1.1 Introduction

A glass is defined as 'an inorganic product of fusion which has been cooled to a rigid condition without crystallization' according to ASTM [1] and it is a non-crystalline material obtained by a melt-quenching process [2-4]. The words ‘non-crystalline solids’ and ‘glass transition’ suggest that a glass cannot be classified in the category of crystalline materials such as quartz, sapphire, etc. or in the category of liquid. The atomic arrangement of a glass is different from those of crystalline materials and is short-range periodicity [2]. This is similar to the atomic arrangement in a liquid. Thus, glass is an amorphous substance, completely lacking in long range order of periodic atomic structure and exhibiting a region of glass transformation behaviour. Hence, instead of diffraction peaks a halo is seen in the X-ray diffraction patterns of a glass.

Glass can be made with excellent homogeneity in a variety of forms and sizes, from small fibres to meter-sized pieces. In addition, glass can be doped with transition metal, rare earth ions and micro crystallites and a wide range of properties can be chosen to meet the needs of various applications. These advantages of glass materials over crystalline materials are based on the unique structural and thermodynamic features. Glass science, has significantly been progressive with the development of many new glassy materials as novel optical
From literature it has been realized that there is still a great deal of potential research in finding several new optical systems, especially heavy metal oxide (HMO) [GeO$_2$, Sb$_2$O$_3$, Bi$_2$O$_3$] based glasses, to explore their uses in the development of some important electro chromic, laser, photonic materials and also in fibre optic materials [11].

A study of the physico-chemical properties of glasses like density, molar volume, refractive index, molar refraction and even some dielectric properties can be practically described by additive relations. In light of these findings some relations can be estimated which describe the concentration of structural units as a function of modifier oxide concentration in the glass matrix. Such study paved the way for the application of some of the glasses in technology. Further, the physical properties of glasses are controlled by the structure, composition, and the nature of the bonds of glasses. The study of changes in the physical properties of glasses with gradual and controlled variation of different factors such as chemical composition and doping is of considerable interest from the application point of view.

Generally, materials prepared from a melt quenching are referred as glasses. Unlike crystals, these materials do not possess long-range periodicity of the arrangement of atoms. However, the building block AO$_3^-$ is trigonal (where A stands for metal) or tetrahedral, which is a short-range order will be retained in the glass. These materials possess ionic or covalent bonding interactions. When a
liquid is cooled from high temperature, crystallization may take place at the melting point $T_m$. If crystallization takes place then there will be an abrupt change in the volume at $T_m$ and if, glass formation takes place there will be a gradual break in slope. The region where the change of slope occurs is known as glass transition temperature $T_g$. This process of change in volume with temperature as a super cooled liquid through the glass transition temperature $T_g$ is illustrated in Fig. 1.1.

Fig. 1.1 Schematic illustration of the change in volume with temperature of glass forming liquid and non-glass forming liquid.

Why did certain materials readily form glasses on cooling a melt and certain chemical compositions of materials have a greater glass forming tendency?. The perfect knowledge on the answers to these questions is lacking even to the present day. There are several factors which play a significant role in
determining the ease of glass formation for example, chemical, structural properties of the glass system, thermodynamic or free volume aspects of the materials and the average atomic coordination number.

The first successful attempt to categorize materials into glass formers and non-glass formers goes to Zachariasen [12]. He prepared glasses with five oxide materials which are the only known glass formers by themselves: \( \text{SiO}_2 \), \( \text{GeO}_2 \), \( \text{B}_2\text{O}_3 \), \( \text{As}_2\text{O}_3 \) and \( \text{P}_2\text{O}_5 \). Besides this, 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 [13] 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 constructed as shown in Fig. 1.2.
As per these rules, the oxides of the type \( \text{AO} \), \( \text{A}_2\text{O} \) should not form glasses, and the rules are satisfied only for oxides of the type \( \text{A}_2\text{O}_3 \), \( \text{AO}_2 \) and \( \text{A}_2\text{O}_5 \). The presence of cations such as \( \text{A}^+ \) (example \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \) etc.,) \( \text{A}^{2+} \) (example \( \text{Ca}^{2+} \), \( \text{Pb}^{2+} \), \( \text{Cd}^{2+} \) etc.,) other than \( \text{A}^{3+} \) and \( \text{A}^{4+} \) are known as network modifiers. \( \text{Li}_2\text{O} \), \( \text{Na}_2\text{O} \), \( \text{K}_2\text{O} \), \( \text{PbO} \), \( \text{CaO} \) and \( \text{CdO} \) are some of the basic examples of modifiers in glass network. These modifiers break up the continuous network by introducing non-bridging oxygens, as shown 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.

Fig. 1.2 Two dimensional schematic of crystalline and amorphous solids
Fig. 1.3 Structure of a glass with modifier oxide

The examples of such groups 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 [14], Elliott [15], Polk [16], Ingram [17], give useful information. During the last few decades, a large variety of inorganic glasses have been developed with an attempt to achieve suitable electrical, mechanical and optical characteristics. These characteristics are associated with 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 [18-25]. Investigations on electrical properties such as dielectric properties and dielectric breakdown strength of glasses provide an idea about their insulating character. Investigations on the optical properties
such as optical absorption, IR and Raman spectra, can be used as probes to throw some light on the structural aspects of these glasses.

1.2 Scope of the present work

Germania (GeO$_2$) and silica (SiO$_2$) glasses are two of the most commonly studied oxide glasses and are widely considered to be classic network glasses composed of tetrahedra that are linked through their corners to make up a continuous three-dimensional network [26]. The structure of the two networks is considered to be comparable despite differences in bond lengths, angles and the relative size of Ge versus Si [27]. The principle differences between the two oxide glasses is that GeO$_2$ glass has a narrower distribution of T–O–T (T = Ge or Si) angles (~132° versus ~148° – 151°), longer T– O bonds (1.74 versus 1.61 Å), and appears to contain significantly more small 3-membered tetrahedral rings [28-30]. Majérus et al. [31] found that with increasing pressure, Ge in SiO$_2$–GeO$_2$ glasses changes coordination from 4- to 6-fold, with the transformation occurring over larger pressure ranges when the SiO$_2$ content increases.

Recently researchers have focused their attention on glasses based on oxides of heavy metals (TeO$_2$, GeO$_2$, Bi$_2$O$_3$, PbO, etc.) as promising materials for IR technologies, nonlinear optics, and design of laser devices [32]. Germanate glasses, due to the valuable optical properties (high refractive index and dispersion, transmission in the IR region of the spectrum) imparted to the glass by
germanium dioxide (GeO$_2$), are used as specialty glasses, in particular flint glasses with a special dispersion curve; very heavy flint glasses with refractive index 2.14 or higher; glasses for the light-guiding core of an optical fiber; glasses transmitting IR radiation, etc. [33, 34].

Glasses doped with transition metal ions are expected to be promising candidates 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. The outer d-electron orbital functions of transition metal ions have broad 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. Transition metal ions are available in different oxidation states along with various coordinations and it leads significant changes in the physical as well as chemical properties of glass matrix. Heavy metal oxide (HMO) glasses doped with transition metal (TM), therefore, gain importance due to their interesting spectroscopic properties making them suitable for non-linear optical (NLO) applications [35, 36]. The redox ratio (TM$^{n+}$/TM$^{(n+1)+}$) of transition metal ions plays an important role, especially for electrical properties in semiconductor glasses.
Three series of elements are formed by filling the 3d, 4d and 5d shells of electrons, together these constitute the d-block elements. They are often called ‘transition elements’ because their position in the periodic table is between s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of the s-block, which typically form ionic compounds, and the elements of p-block, which are largely covalent. In s- and p-blocks, electrons are added to the outer shell of the atom whereas in d-block they are added to the penultimate shell. Typically transition elements have an incompletely filled d level.

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

One of the most striking features of the transition metal elements is that they usually exist in several different oxidation states (Table 1.1). Furthermore, the oxidation states change in units of one, e.g. Fe$^{2+}$ and Fe$^{3+}$, Mn$^{3+}$ and Mn$^{4+}$. Among the first five transition metal elements, the correlation between the electronic structures and minimum and maximum oxidation states in simple compounds is complete. In the highest oxidation states of these first five elements, all of the s and d electrons are being
Table 1.1

Oxidation states of transition metal elements

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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 d^5 configuration is exceeded, i.e., in the last five elements, the tendency for all the d electrons to participate in bonding decreases.

The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (d electrons shield less efficiently than p electrons, which in turn shield less
effectively than s electrons). Because of this poor screening by d electrons, the nuclear charge attracts all of the electrons more strongly: hence a contraction in size occurs.

In view of these, it is felt worth to have some understanding over the dielectric and spectroscopic properties of ZnF$_2$-R$_2$O$_3$-GeO$_2$ ($R = Bi, Sb$) glasses doped with some para and ferromagnetic transition metal oxides like CuO, Fe$_2$O$_3$, CoO and AgO are investigated.

The investigations on spectroscopic (viz., optical absorption, electron spin resonance, infrared spectra and photoluminescence) properties give the information on the position and oxidation states of the transition metal ions in the glass network and help to assess the suitability of these glasses for practical applications. Further the studies on dielectric properties and their dependence on the composition, structure and various external factors such as dimensions, thermal history of preparation, humidity, radiation effect, mechanical action etc., pave the way for estimating the insulating and mechanical strength of the glasses.

A preliminary description of the above mentioned properties along with their relation to some of the investigations (similar to those of present work) on modified antimony/bismuth germanate 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 estimated from the measured value of density ($\rho$) and the average molecular weight $\overline{M}$, using the following equations [37-40].

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

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

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

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

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

1.2.2 Optical absorption

Optical radiation interacts with materials in a variety of ways depending upon the material and the wavelength of the optical radiation, giving rise to the optical spectra, which could be either emission or absorption spectra in solids, normally it is the absorption 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 around the transition metal ion, 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 [41] and further developed by Schlapp and Penny [42], Van Vleck [43] 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.

Fig. 1.4 (a) Regular Octahedron point group (O\(_h\)).(b) Regular Tetrahedron point group (T\(_d\))

Fig. 1.4 (a) Five d orbitals of T\(_{2g}\) orbitals and e\(_{g}\) orbitals.
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.1.4 a). In a weak field approach, one tries to understand the effect of crystal fields on the free ion terms (Fig. 1.4 b, c, d).
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

$$V_{\text{oct}} = D(x^4+y^4+z^4-(3/5)r^4)$$  \hspace{1cm} (1.4)

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

$$<t_{2g}/V_{\text{oct}}/t_{2g}> = -4D_q$$  \hspace{1cm} (1.5)

$$<e_g/V_{\text{oct}}/e_g> = 6D_q$$  \hspace{1cm} (1.6)

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 - $8Dq$, $2Dq$ and $12Dq$, respectively.
Fig. 1.6 Diagram showing relative energy of $e_g$ and $T_{2g}$ orbitals resulting from the splitting of d orbitals by octahedral environments.

The electrostatic energy values for different states have been calculated by Tanabe and Sugano [44] and Griffith [45] 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.
1.2.3 Electron spin resonance

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

1. Atoms having odd number of electrons, e.g., atomic hydrogen and lithium atom.
2. Molecules with odd number of electrons such as NO, and triplet state molecules like oxygen molecule.
3. Ions having partially filled inner electronic shells, e.g., iron, rare earth ions etc.
4. Defects produced in a solid by irradiation.
5. Free radicals, e.g., CH\(_3\) and diphenyl-picrylhydrazyl.
6. Conduction electrons in metals, semiconductors and dilute alloys etc.
When a system having non zero angular momentum and magnetic moment is placed in an external magnetic field, each degenerate electronic level splits into a number of levels depending upon the value of angular momentum (Zeeman splitting). The ESR technique, basically, is the observation of the transitions induced by an electromagnetic radiation of appropriate polarization and energy (frequency) between these Zeeman levels. The energy separation of these levels is typically of the order of $1 \text{ cm}^{-1}$ (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

$$\hat{J} = \hat{L} + \hat{S}. \quad (1.7)$$

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

$$\hat{\mu} = -g_\beta J \quad (1.8)$$

where

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \quad (1.9)$$

which is known as the Lande splitting factor for free ion
and \[ \beta = \frac{e \hbar}{2mc} = 9.274096 \times 10^{-27} \text{erg/gauss} \quad (1.10) \]

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 [46]

\[ \omega_L = \gamma H \quad (1.11) \]

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

\[ h \nu = g \beta H . \quad (1.12) \]

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 \( H \), will have two energy levels, as shown in Fig. 1.7, if \( g \) is constant. The energies of these levels are
E_{\pm1/2} = \pm(1/2)g\beta H, \quad (1.13)

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

$$\Delta E = g\beta H \quad (1.14)$$

The above equation shows that the energy difference between the two levels increases linearly with $H$. In the ESR 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 (1.12) 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. (1.12) and $\Delta M_J = \pm 1$. Such a situation will give rise to multiple absorption lines. The resonance condition (1.12) 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 [47-51].
a) General Spin- Hamiltonian

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

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

The concept of Hamiltonian was originally developed by Pryce [52] and Abragam and Pryce [53] to interpret the observed resonance of ions in the first transition series. The concept was subsequently extended by Elliott and Stevens [54] to interpret the paramagnetic behaviour observed for the rare earth ions. The
terms in the general Hamiltonian for an ion in a crystalline environment can be written as [55].

\[
H = H_E + H_{LS} + H_{SI} + H_Q + H_V + H_{SH} + H_{lH}
\]

(1.15)

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

\[
H_E = \sum_i \left[ \frac{P_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{ij} \frac{e^2}{r_{ij}}
\]

(1.16)

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 \(10^5\) cm\(^{-1}\).

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

\[
H_{LS} = \sum \lambda_{ij} \cdot l_i \cdot s
\]

(1.17)

Where \(l\) is the orbital angular momentum of the individual electron \(s\) is the spin angular momentum of the individual electron and \(\lambda_{ij}\) is the spin – orbit coupling constant. This can be written in a simple form as
\[ H_{LS} = \lambda \ L \cdot S \]  \hspace{1cm} (1.18)

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 \( 10^3 \) cm\(^{-1}\).

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

\[ H_{SI} = \sum a_i \cdot \mathbf{J}_i \cdot \mathbf{I}_i \]  \hspace{1cm} (1.19)

Where \( \mathbf{J}_i \) is the total angular momentum of the \( i^{th} \) electron and \( \mathbf{I}_i \) is the nuclear spin. The magnitude of this interaction will be of the order of \( 10^{-2} \) cm\(^{-1}\).

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

\[ H_Q = \sum \mathbf{I}_i \cdot \mathbf{Q}_i \cdot \mathbf{I}_i \]  \hspace{1cm} (1.20)

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

\[ H_v = \sum e_i \, V(r_i) \]  \hspace{1cm} (1.21)

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

\[
H_{\text{SH}} = \beta \left( \mathbf{L} + g_e \mathbf{S} \right) \cdot \mathbf{B} \quad (1.22)
\]

\[
H_{\text{IH}} = \hbar / 2 \pi \sum_i -\gamma_i \cdot I_i \cdot \mathbf{B} \quad (1.23)
\]

Where $\gamma_i$ is the gyrometric ratio of the $i^{\text{th}}$ 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.

\[
I = \frac{I_0}{T_2^2(B-B_r)^2 + 1} \quad (1.24)
\]

\[
I = I_0 \exp \left[ -b (B-B_r)^2 T_2^2 \right] \quad (1.25)
\]

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 develops in the 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 nearby host molecules. The observed EPR spectra will be a superposition of shapes from all the spins with their local fields. Since the local

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

fields will be randomly distributed, the total line shape results in a Gaussian line shape according to equation (1.25). 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 $h_r$ of the EPR signal corresponding to the centre of $r^{th}$ interval is noted and the area under the curve can be calculated from the equation.

\[
\text{Fig. 1.9} \quad \text{The method of finding the area under the first derivative absorption curve by numerical double integration method.}
\]

\[
\text{Fig. 1.9} \quad \text{shows the method of finding the area under the first derivative absorption curve by numerical double integration method. The accuracy of this method depends on the number of intervals and complexity of the spectrum. Using}
\]

31
about 8 to 10 intervals per peak, the error in calculating the area will likely be within 2 to 3% in Gaussian curves. For Lorentzian curves, the error may be greater due to the presence of long tails. For ESR signals, the line widths are measured from the maximum and minimum line positions at the first derivative curve. The ESR lines always have a finite width due to electrons interacting magnetically with the environment of the sample. Hence, from the line width and the rate of build up or decay of the line intensity, one can obtain information about spin environment.

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

1.2.4 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 bismuth borate glasses, the basic glass contains $\text{BO}_4/\text{BO}_3$ structural units along with $[\text{BiO}_3]$ pyramids and the distorted $\text{BiO}_6$ polyhedra as the main structural unit in the network and when modifying cations such as $\text{Ca}^{2+}/\text{Sr}^{2+}/\text{Ba}^{2+}$ are added, they 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 [56-58], 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 borate, bismuth and modifying oxide groups. 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:
where \( c \) is the velocity of light, \( \mu \) is the reduced mass of the overall network, \( K \) 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.

**1.2.5 Raman spectra**

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

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

![Schematic Raman spectrum diagram]

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

In the present study the Raman spectroscopy has been used for identifying various structural units like ZnO₄, GeO₄ and BiO₃, in the glass matrix and the change in the concentration of these structural units with the varying concentration of the dopant ions (CuO, Fe₂O₃, CoO and AgO). In certain cases, it could also be possible to identify whether the dopant ion occupy either tetrahedral or octahedral positions in the glass network.
1.2.6 Dielectric properties

When an insulating glass (a dielectric) like ZnF$_2$-Bi$_2$O$_3$-GeO$_2$ glass is placed in an external electric field, two types of polarisations – 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) polarisation can arise. These three polarisations 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 polarisation, called the space charge polrisation comes into play. The total polarisation is sum of these four polarisations (assuming that they act independently) [59].

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 [60].

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

\[
\varepsilon^* = \varepsilon'_\infty + \left[ \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + i\omega\tau} \right]
\]

(1.27)

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 can obtain:

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

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

(1.28)

and

\[
\delta'' (\omega) = (\delta'_s - \delta'_{\infty}) \frac{\omega \tau}{(1 + \omega^2 \tau^2)}
\]

(1.29)

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

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

(1.30)

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

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

(1.31)
1.2.7 *Dielectric breakdown*

The study on the electric breakdown of glass dielectrics is of extreme importance in deciding the insulating character of the glass [61] Breakdown strength $E_b$ is nothing but the destruction of the dielectric by the forces of an electric field. The secondary processes (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.
1.3 Brief review of the previous work

Terakado and Tanaka [62] studied the changes in GeO$_2$ glass in terms of its optical and structural properties and concluded that photo-induced optical changes in GeO$_2$ are similar to those in SiO$_2$. Henderson et al. [63] studied the structure of GeO$_2$–SiO$_2$ glasses using Raman spectroscopy. They reported that SiO$_2$–GeO$_2$ binary are not phase separated, are a continuous random network, but one in which mixing of GeO$_4$ and SiO$_4$ tetrahedra is non-ideal (GeO$_4$ tetrahedra preferring to insert initially into the small SiO$_4$ tetrahedral rings to form larger mixed GeO$_4$/SiO$_4$ rings) with the result that the network has regions that are SiO$_2$-like, GeO$_2$-like and mixed SiO$_2$–GeO$_2$-like. At high temperatures the mixed rings break up to form small 3-membered GeO$_4$ rings and 6-membered SiO$_4$ rings rather than the original 4- and 3-membered SiO$_4$ rings. Differential thermal analysis, X-ray diffraction, Raman scattering and UV–visible spectroscopic investigations of TeO$_2$ – Bi$_2$O$_3$ – GeO$_2$ carried out through the analysis of $T_g$, $T_c$, structural, thermal and optical properties by Shivachev et al. [64]. They reported that, the synthesized glasses can double the frequency of coherent electromagnetic emission with wavelengths higher than 800 nm. Cheng et al. [65] studied the thermal behaviour of GeO$_2$ doped PbO–B$_2$O$_3$–ZnO–Bi$_2$O$_3$ glasses by means of differential scanning calorimetry, infrared spectroscopy, X-ray diffraction and optical microscopy. Results indicate that the addition of GeO$_2$ (0.4–2 wt.%) can suppress crystallization of the glass and decrease the sealing temperature and at the GeO$_2$
content of 0.7 wt.%, showing good mechanical property for sealing process. Knoblochova et al. [66] investigated the structural properties of Bi$_2$O$_3$–PbO–B$_2$O$_3$–GeO$_2$ glasses reported that the substitution of B$_2$O$_3$ by PbO and GeO$_2$ leads to slight molar volume increase, to decrease in the glass-transition temperature and to decrease in the optical energy band gap. Bahgat et al. [67] reported that the conduction mechanism was confirmed to obey the adiabatic small polaron hopping (SPH) and was mainly due to electronic transport between Cu ions. The dominant factor determining conductivity was the hopping carrier mobility in this glass by means of dielectric measurements. Spectroscopic studies of lead, zinc bismuth borate glasses doped with CuO were reported by Rajyasree et al. [68]. In these studies it is concluded that the environment of Cu$^{2+}$ ions is more covalent in lead series and ionic in zinc series. Absorption and emission studies indicate that the concentration of luminescence centers of bismuth ions (Bi$^{3+}$ and Bi$^{+}$ ions) is decreased by the integration of ZnO as well as by increasing the dopant concentration.

K. Horea et al [69] have reported structural investigation of xFe$_2$O$_3$-(100-x) [P$_2$O$_5$-TeO$_2$] glass system by FT-IR study and EPR spectroscopy. In these glasses the addition and the increasing of Fe$_2$O$_3$ content modify progressively the structure of the glass matrix. Effect of divalent metal oxides on absorption spectra of some sodium borate glasses containing mixed nickel and iron oxides have reported by El-Betal et al [70]. Hazra and Ghosh [71] studied structural and
physical properties of Fe$_2$O$_3$ doped lead vanadate glasses; they concluded that there is a strong role of iron both in the glass network and in the conduction mechanism of the glasses. Muralidhara [72] et al. carried out electron paramagnetic resonance (EPR) and optical absorption spectral investigations on Fe$^{3+}$ ions doped sodium boro phosphate glasses. The optical absorption spectrum of sodium boro phosphate glasses exhibits four bands characteristics of Fe$^{3+}$ ions in an octahedral symmetry. The value of inter-electronic repulsion parameter B obtained in the present work suggests that the bonding is moderately covalent. Spectroscopic studies of Fe$_2$O$_3$ and CeO$_2$ doped ZnO–Bi$_2$O$_3$–B$_2$O$_3$ glasses were carried out by Singh et al. [73]. From EPR and optical studies it is observed that iron ions are present in trivalent state with distorted octahedral symmetry. The EPR spectra of Fe$^{3+}$ ions exhibit two resonance signals at $g \approx 4.2$ and $g \approx 6.4$ which are attributed to Fe$^{3+}$ ions in rhombic and axial symmetry sites, respectively. The optical bandgap (E$_{opt}$) decreases with increase of transition metal. Raghavaiah et al. [74] studied the thermoluminescence studies on PbO–Sb$_2$O$_3$–As$_2$O$_3$ glasses doped with iron ions. Thermoluminescence (TL) studies coupled with data on optical absorption, ESR and magnetic susceptibility measurements have been carried out. The TL light output has been observed to decrease with increase in the concentration of Fe$_2$O$_3$ up to 0.6 mol%. For further increase in the content of Fe$_2$O$_3$, the TL light output has been observed to increase.
Optical characterization of Mn$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ ions doped zinc lead borate glasses were reported by Thulasiramudu and Buddhdu [75] In these studies they found through various optical tools suggest that these glasses have potential applications as luminescent optical materials. Optical properties of Co$^{2+}$-doped Li$_2$O–Ga$_2$O$_3$–SiO$_2$ glass-ceramics were studied by Xiulan Duan et al. [76] the samples crystallized to LiGa$_5$O$_8$ nanocrystals with the size of 6 nm and exhibited a broad absorption band near 1500 nm, which is characteristic of tetrahedral Co$^{2+}$ ions in crystals. The emission in the visible and near infrared (NIR) region was observed from the glass - ceramics and attributed to the $^4T_1(4P) \rightarrow ^4A_2(4F)$ and $^4T_1(4P) \rightarrow ^4T_2(4F)$ transitions of tetrahedral Co$^{2+}$, respectively. Sankarappa et al. [77] studied the a. c. conductivity and dielectric studies in V$_2$O$_5$–TeO$_2$ – and V$_2$O$_5$ – CoO – TeO$_2$ glasses. In these studies they found that temperature dependence of ac conductivity at different frequencies and dc conductivity exhibit the behaviour at high temperatures similar to that predicted by the Mott’s small polaron hopping model. The ac conductivity appeared to be behaving as per the Hunt’s expression given for $\omega > \omega_m$ where $\omega_m (= F_0)$ correspond to dielectric peak. Optical and thermal properties of P$_2$O$_5$–Na$_2$O–CaO–Al$_2$O$_3$–CoO glasses were reported by Colak and Aral [78]. The incorporation of CoO at 20% almost destroys absorption in the visible region from the absorption spectra and doping by transition metal ions have a dramatic effect on the properties of sodium–phosphate glasses, that new and alternative glass materials may be produced economically by this process.
It is also concluded that CuO doped (at 0.5%) glass is the best candidate for solar collector applications with its improved absorption characteristics and thermal conductivity values. Al₂O₃–SiO₂–TiO₂ glasses doped with CoO were studied by Bae et al. [79] comparing the variations in corresponding Raman scattering spectra, optical absorption spectra and X-ray diffraction patterns. At low-temperature heat-treatments (660 – 700 °C), CoO enters alumina-titanate amorphous phase, which results in increased temperature interval of existence and increased amount of this phase. Addition of CoO decreases the temperature of crystallization of the main crystalline phase, β-eucryptite solid solution.

Sambasiva Rao et al. [80] studied Dielectric, magnetic and spectroscopic properties of Li₂O–WO₃–P₂O₅ glass system doped with Ag₂O. The analysis of the results of DTA indicated the highest glass forming ability for glass containing 0.4 mol% of Ag₂O. The magnetic susceptibility and the optical absorption measurements suggest the reduction of W⁶⁺ ions into W⁵⁺ ions with higher percentage in glass AW₁₀. ESR spectral studies indicate that tungsten ions exist in W⁵⁺ state with octahedral environment in large concentrations in glass AW₁₀. The examination of the results of IR and Raman spectral studies indicate that there is an increasing degree of deformation in the glass network with increase in concentration of Ag₂O beyond 0.4 mol%. Characterization and transport properties of 10BaO–(85-x)V₂O₅–5TeO₂: xAg₂O glass system are reported by Pant et al. [81]. Conductivity data, which obey the Arrhenius type behavior, shows
minimum at 30 mol% Ag$_2$O, suggesting that the conductivity mechanisms are different above and below these two regions. The minimum in conductivity is accompanied by an inverse behaviour of activation energy. Structural characterization of phosphate glasses doped with silver are reported by Lucacel et al. [82]. A slight structural depolymerization process of these phosphate-based glasses was evidenced for higher silver oxide content. In vitro behavior of the bulk glass sample with the highest silver oxide content was tested by immersion in simulated body fluid (SBF). X-ray diffraction and SEM measurements made on the SBF treated sample revealed growth of a crystalline phase on the surface sample. Structural characterization of the ac conductivity in Ag ion conducting glasses are reported by Ndeugueu et al. [83]. The composition dependence of the FSDP wave number has been used to predict the composition dependence of the ratio, independently on the nature of the glass. The concept of bond fluctuation has been successfully used to explain the results which suggest that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales.

Jime´nez et al. [84] studied the UV-excited luminescence of europium ions in silver/tin-doped glasses. Glasses containing silver, tin and europium were prepared by the melt-quenching technique with silver nano-particles being embedded upon heat treatment (HT). An intensification of Eu$^{3+}$ ions emission was observed for non-resonant excitation around 270 nm, corresponding to UV absorption in the
material. Optical measurements suggest that light absorption occurs at single Ag$^+$ ions and/or two fold-coordinated Sn centers followed by energy transfer to europium which results in populating the $^5D_0$ emitting state in Eu$^{3+}$. The quenching effect shows with the presence of Ag nano-particles which may provide multipole radiationless pathways for excitation energy loss in europium ions. Karthikeyan [85] reported the fluorescent glass embedded silver nano-clusters. The light emitting behavior of silver nanoclusters embedded in sodalime glass through ion-exchange technique is studied. Thermal annealing induces size growth in the clusters. The optical absorption measurements show the presence of Ag clusters and its size growth with annealing temperature. Size determination of Ag clusters using optical spectroscopy agrees well with the low frequency Raman spectral studies. Fluorescence measurements show that smaller clusters exhibit a broad fluorescence, which is due to interband transition. Electrical and optical characterization of Ag$_2$V$_4$O$_{11}$ and Ag$_4$V$_2$O$_6$F$_2$ were studied by Bertoni [86] et al. The electrical and optical properties of these materials have been examined, for the first time in the case of Ag$_4$V$_2$O$_6$F$_2$. Electrical conductivity was measured by the powder-solution-composite (PSC) method. Ag$_4$V$_2$O$_6$F$_2$ (SVOF) has a higher silver-to-vanadium ratio than typical electrochemically active materials, while preserving critical connectivity in the vanadium oxide fluoride framework. However, the conductivity is lower than for the SVO phase, but still higher than
other previously reported electrode materials. SVOF has a larger band gap and lower visible light absorption concomitant with the lower conductivity.

Though there are considerable studies available on different modified borate or bismuth borate glass systems, no devoted studies are available on ZnF$_2$-R$_2$O$_3$-GeO$_2$ (R = Bi, Sb) glasses doped with some transition metal oxides CuO, Fe$_2$O$_3$, CoO and AgO. Hence, there is a lot of scope to investigate the structural aspects of ZnF$_2$-R$_2$O$_3$-GeO$_2$ (R = Bi, Sb) glasses.

1.4 **Aim of the present work**

Heavy metal oxide based glasses, like ZnF$_2$-R$_2$O$_3$-GeO$_2$ (R = Bi, Sb) are known for their significant transmission potential in the infrared region and possess high refractive index along with high density. They possess large non-linear optical susceptibility ($\chi^3$) coefficient, high electrical resistance and are transparent to both UV and visible regions also. These glasses have potential applications in non-linear optical devices such as ultrafast optical switches and power limiters, broad band optical amplifiers and in a number of solid state ionic devices.

Increased demand on diverse applications of modern electronic devices has led to the search for new materials, which will meet the specific requirements. Heavy metal oxide based glasses are among these materials and have a number of technological applications. Besides bismuth mixed glasses have several
advantages over conventional silicate and borate 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. 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 germanate glasses are available in recent years, a thorough survey of the literature on these glasses reveals in particular no detailed investigations on spectroscopic and electrical properties of CuO, Fe₂O₃, CoO and AgO doped ZnF₂-R₂O₃-GeO₂ (R = Bi, Sb) glasses are available.

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

Thus the objective of the present study includes preparation, characterization and

➢ To explore the changes in physical, structural properties that take place with the mixing of VA group oxides (Sb₂O₃, Bi₂O₃) as well as doping of
different CuO concentrations to the zinc germanate glasses by investigating spectroscopic and dielectric properties.

To have a comprehensive understanding after coming to a conclusion that, Bi$_2$O$_3$ effectively modified the zinc germanate glass network, the present study is aimed to explore the changes in conduction mechanism that take place with the varied oxidation states of silver, cobalt and iron ions in the glass network by a systematic study on dielectric properties coupled with spectroscopic properties

1.5 Contents of the present work

The details of composition of the glasses investigated are:

1. $40\text{Sb}_2\text{O}_3 - 20\text{ZnF}_2 - (40-x)\text{GeO}_2: (x)\text{CuO}$ $(x = 0, 0.6)$
2. $40\text{Bi}_2\text{O}_3 - 20\text{ZnF}_2 - (40-y)\text{GeO}_2: (y)\text{CuO}$ $(0 \leq y \leq 1)$
3. $20\text{ZnF}_2 - 40\text{Bi}_2\text{O}_3 - (40-x)\text{GeO}_2: x\text{AgO}$ $(0 \leq x \leq 2)$
4. $20\text{ZnF}_2 - 40\text{Bi}_2\text{O}_3 - (40-x)\text{GeO}_2: x\text{CoO}$ $(0 \leq x \leq 1)$
5. $20\text{ZnF}_2 - 40\text{Bi}_2\text{O}_3 - (40-x)\text{GeO}_2: x\text{Fe}_2\text{O}_3$ $(0 \leq x \leq 2.5)$

The details of investigations carried out are:

a) Differential thermal analyses studies and the evaluation of glass transition temperature $T_g$.  

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b) Optical absorption in the UV, visible and NIR regions at room temperature, identification of various electronic transitions of transition metal ions.

c) Electron spin resonance spectra for CuO, Fe$_2$O$_3$ doped glasses in the X-band frequency to identify the site symmetry and valence states of transition metal ions in the glass network.

d) FTIR spectra in the middle infrared region and the study of the effect of concentration of transition metal ions on the position and intensity of various vibrational bands.

e) Raman spectra in the region 200 to 1000 cm$^{-1}$ at room temperature using He-Ne laser source 632.8 nm as the excitation source.

f) Dielectric studies, like dielectric constant $\varepsilon'$, loss (tan$\delta$), a.c conductivity $\sigma_{ac}$ in the frequency range $10^3$-$10^6$ Hz and in the temperature range 30-300 °C.

References


