

Relaxation of silver ions in fast ion conducting molybdate glasses

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Abstract

The conductivity relaxation in the frequency range from 10 Hz to 2 MHz and in the temperature range from 108 to 303 K for the fast ion conducting AgI–Ag₂O–MoO₃ glasses has been reported. It has been observed that the conductivity relaxation in these glasses is highly non-exponential and that the conductivity relaxation mechanism is independent of temperature but is dependent on composition. It has been further observed that the motion of Ag⁺ ions is decoupled more and more from the viscous motion of the glassy matrix with the increase of AgI content in the composition, giving rise to the increase of the conductivity.

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1. Introduction

AgI-doped fast ion conducting glasses have been paid considerable attention for the last few years for their potential applications in solid state electrochemical devices, such as solid state batteries, sensors, electrochromic displays, etc. [1–3]. These materials offer many advantages over polycrystalline ceramic electrolytes, such as absence of grain boundaries, ease of fabrication, wide available composition ranges, etc. They are also important from the academic point of view. There are many experimental and theoretical reports on ionic conduction of these fast ion conducting glasses [4–10]. However, the conduction mechanism of these glasses is not properly understood yet because of the difficulty in separating the contribution of the ion concentration and mobility from the measured conductivity.

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 [11]. It has been observed that AgI–Ag₂O–MoO₃ glasses contain discrete Ag⁺, I[−] and MoO₄^{2−} ions and MoO₄^{2−} ions do not form connected networks similar to –BO₃– or –PO₄– networks in borate and phosphate glasses, respectively. Diffraction and spectroscopic studies [12] reveal that the origin of the 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 glasses. Infrared spectroscopic results indicate [13] that the frequency of Ag⁺ ion motion in molybdate glasses remains relatively unaffected by AgI content. NMR studies [14] show formation of oxy-iodide sites and rule out the existence of AgI clusters in molybdate glasses. However, recent NMR studies [15] indicate the presence of α-AgI microcrystals in molybdate glasses containing high AgI content. Several studies on the electrical properties of AgI-doped molybdate glasses have also been reported [16–19]. The conductivity was found to increase with the increase in the AgI content similar to the phosphate and borate glasses. There are also several reports on the ac electrical properties of these glasses [19–21].

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In this paper, we report the conductivity relaxation of Ag^+ ions in fast ion conducting $\text{AgI-Ag}_2\text{O-MoO}_3$ glasses to shed more light on the dynamics of Ag^+ ions in these glasses.

2. Experiment

Glass samples of compositions $x\text{AgI-(1-x)}(0.5\text{Ag}_2\text{O-0.5MoO}_3)$, where $x=0.3-0.7$, was prepared from the reagent grade chemicals AgI , AgNO_3 and MoO_3 . The mixtures of these chemicals in appropriate proportions were held at 450°C for 2 h for denitrogenation of AgNO_3 and then melted in the temperature range from 700 to 800°C depending upon composition. The melts were equilibrated for 2 h and were finally quenched between two aluminum plates. Transparent glass samples of thickness ~ 1 mm were obtained for $x=0.3-0.7$. Glass formation was confirmed from X-ray diffraction and scanning electron microscopic studies. For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples of diameter ~ 10 mm. The electrical measurements such as capacitance and conductance of the samples were carried out in the frequency range 10 Hz– 2 MHz using a RLC meter (QuadTech, Model 7600). The measurements were taken in a closed cycle cryostat (Janis Inc. Model CCS-450) in the temperature range $108-303$ K.

3. Results and discussion

Two formalisms such as electric conductivity and electric modulus [22–25] have been employed to study the ion dynamics in glasses under ac electric field. However, there is a debate on which of these formalisms provides better insights into the phenomena of ion dynamics [26–28]. In this paper, we have studied the ionic relaxation in the glass system $x\text{AgI-(1-x)}(0.5\text{Ag}_2\text{O-0.5MoO}_3)$ in the framework of the modulus formalism, i.e. the conductivity relaxation mechanism. In the modulus formalism [24,25], an electric modulus M^* is defined as the inverse of the complex dielectric permittivity ε^* :

$$M^* = 1/\varepsilon^* = (\varepsilon' - j\varepsilon'')/|\varepsilon|^2 = M' + jM''$$

$$= M_\alpha \left[1 - \int_0^\infty \exp(-j\omega t) (-d\phi/dt) dt \right] \quad (1)$$

where M' and M'' are the real and imaginary part of the complex modulus M^* and M_∞ is the high frequency value of M' . The function $\phi(t)$ gives the time evolution of the electric field within the materials.

We have presented the real and imaginary modulus spectra at different temperatures for a glass composition in Fig. 1(a) and (b), respectively. Fig. 1(a) shows that real modulus M' shows dispersion as the frequency is increased

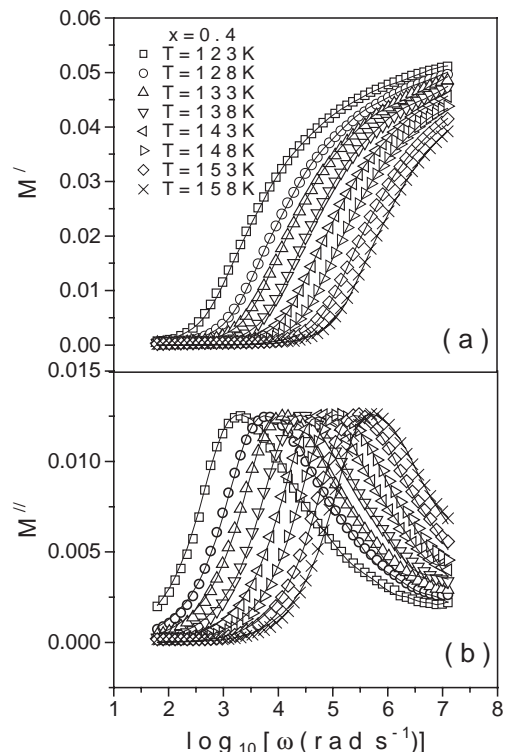


Fig. 1. Frequency dependence of (a) M' and (b) M'' at different temperatures for the $x\text{AgI-(1-x)}(0.5\text{Ag}_2\text{O-0.5MoO}_3)$; $x=0.4$ glass composition. Solid curves are the best fits to Eqs. (1) and (2).

and tends to saturate at M_∞ at higher frequencies. The imaginary modulus M'' [Fig. 1(b)] exhibits a maximum M''_{max} centered at the dispersion region of M' . It is further noted that the position of M''_{max} shifts to higher frequencies as the temperature is increased. The conductivity relaxation frequency ω_c , corresponding to M''_{max} , gives the most probable conductivity relaxation time τ_c by the condition $\omega_c\tau_c=1$ [24]. We also observed similar temperature dependence of M' and M'' for other glass compositions.

Fig. 2(a) shows the reciprocal temperature dependence of the relaxation time τ_c for all glass compositions. It is noted that τ_c exhibits an activated behavior obeying the Arrhenius relation $\tau_c=\tau_0 \exp [E_\tau/kT]$, where E_τ is the activation energy for the conductivity relaxation (Table 1). In Fig. 2(b) Arrhenius temperature dependence of the dc conductivity, obtained from the complex impedance plot, is also shown for different compositions. The activation energy E_σ for the dc conductivity is shown in Table 1. It may be noted that the activation energies for the conductivity relaxation time and the dc conductivity are nearly same.

We have obtained the non-exponential parameter β from the fits of Eq. (1) to the experimental data for M' and M'' for all glass compositions using the procedure of Moynihan et al. [25]. In the fitting process we have used the non-exponential Kohlrausch–Williams–Watts (KWW) function [29]:

$$\phi(t) = \exp[-(t/\tau)^\beta] \quad (2)$$

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