CHAPTER 4

ULTRASONIC STUDY OF
(1-x-y)(B₂O₃)-x(Li₂O)-y(MCl₂) GLASSES
4. Ultrasonic study of \((1-x-y)(B_2O_3)-x(Li_2O)-y(MCl_2)\) (M=Cd, Zn) Glasses

4.1. Introduction

For the last twenty-five years, studies on physical properties of glasses have attracted the attention of solid state physicists mainly because glasses exhibit a number of properties strikingly different from their crystalline counter-parts. In many cases, this difference becomes very prominent at extremely low temperature. These properties are: specific heat, thermal conductivity, thermal expansion, acoustic velocity, acoustic absorption, elastic constants, and pressure coefficient of velocity. The measurement of elastic properties of solids by ultrasonic methods has become an interesting subject, due to the non-destructive nature of the technique. The main reason for extensive ultrasonic investigation of solids is the need for elastic properties of materials like crystals, alloys, plastics, ceramics, etc. in a variety of applications. Elastic and acoustical properties of glasses are significant from the point of view of their application in special devices\(^1\). The old static and dynamic methods of measuring elastic constants of large samples have gained wide acceptance due to their simplicity. Among the various newer techniques, ultrasonic pulse-echo methods are useful where measurements having highest precision are needed.

Ultrasonic investigation of solids will help to understand various solid state phenomena such as grain and domain boundary effects in metals, ferromagnetic and ferroelectric materials, the diffusion of atoms, molecules and vacancies through a solid, the motion of imperfection such as dislocation as well as the interaction between the lattice sound vibration and free electrons in metals at low temperatures. All these effects are studied by measuring elastic properties,
internal friction properties and their change with temperature, frequency and applied electric field²⁻⁴. The measurement of elastic constants of solids is of considerable interest and significance to both science and technology. This measurement yields valuable information regarding the forces operating between the atoms or ions in a solid. Since the elastic properties describe the mechanical behaviour of materials, this information is of fundamental importance in interpreting and understanding the nature of bonding in the solid state. When a material is subjected to a stress it will get strained and within the elastic limit, stress applied on a material is directly proportional to strain (Hooke's Law). The proportionality constant relating stress and strain is the modulus of elasticity or the elastic constant. Commonly there are three types of elastic constants⁵. They are (i) Young's modulus (Y), (ii) Bulk modulus (K), and (iii) Rigidity or Shear modulus (G). The ratio of the linear stress to the linear strain is called the Young's modulus. It also represents the resistance to traction along the axis of thin bar or rod. The Bulk modulus (K) provides a good link between the macroscopic elasticity theory and the atomistic viewpoints such as lattice dynamics. Bulk modulus is the ratio of the hydrostatic stress to the volumetric strain. The shear modulus (G) shows the relation between shear stress and shear strain. In addition to the above elastic constants, the longitudinal modulus (L) may be determined from the density of the solid and velocity of propagation of longitudinal waves through the solid.

There is interest in alkali metal borate glasses in view of their technological interest as solid electrolytes in batteries and other electrochemical devices⁶⁻⁸, and because of the desire to understand how a disordered structure could exhibit the alkali borate anomalies⁹⁻¹¹. Many investigators have particularly made use of spectroscopy to explain the structure of alkali metal borate glasses¹²⁻¹⁴. These
studies reveal that the structure is dependent not only upon the concentration of alkali metal ions but also upon the type of the alkali metal ions. Recently, attention has been paid by many workers to the study of ultrasonic velocity in glasses due to its sensitiveness as a probe to many types of structural changes\textsuperscript{15-17}. Ultrasonic velocity and attenuation in sodium silicate glasses containing another monovalent alkali oxide (K\textsubscript{2}O or Li\textsubscript{2}O) in different concentrations have been measured by the pulse echo overlap method by Rajendran and HaEl-Batal\textsuperscript{15}. The addition of alkali to silica causes the formation of non-bridging oxygens, leading to the weakening of the glass structure or a reduction in the rigidity of the glasses. This results in a decrease in ultrasonic velocity and hence an increase in attenuation\textsuperscript{15}. Ultrasonic velocity in Cs\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3} glasses has been measured by Kodama et al\textsuperscript{16}. Elastic properties of these glasses expressed in terms of the shear modulus are discussed with respect to three kinds of structural units - B\textit{\phi}\textsubscript{3}, Cs\textsuperscript{+}B\textit{\phi}\textsubscript{2}O\textsuperscript{-}, and Cs\textsuperscript{+}B\textit{\phi}\textsubscript{4}, where \textit{\phi} represents a bridging oxygen and O\textsuperscript{-} a non-bridging oxygen. The structural unit Cs\textsuperscript{+}B\textit{\phi}\textsubscript{4} increases the rigidity of the glass and this unit form a three-dimensional covalent bond in the glass network. On the other hand, the structural unit Cs\textsuperscript{+}B\textit{\phi}\textsubscript{2}O\textsuperscript{-} decreases the rigidity of the glass, since this unit acts to break down a covalent bond of the glass network. Kodama et al\textsuperscript{18} have also reported the variation of elastic constants with varying concentration of Li\textsubscript{2}O in B\textsubscript{2}O\textsubscript{3}- Li\textsubscript{2}O glasses. The relationship between elasticity and structure of lithium borate glasses was analysed in terms of the three structural units defined as B\textit{\phi}\textsubscript{3}, Li\textsuperscript{+}B\textit{\phi}\textsubscript{2}O\textsuperscript{-}, and Li\textsuperscript{+}B\textit{\phi}\textsubscript{4}, where \textit{\phi} represents a bridging oxygen and O\textsuperscript{-} a non-bridging oxygen, on the assumption that these structural units exhibit their inherent elastic properties and hence have different elastic constants. The variation in elastic constants is caused partly by the fact that the structural unit Li\textsuperscript{+}B\textit{\phi}\textsubscript{4} forms the glass network by four covalent bonds whereas the structural unit B\textit{\phi}\textsubscript{3} forms the glass networks by
three covalent bonds. In rubidium borate glasses, Kodama\textsuperscript{17} found that ultrasonic velocity exhibits a maximum, a minimum, and another maximum in succession as the concentration of rubidium oxide is increased. But information available on the elastic properties of ternary glass systems is very limited\textsuperscript{15}. It would be of interest to study the velocity of sound and elastic constants of glass samples containing a mixture of an oxide and a halide. In the present chapter, the author reports the study of ultrasonic velocity in the glass systems \((1-x-y)(\text{B}_2\text{O}_3)-x(\text{Li}_2\text{O})-y(\text{MCI}_2)\) (M=Cd,Zn). The elastic constants, Poisson's ratio, thermal expansion coefficient, acoustic impedance and the variation of these quantities with composition of the glasses, were studied.

4.2. Theory

Ultrasonic waves were transmitted through the specimen and the travel time \((t)\) of the waves through the specimen was determined. Then the ultrasonic velocity \((U)\) in the specimen was obtained using the relation

\[
U = \frac{2d}{t}
\]

where \(d\) is the thickness of the sample. Knowing the density \((\rho)\) of the sample, and the longitudinal and the transverse velocities \(U_1\) and \(U_t\) respectively, the longitudinal elastic modulus \((L)\), shear modulus \((G)\), bulk modulus \((K)\), Young's modulus \((E)\), and Poisson's ratio \((\sigma)\) were computed according to the following relations\textsuperscript{15,18}.

\[
L = \rho U_1^2
\]

\[
G = \rho U_t^2
\]
Acoustic impedance \((Z)\), which is a measure of the transmission and reflection of sound energy in the glass samples, was calculated using the relation
\[
Z = U_m \rho
\]  
(7)

where \(U_m\) is the mean sound velocity defined as
\[
U_m = \left[ \frac{1}{3} \left( \frac{2}{U_1^3} + \frac{1}{U_1^3} \right) \right]^{1/3}
\]  
(8)

Thermal expansion coefficient was calculated using the following expression
\[
\alpha_\rho = 23.2 \left( U_1 - 0.57457 \right)
\]  
(9)

4.3. Experimental details

Fourteen glass samples with code numbers BZL1 to BZL7 and BCL1 to BCL7 were prepared from appropriate amount of analar grade \(\text{H}_3\text{BO}_3\), \(\text{Li}_2\text{CO}_3\), and \(\text{CdCl}_2\) or \(\text{ZnCl}_2\) as described in section 3.3 of chapter 3 (Ref: Table 3.1, chapter 3). The glass samples were annealed at a temperature of about 450\(^\circ\)C for 4h and were then polished, so that they had a pair of flat and parallel end faces.

The polished glasses had a diameter of about 1.5cm and a length of 1cm. Ultrasonic velocity of longitudinal and transverse waves in the glass samples were
measured by pulse overlap technique using Matec 700 ultrasonic velocity system (Matec Instruments, Inc, USA), and using respectively X-cut and Y-cut quartz transducers each of frequency 5MHz\textsuperscript{21,19}. The transducers were bonded to the glass samples using salol as the bonding material. The ultrasonic velocity measurements were carried out at room temperature (34 ± 1°C) as described in section 2.7 of chapter 2 of this thesis. In pulse echo method an ultrasonic pulse of small duration is transmitted into the specimen by means of a transducers bonded to it. The pulse traverses the specimen and undergoes several reflections at both the faces. These reflected pulses or echoes are detected either by the transmitting transducers itself or by a separate receiving transducer fixed at the opposite face of the specimen. By measuring the time interval between two successive echoes and knowing the length of the sample, the velocity can be directly computed. The densities of the glass samples were determined making use of Archimede's principle and using water as the immersion liquid.

4.4. Results and discussion

The experimental values of the density of the glass samples, the longitudinal velocity ($U_l$), and transverse velocity ($U_t$) in samples of different compositions are given in the Table 4.1. The computed elastic moduli, acoustic impedance ($Z$), Poisson's ratio ($\sigma$) and thermal expansion coefficient ($\alpha_p$) are tabulated in the Table 4.1. Variations of these quantities with composition of the samples are plotted in the figures 4.1-4.10.

Density of the glass samples was found to increase almost linearly with increase in the concentration of Li$_2$O and ZnCl$_2$ in BZL glasses and with that of Li$_2$O in BCL glasses. But the density showed a conspicuous decrease in its value
Table 4.1. Longitudinal Velocity ($U_l$), transverse velocity ($U_t$), density ($\rho$), longitudinal elastic modulus ($L$), shear modulus ($G$), bulk modulus ($K$), Young's modulus ($E$), acoustic impedance ($Z$), Poisson's ratio ($\sigma$), and thermal expansion coefficient ($\alpha_p$) of BZL and BCL glasses.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$U_l$ m/s</th>
<th>$U_t$ m/s</th>
<th>$\rho$ Kg/m$^3$</th>
<th>$\sigma$</th>
<th>$L$ Gpa</th>
<th>$G$ Gpa</th>
<th>$K$ Gpa</th>
<th>$E$ Gpa</th>
<th>$Z \times 10^{-6}$ Kg/m$^2$s</th>
<th>$\alpha_p$ m/s</th>
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<tr>
<td>BZL1</td>
<td>3884.21</td>
<td>2300.75</td>
<td>2595</td>
<td>.2228</td>
<td>38.49</td>
<td>13.73</td>
<td>20.73</td>
<td>33.57</td>
<td>6.6063727</td>
<td>89172.3</td>
</tr>
<tr>
<td>BZL2</td>
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<td>2557.26</td>
<td>2620</td>
<td>.2945</td>
<td>58.84</td>
<td>17.14</td>
<td>35.99</td>
<td>44.37</td>
<td>7.479594</td>
<td>109954.0</td>
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<tr>
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<td>3036.99</td>
<td>2830</td>
<td>.2633</td>
<td>81.24</td>
<td>26.10</td>
<td>46.44</td>
<td>65.95</td>
<td>9.556765</td>
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</tr>
<tr>
<td>BZL4</td>
<td>5827.38</td>
<td>3159.65</td>
<td>2968</td>
<td>.2918</td>
<td>100.79</td>
<td>29.63</td>
<td>61.28</td>
<td>76.55</td>
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<td>2590.98</td>
<td>2254</td>
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<td>66.72</td>
<td>15.16</td>
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<td>BCL1</td>
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<td>.2343</td>
<td>28.06</td>
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<td>2199</td>
<td>.2748</td>
<td>46.34</td>
<td>14.39</td>
<td>27.15</td>
<td>36.68</td>
<td>6.263146</td>
<td>106482.6</td>
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<td>5379.11</td>
<td>2953.86</td>
<td>2290</td>
<td>.2841</td>
<td>66.26</td>
<td>19.98</td>
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<td>7.540618</td>
<td>124782.1</td>
</tr>
<tr>
<td>BCL4</td>
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<td>.3027</td>
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<td>51.52</td>
<td>61.00</td>
<td>8.237049</td>
<td>138506.5</td>
</tr>
<tr>
<td>BCL5</td>
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<td>2980.76</td>
<td>2301</td>
<td>.3206</td>
<td>77.42</td>
<td>20.49</td>
<td>50.17</td>
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<td>1987</td>
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<td>2230</td>
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<td>21.40</td>
<td>49.22</td>
<td>56.08</td>
<td>7.726941</td>
<td>136986.8</td>
</tr>
</tbody>
</table>
and then an increase with increase in CdCl$_2$ concentration in BCL glasses (Fig. 4.1).

![Graph showing variation of density ($\rho$) with mole percentages of Li$_2$O ($x$) and CdCl$_2$ or ZnCl$_2$ ($y$) in BCL and BZL glasses.]

Figure 4.1. Variation of density ($\rho$) with mole percentages of Li$_2$O ($x$) and CdCl$_2$ or ZnCl$_2$ ($y$) in BCL and BZL glasses

Slow variation of the density with increasing Li$_2$O concentration was the usual trend in Li$_2$O-B$_2$O$_3$ glasses$^{18}$. Results on the study of dependence of density on the mole percentage of Cs$_2$O in Cs$_2$O-B$_2$O$_3$ glasses are also available in the literature$^{16}$. Density of cesium borate glasses is reported to increase almost linearly with increase in the mole percentage of Cs$_2$O.

In present study, longitudinal and transverse velocities in BZL and BCL glasses increase with increase in the concentration of Li$_2$O and ZnCl$_2$ or CdCl$_2$ (Fig. 4.2 & 4.3). Figures 4.4-4.7 show L, K, G and E as a function of concentration of Li$_2$O and ZnCl$_2$ or CdCl$_2$. All these elastic constants were found
to increase with increase in the concentration of the constituents. Recent ultrasonic studies by Kodama on barium borate glasses \((x_2\text{BaO}-x_1\text{B}_2\text{O}_3)\) have shown that both longitudinal and transverse velocity and elastic constants increase at first with increase in the concentration of BaO up to \(x_2 = 0.318\), and then decrease as \(x_2\) increases further. This author has also reported the elastic properties of \(x_2\text{K}_2\text{O}-x_1\text{B}_2\text{O}_3\) glasses. In lithium borate glasses of the composition \(x_2\text{Li}_2\text{O}-(1-x_2)\text{B}_2\text{O}_3\), Kodama et al. reported that the structural unit \(\text{BO}_3\) is converted to the structural unit \(\text{BO}_4\) only in the composition range \(0 \leq x_2 \leq 0.28\) and this conversion caused an increase in velocity of sound. In the present study, the increase in velocity of sound with the increase in concentration of \(\text{Li}_2\text{O}\) \((0.05 \leq x \leq 0.20)\) and \(\text{ZnCl}_2\) or \(\text{CdCl}_2\) \((0.05 \leq y \leq 0.020)\) in the glass composition \((1-x-y)(\text{B}_2\text{O}_3)-x(\text{Li}_2\text{O})-y(\text{MCl}_2)\) \((\text{M} = \text{Cd}, \text{Zn})\) might be due to formation of bridging oxygen as a result of the conversion of \(\text{BO}_3\) units in to \(\text{BO}_4\) units.

![Figure 4.2. Variation of ultrasonic velocities with mole percentages of Li2O (x) and ZnCl2 (y) in BZL glasses.](image-url)
Figure 4.3. Variation of ultrasonic velocities with mole percentages of Li$_2$O (x) and CdCl$_2$ (y) in BCL glasses

Figure 4.4. Variation of elastic constants with mole percentage (x) of Li$_2$O in BZL glasses
Figure 4.5. Variation of elastic constants with mole percentage (y) of ZnCl₂ in BZL glasses.

Figure 4.6. Variation of elastic constants with mole percentage (x) of Li₂O in BCL glasses.
Figure 4.7. Variation of elastic constants with mole percentage (y) of CdCl₂ in BCL glasses

Figure 4.8. Variation of acoustic impedance (Z) with mole percentages of Li₂O (x) and CdCl₂ or ZnCl₂ (y) in BCL and BZL glasses
Figure 4.8 shows the acoustic impedance \((Z)\) of the glass systems as a function of concentration of \(\text{Li}_2\text{O}\) and \(\text{ZnCl}_2\) or \(\text{CdCl}_2\). In the case of sodium silicate glasses containing \(\text{K}_2\text{O}\) or \(\text{Li}_2\text{O}\), it has been reported\(^1\) that the addition of alkali oxide causes the splitting of glass network there by increasing the formation of non-bridging oxygens, resulting in lower impedance to the propagation of ultrasonic waves. It is also reported\(^2\) that the acoustic impedance of sodium silicate glass increases with the addition of \(\text{Cr}_2\text{O}_3\). The addition of \(\text{Cr}_2\text{O}_3\) results in the introduction of new network forming groups \((\text{CrO}_4)^{2-}\) in the already loose sodium silicate glass (40 wt % of \(\text{Na}_2\text{O}\)) which results in larger impedance for the propagation of ultrasonic waves. It is also reported that in \(\text{PbO-SiO}_2\) glasses, the acoustic impedance increased substantially with the increase of \(\text{PbO}\) concentration in the glass\(^3\). In the present study, the concentration changes of \(\text{Li}_2\text{O}\) and \(\text{CdCl}_2\) or \(\text{ZnCl}_2\) in \(\text{B}_2\text{O}_3-\text{Li}_2\text{O}-\text{MCl}_2\), \(\text{M}=\) (\(\text{Cd}, \text{Zn}\)) glasses are found to produce similar variation in the acoustic impedance and increase of acoustic impedance is attributed to the presence of bridging oxygens in the glass structure.

The increase in Poisson's ratio with increasing chalcogen content in \(\text{As-Sb-Se}\) glasses has been attributed to a change in glass structure from an chemically-ordered network to a chain like form\(^4\). The Poisson's ratio was reported to be some-what independent of concentration of \(\text{ZnO}\) in \(\text{ZnO-V}_2\text{O}_5-\text{B}_2\text{O}_3\) glasses\(^5\). The constant value of Poisson's ratio with respect to composition of the glass samples shows that the basic structure of all the glasses remains more or less the same throughout the series\(^6\). Poisson's ratio \((\sigma)\) of the glass samples in the present study is found to decrease slowly with the concentration of \(\text{ZnCl}_2\) or \(\text{CdCl}_2\) (Figure 4.9), while it increases with concentration of \(\text{Li}_2\text{O}\) in both BZL and BCL glasses. This composition dependence of Poisson's ratio might be due to the change in structure of the glass systems.
Thermal expansion coefficient computed using ultrasonic data in the present study shows a regular increase with increasing concentration of Li$_2$O and ZnCl$_2$ or CdCl$_2$ (Figure 4.10).

![Graph showing variation of Poisson's ratio with Li$_2$O concentration](image)

Figure 4.9. Variation of Poisson's ratio (σ) with mole percentages of Li$_2$O (x) and CdCl$_2$ or ZnCl$_2$ (y) in BCL and BZL glasses.

It has been suggested\textsuperscript{26} that the mean atomic volume of the glass structure is not the only factor determining the bulk modulus of the ZnO--V$_2$O$_5$-B$_2$O$_3$ glasses. Besides the mean atomic volume, other factors such as the type of bonding could be effective in determining bulk modulus K. In the above system of glasses, the bulk modulus increases with increase in the concentration of ZnO while Poisson's ratio is found to be independent of concentration of ZnO.
Therefore, the type of bonding, rather than the mean atomic volume, has a greater influence in determining the bulk modulus of these glasses.

![Graph](image)

Figure 4.10. Variation of thermal expansion coefficient ($\alpha_p$) with mole % of $\text{Li}_2\text{O}$ (x) and $\text{CdCl}_2$ or $\text{ZnCl}_2$ (y) in BCL and BZL glasses

The conversion of $\text{BO}_3$ co-ordinated state to $\text{BO}_4$ co-ordinated state increases the connectivity of the glass network, resulting in a progressive and pronounced compact glass structure. The presence of $\text{BO}_4$ tetrahedra with bridging oxygens in $\text{B}_2\text{O}_3 -\text{Li}_2\text{O} - \text{MCl}_2$, ($\text{M} = \text{Cd}, \text{Zn}$) glasses increase the rigidity of the glass, and cause an increase in the value of ultrasonic velocity, density, and elastic constants.
The rates of increase of ultrasonic velocity and elastic constants with concentration variations of CdCl₂ are smaller than those for similar variations of ZnCl₂ concentrations. This might be due to the fact that the process of transformation of boron co-ordination strongly depends on the mass of the cation. Lighter cation (Zn²⁺) favors the formation of tetrahedral groups while Cd²⁺ being heavier than Zn²⁺ does not break the B-O network and therefore does not enter the network interstitially. Hence Cd²⁺ enhances the formation of non-bridging oxygen molecules. Therefore, the formation rate of non-bridging oxygen units is more for heavier cation (Cd²⁺) and it is less for lighter cation (Zn²⁺). Then the connectivity of the structure will be less and the elastic constants will became smaller in BCL glasses.

4.5. Conclusion

Ultrasonic velocities (both longitudinal and transverse) in (1-x-y)(B₂O₃)-x(Li₂O)-y(MCl₂) (M=Cd,Zn) glasses are found to increase with increase in concentration of the constituents. The composition dependence of all the derived parameters such as elastic constants, acoustic impedance, Poisson's ratio and thermal expansion coefficient is discussed. It is found that in BCL glasses, the variation in velocity and elastic constants are smaller than that in BZL glasses. This result may be due to that the heavier cation (Cd²⁺) favors the formation of non-bridging oxygens and causes a decrease in connectivity of the glass structure. The elastic properties of the glasses have been analysed in terms of the structural changes with change in composition of the glasses. The presence of BO₄ tetrahedra with bridging oxygens in the glass structure gives more rigidity to the structure and causes an increase in elastic constants.
References


