Stabilization of Superionic α-AgI at Room Temperature by Heating of AgI–Ag_2O–MoO_3 Glasses

Masahiro Tatsumisago, Taira Saito, and Tsutomu Minami
Department of Applied Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531

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We successfully prepared the superionic composites in which only the high-temperature phase of α-AgI was stabilized at room temperature in a superionic glassy matrix by a simple procedure with heating and consecutive cooling of AgI–Ag_2O–MoO_3 glasses. In the composites, α-AgI microcrystals were dispersed in the glassy matrix.

Nonflammable inorganic solid electrolytes have been getting into the limelight as much safer electrolytes in rechargeable batteries for portable electronic devices like cellular phones.[1,2] The high temperature and superionic phase of AgI, α-AgI, has long been investigated as a prototype of excellent inorganic solid electrolytes.[3] This phase is, however, thermodynamically stable only above 147 °C.

Several years ago, we succeeded in stabilizing α-AgI in superionic glasses at room temperature by a rapid melt–quenching technique.[4] The obtained α-AgI stabilized composites, in which fine particles of α-AgI are dispersed in a matrix glass, exhibited very high conductivity at room temperature.[4,5] However, by this special procedure, it is difficult to control the microstructure of the composite such as crystal size of α-AgI and thus to control the composite properties which are important in their application.

Here we report our success in preparation of the α-AgI stabilized composites by a simple procedure with heating and consecutive cooling[6,7] of AgI–Ag_2O–MoO_3 glasses. The obtained composites, in which α-AgI microcrystals are dispersed in a glass matrix, exhibited high ion conductivities of 10^{-2} to 10^{-1} S cm^{-1} at room temperature.

Reagent grade chemials of AgI, Ag_2O, and MoO_3 were used as starting materials for sample preparation. Batches of the mixed materials were melted at 700 °C for 30 min in a silica glass tube with one open end in an electric furnace. The resultant melts were quenched using twin rollers to form flakelike samples.[8] The samples were heat treated with a constant heating rate of 10 °C/min up to 80–160 °C and then cooled to room temperature by taking them out of an electric furnace. The compositions studied here are 66–82 mol% AgI in the system AgI–Ag_2O–MoO_3 (Ag_2O/MoO_3 mole ratio = 0.5).

X-ray diffraction (XRD) measurements were carried out at various temperatures for flakelike samples glued onto a copper plate using a MAC Science M18XHF^{22}-SRA. The microstructures of the glasses were observed with a Hitachi S-4500 FE-SEM. Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC-7. From the XRD measurements of the rapidly quenched samples of $xAgI\cdot(100-x)(0.33Ag_2O\cdot0.67MoO_3)$ (in mol%), glass formation was observed in the compositions with $x \le 74$. The mixture of the α- and β-phases of AgI was precipitated in the compositions with $74 \le x \le 82$. The composition $74AgI\cdot26(0.33Ag_2O\cdot0.67MoO_3)$ was thus found to correspond to the glass with the largest amount of AgI. DSC of the quenched $74AgI\cdot26(0.33Ag_2O\cdot0.67MoO_3)$ glass showed that two exothermic peaks at 90 and 140 °C were observed and an endothermic peak at 145 °C was observed just after the second exothermic peak in the DSC curve. The XRD measurements for the same quenched glass at various temperatures with a high temperature XRD apparatus in the heating process revealed that the exothermic peaks at 90 °C and 140 °C were due to the crystallization of α-AgI and the transformation of α-AgI to the β-phase. The endothermic peak at 145 °C was attributable to the transformation of β-AgI to the α-phase.

Since the α-AgI crystals were found to be formed by the heat treatment at temperatures higher than 90 °C, the glass was heated up to various temperatures and consecutively cooled down to room temperature in order to stabilize the α-phase at room temperature. Figure 1 shows the XRD patterns at room temperature of the heat-treated $74AgI\cdot26(0.33Ag_2O\cdot0.67MoO_3)$ samples; the heat treatment temperatures are 100, 110, 120 and 130 °C. The pattern for the α-AgI-stabilized $82AgI\cdot18(0.33Ag_2O\cdot0.67MoO_3)$ composite prepared by the rapid quenching of melt is also shown for comparison. Open and closed circles denote the diffraction peaks due to α- and β-AgI, respectively. The halo pattern due to amorphous state without any crystalline peaks is observed in the as-prepared sam-

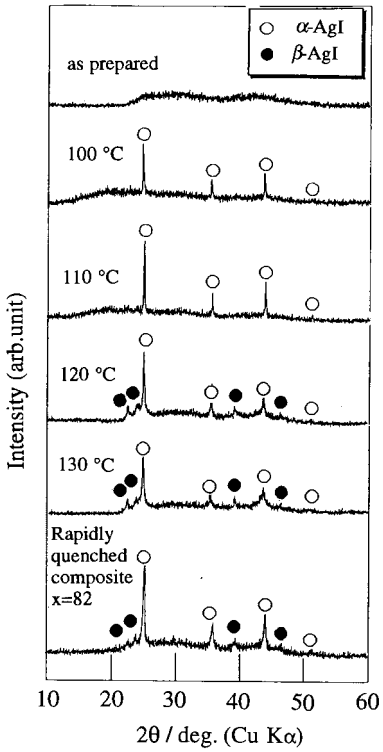

Figure 1. XRD patterns at room temperature of the $74AgI\cdot26(0.33Ag_2O\cdot0.67MoO_3)$ sample prepared by heating and consecutive cooling of glass; the heat treatment temperatures are 100, 110, 120 and 130 °C. The pattern for the α-AgI-stabilized $82AgI\cdot18(0.33Ag_2O\cdot0.67MoO_3)$ composite prepared by the rapid quenching of melt is also shown for comparison.

ple before heating. Intense peaks due to α-AgI are observed for the heat treated samples at 100 and 110 °C, indicating that the α-AgI microcrystals are successfully stabilized at room temperature in a glass matrix by heating and consecutive cooling of the $74AgI{\cdot}26(0.33Ag_2O{\cdot}0.67MoO_3)$ glass. When the heat treatment temperatures are 120 and 130 °C, weak diffraction peaks due to β-AgI are observed in addition to the peaks due to α-AgI. The XRD pattern of the rapidly quenched $82AgI{\cdot}18(0.33Ag_2O{\cdot}0.67MoO_3)$ composite indicates that weak diffraction peaks due to β-AgI are also observed as well as the intense peaks due to α-AgI. In the case of rapid quenching of melt we could not obtain the single phase of α-AgI in the system $AgI–Ag_2O–MoO_3$ as shown in Figure 1.[8] On the other hand, it is noteworthy that the single phase of α-AgI has been obtained at room temperature by the heat treatment of the glass at 100 and 110 °C.

Figure 2 shows a photograph of the FE-SEM cross-section for the $74AgI{\cdot}26(0.33Ag_2O{\cdot}0.67MoO_3)$ sample heat treated at 110 °C. The white particles and the black continuous part are fine α-AgI microcrystals and an $AgI–Ag_2O–MoO_3$ glass matrix, respectively. The α-AgI microcrystals, the size of which are about 10–40 nm in diameter, are apparently present as the dispersed phase in the composite. This morphology is basically similar to that of the rapidly quenched and α-AgI stabilized $AgI–Ag_2O–B_2O_3$ composites and the size distribution of α-AgI microcrystals is a little broader than that in the twin-roller quenched composites.[5]

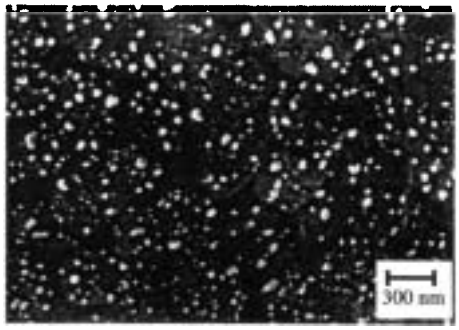

Figure 2. FE-SEM cross section for the α-AgI-stabilized $74AgI{\cdot}26(0.33Ag_2O{\cdot}0.67MoO_3)$ composite prepared by heating and consecutive cooling of glass; the heat treatment temperature is 110 °C.

Figure 3 shows the temperature dependence of conductivity for the α-AgI-stabilized $74AgI{\cdot}26(0.33Ag_2O{\cdot}0.67MoO_3)$ composite prepared by the heating and cooling process of glass. The conductivity of a pure AgI crystal is also shown for comparison. The conductivity at room temperature for the composite is about 1×10^{-1} S cm^{-1}; such extremely high ion conductivity is expected if the composite composed of the stabilized α-AgI microcrystals and the superionic conducting glass are formed. The activation energy in the temperature range 25 to 120 °C was 12 kJ mol^{-1}. These values are reasonable if the stabilized α-AgI phase is present as highly dispersed, discrete particles, the conductivity of which was calculated by the Bruggeman's equation for the conductivity of composite materials.[5] With increasing temperature, a small conductivity drop is observed at 140 °C, which corresponds to the sharp exothermic peak in the DSC curve mentioned above and is due to the α to β transformation of the stabilized α-AgI microcrystals.

In the system $AgI–Ag_2O–MoO_3$, the single phase of α-AgI could not be obtained by rapid quenching of melt as shown in

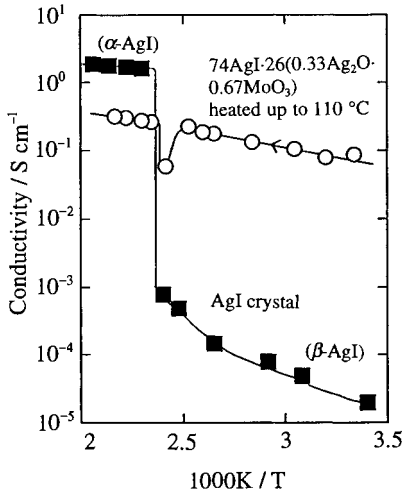

Figure 3. Temperature dependence of conductivity for the α-AgI-stabilized $74AgI{\cdot}26(0.33Ag_2O{\cdot}0.67MoO_3)$ composite prepared by heating and consecutive cooling of glass; the heat treatment temperature is 110 °C.

Figure 1. We reported that it was difficult to stabilize α-AgI in glass matrices with low glass-transition temperatures such a system $AgI–Ag_2O–MoO_3$ because of the low viscosity at the α–β transformation temperature 147 °C.[8] On the other hand, the single phase of α-AgI was successfully obtained in the system $AgI–Ag_2O–MoO_3$ in the case of the heating and consecutive cooling process of glasses, indicating that the high viscosity is not the factor to depress the α-β transformation of AgI at the temperature range below 147 °C.

It is interesting to notice that the XRD peaks of α-AgI in the $74AgI{\cdot}26(0.33Ag_2O{\cdot}0.67MoO_3)$ composite prepared by the glass heating are much sharper than those of the rapidly quenched $82AgI{\cdot}18(0.33Ag_2O{\cdot}0.67MoO_3)$ composite as shown in Figure 1. The Hall's analysis for the XRD peak widths[9] revealed that the $74AgI{\cdot}26(0.33Ag_2O{\cdot}0.67MoO_3)$ composite prepared by heating and consecutive cooling of glass had no lattice strain at room temperature like the pure α-AgI at 150 °C, whereas the α-AgI crystal stabilized by rapid quenching of the $82AgI{\cdot}18(0.33Ag_2O{\cdot}0.67MoO_3)$ melt had a large lattice strain, indicating that the presence of lattice strain in the α-AgI crystal is not indispensable for the stabilization of α-phase at room temperature. Thus, we can obtain the composite in which the single phase of α-AgI is stabilized without any lattice strain in the $AgI–Ag_2O–MoO_3$ glass matrix with such a low glass-transition temperature.

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