Research Article

DSC and DC Conductivity of $\text{Bi}_2\text{O}_3 \cdot \text{LiF} \cdot \text{B}_2\text{O}_3$ Glasses

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Fluoroborate glasses with Bi_2O_3 content and having 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) 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. $\text{LiF-B}_2\text{O}_3$ 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 phenomenons 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 $(70-x)\text{B}_2\text{O}_3 \cdot 15\text{Bi}_2\text{O}_3 \cdot 15\text{LiF} \cdot x\text{Nb}_2\text{O}_5$ glasses. Some interesting results are obtained for the dependence of DC conductivity on temperature. According to the results

FIGURE 1: DSC of 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).

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 fluoroborate 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 Bi_2O_3 , LiF , and H_3BO_3 . The powdered chemicals were mixed thoroughly to obtain a uniform mixture. B_2O_3 was obtained by the decomposition of H_3BO_3 during the melting process. The powdered mixtures were melted at 1273 K 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 $10^\circ\text{C}/\text{minute}$.

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

FIGURE 2: Variation of $\log_{10}\sigma$ with $1000/T$ for 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).

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 Bi_2O_3 except for the sample with $x = 15$. The decrease in T_{g1} can be attributed to the glass forming behavior of Bi_2O_3 . It not only acts as a modifier, but also as a glass former. Bi_2O_3 enters in the glass matrix causing new species to be formed due to change in oxygen packing density. The new species includes BO_2F 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 Bi_2O_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 Bi_2O_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 $\text{Log}_{10}\sigma_0$ for the 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).

x	T_{g1} ($^{\circ}\text{C}$)	T_{g2} ($^{\circ}\text{C}$)	ΔT_{tr} (K)	W (eV)	$\text{Log}_{10}\sigma_0$ ($\text{S}\cdot\text{cm}^{-1}$)
0	352	415	403–408	0.860	10.475
5	355	426	348–377	0.994	9.025
10	370	423	353–382	0.662	10.350
15	351	420	351–395	0.332	10.700
20	376	424	351–400	0.133	10.867

FIGURE 3: Variation of $\log_{10}\sigma$ with $T^{-1/4}$ for glasses with compositions $x\text{Bi}_2\text{O}_3 \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3$ ($x = 5, 10, 15$, 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_2O_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_2O_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_2O_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_2F 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_2O_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:

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

$$\sigma_0 T = \left[\frac{e^2}{2(8\pi)^{1/2}} \right] v_{ph} \left[\frac{N(E_f)}{\alpha kT} \right]^{1/2},$$

where v_{ph} is the phonon frequency, k is Boltzmann's constant, A is a constant, α is the electron wave function decay constant, e 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_2O_3 content. This is understandable as the continuously reduced content of LiF and its formation of BO_2F 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 (ΔT_{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:

$$\sigma = \sigma_0 \exp\left(-\frac{W}{kT}\right), \quad (2)$$

where σ_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

FIGURE 4: Variation of $\log_{10}\sigma$ with Bi_2O_3 content for glasses with compositions $x\text{Bi}_2\text{O}_3 \cdot (40 - x)\text{LiF} \cdot 60\text{B}_2\text{O}_3$ ($x = 5, 10, 15$, and 20) at 323 K , 363 K , and 408 K .

the Arrhenius plots in higher-temperature ranges and are given in Table 1. These plots indicate a continuous decrease in activation energy with the stepwise replacement of LiF by Bi_2O_3 from $x = 5$ to $x = 20$. Variations in the values of W can be attributed to the fact that Bi_2O_3 preferentially occupies the substitution positions in glass network reflecting its glass forming nature in the present glass system. Also there is a change in density of states near the mobility edge due to the above mentioned compositional variation. Values of $\log_{10}\sigma$ are plotted against composition at 323 K , 363 K , and 408 K from three temperature ranges (low, intermediate, and high) in Figure 4.

4. 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_{g1} increases with the increase in the Bi_2O_3 content which is attributed to the strengthening of the structure caused by the Bi_2O_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 Bi_2O_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 Bi_2O_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 Bi_2O_3 and the increase in the density of states near the mobility edge.

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References

- [1] V. R. Kumar, N. Veeraiah, and B. A. Rao, "Optical absorption and photoluminescence properties of Pr^{3+} -doped ZnF_2 - PbO - TeO_2 glasses," *Journal of Luminescence*, vol. 75, no. 1, pp. 57–62, 1997.
- [2] S. Arora, V. Kundu, D. R. Goyal, and A. S. Maan, "Effect of stepwise replacement of LiF by Bi_2O_3 and of annealing on optical properties of $\text{LiF} \cdot \text{Bi}_2\text{O}_3$ glasses," *ISRN Optics*, vol. 2012, Article ID 193185, 7 pages, 2012.
- [3] N. Soga, "Elastic moduli and fracture toughness of glass," *Journal of Non-Crystalline Solids*, vol. 73, no. 1–3, pp. 305–313, 1985.
- [4] I. Z. Hager, "Elastic moduli of boron oxyfluoride glasses: experimental determinations and application of Makishima and Mackenzie's theory," *Journal of Materials Science*, vol. 37, no. 7, pp. 1309–1313, 2002.
- [5] I. Z. Hager and M. El-Hofy, "Investigation of spectral absorption and elastic moduli of lithium haloborate glasses," *Physica Status Solidi A*, vol. 198, no. 1, pp. 7–17, 2003.
- [6] S. Hazra, S. Mandal, and A. Ghosh, "Properties of unconventional lithium bismuthate glasses," *Physical Review B*, vol. 56, no. 13, pp. 8021–8025, 1997.
- [7] M. Subhadra and P. Kistaiah, "Effect of Bi_2O_3 content on physical and optical properties of $15\text{Li}_2\text{O} \cdot 15\text{K}_2\text{O} \cdot x\text{Bi}_2\text{O}_3 \cdot (65-x)\text{B}_2\text{O}_3$: $5\text{V}_2\text{O}_5$ glass system," *Physica B*, vol. 406, no. 8, pp. 1501–1505, 2011.
- [8] N. J. Kim, Y. H. La, S. H. Im, W. T. Han, and B. K. Ryu, "Effect of ZnO on physical and optical properties of bismuth borate glasses," *Electronic Materials Letters*, vol. 5, no. 4, pp. 209–212, 2009.
- [9] Dmitri V. Louzguine-Luzgin, I. Seki, T. Yamamoto, H. Kawaji, C. Suryanarayana, and A. Inoue, "Double-stage glass transition in a metallic glass," *Physical Review B*, vol. 81, Article ID 144202, 6 pages, 2010.
- [10] D. Tonchev, K. Koughia, S. O. Kasap et al., "Thermal stability and optical activity of erbium doped chalcogenide glasses for photonics," in *Functionalized Nanoscale Materials, Devices and Systems*, pp. 351–356, Springer Science + Business Media B.V., 2008.
- [11] H. Kanno, "Double glass transitions in aqueous lithium chloride solutions vitrified at high pressures: evidence for a liquid—liquid immiscibility," *Journal of Physical Chemistry*, vol. 91, no. 7, pp. 1967–1971, 1987.
- [12] Y. Li, S. C. Ng, Z. P. Lu, Y. P. Feng, and K. Lu, "Separation of glass transition and crystallization in metallic glasses by temperature-modulated differential scanning calorimetry," *Philosophical Magazine Letters*, vol. 78, no. 3, pp. 213–220, 1998.
- [13] A. Bajaj and A. Khanna, "Crystallization of bismuth borate glasses," *Journal of Physics*, vol. 21, Article ID 035112, 8 pages, 2009.

- [14] M. Kim, H. W. Choi, H. W. Park, C. H. Song, Y. S. Yang, and Y. H. Rim, "Crystallization process and mixed alkali effect in lithium-potassium borate glass," *Journal of the Korean Physical Society*, vol. 49, no. 2, pp. S495–S499, 2006.
- [15] V. Kundu, R. L. Dhiman, A. S. Maan, D. R. Goyal, and S. Arora, "Characterization and electrical conductivity of Vanadium doped strontium bismuth borate glasses," *Journal of Optoelectronics and Advanced Materials*, vol. 12, no. 12, pp. 2373–2379, 2010.
- [16] M. H. Shaaban, "Structure and electrical conductivity relaxation studies of Nb_2O_5 -doped B_2O_3 — Bi_2O_3 — LiF glasses," *Journal of Material Science*, vol. 47, pp. 5823–5832, 2012.
- [17] S. Arora, V. Kundu, D. R. Goyal, and A. S. Maan, "Effect of stepwise replacement of non-oxide to oxide group on structural properties of Bi_2O_3 . LiF . B_2O_3 glasses," *ISRN Spectroscopy*, vol. 2012, Article ID 896492, 5 pages, 2012.
- [18] N. F. Mott, "Conduction in non-crystalline materials: III. Localized states in a pseudogap and near extremities of conduction and valence bands," *Philosophical Magazine*, vol. 19, pp. 835–852, 1969.