This chapter presents the general introduction, scope, contents and aim of the present work. The basic theory related to spectroscopic, non-linear optical properties, piezoelectric, elastic and electrical properties of \( \text{ZnF}_2-\text{PbO-TeO}_2: \text{TiO}_2 \) glass ceramic system is also included.
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 $R_nO_m$ form most easily when the ionic radius ratio of the cation, $R$, to the oxygen ion lies in the range 0.2 to 0.4. Since radius ratios in this range tend to produce cations surrounded by four oxygen ions in the form of tetrahedra, Goldschmidt believed that only melts containing tetrahedrally-coordinated cations form glasses during cooling. This contention was purely empirical, with no attempt to explain why tetrahedral coordination should be so favorable to glass formation. A few years later, Zachariasen extended the ideas of Goldschmidt and attempted to explain why certain coordination numbers might favor glass formation.

According to Zachariasen [1] there are only five oxide materials which form the glass by themselves viz., SiO$_2$, GeO$_2$, B$_2$O$_3$, As$_2$O$_3$ and P$_2$O$_5$; two more non-oxide compounds viz., As$_2$S$_3$ and BeF$_2$ are also added to this list recently [2]. Though, the glass materials do not possess the long-range periodicity but they retain short range order with AO$_3$ and AO$_4$ basic building blocks and follow certain rules proposed by Zachariasen. 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 AO (CaO, BaO etc.), A$_2$O (Li$_2$O, Na$_2$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.

The summary of the rules for glass formation proposed by Zachariasen is as follows:

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

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

c) The number of corners of polyhedra is less than 6
d) Anions (O\(^2\), S\(^2\), F\(^-\)) should not be linked with more than two cations and do not form additional bonds with any other cations.

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

f) The network modifiers participate in the glass network with the co-ordination number generally greater than 6.

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

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, solgel process techniques, etc. When a liquid is cooled from high temperature, crystallization may take place at the melting point \(T_m\). If the crystallization takes place, there will be abrupt change in the volume/enthalpy at \(T_m\). Continued cooling of the crystal will result in a further decrease in the volume/enthalpy due to the heat capacity of the crystal. If the liquid is cooled below the melting temperature without crystallization, a super cooled liquid is
obtained. In this region, the structure of the liquid continues to rearrange as the
temperature decreases, but there is no abrupt decrease in volume/enthalpy due
to discontinuous structural rearrangement.

As the liquid is cooled further, the viscosity increases. This increase in
viscosity eventually becomes so great that the atoms can no longer completely
rearrange to the equilibrium liquid structure, during the time allowed by the
experiment. The structure begins to lag behind that which would be present if
sufficient time were allowed to reach equilibrium. The enthalpy begins to
deviate from the equilibrium line, following a curve of gradually decreasing
slope, until it eventually becomes determined by the heat capacity of the frozen
liquid, 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 inorganic glasses have been developed with an attempt to achieve suitable electrical, mechanical and optical characteristics. These characteristics are associated with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, IR transmission performance and their ability to accept more transition/rare earth metal ions for their use in solid-state devices. Work along these lines was carried out on a number of glasses giving valuable information [8–13]. 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 and
electron spin resonance can be used as probes to throw some light on the structural aspects of these glasses. Studies on fluorescence spectra especially rare earth doped glasses will help to assess the suitability of the glasses for laser materials.

b. Glass-ceramics

Glass-ceramic processing consists of melting together a mixture of compounds (usually oxides), to form a fluid of high viscosity, which when cooled at moderate rates gradually increase in viscosity until a vitreous (non-crystalline) solid (glass) is formed; as has been discussed above. The cooled glass body is then partially or completely crystallized (devitrified) by heat treatment. A distinctive advantage of the glass-ceramic process is that crystallization may be accomplished at a temperature where the viscosity of the glass is still high, so that the glass body does not deform, but to a first approximation, passes from a solid glass shape to a solid crystal-line shape of the same dimensions. In these materials finely dispersed crystalline structures are stimulated to "grow" within the solidified glass matrix by a process of controlled devitrification (Figs. 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 making the glass opaque, while small crystals evenly scattered throughout the structure have less of an impact on the optical qualities of the finished product. Thus it is of benefit to hold the temperature at the point of maximum seeding for a finite length of time in order to allow numerous tiny seed crystals to nucleate, and then to stop the nucleation process and encourage the ones that have already formed to grow to suitable size.

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

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

Most 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, TiO₂, V₂O₅,
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].

Recently, the nucleation and crystal growth mechanism in TeO$_2$ based glass ceramic with TiO$_2$ as crystallizing agent has been studied in detail [15]. Transmission electron microscopy, X-ray diffraction, and differential thermal analysis showed that at the nucleation temperature, TeO$_2$ reacts with the glass constituents to precipitate PbTeO$_3$, Pb$_3$TeO$_5$, TiTe$_3$O$_8$ [15]. The size and degree of faceting of these crystallites was found to dependent on time at the nucleation temperature.

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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$_2$ is chosen for inducing crystallization in these glasses. Additionally, the transition metal ions like Ti, 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 polar glass ceramics comprising nano/microcrystallites that are capable of exhibiting piezo, pyro, ferroelectric, and non-linear optical (NLO) properties have been in increasing demand and recognized to be potential multifunctional materials. Recently, transparent crystallized glasses (composites of crystalline and glassy phases), consisting of non-linear optical or ferroelectric crystals have received much attention and there have been many reports on the fabrication and characterization of such transparent crystallized glasses [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 silicate, fluoride or oxyfluoride matrices, polymers and thin films [17–21].

Among a variety of polar glass ceramics that were investigated for various physical properties, tellurium dioxide (TeO$_2$)-based glass ceramics were promising for use in optically operated devices because of their
refractive-index compatibility with those of well-known ferroelectric compounds [22]. Further it has been widely accepted that tellurite glasses are promising non-linear optical materials for their high third-order optical non-linear (TONL) susceptibility $\chi^{(3)}$ [23].

1.2 Scope of the present work

TeO$_2$ based glasses are well known due to their high density, high refractive index and high transparency in the far infrared region [24–26]; large third order non-linear susceptibility [27], good chemical resistance and good infrared transmissivity [28]. Photoinduced study on these glasses has been the subject of high interest in recent years due to their potential applications such as IR domes, optical fibers, modulators, memory devices, optical fiber triggers and laser windows. The understanding of the origin of optical susceptibilities in tellurite glasses and the corresponding glass ceramics stimulated by ultra-short laser pulses has gained momentum in the recent years. Such studies in fact help in examining the suitability of the materials for potential applications like three-dimensional photonic devices for integrated optics and other laser-operated devices (such as ultra fast optical switches, optical fiber modulators, power limiters, broad band optical amplifiers) [29, 30].

The origin of these properties has been strongly correlated to the local order around tellurium atoms. The coordination geometry of Te atoms has been shown to be strongly dependent on the composition of the glasses and on the
chemical nature of the glassy network modifier. For example, the addition of transition metal oxides to the TeO$_2$ matrix, changes the coordination of Te from a TeO$_4$ trigonal bipyramid (tbp) group to a TeO$_3$ trigonal pyramid (tp) through intermediate polyhedra TeO$_{3+1}$ (Fig. 1.5). The TeO$_4$ tbp group has two axial and two equatorial oxygen atoms, in which an electron pair occupies the third equatorial position of the sp$^3$d hybrid orbital. The presence of this electron pair plays a key role in the structure building and manifestation of non-linear optical properties of tellurite glasses [31].

We have chosen ZnF$_2$–PbO–TeO$_2$ glasses for the present study. Addition of the modifier like ZnF$_2$ to PbO–TeO$_2$ glass matrix is expected to lower the makes the glass more moisture resistant [32] and also acts as effective mineralizer.viscosity and to decrease the liquidus temperature to a substantial extent and ZnF$_2$ acts as an effective mineralizer and PbO may act as modifier and facilitate glass formation of TeO$_2$, since TeO$_2$ as such is an incipient glass former.

PbO may also act as glass network former and participate in the glass network with [PbO$_{4/2}$] pyramidal units connected in puckered layers. Additionally, earlier it was reported that PbO also plays a crucial role in inducing the non-polar effects in the glass materials [33]. TiO$_2$ is chosen as the crystallizing agent because it is quite likely that the titanium ions do form interesting tetragonal ferroelectric crystalline phases like Pb$_5$Ti$_3$F$_{19}$, PbTiO$_3$ [15] and
PbTeO$_3$ in these samples contributing to second order non-linear optical coefficients, piezoelectric coefficient ($d_{33}$) substantially.

![Illustration of the coordination states of tellurium atom (a) TeO$_4$ trigonal bipyramid (tbp), (b) TeO$_{3+1}$ polyhedron and (c) TeO$_3$ trigonal pyramid (tp)](image)

**Fig. 1.5** Illustration of the coordination states of tellurium atom (a) TeO$_4$ trigonal bipyramid (tbp), (b) TeO$_{3+1}$ polyhedron and (c) TeO$_3$ trigonal pyramid (tp)

Though considerable studies on electrical properties along with optical properties [34–36] of some TeO$_2$ based glasses are available in literature, majority of these studies are devoted to binary tellurite glasses and further they are mainly concentrated on dc conductivity studies [37–40]. Much devoted studies on non-linear optical properties, piezoelectric properties, elastic properties, dielectric relaxation and ac conductivity of ZnF$_2$–PbO–TeO$_2$ glasses crystallized with transition metal oxides like TiO$_2$ are very rare; knowledge on
these properties is highly helpful for assessing the suitability of these materials for non-linear optical devices and design of miniature sensors and actuators.

The first row transition metal ions are very interesting ions to probe in the glass network because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive and also act as crystallizing agents. As a result these ions influence the physical properties of the glasses to a substantial extent. Among various transition metal oxides, TiO$_2$ is expected to be more effective mineralizer especially in the glass systems like tellurite exhibiting high optical susceptibilities. Normally, the ions of titanium, exist in the glass in Ti$^{4+}$ state and participate in the glass network forming with different principal polyhedral: TiO$_4$, TiO$_6$ and some times with TiO$_5$ (comprising of trigonal bipyramids) structural units [41, 42]. However, there are reports suggesting that these ions may also exist in Ti$^{3+}$ valence state in some of the glass matrices [43, 44]. Further the inclusion of Ti$^{4+}$ ions into the tellurite glass ceramic network is substantial advantage to use these materials for optically operated devices, since the empty or unfilled 3d-shells of Ti ions contribute more strongly to the non-linear polarizabilities that can be determined prevailingly by optical/electrical Kerr effect.

In view of these, it is felt worthwhile to have some understanding over the dielectric, dc field and photoinduced second order susceptibilities,
piezoelectric, elastic and spectroscopic properties of ZnF$_2$–PbO–TeO$_2$ glasses crystallized with TiO$_2$. The studies on photoinduced second order susceptibilities coupled with spectroscopic (viz., optical absorption, electron spin resonance, infrared and Raman spectra) help to assess the suitability of these materials for NLO devices; the study on piezoelectric properties will help in examining the aptness of these glass ceramics in the design of miniature sensors and actuators; study on elastic properties will help in estimating the mechanical strength, whereas the studies on dielectric properties give the information on insulating strength of these materials and also help in understanding the structural aspects.

A preliminary description of the above-mentioned properties along with their relation to some of the investigations (similar to those of present work) on ZnF$_2$–PbO–TeO$_2$ glasses is given below:

### 1.2.1 Physical parameters

Some physical parameters useful for characterization ZnF$_2$–PbO–TeO$_2$ glasses crystallized with TiO$_2$ are estimated from the measured value of density (d) and the average molecular weight $\overline{M}$, using the following equations [45–48]:

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

$$N_i = \frac{N_A M(\text{mol\%}) d}{M}$$  \hspace{1cm} (1.1)

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

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

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

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

\[ \text{Field strength (cm}^{-2}), \quad F_i = \frac{z}{r_p^2} \]  \hspace{1cm} (1.4)

### 1.2.2 Dielectric properties

When an insulating glass (a dielectric) like ZnF₂–PbO–TeO₃ glass is placed in external electric field two types of polarizations – the electronic and the ionic – are expected to develop in the glass. If the dielectric contains permanent dipoles, they experience a torque in an applied field that tends to orient them in the field direction. Consequently, an orientational (or dipolar) polarization can arise. These three polarizations are due to charges locally bound in atoms, molecules or in the structures of solids. Additionally to all these, generally there exist charge carriers that can migrate for some distance through the dielectric. Such charge carriers during their motion may be trapped in the material or on interfaces (because they cannot be freely discharged or
replaced at the electrodes); due to these causes, space charges and a microscopic field distortion result. Such a distortion appears as an increase in the capacitance of the sample and may be indistinguishable from a real rise of the dielectric constant. Thus a fourth polarization, called the space charge polarization comes into play. The total polarization is sum of these four polarizations (assuming that they act independently) [49].

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 [50].

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 δ) is given by the expression:

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}$$ \hspace{1cm} (1.8)

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

$$\tan \delta = \frac{4\pi\sigma}{\omega \varepsilon'(\omega)} + \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\varepsilon_s + \varepsilon_\infty \omega^2\tau^2}$$ \hspace{1cm} (1.9)

By plotting log (tanδ) as a function of log (ω), information regarding ac 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 in its valence state, its site preference and determination of the degree of covalency of the metal-ligand bond. When a transition metal ion is embedded in a glass it need not have a centre of symmetry. This leads to
mixing of d– and p– orbitals of the ion and, therefore, an electronic transition involves some charge transfer from a d-orbital 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 has been worked out recently [51–53]. 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. 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. In a weak field approach, one tries to understand the effect of crystal fields on the free ion terms (Fig. 1.7(b)).

For d case, the application of the group theory results in the splitting of $^2D$ state into $e_g$ and $t_{2g}$ representations in octahedral crystal field. The crystal field potential acting on the ion is given by

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

(1.10)

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

$$<t_{2g}/V_{oct}/t_{2g}> = -4D_q$$

(1.11)

$$<e_g/V_{oct}/e_g> = 6D_q$$

(1.12)
Thus, 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.

Fig. 1.7 (a) The five d-orbitals in an octahedral field of ligands
In tetrahedral ($T_d$) 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

**Fig. 1.7 (b)** Detailed spectral information on titanium ($d^1$) transition metal ion.
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 many electron systems are obtained by filling the $t_{2g}$ shell first and then the $e_g$ shell. Thus for example, the $d^2$ ion has $t_{2g}^2$, $t_{2g}^1 e_g^1$ and $e_g^2$ configurations with energies $- 8D_q$, $2D_q$ and $12D_q$, respectively.

![Diagram showing relative energy of e and t orbitals resulting from the splitting of d orbitals by octahedral and tetrahedral environments.](image)

**Fig. 1.8** Diagram showing relative energy of e and t orbitals resulting from the splitting of d orbitals by octahedral and tetrahedral environments.

### 1.2.4 Electron spin resonance

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

1. Atoms having odd number of electrons, e.g., atomic hydrogen and lithium atom.
2. Molecules with odd number of electrons such as NO, and triplet state molecules like oxygen molecule.
3. Ions having partially filled inner electronic shells, e.g., iron, rare earth ions etc.
4. Defects produced in a solid by irradiation.
5. Free radicals, e.g., CH$_3$ and diphenyl−picrylhydrazyl.
6. Conduction electrons in metals, semiconductors and dilute alloys etc.

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

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

\[
\vec{J} = \vec{L} + \vec{S}. \tag{1.13}
\]

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

\[
\vec{\mu} = -g\beta J \tag{1.14}
\]

where

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

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

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

which is known as the Bohr magneton. When a magnetic dipole is placed in a uniform magnetic field B, it precesses about the direction of B with the Larmor angular frequency \(\omega_L\) which is given by [54],
\[ \omega_L = \gamma B \]  
\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. 1.9, 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 \( B \) is

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

**Fig. 1.9** Zeeman energy for a single unpaired electron as function of magnetic field $B$. A magnetic dipole aligned parallel to $B$ has lower energy while a magnetic dipole aligned antiparallel to $B$ has higher energy.
the degenerate energy level will split into (2J+1) levels and the conditions for
the transitions by absorption of energy is given by Eq. (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 [55–59].
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 draw back that various interactions should differ from one another by at least one or two orders of magnitude. Incidentally, this condition is satisfied in EPR spectroscopy.

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

The concept of Hamiltonian was originally developed by Pryce [60] and Abragam and Pryce [61] to interpret the observed resonance of ions in the first transition series. The concept was subsequently extended by Elliott and Stevens [62] 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 [63].

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

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

\begin{itemize}
\item[i.] \(H_E\) is a composite term expressing the total energy of electrons, the columbiaic attractions of the electrons and the nuclei and the repulsion among the electrons.
\end{itemize}

\begin{equation}
H_E = \sum_i \left[ \frac{P_i^2}{2m} - \frac{Ze^2}{r_i} \right] + \sum_{ij} \frac{e^2}{r_{ij}} \tag{1.22}
\end{equation}

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\(^{-1}\).

\begin{itemize}
\item[iii.] \(H_{LS}\) represents the spin-orbit coupling and may be written in the form.
\end{itemize}

$$H_{LS} = \sum \lambda_{ij} \cdot l_i \cdot s$$  \hspace{1cm} (1.23)

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

(1.24)

Where, L and S are the total orbital angular momentum and the spin angular momentum of free ion respectively. The magnitude of this interaction lies in the range \(10^2\) to \(10^3\) cm\(^{-1}\).

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

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

(1.25)

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

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

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

(1.26)

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

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

(1.27)

Where \(V(r_i)\) is the electrostatic potential at the ion with which each electron interacts.

In an external magnetic field \(B\), the terms \(H_{SI}\) and \(H_{IH}\) must be added to represent the interaction of the angular momentum of electrons and nuclei respectively with the magnetic field.
\[ H_{SH} = \beta \left( L + g_e S \right) \cdot B \]  
\[ H_{IH} = \frac{h}{2\pi} \sum_i -\gamma_i \cdot I_i \cdot B \]  

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

b) Line shapes

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

\[ I_1 = \frac{I_0}{T_2^2 (B - B_r)^2 + 1} \]  
\[ I_2 = I_0 \exp \left[ -b (B - B_r)^2 T_2^2 \right] \]  

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

The Lorentzian shape arises due to harmonically bound electron. If the harmonic motion of the electron is interrupted by some process, then the distribution of frequencies follows the Eq. (1.31) for an EPR spectrum, the interruption will be in the form of exchange. Since all the electrons are equivalent, their interchanging between two molecules is quite possible if the molecules are close enough to each other. If this exchange is so rapid to affect the phase coherence of the spins, Lorentzian shape results.
On the other hand, Gaussian shape results from the paramagnetic ion separated from each other by molecules, which are having no unpaired electrons but possessing magnetic nuclei. Each unpaired electron will experience a local static magnetic field which will be dominated by how the nuclear spins are arranged in the near by host molecules. The observed EPR spectra will be a superposition of shapes from all the spins with their local fields. Since the local fields will be randomly distributed, the total line shape results in a Gaussian line shape according to Eq. (1.30). The characteristic Lorentzian and Gaussian line shape are shown in the Fig. 1.10.

![Fig. 1.10 The characteristic Lorentzian and Gaussian line shapes.](image)

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 hr of the EPR
signal corresponding to the centre of $r^{th}$ interval is noted and the area under the curve can be calculated from the equation

$$A = \frac{1}{2} \sum_{r=1}^{n} (n - 2r + 1) h_r$$  \hspace{1cm} (1.32)

Fig. 1.11 shows the method of finding the area under the first derivative absorption curve by numerical double integration method.

![Fig. 1.11 The method of finding the area under the first derivative absorption curve by numerical double integration method.](image)

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 microwaves, (4) the transition probability and (5) the temperature.

1.2.5 Infrared spectra

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

In addition, the investigation of infrared spectra (IR) of glasses enables the assignment of characteristic frequencies to molecular groups in the glass ceramics and hence correlation of IR absorption bands with different units of vitreous structure. In the case of tellurite glasses and glass ceramics, the basic network consists of TeO₄, TeO₃ structural units when a cations such as Zn, Ti are added, it may reside interstitially. Such information about the changes in
the basic glass structure that take place upon the addition of a cation can also be studied from the IR spectra.

The vibrations of structural units in glasses are independent [64–66], unlike the vibrations of complex ions in a glass matrix which are dependent of the vibrations of other groups. In probing the structural units and changes that take place in the network with composition of a ternary glass, infrared spectroscopy lends itself as an effective tool, because the technique is sensitive to short-range ordering and local interactions.

The assignment of the important IR bands observed in ZnF$_2$–PbO–TeO$_2$ glasses of the present work is in general made by comparison of the data with the bands observed in literature, even though some bands attributions have their support from the theory. However, it is possible to provide quantitative justification from the theoretical calculation in the literature [65] for some of the vibrational frequencies assigned to tellurite oxide and other transitional ion groups like TiO$_4$, TiO$_6$ etc.

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

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

(1.33)
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 [65, 66].

1.2.6 **Raman spectra**

Among variety of spectroscopic methods, Raman spectroscopy provides information about molecular symmetry of relatively small molecules and functional groups in large and complex molecules. Raman spectroscopy became a useful technique with the introduction of lasers as a convenient monochromatic light source. It has become widely available only after the introduction of holographic filters to reject the light scattered without frequency change. In this method, the sample is illuminated with monochromatic light (a laser) and the light scattered by the material is analyzed by a conventional optical microscope coupled to a Raman spectrometer or a very sophisticated filter. Most of the scattered light has the same frequency as the laser, but a very tiny amount experiences a frequency shift, which is characteristic of the chemical bonds or molecules present in the material. This inelastic scattering of light is called the Raman effect. The analysis of the scattered frequencies (Raman spectroscopy) gives information on the material chemical composition, state, aggregation, and even factors like stress, orientation etc. The difference 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 (anti-stokes) 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 in Fig. 1.12. In Raman spectrum, the Stokes and anti-Stokes lines are equally displaced from the Rayleigh line.

Fig. 1.12 A schematic representation of Raman spectrum
This occurs because in either case one vibrational quantum of energy is gained or lost. Also, note that the anti-Stokes line is much less intense than the Stokes line. This occurs because only molecules that are vibrationally excited prior to irradiation can give rise to the anti-Stokes line. Hence, in Raman spectroscopy, only the more intense Stokes line is normally measured. For a vibrational motion to be IR active, the dipole moment of the molecule must change. For a transition to be Raman active there must be a change in polarizability of the molecule with the vibrational motion. Thus, Raman spectroscopy complements IR spectroscopy. For example, homonuclear diatomic molecules do not have an infrared absorption spectrum, because they have no dipole moment, but do have a Raman spectrum, because stretching and contraction of the bond changes the interactions between electrons and nuclei, thereby changing the molecular polarizability. For highly symmetric polyatomic molecules possessing a center of inversion (such as benzene) it is observed that bands that are active in the IR spectrum are not active in the Raman spectrum (and vice-versa). In molecules with little or no symmetry, modes are likely to be active in both infrared and Raman spectroscopy.

In the present study, the Raman spectroscopy has been used for identifying various structural units like TiO$_4$, TiO$_6$, TeO$_4$ structural groups in the ZnF$_2$–PbO–TeO$_2$ glass ceramic matrix and the changes in the concentration of these structural units with the varying concentration of TiO$_2$. 
1.2.7 Photoinduced second order susceptibility

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

\[
P = \sum_i P_i = \chi E
\]  

(1.34)

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

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

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

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

In these Eqs., \( \chi_{ij}, \chi_{ijk}, \chi_{ijkl} \) represent first, second and third order susceptibilities respectively and \( L_{ij,k} \) representing Lorenz field factors. \( \chi_{ijk} \) and \( \chi_{ijkl} \) define the degree of non-linearity and are known as non-linear susceptibilities.
A polarization, oscillating at frequency $2\omega$, radiates an electromagnetic wave of the same frequency. The wave thus produced has the same characteristics of directionality and the monochromacity as the incident wave and emitted in same direction. This phenomenon is known as second harmonic generation (SHG). This polarization is represented by

$$P_i^{(2)} = \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k$$  \hspace{1cm} (1.37)

For amorphous material as such this $\chi_{ijk}$ is zero and it is non-zero when exposed to high intense laser beam. The development of Q-switched laser has made possible to generate third harmonic represented by

$$P_i^{(3)} = \sum_{j,k} \chi_{ijk}^{(3)} E_j E_k E_l$$  \hspace{1cm} (1.38)

even in amorphous materials by optical poling. But the energy conversion efficiency in such cases is very low. In case of the optical poling, the IR induced non-centro symmetry of the photo-induced vibrations begins to play a dominant role and it is necessary to consider a process of interaction of at least two photons and three phonons. Interactions of the one or two photons with one or two phonons do not give contribution to the non-zero polarization of the medium (Fig. 1.13)
For getting birefringence, anharmonic electron-phonon interactions with at least three phonons as shown in Fig. (1.15) are required. Otherwise, we shall have harmonic electronic-phonon interactions which would not give non-centro symmetry as shown in Fig. (1.14).
Tellurium oxide as mentioned earlier participates in the glass network with TeO$_4$ tbp structural units and can be viewed as tetrahedrons with the oxygen situated at four vertices and the lone pair of electrons of tellurium at the fourth corner localized in the third equatorial direction of Te atom (Fig. (1.16)).

The deformability of this pair probably favor different optically polarized effects and make these glass ceramics to exhibit non-linear optical susceptibility described by third rank polar tensors.
1.2.8 *Piezoelectric properties*

Certain single crystals, ceramic materials, glasses and glass ceramics when subjected to mechanical stress or strain, electric polarization is produced which is proportion to the magnitude and sign of the strain applied on certain surfaces of the samples and if the material is not short-circuited, the resultant charge induces a voltage across the material. This is called the direct piezoelectric effect, and the materials that exhibit this phenomenon are classified as piezoelectric materials (Fig. 1.17).

![Fig. 1.17 The phenomenon of piezoelectric effect.](image)

The origin of the piezoelectric effect in all the materials that exhibit this effect related to an asymmetric in the unit cell of the material and the resultant generation of electric dipoles due to the mechanical distortion leading to a net polarization at the crystal surface and the induced polarization varies directly with the applied surface and it is direction dependent, so that compressive and
tensile stresses will generate electric fields and hence voltages of opposite polarity.

Piezoelectric glasses and glass ceramics are more versatile such that their physical, chemical, and piezoelectric characteristics can be tailored to specific applications. Conventional piezoelectric ceramic materials viz., BaTiO$_3$, PZT, LNB lose their piezoelectric and pyroelectric properties due to the aging and degradation. In view of this, transparent polar glass ceramics which possess fatigue endurance and minimal degradation effects and containing well defined, randomly oriented inter-twinned polar crystal phases have been in an increasing demand and recognized as potential multifunctional materials.

Any glass ceramic material to exhibit piezoelectric and pyroelectric effects should contain non centrosymmetric crystalline phases because the effect is described by third rank polar tensor. Additionally, nucleation and growth behavior of the glass ceramics, as well as the spatial distribution of the polar crystallites should have a significant effect on the piezoelectric and pyroelectric features of such an acentric media.

In the present investigation we have measured piezoelectric coefficients for ZnF$_2$-PbO-TeO$_2$ glasses crystallized with different concentrations of TiO$_2$. Due to crystallization, the studied glass ceramics are expected to be embedded with PbTi$_2$O$_6$, PbTeO$_3$, Pb$_3$TeO$_5$, and TiTe$_3$O$_8$ acentrosymmetric ferroelectric crystal
phases which exhibit piezoelectric phenomenon. The measurements were performed by connecting sample condenser in parallel to an external capacitor. The application of the mechanical stress on the sample condenser induces the charges and thereby changes the resultant capacitance. By measuring this change in capacitance, we have evaluated the voltage induced on the surface of the sample and evaluated piezoelectric coefficient $d_{33}$ using the standard relation:

$$d_{33} \cdot F = C_V \cdot V$$  \hspace{1cm} (1.39)

### 1.2.9 Elastic properties

Ultrasonic non-destructive characterization of materials is a versatile tool for investigating the change in microstructure, deformation process and mechanical properties of materials [67]. This is possible due to the close association of the ultrasonic waves with elastic and inelastic properties of the materials. Interest in glasses has rapidly increased in recent years because of diverse applications in electronic, nuclear, solar energy and acousto-optic devices. The acoustic wave propagation in bulk glasses has been of considerable interest to understand their mechanical properties [68]. The velocity of sound is particularly suitable for characterising glasses as a function of composition because it gives information about the microstructure and dynamics of glasses [69]. The study of elastic properties of glasses has inspired many researchers [70, 71] and significant information about the same has been
obtained. The dependence of ultrasonic velocity on the composition of glass provides the information on various changes in the structural configuration between the network former and modifiers [72, 73]. Recent ultrasonic studies on BaTiO3 doped vanadate lead glasses [74], bismuthlead tellurite [75], vanadium tellurite [76] and copper tellurite glasses [77] show interesting features with addition of second/third component.

In view of this a part of the thesis is devoted to studies on ultrasonic velocities in TeO2 glass ceramics and their variation with composition. From these studies we have evaluated various mechanical and elastical parameters such as elastic moduli, acoustic impedance, internal friction and micro-hardness of the glass ceramics with the conventional equations.

1.3 Brief review of the previous work

The studies as such on TeO2 glasses crystallized with TiO2 are very few. In view of this a brief summary on the available studies of TeO2 based glasses and TiO2 mixed glasses and glass ceramics is given below.

a) On TeO2 based glasses

Vosejpková et al [78] have investigated boron and tellurium coordination in zinc borophosphate glasses by B MAS NMR and Raman spectroscopy. Their studies have revealed changes in boron coordination depends on changes in TeO2 content and in B2O3/P2O5 ratio in the borophosphate glasses. Sahar et al [79] have studied the effects of chloride ion
in TeO$_2$–ZnO–ZnCl$_2$–Li$_2$O–Eu$_2$O$_3$ glass system. Their studies have indicated that the luminescence efficiency of Eu$^{3+}$ ions depends on the concentration of ZnCl$_2$. Ersundu, et al. [80] have investigate glass formation area and characterization of CdO–WO$_3$–TeO$_2$ ternary system. These studies have indicated that structural transformations on the glass network is resulted by the changing WO$_3$+CdO/TeO$_2$ ratio. Munoz-Martín et al. [81] have studied structural and optical properties of tellurite thin film glasses deposited by pulsed laser deposition. Apakova et al. [82] have applied the constant stoichiometry grouping concept to the Raman spectra of Pb(PO$_3$)$_2$–TeO$_2$ glasses. This concept has opened the way for elaboration of low scattering glasses as candidates for Raman amplifiers. Upender et al. [83] have reported the structural and spectroscopic properties of ternary tellurite glasses, doped with copper. The observed variations in spin-Hamiltonian parameters and bonding parameters have been correlated to the structural modifications due to the WO$_3$ and Ag$_2$O incorporation into the TeO$_2$ glass network. Surendra Babu et al. [84] have recently reported spectroscopic investigations of 1.06 μm emission in Nd$^{3+}$-doped alkali niobium zinc tellurite glasses. In this system the authors have observed that the quantum efficiency of the $^4$F$_{3/2}$ level is higher than the typical value of the other tellurite based glasses. Sandhya Rani et al. [85] have studied the electrical and magnetic properties of copper doped tellurite glass system. These studies have indicated the coexistence of
antiferromagnetic (AFM) as well as ferromagnetic (FM) interactions between Cu\(^{2+}\) ions in these glasses.

Yousef et al. [86] have reported thermal characteristics and crystallization kinetics of tellurite glass with small amount of additive As\(_2\)O\(_3\). In this study the authors have reported crystallization results are analyzed, and both the activation energy of crystallization process and the crystallization mechanism were discussed in detail. Upender et al. [87, 88] have reported the structure, physical and thermal properties of WO\(_3\)–TeO\(_2\) glasses. In this study the variations in the optical band gap energy (E\(_{\text{opt}}\)) and optical basicity (\(\Lambda_{\text{th}}\)) with WO\(_3\) content have been discussed in terms of the glass structure. Jlassi et al. [89] have studied photoluminescence quenching in Er\(^{3+}\)-doped tellurite glasses. In this study it was found that PL quenching with Er concentration in the tellurite glass is independent of OH- content. The authors have also determined stimulated cross-section at 1.53 \(\mu\)m and have discussed using the McCumber theory. Cherif et al. [90] have reported red fluorescence under 980 nm excitation in Er\(^{3+}\) doped TeO\(_2\)–ZnO glasses. The dynamics of the red up-conversion was well explained in this report. Starvou et al. [91] have investigated Raman scattering boson peak and differential scanning calorimetry studies of the glass transition in tellurium-zinc oxide glasses. The studies of these results have indicated that the Boson peak is highly sensitive to dynamical effects over the glass transition and provides a means for an equally
reliable (to DSC) determination of $T_g$ in tellurite glasses and other network glasses. Ardelean et al. [92] have reported Infrared and Raman spectroscopic studies of MnO–As$_2$O$_3$–TeO$_2$ glass system. In this study the authors have reported the presence of MnO$_2$ units in this glass network. Soulis et al. [93] have studied second harmonic generation induced by optical poling in TeO$_2$–Tl$_2$O–ZnO glasses. In this study the authors have concluded that the second order non-linearity amplitude is increasing with increase of Tl$_2$O concentration in the glass network.

Ozdanova et al. [94] reported optical band gap and Raman spectra some tellurite glass systems. In this study the authors have found that structural changes are induced by chemical composition in TeO$_2$ network due to conversion from TeO$_4$ trigonal bipyramids to TeO$_3$ and TeO$_{3+1}$ units. Hayakawa et al. [95] have investigated the non-linear optical properties and glass structure for MO–Nb$_2$O$_5$–TeO$_2$ (M = Zn, Mg, Ca, Sr, Ba) glasses. In this study the authors have measured the third-order non-linear optical susceptibilities $\chi(3)$ of these glasses by Z–scan measurement using Ti:Sapphire femtosecond laser pulses. Wang et al. [96] have reported optical properties and supercontinuum generation of TeO$_2$-based glass. In this report the authors have studied thermal stability, optical transmittance, non-linear optical properties and supercontinuum generation of TeO$_2$–based glass and demonstrated and it is a potential candidate in application in optical devices. Sidek et al. [97] have
studied optical properties of ZnO–TeO$_2$ glass system. In this study the authors have found that the optical band gap ($E_{\text{opt}}$) of zinc tellurite glass decreases with increasing of ZnO content and attributed to the increment of Non-Bridging Oxygen (NBO) ion contents in the glass network.

Dimitrov and Komastru [98] have reported changes of coordination number of tellurium and group optical basicity of ZnO–TeO$_2$ glasses. In this study it has been proposed that the optical basicity of ZnO–TeO$_2$ glasses decreases with increasing modifier content due to the formation of TeO$_3$ groups in the structure which possess lower group optical basicity than that of TeO$_4$ groups. Ozdanova et al. 99] have reported optical band gap and Raman spectra of bismuth tungsten tellurite and lead tungsten tellurite glasses. In this study it was reported that tungsten ions participate in the glass network with WO$_6$ corner shared octahedral units and the linkages of the type Bi–O–Te, Pb–O–Te and W–O–Te are also possible in the glass network. Sidkey et al. [100] have studied relaxation of longitudinal ultrasonic waves in binary TeO$_2$–Nb$_2$O$_5$ and ternary TeO$_2$–Nb$_2$O$_5$–LiO$_2$ tellurite glass systems in the temperature range 200-280 K. The results showed that the mean activation energy is dependent on the modifier content. Abd El-Moneim [101] has investigated DTA and IR absorption spectra of vanadium tellurite glasses and reported that the structure of the glass system changes at 20 mol% of V$_2$O$_5$. Silva et al. [102] have prepared TeO$_2$–PbO glasses and investigate the
structure by means of Raman scattering and X-ray absorption spectroscopy. Lezal et al. [103] have studied physical properties of TeO₂–PbO–PbCl₂, TeO₂–ZnO and Ga₂O₃–PbO–Bi₂O₃ glasses. Vijaya Prakash et al. [104] have investigated physical and optical properties of niobium based tellurite glasses and concluded that the large refractive index values obtained are due to the hyperpolarisability of the Nb–O bands. Pal et al. [105] have prepared MoO₃–TeO₂ glasses by melt quenching and studied the d.c. conductivity. Elkholy and Sharaf [106] has studied the dielectric properties of TeO₂–P₂O₅ glasses and found the dielectric constant and loss decreased with increasing frequency and increased with increasing temperature. El-Damarawi et al. [107] have investigated ionic conductivity of mixed cationic glasses containing silver ions and observed that the values of conductivity in both phosphate and tellurite glasses are similar. Mori et al. [108] prepared V₂O₅–Sb–TeO₂ glasses by press quenching and studied the small polaron hopping conduction in the glasses. Iwadate et al. [109] investigated the short-range structure of K₂O–TeO₂ by XRD and semi-empirical molecular orbital calculation method and found that amorphous alkali tellurites consisted of TeO₄ trigonal bipyramids and TeO₃ trigonal pyramids. Murali and Rao et al [110] have carried out spectroscopic investigations on Cu (II) ions doped in alkali lead boro tellurite glasses and observed that optical energy gap decreased and Urbach energy increased with increase in concentration of copper ion.
Kosuge *et al.* [111] have reported that the K$_2$O–WO$_3$–TeO$_2$ glasses with 60-70 mol % of TeO$_2$ are thermally stable against crystallization. Chowdari and Kumari [112] studied the structure and ionic conduction in the Ag$_2$O–WO$_3$–TeO$_2$ glass system. The results showed that the glass network consists of TeO$_4$, TeO$_3$, WO$_4$ and WO$_6$ polyhedra. Ravikumar *et al.* [113] have investigated the dielectric properties of CuO doped ZnF$_2$–PbO–TeO$_2$ glasses and concluded that the dielectric parameters are strongly dependent on the concentration of CuO. Their infrared spectral investigations [114] on these glasses showed that an increase in the concentration of PbO leads to an increase in the degree of depolymerisation of the glass network. Turrell *et al.* [115] have investigated the effect of doping metal on the structure of binary tellurium oxide glasses by Raman spectroscopy and found that the positions of Raman bands depend both on the metal oxide and the amount of doping. Pan and Morgan [116] have studied the Raman spectra and thermal analysis of lead tellurium germanate glasses and observed that the glass transition temperature decreased with increase in TeO$_2$ content up to 40 mol%. Shaltout *et al.* [117] have studied the optical properties of TeO$_2$–WO$_3$ glass system by Fourier transform infrared spectroscopy in the spectral range 150-25,000 cm$^{-1}$ and reported that the optical band gap decreased while the refractive index increased with increase in WO$_3$ content. Sakata *et al.* [118] have studied the dc conductivity of V$_2$O$_5$–PbO–TeO$_2$ glasses and explained it on the basis of small
polaron hopping theory. Ravikumar and Veeraiah [119] carried out a considerable work on various physical properties of ZnF$_2$–PbO–TeO$_2$ glass system doped with certain rare earth ions. They studied the optical absorption and photoluminescence properties of Eu$^{3+}$ doped ZnF$_2$–PbO–TeO$_2$ glasses.

Mazzuca et al. [120] have undertaken structural studies of ZnO–TeO$_2$ glass system by Raman scattering and interpreted the sharp bands in the final spectra on the basis of chains of TeO$_3$–TeO$_4$ polyhedra interlaced with chains of ZnO$_6$ groups. Sekiya et al. [121] have investigated the MoO$_3$–TeO$_2$ glasses by Raman spectroscopy and differential thermal analysis and reported that the glasses contain TeO$_4$ trigonal bipyramids, TeO$_{5+1}$ polyhedra and MoO$_6$ octahedra as basic structural units. Balaya and Sunanda [122] have investigated the mixed alkali effect, in the conductivity of TeO$_2$ glasses. They have discussed their results in the light of intercharge transportation phenomenon. Mallawany [123] gave a detailed theoretical analysis of electrical properties of tellurite glasses containing some transition metal ions and concluded that the conduction in these glasses is mainly due to hopping of small radius polarons. Mori et al. [124] have reported the electrical conductivity of V$_2$O$_5$–Sb$_2$O$_3$–TeO$_2$ glasses. They have found that these glasses are of n-type semiconductors. Mallawany [125] has studied the longitudinal elastic constants of ZnO–TeO$_2$ glass system. His results have indicated that the longitudinal elastic constants are strongly dependent on the composition of the glasses. Also
Mallawany with Sidkey \textit{et al.} [126] has measured the ultrasonic velocity in MoO$_3$–TeO$_2$ glass system using pulse echo technique and they have used this data to determine the elastic moduli, Debye temperature and Poisson’s ratio of the glasses. Satyanarayana and Buddhudu [127] have measured the elastic properties of Nd$^{3+}$ doped TeO$_2$–V$_2$O$_5$, GeO$_2$–V$_2$O$_5$–TeO$_2$ and TeO$_2$–V$_2$O$_5$–R$_2$O (R$_2$O is alkali oxide) glasses by the ultrasonic technique. Dimitrov \textit{et al.} [128] have investigated the effect of WO$_3$ on IR spectra of tellurite glasses. Ahmed [129] has reported the optical absorption spectrum of tellurium in alkali borate glasses. Khan \textit{et al.} [130] have reported d.c. conduction phenomenon along with some other physical properties of TeO$_2$–Fe$_2$O$_3$ glasses doped with certain rare earths. They found that the activation energy and dc conductivity are the function of atomic number Z of the rare earth cations. Wang \textit{et al.} [131] have studied the infrared properties of TeO$_2$–PbO–PbCl$_2$ glass system and assigned the various bands obtained due to TeO$_3$ and TeO$_4$ units.

\textbf{b) On TiO$_2$ mixed glasses}

The studies as such on TiO$_2$ mixed glasses are very rare. However the brief summary of some recent studies on the role of titanium ions on the structural aspects and physical properties of various glass systems including tellurite, silicate, phosphate, borate, glasses is presented below.
Inoue et al. [132] reported that the TiO$_2$-containing glasses are expected as alternatives of Pb-containing glasses and optical materials, and they have been extensively studied in recent years. In oxide glasses, Ti$^{4+}$ ions take various coordinate structures as TiO$_4$, TiO$_5$, and TiO$_6$, resulting in the specific characteristics. Ti ions in tetrahedral TiO$_4$ units are regarded as network former (NWF), and those in octahedral TiO$_6$ units are as network modifier (NWM). Ti ions in TiO$_5$ units play an intermediate role between NWF and NWM. TiO$_5$ units are in a tetragonal pyramid structure with an extremely short Ti–O bond in the axial direction. The oxygen atom in the axial Ti–O bond is regarded as non-bridging oxygen (NBO), and the rest are attributed to bridging oxygen (BO). A number of reports have been published concerning the coordination structures of Ti ions in glass. Sakka et al. [133, 134] reported that Ti ions mostly existed in TiO$_4$ units in K$_2$O–TiO$_2$ and Cs$_2$O–TiO$_2$ glass systems. Kusabiraki et al. [135] reported that coordination number of Ti ions in Na$_2$O–TiO$_2$–SiO$_2$ glasses changed from 4 to 6 with increasing Na$_2$O content. Balda et al. [136] have studied the optical properties and upconversion luminescence of Er$^{3+}$ ions in TeO$_2$–WO$_3$–PbO–BaF$_2$ and TeO$_2$–TiO$_2$–Nb$_2$O$_5$–BaF$_2$ fluorotellurite glasses and their comparison with those of TeO$_2$–TiO$_2$–Nb$_2$O$_5$ glass. These authors have reported that emission cross-section has been determined from the line shape of the emission spectrum and the calculated emission probability for the $^4$I$_{13/2}$ level. Kabalci et al. [137] have measured
Optical absorption and spectroscopic properties of thulium doped \((\text{TeO}_2)(\text{Nb}_2\text{O}_5)(\text{TiO}_2)\) glasses. In this experiments, the effect of different \(\text{Tm}^{3+}\) ion concentration and glass composition on optical properties of glasses have been investigated by using UV-VIS-NIR optical spectrophotometry. Kabalci \textit{et al} [138] have investigated the optical properties and crystallization kinetics of \((\text{TeO}_2)(\text{ZnO})(\text{TiO}_2)\) glasses. All the glasses were found to be transparent from visible to near infrared region for different \(\text{ZnO}\) glass compositions \((x=0.05, 0.10, 0.20, \text{and} 0.30 \text{ mol})\). These authors suggesed that the addition of \(\text{ZnO}\) to the glass composition from 0.05 to 0.30 mol increases the optical band gap energy from 2.94 to 3.0 eV. Hayakawa \textit{et al} [139] have measured the third-order non-linear optical susceptibilities \((\chi^{(3)})\) of thallium-tellurite \((\text{Ti}_2\text{O-TeO}_2)\) glasses doped separately with various metal oxides \((\text{MOY/X}; \text{M} = 22\text{Ti(IV)}, 30\text{Zn(II)}, 31\text{Ga(III)}, 82\text{Pb(II)} \text{and} 83\text{Bi(III)})\) by using a femtosecond Z-scan technique. They observed that the highest change in refractive index for \(\text{M} = \text{Ti}\) other than \(\text{Pb}\) and \(\text{Bi}\), This was attributed to the formation of the \(\text{TeO}_2/\text{TiO}_2\) glass structure without destruction of the initial three-dimensional network. Chen \textit{et al} [140] have studied microcrystalline \(\text{TeO}_2-\text{Bi}_2\text{O}_3-\text{Nd}_2\text{O}_5-\text{TiO}_2\) quaternary glasses and studied third-order non-linearities of by using Z-scan technology at 730nm. Cascales \textit{et al} [141] have studied fluorescence spectroscopy of \(\text{Eu}^{3+}\) in \(\text{TeO}_2-\text{TiO}_2-\text{Nb}_2\text{O}_5\) glass. In this work the authors reported that the time-resolved line-narrowed fluorescence spectra of the \(^5\text{D}_0\)
$\rightarrow {^7}F_{0.6}$ transitions of Eu$^{3+}$ at 10 K in 80TeO$_2$–5TiO$_2$–15Nb$_2$O$_5$ glass. Gu et al [142] have studied second harmonic generation effect of transparent Li$_2$OBaOTiO$_2$TeO$_2$ crystallized glasses by using Maker fringe technique. These authors found that Li$_2$TeO$_3$ phase in the glass induced the SHG effect, which reached the maximum when the incidence angle was near $\pm 60^\circ$. The SHG intensity gradually increased and then apparently decreased with the increase of temperature and period heat treated. The gradual growing up of the Li$_2$TeO$_3$ microcrystal led to the increase of crystalline degree and formation of Li$_2$TeO$_3$ microcrystal in a preferred orientation in the glass, in addition, the continuously growing-up of Li$_2$TeO$_3$ microcrystal can also be responsible in the enhancement of scattering and decrease of transmittance.

Udovic et al [143] investigated formation domain and characterization of Tl$_2$O–TiO$_2$–TeO$_2$ glass system. They have also measured linear and non-linear optical, thermal and mechanical characteristics of these glasses and reported that these materials promising for applications in non-linear optical designs. The chemical, lattice-dynamical and structural effects of the Tl$_2$O and TiO$_2$ modifiers are discussed by using the Raman spectroscopy data. These authors have also concluded that the former modifier favours the non-linear optical properties of the glasses, whereas the latter improved their thermal and mechanical stabilities. Ozdanova et al [144] have measured some physical properties of Li$_2$O–TiO$_2$–TeO$_2$ and BaO–TiO$_2$–TeO$_2$ glasses. For prepared
glasses the optical gap values were found in the region 3.2 eV - 3.4 eV and the temperature (T) coefficient of the optical gap varies in the narrow region $5.3 \times 10^{-4}$ eV/K to $5.9 \times 10^{-4}$ eV/K for $300 \text{ K} < T < 580 \text{ K}$. They observed the values of non-linear refractive index ($n_2$) were found in the region $n_2 \text{[m}^2\text{W}^{-1}] = 2.7 \times 10^{-18}$ - $3.5 \times 10^{-18}$ close to $n_2$ values for similar glasses. The analysis of Raman spectra indicate that connectivity of $(\text{BaO})_x(\text{TiO}_2)_x(\text{TeO}_2)_{1-2x}$ network is more evolved than that one for $(\text{Li}_2\text{O})_x(\text{TiO}_2)_x(\text{TeO}_2)_{1-2x}$ glasses. TiO$_2$ most probably assists to continuous network formation due to appearance of Te–O–Ti bridges.

Wang et al [145] have studied crystallization and microcrystalline of TeO$_2$–Bi$_2$O$_3$–Nb$_2$O$_5$–TiO$_2$ glasses These authors have used Avrami parameter to demonstrate the three-dimensional growth of crystals in the glass matrices. The main crystal phase in the samples was found to be Bi$_2$TeO$_5$. Villegas et al [146] have studied physical and structural properties of TeO$_2$–TiO$_2$–Nb$_2$O$_5$ glasses. These authors have determined structural role of each component was studied by FTIR and some of their physical properties (density, molar volume, oxygen molar volume, transition temperature, thermal expansion coefficient, optical absorption and energy gap). They have further reported that the glass structure is mainly built by [TeO$_4$] groups, while Nb$^{5+}$ and Ti$^{4+}$-ions play as network modifiers. As the Nb$_2$O$_5$ and TiO$_2$ concentration increases, [TeO$_4$] groups progressively change to [TeO$_3$] groups as a consequence of the network
opening. The contribution of the three ions to the oxygen molar volume is found to follow the order: $\text{Te}^{4+} > \text{Ti}^{4+} > \text{Nb}^{5+}$. TiO$_2$ incorporation and even more Nb$_2$O$_5$ is found to improve the glasses thermal stability and the network reinforcement. Sae-Hoon and Toshinobu et al [147] has reported The third-order non-linear optical susceptibilities of TeO$_2$-based glasses containing transition metal oxides ($M = \text{Sc}_2\text{O}_3$, TiO$_2$, V$_2$O$_5$, Nb$_2$O$_5$, MoO$_3$, Ta$_2$O$_5$, and WO$_3$). They used third harmonic generation (THG) method in order to investigate the effect of the empty d-orbital contributions to the third-order non-linear optical susceptibilities. They found that the addition of TiO$_2$, Nb$_2$O$_5$, and WO$_3$ to TeO$_2$ glass increases the $\chi(3)$ value as well as the refractive index, while others decrease both of them. The positive effect of the TiO$_2$, Nb$_2$O$_5$, or WO$_3$, on the $\chi(3)$ of TeO$_2$ glass was interpreted in terms of the cationic empty d-orbital contribution. Komatsu et al [148] have reported optical properties of transparent TeO$_2$-based glasses containing BaTiO$_3$ crystals.

Gulati et al [149] reported that the Ti doped glass can be used in the ground and space-based telescope industry for many years. More recently, Ti-doped silica glass was chosen as a material for reflective mirrors in an extreme ultraviolet lithography (EUVL) system [150]. In addition to its thermal expansion properties, Ti-doped silica glass possess optical absorption
characteristics that are useful in making mirrors and other optical components, such as the high index core of low loss fiber optical waveguides [151].

Hashimoto et al [152] have reported that TiO$_2$–B$_2$O$_3$–P$_2$O$_5$ (TBP) based glasses are promising materials as molding glasses with high transparency, low $T_g$, and high $n_d$. Ma et al [153] have studied the effect of TiO$_2$ on phase separation and crystallization of glass ceramics in CaO–MgO–Al$_2$O$_3$–SiO$_2$–Na$_2$O system. From FESEM observation and EDS analysis, they concluded that the more TiO$_2$ content of glass, the more droplet separated phase and crystal seeds are found after nucleation heat treatment. Tiefeng et al [154] have studied the third-order optical non-linear properties of Bi$_2$O$_3$–B$_2$O$_3$–TiO$_2$ glasses using femto-second Z-scan method at 800 nm. The results have showed that third-order optical non-linearities are influenced by TiO$_2$ concentration; the largest value of non-linear refraction $γ$ obtained for these glasses is $\sim 8.85\times10^{-14}$ cm$^2$/W. Gorokhovsky et al [155] have investigated the vitrification and crystallization behavior of melts produced at 1400 °C in the K$_2$O–B$_2$O$_3$–TiO$_2$ ternary system. They have discussed that the obtained glass ceramic materials as a source of fibrous TiO$_2$, for composite reinforcement and as solid lubricants. Hamzawy et al [156] have studied the effect of different concentrations of titanium oxide (TiO$_2$) on the crystallization behavior of Li$_2$O–Al$_2$O$_3$–SiO$_2$ glasses prepared from local raw materials. Duhan et al [157] have reported the frequency and temperature dependent
conductivity measurements on heat treated titanium bismuth silicate glasses by using impedance spectroscopy in the frequency range from 20 Hz to 1 MHz. They have observed an enhancement in conductivity of about $10^1$-$10^2$ order is in heat treated sample as compared to parent glass.

Chen et al [158] have investigated the third order optical non-linear properties in $\text{Bi}_2\text{O}_3$–$\text{B}_2\text{O}_3$– $\text{TiO}_2$ transparent glass ceramics and they found that large values of non-linear refractive indices $n_2$ in both as-quenched ($1.983\times10^{-13}$ cm$^2$/W) and heat treated ($2.645\times10^{-13}$ cm$^2$/W) transparent samples. The influence of titanium ions on various physical properties including colour, thermal expansion, compressibilities, elastic constants, sound velocities, densities, viscosities, nucleation rates etc on a variety of inorganic glasses has been reported by a number of researchers [159–168]. Kishioka et al [169] have reported that the addition of TiO$_2$ to phosphate glasses stabilizes the glass structure. Lange and Navrotsky [170] have measured anomalously high variations in heat capacities in some titanosilicate melts at temperatures just above the glass transition temperatures. Information on the local structure environment of Ti$^{4+}$ ions in oxide glasses under ambient conditions has been provided by a number of investigators by a variety of techniques like, Raman spectroscopy [171–176], neutron scattering experiments [177], X-ray photo electron spectroscopy [178], X-ray scattering experiment [179], X-ray
absorption fine spectroscopy [180-182] etc. Wu et al [183] have reported the
dissolution of TiO\textsubscript{2} in calcium zirconoboro silicate glasses.

Lacerda et al [184] have investigated TiO\textsubscript{2} - induced phase separation
and crystallization in SiO\textsubscript{2}–CaO–P\textsubscript{2}O\textsubscript{5}–MgO glasses. Laudisio et al [185]
have studied the devetrification behaviour of titanium in lithium germanate
glasses. Barbieri et al [186] have reported the effect of TiO\textsubscript{2} on properties of
alumino silicate glasses and glass ceramics by thermal, microscopic and
diffractometric techniques. Fei Duan et al [187] have prepared
BaO–SrO–TiO\textsubscript{2}–SiO\textsubscript{2} glass system and reported the piezoelectric properties of
these glasses. Duan et al [188] have studied the effect of changing TiO\textsubscript{2}
content on structure and crystallization of CaO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} glass system.

Abrahams and Hadzifejzovic [189] have measured conductivity due to lithium
ions in lithium alumino phosphate glasses crystallized with TiO\textsubscript{2}. Grussaute et
al [190] have reported phosphate speciation in sodium phosphate silicate
glasses containing TiO\textsubscript{2}. Their studies revealed the formation of Ti–O–P
covalent bonds, which they have attributed to the electrostatic field strength of
Ti\textsuperscript{4+} ions. Chowdari et al [191] have recently reported XPS and ionic
conductivity studies on lithium alumino phosphate glass ceramics containing
TiO\textsubscript{2}. Jivov et al [192] have studied the crystalline nature of P\textsubscript{2}O\textsubscript{5}–CaO–ZnO
glass system containing titanium ions. Shaim et al [193] have reported the role
of titanium in Na\textsubscript{2}O–Bi\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5} glasses on the structural properties.
1.4 Motivation and objective of the present work

TeO\textsubscript{2} based glasses and glass ceramics are well known due to their high density, high refractive index and high transparency in the far infrared region. Photoinduced study on these glasses has been the subject of high interest in recent years due to their potential applications such as IR domes, optical fibers, modulators, memory devices, optical fiber triggers and laser windows. The understanding of the origin of optical susceptibilities in these glasses and glass ceramics stimulated by ultra-short laser pulses has gained momentum because such studies help in examining the suitability of the materials for potential applications like three-dimensional photonic devices for integrated optics and other laser-operated devices (such as ultra fast optical switches, optical fiber modulators, power limiters, broad band optical amplifiers).

Conventional piezoelectric ceramic materials viz., BaTiO\textsubscript{3}, PZT, LNB lose their piezoelectric and pyroelectric properties due to the aging and degradation. In view of this, transparent polar glass ceramics (like ZnF\textsubscript{2}–PbO–TeO\textsubscript{2} glass ceramics containing TiO\textsubscript{2}) which posses fatigue endurance and minimal degradation effects and containing well defined, randomly oriented inter-twinned polar crystal phases (viz., PbTeO\textsubscript{3}, Pb\textsubscript{3}TeO\textsubscript{5} and TiTe\textsubscript{3}O\textsubscript{8}) have been recognized as potential piezoelectric materials. The studies on piezoelectric properties on these materials will, therefore, help to asses the suitability of these materials for various electronic devices, particularly opto-mechanical
switches, electromechanical actuators and sensors, ultrasonic transducers, medical imaging, automotive and aeronautic industries etc.

Study on ultrasonic velocities in glass ceramics and their variation with composition may clarify various mechanical and elastical changes taking place in the structural configuration between network formers and modifiers in the glass ceramic network. Different parameters such as elastic moduli, acoustic impedance, internal friction and micro-hardness of the glass ceramics can be obtained from this study.

The study of dielectric properties such as dielectric constant \( \varepsilon' \), loss tan \( \delta \) and AC conductivity \( \sigma_{\text{ac}} \), over a wide range of frequency and temperature of the glasses and glass ceramic materials not only help in accessing the insulating character and understanding the conduction phenomenon but also throw information on the structural aspects of the glass and glass ceramic materials to a large extent.

The studies on optical absorption, ESR, IR and Raman spectra give information on the structural aspects.

Thus the clear objectives of the present study are

- To synthesize \( \text{ZnF}_2-\text{PbO-TeO}_2 \) glasses, crystallize them with different concentrations of \( \text{TiO}_2 \) as nucleating agent and characterize them by a variety of techniques viz., XRD, SEM, TEM and DSC.
• To study optical absorption, ESR, IR and Raman spectra to have some pre-assessment over the structural aspects of the titled glass ceramics.

• To study second order susceptibility (after the samples were dc field poled at elevated temperatures), photo-induced changes (change in the refractive index with the probe wavelength) and to discuss the correlation between glass structure and non-linear optical (NLO) susceptibilities.

• To study the piezoelectric coefficients coupled with elastic properties as a function of the concentration of crystallizing agent and to analyze the results within a framework of different crystal phases formed in the glass ceramics.

• To investigate dielectric dispersion behavior over a frequency range of $10^{-2}$ to $10^6$ Hz and within the temperature range 303 to 523 K and to obtain some information on insulating character of these glass ceramics.
1.5 Contents of the present work

The glasses used for the present studies are:

$$30\text{ZnF}_2-(10-x)\text{ PbO} - 60\text{TeO}_2: x\text{TiO}_2\,(0 \leq x \leq 2.0)$$

The studies carried out are:

(x) XRD, SEM and TEM studies to identify various crystalline phases in the samples;

(xi) differential scanning calorimetry and the evaluation of glass transition temperature, \( T_g \), crystallization temperature, \( T_C \);

(xii) infrared spectra (in the range 400–2000 cm\(^{-1}\)) and Raman spectra (in the range 300–1500 cm\(^{-1}\));

(xiii) optical absorption studies in the wavelength range 300–900 nm and identification of electronic transitions of titanium ions;

(xiv) electron spin resonance measurements and the identification of the positions and valence states of titanium ions in the glass network;

(xv) second order optical susceptibility as a function of the concentration of crystallizing agent TiO\(_2\) by recording the power of the output spectrally separated second-harmonic wave generated (SHG) intensity for the dc-poled (4 kV/cm and at 400 °C) samples;

(xvi) the non-linear optical effects (change in refractive index) as a function of wavelength after the achievement of maximal sample’s
polarization by applying electrostatic strength 4 kV/cm with simultaneous heating of the sample up to 400 °C;

(xvii) variation of piezoelectric coefficient $d_{33}$ with the concentration of nucleating agent TiO$_2$;

(xviii) ultrasonic velocity in the samples by echo pulse technique (PE) and to estimate different elastic coefficients and acoustic parameters;

(xix) dielectric properties viz., dielectric constant $\varepsilon^l$, dielectric loss tan $\delta$ and ac conductivity $\sigma_{ac}$ in the frequency range $10^{-2} - 10^6$ Hz and in the temperature range 303–523 K and also dc conductivity.
References


