Chapter 3
Structure and Dielectric Properties of
Li$_2$O·MO·Bi$_2$O$_3$·B$_2$O$_3$
(M = Zn, Cd) glasses
Introduction

Discovery and studies of different amorphous glass materials, whose property can be tailored, constitute a great potential in the field of information technology. One of these materials is bismuth borate glasses which are known due to their superior properties such as high transparency in the far infrared regime, large polarizability, high refractive index, density, optical basicity and also large third order non-linear susceptibility [1-4]. Because of above advantages these glasses are suitable for infrared transmission components, ultrafast optical switches and photonic devices and also for radiation shielding windows and scintillation counters [2-4]. Again, Sugimoto [5] has studied the optical properties of Bi-doped borate glasses by using femtosecond lasers and found that these glasses exhibit an ultrafast response in Optical Kerr Shutter (OKS) operation. Chemical durability is also improved on the addition of Bi$_2$O$_3$ in borate glasses. Furthermore, the study of the charge transport in ionically conducting glasses is today a current topic due to their notable application as solid electrolyte in electrochemical devices [6, 7]. The doping of alkali metal ions such as Li$^+$ in bismuth borate glasses which modify the glass structure and enhance the ionic conductivity [8] is own interest. Bismuth oxide is a conditional glass former. It occupies both network forming and network modifying positions in oxide glasses, therefore, the physical properties mainly glass transition temperature and conductivity of glasses (containing Bi$_2$O$_3$) exhibit anomalous changes when the structural role of the cation switches over in this way [8-10]. The role of Bi$_2$O$_3$ in borate glasses has been investigated by the different authors in several studies [2, 8, 10-14] and suggested the sharing of Bi$^{3+}$ in the glass matrix as octahedral [BiO$_6$] units and the possibility of the presence of [BiO$_3$] units. The glasses containing transition metal ion such as ZnO/CdO have gained special interest in recent years owing to their applications in different fields of electronic products. On doping of these metal ions in the host glass the glass matrix is highly influenced. This is because the heavy metal ions enter in the glass network as network modifier as well as network former [15] which further depends on the concentration of the oxide itself. The spectral studies on
the zinc/cadmium bismuth borate glasses containing small rare earth ions have done in the visible and NIR region by some authors and reported that by varying the amount of Bi$_2$O$_3$ in the host glass there is considerable increase in the luminescence intensity and radiative properties which make them suitable for various optical devices [16-19].

In this chapter, the following glass systems have been prepared and detailed investigation has been carried out to study the changes induced in the structure, physical, thermal, optical and electrical properties of lithium zinc/cadmium borate glasses when the conventional glass former (B$_2$O$_3$) is replaced by unconventional glass former (Bi$_2$O$_3$). Further, a more interesting investigation in the prepared glass systems is determined by the presence of Bi$_2$O$_3$ that plays dual role as network modifier and as network former in these glasses.”

$$\text{30Li}_2\text{O-20ZnO-}x\text{Bi}_2\text{O}_3(50-x)\text{B}_2\text{O}_3$$ (LZBB glasses)  
\((x = 0, 10, 20, 30, 40 \text{ and } 50 \text{ mol%})\)

$$\text{30Li}_2\text{O-20CdO-}x\text{Bi}_2\text{O}_3(50-x)\text{B}_2\text{O}_3$$ (LCBB glasses)  
\((x = 0, 10, 20, 30, 40 \text{ and } 50 \text{ mol%})\)

**Experimental**

The glass systems 30Li$_2$O·20ZnO·xBi$_2$O$_3$·(50-x)B$_2$O$_3$ and 30Li$_2$O·20CdO·xBi$_2$O$_3$·(50-x)B$_2$O$_3$, (with x = 0 to 50 mol%) were synthesized by normal melt quench technique (Section 2.2.1). Commercial powder of analytical grade Li$_2$CO$_3$, ZnO, CdO, Bi$_2$O$_3$ and H$_3$BO$_3$ (purity > 99%) was used as starting material. The appropriate amount of these chemicals was taken in a porcelain crucible and was thoroughly mixed to form the batches of 20 g. The batch mixture was then melted at temperature 1373 K in a programmable electric furnace for 30 minutes and stirred constantly for better mixing. Finally the transparent and yellowish glasses were formed by pouring the melt at room temperature onto a stainless steel plate and rapidly quenching it by another stainless steel plate. The exact composition along with the sample code of each glass is presented in Table 3.1 and 3.2.

The amorphous state of the glasses was confirmed by X-ray diffraction using a Rigaku Miniflux-II diffractometer with CuK$_\alpha$ radiation at room temperature (RT) in the 20 range 10$^\circ$ - 80$^\circ$ at scanning rate of 2 $^\circ$/min (Section 2.3.1). IR transmission
spectra of all the samples were recorded at RT using KBr pellet techniques with Perkin-Elmer spectrometer (BX-II) in the spectral range of 450-4000 cm\(^{-1}\) (Section 2.3.2). Densities of the glass samples were calculated at room temperature using Archimede’s method with deionized water as the immersing liquid. Molar volume of each sample (\(V_g\)) was also computed (Section 2.4.1). To obtain the thermal behavior of the glasses, differential scanning calorimetry traces were recorded using Q600 SDT TA instruments with a programmed heating rate of 10 K/min in the temperature range 473-1273 K (Section 2.5.1). The characteristic temperatures such as glass transition temperature, crystalline temperatures and melting temperature etc. were determined with accuracy ±2 K using the software associated to the equipment. The optical transmittance spectra of the polished samples were recorded with a UV-Vis-NIR spectrometer (Cary 5000) in the wavelength range 200-3300 nm at RT (Section 2.6.1). For the electrical measurements, the silver paint as glass electrode was deposited on both surfaces of the polished samples. The temperature and frequency dependent electrical data for all glass samples were recorded by using an impedance gain/phase analyzer (Newton’s 4th Ltd.) over a frequency range from 10 Hz to 1 MHz and in temperature range from 473 K to 673 K (Section 2.7.1).

Table 3.1 Density (\(D_g\)), molar volume (\(V_g\)), crystalline molar volume (\(V_C\)) and difference between \(V_g\) and \(V_C\) (\(\Delta V\)) for all LZBB glasses.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>(\text{Bi}_2\text{O}_3) (mol %)</th>
<th>(D_g) (g/cm(^3))</th>
<th>(V_g) (cm(^3)/mol)</th>
<th>(V_C) (cm(^3)/mol)</th>
<th>(\Delta V) (cm(^3)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LZBB 0</td>
<td>0</td>
<td>2.70</td>
<td>22.27</td>
<td>21.01</td>
<td>1.26</td>
</tr>
<tr>
<td>LZBB 1</td>
<td>10</td>
<td>3.75</td>
<td>26.59</td>
<td>23.51</td>
<td>3.08</td>
</tr>
<tr>
<td>LZBB 2</td>
<td>20</td>
<td>4.48</td>
<td>31.12</td>
<td>26.02</td>
<td>5.10</td>
</tr>
<tr>
<td>LZBB 3</td>
<td>30</td>
<td>4.97</td>
<td>35.71</td>
<td>28.52</td>
<td>7.19</td>
</tr>
<tr>
<td>LZBB 4</td>
<td>40</td>
<td>5.52</td>
<td>39.60</td>
<td>31.03</td>
<td>8.57</td>
</tr>
<tr>
<td>LZBB 5</td>
<td>50</td>
<td>5.55</td>
<td>46.52</td>
<td>33.54</td>
<td>12.98</td>
</tr>
</tbody>
</table>
Table 3.2 Physical parameters such as density \( (D_g) \), molar volume \( (V_g) \), crystalline molar volume \( (V_C) \) and difference between \( V_g \) and \( V_C \) \( (\Delta V) \) for all LCBB glasses.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>( \text{Bi}_2\text{O}_3 ) (mol %)</th>
<th>( D_g ) (g.cm(^{-3}))</th>
<th>( V_g ) (cm(^3) mol(^{-1}))</th>
<th>( V_C ) (cm(^3) mol(^{-1}))</th>
<th>( \Delta V ) (cm(^3) mol(^{-1}))</th>
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</thead>
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<tr>
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<td>3.02</td>
<td>22.96</td>
<td>21.77</td>
<td>1.19</td>
</tr>
<tr>
<td>LCBB 1</td>
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<td>4.04</td>
<td>27.01</td>
<td>24.30</td>
<td>2.71</td>
</tr>
<tr>
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<td>4.63</td>
<td>32.10</td>
<td>26.81</td>
<td>5.29</td>
</tr>
<tr>
<td>LCBB 3</td>
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<td>5.62</td>
<td>33.24</td>
<td>29.32</td>
<td>3.92</td>
</tr>
<tr>
<td>LCBB 4</td>
<td>40</td>
<td>6.22</td>
<td>36.67</td>
<td>31.82</td>
<td>4.85</td>
</tr>
<tr>
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<td>49.47</td>
<td>34.33</td>
<td>15.14</td>
</tr>
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**X-Ray Diffraction Analysis**

The X-ray diffraction pattern gives valuable information about the nature and structure of the sample. The XRD traces for both the LZBB and LCBB systems were taken at room temperature and are shown in Fig. 3.1 and Fig. 3.2, respectively and found that all samples have similar trends. They exhibit a large broad hump around 2\( \theta \) = 20\(^0\) to 35\(^0\) rather than sharp structural peak which confirm the non-crystalline nature of the sample.

**FTIR Spectroscopy Analysis**

0\( \text{Li}_2\text{O} \cdot 2\text{ZnO} \cdot x\text{Bi}_2\text{O}_3 \cdot (50-x)\text{B}_2\text{O}_3 \) (LZBB) glasses

IR vibrations are mainly active in the mid of infrared spectrum region (450-2000 cm\(^{-1}\)), therefore, Fig. 3.3 depicts the IR transmission spectra in this range for all the LZBB glasses. As can be seen from Fig. 3.3 that the IR spectra of the studied glasses exhibit a sharp peak centered at 707 cm\(^{-1}\), attributed to the symmetrical bending vibration of B-O-B bond in [BO\(_3\)] \([20-22]\). With increase of Bi\(_2\)O\(_3\) content, this band is shifted towards higher wavenumber and this large shift may be due to influence of the electrostatic field associated with the strongly polarizing Bi\(^{3+}\) ions.
[13]. Within the low wavenumber region, a more prominent band around 543 cm$^{-1}$ ($x > 0$ mol%) assigned to the vibration of Bi-O bonds in the highly distorted [BiO$_6$] pyramidal units [13, 23, 24] was observed, and shifted towards lower wave number with increase in Bi$_2$O$_3$ content. The red shift in this band can be attributed to decrease of the degree of distortion [25]. Dimitriev and Mihalova [26] have also attributed the shift in band around 482-520 cm$^{-1}$ to the variation in the local symmetry of highly distorted in [BiO$_6$] polyhedra. From IR spectra, it is also observed that for $x < 30$ mol%, the intensity of band at 516-543 cm$^{-1}$ increases due to increase of non-bridging oxygen (NBO) ions with Bi$_2$O$_3$ content. In the region $30 \leq x \leq 40$ mol%, the intensity of this band decreases which may result in the increase of bridging oxygen atoms in the glass network. When Bi$_2$O$_3$ content exceed 40 mol %, the contribution of NBOs in the glass network again increases. The IR band observed at 1020 cm$^{-1}$ attributes the B-O stretching vibration in [BO$_4$] units from tri-, tetra-, and penta borate groups [21, 27] while the band observed at 1384 cm$^{-1}$ attributes the B-O stretching vibration of [BO$_3$] units in metataborate, pyroborate and orthoborate groups [28]. When increasing the Bi$_2$O$_3$:B$_2$O$_3$ ratio a systematical change in both bands at 1384 cm$^{-1}$ and at 1020 cm$^{-1}$ is observed. This systematical change in these bands can be explain in three ways; firstly, with increase of Bi$_2$O$_3$:B$_2$O$_3$ ratio the intensity of
band observed at 1020 cm$^{-1}$ increases whilst the intensity of band at 1384 cm$^{-1}$ decreases. This result indicates that the addition of Bi$_2$O$_3$ in borate glasses leads to progressive conversion of sp$^2$ planar triangular [BO$_3$] units into more stable sp$^3$ tetrahedral [BO$_4$] units and formation of non-bridging oxygens [29]. Secondly, the relative area for both bands increases with raising Bi$_2$O$_3$ content up to a particular value of Bi$_2$O$_3$. Thirdly, with increase of Bi$_2$O$_3$:B$_2$O$_3$ ratio the frequency of [BO$_3$] units is rapidly shifted from 1384 cm$^{-1}$ to 1305 cm$^{-1}$. Boulous and Kreide [30] had reported that the broad band observed at 1300 cm$^{-1}$ attributes the vibration of boron-oxygen rings composed by [BO$_3$] and [BO$_4$] units. Therefore it may be assumed that boron-oxygen rings are formed in LZBB glasses by the connection of bridge oxygen ions between [BO$_3$] and [BO$_4$] tetrahedrons can be made, due to the decreasing intensity of the stretching vibration of B-O-B bond. Further addition of Bi$_2$O$_3$ content
i.e. for LZBB 5 sample, the band observed at 1384 cm\(^{-1}\) is completely disappeared. A red shift in band at 1020 cm\(^{-1}\) with increase of Bi\(_2\)O\(_3\):B\(_2\)O\(_3\) ratio, upto x ≤ 40 mol\%, is connected with the formation of B-O-Bi bridging bonds in the glass structure. Since the stretching force constant of Bi-O bonding is extensively lower than that of the B-O, the stretching frequency of B-O-Bi might tend to be lower [13]. From the studies of Raman spectroscopy, Inue et al. [31] revealed that the band around at 920 cm\(^{-1}\) is mainly attributed to asymmetric stretching anion motion in B-O-Bi and B-O-Zn bonds. Some authors have observed the band in the wavenumber range 890-926 cm\(^{-1}\) and assigned to symmetrical stretching vibration of Bi-O bond in [BiO\(_3\)] polyhedral [23, 32, 33]. Thus at x = 40 mol% composition the band near 915 cm\(^{-1}\) may compose of three bands but most of the intensity comes from stretching vibration of Bi-O bond in [BiO\(_3\)] polyhedral. As mentioned in DSC studies (below), the formation of second glass transition temperature may be due to the presence of network forming units as [BiO\(_3\)] in the glass structure. The IR band around 1200-1400 cm\(^{-1}\) is accompanied by a shoulder centered around 1274 cm\(^{-1}\), assigned to B-O stretching vibration of (BO\(_3\))\(^-\) unit in the meta and orthoborates as well as to vibration of boroxol rings [29, 34]. It is seen from Fig. 3.3 that as the content of Bi\(_2\)O\(_3\) increases this shoulder becomes more prominent and is converted into a band. At x = 40 mol% composition the intensity of this band becomes equal to intensity of IR band at 1305 cm\(^{-1}\). In the light of above discussion, it can be concluded that in the concentration ranges 0 ≤ x ≤ 30 mol\%, Bi\(^{3+}\) ions occupy the octahedral positions and for x > 30 mol% concentration it take up octahedral as well as pyramidal positions.

0Li\(_2\)O-20CdO-xBi\(_2\)O\(_3\)-(50-x)B\(_2\)O\(_3\) (LCBB) glasses

The FTIR spectra of the LCBB glasses have been recorded in the spectral range 450-4000 cm\(^{-1}\) to identify the structural units and type of bonds present in the glass and are shown in Fig. 3.4. The host glass has exhibited the four absorption bands in the wavelength range 1250-1500 cm\(^{-1}\), 800-1200 cm\(^{-1}\), 650-750 cm\(^{-1}\) and 450-600 cm\(^{-1}\) centered at 1392 cm\(^{-1}\), 992 cm\(^{-1}\), 707 cm\(^{-1}\) and 477 cm\(^{-1}\) respectively, along with a shoulder around 1278 cm\(^{-1}\). On the addition of heavy metal ions such as Bi\(_2\)O\(_3\) in the base glass, the intensity as well as position of observed bands changes which can be briefly explained in below:

In the present study, the absorption band observed at 1392 cm\(^{-1}\) is attributed to the B-O stretching vibration of [BO\(_3\)] units in meta-, pyro- and ortho-borates [28]. From
Fig. 3.4 IR transmission spectra at RT for all the LCBB glasses (in MIR region).

Fig. 3.4, it can be seen that with increase in bismuth content, the intensity of band at 1392 cm\(^{-1}\) decreases and it shifts towards lower wavenumber. However, at higher Bi\(_2\)O\(_3\) content (x = 30 and 40 mol%), the frequency of [BO\(_3\)] units is sharply shifted from 1351 cm\(^{-1}\) to 1281 cm\(^{-1}\). Boulous and Kreide [30] observed a broad band at 1300 cm\(^{-1}\) and attributed it to the vibration of B-O rings composed by [BO\(_3\)] and [BO\(_4\)] units. As a result, it may be supposed that B-O rings are formed in the glasses by the association of bridging oxygen ions between [BO\(_3\)] and [BO\(_4\)] tetrahedrons. The IR band observed at 1392 cm\(^{-1}\) is completely disappeared on further substitution of Bi\(_2\)O\(_3\) content i.e. for LCBB 5 sample. Additionally, in the high frequency region (1250-1500 cm\(^{-1}\)) a shoulder around 1274 cm\(^{-1}\) attributes the B-O stretching vibration of (BO\(^3\))\(^-\) unit in the meta- and ortho-borates as well as to vibration of boroxol rings.
From Fig. 3.4 it is observed that with increase of Bi$_2$O$_3$:B$_2$O$_3$ ratio this shoulder becomes more prominent and is converted into a band. In the mid-infrared region, the FTIR spectra of the titled glasses depicts another broad and strong band centered at 992 cm$^{-1}$, assigned to the B-O stretching vibration in [BO$_3$] units from tri-, tetra-, and penta borate groups [21, 27]. Further, with increase of bismuth content the intensities of [BO$_4$] group stretching vibrational frequencies (800-1200 cm$^{-1}$) increases whilst the intensity of band at 1392 cm$^{-1}$ represent [BO$_3$] group decreases which suggests that the addition of heavy metal ion in borate glasses leads to progressive conversion of sp$^2$ planar triangular [BO$_3$] units into more stable sp$^3$ tetrahedral [BO$_4$] units and formation of non-bridging oxygens [29]. As the Bi$_2$O$_3$ content is increased, upto x \( \leq 40 \) mol%, a red shift in band at 992 cm$^{-1}$ is observed which causes the formation of B-O-Bi bridging bonds in the glass structure.

Moreover, the band lying in between 890 and 926 cm$^{-1}$ attributes to symmetrical stretching vibration of Bi-O bond in [BiO$_3$] polyhedral as reported by various authors [23, 32, 33]. Thus, for x = 30 to 40 mol%, the band near 899 cm$^{-1}$ may compose of two bands one is stretching vibration B-O bond in [BO$_4$] units and another is symmetrical stretching vibration of Bi-O bond in [BiO$_3$] units. But the most of intensity comes from stretching vibration of Bi-O bond in [BiO$_3$] polyhedral, also supported by the DSC result. The infrared band situated at 707 cm$^{-1}$ is attributed to the bending vibrations of B-O-B linkages in the borate network [8, 21]. From the figure it is observed that the band lying in between 650 and 750 cm$^{-1}$ shifts towards higher wavenumber with the increase in Bi$_2$O$_3$ content. The blue shift in this band may be due to effect of the electrostatic field associated with the strongly polarizing Bi$^{3+}$ ions [13]. Within the low wavenumber region, a more prominent band, ascribed to the combined vibration of tetrahedral [CdO$_4$] [35] units and the Bi-O-Bi vibration of distorted [BiO$_6$] octahedral units [8, 34] was observed. As can be seen from Fig. 3.4 that with increase in Bi$_2$O$_3$ content (x \( \leq 40 \) mol%) the intensity of band observed around 450 - 600 cm$^{-1}$ increases due to increase of non-bridging oxygen ions and after that it decreases (for x = 50 mol%). A red shift in this band was also observed which attributes the decrease of the degree of distortion [10]. Dimitriev and Mihalova [26] have also ascribed the shift in band from 482 to 520 cm$^{-1}$ to the variation in the local symmetry of highly distorted in [BiO$_6$] polyhedra. From the above discussion, it can be assumed that for x < 30 mol%, Bi$^{3+}$ ions occupy the octahedral positions and for x \( \geq 30 \) mol% concentration it take up octahedral as well as pyramidal positions.
Density and Molar Volume

$0\text{Li}_2\text{O} \cdot 20\text{ZnO} \cdot x\text{Bi}_2\text{O}_3 \cdot (50-x)\text{B}_2\text{O}_3$ (LZBB) glasses

Density is a powerful tool to examine the changes occurring in the glass structure. The density is affected by the structural softening/compactness, change in geometrical configuration, cross-link density, co-ordination number and dimension of interstitial spaces of the glass. The compositional variation of density ($D_g$) and molar volume ($V_g$) of glasses are shown in Fig. 3.5 and their corresponding values are given in Table 3.1. It is seen from the table that $D_g$ increases with an increase in Bi$_2$O$_3$ content. This is an expected result and is due to high relative molecular mass of Bi$_2$O$_3$ (465.98 a.m.u.) as compared to B$_2$O$_3$ (69.62 a.m.u.). A keen observation of these variations show that $D_g$ increases with increase in Bi$_2$O$_3$:B$_2$O$_3$ ratio but the rate of

![Graph showing composition variation of density ($D_g$), molar volume ($V_g$) and hypothetical crystalline volume ($V_C$) and inset: difference between $V_g$ and $V_C$ ($\Delta V$) of LZBB glasses. (The solids lines are guide to eye)](image)

**Fig. 3.5** Composition variation of density ($D_g$), molar volume ($V_g$) and hypothetical crystalline volume ($V_C$) and *inset*: difference between $V_g$ and $V_C$ ($\Delta V$) of LZBB glasses. (The solids lines are guide to eye)
increase is linearly reduced when Bi₂O₃ reaches 40 mol%. For Bi₂O₃ > 40 mol% the increase in density remains negligible small. This anomalous behavior of density around x = 40 mol % suggests that a peculiar change occur in the structure of these glasses. A linear increase in Vₕ with increase in Bi₂O₃ content is mainly attributed to the larger atomic radii and bond length of Bi₂O₃ compared to those of B₂O₃ and thus results in the extension of free volume [27]. Again a close investigation of Fig. 3.5 reveals that there is a slight departure from linear increase in Vₕ around x = 40 mol% which supports the formation of different structural groups at this composition. A similar type of variation is reported by Sindhu et.al [2]. The corresponding molar volume for their crystalline phase, (Vₖ) is also calculated (Table 3.1) simply by adding molar volumes of crystalline Li₂O (14.84 cm³), ZnO (14.52 cm³), Bi₂O₃ (52.36 cm³) and B₂O₃ (27.30 cm³) in the molar ratio. Vₖ is found to increase continuously with Bi₂O₃ content (Fig. 3.5). The higher values of Vₕ than Vₖ reveal the presence of excess structural volume in the glasses. Also ΔV (Vₕ-Vₖ) increases continuously with increase in Bi₂O₃ content in the glass (see inset of Fig. 3.5).

0Li₂O·20CdO·xBi₂O₃·(50-x)B₂O₃ (LCBB) glasses

The compositional variation of the physical properties, for instance, density (D₈) and molar volume (Vₕ) of all LCBB glasses under study are shown in Fig. 3.6 and their values are listed in Table 3.2. It is obvious that D₈ and Vₕ values increases with increase in Bi₂O₃ content. The increase in density on introduction of bismuth oxide (Fig. 3.6) is an expected result and can be related to the replacement of the Bi₂O₃ (atomic mass 465.95) with B₂O₃ (atomic mass 69.62). This can be also explained in terms of the structural changes. Shelby observes that the boron atoms are directly involved in the densification process [36]. The addition of Bi₂O₃ in the glass network can cause compaction of B₂O₃ by breaking the bond between trigonal elements allowing the formation of tetrahedral [BO₄] units (according to IR results). The [BO₄] tetrahedral structural units are strongly bonded than [BO₃] trigonal structural units and thus a compact structure of the glass network is formed, leading to higher density. A further increase in Bi₂O₃ concentration (> 40 mol%) observes a sharp decrease in D₈ which may be related to the absence of [BO₄] structural units in the more flexible structure of bismuth oxygen polyhedral, [BiOₙ] and hence evidence an anomalous decrease in D₈ on substitution of Bi₂O₃ in the present glass system. The glass molar volume behavior (Fig. 3.6) reveals that addition of Bi₂O₃ content leads to expand the
structure of the rigid network of the base glass 30Li2O·20CdO·50B2O3. This may be due to the largest value of ionic radii and bond length of bismuth oxide compared to that of borate oxide results in the formation of excess free volume, which increases the overall molar volume of these glasses [27]. Further, a remarkable note is seen from Fig. 3.6 that $V_g$ increases with increase in $\text{Bi}_2\text{O}_3$ : $\text{B}_2\text{O}_3$ ratio but the rate of increase is linearly reduced when $\text{Bi}_2\text{O}_3$ reaches 30 mol%. For $\text{Bi}_2\text{O}_3 = 30$ to 40 mol%, a slight increase in $V_g$ is observed. Further substitution of $\text{Bi}_2\text{O}_3$ (> 40 mol%) in the glass matrix gives a sharp increase in molar volume. Thus the anomalous behavior of both molar volume and density around $x = 30$ mol% and $x = 40$ mol%, respectively suggests a peculiar change occur in the structure of the glass. The corresponding molar volume of the hypothetic mixture of the component crystalline oxides ($V_C$) is also evaluated (Table 3.2). It is observed from Fig. 3.6 that the molar volume ($V_g$) of the glasses is higher than that of their hypothetical mixed crystalline phases ($V_C$),
indicating the presence of excess structural volume. Again a close investigation of Fig. 3.6 (insert) reveals that for $\text{Bi}_2\text{O}_3 = 30$ and $40 \text{ mol}\%$, the $\Delta V$ variations show departure from linear increase. This may be due to the fact that the substitution of $\text{Bi}_2\text{O}_3$ content in the host glass reduces excess structural volume. These consequences are significant when one considers the transport properties, mainly conductivity, which is associated to the free volume available within the glass matrix for the motion of the charge carrier ions [37].

**Differential Scanning Calorimetry**

0$\text{Li}_2\text{O} \cdot 2\text{ZnO} \cdot x\text{Bi}_2\text{O}_3 \cdot (50-x)\text{B}_2\text{O}_3$ (LZBB) glasses

The information regarding glass network structure and crystalline behavior of LZBB glasses is obtained from DSC curves. Thermal parameters such as glass transition temperature ($T_g$), melting temperature ($T_m$) etc. for all samples are determined from the DSC curves (Fig. 3.7). It can be seen from Fig. 3.7 that the glass sample LZBB 4 possessed two glass transition temperatures marked as $T_{g1}$ and $T_{g2}$ and also has two melting temperatures ($T_{m1}$ and $T_{m2}$) whilst other glasses exhibited a single glass transition and melting temperatures (Table 3.3). The formation of two glassy states for $x = 40 \text{ mol}\%$ glass sample suggested that with increase in $\text{Bi}_2\text{O}_3: \text{B}_2\text{O}_3$ ratio the amorphous glass might have separated in two amorphous phases. One phase may be rich with borate [38] and other phase may be rich with bismuthate. From DSC curves, it is also observed that the two glassy state of LZBB 4 glass has followed two exothermic peaks, at $T_{p1} = 727$ K and $T_{p2} = 746$ K, which might be attributed to the formation of some crystalline phase. In addition, the presence of exothermic peaks for high $\text{Bi}_2\text{O}_3$ content ($= 40 \text{ mol}\%$ ) may indicate a two stage phase separation of modifier cations, as reported in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3$ glass system with increase in $\text{Bi}_2\text{O}_3$ at constant modifier [8]. This result may be attributed to the high coordination number of $\text{Bi}^{3+}$ and the tendency of $\text{BiO}_6$ polyhedra to corner and edge sharing which prevents the formation of a continuous random network of tetrahedral complexes and hence leads to a phase separation. Further, LZBB 5 glass has exhibited three exothermic peaks which can be related to the presence of more crystalline phases in it. The compositional variation of $T_g$ shown in Inset of Fig. 3.7 represents a negative deviation from linearity when the conventional glass former ($\text{B}_2\text{O}_3$) is successfully substituted by the unconventional glass former ($\text{Bi}_2\text{O}_3$). The observed non-linear
behavior (inset of Fig. 3.7) in glass transition temperature is more pronounced at a particular value of Bi$_2$O$_3$ (40 mol%) which can be attributed to mixed glass former effect (MGFE) in these glasses. Recently, Christensen et al. have examined the glass transition temperature of mixed glass former glasses and observed a positive non-linear change in T$_g$ that could cause or contribute to the mixed glass former effect [39]. Further it has been reported that Bi$_2$O$_3$ does not simply act as network modifying oxide but also acts as a network forming oxide [10, 40]. Thus the observed minima in T$_g$ for Bi$_2$O$_3$:B$_2$O$_3$ = 4:1 reveals that the role of Bi$_2$O$_3$ in the studied glasses is changed from the network modifying (below 40 mol%) to network forming oxide (above

\[\begin{array}{c}
\text{Fig. 3.7 DSC curves for all LZBB glasses showing characteristics temperatures such as glass transition temperature, exothermic peak and melting temperature are marked on the plot. The inset shows the variation of T}_g\text{ with Bi}_2\text{O}_3\text{ content.}
\end{array}\]
Table 3.3 Thermal parameters of \(30\text{Li}_2\text{O}\cdot20\text{ZnO}\cdot\text{xBi}_2\text{O}_3\cdot(50-\text{x})\text{B}_2\text{O}_3\) glasses \((0 \leq \text{x} \leq 50 \text{ mol\%})\).

<table>
<thead>
<tr>
<th>Glass Code</th>
<th>(T_{g1}) (K)</th>
<th>(T_{g2}) (K)</th>
<th>(T_{p1}) (K)</th>
<th>(T_{p2}) (K)</th>
<th>(T_{p3}) (K)</th>
<th>(T_{m1}) (K)</th>
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<td>--</td>
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<td>--</td>
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</table>

40 mol\% when borate oxide was completely replaced by bismuth oxide keeping constant modifier (also supported by the FTIR analysis). On the other hand, it has been reported that the glass transition temperature is strictly related to the density of cross-linking, the tightness of packing in the network etc. [41]. Therefore, an overall decrease in \(T_g\) with increase of \(\text{Bi}_2\text{O}_3\) content (up to 40 mol\%) is due to decrease in density of cross linking of the bismuth network. The replacement of strong B-O-B cross-linkage by the weak Bi-O-Bi cross-linkage forms a looser macromolecular structure which requires smaller internal energy for the chain mobility and hence reduces the glass transition temperature [10].

The stability of glass has been estimated by calculating the glass stability factor (\(\Delta T\)) and the Hruby’s parameter (\(K_g\)) using Eqns. (1.4) and (1.5) for LZBB 4 and LZBB 5 glass samples (Table 3.3). From the Table 3.3, it is also found that the value of \(\Delta T\) and \(K_g\) for LZBB 4 glass is larger than for LZBB 5 glass sample which reveals the higher stability of LZBB 4 glass.

**0\text{Li}_2\text{O}\cdot20\text{CdO}\cdot\text{xBi}_2\text{O}_3\cdot(50-\text{x})\text{B}_2\text{O}_3\) (LCBB) glasses**

The DSC thermo-grams of the investigated glasses obtained at heating rate 10 K/min are shown in Fig. 3.8. DSC thermo-grams depict the three characteristic temperatures, viz., glass transition temperature \((T_g)\), crystalline peak temperature \((T_p)\) and melting
Fig. 3.8 DSC curves for all LCBB glasses indicating the characteristic temperatures such as glass transition temperature, exothermic peak and melting temperature. **Inset:** The compositional variation of $T_g$.

temperature ($T_m$). It is observed from Fig. 3.8 that for LCBB 4 sample a single endothermic peak (corresponding to $T_g$) followed by three exothermic peaks (manifest crystallization) and two melting peaks. However, the endothermic peak for all other LCBB glasses exhibits a single melting temperature. The value of these characteristic temperatures; $T_g$, $T_{p1}$, $T_{p2}$, $T_{p3}$, $T_{m1}$ and $T_{m2}$ (depending upon compositions) are indicated in Table 3.4. Inset of Fig. 3.8 demonstrates the variation of $T_g$ with Bi$_2$O$_3$ content in the glass matrix. A negative slope of $T_g$ with Bi$_2$O$_3$ content upto 30 mol% suggests the modifying role of Bi$_2$O$_3$ on the glass network, through the disturbed B-O bond present in the glasses. This result is in consonance with the IR studies (mentioned above), i.e. transformation from [BO$_3$] units to [BO$_4$] units, due to which NBO’s atoms increase in the glass network. Further, it is well known that Bi$^{3+}$ ion is
highly polarizing because of its large ionic radius, small cation field strength and a lone pair in the valence shell. The electronic shell of the oxygen ions is influenced by the high polarization of Bi$^{3+}$ [1], therefore the concentration of NBO’s increases when the Bi$_2$O$_3$ content is increased [42]. This increase in turn made the glass network loose and a loose network structure acquires smaller internal energy for the chain mobility, hence the glass transition temperature decreases. A further substitution of heavy metal oxide in the host glass (> 30 mol%) indicates that bismuth does not simply act as network modifier but also acts as a network former. Thus, the observed minima in $T_g$ suggests that bismuth oxide plays dual role in the studied glasses at a particular composition. This finding is also supported by the FTIR results. In LCBB glasses, the value of $\Delta T$ for LCBB 4 glass sample is 85 K (Table 3.4) which reflects the higher stability of glass.

Table 3.4 Thermal parameters such as glass transition temperature $T_g$, crystallization peak temperatures $T_{p1}$, $T_{p2}$, $T_{p3}$ and melting temperatures $T_{m1}$, $T_{m2}$, thermal stability ($\Delta T$) and glass forming ability ($K_g$) for LCBB glasses at heating rate 10K/min.

<table>
<thead>
<tr>
<th>Glass Code</th>
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<th>$T_{p2}$ (K)</th>
<th>$T_{p3}$ (K)</th>
<th>$T_{m1}$ (K)</th>
<th>$T_{m2}$ (K)</th>
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Optical Absorption Analysis

30Li$_2$O·20ZnO·xBi$_2$O$_3$·(50-x)B$_2$O$_3$ (LZBB) glasses

Fig. 3.9 shows the optical transmission spectra for all the studied lithium zinc bismuth borate glasses. A distinct cutoff ($\lambda_c$) has been observed for all samples which strongly
depends on Bi$_2$O$_3$ content and varies from 316 nm to 436 nm (Table 3.5). The red shift in $\lambda_c$ suggests that the concentration of NBO in the glass matrix increase with Bi$_2$O$_3$ content. Further, it is clearly seen from Fig. 3.9 that these glasses have a wide transmission region in the wavelength range from 0.5 $\mu$m to 2.2 $\mu$m thus making them useful candidate in IR transmission window. From the figure, it is also observed that LZBB 4 sample has a large and stable transmission region than other LZBB samples, which reveals its large stability. The optical band gap of the samples was calculated by using the optical absorption method. The fundamental absorption refers to band to band transitions and it manifests itself by a fast increase in the absorption applied to evaluate the optical band gap. Fig. 3.10 illustrates the optical absorption spectra for LZBB glasses at various composition of Bi$_2$O$_3$. From the figure it is observed that optical absorption edge is not sharply defined and suggests the amorphous nature of the present glasses. The optical absorption coefficient, $\alpha(\nu)$ was determined at various wavelength using Eq. (1.14) for all samples. For amorphous materials, the indirect transitions i.e. $n = 2$ and $n = 3$ (Section 1.7) are valid according to the Tauc's relations [43]. The Tauc's plots for $n = 2$ and $n = 3$ are shown in Fig. 3.11(a) and Fig. 3.11(b), respectively. The value of $E_g$ can be estimated using Eq. (1.15) by extrapolating the linear region of the curves to zero absorbance i.e. $[\alpha(\nu)h\nu]^{1/2} = 0$ and $[\alpha(\nu)h\nu]^{1/3} = 0$ for $n = 2$ and 3, respectively [32] (Table 3.5). The compositional variation of $E_g$ for the two types of transitions (for $n = 2$, $n = 3$) is shown separately in Fig. 3.12 and is found to decrease with increasing Bi$_2$O$_3$ content. These variations in $E_g$ values on addition of Bi$_2$O$_3$ content can be understood in terms of structural changes occurring in the studied glasses and supports the increase in NBO ions. These non-bridging oxygen ions participate to valence band maximum (VBM). When a metal oxygen bond is broken, the bond energy is released and the non-bonding orbitals have higher energies than the bonding orbitals [44]. This suggests that the increase in concentration of NBO ions results in shifting of VBM to higher energies and thus decreases the optical band gap [32]. Further it is also reported that at a particular Bi$_2$O$_3$:B$_2$O$_3$ ration ($x = 40$ mol%) the band gap becomes constant. This may be due to the change of the role of Bi$_2$O$_3$ from modifier to a glass former (as reported in IR studies) which leads to a small decrease in number of non-bridging oxygen ions and thus band gap becomes constant. The values of 'B' calculated from the linear portion of the Tauc's plot for $n = 2$ and $n = 3$ are also included in Table 3.5. These values lie between 17.25 and 36.70 (cm eV)$^{-1}$ and between 5.64 and 10.79 (cm eV$^2$)$^{-1}$ for $n = 2$, 3.
respectively. The values of $\Delta E$ are obtained for all the LZBB glasses from the reciprocal of the slope [45] of $\ln \alpha(\nu)$ vs. $\hbar \nu$ plot (Fig. 3.13). Since $\Delta E$ measure the width of localized states within the optical band gap, therefore the large $\Delta E$ reveals that defects are maximum and reducing the long range order. For the present glass systems, the value of $\Delta E$ varies from 0.14 eV to 0.24 eV (Table 3.5). The small value of $\Delta E$ reveals that the exponential tail for these glasses arises because of phonon-
assisted indirect electronic transitions between localized states [32, 46]. Referring to Table 3.5, it is obtained that the glasses with higher Bi$_2$O$_3$ contents have low value of Urbach’s energy which suggests the possibility of long range order locally arising from the minimum in the defects concentration as compared to other compositions [46]. It is also observed that LZBB 4 glass with lowest $\Delta E$ value is found to have higher glass stability. This interpretation is also supported by the large value of glass
stability factor from DSC analysis. The theoretical optical basicity, $\Lambda_{th}$ for the present glass system has been estimated using the Eq. (1.18). Here the values of $\Lambda_{Li_2O} = 0.87$, $\Lambda_{ZnO} = 1.03$, $\Lambda_{Bi_2O_3} = 1.19$ and $\Lambda_{B_2O_3} = 0.43$ are taken from the literature [47]. The calculated values of $\Lambda_{th}$ are presented in Table 3.5. The optical basicity expresses the basicity of a glass in terms of electron density carried by oxygen and it represents the state of oxide (II) species after the tightening of their electron clouds by constituent cations [2]. From Table 3.5, it has been established that the theoretical optical basicity ($\Lambda_{th}$) increases with increase in Bi$_2$O$_3$ content. This increase may be understood by the relation given by Duffy et al. [48]. According to the Eq. (1.19), the optical basicity increases with increase in oxide ion polarizability. Zhao et al. [49] reported that Bi$^{3+}$ cation possess a very high polarizability (above3Å$^3$), which is due to its large ionic radii and small cation unit field strength. Moreover, Bi$^{3+}$ ions have a lone pair in valence shell. Therefore, with increase in Bi$_2$O$_3$ content in the present glass system, the number of NBOs and oxide ion polarizability increases and also increases the optical basicity. This interpretation is also supported by decrease in optical band gap.

Table 3.5 Cutoff wavelength ($\lambda_c$), indirect optical band gap ($E_g$), band tailing parameter (B), Urbach’s energy ($\Delta E$) and theoretical optical basicity ($\Lambda_{th}$) for 30Li$_2$O·20ZnO·xBi$_2$O$_3$·(50-x)B$_2$O$_3$ (LZBB) glasses.

<table>
<thead>
<tr>
<th>Glass Code</th>
<th>$\lambda_c$ (nm)</th>
<th>$E_g$ (eV)</th>
<th>B (cm eV$^{-1}$)</th>
<th>$E_g$ (eV)</th>
<th>B (cm eV$^2$)$^{-1}$</th>
<th>$\Delta E$ (eV)</th>
<th>$\Lambda_{th}$</th>
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<td>n = 3</td>
<td></td>
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</tr>
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<td>0.18</td>
<td>0.79</td>
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The study of the optical absorption spectra, which involve the transfer of an electron from the glass network to the metal ions, provides important information about the band structure and energy gap in the amorphous materials. The UV-Vis-NIR spectra for all LCBB glasses are shown in Fig. 3.14. The absence of sharp edges in the optical absorption spectra (Fig. 3.14) of the present glass system is clear indication of glassy natures of the samples. The cut off wavelength $\lambda_g$ for LCBB 0 glass is observed at 324 nm and is red shifted to 450 nm (Table 3.6) with an increase of Bi$_2$O$_3$ concentration in the glass network. The red shifts in $\lambda_g$ is attributed to the structural
changes occurring as a result of the different site occupations i.e. interstitial or substitution of the Bi$^{3+}$ ions, which add to the lithium cadmium borate matrix and modify the network [6]. Using the Eq. (1.14), the optical absorption coefficient, $\alpha(\nu)$ was estimated at various wavelength for all samples. The Tauc’s plots for indirect allowed and forbidden transitions are shown in Figs. 3.15 and 3.16, respectively. The values of $E_g$ for $n = 2$ and $3$ were determined from the Tauc’s relation (Eq. (1.15)) by extrapolating the linear region of the curves for $(\alpha h \nu)^{1/2} = 0$ and $(\alpha h \nu)^{1/3} = 0$ as shown in Fig. 3.15 and 3.16 and presented in Table 3.6. The values of „B” calculated from the linear region of the portion of the Tauc’s plot for $n = 2$ and $3$ are also included in Table 3.6 for the studied glasses. It is clear from the Table 3.6 that optical band energy becomes smaller with increasing amount of Bi$_2$O$_3$ content. Since Bi$^{3+}$ ions are highly polarizing cation, it affects the electronic shell of O$^{2-}$ ions. Introduction of Bi$^{3+}$ cation in the glass matrix gives a progressive transformation of [BO$_3$] groups into [BO$_4$], which creates appearance of non-bridging oxygens (NBO) in the glass network [2]. The shifting of energy gap to lower energies can be due to the formation of NBOs. Moreover, the negative charge on non-bridging oxygens has greater significance than bridging oxygens. When the ionicity of oxygen atoms is increased by converting them from bridging to non-bridging, then the top of valence

\[ \text{Fig. 3.14 Optical absorption spectra at RT for all LCBB glasses.} \]
band is raised resulting in reduced energy gap [50]. It is well reported in the literature that the substitution of heavy metals like bismuth in glass composition decreases the optical band gap [2, 34]. Fig. 3.17 shows the optical transmission spectra for lithium zinc bismuth silicate glasses. A sharp cutoff has been observed for all LCBB glass samples. Also a wide transmission in the wavelength range from 0.5 \( \mu \text{m} \) to 2.15 \( \mu \text{m} \)
makes them suitable for IR transmission window. The Urbach tailing of the absorption coefficient $\alpha(\nu)$ is described by the Eq. (1.16) (according to Urbach’s Rule [45]). The materials which have large value of $\Delta E$ would have greater tendency to convert weak bonds into defects. It is well known that at the absorption edge, the broadening of the excitation levels is dominated by the random internal electric fields due to the lack of long range order or presence of defects [51]. The calculated value of $\Delta E$ varies from 0.13 eV to 0.22 eV (Table 3.6). From the table, it is obtained that the glasses with higher Bi$_2$O$_3$ contents have low value of Urbach’s energy which suggests the possibility of long range order locally arising from the minimum in the defects concentration as compared to other compositions. It is also observed that LCBB 4 glass with lowest $\Delta E$ value is found to have higher stability than other glasses. The theoretical optical basicity, $\Lambda_{th}$ for all LCBB glasses has been calculated using basicities assigned to the individual oxides on the basis of Eq. (1.18). The values of $\Lambda_{th}$ thus obtained are presented in Table 3.6. From the table it is observed that $\Lambda_{th}$ increases when bismuth oxide with lower field strength and more ionic character is replaced by borate oxide with higher field and with smaller ionic radii. Such high optical basicity means high ability of the oxide ions to transfer electrons to the surrounding cations [49].

<table>
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<tr>
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<th>$B$ (cm eV$^{-1}$)</th>
<th>$E_g$ (eV)</th>
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Table 3.6 Cutoff wavelength ($\lambda_c$), indirect optical band gap ($E_g$), band tailing parameter (B), Urbach’s energy ($\Delta E$) and theoretical optical basicity ($\Lambda_{th}$) for 30Li$_2$O·20CdO·xBi$_2$O$_3$·(50-x)B$_2$O$_3$ (LCBB) glasses.
3.8 Impedance Spectroscopy

3.8.1 30Li₂O·20ZnO·xBi₂O₅·(50-x)B₂O₃ (LZBB) glasses

Impedance spectroscopy is a well-known method for assessing the migration of charge carrier ions in solids like-glasses. Nyquist plots, (Im (Z) vs. Re (Z), Z being impedance of sample) commonly represent the experimental data and are mostly semicircles or semicircle arcs. A single semicircle for LZBB 4 glass sample at different temperatures observed (Fig. 3.19) is related to bulk effects, which is characteristic for electronic conductors [52]. Figure 3.19 also depicts that the centre of each semicircle is depressed below real axis and the intercept on real axis shifts towards origin with increase in temperatures. This reveals that the associated relaxation of ions is non-Debye in nature [53]. As the temperature increases the radius of semi-circular arc, corresponding to the bulk resistance of the glass samples reduces, suggesting that the migration of charge carrier ions is thermally stimulated. Similar results have been observed in all other studied glasses.

The dc conductivity ($\sigma_{dc}$) was calculated using the geometrical dimensions. The value of $\sigma_{dc}$ increases with increase in temperature (Fig. 3.20) and obeys Arrhenius relation (Section 1.8.2). The activation energy ($E_{dc}$) for the conduction process was extracted from the least square fitting of plots shown in Fig. 3.20. The values of $\sigma_{dc}$ (at 633 K) and $E_{dc}$ are presented in Table 3.7. It is observed that the dc conductivity decreases with increase in Bi₂O₅:B₂O₃ ratio (upto x ≤ 30 mol%). This may be attributed to the
Fig. 3.19 Experimental Nyquist plots for LZBB 4 glass sample at different temperatures.

Fig. 3.20 Reciprocal temperature dependence of dc conductivity ($\sigma_{dc}$) at different composition. Inset: The compositional variation of $E_{dc}$ with Bi$_2$O$_3$ (mol%).
large difference in size of the two ions (B, Bi) which increases the stability and therefore decreases the mobility of charge carrier ion in the glass matrix. Rani et al. [54] have investigated the electrical conductivity of Li$_2$O-Fe$_2$O$_3$-Bi$_2$O$_3$-B$_2$O$_3$ glasses in the temperature range of 513 K-623 K and reported that the decrease in conductivity with increase in Fe$_2$O$_3$ content mainly arise due to blocking effect of iron ions on the overall mobility of lithium ions. Also, Sindhu et al. [2] have reported an analogous effect for decrease in conductivity when Bi$_2$O$_3$ content was increased up to 30 mol%. Similar argument was considered by El-Desoky for ternary glass system [55]. Thus, we can say that Bi$_2$O$_3$ shows a “blocking effect” on the overall mobility of the ions and as a result of this, upto $x \leq 30$ mol%, the conduction mechanism is mainly due to migration of the mobile ions (Li$^+$ ions). Further $\sigma_{dc}$ marginally varies and becomes almost constant for $x > 30$ mol% (Table 3.7). The inset of Fig. 3.20 depicts the non-linear variation of the activation energy with composition. The activation energy exhibits two maxima (Fig. 3.20-inset); first maximum corresponds to the substitution of one ion, whilst the second maximum is observed for Bi$_2$O$_3$:B$_2$O$_3$ ratio (4:1). The second maximum is more prominent than the first one, which suggests the presence of mixed glass former effect in these glasses. The mixed glass former effect with two maxima in $E_{dc}$ was also reported in ZnO-Bi$_2$O$_3$-Li$_2$O-B$_2$O$_3$ glasses [9].

(a) Electric Modulus Analysis

The electric modulus approach was invoked to explain the electrical transport mechanism in LZBB glasses. The electric modulus provides an unconventional approach to perceive the phenomenon such as electrode polarization and bulk conductivity properties in terms of conductivity relaxation times ($\tau$). The complex electric modulus corresponds to relaxation of electric field in the system when the electric displacement is constant as described in detail in Section 1.8.3 (a). The imaginary part of the electric modulus ($M''$) is symptomatic of the energy loss under electric field. The degree of correlation between ions in ionic transport can be well understood by knowing the value of $\beta$ the stretching coefficient. The $\beta$ parameter has been calculated using full width at half maxima value of $M''$ peak and is found to vary from 0.80 to 0.86 (Table 3.7) for different glass samples. The nearly constant value of $\beta$ for a single composition has also been reported by K. Majhi [56]. Figure 3.21 shows the frequency dependence of real ($M'$) and imaginary ($M''$) part of electric modulus at
Fig. 3.21 Frequency dependence of the real ($M'$) and imaginary ($M''$) parts of modulus isotherms for LZBB 4 glass at various temperatures. Inset (a) and (b): Normalized plots of real ($M'$) and imaginary ($M''$) electrical modulus against normalized frequency for LZBB 4 glass at same temperatures as shown in Fig. 3.21.
Fig. 3.22 Inverse temperature dependence of relaxation time ($\tau_M$) for all the LZBB glasses
(Solid lines represent the linear fittings)

different temperatures for LZBB 4 glass sample. In this case, the real part of electric modulus $M'(\omega)$ exhibits very small values at lower frequencies baring the ease of migration of conducting ions. As the frequency is increased, $M'(\omega)$ shows a dispersion tending to $M_\infty$ at higher frequencies. The imaginary part of electric modulus, $M''(\omega)$ (Fig. 3.21) show an asymmetric maximum at the dispersion region of $M'(\omega)$. The electrode polarization effects can be avoided since the electrical modulus peak, $M''_{\text{max}}(\omega)$, shifts to higher frequency. The $M''(\omega)$ plots show a maximum at a characteristic frequency, known as relaxation frequency, $f_M$. Fig. 3.21 describes two relaxation regions: the low frequency side of $M''_{\text{max}}(\omega)$ represents the range of frequencies in which charge carriers are mobile over long distances and associated with hopping conduction. The high frequency side of the $M''_{\text{max}}(\omega)$ represents the range of frequencies in which the charge carriers are spatially confined to their potential wells, being mobile over short range distances and associated with the relaxation polarization processes [57]. Thus, the peak frequency $f_M$ is an indication of the transition from long range to short range mobility. Qualitatively similar types of variation of $M'$ and $M''$ vs. frequency are observed for other presently studied glasses. The relaxation time can be evaluated from $f_M$ ($=1/2\pi \tau_M$) and it satisfied Arrhenius law as shown in Fig. 3.22. The values of $\tau_M$ at 633 K for all the glasses are presented.
Table 3.7 Dc and ac conductivity ($\sigma_{dc}$, $\sigma_{ac}$), activation energy for dc conduction ($E_{dc}$) and relaxation ($E_{M''}$), power law exponent ($s$), stretched exponential parameter ($\beta$) and relaxation time ($\tau_{M''}$) for 30Li$_2$O·20ZnO·xBi$_2$O$_3$·(50-x)B$_2$O$_3$ glasses ($0 \leq x \leq 50$ mol%).

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$\sigma_{dc}$ (at 633K) (S m$^{-1}$)</th>
<th>$E_{dc}$ (eV)</th>
<th>$\sigma_{ac}$ (at 633K, 10kHz) (S m$^{-1}$)</th>
<th>$E_{M''}$ (eV)</th>
<th>$s$ (at 633K)</th>
<th>$\beta$</th>
<th>$\tau_{M''}$ (at 633K) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LZBB 0</td>
<td>0.99 x 10$^{-2}$</td>
<td>0.84</td>
<td>1.17 x 10$^{-2}$</td>
<td>0.87</td>
<td>0.01</td>
<td>0.85</td>
<td>1.30 x 10$^{-6}$</td>
</tr>
<tr>
<td>LZBB 1</td>
<td>1.43 x 10$^{-3}$</td>
<td>1.09</td>
<td>1.48 x 10$^{-3}$</td>
<td>1.09</td>
<td>0.03</td>
<td>0.83</td>
<td>4.67 x 10$^{-6}$</td>
</tr>
<tr>
<td>LZBB 2</td>
<td>2.70 x 10$^{-4}$</td>
<td>1.29</td>
<td>2.86 x 10$^{-4}$</td>
<td>1.29</td>
<td>0.18</td>
<td>0.83</td>
<td>7.44 x 10$^{-5}$</td>
</tr>
<tr>
<td>LZBB 3</td>
<td>8.07 x 10$^{-5}$</td>
<td>1.28</td>
<td>8.39 x 10$^{-5}$</td>
<td>1.27</td>
<td>0.30</td>
<td>0.86</td>
<td>1.41 x 10$^{-4}$</td>
</tr>
<tr>
<td>LZBB 4</td>
<td>7.14 x 10$^{-5}$</td>
<td>1.42</td>
<td>8.40 x 10$^{-5}$</td>
<td>1.43</td>
<td>0.31</td>
<td>0.80</td>
<td>1.41 x 10$^{-4}$</td>
</tr>
<tr>
<td>LZBB 5</td>
<td>3.00 x 10$^{-5}$</td>
<td>1.30</td>
<td>4.38 x 10$^{-5}$</td>
<td>1.30</td>
<td>0.50</td>
<td>0.83</td>
<td>5.06 x 10$^{-4}$</td>
</tr>
</tbody>
</table>
in Table 3.7. The activation energy for relaxation process \( (E_{M''}) \) has been determined from the slope of the plots between \( \log f_{M'} \) vs. \( 1000/T \) (Fig. 3.22). The values of conduction energy and the relaxation energy for each glass compositions are nearly equal which indicates that the charge carrier ions have to overcome the same energy barrier during conduction as well as relaxation [46, 58]. Fig. 3.21(inset (a and b)) shows the normalized plots of modulus isotherm for LZBB 4 sample, where the frequency axis is scaled by peak frequency \( f_{M''} \), \( M' \) axis is scaled by \( M' \) (inset (a)) and \( M'' \) axis is scaled by \( M''_{\text{max}} \) (inset (b)). The perfect overlapping of all the curves on a single 'master curve' for all temperatures reveals that the conductivity relaxation occurring at different frequencies exhibit temperature independent dynamical processes [46].

(b) Conductivity Formalism

The ac conductivity of all samples is assessed from real and imaginary parts of the impedance data computed at various temperatures in the frequency range from 10 Hz to 1 MHz. Fig. 3.23 shows the frequency dependence of total conductivity, \( \log \sigma(\omega) \) at various temperatures for LZBB 4 glass sample. The phenomenon of the conductivity dispersion in solids is generally described using power law (Section 1.8.3 (b) - Eq. (1.28)). It is evident from Fig. 3.23 that the frequency dependence of conductivity in studied frequency window shows two distinct regimes: (i) the low frequency plateau regime corresponding to frequency independent conductivity, \( \sigma_{\text{dc}} \), and (ii) high frequency dispersion region. The changeover from the frequency independent region to frequency-dependent region is the signature of the onset of conductivity relaxation and it is shifted to higher frequency as the temperature increases. In the present glasses constant Li$^+$ ions concentration is mainly responsible for the conduction processes. The dispersion behavior in conductivity is assigned to the microscopic nature of inhomogeneities with the distribution of relaxation processes through distribution of energy barriers in the glass [59]. The values of \( \sigma_{\text{ac}} \) (at 633 K, 10 kHz) for all the samples are also given in Table 3.7. Deviation from linear variation with composition in conductivity parameters further confirms the anomalous behavior of the LZBB 4 sample. The values of dimensionless frequency exponent \( s' \) are obtained from the slope of \( \log \sigma_{\text{ac}} \) vs. \( \log f \) in high frequency region and are listed in Table 3.7. It is observed that the exponent
Fig. 3.23 Frequency dependence of the conductivity, $\sigma (\omega)$, at various temperatures for LZBB 4 glass. Inset: The normalized conductivity isotherms for LZBB 4 glass at the various temperatures.

The parameter “s” decreases with increase in temperature and is significantly lower than unity. The values are also found to be material dependent (Table 3.7) and the glasses with lower Bi$_2$O$_3$ content have lower “s” values. After applying the scaling law as described by Eq. (1.29), all the ac conductivity spectra obtained at different temperatures collapse into a single master curve, as shown in Fig. 3.23 (insert) and suggest temperature independent relaxation behavior. Similar scaling behavior was observed for other LZBB glasses.

3.7.2 30Li$_2$O·20CdO·xBi$_2$O$_3$·(50-x)B$_2$O$_3$ (LCBB) glasses

Fig. 3.24 illustrates the complex impedance plots for 30Li$_2$ 20CdO 30Bi$_2$O$_3$·20B$_2$O$_3$ glass sample at various temperatures. It is observed that at low temperatures, these plots (inset Fig. 3.24) exhibit a single arc and when the temperature of the sample is
increased this arc becomes a slightly depressed semicircle. This is because of the migration of ions in the glass matrix and also due to the distribution of relaxation times [60]. Again, the study of the impedance plots show that the intercept of depressed semicircle on real axis (Fig. 3.24) is shifted to higher frequencies as the temperature increases and gives the value of bulk resistance offered by the sample at various temperatures. Also, the centre of observed depressed semicircle is situated below the real impedance axis, revealing a non-Debye relaxation behavior of ions. Fig. 3.25 exhibits the reciprocal temperature dependence of dc conductivity, $\sigma_{dc}$ which was calculated using the sample dimensions and the resistance obtained from the intercept on the real axis. The temperature variation of $\sigma_{dc}$ obeys an Arrhenius law which is characteristic of thermally activated transport (Fig. 3.25) as described by the Eq. (1.21). The activation energy for dc conduction ($E_{dc}$) is determined from the linear fitting of Arrhenius plots (Fig. 3.25) for all glass samples under study. The values of $\sigma_{dc}$ at 593 K and $E_{dc}$ for different compositions are given in Table 3.8. The variation of $\sigma_{dc}$ with composition (Table 3.8) shows a decrease in conductivity values when

![Fig. 3.24 Complex impedance plots (experimentally) for LCBB 3 glass sample at different temperatures.](image)
going from ternary Li$_2$O·CdO·B$_2$O$_3$ glass (x = 0 mol%) to quaternary Li$_2$O·CdO·Bi$_2$O$_3$·B$_2$O$_3$ glass by replacing B$_2$O$_3$ with Bi$_2$O$_3$ up to x = 20 mol%. However, the conductivity values marginally vary and become almost constant in the composition range $30 \leq x \leq 40$ mol% and thereafter it again decreases when the glass system is changed from quaternary to ternary i.e. at x = 50 mol%. The decreasing behavior of $\sigma_{dc}$ at lower Bi$_2$O$_3$ content reveals the blocking effect of bismuth on the mobility of Li$^+$ ion. The blocking effect of Bi$^{3+}$ ions was also reported by Sindhu et al. [2]. The constancy in dc conductivity around x = 30 and 40 mol% may indicate that on the addition of Bi$_2$O$_3$ content in the glass matrix, no more structural changes is formed due to which conduction mechanism arises i.e. it does not provide any more open channel to the mobility of charge carrier ions. Further, at higher Bi$_2$O$_3$ content, x = 50 mol%, bismuth oxide may take the network modifying positions in the glass matrix because of the formation of bridging oxygen atoms and hence decreases the dc conductivity (also supported by the DSC results obtained at higher bismuth concentration). Again, from Table 3.8, $E_{dc}$ value shows a minima at x = 30 mol%. Singh [8] also reported the same results for the series Li$_2$O·B$_2$O$_3$·Bi$_2$O$_3$ keeping constant lithium concentration and suggested the mixed glass former effect.

![Fig. 3.25 Arrhenius plots of dc conductivity ($\sigma_{dc}$) for all the LCBB glasses (Solid lines represent the linear fittings).](image-url)
(a) Electric Modulus Analysis

In the present glasses, the relaxation of charge carrier can be understood by invoking the electric modulus analysis. The electric modulus approach is particularly valuable in the absence of well-defined loss peaks and its depiction is governed by the capacitive elements. Further, the physical nature of the complex electric modulus is used to make a correlation between the conductivity and the relaxation of charge carriers in the prepared glasses [61]. The frequency dependence of electric modulus defined in Section 1.8.3(a) at several temperatures is displayed in Fig. 3.26 for a particular composition i.e. 30Li2O 20CdO 30Bi2O3·20B2O3 glass sample. It is clearly noted from the figure that the real part of electric modulus, \(M'(\omega)\), at lower frequencies shows very small values (almost zero), informative the ease of migration of charge carriers. Moreover, as the frequency of the electric field increases, \(M'(\omega)\) value shows a dispersion tending to \(M_{\infty}\), the high-frequency asymptotic value of \(M'(\omega)\), (Fig. 3.26). This is because of immobilization of the charge carrier ions into the glass structure in the high frequency region which makes the glass stiffer and thus \(M'(\omega)\) goes to \(M_{\infty}\) [61]. The imaginary part of electric modulus, \(M''(\omega)\), indicative of the energy loss under the electric field, show a maximum peak at frequency \(f_{M''}\) centered at the dispersion region of \(M'(\omega)\) (Fig. 3.26). The peak \(= M'_{\text{max}}(\omega)\) shifts towards higher frequencies as the temperature increases, which suggests suppression of the electrode polarization in the investigated glasses. Again, the investigations of modulus isotherms in Fig. 3.26 show that within the measured frequency window two relaxation regions appeared about \(M'(\omega)\) peak as already described earlier. The peak frequency \(f_{M'}\) is a suggestive of the transition from long range to short range mobility.

Similar types of variation of electric modulus are obtained for other glass samples under study. Fig. 3.27 shows the reciprocal temperature dependence of the most probable relaxation time, \(\tau_{M'}\) provided by the relation \(f_{M'} = 1/2\pi \tau_{M'}\), and their values at 593 K for different glass compositions are listed in Table 3.8. The relaxation time \(\tau_{M'}\) for all compositions (Fig. 3.27) follows the Arrhenius law represented by \(\tau_{M'} = \tau_0 \exp(E_{M'}/kT)\), where \(E_{M'}\) is the activation energy for the electrical relaxation. The activation energy \(E_{M'}\) value (Table 3.8) for the conductivity relaxation time has been obtained from the linear fits of the data in Fig. 3.27 and found to be very close to the value of activation energy of dc conductivity for each glass composition, suggesting
Fig. 3.26 The real ($M'$) and imaginary ($M''$) electric modulus spectra as a function of frequency for 30Li$_2$O·20CdO·30Bi$_2$O$_3·20$B$_2$O$_3$ glass at several temperatures.

The charge carrier ions overcome the same energy barrier while conducting as well as when relaxing. Further, the electric modulus could be expressed in terms of the stretched exponential function, $\phi(t)$ given by Eq. (1.26) which measures the evolution of electric field within the materials, is usually taken as the Kohlrausch-Williams-Watts (KWW) function represented by $\phi(t)$:

$\phi(t) = A e^{-(t/\tau)^\beta}$

where $\beta$ is the Kohlrausch stretched coefficient and tends to one for Debye type relaxation i.e. a completely uncorrelated motion of mobile ions. In addition, $\beta$ describes the degree of correlation between ions in ionic transport and also notifies about the non-exponential character of the relaxation [63]. The value of stretched exponential parameter $\beta$ obtained from $M'$ vs. frequency curves is found to be almost constant (Table 3.8) for different glass samples. Furthermore, Ngai [62] has proposed a relation between the power-law exponent and the non-exponential parameter given by $s = 1 - \beta$. However, for the present glasses, this relation is not satisfied. The
normalized plots of modulus isotherm for LCBB 3 sample is displayed in Fig. 3.28, where the frequency axis is scaled by peak frequency $f_M$ and $M^*\ (M''\ \text{axis is scaled by } M_\infty\ (M_{\text{max}}))$. The exact merge of all curves/peaks into a single 'master curve' for all temperatures reveals temperature independent behavior of dynamical processes [64]. Similar behavior was observed for other investigated glasses. Fig. 3.29 illustrates the normalized $M''$ versus the scaled frequency curves for all prepared compositions under study at 593 K. From the figure, it is found that the $M^*$ scaled curves for all compositions almost merge into each other, which also suggests the composition independent nature of dynamical processes. The superimposability of the scaling plot of $M^*/M^*_{\text{max}}\ \text{vs. } \log (f/f_M)$ also supports the temperature as well as composition independent nature of $\beta$.

(b) Conductivity Formalism

The frequency dependence of ac conductivity for all LCBB glasses at different temperatures has been studied through the real part of ac conductivity. Fig. 3.30 displays the frequency dependent conductivity spectra of LCBB 3 glass at various temperatures and the same behavior is observed for all other glass samples. It is obvious from Fig. 3.30(a) that at lower frequency the conductivity remains constant.

![Fig. 3.27 Arrhenius plots of relaxation time ($\tau_{M''}$) for all the LCBB glasses (Solid lines represent the linear fittings)](image)
Fig. 3.28 Variation of $M'/M_\infty$ and $M''/M''_{\max}$ with $\log (f/f_{M''})$ for LCBB 3 glass.

Fig. 3.29 Normalized plots of electrical modulus against normalized frequency for all LCBB compositions at 623 K.
Fig. 3.30(a) Frequency dependent conductivity spectra (experimental) for LCBB 3 glass sample at various temperatures. Inset: Variation of $s$ factor with the Bi$_2$O$_3$ content. Fig. 3.30(b) The normalized conductivity isotherms for LCBB 3 glass at the same temperature as shown in Fig. 3.30(a).

and as the frequency is increased, it shows dispersion. The low frequency constant region, reflects the dc conductivity, may be assigned to the long-range transport of mobile lithium ions in response to the applied electric field, where only successful diffusion contributes to dc conductivity, $\sigma_{dc}$. The changeover from the frequency independent dc region to higher frequency region is the sign of the onset of the
Table 3.8 Dc and ac conductivity ($\sigma_{dc}$, $\sigma_{ac}$), activation energy for dc conduction ($E_{dc}$) and relaxation ($E_{M''}$), power law exponent ($s$), stretched exponential parameter ($\beta$) and relaxation time ($\tau_{M''}$) for all LCBB glasses ($0 \leq x \leq 50$ mol%).

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$\sigma_{dc}$ (at 593 K) (S m$^{-1}$)</th>
<th>$E_{dc}$ (eV)</th>
<th>$\sigma_{ac}$ (at 593 K, 11 kHz) (S m$^{-1}$)</th>
<th>$E_{M''}$ (eV)</th>
<th>$\beta$ (at 593 K)</th>
<th>$s$ (at 593 K)</th>
<th>$\tau_{M''}$ (at 593 K) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCBB 0</td>
<td>$2.12 \times 10^{-3}$</td>
<td>0.95</td>
<td>$2.25 \times 10^{-3}$</td>
<td>0.99</td>
<td>0.83</td>
<td>0.04</td>
<td>$5.77 \times 10^{-6}$</td>
</tr>
<tr>
<td>LCBB 1</td>
<td>$1.81 \times 10^{-4}$</td>
<td>1.02</td>
<td>$1.89 \times 10^{-4}$</td>
<td>1.01</td>
<td>0.83</td>
<td>0.13</td>
<td>$3.93 \times 10^{-5}$</td>
</tr>
<tr>
<td>LCBB 2</td>
<td>$5.94 \times 10^{-5}$</td>
<td>1.10</td>
<td>$6.73 \times 10^{-5}$</td>
<td>1.07</td>
<td>0.83</td>
<td>0.32</td>
<td>$1.74 \times 10^{-4}$</td>
</tr>
<tr>
<td>LCBB 3</td>
<td>$6.14 \times 10^{-5}$</td>
<td>0.81</td>
<td>$7.23 \times 10^{-5}$</td>
<td>0.77</td>
<td>0.83</td>
<td>0.29</td>
<td>$1.41 \times 10^{-4}$</td>
</tr>
<tr>
<td>LCBB 4</td>
<td>$4.50 \times 10^{-5}$</td>
<td>0.94</td>
<td>$6.08 \times 10^{-5}$</td>
<td>1.01</td>
<td>0.83</td>
<td>0.37</td>
<td>$2.16 \times 10^{-4}$</td>
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<tr>
<td>LCBB 5</td>
<td>$4.73 \times 10^{-6}$</td>
<td>1.21</td>
<td>$1.36 \times 10^{-5}$</td>
<td>1.27</td>
<td>0.83</td>
<td>0.66</td>
<td>$3.44 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
conductivity relaxation phenomena. Further, as the temperature increases the observed dispersion in conductivity shifts towards higher frequency and obeys Jonscher universal power law [65] of the form: \( \sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s \), where \( \omega \) is the angular frequency, \( A \) is the pre-exponential factor and \( s \) is the frequency exponent which varies from zero to one. Also, the exponent \( s \) is ascribed to the interaction between the charge carrier ion with the lattice. Values of parameter \( s \) are calculated from the slope of \( \log \sigma(\omega) \) vs. \( \log f \) curves at different temperature for all titled glasses and listed in Table 3.8. From the table it is found that \( s \) value is considerably smaller than unity and increases with decrease in temperature, satisfying the Correlated Barrier Height (CBH) model [66]. Further, the variation of \( s \) values with the composition is shown in inset of Fig. 3.30(a) and observed that the interaction between mobile ions increases with increase of bismuth concentration in the host glass except \( x = 30 \text{ mol\%} \). The frequency dependence may be normalized with respect to dc conductivity, and temperature by plotting \( \sigma(\omega)/\sigma_{dc} \) vs. \( f/\sigma_{dc}T \) (Fig. 3.30(b)) as described in detail in Section 1.8.3(b) The conductivity data corresponding to different temperatures are superimposable into a single master curve, evoking temperature independent relaxation behavior and which proves Summerfield scaling function. However, a little deviation is observed in high frequency dispersion region which can be neglected. Similar scaling behavior was observed for other LCBB glasses.

**Conclusions**

In the present work, 30Li2O·20ZnO·xBi2O3·(50-x)B2O3 (LZBB: with \( x = 0, 10, 20, 30, 40 \text{ and 50 mol\%} \)) and 30Li2O·20CdO·xBi2O3·(50-x)B2O3 (LCBB: with \( x = 0, 10, 20, 30, 40 \text{ and 50 mol\%} \)) glasses have been synthesized. The different structural, physical, thermal, optical and electrical properties of these glasses have been discussed. The obtained results are reported below:

**LZBB glasses**

- The presence of broad hump in XRD patterns demonstrates the glassy nature of all the samples.
- IR studies revealed that at lower Bi2O3 content (upto \( x < 40 \text{ mol\%} \)) Bi\textsuperscript{3+} cations are incorporated in the glass network as [BiO\textsubscript{6}] octahedral units and at
higher Bi$_2$O$_3$ content (for x \(\geq 40\) mol%), it enter in the glass matrix both as [BiO$_6$] octahedral units and as [BiO$_3$] pyramidal units.

- The variation in density, molar volume and difference between \(V_g\) and \(V_C\) with Bi$_2$O$_3$: B$_2$O$_3$ ratio is related to structural changes occurring in the glass.

- From the DSC analysis, at a particular Bi$_2$O$_3$: B$_2$O$_3$ (4:1) ratio the glasses exhibit two glass transition temperatures and two melting temperatures. The presence of two or three exothermic peaks at higher concentration of bismuth oxide (\(\geq 40\) mol%) may indicate two or more phase separation of modifier cations. The stability of these glasses was confirmed by measuring the glass stability factor.

- The large transmitting windows in UV-Vis-NIR region and the occurrence of sharp cutoff make these glasses promising candidate for IR transmission window. Decrease in \(E_g\) with increase in Bi$_2$O$_3$:B$_2$O$_3$ ratio confirm the increase in number of non-bridging oxygen ions. The low values of \(\Delta E\) further supports the existence of phonon assisted transitions.

- Complex impedance plots suggest the non-Debye nature of relaxing ions. The dc conductivity followed Arrhenius law and decreased with increase in Bi$_2$O$_3$ content (for x < 40 mol%) because of blocking effect. The observed minima in glass transition temperature and maximum in the activation energy reveals mixed glass former effect. The activation energies for conduction and relaxation were found to have almost similar for these glasses, which indicate that the charge carrier ions overcome the same energy barrier while conducting as well as when relaxing. The perfect overlapping of all the electric modulus curves on a single ,,master curve“ in the studied temperature range reveals that the conductivity relaxation mechanism is temperature independent.

**LCBB glasses**

- XRD analysis at room temperature is used to confirm the amorphous nature of all prepared samples.

- From FTIR analysis, it is observed that the addition of heavy metal ion in borate glasses leads to progressive conversion of sp$^2$ planar triangular [BO$_3$] units into more stable sp$^3$ tetrahedral [BO$_4$] units and formation of non-bridging oxygens. It is also observed that for x < 30 mol\%, Bi$^{3+}$ ions occupy
the octahedral positions and for $x \geq 30$ mol% concentration it takes up octahedral as well as pyramidal positions.

- The compositional dependence of $D_g$, $V_g$ and $\Delta V$ with $\text{Bi}_2\text{O}_3$:$\text{B}_2\text{O}_3$ ratio reveals the structural changes occurring in the glass matrix.

- From optical absorption studies it is observed that the optical band gap decreases with increase in $\text{Bi}_2\text{O}_3$ content. The low values of $\Delta E$ also suggested that the defects are reduced by introducing the $\text{Bi}_2\text{O}_3$ in the glass matrix.

- The temperature dependence of dc conductivity obeys an Arrhenius law which is characteristic of thermal activated transport. The decrease in $\sigma_{dc}$ at low content reflects the blocking effect of $\text{Bi}^{3+}$ ions. The observed minima in $E_{dc}$ and $T_g$ values around $x = 30$ mol% reveals the presence of mixed glass former effect in these glasses which is also supported by FTIR results. Also the compositional variation of $s$ values shows that the interaction between mobile ions increases with increase of $\text{Bi}_2\text{O}_3$ content in the host glass except at $x = 30$ mol%.

- Similar values of $E_{dc}$ and $E_M$ suggest that the charge carrier ions face the same energy barrier during conduction as well as when relaxing. The ionic relaxation was analyzed in the framework of conductivity and relaxation formalisms. The occurrence of super curve of electrical conductivity and master curve for modulus isotherms for a given composition signified the temperature independence of the dynamic processes for ions in the present glasses. The superimposing of normalized plots of electric modulus for all LCBB glasses into a single „master curve” reveals composition independent dynamical process at various frequencies, which is also supported by the almost constant value of $\beta$ for different compositions.
References