Transport Properties of Superionic Conducting Glasses (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl)

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In order to identify the dominant mechanism of ionic conduction, the electrical conductivity and ionic mobility of the glasses (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) were measured separately in the temperature range from 293 to 393 K by coupling the AC technique with the TIC method. Electronic conductivity was also measured at 293 K by the Wagner polarization method. The total electrical conductivity of these glasses was found to be as high as $10^{-1} \Omega^{-1} \text{ m}^{-1}$, and the mobility about $10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The variation of total electrical conductivity and mobility at constant temperature and composition with the type of halide occurred in the sequence, Cl < Br < I. For each composition, both conductivity and mobility increased with temperature. The mobile ion concentration was found to be about 10^{23} m^{-3} at 293 K, and it was insensitive to the type of halide as well as temperature. The results suggest that the change in ionic conductivity with the temperature and the type of halide present is mainly attributable to the change in ionic mobility rather than carrier concentration. Moreover, the electronic conductivity was found to be about $10^{-6} \Omega^{-1} \text{ m}^{-1}$ at 293 K. Thus, the electronic contribution to the total conductivity is negligibly small.

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1. Introduction

Superionic conducting (hereafter referred to as SIC) glasses containing Ag⁺ ion have received much attention because of scientific interest in their conduction mechanism as well as their potential application in solid state electrochemical devices. Extensive studies have been carried out to unravel the ion transport mechanism in these glasses. ‘Strong electrolyte’ and ‘weak electrolyte’ models have been proposed to explain Ag⁺ conduction mechanism.^{1,2} Each model is supported by some experimental results. For example, Fontana *et al.*³ support the weak electrolyte model by comparing the Raman scattering intensities of AgI doped borate glasses measured at various temperatures with conductivity data to show that thermally activated ions determine ionic conduction. On the contrary, the results of the Brillouin scattering reported by Börjesson *et al.*^{4,5} suggest that the number of carrier ions is independent of temperature in AgI doped borate glasses. In addition to these two general models, diffusion path model, random site model, cluster-bypass model, and ion association model have also been proposed for explaining the ion conduction mechanism in these glasses.^{6–11} Although these models seem to be successful in explaining the ionic conduction phenomenon in particular glass systems, no general conclusion regarding the conduction mechanism has emerged from the studies reported in the literature. Since, ionic conductivity σ is the product of concentration and mobility of the carrier, it may be possible to distinguish between the two models by focusing attention on both concentration n and mobility μ of the mobile ion.

Although some structural studies on the glass systems (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) have been conducted using spectroscopic methods,^{12–17} no comprehensive study of the transport parameters have been reported. Hence, Ag⁺ ion transport properties in (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3}

(X = I, Br, Cl) glasses have been measured in this study using three different experimental methods in order to shed further light on the conduction mechanism. Conductivity and mobility were measured separately as a function of temperature for different halide dopants. The concentrations of mobile Ag⁺ ion in the various glasses were estimated from measured conductivity and mobility data. In addition, the electronic conductivity was measured using the Wagner polarization method and the ion transport number was evaluated at room temperature (293 K).

2. Experimental Procedure

The glass samples having the composition (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) were prepared from high-grade chemical reagents AgI, AgBr, AgCl, Ag₂O, and GeO₂ (Wako chemical Co. Ltd.). Calculated amounts of the materials were weighed, dried in the oven, and heated in a silica glass tube. After melting in temperature range from 800 to 840 K, the melt sample was quenched between two copper plates. The glassy state of each sample was checked by X-ray diffraction. Samples for conductivity measurement were fabricated with dimensions $8 \times 8 \times 0.5 \text{ mm}^3$. Mass densities of the samples (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) determined by the Archimedeian method with toluene as the liquid medium were 6.53, 6.32 and 5.85 Mg/m³.

Frequency response analyzer (hereafter referred to as FRA, Solatron Instruments model-1260), electrochemical interface (Solatron Instruments model-1287) and electrochemical impedance analysis software (Scribner Associates Inc. Z-plot) were used for electrical conductivity measurement. Frequency and temperature ranges were 1 Hz to 1 MHz and 293 to 393 K, respectively. The following cell using silver paste as electrodes was used for the measurement.

$$(-)\text{Ag/glass}/(+)\text{Ag} \quad (1)$$

Wagner's polarization method was used for evaluating electronic conductivity at 293 K. The electrochemical interface and electrochemical analysis software (Scribner Associates Inc. Corrware) were used for electronic conductivity measurement. Silver paste was coated on one face of a glass sample to act as the reversible electrode, whereas the other face of the sample was coated with graphite paste to form an irreversible electrode. The arrangement can be represented as,

A fixed DC potential of 150 to 300 mV was applied across the sample. The current was monitored as a function of time.

The mobility of the Ag⁺ ion was evaluated in the temperature range between 293 and 393 K from the transient ionic-current (hereafter referred to as TIC) measurement. The electrochemical interface and electrochemical analysis software (Scribner Associates Inc. Corrware) were used for the measurement of mobility. Graphite paste was used to coat as the blocking electrode on both sides of the glass sample.

Firstly, the sample was polarized by applying a fixed DC potential of 50 to 160 mV. After 5 seconds, the polarity of the applied potential was reversed. The current was monitored as a function of time.

3. Results and Discussion

3.1 Electrical conductivity σ measured by the alternating current (AC) method

Figure 1 shows the temperature dependence of electrical conductivity of (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) glasses measured by the AC method. Electrical conductivity of these glasses increases with temperature. The electrical conductivity data fit the Arrhenius equation,^{18,19)}

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (4)$$

where σ_0 is the pre-exponential factor and E_a the activation energy for conduction. k is the Boltzmann constant.

The activation energies of (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} glasses, calculated from the measured conductivity data are shown in Table 1. The activation energy for conduction of these glasses tends to decrease slightly with the type of halide present in the glass in the sequence Cl > Br > I. Generally, pre-exponential factor of superionic conducting materials is lower than that of simple ionic conductors by many orders of magnitude. The magnitude of the pre-exponential factor for the glasses (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl), calculated from the measured conductivity data is of the order of 10⁵ Ω⁻¹ m⁻¹ K, lower than that of crystalline NaCl by a factor of 10² in the temperature range 800 to 1000 K.^{19,20)}

The electrical conductivity of (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) glasses measured by AC method at 293 K, is shown in Fig. 2. Electrical conductivity falls in the range 10⁻² to 10⁻¹ Ω⁻¹ m⁻¹ at 293 K and increases with the size of the halide species.

Fig. 1 Temperature dependence of electrical conductivity σ of the glass (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl).

Fig. 2 Comparison of the electrical conductivity σ of the glass (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) with different halides at room temperature (293 K).

Table 1 Activation energy for conduction E_a , activation energy for migration E_m , electronic conductivity σ_e , and ion transport number t_i of (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) glasses.

	Halogen species X			Unit
	I	Br	Cl	
E_a	0.26 ± 0.02	0.28 ± 0.02	0.29 ± 0.02	eV
E_m	0.20 ± 0.02	0.24 ± 0.02	0.24 ± 0.02	eV
σ_e^*	2.27 ± 0.60	3.85 ± 0.70	3.89 ± 0.80	Ω ⁻¹ m ⁻¹
	× 10 ⁻⁶	× 10 ⁻⁶	× 10 ⁻⁶	
t_i	≈ 1	≈ 1	≈ 1	—

*measured at 293 K

3.2 Electronic conductivity σ_e measured by the Wagner polarization method

It is possible to measure the electronic conductivity and to discern the type of electronic carrier for current by using the Wagner polarization method.²⁰⁻²³⁾ Following Wagner,²¹⁾ the current density J in cell (2) as a function of applied voltage E is given by,

$$J = \frac{I}{A} = \frac{I_e + I_h}{A} = \frac{RT}{LF} \left\{ \sigma_e \left[1 - \exp\left(-\frac{EF}{RT}\right) \right] + \sigma_h \left[\exp\left(\frac{EF}{RT}\right) - 1 \right] \right\} \quad (5)$$

where, I_e and I_h are the currents due to electrons and holes, respectively, R is the gas constant, T is the absolute temperature, A is the electrode area, L is the sample thickness, F is the Faraday constant, E is the applied voltage, and σ_e and σ_h are the conductivities due to free electrons and electron holes, respectively. The electronic conductivity is generally due to electrons or electron holes. If the concentration of electrons is considerably larger than that of holes, $\sigma_e \gg \sigma_h$, the term $\sigma_h[\exp(EF/RT) - 1]$ is negligibly small, and the current density J is dependent directly on the first term of right hand side of eq. (5). Thus, J should exhibit a constant value. In the reverse case, $\sigma_e \ll \sigma_h$, the term $\sigma_e[1 - \exp(-EF/RT)]$ appears to be negligibly small and J increases exponentially with increasing E .

The electronic conductivity of $(\text{AgX})_{0.4}(\text{Ag}_2\text{O})_{0.3}(\text{GeO}_2)_{0.3}$ ($X = \text{I, Br, Cl}$) glasses measured by the Wagner polarization method using the cell (2) at 293 K is shown in Fig. 3. The electronic conductivity of these glasses is nearly independent of voltage in the range from 0.20 to 0.28 V. This current-voltage characteristic indicates that the electronic conductiv-

Fig. 3 Electronic conductivity σ_e of the glass $(\text{AgX})_{0.4}(\text{Ag}_2\text{O})_{0.3}(\text{GeO}_2)_{0.3}$ ($X = \text{I, Br, Cl}$) with a variation of voltage at room temperature (293 K).

ity in this voltage range is mainly caused by electrons rather than holes. The electronic conductivity σ_e at 293 K determined from eq. (5) has a value of about $10^{-6} \Omega^{-1} \text{m}^{-1}$, as shown in Table 1. The ionic contribution to the total electrical conductivity can be expressed by the ion transport number t_i , defined as

$$t_i = 1 - \frac{\sigma_e}{\sigma_{\text{tot}}} \quad (6)$$

where, σ_e is the electronic conductivity and σ_{tot} the total electrical conductivity. The values of ionic transport numbers t_i are also summarized in Table 1. The transport number of Ag^+ ions in these glasses is almost unity and the contribution of electrons to total conductivity is found to be negligibly small since its magnitude is about 4 to 5 orders of magnitude smaller than the total conductivity.

3.3 Mobility μ of mobile Ag^+ ion measured by the TIC method

For the assessment of the dominant factor controlling ionic conductivity in SIC glasses, it is useful to measure the mobility independently. The TIC technique is one of the methods providing direct information on ionic mobility.^{9, 24-28)} In TIC measurement, the mobility μ can be calculated using the relation²⁹⁾

$$\mu = \frac{d^2}{\tau V} \quad (7)$$

where d is the thickness of the sample, V is the reversed constant DC voltage applied, and τ is the time at which the depolarization current attains its maximum value. The value of τ represents the time of flight of the carrier ions across the thickness of the sample. A typical transient ionic current curve for $(\text{AgBr})_{0.4}(\text{Ag}_2\text{O})_{0.3}(\text{GeO}_2)_{0.3}$ glass at 293 K with an applied voltage of 50 mV is shown in Fig. 4. Only one peak is observed in the plot of current versus time. This indicates that only one type of mobile ionic species is present.

Figure 5 shows the temperature dependence of ionic mobility of $(\text{AgX})_{0.4}(\text{Ag}_2\text{O})_{0.3}(\text{GeO}_2)_{0.3}$ ($X = \text{I, Br, Cl}$) glasses measured by the TIC method. All the three results can be represented by an Arrhenius-type equation,

Fig. 4 A typical transient ionic current plot of $(\text{AgBr})_{0.4}(\text{Ag}_2\text{O})_{0.3}(\text{GeO}_2)_{0.3}$ glass at 293 K.

Fig. 5 Temperature dependence of mobility μ of (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) glasses.

$$\mu T = \mu_0 \exp\left(-\frac{E_m}{kT}\right) \quad (8)$$

where μ_0 is the pre-exponential factor and E_m the activation energy for ion migration.

Figure 6 shows the ionic mobilities of (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) glasses with the type of halide dopant used at 293 K. The values fall in the range 10^{-7} to 10^{-5} m² V⁻¹ s⁻¹. The variation observed in ionic mobility is similar to that of ionic conductivity, *i.e.* the ionic mobility increases in the order of AgCl < AgBr < AgI.

The activation energy E_m for ion migration of glass samples calculated by using eq. (8) is shown in Table 1 together with total activation energy E_a for conduction. The activation energy E_m for migration in these glasses increases from 0.20 to 0.24 eV as the doping halide is changed from AgI to AgCl. Activation energy E_a for conduction is expressed as the sum of activation energy E_m for migration and the energy E_f for formation. Table 1 indicates that the values of E_m and E_a are almost the same within the experimental uncertainties. Thus, the energy barrier for ionic conduction is primarily controlled by the activation energy for mobile ion migration rather than the energy required for mobile ion generation.

3.4 Concentration of mobile ion Ag⁺ ion n calculated from σ and μ

Concentration of the mobile Ag⁺ ion n can be calculated from measured values of σ and μ by using the equation:¹⁹⁾

$$n = \frac{\sigma}{q\mu} \quad (9)$$

where q is the charge of the mobile ion. Figure 7 shows temperature dependence of Ag⁺ mobile ion concentration of the

Fig. 6 Comparison of mobility μ of the glass (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) for different halides at room temperature (293 K).

Fig. 7 Temperature dependence of concentration of mobile ion n in the glass (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl).

glasses calculated by using eq. (9) from the measured values of σ and μ . The number of mobile Ag⁺ ions is found to be insensitive to temperature in the range 293 to 393 K. This result is consistent with the conclusions for AgI doped silver borate glasses obtained from Brillouin scattering^{4,5,30)} and for AgI doped silver molybdate glasses from AC conductivity measurement.^{31,32)}

Figure 8 shows mobile Ag⁺ ion concentration n at 293 K for different doping halides. The concentration of mobile Ag⁺ in (AgX)_{0.4}(Ag₂O)_{0.3}(GeO₂)_{0.3} (X = I, Br, Cl) glasses is found to be of 10^{23} m⁻³ and it appears to be insensitive to the type of halogen species present. Moreover, this value is

Fig. 8 Comparison of the concentration of mobile ion n in the glass $(AgX)_{0.4}(Ag_2O)_{0.3}(GeO_2)_{0.3}$ ($X = I, Br, Cl$) glasses with different halides at room temperature (293 K).

much less than the concentration of total Ag^+ ions, order of $10^{33} m^{-3}$ calculated from the chemical composition and measured density of the glasses by using the equation;⁶⁾

$$n_{tot} = \frac{N_A d [Ag^+]}{M} \quad (10)$$

where N_A is the Avogadro number, M is the formula weight and $[Ag^+]$ is the mole ratio of silver in the sample and d is the density of the glassy sample. Then, it is quite likely that extremely small amount of Ag^+ ion contributes to the conduction in these glasses.

The results obtained in this study for $(AgX)_{0.4}(Ag_2O)_{0.3}(GeO_2)_{0.3}$ ($X = I, Br, Cl$) glasses indicate that the concentration of mobile Ag^+ ions is insensitive to change in both halogen species and temperature, whereas ionic mobility increases with temperature and with the doping halide in the sequence, $\mu_{AgI} > \mu_{AgBr} > \mu_{AgCl}$ at constant temperature. These results suggest that the change in ionic conductivity is mainly governed by ionic mobility rather than concentration of the carrier ion.

4. Concluding Remarks

In order to investigate the transport properties in superionic conducting glasses $(AgX)_{0.4}(Ag_2O)_{0.3}(GeO_2)_{0.3}$ ($X = I, Br, Cl$), electrical conductivity and ionic mobility have been measured separately using the standard AC method and the less frequently used the TIC method, respectively. Electronic conductivity was also measured at 293 K by the Wagner polarization method. The results can be summarized as follows:

(1) The total electrical conductivity σ of the glasses is found to be as high as $10^{-1} \Omega^{-1} cm^{-1}$ and the electronic conductivity σ_e about $10^{-6} \Omega^{-1} m^{-1}$ at 293 K. The contribution of electronic conductivity to the total conductivity is negligibly small and ionic transport number is almost unity. The electrical conductivity increases with a change of doping halide in the order $AgCl < AgBr < AgI$.

(2) The mobility μ of mobile Ag^+ ion is as high as $10^{-6} m^2 V^{-1} s^{-1}$ at 293 K and it increases with the type of doping halide in the order of $AgCl < AgBr < AgI$.

(3) The concentration of mobile Ag^+ ion n is about $10^{23} m^{-3}$ at 293 K. It is found to be insensitive to the type of doping halide as well as temperature.

(4) These results suggest that the change in ionic conductivity of superionic conducting glasses $(AgX)_{0.4}(Ag_2O)_{0.3}(GeO_2)_{0.3}$ ($X = I, Br, Cl$) with variations of doping halide and temperature is mainly attributable to the change in ionic mobility rather than carrier concentration.

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