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Fabrication of mesoscopic composites composed of α-AgI and AgI-based superionic glass[1]

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Abstract

The superionic conducting phase of α-AgI, which is thermodynamically stable only above 147°C, was frozen at room temperature in AgI–Ag_2O–B_2O_3 glasses prepared by twin-roller rapid quenching. Such α-AgI frozen samples exhibited extremely high ion conductivities of about 10^{-2}–10^{-1} S cm^{-1} at room temperature. Spherical particles of α-AgI (about 30 nm in diameter) were observed to be homogeneously dispersed in a glass matrix. Heating the composite up to temperatures higher than 80°C, which is near the glass transition temperature of the matrix glass, brought about the relaxation of the lattice strain of α-AgI originally generated by the presence of the rigid glass matrix, and accelerated the α- to β-phase transformation. At low temperatures, much larger lattice strain, instead of the $\alpha \rightarrow \beta$ transformation, was observed below −10°C, where the activation energy for conduction changed abruptly and the heat capacity was maximized. Such anomalies at around −10°C were associated with the ordering of Ag^+ ions in the frozen α-AgI.

Keywords: Activation energy; DSC; Glass composite; Phase transformation; Superioniccon-ductor; XRD

1. Introduction

A process in which some special crystals are precipitated from homogeneous glasses has produced several kinds of new functional materials like the CdS_xSe_{1-x} semiconductor microcrystallite-doped glasses which are of growing interest as nonlinear optical materials [1]. In such a process, the products can be considered as glass-crystal mesoscopic composite materials.

Recently, we have discovered that the superionic conducting crystalline phase of α-AgI, which is thermodynamically unstable below 147°C, is successfully frozen in

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[1] Dedicated to Professor Hiroshi Suga.

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superionic glass matrices at room temperature by the rapid quenching of AgI supersaturated melts [2]. The glass-crystal composites produced containing α-AgI were found to exhibit extremely high ionic conductivities. The rapid quenching of supersaturated melts, which was essential to obtain the frozen α-AgI, must be a potential technique to obtain new types of glass-crystal mesoscopic composite materials.

In the present paper, we report the formation, structure, phase transformation, and low-temperature behavior of the α-AgI-frozen composite $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ (in mol%) prepared by the rapid quenching technique.

2. Experimental

Commercial powders of AgI, Ag_2O, and B_2O_3 were used as starting materials for the preparation of the $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ (mol%) composite. Details of the preparation technique were described in a previous paper [3].

X-ray diffraction measurements were carried out on the flake-like samples glued on a glass substrate, using a Rigaku Denki Rotaflex instrument. Differential scanning calorimetry (DSC) was performed using a Rigaku Denki TAS-100 thermal analyzer. Conductivity was measured for the flakes, on which two parallel gold electrodes were evaporated, using an impedance analyzer (HP4192A) in dry nitrogen atmosphere.

3. Results and discussion

3.1. *Formation of α-AgI frozen superionic composites*

Fig. 1 shows the X-ray diffraction patterns at room temperature for the $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ samples quenched at several cooling rates. Open and solid circles denote the diffraction peaks due to α- and β-AgI, respectively. The metal-plate press-quenching results in the formation of only β-AgI, as expected. However, when twin-roller quenching is used, diffraction peaks due to α-AgI are observed and the peak intensity is increased with an increase in the cooling rate [2, 3].

Fig. 2 shows an FE-SEM photograph for the twin-roller-quenched sample of $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ in which α-AgI was frozen at room temperature. The upper and lower parts of the photograph show the surface and the cross-section of the flake-like sample, respectively. The white particles and the black continuous area observed in the cross-section are small α-AgI crystal and $AgI-Ag_2O-B_2O_3$ glass matrix, respectively. The α-AgI crystals, the size of which are about 20–40 nm in diameter, apparently exist as the dispersed phase in the composite [4].

Fig. 3 shows the temperature dependence of the ionic conductivity for the twin-roller-quenched $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composite. The conductivity of an AgI crystal flake prepared by twin-roller-quenching of pure AgI melt is also shown for comparison. The conductivity at room temperature for the composite is about 10^{-1} S cm^{-1} and the activation energy in the temperature range 25–140°C is 15 kJ mol^{-1} [5]. These values are reasonable if the frozen α-AgI phase is present as highly dispersed,

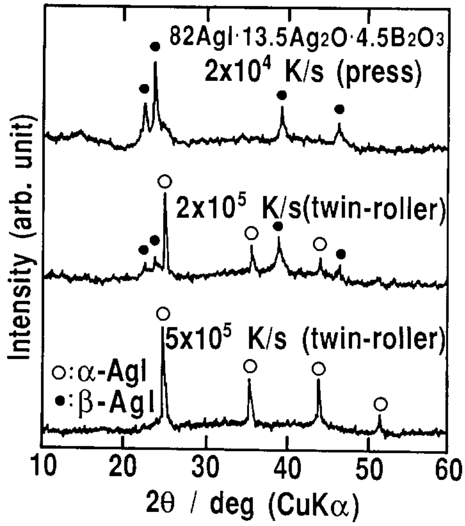

Fig. 1. X-ray diffraction patterns for the melt-quenched samples of $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ with different cooling rates.

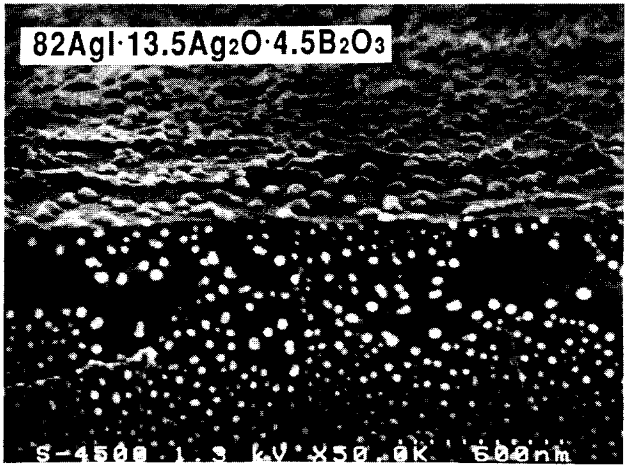

Fig. 2. FE-SEM photograph of the twin-roller-quenched $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composite in which α-AgI was frozen at room temperature.

discrete particles, as shown in Fig. 2, the conductivity of which is calculated by Bruggeman's equation [6].

With increasing temperature, a small conductivity change is observed near the $\alpha \rightarrow \beta$ transformation temperature of 147°C, which is probably due to a small amount of residual β-phase. With decreasing temperature, however, no change in conductivity is

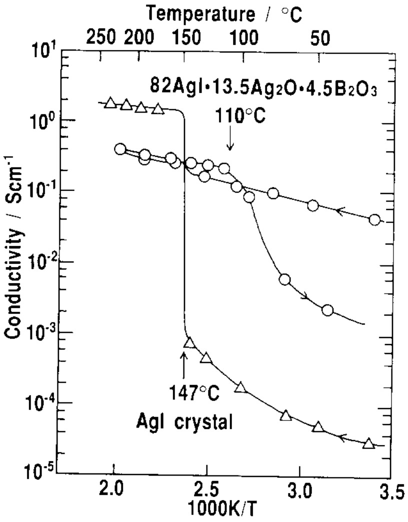

Fig. 3. Temperature dependence of conductivity for the twin-roller-quenched samples of $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ in which α-AgI was frozen at room temperature and for the AgI crystal.

observed at 147°C, and the conductivity starts to decrease considerably at 110°C. The conductivity decrease is due to the $\alpha \rightarrow \beta$ transformation of the AgI crystal in glass matrices. This result indicates that even if the cooling rate is small, as in the conductivity measurements, glass matrices with high viscosity suppress the $\alpha \rightarrow \beta$ transformation.

3.2. *Phase transformation behavior of α-AgI frozen in glass matrices*

As shown in Fig. 3, $\alpha \rightarrow \beta$ transformation of the α-AgI frozen in the composite has been observed when it was heated up to temperatures higher than 147°C. Fig. 4 shows the cooling curves of DSC for the twin-roller-quenched $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composite after heating at a variety of temperatures [7]. The cooling rate is 10°C min^{-1}. The exothermic peaks are observed in cooling curves after heating up to any temperature except for 80°C. These exothermic peaks were confirmed as being due to the $\alpha \rightarrow \beta$ transformation of AgI by the high-temperature X-ray diffraction measurements. The onset temperature and the intensity of the exothermic peaks are decreased with a decrease in heating temperature. However, the exothermic peak due to the $\alpha \rightarrow \beta$ transformation is not observed in the case of the cooling curve from 80°C. These results indicate that the suppressing effect of the $\alpha \rightarrow \beta$ transformation becomes strong with a decrease in the heating temperature of the composites and the transformation cannot be observed when the heating temperature is lower than 80°C.

Incidentally, it has been observed that the diffraction peaks of α-AgI in the composite at 25°C, shown in Fig. 1, were broader than those of pure α-AgI at 150°C. In addition, the full widths at half maximum intensity (FWHM) of each diffraction peak in the

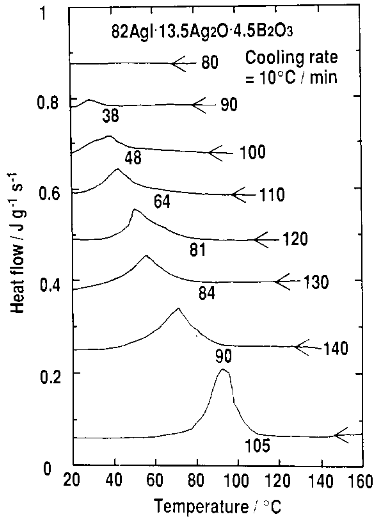

Fig. 4. DSC cooling curves for the α-AgI-frozen $82AgI\cdot13.5Ag_2O\cdot4.5B_2O_3$ composite. The heating temperatures before measurement are different.

composite tended to become larger with increasing Bragg angles, while those in the pure α-AgI were not changed.

Broadening of X-ray diffraction peaks is usually caused by a decrease in a crystallite size and/or an increase in the heterogeneous lattice strain (non-uniform deformation) of the crystal. These two factors can be evaluated separately by Hall's analysis using more than two diffraction peaks [8]. Hall's equation is expressed as

$$\beta_{\mathrm{hkl}} \cos\theta/\lambda = 2\eta \sin\theta/\lambda + K/D \qquad (1)$$

where β_{hkl} is the FWHM of a given (hkl) diffraction peak, λ is the wavelength of the X-ray, D is the crystallite size, η is a measure of heterogeneous lattice strain, θ is the Bragg angle, and K is a constant of 0.9.

Fig. 5 shows the relation between $\beta_{\mathrm{hkl}} \cos\theta/\lambda$ and $\sin\theta/\lambda$ for the (110) and (220) diffraction peaks of α-AgI in the $82AgI\cdot13.5Ag_2O\cdot4.5B_2O_3$ composite at 25°C and the pure α-AgI crystal at 150°C [4]. The values of η in Eq. (1), the measure of lattice strain, are obtained from the slopes of the plots. It is apparent that α-AgI in the composites at 25°C has a larger lattice strain than the pure α-AgI crystal at 150°C. Such a large lattice strain of frozen α-AgI at 25°C must be caused by the stress at the interface between the AgI crystals and the glass matrix during rapid quenching. The surrounding glass matrix suppresses the transformatioin of α-AgI to the β-phase because the β-phase is larger than the α-phase by about 6% in molar volume.

The crystallite size of α-AgI in the composite is estimated to be about 30–40 nm, which is in good agreement with the particle size of α-AgI observed by FE-SEM shown in Fig. 2.

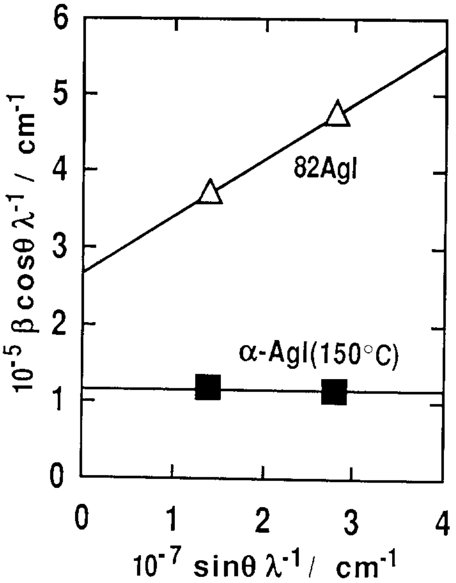

Fig. 5. Hall's plots for the diffraction peaks of the $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composites and the α-AgI crystal at 150°C.

Fig. 6 shows the temperature dependence of the lattice strain η, estimated from the temperature dependence of X-ray diffraction patterns of the $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composite [7]. The $\alpha \rightarrow \beta$ transformation temperatures ($T_{\alpha\text{-}\beta}$) shown in the DSC cooling curves of Fig. 4 are also plotted against the heating temperatures in Fig. 6. The η value is large at room temperature and decreases with increasing temperature. When the

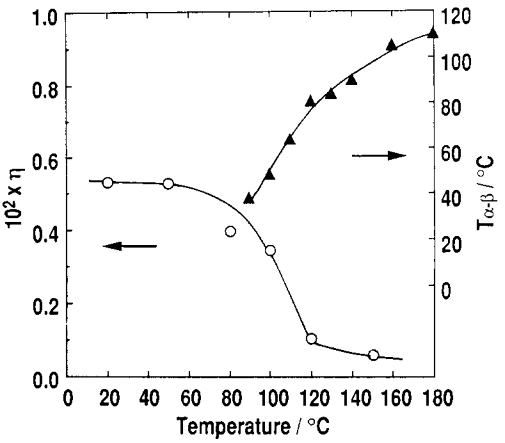

Fig. 6. Temperature dependence of the lattice strain η of α-AgI frozen in the $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composite. The relation between $T_{\alpha-\beta}$ and the heating temperature is also shown.

heating temperature is higher than 80°C, the $\alpha \rightarrow \beta$ transformation only occurs during cooling after the lattice strain of α-AgI frozen in the glass matrix is decreased to some extent by heating at a variety of temperatures above 80°C. The glass transition temperature (T_g) of this matrix glass has been found to be about 80–90°C. The lattice strain caused by the stress in the interface between the AgI crystal and the glass matrix is relaxed largely by annealing near T_g. The $\alpha \rightarrow \beta$ transformation is found to occur on cooling only when the heating temperature is higher than the T_g of matrix glasses, which corresponds to the temperature at which the η value is considerably decreased.

3.3. Low-temperature behavior of the α-AgI frozen composite

Although the α-AgI crystals frozen in the matrix glasses were found to be stable at room temperature, there may be some possibility that the $\alpha \rightarrow \beta$ transformation was observed at much lower temperatures. Fig. 7 shows the X-ray diffraction patterns of the twin-roller-quenched $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composite at various temperatures: (a) the cooling process from 25 to −187°C; (b) the heating process from −130 to 25°C [9]. Intense peaks due to α-AgI with very weak peaks due to β-AgI are observed in the room temperature pattern before cooling. A broadening of the α-AgI peaks is apparently observed with decreasing temperature down to −187°C. It is noteworthy that the growing of any β-AgI peak does not occur at that time, suggesting that the broadening of the α-AgI peaks does not mean the $\alpha \rightarrow \beta$ transformation being present in the

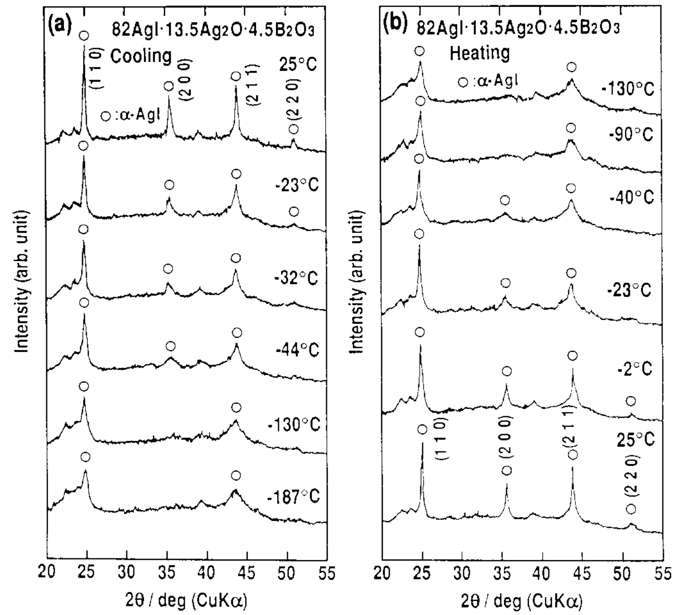

Fig. 7. X-ray diffraction patterns of the α-AgI-frozen $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composite: (a) cooling run; (b) heating run.

low-temperature ranges below room temperature. The broadened α-AgI peaks at low temperature become sharper again with increasing temperature as shown in Fig. 7(b). The profile of the final pattern at 25°C is almost the same as the original one before cooling, indicating that the broadening of the α-AgI peaks with cooling is a reversible phenomenon.

From Hall's analysis, it was found that α-AgI in the composite at lower temperatures had a much larger lattice strain than that at room temperature. Fig. 8 shows the temperature dependence of values of η in Hall's Eq. (1) (heating process). Although the η values are very large at around −100°C, they are decreased drastically at approx.

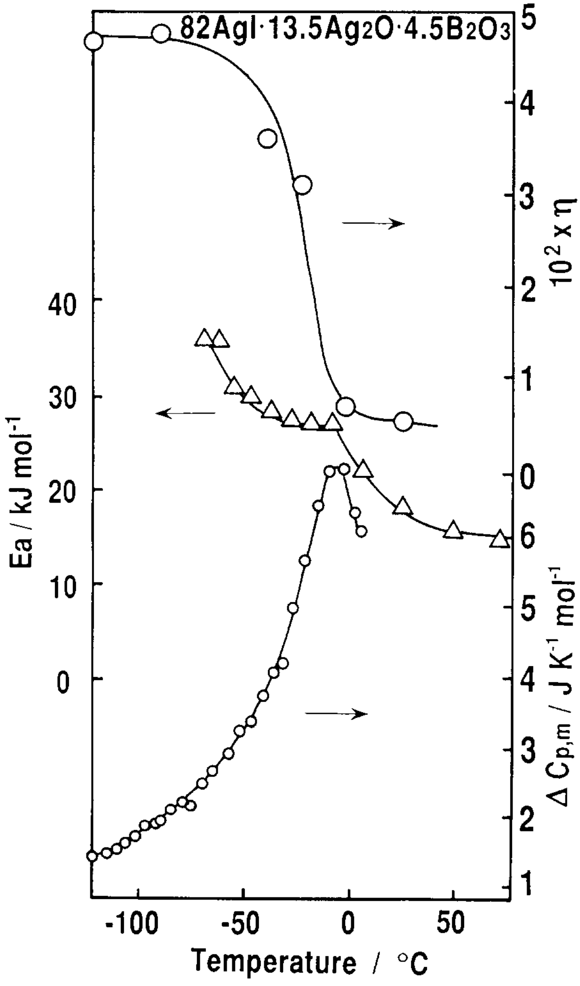

Fig. 8. Temperature dependence of the lattice strain η of frozen α-AgI, activation energy for conduction, and excess heat capacity of the $82AgI \cdot 13.5Ag_2O \cdot 4.5B_2O_3$ composites.

−30–0°C with increasing temperature, indicating that the large lattice strain observed in the α-AgI crystals at low temperatures relaxes at around −10°C in the heating process.

However, the ionic conductivity [10] and the heat capacity [11] of this composite have been found to exhibit an "anomaly" in the same temperature range. Fig. 8 also shows the temperature dependences of the activation energy E_a for conduction and the excess heat capacity $\Delta C_{p,m}$ of the α-AgI frozen composite. A steep decrease in E_a and a maximum in $\Delta C_{p,m}$ are also observed at around −10°C. These anomalous behaviors of E_a and $\Delta C_{p,m}$ are probably caused by the positional ordering of Ag^+ ions in the α-AgI microcrystals in the composite. Since the E_a values and the lattice strain were steeply decreased in the similar temperature range, the positional ordering of Ag^+ ions in the α-AgI microcrystals at temperatures below −10°C may be associated with the large lattice strain generated in the α-AgI microcrystals. The release of the strain of the α-AgI crystals at around −10°C probably results in the disordering of Ag^+ ions to show the heat capacity maximum and the decrease in E_a values.

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