Transport properties of AgI doped silver molybdate superionic glass-nanocomposites

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Abstract
We have reported the dc conductivity as well as the ac conductivity in the frequency range 10 Hz–2 MHz for x AgI–$(1 - x)(0.5Ag_2O$–$0.5MoO_3)$, glass-nanocomposites in the temperature range 100–303 K. We have compared the conductivity and its activation energy for the molybdate nanocomposites with those of the borate and phosphate glasses. We have analysed the ac conductivity using the power law model. We have observed that both the dc conductivity and the crossover frequency obtained from the power law model show an activated behaviour. We have also observed that the power law exponent is almost independent of AgI doping content. Furthermore, the concentration of the mobile Ag^+ ions is found to be independent of temperature as well as the AgI content in the compositions.

1. Introduction

Metal halide doped superionic glasses, for example AgI doped silver borate and phosphate glasses, have been paid much attention for the last few years because of their potential applications in electrochemical devices such as solid state batteries, electrochromic displays, sensors, etc [1]. These materials offer many advantages over polycrystalline ceramic electrolytes, such as no grain boundaries, ease of fabrication, wide available composition ranges, etc. They are also important from the academic point of view. One of the main scientific challenges is to explain how the disorder structure of glasses is related to the high ionic conductivity ($\sim10^{-2}$ Ω^{-1} cm^{-1}) achieved at ambient temperatures [2].

AgI doped silver molybdate glasses are particularly interesting because of the growing evidence of anomalies in the structure as well as in the intensive properties when compared with silver borate and silver phosphate glasses [3]. It has been observed that AgI–Ag_2O– MoO_3 glasses contain discrete Ag^+, I^- and MoO_4^{2-} ions. MoO_4^{2-} ions in molybdate glasses do not form connected networks similar to –BO_3– or –PO_4– networks in borate and phosphate glasses respectively. Diffraction and spectroscopic studies [4] reveal that the origin of the

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first diffraction peak in the AgI doped molybdate glasses is somewhat different from that of borate and phosphate glasses and cannot be simply explained in terms of AgI clustering as in phosphate glass. Infrared spectroscopic results indicate [5] that Ag^+ motion frequency in molybdate glasses remains relatively unaffected by AgI content. NMR studies [6] show formation of oxy-iodide sites and rule out the existence of AgI clusters in molybdate glass. However, recent NMR studies [7] indicate the presence of α-AgI microcrystals in molybdate glasses containing high AgI content. A few studies on the electrical properties of AgI doped molybdate glasses have also been reported [8–10]. The conductivity was found to increase with the increase in the AgI content similar to the phosphate and borate glasses. However, studies of the electrical properties and relaxation of these glasses in details have not been reported.

In this paper we report electrical conductivity of the xAgI–$(1 - x)(0.5Ag_2O$–$0.5MoO_3)$ glass-nanocomposites in a wide composition range.

2. Experiment

Samples of compositions xAgI–$(1-x)(0.5Ag_2O$–$0.5MoO_3)$, where $x = 0.30, 0.40, 0.50, 60,$ 0.70, 0.75 and 0.80 respectively, were prepared by quenching the melts. The appropriate amounts of reagent grade powders AgI, $AgNO_3$ and MoO_3 were thoroughly mixed and preheated in a platinum crucible at 400 °C for 2 h for denitrogenation of $AgNO_3$. The mixtures were then melted at temperatures in the range from 700 to 800 °C depending upon the composition. The melts were equilibrated for 2 h and quenched between two aluminium plates. However, for compositions with $x > 0.70$ the melts were poured onto a twin-roller system for devitrification. Transparent samples of thickness ~1 mm were obtained for $x = 0.30$–0.80. Formation of glass-nanocomposites was confirmed from x-ray diffraction and transmission electron microscopic studies. Electrical measurements such as capacitance and conductance were carried out in the frequency range 10 Hz–2 MHz and in the temperature range 100–303 K using an *LCR* meter (Quad Tech, model 7600) and a closed cycle cryocooler (Janis Inc, model CCS-450) respectively.

3. Results and discussion

The dc conductivity at different temperatures for all compositions was computed from the complex impedance plots. The variation of the dc conductivity with reciprocal temperature for different compositions is shown in figure 1, which shows that the dc conductivity exhibits the Arrhenius relation: $\sigma_{dc}T = \sigma_0 \exp(-E_\sigma/kT)$. The values of the activation energy E_σ for different compositions, obtained from the least squares straight line fits, are shown in table 1. The dependence of the conductivity at 303 K on the AgI content in the composition is shown in figure 2(a). For comparison the dc conductivity data for the phosphate and borate glasses [11–13] are also included in figure 2(a). We note that the conductivity for the molybdate glasses increases with the increase of AgI content similar to borate and phosphate glasses. It may be noted that for AgI content more than 50 mol% the conductivities for the molybdate, phosphate and borate systems are comparable. However, for lower AgI content, the conductivity for the molybdate glasses is lower. Figure 2(b) shows that the activation energy E_σ for the molybdate glasses decreases with the increase of AgI content. It is noteworthy that the activation energy for the molybdate glasses is lower than that for the phosphate and borate glasses. The different behaviour of molybdate glasses in the conductivity and its activation energy from that of the phosphate and borate glasses arises from the difference in their structures as mentioned in the introduction.
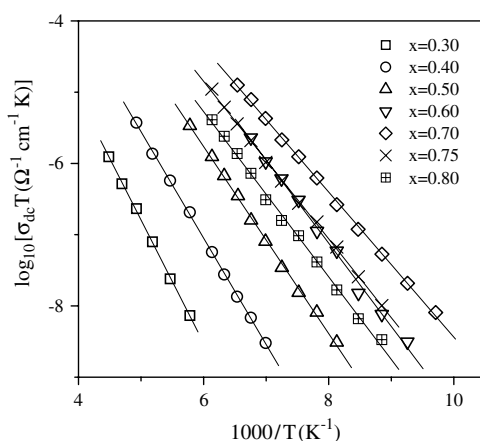
Figure 1. Dc conductivity of xAgI–$(1 - x)(0.5Ag_2O$–$0.5MoO_3)$ glass-nanocomposites shown as a function of reciprocal temperature for different compositions (shown).

Table 1. The dc conductivity and its activation energy, the crossover frequency and its activation energy and the power-law exponent for the xAgI–$(1 - x)(0.5Ag_2O$–$0.5MoO_3)$ glass-nanocomposites.

Composition x	$\log_{10}[\sigma_{dc} \ (\Omega^{-1} \ cm^{-1})]$ at 303 K (± 0.02)	E_σ (eV) (± 0.01)	$\log_{10}[\omega_c \ (rad \ s^{-1})]$ at 303 K (± 0.02)	E_c (eV) (± 0.01)	n (± 0.02)
0.30	−3.92	0.34	3.37	0.28	0.66
0.40	−3.05	0.29	4.35	0.27	0.68
0.50	−2.26	0.26	4.54	0.31	0.68
0.60	−1.68	0.23	4.68	0.22	0.65
0.70	−1.66	0.20	4.70	0.20	0.65
0.75	−1.70	0.22	4.68	0.21	0.67
0.80	−2.14	0.23	4.67	0.21	0.68

It is also noted that the dc conductivity shows a maximum at $x = 0.7$. The reason for this maximum may be understood from the standpoint of their structural studies. From the selected area diffraction in transmission electron microscopic studies of this system (figure 3), it is quite clear that α-AgI nanocrystals are dispersed in the glassy matrix. The transmission electron micrographs also (figure 3(a)) indicated that the size of the dispersed AgI cluster is about 30–45 nm in the compositions for $x < 0.7$. However, for $x > 0.7$ the size of AgI cluster increases and the conductivity decreases for these compositions. The increase of the size of AgI cluster for $x > 0.7$ may be related to the solubility limit of glass formation and is to be understood theoretically.

The ac conductivity at four frequencies for a composition is shown in figure 4 as a function of reciprocal temperature. It is observed that at lower temperatures the ac conductivity is dominant over the dc conductivity. As the temperature is increased, the ac conductivity approaches the dc conductivity. It may also be noted that the ac conductivity increases with the increase in frequency.

We have shown in figure 5 the ac conductivity spectra at several temperatures for a composition. At lower frequencies, the conductivity is independent of frequency and corresponds to the dc conductivity. However, as the frequency is increased, the conductivity
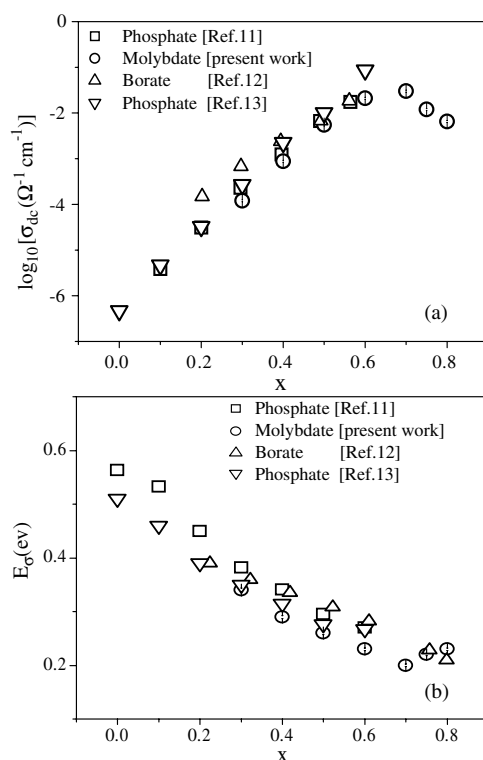
Figure 2. (a) Dc conductivity at 303 K and (b) activation energy shown as a function of AgI content in the glass compositions. The error bars are within the size of the symbols. For comparison the data for the phosphate and borate glasses are included.

shows dispersion. It may be noted that the frequency at which the dispersion occurs shifts to higher frequencies as the temperature is increased. Other compositions also showed similar behaviour. Such a frequency dependence of the conductivity can be well described by the power-law formalism [14, 15], according to which the real part of the conductivity can be given by

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

where ω_c is the crossover frequency from the dc to the dispersive conductivity and n is a power law exponent. We have obtained the values of σ_{dc}, ω_c and n from the best fit of conductivity spectra of figure 5 to equation (1). The Arrhenius temperature dependence of ω_c for different compositions is shown in figure 6, which exhibits an activated behaviour. The activation energy E_c for ω_c, obtained from the least squares straight line fit, is displayed in table 1. We note that the values of E_c are close to the values of activation energy E_σ for the dc conductivity, except for the composition with $x = 0.5$. The reason for deviation for $x = 0.5$ composition is not clear at present. We have observed that the values of n are almost independent of temperature and composition (table 1). The composition independence of n might arise from the structure of these glasses, which is independent of the doping of AgI contents as evidenced by the infrared studies of these glasses [15]. Such values of n can be related to the three-dimensional conduction pathway [16]. However, there is no theoretical explanation for such values of n at present and this needs further studies theoretically.
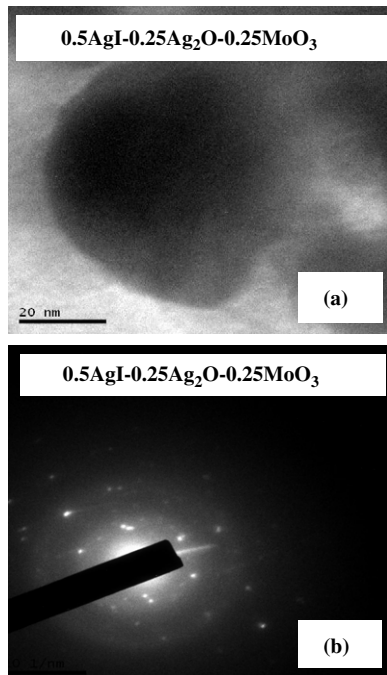
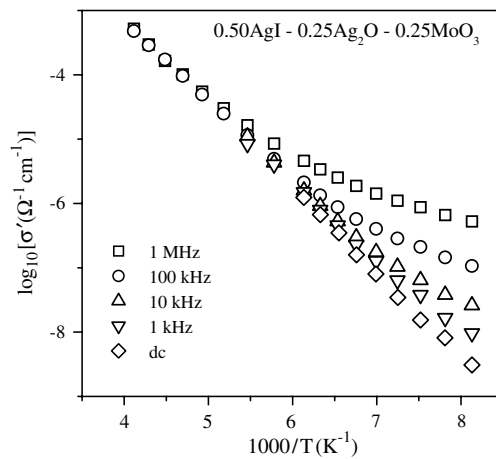**Figure 3.** (a) Transmission electron micrograph and (b) selected area diffraction pattern for the 0.5AgI–0.25Ag$_2$O–0.25MoO$_3$ composition.

Figure 4. Ac conductivity at four frequencies shown as a function of reciprocal temperature for the 0.50AgI–0.25Ag$_2$O–0.25MoO$_3$ composition. The dc conductivity is also included for comparison.

Now assuming the crossover frequency ω_c as the hopping frequency ω_h [16] and thermally activated hopping of the charge carriers, the dc conductivity σ_{dc} can be given by the Nernst–Einstein relation,

$$\sigma_{dc} = n_c q^2 d^2 \omega_h / 12\pi kT \tag{2}$$

where n_c is the mobile ion concentration, q is the charge and d is the average jump distance between the mobile ion sites. We have obtained the mobile ion concentration n_c from
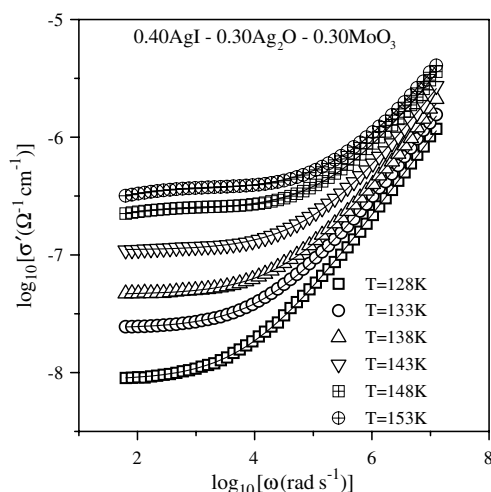
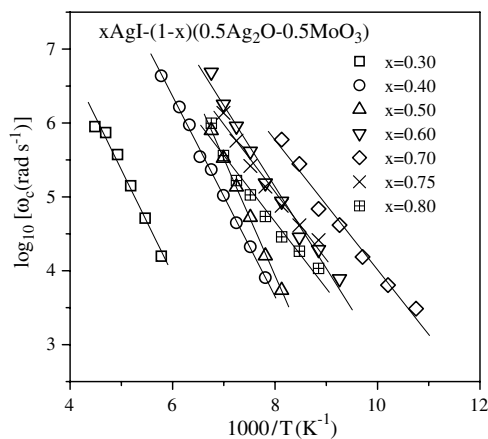**Figure 5.** Ac conductivity spectra at different temperatures (shown) for the composition 0.40AgI–0.30Ag$_2$O–0.30MoO$_3$.

Figure 6. Reciprocal temperature dependence of the crossover frequency for different compositions (shown) of the xAgI–$(1-x)(0.5$Ag$_2$O–0.5MoO$_3$) system.

equation (2) and shown the results in figures 7(a) and (b) respectively as a function of reciprocal temperature and AgI content for different compositions. It may be noted that the mobile ion concentration n_c is almost independent of temperature for all compositions. It is also almost independent of the AgI content in the compositions. Thus the mobility rather than concentration of charge carriers dominates the conductivity of the AgI doped silver molybdate glass-nanocomposites.

4. Conclusions

The dc conductivity as well as the ac conductivity in the frequency range 10 Hz–2 MHz has been studied for the xAgI–$(1-x)(0.5$Ag$_2$O–0.5MoO$_3$) glass-nanocomposites in a wide temperature range. The dc conductivity and its activation energy for the molybdate glass-nanocomposites are lower than those of the borate and phosphate glasses. The growth of the
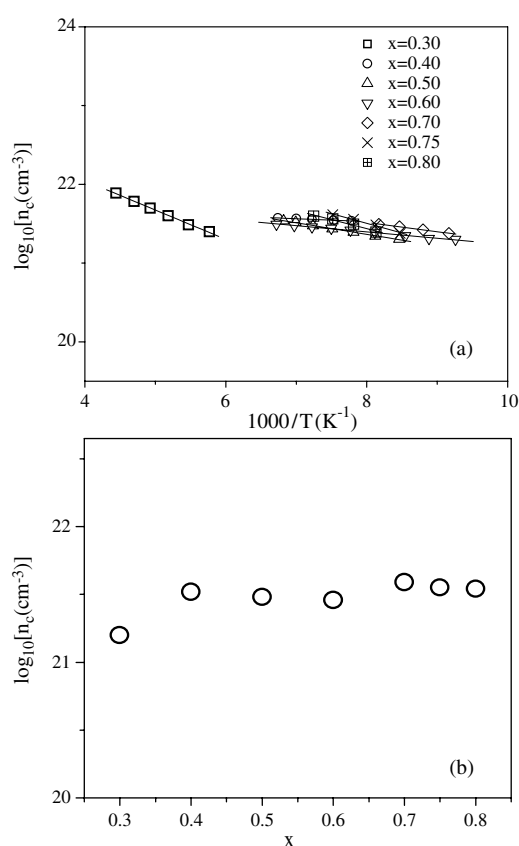
Figure 7. (a) Mobile silver ion concentration shown as a function of reciprocal temperature for different compositions. (b) Mobile silver ion concentration shown as a function of AgI content.

size of α-AgI nanoclusters in the glass matrix is the probable reason for the decrease of dc conductivity with the increase of AgI content beyond 0.70. Both the dc conductivity and the crossover frequency obtained from the power law model show an activated behaviour with the same activation energy. The power law exponent is almost independent of AgI doping content. The mobile Ag^+ ion concentration is also independent of temperature and AgI content in the compositions.

Acknowledgments

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