The objectives of the chapter is to determine piezoelectric and elastic coefficients as a function of the concentration of crystallizing agent and to analyze the results within a framework of different crystal phases formed in ZnF₂–PbO–TeO₂: TiO₂ glass ceramics. The value of piezoelectric coefficient is found to be the maximum for the samples crystallized with 2.0 wt% of TiO₂. This is attributed to the presence of larger concentration of ferroelectric crystal phases viz., Pb₅Ti₃F₁₉ in this sample. The ultrasonic velocities and elastic coefficients measured as function of TiO₂ concentration were found to be the lowest for the samples crystallized with 1.0 wt% of TiO₂. This is ascribed to the larger presence of titanium ions in Ti³⁺ states in this sample that will inculcate more degree of disorder in the glass ceramic network and thereby hamper the propagation of sound waves in the glass ceramic.
Piezoelectric and elastic properties of ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramics

5.1 Introduction

In recent years there has been an enhanced interest on the studies of piezoelectric properties of glass ceramics since such studies help to assess the suitability of these materials for various electronic devices, particularly optomechanical switches, electromechanical actuators and sensors, ultrasonic transducers, medical imaging, automotive and aeronautic industries etc. [1–4]. 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.
Among a variety of polar glass ceramics that were investigated for various physical properties, tellurium dioxide (TeO$_2$) based glass ceramics were found to be promising for use in laser operated devices because of their refractive-index compatibility with the well-known ferroelectric compounds [5]. Moreover, it has been widely accepted that tellurite glasses are promising non-linear optical materials because of their high third-order optical non-linear (TONL) susceptibility $\chi^{(3)}$ coefficient [6].

Among various crystallizing agents, TiO$_2$ is expected to be more effective mineralizer especially in the glass systems like lead tellurite exhibiting relatively high non-linear optical susceptibilities as mentioned earlier. Normally, the ions of titanium, exist in the glass matrices in Ti$^{4+}$ valence state and participate in the glass network forming with different principal polyhedra: TiO$_4$, TiO$_6$ and sometimes TiO$_5$ (comprising of trigonal bipyramids (tbp)) structural units [7, 8]. However, these ions also sporadically exist in Ti$^{3+}$ valence state in some of the glass matrices and may act as modifier [9, 10] as mentioned before. Further, the inclusion of Ti$^{4+}$ ions into the tellurite glass ceramic network provides substantial advantage to use these materials for various electronic devices based on piezoelectric effect such as actuators and sensors, since the empty or unfilled 3d-shells of Ti ions contributing more strongly to the piezoelectric coefficients. In fact in some of the earlier studies on other materials it was established that Ti$^{4+}$ ions in the ceramic materials occupy substitutional positions with TiO$_4$ structural units, suppress the electrical conductivity and improve the piezoelectric properties.
[11–13]. Hence, it is possible to optimize the piezoelectric properties by means of structural modification using appropriate crystallizing agent like TiO$_2$ with proper concentration. As mentioned in the earlier chapters ZnF$_2$–PbO–TeO$_2$ glasses crystallized with TiO$_2$ consists of tetragonal ferroelectric crystalline phases like Pb$_5$Ti$_3$F$_{19}$, PbTiO$_3$ and PbTeO$_3$ in these samples which may contribute to piezoelectric coefficient ($d_{33}$) substantially.

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. These results open a way for the estimation of mechanical strength of the glasses. Study along these lines was carried out on a variety of glasses and glass ceramics yielding valuable information [14 –17].

The objectives of the chapter is to determine 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. For the applications of these materials in the design of miniature sensors and actuators, it is desirable to have a comprehensive knowledge concerning these properties.
5.2 Brief review of previous work on elastic properties of TeO$_2$ glasses

The studies on piezoelectric properties of TeO$_2$ glasses and glass ceramics are very rare. However, a brief review on some recent studies on elastic properties of TeO$_2$ glasses is presented below.

Rajendran et al [15] have measured ultrasonic velocities (both longitudinal and shear) and attenuation of V$_2$O$_5$–Bi$_2$O$_3$–TeO$_2$ glasses through ultrasonic measurements using a transducer operated at the fundamental frequency of 5 MHz in the temperature range from 150 to 480 K. The elastic moduli, Debye temperature, and Poisson’s ratio have been obtained both as a function of temperature and Bi$_2$O$_3$ content. The room temperature study on ultrasonic velocities, attenuation, elastic moduli, Poisson’s ratio, Debye temperature and glass transition temperature show the absence of any anomalies with addition of Bi$_2$O$_3$ content. The observed results confirm that the addition of Bi$_2$O$_3$ modifier changes the rigid formula character of TeO$_2$ to a matrix of regular TeO$_3$ and ionic behaviour bonds (NBOs). A monotonic decrease in velocities and elastic moduli, and an increase in attenuation and acoustic loss as a function of temperature in all the glass samples revealed the loose packing structure, which was attributed to the instability of TeO$_4$ trigonal bipyramid units in the network as temperature increases. Yasser and Lamia [16] have investigated the effect of TeO$_2$ on the elastic moduli of sodium borate glasses measured using ultrasonic technique. The elastic moduli, the Debye temperature, Poisson’s ratio, and the parameters derived from the Makishima–Mackenzie model and the bond compression model have
been obtained as a function of TeO$_2$ content. The monotonic decrease in the velocities and the elastic moduli, and the increase in the ring diameter and the ratio Kbc=Ke as a function of TeO$_2$ modifier content revealed the loose packing structure, which was attributed to the increase in the molar volume and the reduction in the vibrations of the borate lattice. The observed results confirm that the addition of TeO$_2$ changes the rigid character of Na$_2$B$_4$O$_7$ to a matrix of ionic behaviour bonds (NBOs).

Mohamed et al [17] have studied effects of concurrent TeO$_2$ reduction and ZnO addition on elastic and structural properties of TeO$_2$–Nb$_2$O$_5$–ZnO glasses using ultrasonic method. From the combined results of ultrasonic velocity and IR absorption spectra these authors have concluded that the role of TeO$_2$ is very critical in the ternary glass system as, although ZnO addition showed improved rigidity due to recovery of shear modulus, the weakening of longitudinal and Bulk moduli indicates ZnO is not fully effective as glass former in place of TeO$_2$. El-Moneim [18] has recently reported correlations between acoustical properties and many critical compositional parameters and determined the structural role of B$_2$O$_3$, ZnO, BaO, La$_2$O$_3$, TiO$_2$, V$_2$O$_5$, Bi$_2$O$_3$, WO$_3$, Ag$_2$O, Na$_2$O, K$_2$O, and Li$_2$O oxides in the tellurite glass network. This author has evaluated the elastic moduli and Poisson's ratio for the studied glasses using Makishima & Mackenzie theory. The relationship between theoretically calculated and experimentally measured values of elastic moduli and Poisson's ratio has been investigated. It has been found that the theoretical values are in excellent agreement with the corresponding measured
ones, except in V$_2$O$_5$-containing glasses. The disagreement has been discussed in terms of the structure of these glasses. Khafagy et al [19] have reported some mechanical and optical properties of TeO$_2$–15B$_2$O$_3$–15P$_2$O$_5$–Li$_2$O glasses using ultrasonic pulse-echo technique with 5 MHz transducer. These authors have reported the ultrasonic attenuation, longitudinal and shear wave velocities, elastic moduli, Poisson ratio, Debye temperature and hardness of the present glasses. From these studies it was found that the gradual replacement of TeO$_2$ by Li$_2$O in the glass matrix up to 30 mol% leads to decrease the average crosslink density and rigidity of prepared samples which affects the studied properties.

Gaafara et al [20] have investigated acoustic properties viz., longitudinal and shear ultrasonic velocities and elastic moduli, longitudinal and shear moduli of some tellurite glasses using artificial intelligence technique (ANN). The ANN results were found to be in successful good agreement with those experimentally measured parameters. Then the presented ANN model was used to predict the acoustic properties of lead niobium tellurite and bismuth niobium tellurite glasses. The results of ultrasonic velocities and elastic moduli showed that the addition of Nb$_2$O$_5$ as a network modifier provides oxygen ions to change [TeO$_4$] tbps into [TeO$_3$] tps. Abd El-Moneim [21] has investigated the correlation between activation energy of ultrasonic relaxation process through the temperature range from 140 to 300K and some physical properties has been investigated in pure TeO$_2$, TeO$_2$–V$_2$O$_5$ and TeO$_2$–MoO$_3$ glasses according to Bridge and Patel’s theory. The oxygen density (loss centers), number of two-well systems, hopping
distance and mechanical relaxation time have been calculated in these glasses from the data of density, bulk modulus and stretching force constant of the glass. It has been found that the acoustic activation energy increased linearly with both the oxygen density and the number of two-well systems. The correlation between the acoustic activation energy and bulk modulus was achieved through the stretching force constant of the network and other structural parameters.

Souri [22, 23] has investigated thermal stability, Poisson's ratio, fragility and glass forming tendency of tellurite-vanadate glasses containing antimony oxide and also molybdenum oxide. The author has estimated relationship between chemical composition and the thermal stability. Further using Makishima and Makenzie's theory the author has concluded that there exist a strong relation between elastic properties and structure of glass. Baizura and Yahya [24] have studied elastic properties together with structural properties of 75TeO2– (10 - x)Nb2O5–15ZnO–(x) Er2O3 (x = 0.0-2.5 mol%) glass by measuring both longitudinal and shear velocities using the pulse-echo-overlap technique at 5 MHz and Fourier Transform Infrared (FTIR) spectroscopy, respectively. Shear velocity, shear modulus, Young's modulus and Debye temperature were observed to initially decrease at x = 0.5 mol% but remained constant between x = 1.0 mol% to x = 2.0 mol%, before increasing back with Er2O3 addition at x = 2.5 mol%. The initial drop in shear velocity and related elastic moduli observed at x = 0.5 mol% were suggested to be due to weakening of glass network rigidity as a result of increase in non-bridging oxygen (NBO) ions as a consequence of Nb2O5 reduction.
The near constant values of shear velocity, elastic moduli, Debye temperature, hardness and Poisson's ratio between x = 0.5 mol% to x = 2.0 mol% were suggested to be due to competition between bridging oxygen (BO) and NBO ions in the glass network as Er₂O₃ gradually compensated for Nb₂O₅. Further addition of Er₂O₃ (x > 2.0 mol%) seems to further reduce NBO leading to improved rigidity of the glass network causing a large increase of ultrasonic velocity (V_L and V_S) and related elastic moduli at x = 2.5 mol%. FTIR analysis on NbO₆ octahedral, TeO₄ trigonal bipyramid (tbp) and TeO₃ trigonal pyramid (tp) absorption peaks confirmed the initial formation of NBO ions at x = 0.5 mol% followed by NBO/BO competition at x = 0.5 – 2.0 mol%. Appearance of ZnO₄ tetrahedra and increase in intensity of TeO₄ tbp absorption peaks at x = 2.0 mol% and x = 2.5 mol% indicate increase in formation of BO. Sidek et al [25] have measured the elastic properties of ternary tellurite glasses TeO₂–AlF₃–ZnO as a function of composition. The ultrasonic velocity data, the density, the calculated elastic moduli and micro-hardness are composition dependent and were discussed in terms of modifying action of ZnO.

Halimah et al [26, 27] have studied elastic properties, Poisson's ratio, microhardness, softening temperature and Debye temperature of TeO₂–B₂O₃–Ag₂O and glasses and TeO₂–B₂O₃–Ag₂O–AgI using ultrasonic velocity at room temperature. The experimental results indicated that the elastic constants depend upon the composition of the glasses and the role of the Ag₂O inside the glass network. Comparison between the experimental elastic moduli data obtained in the
study and the calculated theoretically by Makishima-Mackenzie theory and bond compression model has been discussed in detail in this paper. The presence of AgI inside the glass network is found to create a loose packing structure of the glass network and reduce the rigidity and the strength of the glass system. Abd El-Aal and Afifi [28] has studied the elastic properties of vanadium tellurite glasses at room temperature with CuO as dopant by ultrasonic velocity measurements using a 4 MHz transducer. Elastic moduli, Poisson ratio, crosslink density, Microhardnes, and Debye temperature of the glasses have been determined using the experimental data. Quantitative analysis has been carried out in order to obtain more information about the structure of the glass based on bond compression model and the Makishima and Mackenzie model. Yousef et al [29] have measured sound velocities in TeO$_2$/WO$_3$ glasses containing small amount of ZrO$_2$ by pulse echo technique. From these velocities and densities values, various elastic moduli were calculated. The variations in the elastic moduli with WO$_3$ content have been discussed in terms of the glass structure. Quantitatively, these authors used the bond compression model for analyzing the room temperature elastic moduli data. By calculating the number of bonds per unit volume, the average stretching force constant, and the average ring size they could extract information about the structure of the studied glasses.
5.3 Experimental

a) Piezoelectric set-up

For measuring of the piezoelectric coefficients, the samples were taken in the form of rectangular bars and the mechanical stress is applied along the vertical direction and resultant voltage is measured by contact of electrodes in the horizontal (Fig. 5.1(a))

Fig. 5.1(a) Photograph of the experimental setup used for measuring piezoelectric coefficients
The magnified picture of sample arrangement used for this study is shown in Fig. 5.1 (b).

![Image of sample arrangement](image)

**Fig. 5.1(b)** The magnified view of the sample arrangement used for measuring the piezoelectric coefficient

A reference condenser of known capacity $C_0$ is connected in parallel to the sample condenser as shown in Fig. 5.1 (c). After the application of the mechanical stress, the surface of sample capacitor acquires charge $q$, the corresponding capacitance of the sample is measured as $C_v$. If the potential across the sample capacitor is $V_1$, after the parallel addition of $C_0$, the potential changes to $V_2$. 
Fig. 5.1(c) The sketch of principal set-up used for measurements of the piezoelectric constant.

Using equation:

\[ q_i = C_v \cdot V_i = d_{33} \cdot F_i = (C_v + C_0) \cdot V_2, \quad (5.1) \]

one can obtain:

\[ C_v = \frac{C_0 V_2}{V_1 - V_2} \]

and

\[ d_{33} = \frac{C_0}{F} \frac{V_1 \cdot V_2}{V_1 - V_2} \quad m/V \quad (5.2) \]

where \( d_{33} \) is the piezoelectric tensor component that represents the induced polarization per applied unit stress in the direction 3 (sometimes it is indicated as
z) or alternatively it is the induced strain per unit electric field in the direction 3. Assuming that in the measurement set-up we have always maintained the same value of the acting force on the sample and the term $\frac{C_0}{F} = k$ represents constriction constant. For reliable measurements, the set-up was constructed in a way allowing applying of multi-time external mechanical forces during short time mechanical action. This action causes an occurrence of the surface charge. The measurement is performed with and without the connection of $C_0$. Afterwards we have measured the voltages $V_1$ and $V_2$, respectively. The typical voltage response versus the applied mechanical action is presented in Fig. 5.2 for two samples (TC$_{15}$ and TC$_{20}$).

Using as a reference single crystal of LiNbO$_3$ (LNB) with the known piezoelectric constant we have determined values of constriction constant $k$ which was used later to evaluate the piezoelectric coefficient for the studied materials after the bicolor optical treatment (i.e. simultaneous treatment by the pulsed coherent fundamental laser 1064 nm 10 ns beam and its second harmonic generation at 532 nm).

The accuracy of the piezoelectric constant determination is dependent on the accuracy of evaluations of the constrictive constant $k$. To ensure a sufficiently good accuracy of piezoelectric constant measurements we have used two methods of determination of piezoelectric coefficients, i.e. A and B.
An inaccuracy of the voltage within a framework of type A measurements was determined as

$$V_A(V_1) = \sqrt{S_V^2} = \sqrt{\frac{\sum (V_i - \bar{V}_1)^2}{n(n-1)}} = 0.00418 \ [V]$$ (5.3)

And similarly $V_A(V_2) = 0.00619 \ [V]$ (5.4)

The corresponding accuracy for the type B measurement was presented as follows:

$$V_B(V_1) = \frac{0.01}{\sqrt{3}} = 0.006 \ [V]$$ (5.5)

$$V_B(V_2) = \frac{0.001}{\sqrt{3}} = 0.0006 \ [V]$$ (5.6)

were the total inaccuracy of the measurement of voltages. In particularly $V_C$ for LNB may be presented as:
\[ V_C(V_1) = \sqrt{V_A^2(V_1) + V_B^2(V_1)} = 0.0073 \text{ [V]} \quad (5.7) \]

And \[ V_C(V_2) = \sqrt{V_A^2(V_2) + V_B^2(V_2)} = 0.0062 \text{ [V]} \quad (5.8) \]

At the same time the constriction constant \( k \) was determined experimentally using the LNB reference crystal:

\[
k = \frac{C_0}{F} = \frac{d_{33}(V_1 - V_2)}{V_1 \cdot V_2} = 4.4 \cdot 10^{-12} \text{ (m/V}^2) \quad (5.9)
\]

Then, the relative mean square inaccuracy is equal to:

\[
\Delta_i = \left[ \frac{\partial k}{\partial V_1} V(V_1) \right]^2 + \left[ \frac{\partial k}{\partial U_2} V(V_2) \right]^2 = 0.05 \cdot 10^{-12} \text{ (m/V}^2) \quad (5.10)
\]

So the use of these two methods A and B was complementary for determination of the piezoelectric coefficients tolerance.

During the experiment it was found that the accuracy of \( d_{33} \) determination depends on reliable evaluation of \( k \). For this purpose the applied mechanical stress should be uniform. This requires a use of renormalized specimen with the same surfaces or to fit the electrode surfaces in a way to establish the uniform attachment of the electrode with material.

The investigations have shown that application of electrodes with the higher diameters than specimen’s dealing with, the perfect attachment of the electrode to the sample requires, the surfaces of the samples which should be perfectly parallel with the electrodes. Otherwise we receive an error up to 20 %. Moreover, due to some surface non-homogeneities of the samples, there may
occur an additional inaccuracy of the same order. To avoid this we have used the electrodes with diameter less than sample’s diameter and one of the electrodes has the spheric-like form (Figs. 5.1 (c) and 5.3). With this modification and using two mentioned methods of error determination (A and B) the accuracy in $d_{33}$ was estimated to be 0.08 pm/V.

**Fig. 5.3** Modified set-up (a – electrodes, b – specimen, c – isolation) used for measuring piezoelectric coefficient

**b) Ultrasound velocity measurements**

The ultrasound velocity in the sample was measured using the measurement card OPCARD 01/100 with the integrated transducer of the pulses and two piezoelectric sensors with frequency 5 MHz. The gating frequency was 100 MHz. Using the card programming we have measured the velocity of the pulse propagation using the time of its propagation between the transducer and receptor for the known distance (Fig. 5.4(a)). The measurements were carried out by two methods: by echo pulse technique (PE), when one of the sensor is used
simultaneously as transmitter as well as receptor or by the transmitting technique for which two tips are used— one as a transmitter and another one as receptor.

**Fig. 5.4(a)** Principal set-up used for measuring the ultrasonic velocity in the glass samples

The longitudinal acoustic signal observed for one of the samples is shown in Fig. 5.4(b). Because the sound velocity consists of measurement of sound time propagation for the fixed given distance, an error in the measurements significantly depends on the accuracy of the time measurements and on the measurements of the sample’s thickness.
Fig. 5.4(b) Sample window program showing longitudinal acoustic signal for the sample TC_{10}.

For example for the sample of thickness 2 mm measured with thickness accuracy 0.01 mm the measurement’s accuracy for the sound velocity 6772 m/s was evaluated as 3.07 m/s using the expression:

$$\Delta_v = \sqrt{\left(\frac{\partial v}{\partial t}\Delta(t)\right)^2 + \left(\frac{\partial v}{\partial s}\Delta(s)\right)^2} = 3.07 \text{ (m/s)}$$  \hspace{1cm} (5.11)

The shear velocities were measured by the same technique using cylindrical rods of samples [30, 31].
5.4 Results and discussion

The variation of measured piezoelectric coefficient $d_{33}$ for ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramic with the concentration of nucleating agent TiO$_2$ is shown in Fig. 5.5; the variation exhibited maximal effect at $x = 1.0$. It should be emphasized here that we have also measured piezoelectric coefficient for the pre-

![Graph showing the variation of piezoelectric coefficient $d_{33}$ with concentration of TiO$_2$. The graph has a peak at $x = 1.0$.]

Fig. 5.5 Variation of piezoelectric coefficient of ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramics with the concentration of TiO$_2$.  

crystallized samples; these values are found to be below the detection level (< 0.1 pm/V). In the Fig. 5.6, the variation of longitudinal ($v_l$) and shear ($v_s$) velocities of ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramics with the concentration crystallizing agent From these TiO$_2$ is presented.

Both the velocities have exhibited minimal effect at x = 1.0. Velocities we have evaluated various elastic and acoustic parameters [30, 20] using the expressions:

- **longitudinal elastic coefficient** $L = \rho v_l^2$, \hspace{1cm} (5.12)

- **shear modulus** $G = \rho v_s^2$, \hspace{1cm} (5.13)

- **the Possion’s ratio** $\sigma = \frac{(L - 2G)}{2(L - G)}$, \hspace{1cm} (5.14)

![Fig. 5.6](image_url)  
**Fig. 5.6** Variation of sound velocities with concentration of TiO$_2$ (wt%) in ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramics.
and the Young’s modulus \( Y = (1+\sigma)2G \). \hfill (5.15)

Using these coefficients, various other parameters such as

Debye temperature \( \theta_D = \frac{\hbar}{k_B} \left( \frac{3N_A}{4\pi V} \right)^{1/3} v_m \), \hfill (5.16)

In Eq. (5.16) \( h \) is Planck’s constant, \( k_B \) is the Boltzmann’s constant, \( N_A \) is the Avogadro’s number and \( V_s \) is the specific volume (volume occupied by the unit mass) and \( v_m \) is the mean velocity, evaluated using

\[
    v_m = \left[ v_i^2 - (4/3)v_s^2 \right]^{1/2}
\]

The acoustic impedance of ZnF\(_2\)-PbO–TeO\(_2\): TiO\(_2\) glass ceramics is estimated using

\[
    Z_t = v_m \rho
\]

The summary of all these parameters is furnished in Table 5.1

From the XRD pattern it is evident that the presence of higher concentration of Pb\(_5\)Ti\(_3\)F\(_{19}\) ferroelectric crystal phases in the glass ceramic sample TC\(_{10}\). The structure of Pb\(_5\)Ti\(_3\)F\(_{19}\) crystal phase, as mentioned earlier consists of infinite chains of eclipsed corner-sharing TiF\(_6\) octahedra as well as individual octahedrons [32]. These phases contribute more to the piezoelectric coefficient \( d_{33} \) and are responsible for higher value of \( d_{33} \) for the samples crystallized with 1.0 and 2.0 wt\% of TiO\(_2\). The increase of piezoelectric coefficient beyond \( x = 1.5 \) is probably due to the increasing concentration of conventional ferroelectric crystal phases viz., PbTiO\(_3\) and PbTeO\(_3\) which also may significantly contribute to \( d_{33} \).
Table 5.1

Various acoustic/ elastic properties of ZnF$_2$–PbO–TeO$_2$:TiO$_2$ glass ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density $\rho$ (kg/m$^3$)</th>
<th>$v_i$ (m/s)</th>
<th>$v_s$ (m/s)</th>
<th>$L$ (x10$^{10}$ N/m$^2$)</th>
<th>$G$ (x10$^{10}$ N/m$^2$)</th>
<th>$Y$ (x10$^{10}$ N/m$^2$)</th>
<th>$\theta_D$ (K)</th>
<th>$Z_i$ (x10$^{7}$ kg/m$^2$-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC$_5$</td>
<td>5617</td>
<td>3519</td>
<td>2361</td>
<td>6.96</td>
<td>3.13</td>
<td>6.83</td>
<td>115.2</td>
<td>1.45</td>
</tr>
<tr>
<td>TC$_7$</td>
<td>5517</td>
<td>3505</td>
<td>2351</td>
<td>6.78</td>
<td>3.05</td>
<td>6.65</td>
<td>114.1</td>
<td>1.42</td>
</tr>
<tr>
<td>TC$_{10}$</td>
<td>5499</td>
<td>3460</td>
<td>2321</td>
<td>6.58</td>
<td>2.96</td>
<td>6.46</td>
<td>112.5</td>
<td>1.39</td>
</tr>
<tr>
<td>TC$_{15}$</td>
<td>5486</td>
<td>3491</td>
<td>2342</td>
<td>6.69</td>
<td>3.01</td>
<td>6.57</td>
<td>113.4</td>
<td>1.40</td>
</tr>
<tr>
<td>TC$_{20}$</td>
<td>5467</td>
<td>3500</td>
<td>2348</td>
<td>6.70</td>
<td>3.02</td>
<td>6.58</td>
<td>113.5</td>
<td>1.41</td>
</tr>
</tbody>
</table>

The acoustic and elastic parameters were found to decrease with increase in the concentration of crystallizing agent TiO$_2$ (up to 1.0 wt%) and with further increase of TiO$_2$ the parameters exhibited an opposite trend. In general, in a more ordered glass framework the energy introduced by the vibrator is distributed more rapidly among the vibrational degrees of freedom of the glass ceramic framework. The time required for the establishment of equilibrium distribution of energy goes on increasing in comparison with the period of oscillation of the vibrator and hence an increase in the mechanical loss factor or coefficient of internal friction which will lead to an increase in the elastic coefficients and acoustical impedance of these glass ceramics. However, the observed decrease in the values of elastic coefficients and acoustical parameters (with the increase of TiO$_2$ from 0.5 to 1.0
wt%) suggests higher degree of disorder in glass ceramics likely due to higher concentration modifying ions viz., Ti$^{3+}$ ions.

5.5 Conclusions

The piezoelectric coefficients of ZnF$_2$–PbO–TeO$_2$: TiO$_2$ glass ceramic materials were measured by applying mechanical stress and also by applied coherent bicolor optical treatment using 10 ns 1064 nm Nd: YAG pulsed laser and its doubled frequency generated signal. The value of piezoelectric coefficient measured with modified piezoelectric set-up is found to be the maximum for the samples crystallized with 2.0 wt% of TiO$_2$. This is attributed to the presence of larger concentration of ferroelectric crystal phases viz., Pb$_3$Ti$_3$F$_{19}$ in this sample.

The ultrasonic velocities and elastic coefficients measured as function of TiO$_2$ concentration were found to be the lowest for the samples crystallized with 1.0 wt% of TiO$_2$. This is ascribed to the larger presence of titanium ions in Ti$^{3+}$ states in this sample that will inculcate more degree of disorder in the glass ceramic network and thereby hamper the propagation of sound waves in the glass ceramic.
References


