Ionic Conductivity of Superionic Conducting Glasses in the Pseudobinary System AgI–Ag$_2$MoO$_4$

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The ionic conductivity was measured in the temperature range 250–300 K as a function of composition of superionic conducting glasses in the pseudobinary system AgI–Ag$_2$MoO$_4$. The conductivity, ranging from 10^{-2} to 10^{-4} Ω^{-1} cm^{-1} at room temperature, increases linearly in logarithmic scale with increasing AgI content, while the total silver ion concentration remains nearly constant in the whole glass-forming region of the present system. Such a composition dependence of conductivity is considered to be evidence that only a fraction of the silver ions in glass contributes to the ionic conduction. The conductivity and the activation energy for conduction differ slightly between bulk glasses and pressed pellets of pulverized glasses. The close agreement in bulk glasses and pellets suggests that bulk rather than grain boundary or surface diffusion dominates the conduction process in the present glasses.

1. Introduction

Recently much attention has been paid to superionic conductors of glassy materials, i.e., "superionic conducting glasses" (*1–7*). In these glasses containing a large amount of silver iodide, ionic conductivities as high as 10^{-2} Ω^{-1} cm^{-1} (at room temperature) were reported, bringing a striking contrast to ordinary insulating glasses such as silicates, borates, phosphates, and so on.

There was a postulation that the high ionic conductivity of these glasses resulted from silver ion migration along the grain boundary or surface of the pulverized samples, which contained conductive silver iodide finely dispersed in the glass matrix (*6*). (As is well known, the conductivity of superionic conductors is usually measured for pressed pellets of powders.)

There are two different points of view concerning the concentration of mobile ions (Ag$^+$) in the crystalline superionic conductors based on silver iodide; all (*8*) or only a fraction (*9, 10*) of silver ions are supposed to contribute to the ionic conduction. For glassy superionic conductors there are very few papers (*5, 7*) reporting on the concentration of mobile ions.

In a previous note (*11*) we reported that the glasses in the system AgI–Ag$_2$O–MoO$_3$ have higher ionic conductivities with silver ion transport number of unity than the crystallized samples. The main purpose of the present paper is to show that in the glasses of this system with the mole ratio Ag$_2$O/MoO$_3$ = 1, i.e., the pseudobinary system AgI–Ag$_2$MoO$_4$, bulk diffusion is predominant in the silver ion migration and only some of silver ions participate in the conduction of the glasses.

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2. Experimental

Mixtures of desired amounts of AgI and Ag_2MoO_4 were melted at 500°C for 5–7 hr in a Pyrex glass tube and the resultant melts were poured onto a stainless-steel plate; AgI and Ag_2MoO_4 were prepared by the wet method from special grade chemicals, $AgNO_3$ and KI or Na_2MoO_4.

Conductivities were measured at 1000 Hz in an electrically shielded chamber filled with dry nitrogen gas by using a universal bridge (YPH, Model 4260A) and/or a G–C bridge (Ando Denki, Model TR-1C). The error in the measurements of conductivity was less than ±10% (11). Two types of samples were used for the measurements. First, as an ordinary method in the measurement for superionic conductors, pulverized glasses were pressed together with electrode mixtures of silver (0.9 g) and glass (0.3 g) powders under 2 tons/cm^2 to form pellets 13 mm in diameter. Second, bulk glasses with evaporated silver electrodes were used; the three-terminal method with a guard ring was employed.

The activation energy for conduction was determined by least squares of the conductivity vs temperature relation: the calculated values of probable errors were in the range ±(0.03 to 0.16) kcal/mole for each sample (both bulk and pellet).

Densities were measured at room temperature (25 ± 2°C) for bulk glasses by the Archimedean method, using ethylene glycol as a medium.

3. Results and Discussion

3.1. Constituent Ion Concentration in the Glasses

According to previous results (12), the glasses in the pseudobinary system AgI–Ag_2MoO_4 are composed of Ag^+, I^-, and MoO_4^{2-} ions only. In such glasses the concentration of each constituent ion can be calculated from the chemical composition and density.

Table I summarizes the composition and calculated ion concentrations for bulk glasses. The compositions shown in this table cover almost the entire region of glass formation in the system AgI–Ag_2MoO_4 (13). The packing density, which is the volume percentage of space occupied by the ions in the glass, was calculated by assuming that Ag^+, I^-, and MoO_4^{2-} ions are hard spheres of 1.12, 2.20, and 2.54 Å radius, respectively (14). It is worth noting in the table that the silver ion concentration is nearly constant with the variation of composition and the packing density is fairly large in comparison with ordinary silicate glasses (15).

3.2. Contact Resistance

It has been reported that the electrode made of mixtures of electrolyte and silver

TABLE I

COMPOSITION AND ION CONCENTRATION OF BULK GLASSES IN THE SYSTEM AgI–Ag_2MoO_4

Glass number	Composition (mole %)		Density (g/cm^3)	Ion concentration ($\times 10^{-2}$ mole/cm^3)			Packing density (%)
	AgI	Ag_2MoO_4		Ag^+	I^-	MoO_4^{2-}	
1	75	25	6.27	2.90	1.74	0.580	81.3
2	70	30	6.24	2.93	1.58	0.677	81.0
3	66.7	33.3	6.22	2.94	1.47	0.735	80.5
4	60	40	6.20	2.98	1.28	0.852	80.4
5	57	43	6.18	2.99	1.20	0.897	80.1

powders, as described in Section 2, can minimize the contact resistance of the electrode/electrolyte interface (16, 17). A few examples of the resistance measured for pellets with such electrodes are shown in Fig. 1 as a function of thickness of the pellets; Glass 2 was used. Evidently the lines at each temperature pass quite closely through the origin. Thus the contact impedance is bypassed at the employed frequency of 1000 Hz, so that the obtained conductivity values are reasonably considered independent of the electrode/electrolyte interface.

Figure 2 shows the resistance of the bulk glass (Glass 2) with different thicknesses ranging from 0.7 to 2 mm. Evidently the conductivities are again considered independent of the electrode/electrolyte interface.

3.3. Temperature Dependence of Conductivity

The comparison of conductivity between bulk glasses and pellets is shown in Fig. 3 as a function of temperature. Results of three glasses only are presented to avoid the confusion of plots. The conductivity σ is expressed by

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E_\sigma}{RT}\right), \qquad (1)$$

FIG. 2. Resistance of bulk glasses (Glass 2) with different thicknesses. The evaporated silver was used as the electrodes (6.3 mm in diameter).

where T is the absolute temperature, σ_0 a constant, R the gas constant, and E_σ the activation energy for conduction. The conductivities of pellets at a given temperature are slightly smaller than those of bulk glasses, and the slopes are similar.

3.4. Composition Dependence of Conductivity and Activation Energy

Figure 4 shows the composition dependence of conductivity at 25°C, σ_{25}. Circles are for bulk glasses and triangles for pellets. The largest values of σ_{25} reach as high as $1.4 \times 10^{-2} \ \Omega^{-1} \ cm^{-1}$.
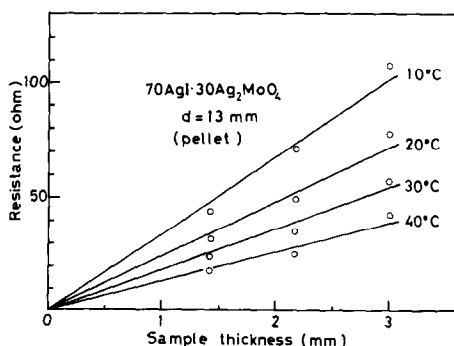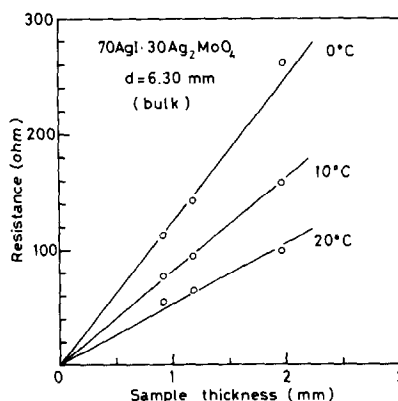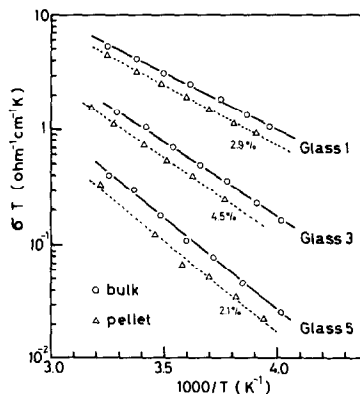

FIG. 1. Resistance of pellets of Glass 2 with different thicknesses. The electrodes (13 mm in diameter) were composed of silver and glass powder mixtures.

FIG. 3. Temperature dependence of conductivity in AgI-Ag₂MoO₄ glasses. Percentages are voids present in the pellets.

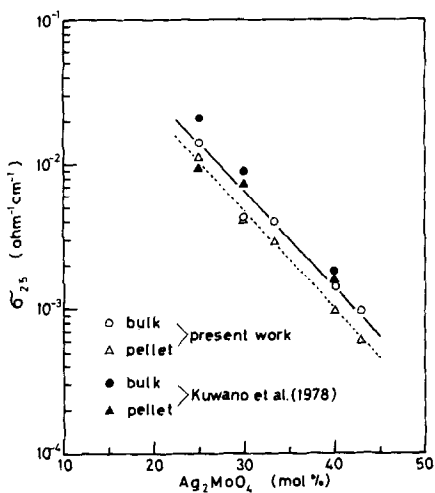FIG. 4. Composition dependence of the conductivity at 25°C, σ_{25}, in the AgI–Ag$_2$MoO$_4$ glasses.

FIG. 5. Composition dependence of the activation energy for conduction, E_σ, in the AgI–Ag$_2$MoO$_4$ glasses.

In spite of the fact that the silver ion concentration in the glasses is nearly constant, as shown in Table I, σ_{25} varies appreciably with composition. A tentative way to explain this composition dependence is to assume that all the silver ions do not participate in the ionic conduction but only a part of the ions contribute to the conduction. Such partial contribution to the conduction has also been reported for some superionic conducting glasses based on silver iodide (5, 7). Conductivities of bulk glasses slighly larger than those of pellets must be evidence that the surface or boundary diffusion of mobile ions (Ag$^+$) is not dominant but that the bulk diffusion plays an important role in the superionic conduction of the present glasses.

Figure 5 shows the composition dependence of E_σ. Open circles are for bulk glasses and triangles for pellets. The values for pellets are slightly larger (about 0.3–0.7 kcal/mole) than those for bulk glasses. The fact that E_σ for bulk glasses is not larger than that for pellets must serve as evidence that the bulk diffusion is the dominant process in the migration of silver ions.
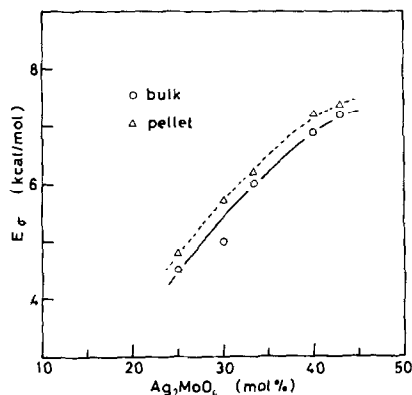
It is noticeable that the roughly extrapolated value of E_σ to 0% Ag$_2$MoO$_4$ is smaller than that of α-AgI (=2.3 kcal/mole) (8). The heat of transport of silver ions in the present glasses is now under study through the measurement of thermoelectric power, and more detailed discussion on E_σ and the conduction mechanism will be published in the future.

Acknowledgments

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