Li^{+} ion dynamics in strontium bismuthate glasses

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Abstract

Ion transport in Li_2O–Bi_2O_3–SrO glasses has been studied in the frequency range 10 Hz–2 MHz and in the temperature range 263–483 K. The variation of the dc conductivity and the activation energy of these glasses with composition has been compared with those of bismuthate and lead bismuthate glasses. The frequency dependent conductivity has been studied using both modulus and conductivity formalisms. We have observed that the variation of the power law exponent with Li_2O content is in contrast to that for the Li_2O–Bi_2O_3 and Li_2O–Bi_2O_3–PbO glasses. The values of the non-exponential parameter for the Li_2O–Bi_2O_3–SrO glasses are lower than those for the binary Li_2O–Bi_2O_3 glasses.

1. Introduction

Glasses formed with Bi_2O_3 as a network former have been paid considerable attention recently due to their excellent optical properties, which make them appealing for applications as infrared transmission components, ultrafast optical switches, third order optical nonlinear materials and other photonic devices [1–3]. These glasses are also interesting from the point of view of glass formation and structure [1–7] as these glasses do not contain any conventional network formers such as SiO_2, P_2O_5, B_2O_3 etc. Also, Bi_2O_3 based glasses with high alkali content exhibit high electrical conductivity [8] and hence have recently attracted great interest as possible solid electrolytes for application in high energy density batteries and sensors. There are a few preliminary reports on the structure of the Bi_2O_3 based glasses [5, 9–11] containing Li$^+$ ions. These studies show the presence of BiO_6 octahedra as a main structural unit for these glasses. For the glasses with low alkali content, Li$^+$ ions occupy the structural interstices to compensate the excess negative charge of BiO_6 octahedra. However, for the glasses with high Li_2O content, the charge compensation is exceeded and hence some of the relatively strong Bi–O bonds in the glass network are replaced by weak ionic Li$^+$–O$^-$ bonds. This change causes a decrease in the mean bond strength and connectivity of the glass network, resulting in a more open structure,

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Table 1. Activation energy for the dc conductivity, high-frequency dielectric constant, activation energy for conductivity relaxation, stretched exponential parameter, activation energy for crossover frequency and frequency exponent for xLi$_2$O–(80 − x)Bi$_2$O$_3$–20SrO glasses.

mol% of Li$_2$O (x)	E_σ (eV) (± 0.01)	ε_∞	E_τ (eV) (± 0.01)	β (± 0.01)	E_{H} (eV) (± 0.01)	n (± 0.01)
40	0.94	19.083	0.94	0.50	0.94	0.63
50	0.79	21.097	0.80	0.50	0.81	0.64
60	0.76	14.925	0.75	0.49	0.76	0.66
70	0.67	12.315	0.63	0.47	0.67	0.67

which might be responsible for the high ionic conductivity of these glasses and thus it will be of interest to investigate the Li$^+$ ion dynamics in these glasses. Introduction of alkali earth oxides may further create open structure by breaking the bond forming network and these may influence the dynamics of Li$^+$ ions. In this paper, we have reported the dynamics of Li$^+$ ions in the strontium bismuthate glasses, which form glass for Li$_2$O content from 40 to 70 mol%. The wide composition range provides us an opportunity to study ion dynamics in these materials as a function of composition.

2. Experiment

Glasses of compositions xLi$_2$O–(80 − x)Bi$_2$O$_3$–20SrO, where x = 40–70 mol%, were prepared from the reagent grade chemicals Li$_2$CO$_3$ (Aldrich, 99+%), Bi$_2$O$_3$ (Loba Chemie, 99%) and SrCO$_3$ (Loba Chemie, 99%). The appropriate mixtures of these chemicals were first decarbonated in an alumina crucible at 450 °C for two hours and then melted in an electric furnace in the temperature range 850–950 °C in air for half an hour. Glass samples were obtained by quenching the melt in between two aluminium plates. All the samples were transparent and rather yellowish in colour. The glassy nature of all the prepared samples was confirmed from x-ray diffraction patterns recorded in a x-ray diffractometer (Seifert, model-3000P). The density was measured at room temperature by the liquid displacement method using acetone as the immersion liquid. Gold electrodes were deposited on both surfaces of the prepared samples of thickness ∼0.03–0.05 cm and diameter ∼1.2 cm. Electrical measurements such as capacitance and conductance were carried out using a precision RLC bridge (QuadTech, model 7600) in the temperature range 263–483 K and the frequency range 10 Hz–2 MHz. The dc conductivity was obtained from the complex impedance plots.

3. Results and discussion

3.1. dc conductivity

The variation of the dc conductivity with reciprocal temperature for different compositions is shown in figure 1. The plots show that the dc conductivity obeys the Arrhenius relation $\sigma_{\mathrm{dc}} = \sigma_0[\exp -(E_\sigma/kT)]$. The activation energy E_σ of the different compositions, calculated from the least squares straight-line fits, is given in table 1. The dependence of the dc conductivity and the activation energy on the lithium ion content for the present glasses is also compared in figures 2(a) and (b) respectively with those for the other bismuthate [12] and lead bismuthate [13] glasses containing Li$^+$ ions. It is observed that the dc conductivity for lead bismuthate glasses is maximum for a fixed Li$_2$O content (figure 2(a)). It is due to the
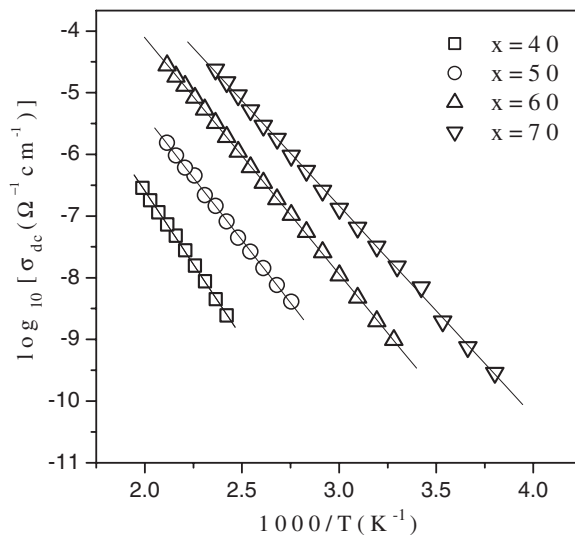
Figure 1. The dc conductivity shown as a function of the reciprocal of the temperature for different compositions (shown) of $x\text{Li}_2\text{O}$–20SrO–$(80 - x)\text{Bi}_2\text{O}_3$ glasses. The solid lines are the least squares straight-line fits.

fact that, in lead bismuthate glasses, a fraction of Li^+ ions coordinate with PbO_3 polyhedra through PbO^-–Li^+ bonds, leading to the increase in conductivity [13]. But in the case of lithium strontium bismuthate glasses there is no existence of SrO polyhedra and SrO solely acts as a modifier in this case. It can be seen from figure 2 that the conductivity as well as the activation energy changes very little from the bismuthate glasses to strontium bismuthate glasses after introduction of SrO.

3.2. Ac conductivity

We have analysed the ac conductivity of lithium ions in Li_2O–Bi_2O_3–SrO glasses in the framework of the modulus [14] as well as the conductivity formalism [15]. We have used both the formalisms, as there is a debate on which of these formalisms provides a better description of the dynamic process [16, 17]. In the modulus formalism [14] an electric modulus is defined as $M^*(\omega) = 1/\varepsilon^*(\omega)$, where $\varepsilon^*(\omega)$ is the complex dielectric permittivity. We can write $M^*(\omega)$ as

$$M^*(\omega) = 1/\varepsilon^*(\omega) = (\varepsilon' - j\varepsilon'')/|\varepsilon^*|^2 = M'(\omega) + jM''(\omega)$$
$$= M_\infty \left[1 - \int_0^\infty \exp(-j\omega t)(-d\varphi(t)/dt)\,dt \right]. \tag{1}$$

Here $M_\infty = 1/\varepsilon_\infty$ is the high frequency asymptotic value of the real part of the dielectric constant and $\varphi(t)$ is defined as the relaxation function which evolves the electric field within the dielectric. We have taken the relaxation function $\varphi(t)$ as the Kohlrausch–Williams–Watts (KWW) [18] function given by

$$\varphi(t) = \exp\{-(t/\iota_m)^\beta\} \tag{2}$$

where β is a non-exponential parameter. Figures 3(a) and (b) show the frequency dependence of the modulus isotherms for the composition $60\text{Li}_2\text{O}$–$20\text{Bi}_2\text{O}_3$–20SrO. It has been observed that as the frequency of the applied field is increased, $M'(\omega)$ shows a dispersion tending to M_∞ at higher frequencies. The imaginary part of the electrical modulus $M''(\omega)$ shows an asymmetric maximum at frequency ω_m centred at the dispersion region of $M'(\omega)$. The frequency corresponding to the peak of $M''(\omega)$ gives the most probable conductivity relaxation time τ_m
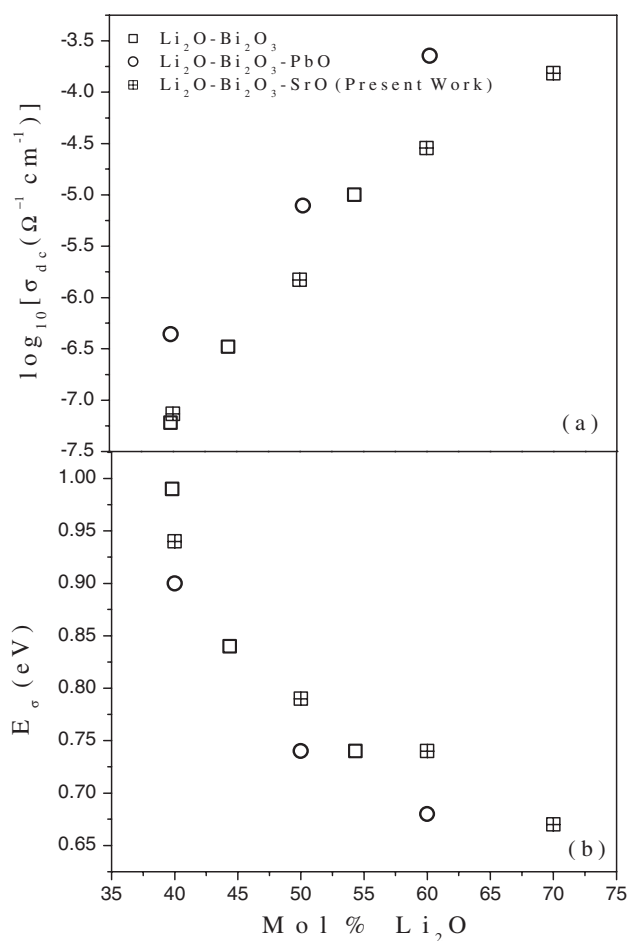
Figure 2. (a) Comparison of the dc conductivity at 200 °C and (b) dc activation energy of strontium bismuthate glasses with those of bismuthate [12] and lead bismuthate [13] glasses.

given by the condition $\omega_m \tau_m = 1$. The reciprocal temperature dependence of the conductivity relaxation time (shown in figure 4) obeys the Arrhenius relation $\tau_m = \tau_0 \exp(E_\tau/kT)$. The activation energy E_τ (table 1) obtained from figure 4 by least squares straight-line fits is close to the activation energy obtained from dc conductivity. A master plot of the electric modulus is shown in figure 5 in which each frequency is scaled by the peak frequency ω_m and M' (or M'') is scaled by M_∞ (or M''_{max}). The perfect overlap of the curves for all temperatures on a single master curve indicates that the dynamical processes are temperature independent.

The fits of equations (1) and (2) to the data give the values of the non-exponential parameter β, which are listed in table 1. We note that the values of β remain almost constant within the experimental errors for different compositions. Comparing the values of β for the present glasses with those for Li$_2$O–Bi$_2$O$_3$ glasses [12], we have observed that the values of β decrease due to introduction of SrO.

In the conductivity formalism the real part of the frequency dependent conductivity $\sigma'(\omega)$ is expressed as [15]

$$\sigma'(\omega) = \sigma_{dc}[1 + (\omega/\omega_H)^n] \tag{3}$$

where ω_H is a crossover frequency, separating the dc regime from the dispersive conduction, and n is the frequency exponent which lies between zero and unity. The fractional exponent n has
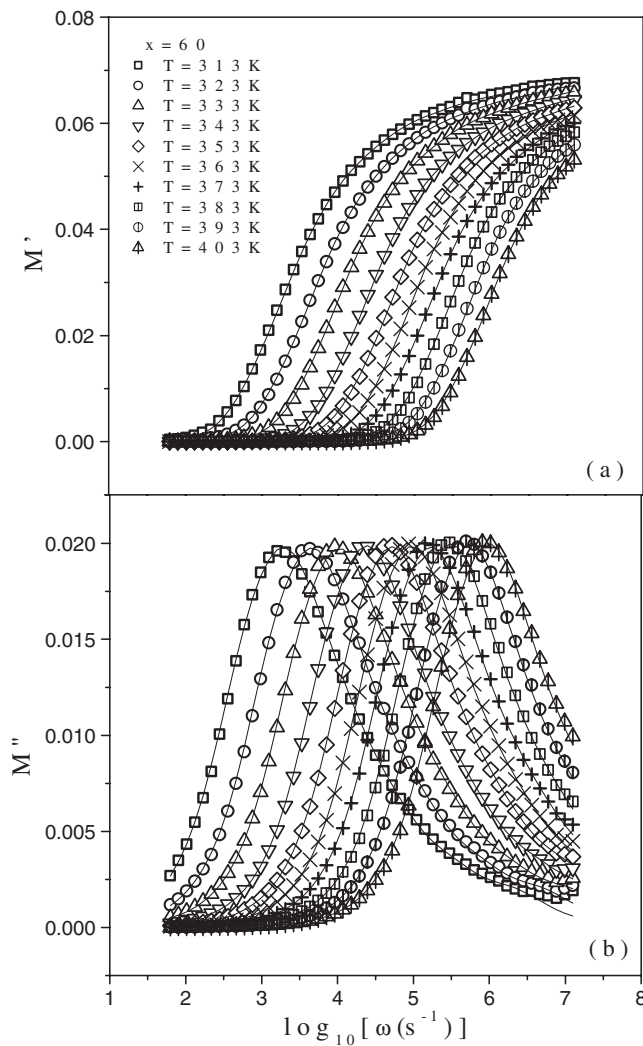
Figure 3. Frequency dependence of the (a) real and (b) imaginary parts of the modulus isotherms for different temperatures (shown) for the 60Li$_2$O–20SrO–20Bi$_2$O$_3$ glass. The solid curves are the best fits to equation (5).

long been discussed by Jonscher [19]. Equation (3) can be obtained from the imaginary parts of the complex dielectric susceptibility [19], assuming that the crossover frequency is close to the hopping frequency [15]. The frequency exponent n measures the interaction between the mobile ions. By using the Nernst–Einstein relation and assuming thermally activated hopping of the charge carriers, the value of σ_{dc} can be given by

$$\sigma_{dc} = [N_0 q^2 \lambda^2 \omega_H]/12\pi kT \tag{4}$$

where N_0 is the mobile ion concentration, q is the electronic charge, λ is the average jump distance between the mobile ion sites and ω_H is the crossover frequency. Thus, assuming the crossover frequency as the hopping frequency [15] the bulk ac conductivity can be written by using equations (3) and (4) as

$$\sigma'(\omega) = [N_0 q^2 \lambda^2 \omega_H]/12\pi kT[1 + (\omega/\omega_H)^n]. \tag{5}$$

For the present glasses we have taken the ion jump distance λ equal to the cation–cation separation distance obtained from glass composition and density. The frequency spectra of
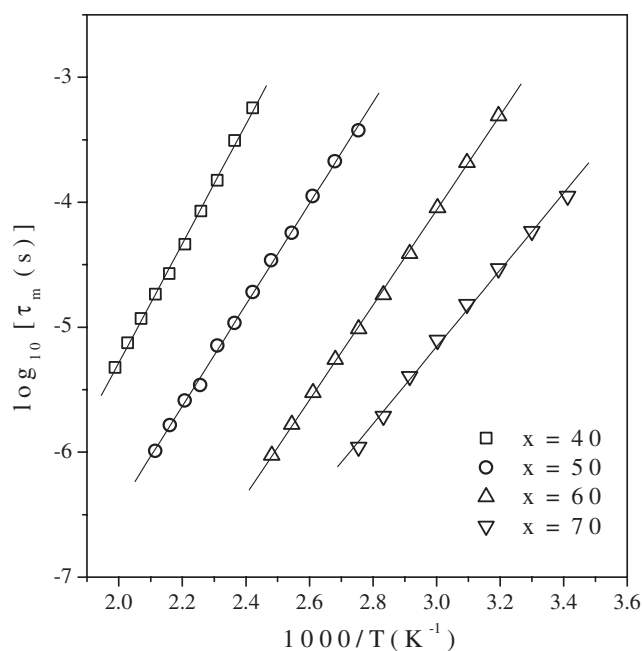
Figure 4. Reciprocal temperature dependence of conductivity relaxation time for different compositions (shown) of xLi$_2$O–20SrO–(80 − x)Bi$_2$O$_3$ glasses. The solid lines are the least squares straight-line fits.
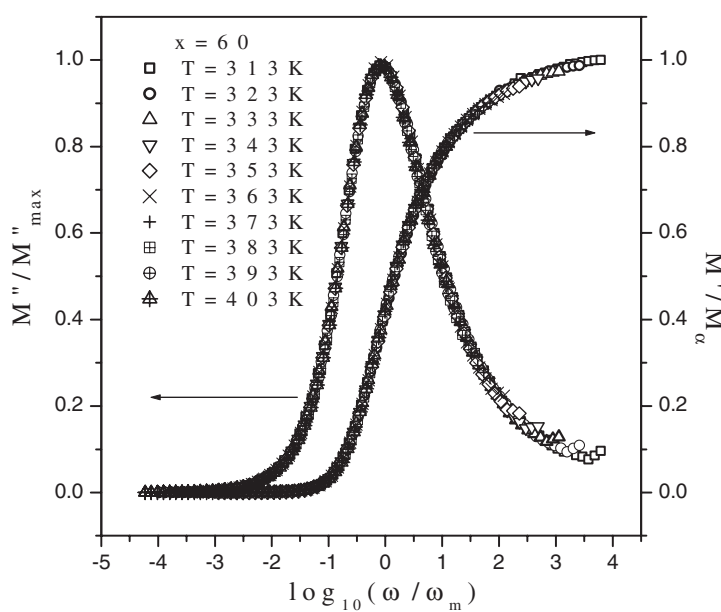
Figure 5. Master plot of the electrical modulus for the 60Li$_2$O–20SrO–20Bi$_2$O$_3$ glass for different temperatures (shown).

the real conductivity $\sigma'(\omega)$ at different temperatures for a composition are shown in figure 6. It is observed that the conductivity remains almost constant (i.e independent of frequency) at low frequencies but it exhibits dispersion for the higher frequencies. The experimental conductivity data were fitted to equation (5) with N_0, ω_H and n as variables. The best fits to the conductivity spectra are shown by the solid curves in figure 6. An Arrhenius plot of the ion concentration N_0 with reciprocal of temperature is shown in figure 7(a). This figure indicates that mobile ions are independent of temperature, but are dependent weakly on Li$_2$O content
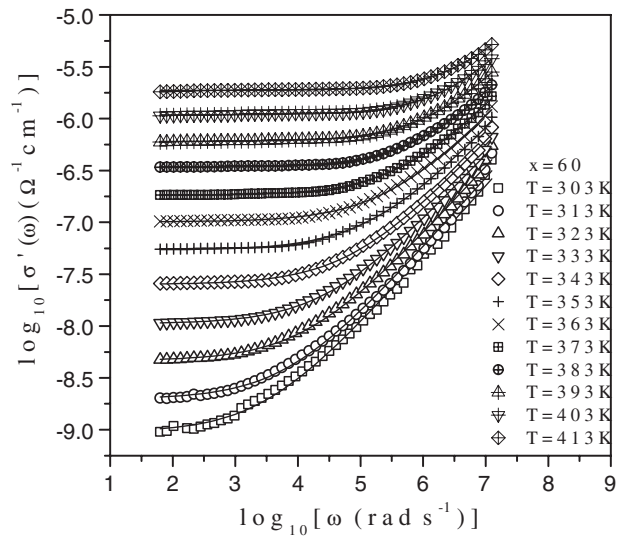
Figure 6. Conductivity isotherms at different temperatures (shown) for the 60Li$_2$O–20SrO–20Bi$_2$O$_3$ glass as a function of frequency. The solid curves are the best fits to equation (5).
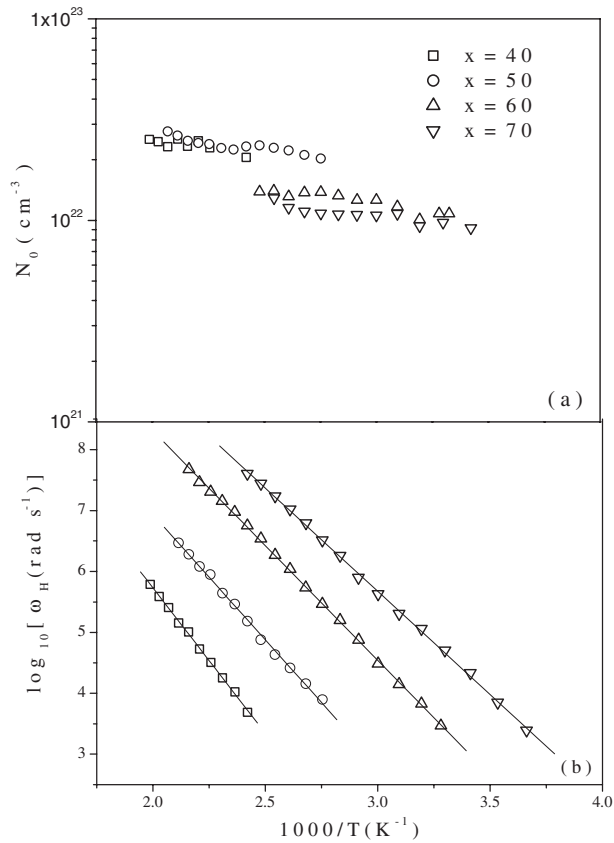
Figure 7. (a) Charge carrier concentration and (b) crossover frequency for xLi$_2$O–20SrO–$(80 - x)$Bi$_2$O$_3$ glasses shown as a function of the reciprocal of the temperature. The solid lines are the least squares straight-line fits.

in the compositions. A reciprocal temperature dependence of the crossover frequency ω_H (figure 7(b)) shows that it obeys the Arrhenius relation. The values of activation energy (E_H) of ω_H (table 1) are close to the activation energy for the dc conductivity. This is in contrast with the previous results for Li_2O–Bi_2O_3 [12] and Li_2O–Bi_2O_3–PbO glasses [13] for which thermally activated mobile ions were observed. We have observed that the values of n are also independent of temperature. The variation of the values of the parameter n (shown in table 1) increases slightly with the increase in the Li_2O content in the composition. We have noted that this compositional variation of n is quite the opposite of that of the Li_2O–Bi_2O_3 [12] and Li_2O–Bi_2O_3–PbO [13] glasses in which the value of n decreases with the increase of Li_2O content.

4. Conclusions

The dc conductivity and the ac relaxation of $x Li_2O$–$(80 - x)Bi_2O_3$–20SrO glasses of variable Li_2O content were analysed in a wide frequency and temperature range. The results obtained for dc conductivity and activation energy for these glasses were compared with the results for Li_2O–Bi_2O_3 and Li_2O–Bi_2O_3–PbO glasses. The ac conductivity of the present glasses has been analysed using both the modulus and the conductivity formalisms. It was noted that the compositional variation of the power law exponent is in contrast with those of Li_2O–Bi_2O_3 and Li_2O–Bi_2O_3–PbO glasses. We have also found that the values of the non-exponential parameter for the present glass system are low in comparison to those for the binary Li_2O–Bi_2O_3 glasses.

Acknowledgments

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