This chapter presents the general introduction, scope, contents and aim of the present work. In this chapter, the basic theory related to electrical and spectroscopic properties and ZnO–ZnF$_2$–B$_2$O$_3$ glasses crystallized with TiO$_2$, MoO$_3$ and CoO.
General introduction Scope and Contents of present work

1.1 Introduction

a. Glasses

Glass is an inorganic solid material that is usually clear or translucent with different colors. It is hard, brittle and stands up to the effects of wind, rain or Sun. In more precise terminology, glass is an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior. Any material, inorganic, organic or metallic, formed by any technique, which exhibits glass transformation behavior, is a glass.

The exceptionally rapid development of technological research in all fields of knowledge is accompanied by intense work by scientists and technologists on glass materials. These materials have potential applications as laser materials, IR domes, optical fibers, modulators, and memory devices, photonic devices for communication and advanced computer applications and as semi conducting devices. Applications of these materials can also be found in nuclear waste management, optical fibers, solid electrolytes, electronic displays, biocompatible implants, dental posterior materials, high performance composites etc. In view of such vast and diversified applications, the investigation on the development and characterization of different glass materials has gained momentum in the recent years.
The literature survey on the formation of glass theories indicates that it was the Goldschmidt who proposed the theory of glass formation based on the examination of various glass systems that glasses of the general formula \( \text{R}_n\text{O}_m \) form most easily when the ionic radius ratio of the cation, \( \text{R} \), to the oxygen ion lies in the range 0.2 to 0.4. Since radius ratios in this range tend to produce cations surrounded by four oxygen ions in the form of tetrahedra, Goldschmidt believed that only melts containing tetrahedrally-coordinated cations form glasses during cooling. This contention was purely empirical, with no attempt to explain why tetrahedral coordination should be so favorable to glass formation. A few years later, Zachariasen extended the ideas of Goldschmidt and attempted to explain why certain coordination numbers might favor glass formation.

According to Zachariasen [1] there are only five oxide materials which form the glass by themselves viz., \( \text{SiO}_2 \), \( \text{GeO}_2 \), \( \text{B}_2\text{O}_3 \), \( \text{As}_2\text{O}_3 \) and \( \text{P}_2\text{O}_5 \); two more non-oxide compounds viz., \( \text{As}_2\text{S}_3 \) and \( \text{BeF}_2 \) are also added to this list recently [2]. Though, the glass materials do not possess the long-range periodicity but they retain short range order with \( \text{AO}_3 \) and \( \text{AO}_4 \) basic building blocks and follow certain rules proposed by Zachariasen. Basing on these rules, a continuous random network for a glass can be constructed as shown in Fig. 1.1.

As per these rules, the oxides of the type \( \text{AO} \) (\( \text{CaO}, \text{BaO} \) etc.), \( \text{A}_2\text{O} \) (\( \text{Li}_2\text{O}, \text{Na}_2\text{O} \) etc.) cannot form glasses on their own and the rules are satisfied
only for oxides of the type A$_2$O$_3$, AO$_2$ and A$_2$O$_5$ and for non-oxide compounds As$_2$S$_3$ and BeF$_2$.

The cations 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. Alkali oxides/fluorides, alkali earth oxides/fluorides, ZnO, PbO, CdO etc., are some of the basic examples of modifiers in glass network. These modifiers break-up the continuous network by introducing non-bridging oxygens (Fig.1.2). A third group of oxides known as intermediate class of oxides also exist which by themselves not readily form glasses but do so when mixed with other oxides; such oxides are known as intermediate glass formers. The examples of this group include TeO$_2$, Sb$_2$O$_3$, Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$, WO$_3$, MoO$_3$, V$_2$O$_5$ etc.

Fig. 1.1 Two dimensional schematic of crystalline and non-crystalline (glass) materials

Crystalline A$_2$O$_3$     Glassy A$_2$O$_3$
The summary of the rules for glass formation proposed by Zachariasen is as follows:

a) A high proportion of glass network forming cations (Si, B, P, Ge, As, etc..) is surrounded by oxygen tetrahedra or triangles.

b) The polyhedra, share should not more than one corner with each other.

c) The number of corners of polyhedra is less than 6.

d) An-ions (O²-, S²-, F⁻) should not be linked with more than two cations and do not form additional bonds with any other cations.

e) At least three corners of polyhedra must connect with the neighboring polyhedra.

f) The network modifiers participate in the glass network with the coordination number generally greater than 6.
g) Intermediate glass formers (do not form the glass on their own) but either reinforce network or loosen the network with coordination number 6 to 8 and may participate in the network with coordination number 3 or 4 in the presence of modifiers.

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

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

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

This process of changes in volume/enthalpy with temperature as a super cooled liquid is cooled through the glass transition region is illustrated in Fig. 1.3.

During the last few decades a variety of in-organic glasses have been developed with an attempt to achieve suitable electrical, mechanical and optical characteristics. These characteristics are associated with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, IR transmission performance and their ability to accept more transition/rare earth metal ions for their use in solid-state devices. Work along these lines was carried out on a number of glasses giving valuable information [8–13]. Investigations on electrical properties such as dielectric properties of glasses help to have an idea over their insulating character. Investigations on
the spectroscopic properties such as optical absorption, infrared spectra, electron spin resonance and photoluminescence can be used as probes to throw some light on the structural aspects of these glasses.

b. Glass-ceramics

Glass-ceramic processing consists of melting together a mixture of compounds (usually oxides), to form a fluid of high viscosity, which when cooled at moderate rates gradually increase in viscosity until a vitreous (non-crystalline) solid (glass) is formed; as has been discussed above. The cooled glass body is then partially or completely crystallized (devitrified) by heat
treatment. A distinctive advantage of the glass-ceramic process is that crystallization may be accomplished at a temperature where the viscosity of the glass is still high, so that the glass body does not deform, but to a first approximation, passes from a solid glass shape to a solid crystal-line shape of the same dimensions. In these materials finely dispersed crystalline structures are stimulated to "grow" within the solidified glass matrix by a process of controlled devitrification (Fig.s 1.4 (a) and (b)).

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

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

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

The presence of native crystalline inclusions strengthens the glass and makes it more flexible, reducing the presence and severity of micro-cracks and acting as crack stoppers. Further, glass-ceramics are stronger at high temperatures than glasses.
The advantages of the glass-ceramic process have been applied to a whole spectrum of compositions and applications. Their high mechanical strength and chemical inertness makes them suitable for prosthetic implants, for missile radomes. Yet, their low thermal expansion coefficients, makes these materials suitable for gas tight electrical feed-throughs. These materials are very poor conductors of electricity.

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

Although the nucleation and growth process in glass ceramics has been extensively studied for the last 25 years since it was discovered, at present there is no general theory that explains how the nucleating agents operate. Most available models are specific to a given system, and they commonly postulate the formation of some sort of heterogeneity by the nucleating agent that catalyzes the subsequent crystallization [14].

The nucleation and crystal growth mechanism in a variety of glass materials has been studied in detail [4, 15].

The characteristics of glass ceramic however depend on the kind and quantity of the crystal phase formed as well as on the residual glass composition. Hence, the selection of a suitable nucleating agent in the correct
concentration and determination of the temperature and the time of nucleation and growth are important factors, in the formation of a glass-ceramic. The nucleating agents that are generally used for controlled crystallization processes, giving rise to enormous numbers of nucleation centres in the original glass are, gold, silver, platinum or the oxides of Ti, Cr, Mn, Ce, V, Ni and Zr or certain sulfides or fluorides. In the present study TiO$_2$, MoO$_3$, CoO is chosen for inducing crystallization in these glasses. Additionally, the transition metal ions are very interesting ions to probe in the glass ceramic networks because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent.

Transparent glass ceramics comprising nano/microcrystallites that exhibit superior physical properties over the amorphous materials are under extensive investigation [16]. Transparency of glass-ceramics can be retained by controlling the crystallization of a glass precursor with appropriate chemical compositions and appropriate nucleating agent. The general conditions for retention of transparency of glass even after the crystallization include small refractive index difference between the crystalline and residual glass phases, a small birefringence of the crystallites and smaller wavelength of the incident light when compared with that of size of crystallites. Investigations along these
lines have been carried out on several glass systems including some zinc, fluoride or oxyfluoride matrices, polymers and thin films [17-22].

1.2 Scope of the present work

Among different glass systems ZnO mixed borate or silicate glasses possess low specific heat, high thermal conductivity and ZnO in these glasses dissipates heat more rapidly when compared with that of glasses containing heavy metal oxide modifiers like BaO and PbO. Further, dielectric breakdown strength of ZnO mixed glasses was found to be abnormally high probably because the electrons in the outer most shell of Zn$^{2+}$ cations is 18. For this reason thin layers of these glasses are being extensively used as insulating layers in plasma display panels [23, 24]. Zinc oxide based glasses are being widely used in plasma display panels in large area hang-on-wall TVs and computer monitors for high quality and performance. In plasma display panels, a dielectric layer is formed on the glass substrate (Fig.1.5) so as to cover the display electrodes. It is necessary for the dielectric layer to maintain discharge, to have a high dielectric strength and to have good transparency, high dielectric break down voltage. ZnO based glass material meet these requirements.

The breakdown strength of these glasses can further be improved if the glasses are crystallized with transition metal oxides like TiO$_2$, MoO$_3$, CoO as nucleating agents.
Three series of elements are formed by filling the 3d, 4d and 5d shells of electrons. Together these comprise the d-block elements. They are often called ‘transition elements’ because their position in the periodic table is between s-block and p-block elements. Their properties are transitional between the highly reactive metallic elements of the s-block, which typically form ionic compounds and the elements of p-block, which are largely covalent. In s- and p-blocks, electrons are added to the outer shell of the atom where as in d-block they are added to the penultimate shell. Typically transition elements have an incompletely filled d-level.

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

One of the most striking features of the transition metal elements is that they usually exist in several different oxidation states (Table 1.1). Furthermore, the oxidation states change in units of one, e.g. Fe$^{3+}$ and Fe$^{2+}$, Mn$^{3+}$ and Mn$^{4+}$. Among the first five transition metal elements, the correlation between the electronic structures and minimum and maximum oxidation states in simple compounds is complete. In the highest oxidation states of these first five elements, all of the s and d electrons are used for bonding. Thus the properties depend only on size and valency; consequently show some similarities with elements of the main groups in similar oxidation states. Once the d$^5$ configuration is exceeded, i.e., in the last five elements, the tendency for all the d electrons to participate in bonding decreases. Thus Fe has a maximum oxidation state of (+VI). 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.
The covalent radii of the elements decrease from left to right across a row.

### Table 1.1
Oxidation states of transition metal elements

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In view of these, the thesis is mainly devoted to the studies on dielectric properties and dielectric breakdown strength of ZnO–ZnF$_2$–B$_2$O$_3$ glasses crystallized with TiO$_2$, MoO$_3$, and CoO. The studies were further extended to the spectroscopic properties (like optical absorption and IR spectra) so as to use as tools for understanding the changes in the insulating strength of glass-ceramics.

The studies on dielectric properties, and the dependence of these properties on the composition, structure and on various external factors such as humidity, radiation effect, mechanical action etc., pave the way for estimating the insulating character of the glass ceramics. Whereas, the investigations on spectroscopic (viz., optical absorption, electron spin resonance, infrared spectra and photoluminescence) give the information on the environment and oxidation states of the transition metal ions (nucleating agents) in the glass ceramic network and help to assess the suitability of these materials for practical applications.

A preliminary description of the above mentioned properties along with their relation to some of the investigations (similar to those of present work) on ZnO–ZnF$_2$–B$_2$O$_3$ glasses crystallized with TiO$_2$, MoO$_3$, CoO is presented below.

1.2.1 Physical parameters

Some physical parameters useful for characterization ZnO–ZnF$_2$–B$_2$O$_3$ glasses crystallized with some transition metal oxides are estimated
from the measured value of density \(d\) and the average molecular weight \(\overline{M}\), using the following equations [25]:

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

\[
(i) \quad N_i \left(10^{22} \text{ ions/cm}^3\right) = \frac{N_A M (\text{mol} \%)}{M d} \tag{1.1}
\]

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

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

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

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

\[
(iv) \quad \text{Field strength } F_i (\text{cm}^{-2}) = \frac{z}{r_p^2} \tag{1.4}
\]

### 1.2.2 Dielectric properties

When an insulating glass ceramic (a dielectric) like ZnO–ZnF\(_2\)–B\(_2\)O\(_3\) is placed in external electric field two types of polarizations – the electronic and the ionic – are expected to develop in the glass ceramic. If the dielectric
contains permanent dipoles, they experience a torque in an applied field that
tends to orient them in the field direction. Consequently, an orientational (or
dipolar) polarization can arise. These three polarizations are due to charges
locally bound in atoms, molecules or in the structures of solids. Additionally to
all these, generally there exists charge carriers that can migrate for some
distance through the dielectric. Such charge carriers during their motion may
be trapped in the material or on interfaces (because they cannot be freely
discharged or replaced at the electrodes); due to these causes, space charges
and a microscopic field distortion result. Such a distortion appears as an
increase in the capacitance of the sample and may be indistinguishable from a
real rise of the dielectric constant. Thus a fourth polarization, called the space
charge polarization comes into play. The total polarization is sum of these four
polarizations (assuming that they act independently) [26].

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 [27].

The complex dielectric constant, according to Debye for a material
having permanent dipoles characterized by single relaxation time $\tau$, given by:
\[ \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau} \]  

(1.5)

where \( \varepsilon_s \) is the static dielectric constant and \( \varepsilon_\infty \) is the dielectric constant value of the material corresponding to its electronic and atomic polarization. Separating this equation into its real and imaginary parts, one obtains:

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

(1.6)

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

(1.7)

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

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

(1.8)

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

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

(1.9)

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

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

Most of the physical properties of the transition metal complexes are studied with the help of crystal field, ligand field and molecular orbital theories. The ligand field theory explains the optical levels by energy splitting of the states of the central ion in the field of the surrounding atoms. The theory
of this splitting under the influence of fields produced by various symmetries was worked out by Bethe [28] and further developed by Schlapp and Penny [29], Van Vleck [30] and others. The principal symmetry of the transition metal complexes is usually an octahedral one while in a few cases, tetrahedral, square planar and lower symmetries occur. In a complex the site symmetry of anions is always degraded from the extremely high spherical one to a lower symmetry. Two types of symmetries, known as octahedral (designated by $O_h$) and tetrahedral (designated by $T_d$) are important. The corresponding molecular structures having these symmetries are shown diagrammatically in Fig. 1.6.

![Diagram of octahedral and tetrahedral point groups](image)

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

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

In a weak field approach, one tries to understand the effect of crystal fields on the free ion terms. For d, the application of the group theory results in the splitting of $^2D$ 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} (1.10)

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

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

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

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

In $T_d$ symmetry the nature of the splitting is the same but ordering of the levels is inverted as shown in Fig. 1.8. If the symmetry is lower than octahedral, say tetragonal or orthorhombic, then these levels will split into levels of lesser degeneracy. The above discussion is valid for single electron d-orbitals.
Fig. 1.7 (a) The five d-orbitals in an octahedral field of ligands
Fig. 1.7 (b) Detailed spectral information on various transition metal (from d$^1$ to d$^4$) ions.
Fig. 1.7 (c) Detailed spectral information on various transition metal (from d$^6$ to d$^9$) ions.
Fig. 1.7 (d) Energy spectra of transition metal ions.
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\textsubscript{2g} and e\textsubscript{g} functions become the basis. The various configurations of many electron systems are obtained by filling the t\textsubscript{2g} shell first and then the e\textsubscript{g} shell. Thus for example, the d\textsuperscript{2} ion has t\textsubscript{2g}\textsuperscript{2}, t\textsubscript{2g}\textsuperscript{1}.e\textsubscript{g}\textsuperscript{1} and e\textsubscript{g}\textsuperscript{2} configurations with energies - 8Dq, 2Dq\textsubscript{t} and 12Dq\textsubscript{t}, respectively.

The electrostatic energy values for different states have been calculated by Tanabe and Sugano [31] and Griffith [32] 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 Dq/B for various d\textsuperscript{n} configurations popularly known as Tanabe-Sugano diagrams. Fig. 1.9 indicates the TS diagram for d\textsuperscript{7} ion. Here, 

E corresponds to the energy level of a d\textsuperscript{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 Dq\textsubscript{t} and parameters B and C. From these diagrams, it is possible to obtain a quantitative measure of the ease of spin pairing. These diagrams also help in assigning the transitions correctly.

1.2.4 Electron spin resonance

Electron spin resonance (ESR) has been developed as an extremely sensitive and important spectroscopy technique, which is widely used to study
Fig. 1.8 Diagram showing relative energy of $e_g$ and $T_{2g}$ orbitals resulting from the splitting of d orbitals by octahedral environments.

Fig. 1.9 Tanabe – Sugano diagram for $d^7$ ions
systems having unpaired electrons. In condensed matter physics, ESR is used as a powerful technique to study the lowest energy levels, hence, the electronic state of the unpaired electrons of paramagnetic species in solids. This technique provides information on understanding of the symmetry of the surroundings of the paramagnetic ion and the nature of its bonding to the nearest diamagnetic neighbours. Following are a few examples of systems containing unpaired electrons.

1. Atoms having odd number of electrons, e.g., atomic hydrogen and lithium atom.
2. Molecules with odd number of electrons such as NO, and triplet state molecules like oxygen molecule.
3. Ions having partially filled inner electronic shells, e.g., iron, rare earth ions etc.
4. Defects produced in a solid by irradiation.
5. Free radicals, e.g., CH₃ and diphenyl-picrylhydrazyl.
6. Conduction electrons in metals, semiconductors and dilute alloys etc.

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

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

\[
\mathbf{J} = \mathbf{L} + \mathbf{S}.
\] (1.13)

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

\[
\mu = -g\beta \mathbf{J}\] (1.14)

where

\[
g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}
\] (1.15)

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

\[
\beta = \frac{e\hbar}{2mc} = 9.274096 \times 10^{-27} \text{ erg/gauss}
\] (1.16)

which is known as the Bohr magneton. When a magnetic dipole is placed in a uniform magnetic field H, it precesses about the direction of H with the Larmor angular frequency \(\omega_L\) which is given by [33]
\[ \omega_L = \gamma B \]  \hspace{1cm} (1.17)

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

\[ h\nu = g \beta B. \]  \hspace{1cm} (1.18)

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

The energy level of an electron with total angular momentum \( J \) has a degeneracy of \( (2J + 1) \). The application of an external magnetic field removes this degeneracy and the energy level splits into \( (2J + 1) \) levels. When angular momentum \( L \) is zero then \( J \) becomes equal to \( S \). The transitions between these levels are governed by the selection rules \( \Delta M_s = \pm 1 \), where \( M_s \) is the spin magnetic quantum number. An unpaired electron with \( S = \pm 1/2 \), when placed in a uniform magnetic field \( B \), will have two energy levels, as shown in Fig. 1.10, if \( g \) is constant. The energies of these levels are

\[ E_{\pm 1/2} = \pm (1/2) g \beta B, \]  \hspace{1cm} (1.19)

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

\[ \Delta E = g \beta B \]  \hspace{1cm} (1.20)
The above equation shows that the energy difference between the two levels increases linearly with $B$ in the ESR technique. The magnetic dipole transitions between the levels are induced between the two levels in the presence of a uniform polarized perpendicular to $B$ by an incident radiation of frequency $\nu$ if the quantum condition (1.18) and $\Delta M_s = \pm 1$ are satisfied. This will give rise to only one absorption line. When the orbital angular momentum is not zero then

**Fig. 1.10** 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 uniform polarized perpendicular to $B$ by an incident radiation of frequency $\nu$ if the quantum condition (1.18) and $\Delta M_s = \pm 1$ are satisfied. This will give rise to only one absorption line. When the orbital angular momentum is not zero then
the degenerate energy level will split into \((2J+1)\) levels and the conditions for the transitions by absorption of energy is given by eqn. (1.18) and \(\Delta M_J = \pm 1\). Such a situation will give rise to multiple absorption lines. The resonance condition (1.18) can be satisfied either by changing the magnetic field or the frequency of the radiation incident on the magnetic dipole. Practically, it is more convenient to vary the uniform magnetic field rather than the frequency of the incident radiation since the frequency variation of a microwave source is possible within a very small range only.

Thus, from an ESR spectrum recording one can get information about the resonance field at a fixed frequency of the electromagnetic radiation, hence, the ‘g’ value, the shape, amplitude and width of the absorption line. The ‘g’ value may be modified by the crystal field surrounding the free ion from the value of the “free ion value”. All of these parameters, when interpreted properly and in conjunction with the appropriate theoretical ideas, provide valuable information on the system studied. In addition, one may vary certain other external parameters like temperature, composition etc., which would possibly change ESR parameters leading to additional information on the system under study. A vast discussion on ESR technique and its applications is available in a number of pioneering books written by many authors [34-38].
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 [39] and Abragam and Pryce [40] to interpret the observed resonance of ions in the first transition series. The concept was subsequently extended by Elliott and Stevens [41] 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 [42].
\[ H = H_E + H_{LS} + H_{SI} + H_Q + H_V + H_{SH} + H_{HI} \]  \quad (1.21)

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

i. \( H_E \) is a composite term expressing the total energy of electrons, the cumblic 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 (1.22)

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

\[
H_{LS} = \sum \lambda_{ij} \cdot I_i \cdot S \]  \quad (1.23)

Where \( I \) is the orbital angular momentum of the individual electron, \('s'\) is the spin angular momentum of the individual electron and \( \lambda_{ij} \) is the spin – orbit coupling constant. This can be written in a simple form as

\[
H_{LS} = \lambda \cdot L \cdot S \]  \quad (1.24)
Where, L and S are the total orbital angular momentum and the spin angular momentum of free ion, respectively. The magnitude of this interaction lies between $10^2$ to $10^3$ cm$^{-1}$.

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

$$H_{SI} = \sum \mathbf{a}_i \cdot \mathbf{J}_i \cdot \mathbf{I}_i$$  \hspace{1cm} (1.25)

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 $\mathbf{I} > \frac{1}{2}$, 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} (1.26)

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

$$H_v = \sum \mathbf{e}_i \mathbf{V}(r_i)$$  \hspace{1cm} (1.27)

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

$$H_{SH} = \beta \left( \mathbf{L} + g_e \cdot \mathbf{S} \right) \cdot \mathbf{B}$$  \hspace{1cm} (1.28)

$$H_{IH} = \hbar / 2 \pi \sum_i -\gamma_i \cdot \mathbf{I}_i \cdot \mathbf{B}$$  \hspace{1cm} (1.29)
Where $\gamma_i$ is the gyrometric ratio of the i\textsuperscript{th} nucleus and the latter terms (about $10^{-4}$ cm\textsuperscript{-1}) may be neglected expect in considering second order effects in the nuclear hyperfine interaction.

\textbf{b. Line shapes}

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

\begin{equation}
I = I_0 \frac{T_2^2 (B - B_r)^2}{T_2^2 (B - B_r)^2 + 1}
\end{equation}

\begin{equation}
I = I_0 \exp [-b (B - B_r)^2 T_2^2]
\end{equation}

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

The Lorentzian shape arises due to harmonically bound electron. If the harmonic motion of the electron is interrupted by some process, then the distribution of frequencies follow the equation [1.31] for an EPR spectrum, the interruption will be in the form of exchange. Since all the electrons are equivalent, their interchanging between two molecules is quite possible if the molecules are close enough to each other. If this exchange is so rapid to affect the phase coherence of the spins, Lorentzian shape results.

On the other hand, Gaussian shape results from the paramagnetic ion separated from each other by molecules, which are having no unpaired
electrons but possessing magnetic nuclei. Each unpaired electron will experience a local static magnetic field which will be dominated by how the nuclear spins are arranged in the near by host molecules. The observed EPR spectra will be a superposition of shapes from all the spins with their local fields. Since the local fields will be randomly distributed, the total line shape results in a Gaussian line shape according to equation (1.30). The characteristic Lorentzian and Gaussian line shape are shown in the Fig. 1.11.

**Fig. 1.11** The characteristic Lorentzian and Gaussian line shapes.

c. **Line Width and Intensities**

Generally the EPR signals are recorded as the first derivative of the absorption curve and hence the area under the EPR signal can be calculated by numerical double integration method. In this method, the EPR spectrum is divided in to ‘n’ small intervals having length‘d’. The height $h_r$ of the EPR signal corresponding to the centre of $r^{th}$ interval is noted and the area under the curve can be calculated from the equation
\[ A = \frac{1}{2} \left( \frac{d}{dB} \right)^2 \sum_{r=1}^{n} (n - 2r + 1) h_r \]  

(1.32)

Fig. 1.12 shows the method of finding the area under the first derivative absorption curve by numerical double integration method. The accuracy of this method depends on the number of intervals and complexity of the spectrum.

Using about 8 to 10 intervals per peak, the error in calculating the area will likely be within 2 to 3% in Gaussian curves. For Lorentzian curves, the error may be greater due to the presence of long tails.

For ESR signals, the line widths are measured from the maximum and minimum line positions at the first derivative curve. The ESR lines always have a finite width due to electrons interacting magnetically with the environment of the sample. Hence, from the line width and the rate of build up
or decay of the line intensity, one can obtain information about spin environment.

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

1.2.5 Infrared spectra

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

In addition, the investigation of infrared spectra (IR) of these materials enables the assignment of characteristic frequencies to molecular groups in the glass and hence correlation of IR absorption bands with different units of vitreous structure. In the case of borate glasses, the basic glass contains BO$_3$ and BO$_4$ structural units in the glass network and when a cation such Zn$^{2+}$ is added, it participates in the glass network with ZnO$_4$ structural units or may reside in interstitial positions as modifiers depending upon the concentration of ZnO. 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 [43-45], unlike the vibrations of complex ions in a crystalline matrix which are dependent of the vibrations of other groups. In probing the structural units and changes that take place in the network with composition of a ternary glass, infrared spectroscopy lends itself as an effective tool, because the technique is sensitive to short-range ordering and local interactions.

The assignment of the important IR bands observed in ZnO–ZnF$_2$–B$_2$O$_3$ glasses and glass ceramics of the present work is in general made by comparison of the data with the bands observed in literature, even though some bands attributions have their support from the theory. However, it is possible to provide quantitative justification from the theoretical calculation in the literature [46] for some of the vibrational frequencies assigned to borate and other transitional ion groups like Ti, Mo, Co, provided the force constant corresponding to Ti-O, Mo-O and Co-O stretchings are known.

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

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

(1.33)

where $c$ is the velocity of light, $m$ is the reduced mass of the diatomic or triatomic group, $K$ is the stretching or bending force constant. For certain
diatomic and triatomic groups, the force constant was evaluated using various empirical formulae available in the literature [46, 47].

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

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

SEM inspection is often used to identify whether the prepared material is amorphous or crystalline in nature. The formation of crystal grains, their size and sometimes their orientation and physical defects on the surface of the specimen can also be identified by the images of SEM. During SEM inspection, a beam of electrons is focused on a spot volume of the specimen, resulting in the transfer of energy to the spot. These bombarding electrons, also referred to as primary electrons, dislodge electrons from the specimen itself. The dislodged electrons, also known as secondary electrons, are attracted and collected by a positively biased grid or detector, and then translated into a signal. To produce the SEM image, the electron beam is swept across the area being inspected, producing many such signals. These signals are then amplified, analyzed, and translated into images of the topography being inspected. Finally, the image is recorded. The schematic representation of SEM and SEM pictures of an amorphous material and a glass ceramic material recorded are shown in Fig. 1.13.
Fig. 1.13 (a) Schematic representation of SEM

A SEM may be equipped with an EDX analysis system to enable it to perform compositional analysis on specimens. EDX analysis is useful in identifying materials and contaminants, as well as estimating their relative concentrations on the surface of the specimen. EDX Analysis stands for Energy Dispersive X-ray analysis. It is sometimes referred to also as EDS or EDAX analysis. The EDX analysis system works as an integrated feature of a SEM.
During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

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

**Fig. 1.13** Scanning electron microscopic pictures.
The output of an EDX analysis is an EDX spectrum (Fig. 1.14). The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks are unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.

1.3 Brief review of the previous work on ZnO-B$_2$O$_3$ glasses and glass ceramics

Masai et al. [48] have investigated crystallization behavior of the oxide semi conductor ZnO in Al$_2$O$_3$ doped zinc borate glass ceramics and results suggest that crystallization of ZnO from multi-component glass is dominated by the local coordination state of the host glass. Rada et al. [49] have studied
the Spectroscopic properties and ab initio calculations on the structure of erbium–zinc-borate glasses and glass ceramics. Swapna et al. [50] have prepare the zinc alumino bismuth borate optical glasses of different compositions doped with 1 mol% of Dy$^{3+}$ ions to explore the feasibility of these glasses for optoelectronic devices. Saroj Rani et al. [51] have reported the Influence of Bi$_2$O$_3$ on thermal, structural and dielectric properties of lithium zinc bismuth borate glasses. El-Falaky et al. [52] have studied the A.C. conductivity and relaxation dynamics in zinc–borate glasses. Shanmugavelu and Ravi Kanth Kumar [53] have investigated the thermal, structural and electrical studies of bismuth zinc borate glasses. Razvan Stefan et al. [54] have investigate the effect of copper ions addition in 55B$_2$O$_3$–45ZnO glass matrix together with the matrix effect on paramagnetic behavior and they concluded that the increase of the number of non-bridging oxygen (NBO) atoms as a function of CuO content in these glasses leads to the decrease of glass polymerization which reduces the stability of the glasses. Ledemi et al. [55] have reported the refractive index modification in fluoro-borate glasses containing WO$_3$ have been exposed to 800 nm femtosecond pulses of 70 fs width at a repetition rate of 100 kHz from a Ti-sapphire regenerative amplifier system. Gupth et al. [56] have studied the influence of bismuth addition on structural, elastic and spectral properties Nd$^{3+}$ doped zinc–boro–bismuthate glasses and they have conclude that these materials may be promising for compact solid state infrared lasers. Hua et al. [57] have reported structural and
luminescence properties of Mn$^{2+}$ ions doped calcium zinc borophosphate glasses. They have showed that these glasses could have potential applications as luminescent optical materials, visible lasers and fluorescent display devices. Abdel et al. [58] have investigated lithium tungsten borate glass doped with ZnO for phonic applications. Their results suggested that the replacement of ZnO by B$_2$O$_3$, increased the Uv glass transmission window and transmittance. Bale and Rahman [59] have reported optical absorption and EPR studies on Bi$_2$O$_3$–Li$_2$O–ZnO–B$_2$O$_3$ glasses. Sontakke et al. have [60] reported the photoluminescence properties of Bi$^{3+}$ co-doped Eu$^{3+}$ containing ZnO-B$_2$O$_3$ glasses. Sava et al. [61] have investigated the Raman and ESR study of ZnO–TiO$_2$–B$_2$O$_3$ ternary system. Hsiang et al. [62] have studied the crystallization behavior and dielectric properties of BaO–ZnO–SrO–CaO–Nd$_2$O$_3$–TiO$_2$–B$_2$O$_3$–SiO$_2$ glass-ceramics for LTCC applications. Inoue et al. [63] made a systematic study on thermal properties and electron polarizability from average single bond strength in ZnO–Bi$_2$O$_3$–B$_2$O$_3$ glasses. Shiv Prakash et al. [64] reported 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. Shengchun et al. [65] have investigated the structural and physical properties in the system ZnO–B$_2$O$_3$–P$_2$O$_5$–R$_n$O$_m$.

Kim et al. [66] have carried out thermal and dielectric properties of ZnO–B$_2$O$_3$–MO$_3$ glasses (M= W, Mo) and have examined suitability of these glasses for plasma display panels. Naga Raju et al. [67] have studied the
analysis of various spectroscopic and magnetic properties on of ZnO—ZnF$_2$—B$_2$O$_3$ glasses doped with different concentrations of Cr$_2$O$_3$. These studies have indicated, there is an increasing the presence of Cr$^{6+}$ ions in the glass network that take part network forming positions with CrO$_2$$^{-4}$ structural units and decreased the degree of disorder in the glass, when Cr$_2$O$_3$ is present in higher concentrations. In this study the formation of Zn$^{2+}$ in tetrahedral coordination was observed. The average electronic polarizability of the oxide ion ($\alpha_O$$^2$), optical basicity (A), and Yamashita-Kurosawa’s interaction parameter (A) were also evaluated based spectroscopic studies of Bi$_2$O$_3$–Li$_2$O$_3$–ZnO–B$_2$O$_3$ glasses [68]. Jayasimhadri and Jung-Hyun Jeong [69] have reported the efficiency of ZnO–B$_2$O$_3$–P$_2$O$_5$ glasses to emit white light under 400 and 453 nm excitations, which are nearly match with the emission of commercial GaN blue LEDs and InGaN LED, respectively. Wookyung Sung et al. [70] have investigated the thermal properties such as glass transition temperature, dilatometer softening point and coefficient of thermal expansion and chemical properties (aqueous durability) of P$_2$O$_5$–V$_2$O$_5$–ZnO/B$_2$O$_3$(PVZ/B) glass system in order to determine their applicability as barrier-ribs in plasma display panels that can be fired at low temperature (500°C). Motke et al. [71] have studied The Infrared spectra of zinc doped lead borate glasses were systematically.

Kim et al. [72] have carried out thermal and electrical properties of zinc borate glasses for plasma display panels. Montagne et al. [73] have reported the effect of ZnO on some physical properties of sodium phosphate glasses.
Wang and Wang [74] have studied the influence of ion-implantation on crystallization of zinc borate glasses mixed with PbO. Koffyberg and Benko [75] have investigated conductivity and optical absorption of zinc borate glasses mixed with 80% of WO$_3$ and analyzed the results using small polaron hopping theory. Musiun et al. [76] have reported detailed investigations of influence of ZnO on alkali phosphate glasses. Lee et al. [77] have reported the devetrification studies zinc borate glasses mixed with varying concentrations of PbO. Huang et al. [78] have prepared ZnO based glass ceramic films and studied their electrical properties. Patil [79] have reported synthesis and spectroscopic studies of Na$_2$O–ZnO–ZnF$_2$–B$_2$O$_3$ glasses.

In spite of vast literature available on some zinc borate glasses studies as such on insulating characteristics of these glasses are very rare. In view of this we have devoted the present study mainly to investigate the dielectric properties and to assess their insulating character.

1.4 Motivation and objective of the present work

The crystalline glass materials containing fine-grained uniform structure, consisting of small crystals of irregular and distorted form, often aggregated into spherulites with residual glass inter-layers cementing the crystalline glass-ceramic concretion. These materials possess very small and strain free intertwined crystals that hinder the crack growth. As a result, glass ceramics are expected to possess outstanding mechanical, electrical and thermal properties. These materials also possess high chemical durability and
very low coefficient of thermal expansion. In view of such features, the glass-ceramic materials are better candidates over the glass materials for applications as transparent insulating layers in display panels since the heat liberated in the bulk ceramic material would easily be dissipated.

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

Among different glass systems ZnO mixed borate glasses possess low specific heat, high thermal conductivity and ZnO in these glasses dissipates heat more rapidly when compared with that of glasses containing heavy metal oxide modifiers. Further, dielectric breakdown strength of ZnO mixed glasses was found to be abnormally high probably because the electrons in the outer most shell of Zn$^{2+}$ cations is 18. Insulating strength of these glasses can be further improved if the material is crystallized with appropriate concentrations of transition metal oxides like TiO$_2$, MoO$_3$ and CoO. Thin layers of such glass
ceramics are being extensively used as insulating layers in plasma display panels. In display panels, it is necessary for the dielectric layer to maintain discharge, to have a high dielectric strength and to have good transparency, high dielectric breakdown voltage. Since ZnO based glass ceramic material posses all these properties, it is felt worth to throw some light on the insulating strength of these materials by studying their dielectric properties and dielectric breakdown strength coupled with spectroscopic properties.

Thus the clear objectives of the present study are

- To prepare ZnO–ZnF$_2$–B$_2$O$_3$ glass ceramics with three different nucleating agents viz., TiO$_2$, MoO$_3$ and CoO.
- To characterize them by a variety of techniques those include XRD, SEM, EDS and DSC.
- To have a comprehensive understanding over the influence of transition metal ions on structural aspects of ZnO–ZnF$_2$–B$_2$O$_3$ glass ceramics by investigating optical absorption, ESR, IR, photoluminescence
- To study the dielectric properties and breakdown strength, and to identify the optimal concentration of nucleating agents that makes the glass ceramic more electrical resistant.
1.5 Contents of the present work

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

1. \((10-x)\text{ZnO}\text{–}30\text{ZnF}_2\text{–}60\text{B}_2\text{O}_3: x\text{TiO}_2\) \((0 \leq x \leq 0.5)\)

2. \((10-x)\text{ZnO}\text{–}30\text{ZnF}_2\text{–}60\text{B}_2\text{O}_3: x\text{MoO}_3\) \((0 \leq x \leq 1.0)\)

3. \((10-x)\text{ZnO}\text{–}30\text{ZnF}_2\text{–}60\text{B}_2\text{O}_3: x\text{CoO}\) \((0 \leq x \leq 2.0)\)

The studies undertaken and their purposes are:

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

(ii) dielectric properties viz., dielectric constant \((\varepsilon_1)\), dielectric loss \((\tan \delta)\) and ac conductivity \((\sigma_{\text{ac}})\) in the frequency range \(10^2\text{–}10^6\) Hz and in the temperature range 30-300 °C and dielectric breakdown strength at room temperature to assess the insulating character.

(iii) infrared spectral studies in the wave number range 400-4000 cm\(^{-1}\) to understand the effect of concentration of nucleating agents on the structural aspects of glass ceramics.

(iv) electron spin resonance measurements, optical absorption and photoluminescence studies to identify the valence states and the environment of the transition metal ions.
References


