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Ionic relaxation in AgI–Ag₂O–TeO₂ glasses

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Abstract

We report the ionic conductivity relaxation in fast ion conducting glasses in the system $x\text{AgI}-(1-x)(0.40\text{Ag}_2\text{O}-0.60\text{TeO}_2)$ in the temperature range 128–303 K and in the frequency range 10 Hz–2 MHz. We have observed that the conductivity relaxation can be described by the highly non-exponential Kohlrausch–Williams–Watts function. The Ag⁺ ions have to overcome the same barrier while relaxing as well as while conducting. We have further observed that the migration of Ag⁺ ions in the glassy matrix is highly cooperative and the cooperation is extended as the AgI content is increased.

1. Introduction

Fast ion conducting glasses are of current interest because of their potential application in solid state electrochemical devices [1–3]. Although there are many experimental and theoretical reports on the ionic conductivity of these glasses [1, 4–11], the conduction mechanism in these glasses is not well understood yet because of the difficulty in separating the contribution of the ionic conductivity and the mobility from the measured conductivity. Glass formation and ionic conductivity of several fast ion conducting glasses in the AgI–Ag₂O–TeO₂ system have been recently reported [12–18]. It has been observed that the ionic conductivity increases with the increase of AgI content in the glass composition. The composition dependence of the ionic conductivity showed that the conductivity for these fast ion conducting glasses is bound essentially to the mobility of Ag⁺ ions located in an iodide environment similar to other fast ion conducting glasses [13, 14]. The structure of these glasses has also been investigated by infrared and Raman spectroscopy [12, 15]. These studies indicate the existence of weak interaction between AgI and the tellurite glass network similar to other fast ion conducting glasses formed with other network formers. It thus seems that the Ag⁺ ions from AgI and those involved in the glass network have different roles in the conduction process.

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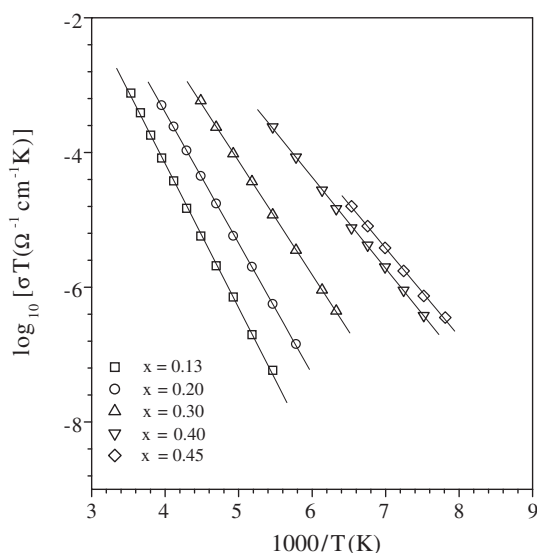


Figure 1. The dc conductivity of different compositions of $x\text{AgI}-(1-x)(0.40\text{Ag}_2\text{O}-0.60\text{TeO}_2)$ glasses shown as a function of reciprocal temperature. The solid lines are the least-squares straight-line fits.

In this paper, we report the conductivity relaxation in $x\text{AgI}-(1-x)(0.40\text{Ag}_2\text{O}-0.60\text{TeO}_2)$ glasses to shed further light on the dynamics of Ag^+ ions in these glasses.

2. Experiment

Glass samples of compositions $x\text{AgI}-(1-x)(0.40\text{Ag}_2\text{O}-0.60\text{TeO}_2)$, where $x = 0.13-0.45$, were prepared from reagent grade AgI , AgNO_3 and TeO_2 . Mixtures of these chemicals in appropriate proportions were held at 340°C for 1 h and then melted in the temperature range from 700 to 800°C depending upon composition. After homogenization for 20 min, the melts were finally quenched between two aluminium plates. Transparent glass samples of thickness ~ 1 mm were obtained for $x = 0.13-0.45$. Glass formation was confirmed from x-ray diffraction studies. For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples of diameter ~ 10 mm. The measurements of capacitance and conductance of the samples were carried out in the frequency range 10 Hz– 2 MHz using an RLC meter (Quad Tech, model 7600). The measurements were made in the temperature range $128-303$ K. The dc conductivity was obtained from the complex impedance plots.

3. Results and discussion

The dc ionic conductivity for different compositions of $x\text{AgI}-(1-x)(0.40\text{Ag}_2\text{O}-0.60\text{TeO}_2)$ glasses is shown in figure 1 as a function of reciprocal temperature. It is observed that the conductivity for all compositions exhibits the Arrhenius temperature dependence. The activation energy for different compositions was obtained from the least-squares straight-line fits (table 1). The variation of the dc conductivity at 303 K and the activation energy with the AgI content in the compositions is shown in figure 2. It may be noted that the conductivity increases and the activation energy decreases with the increase of AgI content. However,

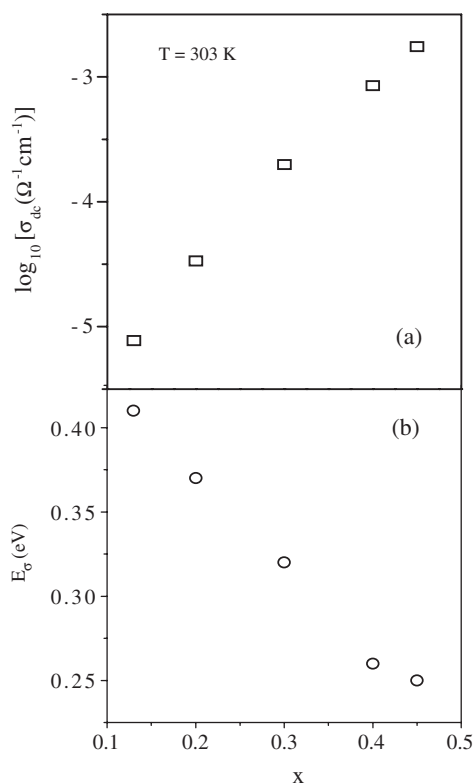


Figure 2. (a) Variation of the dc conductivity at 303 K and (b) variation of the activation energy with composition for $x\text{AgI}-(1-x)(0.4\text{Ag}_2\text{O}-0.6\text{TeO}_2)$ glasses.

Table 1. The activation energies for the dc conductivity and the conductivity relaxation frequency, high-frequency modulus and non-exponential parameter for $x\text{AgI}-(1-x)(0.6\text{Ag}_2\text{O}-0.4\text{TeO}_2)$ glasses.

Composition x	E_{σ} (eV) (± 0.01)	E_c (eV) (± 0.01)	M_{∞}	β (± 0.01)
0.13	0.41	0.40	0.044	0.49
0.20	0.37	0.37	0.043	0.47
0.30	0.32	0.32	0.041	0.45
0.40	0.26	0.26	0.044	0.43
0.45	0.25	0.25	0.044	0.41

the rate of decrease of the activation energy for glasses with higher AgI content is small. Recently, ionic conductivities of some compositions of AgI doped tellurite glasses have been reported [17, 18]. The increase of the conductivity with AgI content has been observed for AgI content up to 50 mol%, for which compositions homogeneous glasses were obtained. However, the conductivity decreased for the compositions with AgI content more than 50 mol% due to formation of crystalline phases.

The measured ac conductivity for the $0.4\text{AgI}-0.6(0.4\text{Ag}_2\text{O}-0.6\text{TeO}_2)$ glass composition is shown in figure 3 for different temperatures as a function of frequency. It is observed that at low frequencies the conductivity is independent of frequency and corresponds to the

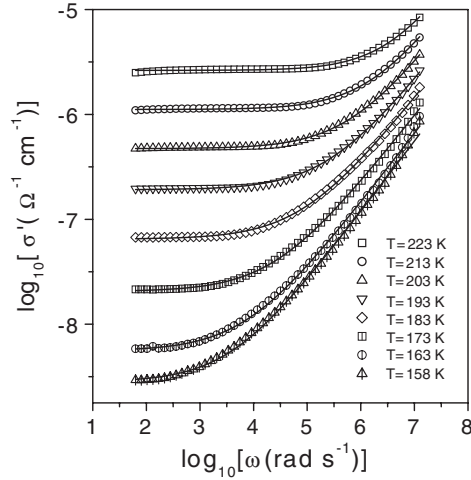


Figure 3. Ac conductivity at different temperatures shown as a function of frequency for the 0.3AgI–0.7(0.4Ag₂O–0.6TeO₂) glass composition. The solid curves are drawn to guide the eye.

dc conductivity. However at higher frequencies it shows dispersion. In the following, we have analysed the above results in the framework of the modulus formalism. In the modulus formalism [19, 20], an electric modulus M^* is defined as the inverse of the complex dielectric permittivity ε^* by [19, 20]

$$\begin{aligned}
 M^* &= M' + jM'' = 1/\varepsilon^* \\
 &= (\varepsilon' - j\varepsilon'')/|\varepsilon|^2 \\
 &= M_\infty \left[1 - \int_0^\infty \exp(-j\omega t) (-d\phi/dt) dt \right]
 \end{aligned} \quad (1)$$

where M' and M'' are the real and imaginary parts 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.

The real and imaginary modulus spectra for a glass composition at different temperatures are displayed in figures 4(a) and (b) respectively. We note in figure 4(a) that the real modulus M' shows dispersion as the frequency is increased and tends to saturate to M_∞ at higher frequencies. The imaginary modulus M'' exhibits a maximum, M''_{\max} , centred at the dispersion region of M' . It is noted that the position of M''_{\max} shifts to higher frequencies for higher temperatures. The conductivity relaxation frequency ω_c , corresponding to M''_{\max} , which indicates transition from a short-range to a long-range mobility at decreasing frequency, gives the most probable conductivity relaxation time τ_c by the condition $\omega_c \tau_c = 1$ [19]. Similar temperature dependence of the modulus spectra of other glass compositions was observed.

Figure 5 shows the reciprocal temperature dependence of the conductivity relaxation frequency ω_c for different glass compositions. We note that ω_c exhibits an activated behaviour obeying the Arrhenius relation $\omega_c = \omega_0 \exp(-E_c/kT)$, where E_c (table 1) is the activation energy for the conductivity relaxation. It may be noted in table 1 that the activation energies for the conductivity relaxation and the dc conductivity are the same within the experimental error. These results imply that the Ag⁺ ions have to overcome the same barrier while conducting as well as while relaxing. We have fitted the experimental data for M' and M'' in figures 4(a) and (b) to equation (1) given by the modulus formalism, following the procedure given by

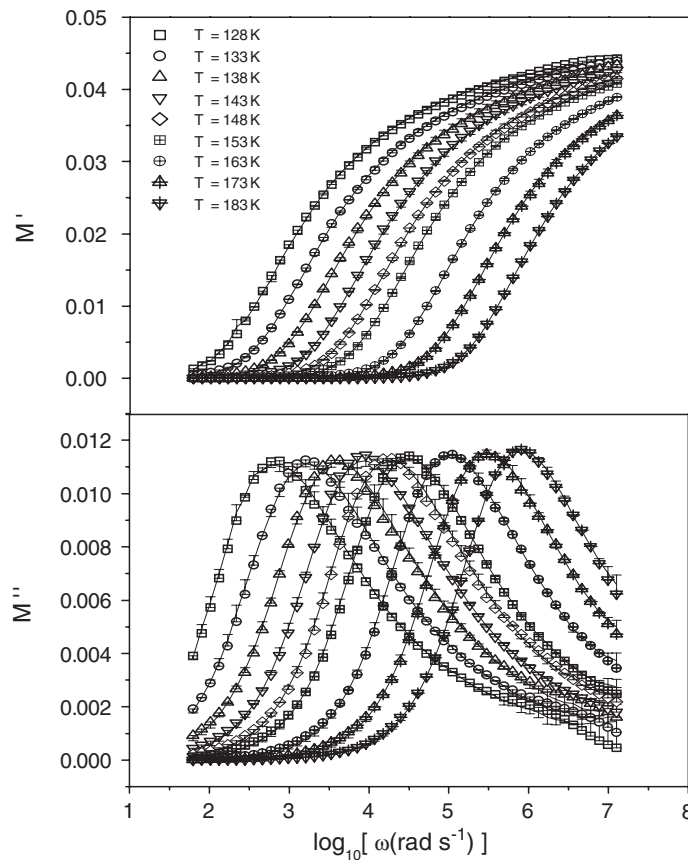


Figure 4. (a) Real and (b) imaginary modulus spectra at different temperatures for the 0.4AgI–0.6(0.4Ag₂O–0.6TeO₂) glass composition. The solid curves are the best fits to equation (1). Error bars are also shown in the figure.

Moynihan *et al* [20]. In the fitting process, we have used the non-exponential Kohlrausch–Williams–Watts (KWW) function [21]:

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

where β is an exponent, which indicates deviation from the Debye relaxation. The values of β and M_∞ obtained from the fit are shown in table 1. We have observed that the values of β are almost independent of temperature and are smaller than unity. The small values of β clearly indicate that the relaxation is highly non-exponential. The composition variation of β is displayed in figure 6. It is noted that values of β decrease with the increase of AgI content in the composition in sharp contrast to the results reported earlier for other series of tellurite glasses [16], where values of β were found to increase with increasing AgI content in the composition. The reason for the difference is not known at present. However, we expect difference in structure might be a reason. It may be further noted that the variation of β for the present glasses with AgI content is consistent with that for the activation energy (figure 2(b)), suggesting the validity of the coupling model of Ngai [22] for the present glasses.

We have shown the scaled spectra for M' and M'' for different temperatures for a glass composition in figure 7. In the scaling process, M' and M'' have been scaled by M_∞ and

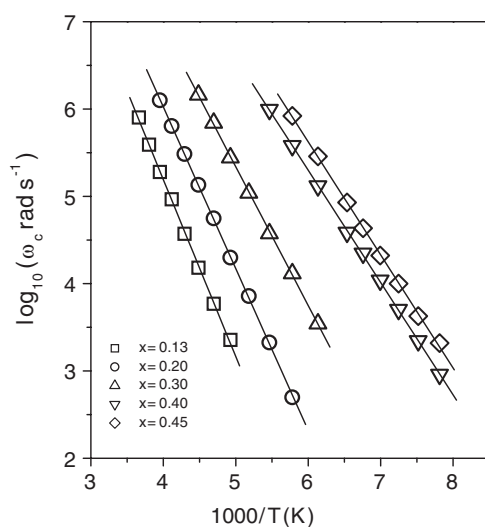


Figure 5. Reciprocal temperature dependence of the conductivity relaxation frequency ω_c for different $x\text{AgI}-(1-x)(0.4\text{Ag}_2\text{O}-0.6\text{TeO}_2)$ glass compositions.

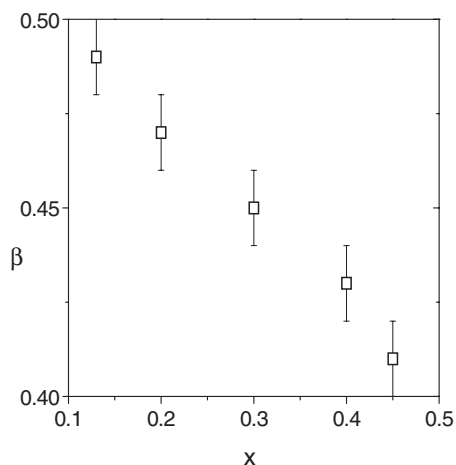


Figure 6. Variation of the non-exponential parameter β with composition for $x\text{AgI}-(1-x)(0.4\text{Ag}_2\text{O}-0.6\text{TeO}_2)$ glasses. Error bars are also shown in the figure.

M''_{\max} respectively, while the frequency axis has been scaled by the conductivity relaxation frequency ω_c . We note that the scaled spectra for M' and M'' for different temperatures merge on a single curve. These results suggest that the dynamic processes occurring at different temperatures are independent of temperature. Such results were also observed for other glass compositions. These results also indicate that the distribution of activation energy is not an appropriate picture for the non-exponential relaxation [23]. It has been proposed that the migration of charge carriers in glasses is highly cooperative [24]. When an ion migrates from one equilibrium position to another, it causes a time dependent movement of other charge carriers in the surroundings, leading to additional relaxation of the applied field. It has been further observed that the smaller the value of β , the larger is the cooperation between charge

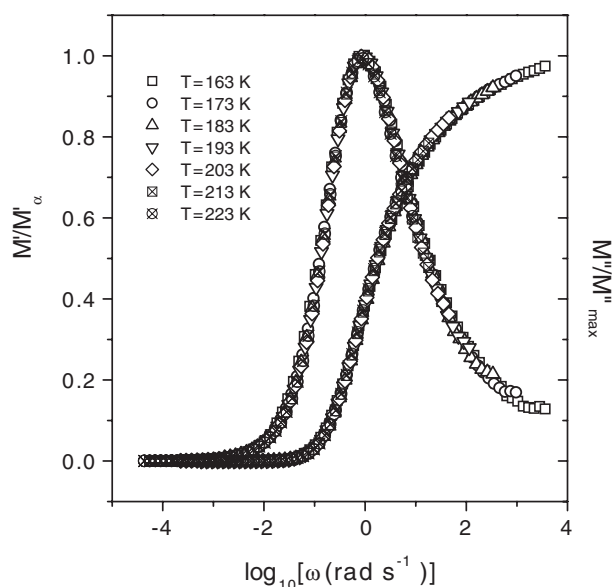


Figure 7. Scaled M' and M'' spectra for different temperatures (shown) for the 0.3AgI–0.7(0.4Ag₂O–0.6TeO₂) glass composition.

carriers [24]. Figure 6 indicates that as the AgI content in the composition is increased, the migration of Ag⁺ ions becomes more cooperative.

4. Conclusions

The conductivity relaxation in the different compositions of x AgI–(1 – x)(0.40Ag₂O–0.60TeO₂) glasses has been studied in the frequency range 10 Hz–2 MHz and in the temperature range 128–303 K. We have observed that the conductivity relaxation is highly non-exponential. The Ag⁺ ions have to overcome the same barrier while relaxing as well as while conducting. Furthermore, the migration of Ag⁺ ions is highly cooperative and the cooperation between Ag⁺ ions increases as the AgI content in the glass composition is increased.

Acknowledgment

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