Research Article
DSC and DC Conductivity of Bi$_2$O$_3$·LiF·B$_2$O$_3$ Glasses

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Received 17 December 2012; Accepted 3 January 2013

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Fluoroborate glasses with Bi$_2$O$_3$ content and having compositions $x$Bi$_2$O$_3$·(40–$x$)LiF·60B$_2$O$_3$ ($x = 0, 5, 10, 15$, and 20) are prepared using melt-quench technique. DSC characterization is carried out to observe glass transition temperature. Two such temperatures are observed for each of the reported samples. DC conductivity of the reported samples is studied with the variation in temperature from 313 K to 413 K by dividing this range into three regions, namely, low-, intermediate-, and high-temperature regions. DC conductivity responses for these temperature regions are explained using different conductivity models.

1. Introduction

Fluoroborate glasses have attracted the attention of researchers in the recent times due to their wide application range. LiF-B$_2$O$_3$ glasses doped with rare earth ions are used as efficient lasing materials [1]. When alkali halides are introduced into the glass structure, they exhibit their presence by changing the glass structure [2–5], which is observed with the help of a number of experimental techniques. Differential scanning calorimetry (DSC) is an important technique to study the glass forming ability of a melt which in turn depends on the cooling rate. The difference in the glass transition temperature ($T_g$) and crystallization temperature ($T_c$) indicates the stability of the glass [6]. $T_g$ depends upon the coordination number of the network forming ions of network forming atoms and the number of nonbridging oxygen atoms (NBOs) [7]. Therefore, a change in $T_g$ is always attributed to the variations occurring in the glass structure. A decrease in $T_g$ indicates the decrease in oxygen packing density and that the structure becomes loosely packed [8].

Louzguine-Luzgin et al. [9] designated the glass transition process as “dark area” in material science while investigating about double-stage glass transition in some metallic glasses. A multiphase relaxation is reported in a number of research papers. Many of them have reported two or even three crystallization temperatures. This happens due to the separation out from the matrix by crystallization [10]. Kanno [11] has reported two values of $T_g$ of an aqueous LiCl solution suggesting two different glassy phases in the quenched solution. Li et al. [12] has also reported two glass transitions in some metallic glasses. Bajaj and Khanna [13] has reported two separate phases in some crystallized bismuth borate glasses. In case of glasses containing two alkali species, mixed alkali effect has also been claimed [14] with the help of two-stage relaxation mechanism.

Basically, electrical properties of a material depend upon the nature of charge particles available for transport and their interaction with the structural heterogeneity of the material and themselves. There can be two categories of charge transport in glasses, namely, electronic and ionic. A number of investigations have been made so far to study these two-charge transport phenomenon. In some cases, it is observed that a glass can have both phenomena dominating at different physical conditions. The presence of two different kinds of ions in glass structure become responsible for electronic and ionic conductivities to dominate in different temperature ranges [15].

Shaaban [16] has recently reported charge transport properties of $(70 - x)$B$_2$O$_3$·15Bi$_2$O$_3$·15LiF·$x$Nb$_2$O$_5$ glasses. Some interesting results are obtained for the dependence of DC conductivity on temperature. According to the results
obtained, there are two models applicable in two different temperature ranges. At higher temperatures it is small-polaron hopping model (SPH) and at low temperatures it is variable-range hopping model (VRH).

In this paper we have reported two independent studies of $x\text{Bi}_2\text{O}_3 \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3$ glasses. One is the study of glass transition temperatures by DSC technique and the other is the study of temperature dependence of DC conductivity in different temperature regions.

2. Experimental Details

2.1. Glass Synthesis. Bismuth fluoroaborate glasses with compositions $x\text{Bi}_2\text{O}_3 \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3$ ($x = 0, 5, 10, 15$ and $20$) were prepared by the traditional melt-quench technique using reagent grade powders of $\text{Bi}_2\text{O}_3$, $\text{LiF}$, and $\text{H}_2\text{BO}_3$. The powdered chemicals were mixed thoroughly to obtain a uniform mixture. $\text{B}_2\text{O}_3$ was obtained by the decomposition of $\text{H}_2\text{BO}_3$ during the melting process. The powdered mixtures were melted at $1273^\circ\text{C}$ up to 30 minutes to obtain a bubble-free mixture. The melt was pressed between two carbon plates placed at room temperature. Thin pallets having a thickness nearly 1 mm each were obtained.

2.2. Differential Scanning Calorimetry (DSC). DSC characterization was carried out for the reported samples within temperature range of 199°C to 740°C using the instrument model Q600SDT of TA Instruments at a heating rate of 10°C/minute.

2.3. DC Conductivity. DC conductivity of the reported samples was examined using Keithley Electrometer (Model 617) within temperature range of 313 K to 413 K. Silver paste electrodes were deposited on both sides of well-polished sample pallets. The absence of barrier layers was confirmed by linear $I$-$V$ characteristics.

3. Results and Discussion

3.1. Differential Scanning Calorimetry. DSC thermograms for the reported samples are depicted in Figure 1. There appears two glass transition temperatures $T_{g1}$ and $T_{g2}$ for each of the samples. These transitions are relatively weak as compared to the conventional transitions reported so far. Therefore, the reported glasses may be called “soft glasses.” Values of both transition temperatures are given in Table 1. There is a continuous increase in the value of $T_{g1}$ with introduction and then increase in the concentration of $\text{Bi}_2\text{O}_3$ except for the sample with $x = 15$. The decrease in $T_{g1}$ can be attributed to the glass forming behavior of $\text{Bi}_2\text{O}_3$. It not only acts as a modifier, but also as a glass former. $\text{Bi}_2\text{O}_3$ enters in the glass matrix causing new species to be formed due to change in oxygen packing density. The new species includes $\text{BO}_3^-$ units whose formation is reported earlier [17] using FTIR spectroscopy. This process makes the structure relatively strongly packed thereby increasing the value of $T_{g1}$. On the other hand there are small changes in the values of $T_{g2}$, with increase in $\text{Bi}_2\text{O}_3$ concentration.

3.2. DC Conductivity. Temperature-dependent responses of DC conductivity for the reported samples are depicted in Figure 2. Some interesting results are obtained for the reported samples.

To start with, a transition in the nature of conduction is observed in the sample without any concentration of $\text{Bi}_2\text{O}_3$ (i.e., $x = 0$). This transition is the change in ionic conductivity to the electronic one with rise in temperature. For $x = 0$, the transition lies in the temperature range 403 K–408 K. Mentioning a range instead of a single value of temperature...
Table 1: Glass transition temperatures, temperature range for DC conductivity transition, activation energy and Log$_{10}$\(\sigma_0\) for the glasses with compositions \(x\)Bi$_2$O$_3 \cdot (40 - x)$LiF $\cdot 60$B$_2$O$_3$ \((x = 0, 5, 10, 15 \text{ and } 20)\).

<table>
<thead>
<tr>
<th>(x)</th>
<th>(T_g) (°C)</th>
<th>(T_g^2) (°C)</th>
<th>(\Delta T_{\text{tr}}) (K)</th>
<th>(W) (eV)</th>
<th>Log$_{10}$(\sigma_0) (S-cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>352</td>
<td>415</td>
<td>403–408</td>
<td>0.860</td>
<td>10.475</td>
</tr>
<tr>
<td>5</td>
<td>355</td>
<td>426</td>
<td>348–377</td>
<td>0.994</td>
<td>9.025</td>
</tr>
<tr>
<td>10</td>
<td>370</td>
<td>423</td>
<td>353–382</td>
<td>0.662</td>
<td>10.350</td>
</tr>
<tr>
<td>15</td>
<td>351</td>
<td>420</td>
<td>351–395</td>
<td>0.332</td>
<td>10.700</td>
</tr>
<tr>
<td>20</td>
<td>376</td>
<td>424</td>
<td>351–400</td>
<td>0.133</td>
<td>10.867</td>
</tr>
</tbody>
</table>

Figure 3: Variation of log$_{10}$\(\sigma\) with \(T^{-1/4}\) for glasses with compositions \(x\)Bi$_2$O$_3 \cdot (40 - x)$LiF $\cdot 60$B$_2$O$_3$ \((x = 5, 10, 15\text{, and } 20)\). for this transition is because of the results obtained for other samples with broad regions of such transitions. At low-temperature values, DC conductivity is very low. It increases with the increase in temperature. This trend is followed at low temperatures by all other samples with varied concentration of Bi$_2$O$_3$. It is interesting to note that for the sample with \(x = 5\), DC conductivity in low-temperature range is more than that for \(x = 0\) and having a small variation for all other samples. Observed variations in DC conductivity in this temperature range can be explained by considering its nature as ionic one.

With the introduction of Bi$_2$O$_3$ content into the glass composition, the structural disorder increases due to the increase in the number of NBO sites as compared with the number of such sites in the sample with \(x = 0\). Therefore, halide ions can hop from one NBO site to another, thereby increasing the ionic conductivity. There can be three simultaneous processes involved while changing the composition of the glass with increasing Bi$_2$O$_3$ content and decreasing LiF content. First one is the availability of more NBO sites which in turn should encourage the ionic transport. Second one is the decrease in the number of hopable ions available for transport due to decrease in the LiF concentration. It leads to a decrease in the ionic conductivity. Third process is the formation of BO$_2$F and B-F units reported by us earlier [17]. Formation of such units also results in the decrease in the number of hopable ions. Second and third processes compete with the first one and so a small variation in the ionic conductivity occurs with change in composition. There is a linear increase in this ionic conductivity with the increase in the temperature for a small temperature range above room temperature.

In the intermediate temperature range, the DC conductivity response deviates from that in low-temperature range with a decrease in the slopes of log$_{10}$\(\sigma\) versus 1000/\(T\) plots for all the samples except \(x = 0\). By applying VRH model to these samples over intermediate temperature ranges, one can observe the linear dependence of log$_{10}$\(\sigma\) over \(T^{-1/4}\) which approves the validity of VRH model in this intermediate range. Such plots are given in Figure 3. According to VRH model at low temperatures, the charge carriers hop from one site to another because of the dominating static disorder energy [18]. As said earlier that with increase in the Bi$_2$O$_3$ content, the number of NBOs increases, thereby increasing the static disorder energy. In VRH model, DC conductivity can be related to temperature as follows:

\[
\sigma = \sigma_0 \exp \left(-\frac{A}{T^{1/2}}\right) \quad \text{with} \quad A = 2.06 \left\{\frac{\alpha^3}{kN(E_f)}\right\}^{1/4},
\]

\[
\sigma_0 T = \left[\frac{\varepsilon^2}{2(8\pi)^{1/2}}\right] N(E_f) \frac{\varepsilon^2}{\alpha k T}^{1/2}
\]

where \(\alpha\) is the phonon frequency, \(k\) is Boltzmann’s constant, \(A\) is a constant, \(\alpha\) is the electron wave function decay constant, \(\varepsilon\) is the charge on electron, and \(N(E_f)\) is the density of states at Fermi level.

Temperature range for application of VRH model increases with the increase in the Bi$_2$O$_3$ content. This is understandable as the continuously reduced content of LiF and its formation of BO$_2$F and B-F units makes it more difficult for fluoride ions to hop due to static disorder energy only. Therefore, higher temperature triggers from \(x = 5\) to \(x = 20\) are required for conduction process to step up again. Temperature ranges \((\Delta T_{\text{tr}})\) for the transition from ionic to electronic in DC conductivity are given in Table 1.

At higher-temperature range, DC conductivity and temperature are related by the Arrhenius equation:

\[
\sigma = \sigma_0 \exp \left(-\frac{W}{k T}\right),
\]

where \(\sigma_0\) is the preexponential factor, \(k\) is Boltzmann’s constant and \(W\) is the activation energy for conduction. Values of \(W\) and log$_{10}$\(\sigma_0\) for the reported samples are calculated from

\[
\log_{10}\sigma_0 = \log_{10}\sigma_0 - \frac{W}{k T},
\]

Conclusions

Reported results include DSC and temperature-dependent DC conductivity studies of glasses with compositions \( \text{Bi}_2\text{O}_3 \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3 \) \( x = 0, 5, 10, 15, \) and \( 20 \). Two glass transition temperatures are obtained for each reported sample. \( T_g \) increases with the increase in the \( \text{Bi}_2\text{O}_3 \) content which is attributed to the strengthening of the structure caused by the \( \text{Bi}_2\text{O}_3 \) by entering the glass network and showing its glass-forming character. DC conductivity is explained on three temperature ranges: low, intermediate, and high. In low-temperature ranges, DC conductivity is ionic in nature and increases with the increase in temperature. With the increase in \( \text{Bi}_2\text{O}_3 \) content, it shows a small variation due to the increase in NBO sites and decrease in hopable ions. In the intermediate-temperature range, VRH model is applied to explain linear dependence of \( \log_{10}\sigma \) over \( T^{-1/4} \). Temperature ranges of VRH model regions are observed to increase with the increase in \( \text{Bi}_2\text{O}_3 \) content. In the higher-temperature range, DC conductivity follows the Arrhenius equation. A decrease in activation energy is observed which may be due to the glass-forming nature of \( \text{Bi}_2\text{O}_3 \) and the increase in the density of states near the mobility edge.

Acknowledgments

The financial support provided to one of the authors (S. Arora) by CSIR, New Delhi, India, is gratefully acknowledged.

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