1. Introduction

Glasses based on heavy metal oxides viz., Bi₂O₃, PbO and Ga₂O₃ have wide applications in the field of glass ceramics, layers for optical and electronic devices thermal and mechanical sensors, reflecting windows, etc. [1]. Because of small field strength of Bi³⁺ ions, bismuth oxide cannot be considered as network former, however, in combination with B₂O₃, glass formation is possible in a relatively large composition range [2]. The large glass formation region in boro-bismuthate glasses has been attributed to the high polarizability of Bi³⁺ ions. This property of Bi³⁺ ions also makes the glass suitable as non-linear optical/photon material with high non-linear optical susceptibility [3]. Lithium borate glasses system have been studied extensively because of their important advantages as solid electrolytes in storage batteries. The small size, light weight and highly electro-positive character of lithium ions are considered as factors which give rise to high voltage and high energy density micro-batteries [4–7].

The study of dielectric properties, such as dielectric constant, loss factor, and ac conductivity over a wide range of frequency and temperature not only help in assessing the insulating character of the glasses but also throw some light on the structural aspects of these glasses. work along these lines was carried out in recent years on a variety of inorganic glasses by a number of researchers yielding valuable information [8–10]. The objective of the present study is therefore, to explore the structural influence of Bi₂O₃ on xBi₂O₃-(75–x) B₂O₃–25Li₂O glass system through detailed investigations on dielectric properties.

2. Experimental

The bismuth borate glasses were prepared by normal melt quenching. The starting materials used were analar (AR) grade regents of Li₂CO₃, H₃BO₃ and Bi₂O₃. The mixtures corresponding to the desired composition (see Table 1) were melted in a porcelain crucible at about 1100 °C, the fused materials were kept at melting temperature for 30 min and shaken frequently to make the mixture homogeneous. The melts were then quickly cooled at room temperature by pouring and pressing between two carbon plates. The as prepared glasses were grind and finally polished to a thickness of ≈0.2 cm. The sample was sandwiched between two copper electrodes and then fitted in designed holder connected to programmable oven with heating rate 1 °C/min. Temperature was measured using a copper — constant thermo-couple kept in perfect contact with the specimen. Measurements of dielectric constant (ε), loss tangent factor (tan δ) were carried out using (Type Hioki 3531Z Hitester programmable automatic RLC meter). The ac electrical conductivity σ ac, was obtained using the relation (σ ac = ω ε d ε' tan δ). The accuracy of both ε and tan δ was about ±3%.

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Borate glasses
ac Conductivity
CBH model

Glasses with compositions xBi₂O₃–(75–x) B₂O₃–25Li₂O with, x = 0, 5, 20, 25,30,35,40 mol % have been prepared using the normal melt quenching technique. The dielectric constant (ε) dielectric loss tangent tan δ, electric modulus behaviour was studied as a function of temperature in the frequency range 0.1–100 kHz. The detailed analysis of the results showed that the dielectric dispersion consists of both dipolar and interfacial polarization. Also the activation energy of the dielectric relaxation process from the electric modulus measurements was calculated. Measurements of the ac conductivity as a function of frequency at different temperatures indicated that the correlated barrier hopping (CBH) model is the most suitable mechanism for the ac conduction behaviour. The ac parameters, such as hopping distance (R, R min), polaron binding energy (U M) and Columbic barrier height (U b) were calculated.

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3. Results and discussion

3.1. Dielectric properties

3.1.1. Dielectric constant ($\varepsilon$)

Generally the dielectric constant of a material is determined by electronic, ionic, dipolar and space charge polarization. Out of these the space charge contribution depends on the purity and the perfection of glass samples. Its influence is in general negligible at very low temperatures and noticeable in the low frequency region. The increase in dielectric constant of the sample with increase in temperature is usually associated with the decrease in bond energies [11]. That is, as the temperature increases two effects on the dipolar polarization may occur: (i) it weakens the intermolecular forces and hence enhances the orientational vibration, (ii) it increases the thermal agitation and hence strongly disturbs the orientational vibrations. The dielectric constant becomes larger at low frequencies and at high temperatures which is normal in oxide glasses and this cannot be taken as indication for spontaneous polarization [11]. This could be due to the fact that as the frequency increases, the polarizability contribution from ionic and orientation sources decreases and finally disappear due to their inertia.

Fig. 1 shows the temperature dependence of the dielectric constant ($\varepsilon$) at frequencies 1, 5, 10, 15, 20, 100 kHz, for glass samples G0, G40. The temperature dependence of dielectric constant for other glass samples is represented at 1 kHz. The variation of $\varepsilon_{\text{max}}$ with Bi content is also represented in the same figure. We see that in Fig. 1 as temperature increases the dielectric constant increases and at high temperature it increases very rapidly. This behaviour is typical to the polar dielectrics in which the orientation of dipoles is facilitated with rising temperature and thereby the dielectric constant is increased. At the low temperatures, the contribution of electronic and ionic components to the total polarizability will be small. As the temperature is increased the electronic and ionic polarizabilities start to increase. The variation of $\varepsilon_{\text{max}}$ with Bi content is represented also in Fig. 1. It is seen that as Bi content increases $\varepsilon_{\text{max}}$ increases until 30 mol % then $\varepsilon_{\text{max}}$ decreases. The increase of $\varepsilon_{\text{max}}$ is due to bonding defects generated in the glass network. The defects thus produced create easy path ways for the

**Table 1**

Compositions of $x$Bi$_2$O$_3$–(75–$x$)B$_2$O$_3$–25Li$_2$O glass system.

<table>
<thead>
<tr>
<th>$x$ (mol %)</th>
<th>Glass composition</th>
<th>Glass number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75B$_2$O$_3$–25Li$_2$O</td>
<td>G0</td>
</tr>
<tr>
<td>5</td>
<td>70B$_2$O$_3$–30Li$_2$O</td>
<td>G5</td>
</tr>
<tr>
<td>20</td>
<td>55B$_2$O$_3$–45Li$_2$O</td>
<td>G20</td>
</tr>
<tr>
<td>25</td>
<td>50B$_2$O$_3$–50Li$_2$O</td>
<td>G25</td>
</tr>
<tr>
<td>30</td>
<td>45B$_2$O$_3$–55Li$_2$O</td>
<td>G30</td>
</tr>
<tr>
<td>35</td>
<td>40B$_2$O$_3$–60Li$_2$O</td>
<td>G35</td>
</tr>
<tr>
<td>40</td>
<td>35B$_2$O$_3$–65Li$_2$O</td>
<td>G40</td>
</tr>
</tbody>
</table>

Fig. 1. Variation of $\varepsilon$ with temperature for xBi$_2$O$_3$–(75–$x$)B$_2$O$_3$–25Li$_2$O glass system, and variation of $\varepsilon_{\text{max}}$ with Bi content.
migration of charges that would build up space charge polarization and facilitate to an increase in the dielectric parameters [12–14]. The decrease of $\varepsilon_{\text{max}}$ after 30 wt.% Bi can be attributed to the hindering effect for electronic motion (Fig. 2).

Fig. 2 shows the behaviour of dielectric constant of glass samples in the frequency range 0.1–100 kHz at some selected temperatures. The change in $\varepsilon$ is significant at low frequencies for all samples. The decrease in $\varepsilon$ with frequency for the investigated samples may be attributed mainly to the decreasing number of dipoles which contribute to polarization.

3.1.2. Dielectric loss tangent and electric modulus

The dielectric loss factor is the phase difference due to the loss of energy within the sample at a particular frequency and is expressed as $\tan \delta (\varepsilon''/\varepsilon')$. The contribution to the dielectric loss is mainly attributed to thermally activated relaxation of freely rotating dipoles where thermal energy is the only type of relaxation and at higher temperatures it is due to electrical conduction with hopping motion of ions. The variation of dielectric loss with temperature is represented in Fig. 3 for all glass samples at 1 kHz. From Fig. 3 the dielectric loss has exhibited distinct maxima.
The increase in the content of B$_2$O$_3$ form non-bridging oxygens (NBOs) and expanded (opened up) the structure of the tightly network of glass system. The larger values in the radii and the bond length of B$_2$O$_3$ than that of the B$_2$O$_3$ results in the formation of excess free volume, which increases the overall molar volume of these glasses [15]. This will facilitate the rotation of dipoles and consequently higher values of dielectric loss (tan δ). In the case of G30, G40 samples the dielectric constant decreases and this leads to decrease of dielectric loss, in case of G35 sample the increase of conductivity values leads to increase of dielectric loss [14]. This relaxation can be dielectric relaxation to confirm this we studied the electric modulus formalism ($M''(\omega)$).

This formalism is notably suitable to detect electrode polarization phenomena and bulk effects as average conductivity relaxation [16]. For sake of brevity we represented $M''$ for G20 sample only as shown in Fig. 4. $M''(\omega)$ exhibits low value at low frequencies which may be due to large value of capacitance associated with electrodes”(w) plots show asymmetric maxima at the dispersion region of $\epsilon''(w)$ .The maximum ($=M''_{\text{max}}$) shifts to higher frequency with increase of temperature, which suggests the effect of electrode polarization can be avoided. The peak frequency corresponding to $M''_{\text{max}}$ is known as relaxation frequency $f_m$ when $f < f_m$ the charge carriers are mobile over large distance and are associated with the hopping conductivity. For $f > f_m$ the carriers are spatially confined to their potential wells, being mobile over short distances and associated with the relaxation polarization process [17].Thus the peak frequency $f_m$ is indication of transition from long range to short range mobility and is defined by the condition $2\pi f_m \tau_m = 1$ where $\tau_m$ is the relaxation time .The asymmetric $M''$ peak originates from the nature of relaxation behaviour. This non-Debye behaviour of the $M''$ spectrum can be associated to the distribution of relaxation times .The amorphous nature of glasses and hence a distribution of mobile ion sites having different environments is thought to be the cause for the non-Debye peak.

The relaxation process can be modeled by Arrhenius temperature dependence as following:

$$ f_m = f_0 e^{-\frac{W}{kT}}, $$

where $f_0$ is the relaxation frequency at which $M''$ is maximum, $W$ is effective activation energy for relaxation and $f_c$ is the constant parameter characteristic for particular relaxation. The shift in the frequency of the loss peak is represented in Fig. 7 as a function of reciprocal temperature for all glass samples. The data were fitted to a straight line whose slope is the activation energy. The activation energies are 0.146, 0.09, 0.092, 0.093, 0.07, 0.092, 0.04 eV for Go, G5, G20, G25, G30, G35 and G40 respectively.

Boron and bismuth are known to have more than one stable configuration, i.e., boron triangles and tetra borate for boron and bismuth pyramidal and octahedral units for bismuth, respectively [18]. Therefore increasing of B$_2$O$_3$ content, creates, more NBO. These factors besides the weaker bond strength of Bi–O (80.3 kcal mol$^{-1}$) compared to the bond strength of B–O (192.7 kcal mol$^{-1}$), and Li–O (333.5 kcal mol$^{-1}$) will affect the physical properties.

### 3.2. ac Conductivity ($\sigma_{ac}$)

Fig. 5 shows the frequency dependence of $\sigma_{ac}(w)$ at different temperatures for the glass samples. As can be seen, each curve displays the conductivity dispersion, which is strongly dependent on frequency at room temperature and show weaker frequency dependence at higher temperatures. The ac conductivity is a monotonically increasing function of frequency. This type of behaviour reveals that the mechanism responsible for ac conduction could be hopping one .It is found to be consistent with that observed in many hopping systems [19] .In general, the ac conductivity as a function of frequency can be represented over many decades by Almond-West type power law of the form:

$$ \sigma_{ac}(\omega) = A\omega^{s}, $$

where $A$ is temperature dependent constant and $s$ is a material and temperature dependent power law exponent [20]. At low frequencies, random distribution of the ionic charge carriers via activated hopping gives rise to a frequency-independent conductivity while at higher frequencies, conductivity exhibits dispersion which increases roughly in a power law fashion and eventually becomes almost linear at even higher frequencies [20]. The changeover of the conductivity is shifted toward higher frequencies with increase in temperature because mobile ions acquire more thermal energy and cross the barrier more easily. The values of the exponent $s$ were derived by calculating the slopes of the curves in Fig. 5.

Fig. 6 illustrates the variation of the exponent $s$ with temperature for different glass compositions .It is observed that the exponent $s$ decreases with increasing temperature and its value is less than unity i.e. $0 < s < 1$. Parameter $s$ is associated with the modification of network structure and its smaller value signifies higher degree of modification [21]. Accordingly these results lead to the prediction that the correlated barrier hopping (CBH) is the most suitable mechanism to explain the ac conduction behaviour in the considered system [22,23]. In the CBH model [24] the exponent $s$ was found to obey the equation:

$$ S = 1 - \frac{6kT}{U_m - kT \ln\left(\frac{1}{e}\right)}, $$

where $U_m$ is the effective activation energy.
where $U_M$ is the maximum barrier height at infinite separation, which is called the “polaron binding energy”, i.e. the binding energy of the carrier in its localized sites and $\tau_0$ is a characteristic relaxation time which is in the order of an atom vibrational period $\tau_0 = 10^{-13}$ s. For neighboring sites at a separation $R$, the Coulomb wells overlap, resulting in a lowering of the effective barrier from $U_M$ to value $U_h$, which for the case of a single electron transition is given by:
Table 2
ac Conductivity parameters for xBi2O3 (75–x) B2O3 25Li2O glass system at 1 kHz and different temperatures.

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>293 K</th>
<th>323 K</th>
<th>333 K</th>
<th>353 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R$(A)</td>
<td>$R_{min}$(A)</td>
<td>$U_{o}$(eV)</td>
<td>$U_{d}$(eV)</td>
</tr>
<tr>
<td>G0</td>
<td>4.8</td>
<td>4.7</td>
<td>1.14</td>
<td>1.51</td>
</tr>
<tr>
<td>G5</td>
<td>33.29</td>
<td>28.88</td>
<td>0.23</td>
<td>0.3</td>
</tr>
<tr>
<td>G20</td>
<td>4.56</td>
<td>4.42</td>
<td>0.95</td>
<td>1.26</td>
</tr>
<tr>
<td>G25</td>
<td>3.77</td>
<td>3.66</td>
<td>1.04</td>
<td>1.37</td>
</tr>
<tr>
<td>G30</td>
<td>4.42</td>
<td>4.26</td>
<td>1.27</td>
<td>1.68</td>
</tr>
<tr>
<td>G35</td>
<td>2.13</td>
<td>2.07</td>
<td>1.14</td>
<td>1.51</td>
</tr>
<tr>
<td>G40</td>
<td>3.05</td>
<td>2.93</td>
<td>1.44</td>
<td>1.89</td>
</tr>
</tbody>
</table>

$U_{h} = U_{M} - \frac{e^{2}}{4\pi\varepsilon_{0}\varepsilon R}$ (4)

where the hopping distance ($R$) at frequency $\omega$ is given by:

$R = \frac{e^{2}}{\varepsilon_{0}\omega^{2}(U_{M} - kT\text{ln} \left( \frac{1}{\omega R} \right))}$ (5)

For large values of $U_{M}/kT$, the exponent $s$ becomes [23]:

$S = 1 - \frac{6kT}{U_{M}}$ (6)

And the lower bound (cut-off) to hopping distance becomes:

$R_{min} = \frac{e^{2}}{4\pi\varepsilon_{0}\varepsilon U_{M}}$ (7)

Using the values of $s$ derived from Fig. 6 $U_{h}$ is calculated according to equation (6) and listed in Table 2. $U_{h}$ values are somewhat decreased with increasing the temperature. The values of $s$ and $U_{M}$ changed irregularly with glass composition. The hopping distance $R$, the lower bound (cut-off) $R_{min}$ and the Columbic barrier height $U_{h}$ are calculated using equations (4), (5) and (7), respectively. It must be remembered that the value of the relaxation time ($\tau_{0}$) at which electric modulus is maximum is used in calculation of $R$ in eq. (5). The values of ac parameters $R$, $R_{min}$ and $U_{h}$ at different temperatures are listed in Table 2 at 1 kHz. It is clear that the values of these parameters change irregularly with both temperature and glass composition. This suggests that the correlated barrier hopping mechanism depends on composition and temperature of composite matrix.

4. Conclusions
1- The dielectric dispersion is found to occur for the investigated samples in the audio frequency range.
2- The magnitude of the frequency dispersion depends on the temperature and the dielectric increment tends to become largely noticeable as temperature increases.
3- The increase of Bi$_2$O$_3$ content on the expense of B$_2$O$_3$ varies the dielectric properties of the studied glass system xBi$_2$O$_3$–(75–x) B$_2$O$_3$–25Li$_2$O.

4- The correlated barrier hopping model (CBH) is found to be the most suitable ac conduction mechanism for the investigated samples.

Ethical approval
We do our best to do good scientific work. We cooperate well to represent our selves.

References