Journal of Physics and Chemistry of Solids 74 (2013) 189–195

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

AC conductivity and its scaling behavior in $MgO–Li_2O–B_2O_3–Bi_2O_3$ glasses

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ARTICLE INFO

Article history:
Received 27 May 2012
Received in revised form
26 August 2012
Accepted 2 September 2012
Available online 26 September 2012

Keywords:
A. Glasses
C. Differential Scanning Calorimetry (DSC)
D. Electrical conductivity
D. Transport properties

ABSTRACT

In the present work, the compositional dependence of density, refractive index and glass transition temperature of xMgO-(25-x)$Li_2O–50B_2O_3–25Bi_2O_3$ glasses is studied. Impedance spectroscopy technique is employed on these samples and the data are analyzed using Cole–Cole type impedance response function. The AC conductivity behavior of the present glasses has been investigated in the frequency range from 100 Hz to 1 MHz and as a function of temperature the measured AC data are analyzed using the Jonscher's universal power law to explain the observed dispersive behavior of the electrical conductivity. The temperature and composition dependence scaling behavior in the AC conductivity are satisfactorily explained by scaling the AC conductivity $\sigma'(\omega)$ by hopping frequency ω_p. The frequency response of dielectric constant ε' and dielectric loss tanδ as a function of temperature were studied. The tanδ peak shifts to higher frequency with increasing temperature, indicating dipolar relaxation character of dielectric loss in the present glasses.

1. Introduction

The dispersion in AC conductivity has been seen in wide variety of disordered solids like, ion conducting glasses, amorphous semiconductors, ionic and electronic conducting polymers, organic semiconductors, non-stiochiometric or highly defective crystals, doped semi conductors, single crystals, etc. [1–5]. At low frequencies, one observes a constant conductivity while at higher frequencies the conductivity becomes strongly frequency dependent. The generality of this behavior for many widely different classes of materials was pointed out by Jonscher et al. [6].

Heavy metal oxide glasses (HMO) containing bismuth oxides have received increased interest due to their manifold possible applications [7–9]. These glasses were found to be efficient X-ray absorbers and also considered for use in scintillation detectors for high energy physics. The large polarizability and small field strength of Bi^{3+} in oxide glasses makes them suitable for optical devices such as ultra fast all-optical switches, optical isolators, optical Kerr shutter (OKS) and environmental guidelines. Despite the fact that Bi_2O_3 is not a classical glass former, in the presence of conventional glass formers (such as B_2O_3, SiO_2, etc.) it may build a glass network of $[BiO_n]$ ($n=3, 6$) pyramids [10]. Due to its dual role, as modifier with $[BiO_6]$ octahedral and as glass former with $[BiO_3]$ pyramidal units, bismuth ions may influence the electrical properties of glasses. The addition of Li, Mg, Zn, Fe oxides to these glasses [11–13] results in large glass formation domain.

The ionic conductivity and other electrical properties of some lithium-containing bismuthate glasses have been studied recently [14–16]. The introduction of alkaline earth ions in lithium bismuthate glasses may cause more open structure of the glass network and thus this is of much interest to explore the mobile ion dynamics in these glasses. Rolling et al. [17,18] have reported that the alkaline earth ions may be mobile in the presence of alkali ions. They have also concluded that the mobility of the alkaline earth ions is mainly dependent on the difference between the radii of alkali and alkaline earth ions. The smaller the difference between their radii, the higher is the mobility of the alkaline earth ions. These ions are most mobile when the ratio of their ionic radii approaches to unity.

The objective of the present study is to investigate the mixed mobile ion effect in xMgO-(25-x)$Li_2O–50B_2O_3–25Bi_2O_3$ $(0 \le x \le 25)$ glasses by measuring density, glass transition temperature, refractive index and AC conductivity from room temperature to 300 °C and in the frequency range from 100 Hz–1 MHz as a function of compositional parameter R_{Mg} defined as R_{Mg}=MgO mol%/(MgO+Li_2O) mol% which takes the values of 0, 0.2, 0.4, 0.6, 0.8 and 1.

2. Experimental

Glass samples of composition xMgO-(25-x)$Li_2O–50B_2O_3–25Bi_2O_3$ (where x=0, 5, 10, 15, 20 and 25 mol%) were prepared by conventional melt-quench technique using analytical grade Li_2CO_3, H_3BO_3, Bi_2O_3 (May and Baker) and MgO (Fluka) chemicals. The well ground mixture of chemicals in appropriate weight ratios were taken in porcelain crucible and melted in electrical

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http://dx.doi.org/10.1016/j.jpcs.2012.09.001

furnace at a constant temperature in the range 1000–1150 °C for 2 h. The liquids were agitated to ensure homogeneous mixture. In this technique, the clear liquid (free of bubbles) is quickly cast in a stainless steel mold kept at 200 °C and pressed with another steel disc maintained at the same temperature. All the glass samples were annealed at 200 °C for duration of about 12 h. For samples taken from different regions of the bulk specimen, the absence of any Bragg peaks in the X-ray diffraction pattern confirmed that they are amorphous and homogeneous.

Density (ρ) is measured at room temperature by Archimedes principle with xylene (ρ=0.86 g/cm^3) as an immersion liquid. Refractive index of the present glasses was measured using Brewster's angle method at wavelength 632.8 nm (He–Ne laser). The thermal behavior of the glass samples was investigated using a differential scanning calorimeter (TA Instruments DSC 2010). Samples in the form of powder weighing about 15 mg were sealed in copper pans and scanned from room temperature to above the exothermic peak at heating rate 10 °C/min. During all runs the sample chamber was purged with dry nitrogen.

AC conductivity measurements were carried out using AUTOLAB (PGSTAT 30) low frequency impedance analyzer interfaced to a PC using a frequency response analyzer (FRA) software. Parallel glass discs of thickness around 1.5 mm and diameter 12 mm were grounded and polished. The flat surfaces of the samples were painted with silver paste. The samples were scanned in the frequency range 100 Hz–1 MHz and in the temperature range 300–573 K.

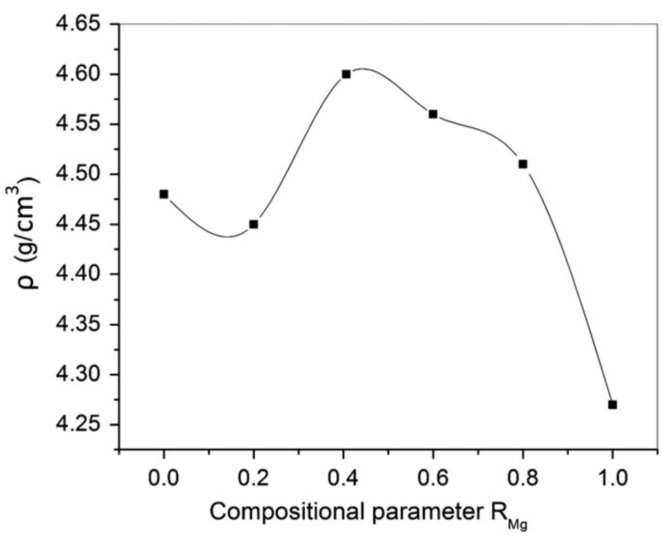

Fig. 1. Compositional dependence of density in xMgO-(25-x)Li_2O–50B_2O_3–25Bi_2O_3 glasses.

3. Results and discussion

3.1. Density, refractive index and glass transition temperature

The density data for the present xMgO-(25-x)Li_2O–50B_2O_3–25Bi_2O_3 glasses as a function of compositional parameter R_{Mg} which is defined as $R_{MgO}/(R_{MgO}+R_{Li_2O})$ is shown in Fig. 1. From the figure it is clear that the density increases and then decreases exhibiting a positive deviation, when alkali oxide is substituted by alkaline earth oxide. The maxima in density is observed at $R_{Mg}=0.4$ which is the distinct feature of the mixed alkali alkaline earth effect.

The measured densities of the present glass system along with evaluated values of molar volume, oxygen packing density, lithium ion and magnesium ion concentrations N and the average inter ionic separation $R=(1/N)^{1/3}$ of all the glasses are presented in Table 1. The molar volume and the oxygen packing density in the present glasses also vary non-linearly.

Density of glass, in general, is explained in terms of a competition between the masses and sizes of the various structural groups present in glass. Accordingly, density is related to how tightly the ions and ionic groups are packed together in the substructure. In mixed alkali or alkali-alkaline earth glass systems density may exhibit either positive or negative deviation from linearity [19]. Stevels [20] visualized the glass structure as containing interstices of varying diameter so that alkali, alkaline ions of different sizes are more easily accommodated than all ions have the same size. Thus in Stevels theory the higher density of alkali alkaline earth glasses is due to a more efficient packing. In the present studied glass system, the density and oxygen packing density exhibited positive deviation from linearity which is supported by Stevel's theory.

Refractive index, η of the present glass system measured by Brewster's angle technique is presented in Fig. 2. The refractive index of the bismuthate glass system increases with MgO content. The refractive index of any glass depends on glass formers. In the present glass system since B_2O_3 and Bi_2O_3 are fixed around 50 mol% and 25 mol%, respectively, the refractive index varies from 1.80 to 1.88. The small increase in the refractive index of the present glass system is attributed to the high field strength of Mg^{2+} ions compared to Li^+ ions. These measured η values of the present glasses are in agreement with the reported η values for similar glass system [21,22].

The DSC thermograms, shown in Fig. 3 exhibit endothermic peaks in the range (398–470 °C) selected as the glass transition temperature, T_g. Crystallization processes taking place in the glass matrix are marked by exothermic peaks T_p in the range (442–580 °C) for all glass samples. Fig. 4 illustrates the compositional dependence of the glass transition temperatures in the present glasses. Table 2 presents the

Table 1
Density (ρ), molar volume (V_m), oxygen packing density (OPD), ionic concentrations and inter ionic distance of xMgO–(25-x)Li_2O–50B_2O_3–25Bi_2O_3 glasses.

Glass composition	Average molecular weight (g/mol)	ρ (g/cm^3)	V_m (cm^3/mol)	OPD (g-atm/l)	Mg^{2+} ion concentration $\times 10^{21}$/cc	Mg^{2+} inter ionic distance (Å)	Li^+ ion concentration $\times 10^{21}$/cc	Li^+ inter ionic distance (Å)
25Li_2O–50B_2O_3–25Bi_2O_3	154.39	4.48	40.15	62.25	–	–	4.35	1.63
5MgO–20Li_2O–50B_2O_3–25Bi_2O_3	155.40	4.45	38.16	65.51	0.79	0.92	3.31	1.49
10MgO–15Li_2O–50B_2O_3–25Bi_2O_3	155.91	4.60	34.15	73.01	1.55	1.15	2.25	1.31
15MgO–10Li_2O–50B_2O_3–25Bi_2O_3	156.44	4.56	34.24	72.21	2.73	1.39	1.76	1.20
20MgO–5Li_2O–50B_2O_3–25Bi_2O_3	156.96	4.51	40.07	62.39	3.10	1.45	0.75	0.90
25MgO–50B_2O_3–25Bi_2O_3	157.48	4.27	40.57	61.62	3.85	1.56	–	–