3.1 Introduction

The ultrasound waves are having frequency, higher than 20 kHz. Normally these ultrasonic waves are used to determine material characteristics of interest such as the presence of cracks, voids, inclusions, porosity, part thickness, weld penetration and joint integrity by measuring the speed of sound. From the velocity measurements one can calculate the elastic moduli and Poisson’s ratio for the material. The pulse-echo technique used to send and receive ultrasound is a simple, quick, and accurate method of measuring the speed of sound in solids [1, 2]. Since glasses/glass-ceramics are solids, the measurement of the velocity with which sound waves propagated through them has become an important tool to understand the mechanical behaviour. The techniques employing high frequency acoustic waves are both experimentally more convenient and inherently more precise. Since glasses are basically isotropic solids, we see that the elastic moduli are not the functions of direction of propagation of sound waves through them [3]. In the following sections a brief theory of elasticity and the experimental techniques to measure elastic moduli is given.

3.2 Brief Theory of Elasticity

3.2.1 The Characterization of Elastic Properties of Solids

The mechanics of solids, regarded as continuous media, forms the basic assumption of the theory of elasticity. The macroscopic behavior of a solid is described by a continuum field theory, the theory of elasticity, which describes the way a solid deforms when external stresses are applied [4]. Under the action of applied stress, solid body exhibits shape and volume changes to some extent, and every point in the solid body is in general displaced. Under deformation, the body ceases to be in its original state
of equilibrium, and the forces, which are called internal stresses, therefore arise which tend to return the body to its equilibrium state. If the deformation of the body is fairly small, it returns to its original un-deformed state when the external forces cease to act. Such deformations are called elastic. For large deformations, the removal of the external forces does not result in the fully recovery of the deformation. Such deformations are plastic [4].

The bulk modulus describes the strain response of a body to hydrostatic stress involving change in volume without change of shape. The shear modulus relates to strain response of a body to shear or torsional stress. It involves change of shape without change of volume. For an isotropic solid, its elastic behavior is fully described by the longitudinal modulus \( L \) and shear modulus \( G \). If in addition the atoms interact through a central potential, then according to the Cauchy’s identity one obtains a reduction to only one independent elastic modulus i.e., \( L = 3G \). This is Cauchy’s identity, valid for an isotropic solid composed of molecular interacting two-body central force, may be stated as:

\[
K = \frac{5}{3} G
\]  \hspace{1cm} 3.1

which implies that \( L \) and \( K \) are equal to 0 when \( G = 0 \). For the Lennard Jones interaction potential [4], this identity changes to,

\[
L = a + bG
\]  \hspace{1cm} 3.2

where \( a \) and \( b \) are constants. This leads to the relation,

\[
K = a + (b - 1.33G)
\]  \hspace{1cm} 3.3

which is known as the generalized Cauchy’s relation. Its parameters ‘\( a \)’ and ‘\( b \)’ remain constant with changing temperature and pressure, but are sensitive to small changes in the
potential. This relation is valid for both liquids and glasses [4]. Suppose the deformation is proportional to the applied forces then this law is called Hooke’s law, which is actually applicable to almost all elastic deformations in solids [4].

Young’s modulus also known as the tensile modulus is a measure of the stiffness of an isotropic elastic material. It is defined as the ratio of the uniaxial stress to the uniaxial strain in the elastic regime. This can be experimentally determined from the slope of a stress–strain curve obtained during tensile or compression applied on a material. Young’s modulus is also commonly, but loosely, called the elastic modulus or modulus of elasticity, because Young’s modulus E is the best-known elastic constant, which is most commonly used in engineering design. There are other elastic moduli, such as the bulk modulus (K) and the shear modulus (G). The expression for E may be expressed in terms of G and K by

\[ E = \frac{9KG}{3K+G} \]  

The ratio of the transverse compression to the longitudinal extension is called Poisson’s ratio (\( \sigma \)), named after Simeon Poisson. Poisson’s ratio is an important material property used in elastic analysis of the material. When a material is compressed in one direction, it usually tends to expand in the other two directions perpendicular to the direction of compression. This phenomenon is called the Poisson effect. Poisson’s ratio \( \sigma \) is a measure of the Poisson effect. When the solid is stretched, the Poisson ratio will be the ratio of relative contraction to relative stretching, and will have the same value as in the case of compression instead of stretch. The relation of Poisson’s ratio with other elastic moduli is expressed (for isotropic solids) as

\[ \sigma = \frac{1}{2} \frac{(3K - 2G)}{(3K + G)} \]
since K and G are always positive, the Poisson’s ratio is found to vary between -1 (for K = 0) and 0.5 (for G = 0), that is \(-1 \leq \sigma \leq 0.5\). One might see Poisson’s ratios larger than 0.5 reported in the literature; however, this implies that the material was stressed beyond the elastic limit to cracking. Generally, “harder” materials will have lower Poisson’s ratios than “softer” materials. While only in very rare cases, a material will actually shrink in the transverse direction when compressed (or expanded when stretched) which will yield a negative value of the Poisson’s ratio. For most crystalline metals and alloys, \(\sigma = 1/3\) [5].

For the isotropic solids or media, the three elastic constants G, E and K correlate with \(\sigma\) as [4, 5].

\[
G = \frac{E}{2} (1 + \sigma) \\
K = \frac{E}{3} (1 - 2\sigma)
\]

The glasses are macroscopically isotropic in structure and homogeneous in physical and mechanical properties, and therefore, the above equations may be applied to glasses.

### 3.2.2 Experimental Methods

The elastic moduli of a matter are determined by its inter-atomic forces, the structure and its vibration properties. Hence the values of the elastic moduli K, G, and E and Poisson’s ratio \(\sigma\) may be experimentally measured by methods such as mechanical deformation or ultrasonic-wave propagation. For liquids, instantaneous elastic moduli may be obtained from velocity measurements of high-frequency sound waves in order to avoid contributions of fast structural relaxations. In solids, the elastic moduli can be determined from two different methods, (i) static methods and (ii) dynamic methods. The
static and dynamic methods may be regarded as isothermal and adiabatic measuring conditions, respectively. The basic theory for static method is to obtain the stress–strain curve in the elastic deformation limit, and then calculate the elastic moduli based on these curves. The experimental conditions such as loading as well as the loading rate significantly affect the measuring accuracy of the elastic moduli. The static method is also difficult to apply to brittle materials such as glassy materials. The dynamic method has relatively high accuracy. According to the applied frequency range, the dynamic methods are classified as, *acoustic method* (the frequency is below $10^4$ Hz) and *ultrasonic method* (the frequency is between $10^4$ and $10^8$ Hz). The dynamic methods are widely applied to study the elastic properties and determine the elastic moduli of glasses and glass-forming liquids. Therefore, in the following section, an introduction of one of the dynamic methods, namely the ultrasonic method is described with the associated theory.

### 3.3 Pulse Echo and Pulse Echo Superposition Techniques

#### 3.3.1 Pulse Echo Technique

When a short duration pulses of ultrasonic waves obtained from the pulsed repetition frequency (PRF) oscillator are introduced into the specimen by exciting quartz transducer. The mechanical vibrations propagating within the specimen are reflected back and forth between the parallel faces of the specimen. Several such reflections occur and the echo pattern can be detected by the same transducer (pulse echo mode, single ended operation). The transducer transmits the signal from the oscillator and functions as a receiver of the return echoes in the interval between pulses. The measured time interval
between successive echoes corresponds to the phase delay of the acoustic wave in a given length of the specimen.

In pulse echo mode the round trip phase delay is the time between certain cycle on one and the proper cycle of the next echo, due to the finite rise time of the echoes, introduces ambiguity for the timing purpose. Therefore, the method involving cycle for cycle matching of an echo is needed to determine the round trip delay time. There are number of techniques to determine the transit time of the pulse travelling in the specimen [2, 6-13]. The pulse superposition method by McSkimin [2, 7, 9-12] and the pulse echo overlap method by Papadakis [1,6] and May [2] are popularly used.

In solids, sound waves can propagate in four principle modes that are based on the way the particles oscillate. Sound can propagate as longitudinal waves, shear (transverse) waves, surface waves and in thin materials as plate waves (These are also called as Lamb waves). Longitudinal and shear waves are the two modes of propagation most widely used in ultrasonic measurements. The particle movement responsible for the propagation of longitudinal and shear waves is illustrated in Figure 3.1.

Figure 3.1: Propagation of longitudinal and shear waves.
The common types of piezoelectric materials used are quartz (SiO₂), lead–
zirconate-titanate (PZT), lithium-niobate (LiNbO₃) etc. Longitudinal waves can be
generated in solids by cutting a quartz crystal such that its radiating surfaces are
perpendicular to one of the X-axes (X-cut plate). Transverse waves can be generated in
solids by cutting a quartz crystal such that its radiating surfaces are perpendicular to one
of the Y-axis (Y-cut plate).

When a plane sound wave is made to incident normally to the boundary between
two media, the conservation of energy requires the incident wave energy to be equal to
the sum of the wave energy that is reflected back into the medium-1 and the wave energy
that is transmitted into the medium-2. The ability of the material to transmit ultrasonic
waves is measured by its acoustic impedance \( Z \) which is given by

\[
Z = \rho v
\]

where \( \rho \) the density and \( v \) is the velocity. For solids, acoustic impedance depends on the
type of the ultrasonic wave being propagated such as longitudinal, transverse etc. It is
mentioned that gasses and liquids possess only longitudinal acoustic impedance differs
very much from one medium to another, almost complete reflection will occur at the
interface between the two media. The values of the acoustic impedance of quartz and
salol are in the order of \( 10^5 \) mechanical \( \Omega \)cm² at room temperature.

The simplest form of block diagram of the pulse echo systems is shown in Fig
3.2. The transducer must be coupled to the specimen in such a manner as to exclude the
presence of air voids. It is also desirable to produce thin bonds so that the phase shift
correction to the measured transit times remains small.
The repetition rate of the oscillator is low so that the echo train will have completely attenuated before the oscillator is pulsed again. In this operation the transducer transmits the signal applied from the oscillator and functions as a receiver of the return echoes in the interval between pulses. The sample-transducer arrangement and the resultant echo signal are shown in Figure 3.3.

The accuracy in the pulse echo method depends on the speed and linearity of the time base of the oscilloscope. Lazarus [14] pointed out that a small transit time error is incurred due to the ultrasonic wave propagation into the transducer and the couplant (bond). This could be eliminated by the measurement of transit time in different lengths of the samples. The intercept of the plot of transit times as a function of the ultrasonic pulse at the sample-transducer interface changes the shape of the pulse with each successive echo. This leads to an inaccuracy in the transit time measurement.
The matches of the leading edges of the echoes also cause an error in the measurement [6]. A pulse superposition technique developed by MsSkimin et al. [9,10], which allows cycle-for-cycle matching of the echoes and could eliminate the above problem.

![Sample-transducer arrangement and the resultant echo signals](image)

**Figure 3.3:** Sample-transducer arrangement and the resultant echo signals

### 3.3.2 Pulse Echo Superposition Technique

In pulse superposition technique, the frequency of the applied pulses is most important rather than the carrier frequency. This technique has the operating advantage of greater energy in the return echoes. A block diagram of the typical arrangement of the pulse superposition technique is shown in Fig. 3.4.
Fig 3.4 Block diagram of pulse superposition technique.

Figure 3.5: Resulting echoes when RF pulse is repeated at every t sec interval.
The continuous wave oscillator is of variable frequency arrangement, permitting the use of a wide range of transducers. The continuous wave oscillator is pulsed at PRF. The output of the pulsed oscillator consists of a sequence of repetition frequency (RF) pulses which activates the X-cut or Y-cut transducers. The return echoes are received by the same amplifier-detector. The detected signal is applied to (Hewlett Packard 54600B 100MHz) oscilloscope on which envelops of the pulses are displayed. The PRF is accurately determined to six significant figures. In the present study Ultrasonic Pulse echo Interferometer (System Dimensions, Model SDUI/003, Bangalore) was used for the ultrasound velocity measurement. The X-cut and Y-cut coaxial quartz transducers (10 mm diameter, BEL, Bangalore), resonating at a frequency of 10 MHz were used for the longitudinal and transverse waves respectively. The carrier frequency of the PRF oscillator is set to the transducer resonance frequency. Phenyl salicilate (Salol) has been used in the present study to couple the quartz transducers onto the glass specimen. A thin layer of the bond was obtained as follows. A small quantity of salol which is a solid at room temperature and melts around 40°C is introduced between the transducer and the sample and this region is slightly heated using a hot air blower. A small load applied by a spring loading arrangement [see the Plate-3.1(a)] makes the liquid spread uniformly over the surface. The excess liquid salol is squeezed out beyond the transducer is removed with a filter paper. Plate-3.1 (b) shows the pulse echo pattern seen on the CRO screen. When a short duration RF pulse is initiated in the specimen, a series of echoes will result and is shown by V_1, V_2 and V_3 etc., in the Fig 3.5 (also see the Plate-3.1 (b)). The time ‘t’ can be adjusted further to maximize the amplitude of summed echoes by superimposing a particular crests of radio frequency within a pulse. Since various combinations of crests
are possible, it is not certain at first which crests are actually involved in a particular maximization, because of lack of resolution or distortion of the leading edges of pulses resulting from reflection within the transducer. In principal, the PRF is adjusted so that its period is equal to some integral multiple of the delay time in the specimen. That is the time delay between the applied pulses is exactly equal to an integral number of round trips in the specimen. Whenever this condition is achieved, the applied pulses are superimposed upon the specimen echoes. If the integer is 1, then every specimen echo will have an applied pulse superimposed upon it. If the integer is 2, the applied pulse will be superimposed upon every other echo and so on. It is preferable to operate with this integer equal to unity, for then the large amount of energy is being impressed upon the specimen.
Plate 3.1: (a) Sample-transducer arrangement

(b) Pulse-echo pattern seen on the CRO
3.3.3 Analysis of the Pulse Superposition Time.

The relation between the measured time delay ($t$) and the actual time delay ($\delta$) is given by

$$t = p\delta - \frac{p\gamma}{360f} + \frac{n}{f}$$  \hspace{1cm} (3.9)

where $t$ is the measured period of the PRF at the interference condition, $P$ is the number of round trips in the measurement, $\delta$ is the true time delay in the specimen, $\gamma$ is the phase shift introduced by the bonding material between transducer and the sample (seal), $f$ is the frequency of the continuous wave oscillator and $n$ is an integer which gives the number of cycles mismatched. If $t$ corresponds to $n = 0$ is determined and by knowing the reflection angle $\gamma$ at the transducer, delay time $\delta$ can be obtained. This is done by comparing experimental and theoretical values by McSkimin’s $\Delta t$ criteria and is defined by

$$\Delta t = \frac{1}{f_L} \left(n - \frac{P\gamma_L}{360}\right) - \frac{1}{f} \left(n - \frac{P\gamma_H}{360}\right)$$  \hspace{1cm} (3.10)

where $\Delta t$ is the change required to maintain the “in phase” condition as the frequency is changed from $f_H$ (the resonant frequency of the transducer) to $f_L$ which is about 10% lower than $f_H$. The phase angles $\gamma_H$ and $\gamma_L$ associated with $f_H$ and $f_L$ are calculated from the standard relation [9-12].

The round trip delay time can be calculated using the relation

$$\delta = \left(\frac{1}{P}\right) + \left(\frac{\gamma}{360f}\right)$$  \hspace{1cm} (3.11)

By finding delay time $\delta$ and the length $l$ of the sample, the velocity of sound in the sample can be obtained using the relation

$$V = \frac{2l}{\delta}$$  \hspace{1cm} (3.12)
Further by knowing the velocity and the density of the samples various elastic moduli, Poisson’s ratio and the Debye temperatures were calculated using the following standard relations [15,16].

\[
\begin{align*}
\text{Longitudinal modulus,} & \quad L = \rho V_l^2 \tag{3.13} \\
\text{Shear modulus,} & \quad G = \rho V_t^2 \tag{3.14} \\
\text{Bulk modulus,} & \quad K = L - (4/3)G \tag{3.15} \\
\text{Young’s modulus,} & \quad E = (1+\sigma)2G \tag{3.16} \\
\text{Poisson’s ratio,} & \quad \sigma = (L-2G)/(2(L-G)) \tag{3.17} \\
\text{Debye temperature,} & \quad \Theta_D = (h/k)(3\rho q N_A)/(4\pi M)^{\frac{1}{3}}V_m \tag{3.18}
\end{align*}
\]

where \(V_l\) and \(V_t\) are the longitudinal and shear ultrasonic sound wave velocities, \(\rho\) is the density and \(M\) is the molecular weight of the corresponding samples, \(q\) is the number of atoms in the unit formula. \(N_A\) is the Avogadro number. The mean sound velocity \(V_m\) in the Eq. 3.18 is estimated by the following defined relation

\[
3/V_m^3 = 1/V_l^3 + 2/V_t^3 \tag{3.19}
\]

The density of the sample (\(\rho\)) was measured from the Archimedes principle using toluene as buoyant liquid.
3.4 Elastic Properties of 0.3Li$_2$O-0.2LiCl-0.5B$_2$O$_3$ and 0.7[0.8V$_2$O$_5$-0.2P$_2$O$_5$]-0.25PbO-0.05TiO$_2$ Glass-Ceramics

It has been observed that, borate glasses containing lithium ions have been studied extensively because of their technological applications in solid state batteries [17-19]. Small size, light weight and highly electropositive character of lithium ions are considered as factors which give rise to high voltages and high energy densities [20]. Stable lithium modified borate glasses are known to form over wide range of compositions and the inclusion of metal halides / salts such as LiCl, AgI, NaI, CuI into the glass enhances the ionic conduction [21]. But on mechanical and structural stability point of view, the research work on such glasses is also important. In the present work, lithium-chloro-borate (LCB) and vanadium-phosphate-lead-titanate (VPPT) glass-ceramics (GC) have been synthesized by heat treatment method. The ultrasonic measurements were carried out to study the effect of heat treatment on the elastic moduli, density, molar volume, Poisson’s ratio and Debye temperature of the LCB and VPPT samples. In the following section we describe the experimental results and discussion.

3.4.1 Density and Molar Volume Measurements

The synthesis and characterization of LCB and VPPT glasses and the respective glass-ceramics have been described in the Chapter-2A. The cylindrical shaped samples were prepared to serve the purpose of ultrasonic measurements. The same samples are also used to find the density using electronic balance up to the accuracy of ±0.001gm by Archimedes principle using toluene as immersion liquid.
The molar volumes $M_v$ were calculated $M/\rho$ where $M$ is the molecular weight and $\rho$ is the density of the corresponding glass/GC samples. The densities and molar volumes of LCB and VPPT GC samples are given in Table 3.2 (a) and (b) respectively.

3.4.2 Ultrasound Velocity Measurements.

A pulse superposition method was employed using ultrasonic interferometer to find the round trip delay time ‘$\delta$’ as we have already discussed in Section 3.3.3. By measuring the length of the sample ($l$), longitudinal ($v_l$) and transverse ($v_t$) velocities were calculated using the Eq.3.12 and mean velocity from the Eq. 3.19. The various elastic moduli, the poison’s ratio and Debye temperature of the samples investigated were calculated using the standard relations mentioned in section 3.3.3. All these calculated values for LCB and VPPT series are given in the Table 3.3.

3.5 Results and Discussion

3.5.1 Effect of Heat Treatment on Density and Molar Volume.

Density ($\rho$) measurements are widely used to study the effects of composition on glass structure [22-24]. These measurements are usually employed to control the homogeneity of glass, but the value of density itself is not a useful structural parameter. On the contrary, the determination of molar volume ($M_V$) from density data can also provide information on different aspects of the glass structure of glass-ceramics containing the crystalline phases [25].
Table 3.2: The densities and molar volumes of LCB and VPPT glass-ceramic samples

(a) Sample composition: 0.3Li$_2$O-0.2LiCl-0.5B$_2$O$_3$
   Heat treatment temperature: 150°C

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Heat treatment time (h)</th>
<th>Density (g/cc)</th>
<th>Molar volume (cc/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCB1</td>
<td>0</td>
<td>2.312</td>
<td>22.59</td>
</tr>
<tr>
<td>LCB2</td>
<td>2</td>
<td>2.293</td>
<td>22.78</td>
</tr>
<tr>
<td>LCB3</td>
<td>4</td>
<td>2.279</td>
<td>22.92</td>
</tr>
<tr>
<td>LCB4</td>
<td>6</td>
<td>2.289</td>
<td>22.82</td>
</tr>
<tr>
<td>LCB5</td>
<td>8</td>
<td>2.330</td>
<td>22.42</td>
</tr>
</tbody>
</table>

(b) Sample composition: 0.7[0.8V$_2$O$_5$-0.2P$_2$O$_5$]-0.25PbO-0.05TiO$_2$
   Heat treatment temperature: 150°C

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Heat treatment time (h)</th>
<th>Density ($\rho$) (g/cc)</th>
<th>Molar volume ($M_v$) (cc/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPPT1</td>
<td>0</td>
<td>3.864</td>
<td>45.94</td>
</tr>
<tr>
<td>VPPT2</td>
<td>2</td>
<td>3.870</td>
<td>45.86</td>
</tr>
<tr>
<td>VPPT3</td>
<td>4</td>
<td>3.879</td>
<td>45.75</td>
</tr>
<tr>
<td>VPPT4</td>
<td>6</td>
<td>3.894</td>
<td>45.58</td>
</tr>
<tr>
<td>VPPT5</td>
<td>8</td>
<td>3.918</td>
<td>45.30</td>
</tr>
</tbody>
</table>
Table 3.3: Sample Code, sound velocities, elastic moduli, Poisson’s ratio and Debye temperature

<table>
<thead>
<tr>
<th>Code</th>
<th>Sound velocity (m/s)</th>
<th>Elastic moduli (G pa)</th>
<th>Poisson’s ratio σ</th>
<th>Debye Temp θD (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V_l</td>
<td>V_t</td>
<td>V_m</td>
<td>L</td>
</tr>
<tr>
<td>LCB-Series</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCB1</td>
<td>6594</td>
<td>3697</td>
<td>4114</td>
<td>100.54</td>
</tr>
<tr>
<td>LCB2</td>
<td>6645</td>
<td>3745</td>
<td>4166</td>
<td>101.24</td>
</tr>
<tr>
<td>LCB3</td>
<td>6676</td>
<td>3872</td>
<td>4297</td>
<td>101.57</td>
</tr>
<tr>
<td>LCB4</td>
<td>6681</td>
<td>3923</td>
<td>4349</td>
<td>102.17</td>
</tr>
<tr>
<td>LCB5</td>
<td>6843</td>
<td>3982</td>
<td>4582</td>
<td>109.11</td>
</tr>
<tr>
<td>VPPT-Series</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VPPT1</td>
<td>3656</td>
<td>2157</td>
<td>2390</td>
<td>51.64</td>
</tr>
<tr>
<td>VPPT2</td>
<td>3883</td>
<td>2219</td>
<td>2465</td>
<td>58.35</td>
</tr>
<tr>
<td>VPPT3</td>
<td>4042</td>
<td>2226</td>
<td>2882</td>
<td>63.38</td>
</tr>
<tr>
<td>VPPT4</td>
<td>4143</td>
<td>2301</td>
<td>2562</td>
<td>66.84</td>
</tr>
<tr>
<td>VPPT5</td>
<td>3871</td>
<td>2205</td>
<td>2450</td>
<td>58.70</td>
</tr>
</tbody>
</table>
The structural modification due to heat treatment would affect the density and the respective molar volume compared to their base glasses. The variation of density and molar volume as a function of heat-treatment time in the LCB GC’s as a function of heat treatment time is shown in Fig. 3.6 (a) and (b) respectively. Similar variations for the VPPT series are shown in Fig 3.7 (a) and (b) respectively. Although though change is density is marginal, however, the closer look show in LCB series that, initially density decrease with the increase of heat-treatment time (2 to 4h). A further increase of heat-treatment time on the sample gradually increases the density. On the other hand, molar volume varies inversely with the density as expected. Similarly in the case of VPPT-series, a continuous increasing trend of density has been observed with corresponding decrease in the molar volume. This kind of increase in density normally results higher network stability [25]. By considering the structural features of the glass networks [25, 26], for example, in the case of borate based glass (LCB), the structure of both crystalline and amorphous B₂O₃ is made up of planar [BO₃/2]₀ triangles. In amorphous B₂O₃, most of these triangles are arranged into boroxyl rings in which three oxygen atoms are part of the ring and three are out of the ring. These rings are randomly interconnected through the loose [BO₃/2]₀ units. Because of the presence of Li₂O, the three coordinated triangle boron [BO₃/2]₀ units are converted into four coordinated boron tetrahedral [BO₄/2]⁻ units with a non-bridging oxygen. Though the dimensionality and connectivity among the structural units remains unchanged with the increase of heat treatment, the compactness and packing efficiency of the structure increase after heat treatment [27,28]. This is reflected in an increase in density with the corresponding decrease in molar volume. In VPPT samples, the density increase continuously with the increase of heat treatment time
and the corresponding molar volume decrease. These results may attribute to an increase of the structural compactness and reduction in density of the samples. The results are also consistent with the IR results of the samples (Chapter-2A), wherein the peaks correspond to P-O and P-O-P bending vibration, P=O, V-O stretching vibrations and V=O vibration were gradually disappeared with the increase of heat treatment time.
Figure 3.6: Variation of (a) Density (b) Molar volume verses heat treated time for LCB-series.
Figure 3.7: Variation of (a) Density and (b) Molar volume verses heat treated time for VPPT-series
3.5.2 Effect of Heat Treatment on Elastic Properties.

Measured ultrasound wave velocities $V_1$ and $V_t$ for various LCB and VPPT glass-ceramics from a pulse superposition technique are presented in Table 3.3. An overall increase of ultrasound velocities with an increase of heat-treatment time both in LCB and VPPT GC’s has been observed. An increase in sound velocities is an indication of the structural modification related to partial crystallization in the samples. The variations of elastic moduli as a function of heat-treatment time are shown in Fig. 3.8 and Fig 3.9 for LCB and VPPT samples respectively. It may be noted that for LCB samples, when the heat-treatment time is less than 4h, variation of elastic moduli appear to be a small in magnitude. As the heat-treatment time increases beyond 4h, longitudinal modulus ($L$) and Young’s modulus ($E$) tend to increase and the bulk modulus ($K$) tends to decrease. This is attributed to the decrease in longitudinal strain as an indication of the increase in stiffness of the structure. Further it may be noted that moduli tend to increase when the subjected to heat treatment for 6h more. This again indicates the high growth rate of crystallization leading to increase in the bond strength among constituent atoms of GC’s and they become stronger compared to the precursor glass [30]. Further, the variation of rigidity modulus ($G$) found to be least sensitive with the heat-treatment, which is an indication that the sample can sustain more shear strain, probably because of the presence of more covalent bonds [31-33]. These observations are consistent with morphology as seen in the SEM images of Fig. 2A.4 and the characteristic IR spectra of LCB-series shown in the Chapter-2A. As for as VPPT GC’s concerned, the moduli tend to increase with the increase of heat treatment time (up to 6h). Further, an increase of heat treatment time to 8h decreases the elastic moduli may be due to the lack of compactness in the structure.
The rigidity modulus (G) shows almost insensitiveness with the heat treatment time. These observations are consistent with the XRD, SEM and IR characteristic studies of VPPT series discussed in the Chapter-2A.

Figure 3.8: Variation of elastic moduli versus heat-treated time: (a) Longitudinal modulus [L], (b) Young’s modulus [E], (c) Bulk modulus [K] and (d) Shear modulus [G] for LCB-series.
Figure 3.9: Variation of elastic moduli versus heat-treated time: (a) Longitudinal modulus [L], (b) Young’s modulus [E], (c) Bulk modulus [K] and (d) Shear modulus [G] for VPPT-series.
3.5.3 Poisson’s Ratio and Debye Temperature

Variations of Poisson ratio and Debye temperature for different heat-treatment time for LCB series are shown in Fig 3.10 (a) and (b) respectively. Similar variations for VPPT series are shown in 3.11 (a) and (b) respectively. The Poisson ratio is a measure of covalency–rigidity, which also represents the negative ratio of the transverse to longitudinal strains, and hence expected to sensitively reflect the structural dimensionality changes. It is well known that the Poisson’s ratio will be affected by the changes in the cross-link density of the glass network [34, 35]. A high cross-link density has Poisson’s ratio in the order of 0.1 to 0.2, while a low cross-link density has Poisson’s ratio between 0.3 and 0.5 [36,37]. The observed values Poisson’s ratio in the present work lie in a very narrow range for both LCB and VPPT GC samples (0.20 to 0.30).

The Debye temperature $\theta_D$ is characteristic property of a solid lattice related to the acoustic phonon spectrum [38]. It also determines the number of atoms in a chemical formula that participate in the vibrations [24]. Continuous increasing trend of Debye temperature has been observed in LCB GC’s sample. The increasing trend of Debye temperature is seen in the VPPT GC’s series up to 4h of heat treatment time. These results are attributed due to the increase in rigidity and compactness in the structure which arises gradually during the controlled heat treatment [39]. On further heat treatment, Debye temperature decreases due to the lack of compactness and leads to more disorder in the structure. Hence the prepared LCB5 (heat treated at 150°C for 8h) and VPPT3 (heat treated at 150°C for 6h) glass-ceramics will be mechanical stronger than the corresponding base glasses [26]. The results are consistent with the XRD and IR- spectral studies described in the Chapter-2A, wherein it has been observed that relative intensities
and line widths of IR spectra vary significantly because of the effect of heat-treatment. Intensities of the peaks increase, while the line widths decrease in LCB glass-ceramic series. In addition to this, there are also several sharp peaks that appear as a consequence of the heat-treatment. Thus, the heat-treatment on the prepared LCB and VPPT (up to 4h) GC’s enhances the compactness and orderliness of the structure.
Figure 3.10: Variation of (a) Poisson’s ratio and (b) Debye temperature verses heat treated time for LCB-series.
Figure 3.11: Variation of (a) Poisson’s ratio and (b) Debye temperature verses heat treated time for VPPT-series.
3.6 Conclusions

Cylindrical blocks of LCB and VPPT samples suitable for the measurement of ultrasonic sound velocity by pulse echo superposition technique. The thermal treatment on the glasses results in the release of stresses from the glass and the possible formation of crystalline phases along with the residual glassy phases. This microstructural modification leads to a decrease of effective volume. Further, it has been observed that the magnitudes of the density, ultrasound velocity, attenuation for the GC’s are found to increase with the increase of heat treatment on the samples up to certain time. The characteristic modifications are observed in the elastic moduli of the samples as they converted to GC’s so that they become stronger than the parent glasses.

The Debye temperature variation with respect to the increase in heat treatment time in the LCB and VPPT GC’s reveals the structural modification. The continuous increase of Debye temperature in LCB and in VPPT (up to 4h) samples indicates the increase of compactness in the structure due to the increase of crystallite growth rate. On further heat treatment Debye temperature decreases due to lack of compactness. The values of Poisson ratio are typically that of covalently bonded networks (0.2–0.3) for both LCB and VPPT with slight variation on either side due to thermal agitation indicating that Poisson’s ratio is least sensitive to the heat treatment on the samples.
References:


