O$-$B_2O_3$-$Fe_2O_3$ ($R$=Ca, Sr and Ba) and $Li_2O$-$PbO$-$B_2O_3$-$P_2O_5$ glasses doped with different transition metal oxides such as $Cr_2O_3$, $V_2O_5$ and $MnO$ individually.

The studies on dielectric properties, dielectric breakdown strength 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 evaluating the insulating character and mechanical strength of the glasses. Whereas the explorations on spectroscopic (viz., optical absorption, electron spin resonance and infrared spectra) properties give the information on the position and oxidation states of the transition metal ions in the glass network and help to judge the suitability of these glasses 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 $K_2O$-$BaO$-$B_2O_3$, $CaO/SrO/BaO$-$Na_2O$-$B_2O_3$ and $Li_2O$-$PbO$-$B_2O_3$-$P_2O_5$ glasses is given below:

### 1.2.1 Physical parameters

Some physical parameters useful for characterization of the selected glasses doped with transition metal oxides are determined from the measured value of density (d) and the average molecular weight $M$, using the following equations [36-39]:

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

\[
(i) \quad N_i \quad (10^{22} \text{ ions /cm}^3) = \frac{N_i x \rho}{M} \quad (1.1)
\]

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

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

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

### 1.2.2 Dielectric properties

When an insulating glass (a dielectric) like $Li_2O$-$PbO$-$B_2O_3$-$P_2O_5$ glass is kept in an 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. In addition 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) [40].

When the dielectric is situated 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 [41].

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

$$
\varepsilon^* = \varepsilon' + \frac{\varepsilon_s - \varepsilon'_\infty}{1 + i\omega \tau}
$$

(1.4)

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 polarisation. Separating this equation into its real and imaginary parts, one obtains:

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

(1.5)
The dielectric loss of the material (generally expressed by tan\(\delta\)) is given by the expression:

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon'_s - \varepsilon'_\infty) \omega \tau}{\varepsilon'_s + \varepsilon'_\infty \omega^2 \tau^2}
\] (1.7)

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

\[
\tan \delta = \frac{4 \pi \sigma}{\omega \varepsilon'} + \frac{(\varepsilon'_s - \varepsilon'_\infty) \omega \tau}{\varepsilon'_s + \varepsilon'_\infty \omega^2 \tau^2}
\] (1.8)

### 1.2.3 Dielectric breakdown

The study on the electric breakdown of glass dielectrics is of extreme importance in deciding the insulating character of the glass [42]. Breakdown strength \(E_b\) is nothing but the destruction of the dielectric by the forces of an electric field. The secondary process (heating, chemical reactions etc.,) which may occur in a dielectric under the action of an electric field and facilitate the progress of the puncture (which never takes place with a purely electric breakdown). An electric breakdown develops as a result of interaction of free charge particles (electrons, ions) accelerated by an electric field with the particles of a dielectric, or as result of inelastic displacement of bound charges in a dielectric under the action of an external electric field.
The electric breakdown is distinguished by:

(a) a short time of development of breakdown (commonly of the order of microseconds and even less)

(b) a small dependence of $E_b$ on the frequency of the applied voltage

(c) a small dependence of electric breakdown strength on temperature

(d) a comparatively little pronounced (at any rate with a uniform electric field) dependence of electric strength on the dimensions of the dielectric and the electrodes.

1.2.4 Optical absorption

Optical radiation interacts with materials in different ways depending upon the substance 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 spectrum that 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 in 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 [43] and further developed by Schlapp and Penny [44], Van Vleck [45] and others. The principal symmetry of the transition metal complexes is usually an octahedral one while in a few cases, tetrahedral, square planar and lower symmetries occur. In a complex the site symmetry of anions is always degraded from the extremely high spherical one to a lower symmetry. Two types of symmetries, known as octahedral (designated by $O_h$) and tetrahedral (designated by $T_d$) are important. The corresponding molecular structures having these symmetries are shown diagrammatically in Fig. 1.4

![Diagram of Octahedral and Tetrahedral Point Groups](image)

**Fig. 1.4** (a) Regular Octahedron point group ($O_h$)  (b) Regular Tetrahedron point group ($T_d$)

A free d-electron has five-fold degeneracy with all the five d-orbitals, namely $d_{xy}$, $d_{yz}$, $d_{zx}$, $d_{x^2-y^2}$ and $d_{z^2}$ possessing the same energy (Fig.1.5 a). In a weak field
approach, one tries to understand the effect of crystal fields on the free ion terms (Fig. 1.5 b, c, d).

**Fig. 1.5** (a) Five d orbitals of $T_{2g}$ orbitals and $e_g$ orbitals
Fig. 1.5 (b) Detailed spectral information on various transition metal (from $d^1$ to $d^4$) ions.
Fig. 1.5 (c) Detailed spectral information on various transition metal (from $d^6$ to $d^9$) ions
Fig. 1.5 (d) Energy spectra of transition metal ions.
For d case, the application of the group theory results in the splitting of $^2D$ state into $e_g$ and $t_{2g}$ representations in octahedral crystal field. The crystal field potential acting on the ion is given by

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

(1.9)

Where $D = (Ze/4a^5)$. This potential has to be applied on the wave functions which transform as $t_{2g}$ whereas $d_{x^2 - y^2}$ and $d_{z^2}$ transform as $e_g$, and

$$\langle t_{2g}/V_{oct}/t_{2g} \rangle = -4D_q \quad (1.10)$$

$$\langle e_g/V_{oct}/e_g \rangle = 6D_q \quad (1.11)$$

so that the separation $D_q$ 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. 1.6. If the symmetry is lower than octahedral, say tetragonal or orthorhombic, then these levels will split into levels of lesser degeneracy. The above discussion is valid for single electron d orbitals. Similar procedure is adopted for multi electron system where the terms will be split into various irreducible representations.

In the case of strong octahedral crystal fields, the single electron $t_{2g}$ and $e_g$ functions become the basis. The various configurations of many electron systems are obtained by filling the $t_{2g}$ shell first and then the $e_g$ shell. Thus for example, the $d^2$ ion has $t_{2g}^2, t_{2g}^1 e_g^1$ and $e_g^2$ configurations with energies - $8D_q, 2D_q$ and $12D_q$, respectively.
The electrostatic energy values for different states have been calculated by Tanabe and Sugano [46] and Griffith [47] and they have presented these energy values in the form of matrices. For convenient interpretation of the observed optical spectra, Tanabe and Sugano have drawn energy level diagrams between E/B and D_q/B for various d^n configurations 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.

Fig. 1.6 Diagram showing relative energy of e_g and T_{2g} orbitals resulting from the splitting of d orbitals by octahedral environments.
1.2.5 Electron spin resonance

Electron paramagnetic resonance (EPR) has been developed as an immensely sensitive and important spectroscopy technique, which is widely used to study systems possessing unpaired electrons. In condensed matter physics, EPR is used as a powerful tool to study the lowest energy levels, hence, the electronic state of the unpaired electrons of paramagnetic species in solids. This method 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 bearing 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 possessing 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 EPR 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 EPR.

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

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

(1.12)

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

\[
\mu = -g\beta J
\]  

(1.13)

where

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

(1.14)

which is familiar as the Lande splitting factor for free ion

and

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

(1.15)

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 [48]

\[
\omega_L = \gamma H
\]  

(1.16)

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
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.

\[
h \nu = g\beta H. \tag{1.17}
\]

**Fig. 1.7** Zeeman energy for a single unpaired electron as function of magnetic field \( H \). A magnetic dipole aligned parallel to \( H \) has lower energy while a magnetic dipole aligned antiparallel to \( H \) has higher energy.

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 \( H \), will have two energy levels, as shown in Fig. 1.7, if \( g \) is constant. The energies of these levels are

\[
E_{\pm 1/2} = \pm (1/2)g\beta H, \tag{1.18}
\]
and the energy difference between the two levels for a given value of $H$ is

$$\Delta E = g\beta H$$  \hspace{1cm} (1.19)

The above equation shows that the energy difference between the two levels increases linearly with $H$. In the EPR technique, the magnetic dipole transitions between the two levels in the presence of a uniform magnetic field $H$ and an alternating magnetic field polarized perpendicular to $H$ are induced by an incident radiation of frequency $\nu$ if the quantum condition (1.17) and $\Delta M_s = \pm 1$ are satisfied. This will give rise to only one absorption line. When the orbital angular momentum is not zero then the degenerate energy level will split into $(2J+1)$ levels and the conditions for the transitions by absorption of energy is given by Eq. (1.17) and $\Delta M_J = \pm 1$. Such a situation will give rise to multiple absorption lines. The resonance condition (1.17) 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 EPR 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. Besides this one may vary certain other external parameters like temperature, composition etc., which would possibly change EPR parameters leading to additional
information on the system under study. A vast discussion on EPR technique and its applications are available in a number of pioneering books written by many authors [49-53].

a) General Spin- Hamiltonian

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

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

The concept of Hamiltonian was originally developed by Pryce [54] and Abragam and Pryce [55] to interpret the observed resonance of ions in the first transition series. The concept was subsequently extended by Elliott and Stevens [56] to interpret the paramagnetic behavior observed for the rare earth ions. The terms in the general Hamiltonian for an ion in a crystalline environment can be written as [57].
\[ H = H_E + H_{LS} + H_{SI} + H_Q + H_V + H_{SH} + H_{IH} \quad (1.20) \]

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

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

\[
H_E = \sum_i \left[ \frac{p_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{ij} \frac{e^2}{r_{ij}} \quad (1.21)
\]

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

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

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

\[
H_{LS} = \sum \lambda_{ij} \cdot l_i \cdot s \quad (1.22)
\]

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

\[
H_{LS} = \lambda \cdot L \cdot S \quad (1.23)
\]

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 in the range \( 10^2 \) to \( 10^3 \text{ cm}^{-1} \).
iii. $H_{SI}$ describes the magnetic interaction between each electron and the nucleus

$$H_{SI} = \sum a_i \cdot J_i \cdot I_i$$

(1.24)

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

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

$$H_Q = \sum I_i \cdot Q_i \cdot I_i$$

(1.25)

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

$$H_v = \sum e_i \cdot V(r_i)$$

(1.26)

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.

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

(1.27)

$$H_{IH} = \hbar / 2 \pi \sum I_i \cdot B$$

(1.28)

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

b) Line shapes

The most commonly observed shape functions in EPR spectroscopy are Lorentzian and Gaussian, described by the functions given below.
\[ I = \frac{I_0}{T_2^2 (B - B_r)^2 + 1} \]  

(1.29)

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

(1.30)

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 follows the eq. (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. 1.8.
c) Line Width and Intensities

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

![LORENTZIAN and GAUSSIAN line shapes](image)

**Fig. 1.8** The characteristic Lorentzian and Gaussian line shapes.

Fig. 1.9 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.
Fig. 1.9 The method of finding the area under the first derivative absorption curve by numerical double integration method.

For EPR signals, the line widths are measured from the maximum and minimum line positions at the first derivative curve. The EPR 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 EPR signals depends on various factors (1) Concentration of the paramagnetic ion (2) the micro wave frequency (3) the power of micro waves (4) the transition probability and (5) the temperature.

1.2.6 FTIR spectra

Infrared absorption spectra of glasses can provide significant and valuable information regarding the arrangement of atoms, nature of chemical bonding among them, and 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 glass and hence correlation of IR absorption bands with different units of vitreous structure. In the case of arsenate glasses, the basic glass contains AsO$_4$/AsO$_3$ structural units in the phosphate network and when a cation such as Zn$^{2+}$ is added, it may enter the network or 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 a glass are independent [58-60], 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 bands observed in IR spectra of the glasses of the present work, in general, is 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 for some of the vibrational frequencies assigned to arsenate, antimony and zinc oxide groups. Such justification could be extended even for the IR spectrum observed for ZnO, As$_2$O$_3$, Sb$_2$O$_3$ groups provided the force constants corresponding to Zn-O, As-O, Sb-O stretching are known.
When the characteristic group frequencies arise from the vibrations of pure stretching nature or of pure bending nature the wavenumber \( \bar{\nu} \) is 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, \( \mu \) is the reduced mass of the diatomic or triatomic group, \( K \) is the stretching or bending force constant. For certain diatomic and triatomic groups, the force constant has been evaluated using various empirical formulae available in the literature.

1.3 Brief review of the previous work

Nageswara Rao et al [61] have reported the dielectric and optical properties of AF-PbO-B_2O_3 (where A=Na, Li, K) glasses. The comparison of the results of three series indicates the lithium series glasses are the better candidates for the practical applications. They have also carried out the LiF-Sb_2O_3-B_2O_3 glassed doped with copper and nickel ions and the results of these studies were analyzed with the aid of data of optical absorption and EPR spectra on these glasses. Recently, Srilatha et al [62] have reported the electrical, dielectric and spectroscopic studies on LiI-AgI-B_2O_3 glasses doped with some transition metal ions. Sreekanth Chakradhar et al [63] have investigated lead tetraborate glasses by EPR and optical studies. Venkat Reddy et al [64] have reported optical and thermo luminescence properties of R_2O-RF-B_2O_3 (where R= Li and Ni) glass system. They have concluded that the thermo luminescence studies on these glass systems showed a quenching of TL output with increase in the concentration. Venkateswara Rao et al [65] have studied thermo luminescence quenching by manganese ions in MO-CaF_2-B_2O_3 glasses. The probable mechanism
responsible for quenching of TL emission by these glasses has been suggested with the aid of optical absorption, IR spectra and differential scanning calorimetric studies. They are also carried out thermo luminescence studies on X-ray irradiated Li$_2$O-CaF$_2$-B$_2$O$_3$ glasses doped with different concentrations. Veerabhadra Rao et al [66] reported dielectric relaxation and a.c. conduction phenomena of PbO-PbF$_2$-B$_2$O$_3$ glasses and these glasses are characterized by X-ray diffraction and differential thermal analysis. Tercznska-Madej et al [67] investigated coordination and valence state of transition metal ions in alkali-borate glasses and concluded that a decrease of the electronegativity of the modifiers (Li→Na→K) and an increase of the glass matrix basicity cause a shift of the oxidation/reduction equilibrium towards higher valences of the transition metals. Sanjay et al [68] have reported study of structural, optical and transport properties of semiconducting Fe$_2$O$_3$-PbO-B$_2$O$_3$ glasses and the dc conductivity of these samples was measured in the temperature range 473-623 K. Shiv Prakash Singh et al [69] have investigated EPR, FTIR, optical absorption and photoluminescence studies of Fe$_2$O$_3$ and CeO$_2$ doped ZnO-Bi$_2$O$_3$-B$_2$O$_3$ glasses. Zinc-bismuth-borate glasses with iron and cerium doping have been prepared by melt quenching technique. Hulpus et al [70] have reported spectroscopic (FTIR and Raman) studies on CuO-B$_2$O$_3$-PbO-Ag$_2$O glass systems. Both spectroscopic techniques provide information regarding the local structure revealing the presence of borate arrangements such as: di-,tri-, tetra-, ortho-, meta-, pyro-borate and boroxol rings. The conversion between the tri-coordinated boron atoms and tetra-coordinated ones was also followed. Simon and Eniu [71] analysed spectroscopic characterization of local structure in Y$_2$O$_3$-B$_2$O$_3$-Bi$_2$O$_3$ glasses doped with gadolinium. Vibrational spectroscopy has proven
to be powerful and effective tool for characterizing the structure of local arrangements in glasses. Karthikeyan et al [72] have studied optical properties and ultra fast optical nonlinearity of ytterbium doped sodium borate and bismuthate glasses. Local structure of the glasses has been identified by using Fourier Transform Infrared (FTIR) and Raman studies. Sudhakar et al [73] have reported vibrational spectral analysis of structural modifications of Cr$_2$O$_3$ containing oxyfluoroborate glasses. The breaking and reforming of the boroxol ring is explained from the Raman spectral studies of these glasses. Naga Raju et al [74] have investigated the structural role of chromium ions on the improvement of insulating character of ZnO-ZnF$_2$-B$_2$O$_3$ glass system by means of dielectric, spectroscopic and magnetic properties. The analysis of the results indicates that there is a substantial enhancement of insulating strength of these glasses. Ardelean et al [75] have reported the study of copper-doped B$_2$O$_3$, Bi$_2$O$_3$ glass matrix by spectroscopic methods. Complex network structures mainly built by BiO$_3$, BiO$_6$, BO$_3$, BO$_4$ units were revealed for these glasses by means of FTIR measurements. Similar structures were evidenced by means of Raman spectroscopic and additional new structural groups were detected in the glass structures, i.e. pyroborate, chain and ring type metaborate groups. Petru Pascuta et al [76] have studied FTIR and Raman spectroscopic investigation of some strontium-borate glasses doped with iron ions and concluded that in higher concentrations the iron ions break the regulate glass network and determines the appearance of BO$_4$ isolated units. Adamczyk and Handke [77] reported the spectroscopic studies of glasses and glass-ceramics in the Na$_2$O (Li$_2$O)–B$_2$O$_3$-P$_2$O$_5$-SiO$_2$ system. Blaszczak [78] have studied the infrared studies of devetrification of glasses in the Li$_2$O-B$_2$O$_3$-Ge$_2$O$_3$ system.
In spite of the considerable studies are available on different alkali alkaline earth borate and alkali lead borophosphate glass systems, as such no devoted studies are available particularly on \( \text{Li}_2\text{O}\)-PbO-\( \text{B}_2\text{O}_3\)-P\(_2\)O\(_5\) glasses alloyed with transition metal oxides. Hence, there is a lot of scope to investigate on the structural aspects of \( \text{K}_2\text{O}\)-BaO-\( \text{B}_2\text{O}_3\); \( \text{Fe}_2\text{O}_3\), RO-Na\(_2\)O-\( \text{B}_2\text{O}_3\)-Fe\(_2\)O\(_3\) glasses (R=Ca, Sr and Ba) and glass systems like \( \text{Li}_2\text{O}\)-PbO-\( \text{B}_2\text{O}_3\)-P\(_2\)O\(_5\) doped with some transition metal oxides such as Cr\(_2\)O\(_3\), V\(_2\)O\(_5\) and MnO.

1.4 Aim of the present work

Alkali alkaline earth borate glasses like \( \text{K}_2\text{O}\)-BaO-\( \text{B}_2\text{O}_3\), RO-Na\(_2\)O-\( \text{B}_2\text{O}_3\) (where R=Ca, Sr and Ba) and alkali lead borophosphate glasses, like \( \text{Li}_2\text{O}\)-PbO-\( \text{B}_2\text{O}_3\)-P\(_2\)O\(_5\) are known for their significant transmission in the infrared region and possess high refractive index. Thus glasses possessing large non-linear optical susceptibility (\( \chi \)) coefficient, high mechanical strength, and high electrical resistance are transparent to both UV and visible regions. These glasses have potential applications in non-linear optical devices such as ultra fast optical switches and power limiters, broad band optical amplifiers and in a number of solid state ionic devices. Lithium lead borophosphate glasses have several advantages over conventional silicate glasses due to their superior physical properties such as high thermal expansion coefficient, low melting and softening temperatures, and high ultra violet transmission and are expected to be relatively moisture resistant and possess low rates of crystallization. Though few recent studies on certain physical properties of some alkali alkaline earth borate and lithium lead borophosphate glasses are available, the thorough literature survey on these glasses shows detailed investigations on dielectric and spectroscopic properties of
transition metal oxides such as Cr$_2$O$_3$, V$_2$O$_5$ and MnO doped Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses are not available.

Increased demand on diverse applications of modern electronic devices has led to the search for new materials, which will meet the specific requirements. Alkali alkaline earth borate and lithium lead borophosphate glasses are among these materials and have a number of technological applications. These glasses are structurally interesting because they accept a wide range of ion substitution. This glass network expected to show significant improvement in chemical durability while maintaining low glass transformation temperature and softening points. Due to the possibility that a large variety of properties are adjustable by composition and excellent chemical durability these glasses have potential applications. Though a few studies on certain physical properties of some alkali lead borophosphate glasses in general are available in recent years, a thorough literature survey shows that the detailed investigations on dielectric and spectroscopic properties of Cr$_2$O$_3$/V$_2$O$_5$/MnO doped Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$; K$_2$O-BaO-B$_2$O$_3$; Fe$_2$O$_3$, RO-Na$_2$O-B$_2$O$_3$; Fe$_2$O$_3$ (R=Ca, Sr and Ba) glasses in particular are not available.

Study on the dielectric properties helps in estimating the insulating strength of these glasses and enhance the understanding structural aspects of these glasses. Detailed studies on spectroscopic properties (viz., optical absorption, infrared, and EPR spectra) of transitional metal ions doped glasses expected to throw some light on the possible use of these glasses in solid state ionic devices.

Thus the objectives of the present study are to synthesize, characterize and
To have a comprehensive understanding over the influence of iron ions on structural aspects of K$_2$O-BaO-B$_2$O$_3$: Fe$_2$O$_3$ glasses and study the influence of alkaline earth oxides on RO$_2$Na$_2$O-B$_2$O$_3$: Fe$_2$O$_3$ (R=Ca, Sr and Ba) glass system by investigating optical absorption, EPR, FTIR and dielectric properties.

To have an understanding of valence states and the local environment of chromium ions in Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$: Cr$_2$O$_3$ glass network and to probe their role on the structural modifications that take place in the glass network by means of EPR, optical absorption, FTIR and dielectric properties.

To investigate the structural influence of vanadium ions doped Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glasses by studying EPR, optical absorption, FTIR and dielectric properties.

To investigate the structural influence of manganese ions on Li$_2$O-PbO-B$_2$O$_3$-P$_2$O$_5$ glass network with a gradual decrease in the concentration of B$_2$O$_3$ through a detailed investigation on spectroscopic (optical absorption, FTIR and EPR) coupled with dielectric properties.

1.5 Contents of the present work

The glass systems investigated are:

- 10K$_2$O-20BaO-(70-x)B$_2$O$_3$: xFe$_2$O$_3$ \hspace{1cm} (0 \leq x \leq 1) and
- 20RO-10Na$_2$O-69B$_2$O$_3$-1Fe$_2$O$_3$ \hspace{1cm} (R=Ca, Sr and Ba)
- 20Li$_2$O-20PbO-45B$_2$O$_3$-(15-x)P$_2$O$_5$: xCr$_2$O$_3$ \hspace{1cm} (0 \leq x \leq 1)
- 20Li$_2$O-20PbO-45B$_2$O$_3$-(15-x)P$_2$O$_5$: xV$_2$O$_5$ \hspace{1cm} (0 \leq x \leq 2.5)
- 20Li$_2$O-20PbO-45B$_2$O$_3$-(15-x)P$_2$O$_5$: xMnO \hspace{1cm} (0 \leq x \leq 3)

The studies carried out are:
(i) Optical absorption studies in the wavelength range 200-1200 nm, identification of various electronic transitions of transition metal ions.

(ii) Electron spin resonance measurements at room temperature for the identification of structural units and valence states of transition metal ions in the glass network.

(iii) FTIR spectral studies in the wavenumber range 400-1200 cm\(^{-1}\) and the study of the effect of concentration of transition metal ions on the position and intensity of various vibrational band.

(iv) Dielectric properties viz., dielectric constant \(\varepsilon_1\), dielectric loss tan\(\delta\), ac conductivity \(\sigma_{ac}\) and electric modulus \(M\) in the frequency range \(10^3-10^6\) Hz and in the temperature range 30-300 °C and dielectric breakdown strength in air medium at room temperature.
References


