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Anomalous AgI composition dependence of the thermal and dielectric properties of AgI–Ag$_2$O–P$_2$O$_5$ glasses: evidence for the formation of amorphous AgI aggregate regions as dominating the fast Ag$^+$ ion conduction

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Abstract
Heat capacities of $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses with $x = 0.70$ and 0.80 were measured to estimate the jump, ΔC_p, in the β-glass transition due to freezing of the Ag$^+$ ion rearrangement. Dielectric relaxation properties of $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ with $x = 0$, 0.20, and 0.40 and $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses with $x = 0.30$ and 0.40 were examined to estimate the activation energies, $\Delta\varepsilon_a$, along the conduction path. ΔC_p was found to appear only at larger x than a critical value $x_c = 0.60$ for $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses. x_c, depending on the structure of the glass network former, is larger than the values of 0.35 and 0.54 for $(AgI)_x(AgPO_3)_{1-x}$ and $(AgI)_x(Ag_2PO_{3.5})_{1-x}$, respectively, glasses. $\Delta\varepsilon_a$ was found to show its inflection at around the respective x_c values for the $(AgI)_x(Ag_3PO_4)_{1-x}$ and $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ glasses. These observations are discussed to support the 'amorphous AgI aggregate' model for the fast Ag$^+$ ion conduction path.

1. Introduction

Fast ion conducting (FIC) glasses are materials of an interesting class because of their potential applications to an electrolyte for constructing a solid-state battery and also to solid-state electrical devices. Much effort has been made, especially for metal-halide-based FIC glasses, to get the information on the structure of the glasses and to understand the mechanism of the ion conduction for producing higher ionic conductivity in the glasses [1–5]. However, the microscopic structure of the glasses, particularly in a large metal halide composition range, has not been clarified yet and is still under debate. Among the glasses, AgI-based AgI–AgPO$_3$

glasses have been most widely investigated as a model material, and a homogeneous structure, where most Ag^+ ions are coordinated to both I^- and $-O^-$ anions without the existence of AgI clusters, has been claimed from the study done by combining neutron diffraction, x-ray diffraction and EXAFS data together with reverse Monte Carlo modelling [6]. In contrast, the results of precise calorimetry and conductometry for $AgI–Ag_2O–P_2O_5$, including $AgI–AgPO_3$, $AgI–Ag_2PO_{3.5}$ and $AgBr–AgPO_3$ glasses, have strongly suggested the formation of an amorphous silver halide aggregate region in a large silver halide composition range, and an amorphous silver halide aggregate model has been proposed as characterizing the behaviour of Ag^+ ion conduction in this range [7–12].

In this paper, in order to examine the AgI composition dependence of the properties related to the Ag^+ ion conduction and thus to check the validity of the amorphous AgI aggregate model, firstly the precise adiabatic calorimetry was carried out for $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses with large AgI compositions of $x = 0.70$ and 0.80; the anion PO_4^{3-} as the glass former component has a monomer structure, as viewed among a series of polyphosphoric anions, differently from PO_3^- with a one-dimensional chain structure and $PO_{3.5}^{2-}$ with a dimer structure. Secondly, dielectric measurements were performed for $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ with $x = 0$, 0.20, and 0.40 and $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses with $x = 0.30$ and 0.50. Inflection in the AgI composition dependence of the activation energy for the Ag^+ ion conduction was found at around the same AgI composition as that at which the heat capacity data predict the amorphous AgI aggregates to start to be formed.

2. Experimental details

$(AgI)_x(Ag_2PO_{3.5})_{1-x}$ and $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses were prepared under low-light conditions from raw materials of reagent grade, namely AgI, $AgNO_3$, Ag_2O and $NH_4H_2PO_4$, according to the following procedure. The raw materials were weighed to the desired compositions, mixed and ground in a mortar. The mixture was slowly heated up to 873 K and the red melt was quenched to room temperature. The samples for calorimetry of $(AgI)_x(Ag_3PO_4)_{1-x}$ with $x = 0.70$ and 0.80 were quenched at the estimated cooling rate of $10^2–10^3$ K s^{-1} by pressing the melt rapidly between a pair of stainless-steel plates [13]. The samples for dielectric measurements of $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ with $x = 0$, 0.20, and 0.40 and $(AgI)_x(Ag_3PO_4)_{1-x}$ with $x = 0.30$ and 0.50 were quenched by a twin-roller quenching method at the estimated cooling rate of $\sim 10^5$ K s^{-1} [12, 14, 15]. Powder x-ray diffractometry was carried out using Cu Kα radiation, to confirm the successful preparation of glassy sample containing no crystallite.

Heat capacities of the glasses were measured in the temperature region between 13 and 300 K using a high-precision adiabatic calorimeter reported previously [16]. The sample, which was rather coarse flakes obtained by breaking the above-prepared thin plate glass, was loaded into a calorimeter cell under an atmosphere of He gas and the cell was sealed vacuum-tight with indium wire. The masses of the samples used were 28.735 g (corresponding to 0.099 114 mol) for $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and 43.758 g (0.161 15 mol) for $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glass, respectively. A Pt resistance thermometer was used with calibration based on the ITS-90 [17]. 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 [16].

The ac dielectric response of the glasses was measured as a function of both temperature (100–300 K) and frequency (20 Hz–1 MHz) employing an HP4284A *LCR* meter in a He-refrigerator cryostat system under He gas atmosphere. Electrodes were prepared by painting
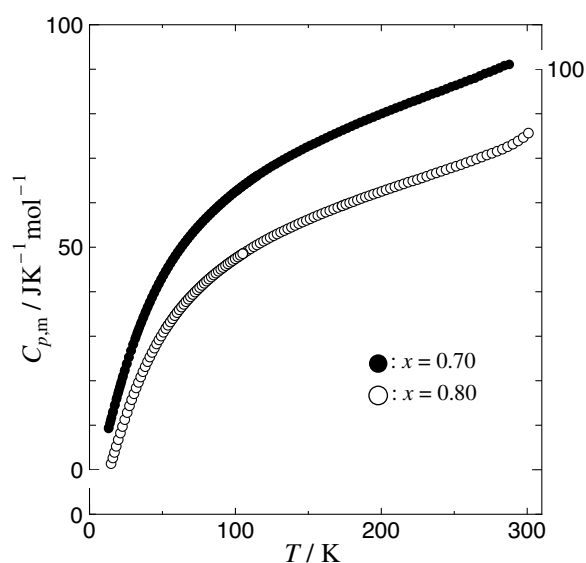
Figure 1. Molar heat capacities of $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses: ●, $x = 0.70$ glass; O, $x = 0.80$ glass.

silver paste on both sides of the flake sample. The results of the dielectric measurements were analysed according to the electric modulus M^* formalism, which has been employed for analysing the ac response of fast ion conducting glasses [18–20], to investigate precisely the relaxation property of conductive Ag$^+$ ions and its dependence on temperature.

3. Results

3.1. Calorimetry for $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses with $x = 0.70$ and 0.80

Figure 1 shows the temperature dependence of molar heat capacities obtained for $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glasses. Although the heat capacity curve of each sample was apparently quite smooth in the measured temperature range, a thermal anomaly was observed as spontaneous heat evolution and absorption in the temperature measurement periods for both the samples in the liquid-nitrogen temperature region. The anomaly was considered to originate from the freezing-in/out phenomenon of the remaining positional disorder of conductive Ag$^+$ ions in the glasses. To obtain more precise information about the thermal anomaly, heat-capacity measurements were performed in the liquid-nitrogen temperature region for the samples subjected to the precooling treatments at different rates. Since heat capacities were measured under the adiabatic condition by an intermittent heating method [8, 21], 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 [22, 23]. Actually in the measurements, such anomalous temperature dependence of the spontaneous temperature drift rates was observed as shown in figure 2. In $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ glass (figure 2(a)), the sample precooled rapidly at a rate of ~ 10 K min^{-1} in the liquid-nitrogen temperature region exhibited an exothermic effect starting at around 70 K and showing its maximum at 83 K, and the sample precooled slowly at a rate of ~ 10 mK min^{-1} exhibited an endothermic effect showing its maximum at 88 K and ending
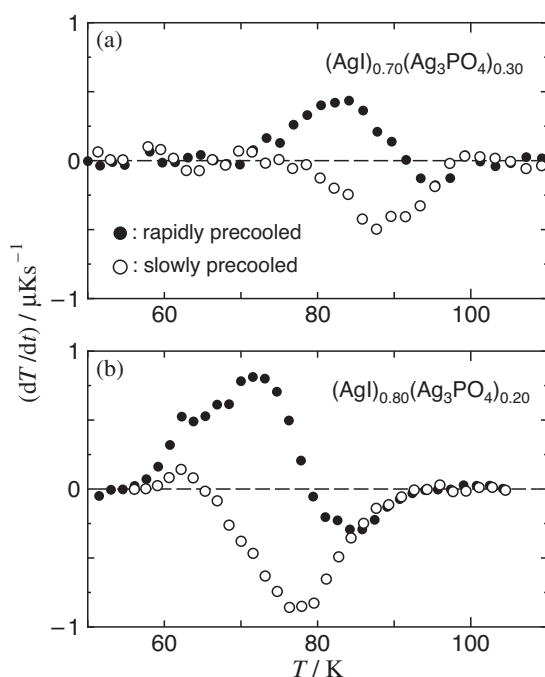
Figure 2. Temperature dependence of spontaneous temperature drift rates observed during the heat-capacity measurements for $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses: (a) $x = 0.70$ glass; (b) $x = 0.80$ glass. Closed circles represent the results for rapidly precooled samples and open circles represent those for slowly precooled samples.

at around 97 K. In $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glass (figure 2(b)), the rapidly precooled sample exhibited an exothermic effect starting around 60 K, having its peak at 72 K and followed by an endothermic effect, and the slowly precooled sample showed only an endothermic effect having its maximum at 78 K. The observation of the exothermic and endothermic effects systematically changing with the precooling rates indicates the existence of a β-glass transition besides the α-glass transition expected above room temperature [13, 24–26]. In these glasses the fast ionic conduction arises from the presence of Ag^+ 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 [16, 23]. The β-glass transition temperatures thus determined were (88 ± 1) and (78 ± 1) K for $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glasses, respectively.

For assessment of the very small heat-capacity jump associated with the β-glass transition, a smooth curve was determined somewhat arbitrarily as a function of temperature by fitting
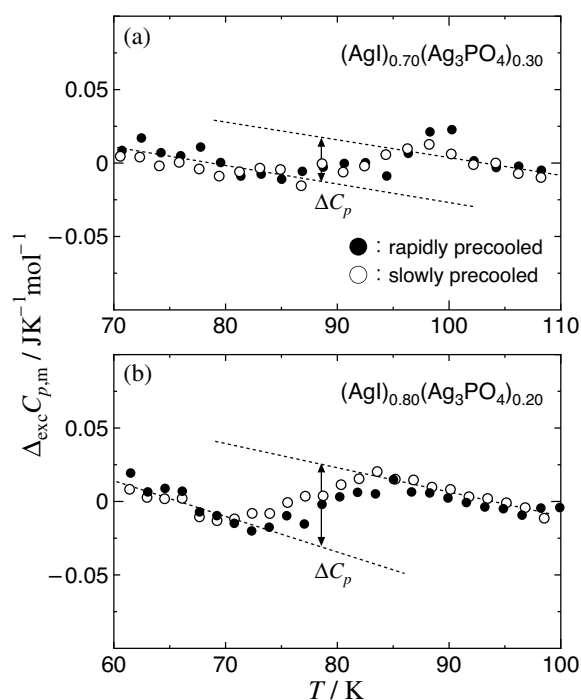
Figure 3. Temperature dependence of excess molar heat capacities around the β-glass transition temperature for $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses: (a) $x = 0.70$ glass; (b) $x = 0.80$ glass. Closed circles represent the results for rapidly precooled samples and open circles represent those for slowly precooled samples. The values were derived as referred to smooth curves somewhat arbitrarily drawn for the molar heat capacities (see the text for details).

to the obtained heat-capacity data and was subtracted from the heat capacity of the glass. The smooth curves for $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glasses were determined by the fitting of fifth-order polynomial functions of T to the heat-capacity data between 50 and 140 K for $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ glass, and the data between 40 and 130 K for $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glass, respectively. Figure 3 shows the excess molar heat capacities over the smooth curves in the β-glass transition temperature region for $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glasses. In the figure, open circles stand for the results of the slowly precooled samples and closed circles for those of the rapidly precooled 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 0.03 ± 0.02 and 0.06 ± 0.02 J K^{-1} mol^{-1} for $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glasses, respectively. The inaccuracy of ± 0.02 J K^{-1} mol^{-1} in the heat-capacity jumps was estimated as the maximum value based on the imprecision of the heat-capacity data. The calorimetric properties of the β-glass transition in the glasses are listed in table 1 along with the previously reported data [7–9, 11].

3.2. Dielectric measurements for $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ and $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses

The temperature dependence of the imaginary component of the complex electrical modulus, M'', measured at several different electric field frequencies for $(AgI)_{0.30}(Ag_3PO_4)_{0.70}$ glass is

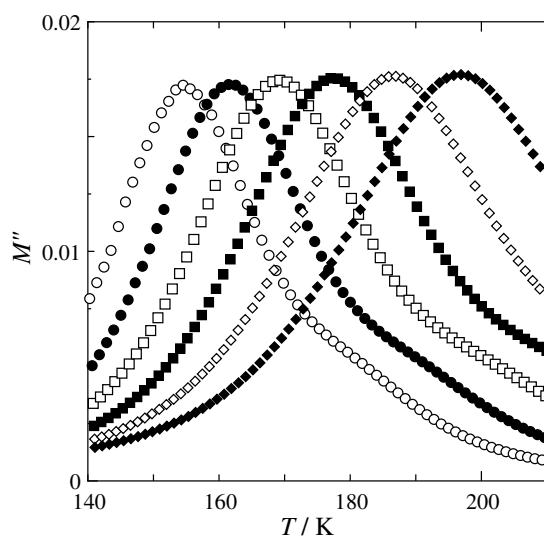**Figure 4.** Temperature dependence of M'' for $(AgI)_{0.30}(Ag_3PO_4)_{0.70}$ glass at different electric field frequencies: ○ 29 Hz; ● 95 Hz; □ 303 Hz; ■ 974 Hz; ◇ 3.13 kHz; ♦ 10 kHz.

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

Glass sample	T_g (K)	ΔC_p (J K^{-1} mol^{-1})	$(x - x_c)/(1 - x_c)$	$\Delta \varepsilon$ (kJ mol^{-1})
$(AgI)_x(AgPO_3)_{1-x}$				
$x = 0.50$[a]	85 ± 1	0.03 ± 0.02	0.23	6.1
$x = 0.60$[a]	76 ± 1	0.05 ± 0.02	0.38	5.3
$x = 0.65$[a]	74 ± 1	0.06 ± 0.02	0.46	5.2
$x = 0.75$[b]	71 ± 1	0.08 ± 0.02	0.62	5.0
$(AgI)_x(Ag_2PO_{3.5})_{1-x}$				
$x = 0.65$[c]	84 ± 1	0.03 ± 0.02	0.24	5.9
$x = 0.75$[b]	76 ± 1	0.06 ± 0.02	0.46	5.3
$x = 0.80$[b]	72 ± 1	0.07 ± 0.02	0.57	5.1
$(AgI)_x(Ag_3PO_4)_{1-x}$				
$x = 0.70$	88 ± 1	0.03 ± 0.02	0.25	6.2
$x = 0.80$	78 ± 1	0.06 ± 0.02	0.50	5.5

[a] Data from [7] and [8].
[b] Data from [11].
[c] Data from [9].

shown in figure 4. The plot shows features typical of a relaxation. The temperature of the M'' peak increases with increasing frequency in the spectra. The M'' peak corresponds to the point of a resonance phenomenon between the applied electric field frequency and the fluctuation of complex modulus M^* at the temperature. With the M^* reflecting the fluctuational motion of conductive Ag$^+$ ions in the glasses, the mean frequency of the motion of the Ag$^+$ ions at the M''-peak temperature is considered to coincide with the specific electric field frequency, f. Thus, the relaxation time, τ, associated with the diffusional motion of conductive Ag$^+$ ions at that temperature was evaluated as $\tau = 1/(2\pi f)$. The M'' spectra exhibited a shoulder on the higher temperature side of the M'' peak. The origin of the small shoulder is not clear. It
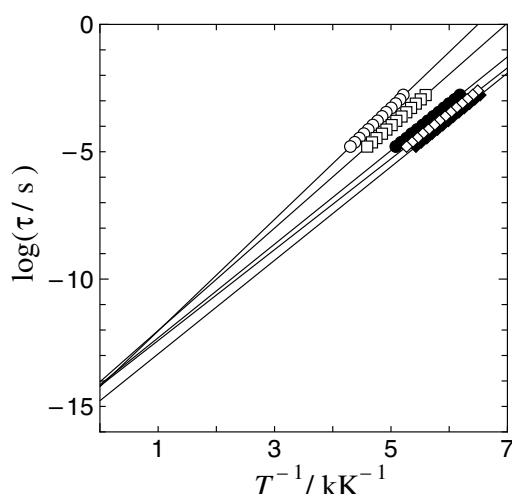
Figure 5. Arrhenius plots of the relaxation times, associated with the Ag$^+$-ion migration in $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ and $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses, evaluated from the results of the dielectric measurements: $\bigcirc$ Ag$_2$PO$_{3.5}$; $\square$ $(AgI)_{0.20}(Ag_2PO_{3.5})_{0.80}$; $\lozenge$ $(AgI)_{0.40}(Ag_2PO_{3.5})_{0.60}$; $\bullet$ $(AgI)_{0.30}(Ag_3PO_4)_{0.70}$; $\blacklozenge$ $(AgI)_{0.50}(Ag_3PO_4)_{0.50}$.

could be due to the interfacial effect between the sample and the electrodes. However, the anomaly is quite small and is considered to be not essential for the dielectric property of the glass samples.

Figure 5 shows Arrhenius plots of the derived dielectric relaxation times for the glasses of $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ and $(AgI)_x(Ag_3PO_4)_{1-x}$. In all the glasses studied, the relaxation times are well on the respective straight lines, and the intercepts at T^{-1} (K^{-1}) $= 0$, being 10^{-14}–10^{-15} s, are within an appropriate order of magnitude in view of the frequency of the translational vibration of Ag$^+$ ions. The good fit of the relaxation times by a straight line indicates that the potential energy curve for the positional rearrangement of the conductive Ag$^+$ ions is virtually unchanged in the temperature range studied here below the α-glass transition temperatures. The activation energies, $\Delta\varepsilon_a$, of Ag$^+$-ion migration were calculated from the slope of the lines to be 41.3, 38.4, and 34.4 kJ mol^{-1} for $x = 0$, 0.20, and 0.40, respectively, in $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ glasses, and 35.1 and 34.9 kJ mol^{-1} for $x = 0.30$ and 0.50, respectively, in $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses.

4. Discussion

4.1. Presence of a critical AgI composition for appearance/disappearance of the heat capacity jump due to the β-glass transition

Both the glasses of $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ exhibited the β-glass transition due to the freezing-in/out of the positional disorder of conductive Ag$^+$ ions. The decrease in the glass transition temperature, T_g, and the increase in the heat-capacity jump, ΔC_p, associated with the transition are found on increasing the AgI composition as a common feature of the β-glass transition in the systems (see table 1). The ΔC_p values are plotted as a function of AgI composition in figure 6 for the present $(AgI)_{0.70}(Ag_3PO_4)_{0.30}$ and $(AgI)_{0.80}(Ag_3PO_4)_{0.20}$ glasses together with those reported previously for $(AgI)_x(AgPO_3)_{1-x}$ and $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ glasses [7–9, 11]. In these glass systems, as a whole, a tendency
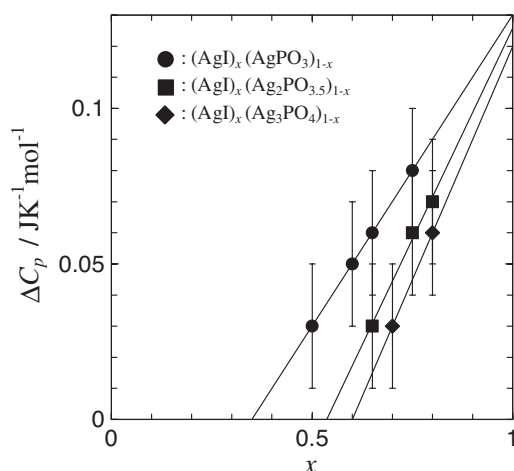
Figure 6. AgI composition dependence of the heat-capacity jump in the β-glass transition associated with rearrangement of Ag^+ ions in the glasses: ● $(AgI)_x(AgPO_3)_{1-x}$ glasses; ■ $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ glasses; ◆ $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses.

of a rather linear decrease in ΔC_p with the decrease of AgI composition, x, is observed, and this characteristic dependence indicates that the β-glass transition appears in the glasses with larger AgI composition than some critical value, x_c, while the Ag^+ ions in the glasses with small x are not excited in their positions at the glass transition temperature expected from the temperature dependence of the dielectric relaxation times [8, 9, 12, 27]. In the currently studied $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses, assuming a linear dependence of ΔC_p on x leads to almost the same value at the limit of $x = 1$ as those expected in $(AgI)_x(AgPO_3)_{1-x}$ and $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ glasses. This indicates that the assumed straight line represents reasonably well the relation between ΔC_p and x in $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses, and the critical AgI composition, x_c, at which the ΔC_p appears based on the β-glass transition is derived from the intercept of the linear line to the abscissa in figure 6 to be 0.60. The x_c value, depending on the structures of the glass network formers, is larger than 0.35 and 0.54 for $(AgI)_x(AgPO_3)_{1-x}$ and $(AgI)_x(Ag_2PO_{3.5})_{1-x}$, respectively, glasses.

The β-glass transition can be observed only in the case where an appreciable number of Ag^+ ions are in the excited sites and it varies with the temperature change. The magnitude of the associated heat capacity jump reflects the change in the number of the ions in the excited sites and the energy for the excitation. Meanwhile, $AgI–Ag_2O–P_2O_5$ systems are generally recognized as mixtures of end compounds of AgI and glass network former $Ag_yPO_{(5+y)/2}$; $y = 1$ for $AgPO_3$, $y = 2$ for $Ag_2PO_{3.5}$, and $y = 3$ for Ag_3PO_4. Although pure melt AgI and Ag_3PO_4 really crystallized during the cooling and could not be captured in the glassy states, it is significant to consider the structural environments of the Ag^+ ions in the respective glassy states of pure AgI and glass network formers. Then, the above observation that the β-glass transition is found only in a larger AgI composition range than a critical x_c indicates that the Ag^+ ions in AgI would have plural accessible sites with relatively small excitation energies. This is reasonable since the Ag^+ ions are surrounded only by iodide ions and the glass is expected to have microscopically a structure somewhat similar to the crystalline α-AgI. On the other hand, it turns out that the Ag^+ ions in any glass network former are surrounded by $–O^-$ oxygen ions and in some cases would be arrested rather by a particular oxygen ion. In the mixture of the end compounds, there appear Ag^+ ions which are surrounded both by

iodide ions and –O$^-$ oxygen ions. Such Ag$^+$ ions would show, in an ordinary expectation, properties in between the above two in the glasses of AgI and glass former and changing with the composition. In view of the presence of the particular x_c, therefore, it is strongly indicated that the fast Ag$^+$ ion conduction is brought about through the existence of amorphous AgI aggregate regions and that x_c is the composition at which the region starts to be formed within the glasses. Further, it is suggested that ΔC_p at the limit of $x = 1$ would correspond to the property of the pure amorphous AgI which has never been realized.

4.2. Excitation energy of Ag$^+$ ion to another accessible site in the amorphous AgI aggregate

The critical AgI composition x_c depends naturally on the glass-former network structures [11]: PO$_4^{3-}$ anion as the glass former with a monomer structure is more dispersive than PO$_3^-$ with a chain and PO$_{3.5}^{2-}$ with a dimer structure. This dispersive property tends to prevent AgI from forming the amorphous aggregate region and hampers its development, resulting in larger x_c for (AgI)$_x$(Ag$_3$PO$_4$)$_{1-x}$ than those for (AgI)$_x$(AgPO$_3$)$_{1-x}$ and (AgI)$_x$(Ag$_2$PO$_{3.5}$)$_{1-x}$ glass systems.

The amount of the AgI, x_{aggr}, forming AgI aggregates and thus contributing to the β-glass transition in the glasses can be expressed by the formula $(x - x_c)/(1 - x_c)$ [8]. By applying the formula, $x_{aggr} = 0.25$ and 0.50 are derived for the currently studied (AgI)$_x$(Ag$_3$PO$_4$)$_{1-x}$ glasses with $x = 0.70$ and 0.80, respectively, to contribute to the β-glass transition and thus to the heat-capacity jump, ΔC_p, at the transition temperature. The values of x_{aggr} for the glasses are also listed in table 1. The fraction, x_{aggr}, forming the AgI aggregates increases abruptly with increasing x above x_c. ΔC_p includes information about the average energy difference $\Delta \varepsilon$ between adjacent lowest-energy sites for the Ag$^+$ ions, as stated above. The β-glass transition was observed at very low temperatures in a liquid-nitrogen temperature region and ΔC_p was quite small. These facts indicate that the heat-capacity jump consists only of the contribution by an excitation to the first excited positional state of Ag$^+$ ion relevant to the β-glass transition. In such a case, a double-minimum potential is a suitable assumption to express the energetic environment with respect to 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 $\Delta \varepsilon$, the energy difference,

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

The molar value C can be related to the magnitude of the observed heat-capacity jump ΔC_p 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 difference between the lowest two potential minima, $\Delta \varepsilon$, was estimated to be 6.2 and 5.5 kJ mol^{-1} for (AgI)$_{0.70}$(Ag$_3$PO$_4$)$_{0.30}$ and (AgI)$_{0.80}$(Ag$_3$PO$_4$)$_{0.20}$ glasses, respectively, and are listed in table 1.

The $\Delta \varepsilon$ values are plotted as a function of x in figure 7 along with the results of our previous works for (AgI)$_x$(AgPO$_3$)$_{1-x}$ and (AgI)$_x$(Ag$_2$PO$_{3.5}$)$_{1-x}$ glasses [8, 11]. In all the glasses of (AgI)$_x$(AgPO$_3$)$_{1-x}$, (AgI)$_x$(Ag$_2$PO$_{3.5}$)$_{1-x}$ and (AgI)$_x$(Ag$_3$PO$_4$)$_{1-x}$, $\Delta \varepsilon$ values are observed to decrease with the AgI composition x, and shows a tendency to converge upon the value of ∼5 kJ mol^{-1} at the limit of $x = 1$. This indicates the formation of the hypothetical bulk amorphous AgI at the limit, and the estimated value of $\Delta \varepsilon$ at $x = 1$ is considered to correspond to that for the bulk amorphous AgI, which has never been obtained experimentally.
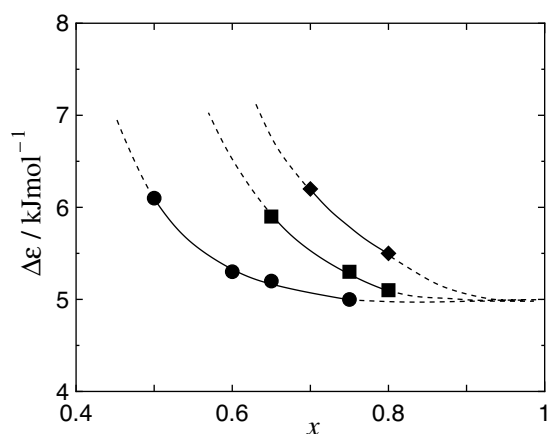
Figure 7. AgI composition dependence of the energy difference between adjacent lowest-energy sites for the Ag$^+$ ions in the glasses: ● $(AgI)_x(AgPO_3)_{1-x}$ glasses; ■ $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ glasses; ◆ $(AgI)_x(Ag_3PO_4)_{1-x}$ glasses.

4.3. Inflection in the AgI composition dependence of $\Delta\varepsilon_a$, as evidencing the changeover in the path of conductive Ag$^+$ ions with the composition

It was mentioned above that there should be typically three kinds of Ag$^+$ ions present in AgI–Ag$_2$O–P$_2$O$_5$ systems: Ag$^+$ ions surrounded only by iodide ions, only by –O$^-$ oxygen ions, and by both ions. Since the structural and energetic environments of these Ag$^+$ ions are different, the potential barriers for the conduction must be different from each other. In view of the fact that the β-glass transition is observed only in the glasses with larger x than an x_c, the Ag$^+$ ions surrounded only by iodide ions are understood to be most mobile, and those surrounded only by –O$^-$ oxygen ions of glass former component to be the most immobile among them. Therefore a possibility exists that, as x increases, a kind of jump in the activation energy for the Ag$^+$ ion conduction appears at the stage where the Ag$^+$ ions surrounded both by iodide ions and –O$^-$ oxygen ions and/or surrounded only by iodide ions rise by an appreciable amount.

Figure 8 shows a plot of the activation energies obtained for the Ag$^+$ ion conduction, $\Delta\varepsilon_a$, against the AgI composition, x, together with the data previously reported for the glasses of $(AgI)_x(AgPO_3)_{1-x}$ [8, 12], $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ [9, 12], and $(AgI)_x(Ag_3PO_4)_{1-x}$ [12]. The dependence exhibits an inflection clearly in $(AgI)_x(Ag_3PO_4)_{1-x}$ glass at around $x_c = 0.60$, and also in $(AgI)_x(Ag_2PO_{3.5})_{1-x}$ glass at around $x_c = 0.54$. The presence of these inflection points indicates that the activation energy of the Ag$^+$ ion conduction changes rather abruptly and thus the mechanism of the conduction path changes in the glasses at around the composition x_c, as the β-glass transition starts to be observed. In view of the character of calorimetry, furthermore, the distinct observation of the β-glass transition means that an appreciable number of Ag$^+$ ions are located in almost the same energetic environments. Such a condition would be fulfilled when the Ag$^+$ ions located within amorphous AgI regions are produced. The appearance of the inflection point also evidences consistently that the amorphous AgI regions start to be formed at around x_c in the glasses.

5. Conclusion

It was observed that the β-glass transition due to the freezing-in/out of the fast Ag$^+$ ion conduction appears in the $(AgI)_x(Ag_yPO_{(5+y)/2})_{1-x}$ glasses with larger x than the respectively

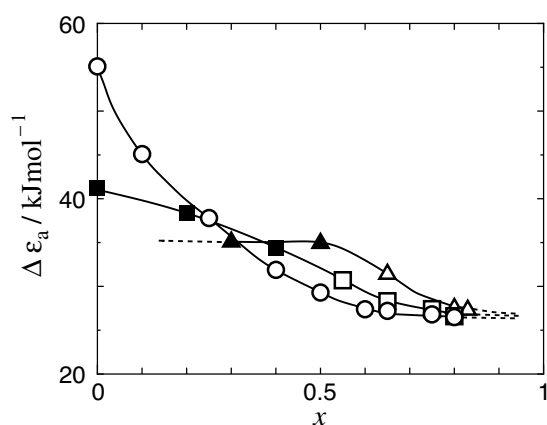**Figure 8.** AgI composition dependence of the activation energy for the Ag$^+$ ion conduction in the glasses: ○ (AgI)$_x$(AgPO$_3$)$_{1-x}$; □ ■ (AgI)$_x$(Ag$_2$PO$_{3.5}$)$_{1-x}$; △ ▲ (AgI)$_x$(Ag$_3$PO$_4$)$_{1-x}$. Open symbols represent the values already reported and closed symbols the present results.

particular critical x_c values and that the x dependence of the activation energies for the conduction shows an inflection at around the same x_c as well. These observations strongly support the validity of the 'amorphous AgI aggregate' model for characterizing the structure of the glasses in connection with the fast Ag$^+$ ion conduction, but not the model assuming a homogeneous arrangement of the constituent ions for the glasses. AgI aggregate regions are formed naturally at high AgI compositions within the interstices between the glass-former networks, and the AgI aggregate has an amorphous structure dependent on the size of the region, which develops with increasing AgI composition. It is reasonable that the calorimetric β-glass transition is observed only in the situations where an appreciable number of Ag$^+$ ions, as surrounded by only iodide ions, are located in almost the same energetic environments and have excitable sites at the temperature. The value x_c is consistently understood as the composition at which the amorphous AgI region starts to be formed in the glasses.

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