

FORMATION OF AMORPHOUS AgI AGGREGATES DOMINATING FAST ION CONDUCTIVITY IN AgI-BASED GLASSES

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Abstract

Precise calorimetry was performed for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_3)_{1-x}$ glasses with very high AgI compositions ($x \geq 0.75$). The glasses showed β -glass transitions due to the freezing-in of the rearrangement of conductive Ag^+ ions. Magnitude of the associated heat-capacity jump increased with increasing the AgI composition in the respective glass systems, and was larger in the former system than in the latter when compared at the same AgI composition. All the results were well explained by the 'amorphous AgI aggregate' model for the AgI-based fast ion conducting glasses, indicating the appropriateness of the model for the structure of the glasses with high AgI compositions. The formation of the hypothetical bulk amorphous AgI was also indicated in the glasses at the highest limit of AgI composition.

Keywords: AgI, amorphous, calorimetry, glass, glass transition, ion conduction

Introduction

Fast ion conducting (FIC) glasses are materials of an interesting class because of their potential applications to solid-state electrical devices, and much effort has been made to clarify the structure of the glasses and to understand the mechanism of the ionic conduction [1-5]. Among them, AgI-based glasses have been most widely investigated as model materials since they have relatively high ionic conductivity and can be easily prepared. Recently, structural study for AgI-AgPO₃ glasses has been developed by the combination of neutron diffraction, X-ray diffraction and EXAFS data with reverse Monte Carlo modeling [6], and strong correlation has been suggested to exist between the ionic conductivity and free volume for the conductive ions in the glasses [7]. However, especially in high AgI composition range, neither AgI-composition dependence of the ionic conductivity nor relation between the microscopic structure of the glasses and their conductivity have been clarified yet.

In the course of our calorimetric studies for the AgI-based FIC glasses, we have discovered a β -glass transition due to the freezing-in of the rearrangement of con-

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ductive Ag^+ ions in the glasses [8–11]. Based on the observation of the β -glass transition, it has been deduced that the positional order/disorder process of Ag^+ ions is essential for the fast ionic conduction in the glasses and that the AgI aggregate region naturally formed at high AgI content mainly contributes to the fast ionic conduction. We have postulated, in consequence, an ‘amorphous AgI aggregate’ model for the structure of the glasses with high AgI composition [9–11]. In this model, the AgI aggregate is considered to have some amorphous structure dependent on the size of the AgI aggregate region and the regions are expected to develop with increase of AgI composition.

In this paper, in order to check the validity of the ‘amorphous AgI aggregate’ model, we tried to prepare glassy samples with very high AgI compositions for AgI– AgPO_3 and AgI– $\text{Ag}_2\text{PO}_{3.5}$ systems by applying a twin-roller quenching method. Then the precise calorimetric measurements were performed for the successfully prepared $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$, $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses. Consequently, each of the glasses exhibited the β -glass transition, and clear dependence was observed in the properties of the β -glass transition on AgI composition and on the glass-network structure. The results were well explained by the ‘amorphous AgI aggregate’ model, implying that the model is appropriate for the structure of the glasses with high AgI compositions. Furthermore, the formation of the hypothetical bulk amorphous AgI was indicated in the glasses at the highest limit of AgI composition independently of the glass-network former.

Experimental

$(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ amorphous samples with rather high AgI composition x were prepared in low-light conditions from raw materials of AgI, AgNO_3 , Ag_2O and $\text{NH}_4\text{H}_2\text{PO}_4$ of reagent grade in the following procedure. The raw materials were weighed to the desired composition, mixed, and ground in a mortar. The mixture was slowly heated up to 873 K and the red melt was quenched to room temperature. In the present work, to avoid the crystallization in the melt during the quenching and to obtain a glassy sample in higher AgI composition region, a twin-roller quenching method was applied. In the quenching, the melt was poured between the rotating twin rollers at the rotation rate of 3000 r.p.m. With this method, much higher cooling rate can be yielded easily than in the press quenching [12] and the cooling rate was estimated to be $\sim 10^5 \text{ K s}^{-1}$ [13]. In the syntheses of AgI– $\text{Ag}_2\text{PO}_{3.5}$ glasses, NH_4NO_3 was added to the mixture as a mild oxidizing agent to suppress the reduction of the Ag^+ cation in the Ag salt to neutral Ag. Powder X-ray diffraction experiment was carried out with Rigaku Rint 2000 powder X-ray diffractometer by using $\text{CuK}\alpha_1$ radiation. The added voltage and electric current were set to 40 kV and 100 mA, respectively. In the measurements, the thin-flake samples formed by the above quenching manner were set on the sample stage without further grinding.

Heat capacities of the glasses were measured in the temperature region between 13 and 300 K using a high-precision adiabatic calorimeter reported previously [14].

The sample, which was of thin flakes, was loaded in a calorimeter cell under an atmosphere of helium gas and the cell was sealed vacuum-tight with indium wire. The masses of the samples used were 23.859 g (corresponding to 0.10709 mol) for $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$, 22.559 g (0.089605 mol) for $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and 23.384 g (0.084738 mol) for $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glass, respectively. A Pt resistance thermometer was used with calibration based on the ITS-90 [15]. The imprecision and inaccuracy of the heat capacities were estimated previously to be less than $\pm 0.06\%$ and $\pm 0.3\%$, respectively, from the results of the heat-capacity measurements for benzoic acid as a standard material [14].

Results

Glass-forming composition region

Figures 1 and 2 show the powder X-ray diffraction patterns of the twin-roller quenched $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ samples with relatively high AgI compositions. In $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ samples, those with AgI composition of $x \leq 0.80$ exhibited only halo patterns characteristic of glassy states. However, part of $x=0.80$ sample showed some diffraction peaks, which indicate the existence of β - and/or γ -AgI crystallites in the sample. This difference within $x=0.80$ sample is considered to come from the presence of distribution in the cooling rates of the sample from part to part during the quenching and the AgI-composition limit for glass for-

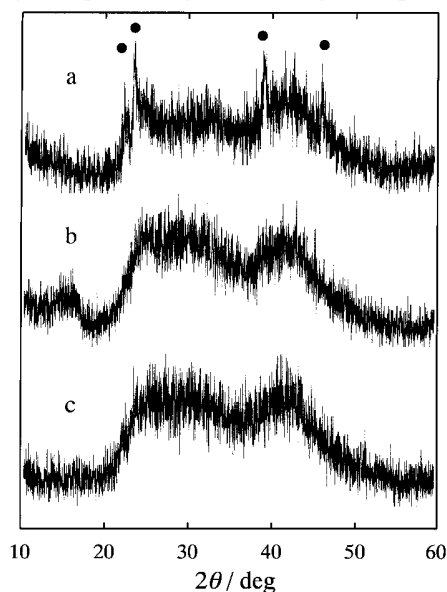


Fig. 1 Powder X-ray diffraction patterns of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ at room temperature: (a), $x=0.80$ sample including crystallites; (b), $x=0.80$ glassy sample; (c), $x=0.75$ sample. The diffraction peaks indicated by closed circles are those of β - and/or γ -AgI crystallites

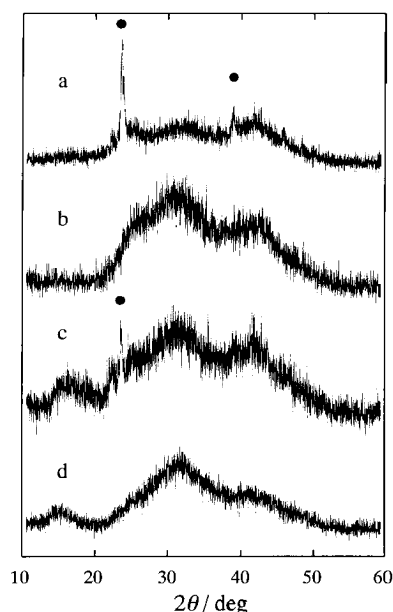


Fig. 2 Powder X-ray diffraction patterns of $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ at room temperature: (a), $x=0.85$ sample; (b), $x=0.80$ sample (immediately after the preparation); (c), $x=0.80$ sample (kept for 2 d at room temperature after the preparation); (d), $x=0.75$ sample. The diffraction peaks indicated by closed circles are those of β - and/or γ -AgI crystallites

mation by the present quenching method was decided to be $x < 0.80$ for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ system. In $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ samples, while $x=0.85$ sample showed distinct diffraction peaks, the samples with $x \leq 0.80$ did not. The $x=0.80$ sample showed some indication of the formation of β - and/or γ -AgI crystallites within the glass only in two days at room temperature.

Heat-capacity measurements

The precise heat-capacity measurements were carried out for $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$, $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses. The sample in which the crystallization of AgI potentially proceeds even at room temperature was loaded into a calorimeter cell, set in a calorimeter cryostat and cooled to liquid nitrogen temperature quickly within a couple of hours after the preparation. Figure 3 shows the temperature dependence of molar heat capacities obtained for the respective samples. Although the heat capacity curve of each sample was apparently quite smooth in the measured temperature range, thermal anomaly was observed for all the samples in liquid-nitrogen temperature region. The anomaly was considered possibly to originate from the freezing-in/-out phenomenon of positional disorder of conductive silver ions in the glasses. To obtain more precise information about the thermal anomaly, heat-capacity measurements were performed in

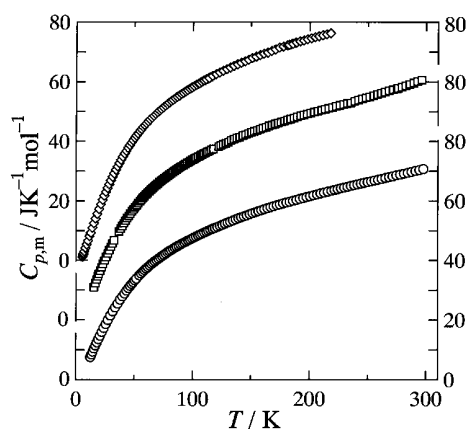


Fig. 3 Molar heat capacities of the glasses: \circ – $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$ glass; \square – $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ glass; \diamond – $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glass. The origin of the ordinate is shifted upward by $20 \text{ J K}^{-1} \text{ mol}^{-1}$ in order from $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$ to $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ to $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses

the liquid-nitrogen temperature region for the samples subjected to the precooling at different rates. Since heat capacities were measured under the adiabatic condition by an intermittent heating method [9, 16], the freezing-out phenomenon should appear, with increase in the temperature, as spontaneous heat evolution and successive absorption effects resulting in anomalous temperature drifts at positive and then negative rates, respectively, of the calorimeter cell in the temperature-rating periods [17, 18]. Actually in the measurements, such anomalous temperature dependence of the spontaneous temperature drift rates was observed as shown in Figs 4–6. In $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$ glass (Fig. 4), the sample pre-cooled rapidly in the liquid-nitrogen temperature region exhibited exothermic effect start-

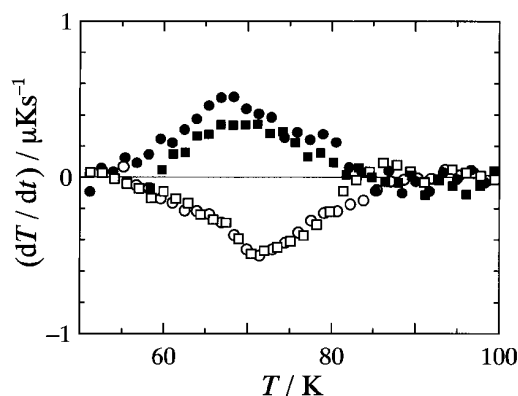


Fig. 4 Temperature dependence of spontaneous temperature drift rates observed during the heat-capacity measurements for $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$ glass: \bullet – pre-cooled rapidly at the rate of 5 K min^{-1} ; \blacksquare – at 2 K min^{-1} ; \circ – pre-cooled slowly at 9 mK min^{-1} ; \square – at 6 mK min^{-1}

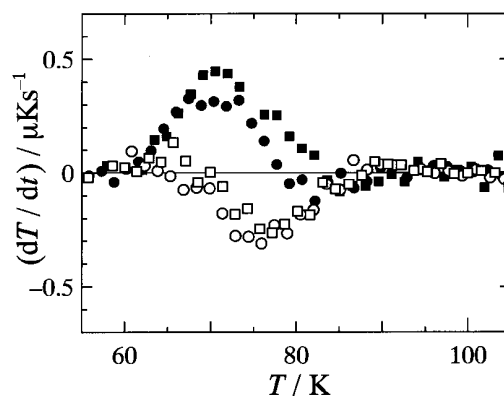


Fig. 5 Temperature dependence of spontaneous temperature drift rates observed during the heat-capacity measurements for $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ glass: ● – pre-cooled rapidly at the rate of 5 K min^{-1} ; ■ – at 9 K min^{-1} ; ○ – pre-cooled slowly at 12 mK min^{-1} ; □ – at 11 mK min^{-1}

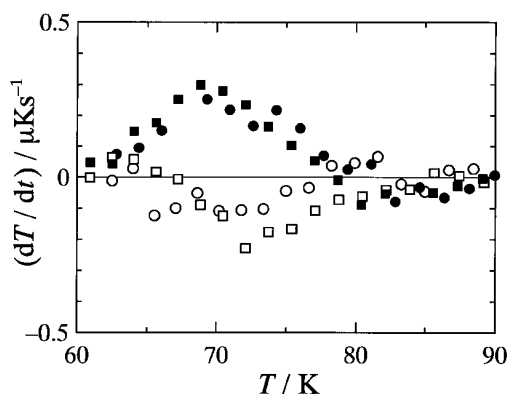


Fig. 6 Temperature dependence of spontaneous temperature drift rates observed during the heat-capacity measurements for $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glass: ● – pre-cooled rapidly at the rate of 7 K min^{-1} ; ■ – at 8 K min^{-1} ; ○ – pre-cooled slowly at 14 mK min^{-1} ; □ – at 13 mK min^{-1}

ing at around 55 and showing its maximum at 67 K, while the slowly pre-cooled sample exhibited endothermic effect showing its maximum at 71 and ending at around 85 K. In $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ glass (Fig. 5), rapidly pre-cooled sample exhibited exothermic effect starting around 60, having its peak at 70 K and followed by endothermic effect, while slowly pre-cooled sample showed only endothermic effect having its maximum at 76 K. Also in $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glass (Fig. 6), rapidly pre-cooled sample showed exothermic effect with its maximum at 69 K and slowly pre-cooled sample exhibited endothermic effect with its peak at 72 K. The observation of the exothermic and endothermic effects which change systematically as the pre-cooling rates change indicates the existence of a β -glass transition besides the α -glass transition expected above room temperature [12, 19–21]. In these glasses the

fast ionic conduction arises from the presence of silver ions with high mobility. Thus the β -glass transition observed here is reasonably assigned to the freezing-in/-out of the rearrangement of Ag^+ ions much below the α -glass transition temperature, at which the positions of the other ions in the glass are virtually fixed.

The enthalpy relaxation effects observed in the β -glass transitions for these samples were too small to estimate experimentally the relaxation time at each temperature. The β -glass transition temperatures, T_g , at which the relaxation time becomes 1 ks were therefore determined according to an empirical relation. In the present work, heat-capacity measurements were performed by an intermittent heating method with a temperature-rating period of about 10 min. In many cases of glass transitions studied in such a condition, samples precooled slowly at a rate of about 10 mK min^{-1} in the transition region have been observed to exhibit a maximum endothermic effect at the temperature where the relaxation time is about 1 ks [14, 18]. The β -glass transition temperatures thus determined were 71 ± 1 , 76 ± 1 and 72 ± 1 K for $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$, $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses, respectively.

For assessment of the very small heat-capacity jump associated with the β -glass transition, the heat-capacity data were treated as follows. In the case of $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$ glass, the observed heat capacities were converted to the apparent partial molar quantities of AgI by subtracting the heat-capacity contribution from the glassy AgPO_3 portion at first [8, 9]. Then a smooth curve was determined somewhat arbitrarily as a function of temperature by fitting to the obtained partial molar AgI heat-capacity data between 20 and 60 K. The function was represented as the sum of Debye and Einstein functions for each of three degenerate vibrational degrees of freedom and a $C_p - C_v$ correction term of $AC_p^2 T$. The excess heat capacities over the smooth curve around the β -glass transition are shown in Fig. 7, which

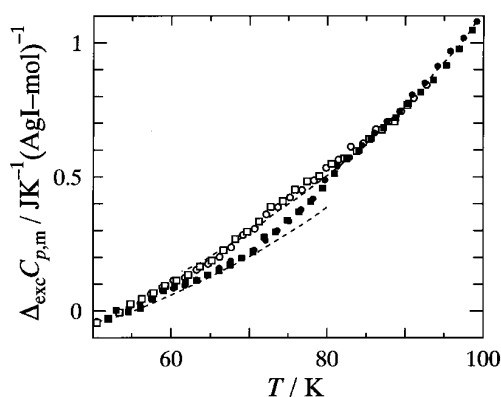


Fig. 7 Temperature dependence of excess part of apparent partial molar heat capacities of AgI in $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$ glass around the β -glass transition temperature:

○, □ – slowly precooled samples at the rate of 9 and 6 mK min^{-1} , respectively;
 ●, ■ – rapidly precooled samples at 5 and 2 K min^{-1} , respectively. The values were derived as referred to a smooth curve somewhat arbitrarily drawn for the apparent partial molar heat capacities of AgI (see text for details)

clearly indicates the heat-capacity jump associated with the transition. Open circles and squares in the figure represent the results of the slowly precooled sample, and closed circles and squares are those for the rapidly precooled sample. In the slowly precooled sample, overshooting effects can be seen in the glass transition temperature region. This is because the heat capacities were evaluated so as to include the contribution from the endothermic enthalpy relaxation associated with the glass transition during the measurements. In the rapidly precooled sample, on the other hand, the heat capacities are due to only the contributions from vibrational degrees of freedom in the glass below T_g , since they were evaluated to exclude the contribution from the exothermic enthalpy relaxation by recognizing the exothermic temperature drift as being attributed to the heat influx to the calorimeter cell from its surroundings [9]. The two dashed lines in the lower and higher temperature regions represent the heat-capacity curves estimated for the frozen-in and the equilibrium, respectively, states with respect to the configurational degrees of freedom of Ag^+ ions relevant to the β -glass transition. From the difference between the two dashed lines, the heat-capacity jump at the β -glass transition temperature, 71 K, was evaluated to be $0.10 \pm 0.03 \text{ J K}^{-1} (\text{AgI} \cdot \text{mol})^{-1}$ and thus $0.08 \pm 0.02 \text{ J K}^{-1} \text{ mol}^{-1}$ as the molar quantity for $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$ glass.

In the cases of $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses, because of lack of the heat-capacity data for $\text{Ag}_2\text{PO}_{3.5}$ glass, smooth curves for heat capacities were determined as follows. The obtained heat-capacity data were multi-

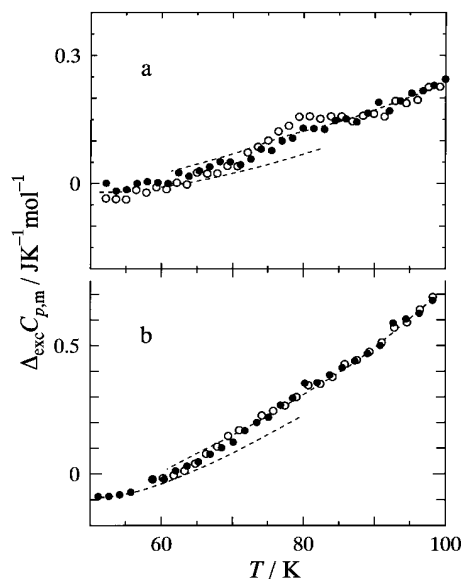


Fig. 8 Temperature dependence of excess molar heat capacities around the β -glass transition temperature: (a), $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ glass; (b), $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glass. Open circles stand for the results of slowly precooled samples and closed circles for those of rapidly precooled samples. The values were derived as referred to smooth curves somewhat arbitrarily drawn for the molar heat capacities (see text for details)

plied by $T^{0.8}$ and $T^{0.85}$ for $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses, respectively. Then first-order functions of T were fitted to the results between 40 and 70 K, and the functions were converted to the smooth curve for the temperature dependence of the heat capacities. Figure 8 shows the excess molar heat capacities over the smooth curves in the β -glass transition temperature region for $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses. In the figure, open circles stand for the results of slowly pre-cooled samples and closed circles for those of rapidly pre-cooled samples. Lower and upper dashed lines represent the estimations for the heat-capacity curves in the lower-temperature frozen-in and the higher-temperature equilibrium, respectively, states with respect to the configurational degrees of freedom of relevant Ag^+ ions. From the difference between the two dashed lines, the heat-capacity jumps at the β -glass transition temperatures were evaluated to be $0.06 \pm 0.02 \text{ J K}^{-1} \text{ mol}^{-1}$ and $0.07 \pm 0.02 \text{ J K}^{-1} \text{ mol}^{-1}$ for $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses, respectively. The calorimetric parameters for the β -glass transition of the glasses are listed in Table 1 along with the previously reported data [8–10].

Table 1 Calorimetric results for the β -glass transition in FIC glasses

Glass sample	T_g/K	$\Delta C_p/\text{J K}^{-1} \text{ mol}^{-1}$	$(x-x_c)/(1-x_c)$	$\Delta\epsilon/\text{kJ mol}^{-1}$
$(\text{AgI})_x(\text{AgPO}_3)_{1-x}$				
$x=0.50^a$	85 \pm 1	0.03 \pm 0.02	0.23	6.1
$x=0.60^a$	76 \pm 1	0.05 \pm 0.02	0.38	5.3
$x=0.65^a$	74 \pm 1	0.06 \pm 0.02	0.46	5.2
$x=0.75$	71 \pm 1	0.08 \pm 0.02	0.62	5.0
$(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$				
$x=0.65^a$	84 \pm 1	0.03 \pm 0.02	0.24	5.9
$x=0.75$	76 \pm 1	0.06 \pm 0.02	0.46	5.3
$x=0.80$	72 \pm 1	0.07 \pm 0.02	0.57	5.1

a) data from [8] and [9]; b) data from [10]

Discussion

In both the glass systems of AgI-AgPO_3 and $\text{AgI-Ag}_2\text{PO}_{3.5}$, the β -glass transition due to the freezing-in/-out of the positional disorder of conductive Ag^+ ions was observed for the glasses with relatively high AgI compositions. With increasing AgI composition, decrease of the glass transition temperature, T_g , and increase of the heat-capacity jump, ΔC_p , associated with the transition were observed as a common feature of the β -glass transition in the systems (Table 1). However, the two glass systems have different glass network structures from each other; AgPO_3 and $\text{Ag}_2\text{PO}_{3.5}$ have, as an average, a one-dimensional chain structure and a dimer structure of corner-shared tetrahedral phosphate groups [22]. Corresponding to the difference,

(AgI) $_x$ (AgPO $_3$) $_{1-x}$ glasses showed lower T_g and larger ΔC_p than (AgI) $_x$ (Ag $_2$ PO $_{3.5}$) $_{1-x}$ glasses when these quantities were compared at same AgI composition between the two systems.

The AgI-composition dependence of ΔC_p is plotted in Fig. 9 for each of (AgI) $_x$ (AgPO $_3$) $_{1-x}$ and (AgI) $_x$ (Ag $_2$ PO $_{3.5}$) $_{1-x}$ glasses. In both the systems, tendency of rather linear decrease in ΔC_p with the decrease of AgI composition, x , is observed. This characteristic dependence of ΔC_p on x indicates that the β -glass transition appears in the glasses with higher AgI composition than some critical value, x_c , and that the x_c is dependent on glass network structures. The values of x_c are evaluated, from the intercept of the linear lines to the abscissa in Fig. 9, to be 0.35 for (AgI) $_x$ (AgPO $_3$) $_{1-x}$ glass system as has been reported previously based on the data for $x \leq 0.65$ glasses [9] and to be 0.54 for (AgI) $_x$ (Ag $_2$ PO $_{3.5}$) $_{1-x}$ glass system.

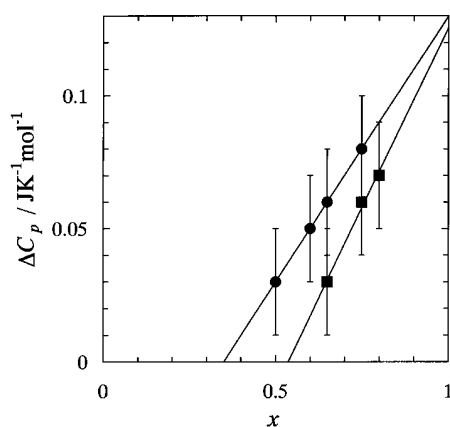


Fig. 9 AgI-composition dependence of the heat-capacity jump in the β -glass transition associated with rearrangement of Ag $^+$ ions in the glasses: ● – (AgI) $_x$ (AgPO $_3$) $_{1-x}$ glasses; ■ – (AgI) $_x$ (Ag $_2$ PO $_{3.5}$) $_{1-x}$ glasses

This result strongly supports validity of ‘amorphous AgI aggregate’ model for the structure of the glasses. The model predicts that AgI aggregate regions are formed naturally at high AgI composition within the interstices between the glass network formers, and that the AgI aggregate has an amorphous structure dependent on the size of the region which develops with increasing AgI composition. In view of the characters of calorimetry, the distinct observation of the β -glass transition means that an appreciable deal of Ag $^+$ ions are located in almost the same energetic environments. Conversely, the Ag $^+$ ions included in the aggregate region and surrounded only by iodide anions are reasonably considered to be responsible for appearance of the β -glass transition, and the ions are expected to contribute the majority of fast ionic conduction in the glasses. As described qualitatively in our previous paper, the development of the amorphous AgI aggregate region is dominated not only by the AgI composition of the glass but also by the glass-former network structures [10]. The glass former Ag $_2$ PO $_{3.5}$ is more dispersive than AgPO $_3$ chain in the glass as a mat-

ter of course. This tendency of dispersion prevents AgI from formation of the amorphous aggregate region and hampers its development, resulting in higher x_c for $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ than for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glass system.

The amount of AgI contributing to the β -glass transition in the glasses can be expressed by the formula $(x-x_c)/(1-x_c)$, since the mole fraction of AgPO_3 or $\text{Ag}_2\text{PO}_{3.5}$ decreases with increasing x and the proportionality constant is deduced to be $1/(1-x_c)$ in the range of x above x_c . By applying the formula to the presently studied glasses*, 0.62, 0.24, 0.46 and 0.57 mol of AgI were calculated to contribute to the β -glass transition per mol of $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$, $(\text{AgI})_{0.65}(\text{Ag}_2\text{PO}_{3.5})_{0.35}$, $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses, respectively, and thus the respective amounts of AgI should contribute to the heat-capacity jump at the transition, ΔC_p . The glass transition observed by calorimetry is the freezing-in/-out phenomenon of the configurational order-disorder process activated by the thermal energy kT . Therefore, the glass transition temperature reflects the activation energy $\Delta\epsilon_a$ of the potential along the path of positional rearrangement of Ag^+ ions, and the heat-capacity jump associated with the glass transition includes information about the energy difference $\Delta\epsilon$ between adjacent lowest-energy sites for the Ag^+ ions. The β -glass transition was observed at very low temperatures in liquid-nitrogen temperature region and the heat-capacity jump at the transition was quite small. These facts indicate that the heat-capacity jump is contributed only by an excitation to the first excited state of a small amount of Ag^+ ions among those relevant to the β -glass transition. In such a case, double-minimum potential is a suitable assumption to express the energetic environment around the Ag^+ ions. When assuming a two-energy-level scheme, the molar heat capacity due to the Ag^+ ions can be expressed by the following equation with $\Delta\epsilon$, the energy difference,

$$C=R[(\Delta\epsilon/RT)^2\exp(\Delta\epsilon/RT)/\{1+\exp(\Delta\epsilon/RT)\}^2].$$

The molar value C can be related to the magnitude of the observed heat-capacity jump by $C=\Delta C_p/[(x-x_c)/(1-x_c)]$, in which the denominator is the amount of AgI contributing to the heat-capacity jump as mentioned above. By using these relations, the energy differences between the lowest two potential minima, $\Delta\epsilon$, are estimated to be 5.0, 5.9, 5.3 and 5.1 kJ mol^{-1} for $(\text{AgI})_{0.75}(\text{AgPO}_3)_{0.25}$, $(\text{AgI})_{0.65}(\text{Ag}_2\text{PO}_{3.5})_{0.35}$, $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ and $(\text{AgI})_{0.80}(\text{Ag}_2\text{PO}_{3.5})_{0.20}$ glasses, respectively, and are listed in Table 1.

The x dependence of $\Delta\epsilon$ is plotted in Fig. 10 along with the results of our previous works for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ ($x\leq 0.65$) glasses [9]. When comparing between $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ glasses, the former show smaller $\Delta\epsilon$ than that of the latter at the same AgI composition of x . However, the glass with smaller $\Delta\epsilon$ showed lower T_g in both the glass systems, and the glasses which have the same

* Calorimetric results and the observation of the β -glass transition for $(\text{AgI})_{0.65}(\text{Ag}_2\text{PO}_{3.5})_{0.35}$ glass have been already reported in [10]. However, the amount of AgI contributing to the transition for the glass was estimated for the first time with the help of the presently obtained value of $x_c=0.54$.

$\Delta\varepsilon$, for example $(\text{AgI})_{0.60}(\text{AgPO}_3)_{0.40}$ and $(\text{AgI})_{0.75}(\text{Ag}_2\text{PO}_{3.5})_{0.25}$ glasses, exhibited the same T_g (Table 1). These facts indicate that there is no difference in the structural property of the amorphous AgI aggregates formed in the glasses between these glass systems. The difference in $\Delta\varepsilon$ at the same AgI composition between the systems is reasonably considered to be due to the difference in the degree of the development of AgI aggregate region, which is hampered in the glass by more dispersed glass network. Thus, the Ag^+ ions relevant to the β -glass transition are concluded to have the same energetic environment when the size of the AgI aggregates develops to the same degree, independently for the glass network structure.

Recently, the glass structure of AgI–AgPO₃ system has been reported by Wicks *et al.* based on the results of neutron, X-ray diffraction and extended X-ray-absorption fine structure spectroscopy with the help of reverse Monte Carlo modeling [6]. They concluded that AgI–AgPO₃ glass has an amorphous complex structure formed of the host glass of AgPO₃ and AgI, and that most Ag^+ ions are coordinated to both I and O anions without the existence of AgI ‘clusters’ on the consideration of their size. However, they assumed the AgI ‘clusters’ of a crystalline type as a kind of α -AgI crystallite and their experiments were limited only for the glasses with the AgI composition of $x \leq 0.5$. The fact that the β -glass transition is observed only in the glasses with the AgI composition higher than some critical value x_c , which is dependent on the glass former network structure, strongly suggests the formation of AgI aggregate region in the interstices between the glass former phosphates. When assuming AgI aggregate has an amorphous structure, which can be much smaller in the size than the crystallites, the formation of AgI aggregate is really possible and the properties of the mobile Ag^+ ions are expected to approach to those proper to hypothetical bulk amorphous AgI as AgI composition increases. In Fig. 9, the extrapolations of ΔC_p to the limit of $x=1$ for the glass systems of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ seem to come to the same value of $-0.13 \text{ J K}^{-1} \text{ mol}^{-1}$. The $\Delta\varepsilon$ shows also the tendency to converge upon the value of $\sim 5 \text{ kJ mol}^{-1}$ at the limit of $x=1$ (Fig. 10). These facts indicate the formation of the hypothetical bulk amorphous AgI

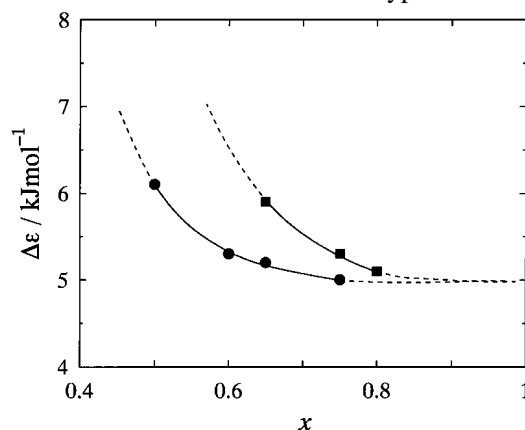


Fig. 10 AgI-composition dependence of the energy difference $\Delta\varepsilon$ between adjacent lowest-energy sites for the Ag^+ ions in the glasses: ● – $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses; ■ – $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ glasses

in the glasses, and the values of ΔC_p and $\Delta \epsilon$ estimated at $x=1$ are, thus, considered to correspond to those for the bulk amorphous AgI, which has never been obtained experimentally.

Concluding remarks

In the present glass systems, glassy AgPO_3 and $\text{Ag}_2\text{PO}_{3.5}$ themselves are ion conducting materials. Therefore, all the Ag^+ ions included in $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ glasses can contribute to their ionic conductivity as has been reported by Roling *et al.* [23]. However, the ion conduction property is mainly decided by the activation energy, $\Delta \epsilon_a$, for Ag^+ ions to migrate in the glasses, and the Ag^+ ions included in the amorphous AgI aggregate region are reasonably considered to have the lowest $\Delta \epsilon_a$ among those included in the glass. Therefore, we believe that the fast ion conduction property of these glass systems is strongly dependent on the formation of the amorphous AgI aggregate region in the glasses and its development in the size, and that the 'amorphous AgI aggregate' model for the glasses are useful for understanding the ion conduction property of these fast ion conducting glasses.

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