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Activation properties of Ag⁺-ion conduction in bulk amorphous AgI: estimation from extrapolation of the AgI composition dependence in AgI–Ag₂O–P₂O₅ glasses

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Abstract

AgI-based fast-ion conducting glasses with very high AgI compositions from the (AgI)_x(AgPO₃)_{1-x}, (AgI)_x(Ag₂PO_{3.5})_{1-x}, and (AgI)_x(Ag₃PO₄)_{1-x} systems were prepared successfully by using a rapid-press quenching and a twin-roller quenching method. The ac dielectric measurements showed common relaxation properties of Ag⁺-ion conduction in the glasses independently of the species of the glass network formers of AgPO₃, Ag₂PO_{3.5}, and Ag₃PO₄, and the activation energies, $\Delta\varepsilon_a$, for Ag⁺-ion conduction were observed to converge upon the same magnitude of ~ 26 kJ mol⁻¹ at the AgI composition limit of $x = 1$. This indicates the formation of amorphous AgI regions in the glasses, and the value of $\Delta\varepsilon_a = 26 \pm 1$ kJ mol⁻¹ estimated at $x = 1$ was concluded to correspond to that for bulk amorphous AgI which has never been obtained experimentally.

1. Introduction

A solid-state electrolyte is a key material for constructing a solid-state battery, which can have higher electrical energy density without the leakage problem of liquid electrolytes. In attempting the realization of solid-state electrolytes, fast-ion conducting (FIC) glasses have been studied widely in efforts to produce higher ionic conductivity, and much effort has been made to clarify the structure of the glasses and to understand the mechanism of the ion conduction [1–5]. Among them, AgI-based glasses have been most widely investigated as

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model materials, since they have relatively high ionic conductivity and can be easily prepared. We have postulated an ‘amorphous AgI aggregate’ model for the structure of the AgI-based FIC glasses, based on the results of high-precision adiabatic calorimetry and ac dielectric measurements [6–9].

According to the model, the amorphous AgI aggregate region is formed in the interstices between the glass former network above some critical AgI composition, and the region grows and develops in size as the AgI composition increases. At very high AgI composition, the properties of the AgI aggregate region are expected to approach those proper to bulk amorphous AgI, and thus the conductive Ag^+ ions would show a certain characteristic property corresponding to bulk amorphous AgI independently of the glass network structures.

We succeeded in preparing glassy samples with very high AgI compositions for the AgI–Ag₂O–P₂O₅ glass systems of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, and $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$ by using a rapid-press quenching and a twin-roller quenching method. In this paper, we show the common relaxation properties observed for conductive Ag^+ ions in the glasses with very high AgI compositions by means of ac dielectric measurements. The properties obtained by extrapolating the AgI composition dependence to $x = 1$ should correspond to those of bulk amorphous AgI, and in this way we estimated the activation energy of Ag^+ -ion conduction in bulk amorphous AgI for the first time.

2. Experimental details

$(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, and $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$ glasses were prepared under low-light conditions from raw materials of reagent grade—namely AgI, AgNO₃, Ag₂O, and NH₄H₂PO₄—according to the following procedure. The raw materials were weighed to obtain the desired composition, mixed, and ground in a mortar. The mixture was slowly heated to 873 K and the red melt was quenched to room temperature. The samples with relatively low AgI compositions of $x \leq 0.65$ for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, and all the samples of $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$ 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 [10]. For the samples with higher AgI compositions of $x \geq 0.65$ and 0.75 for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ and $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, respectively, the twin-roller quenching method was applied to quench them at a higher cooling rate: the melt was poured between the twin rollers rotating at 3000 rpm at room temperature [11]. Thin flakes of the glass were yielded by this quenching method, and the cooling rate was estimated to be $\sim 10^5$ K s⁻¹ from the thickness of the products [11, 12]. Powder x-ray diffractometry was carried out using Cu K α radiation, to confirm the successful preparation of glass samples containing no crystallite. The glass-forming AgI composition regions for producing $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, and $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$ by the above quenching methods were $0 \leq x \leq 0.80$, $0 \leq x \leq 0.80$, and $0.50 \leq x \leq 0.83$, respectively.

The ac dielectric response of the glasses was measured as a function of both temperature (90–370 K) and frequency (10 Hz–1 MHz) employing an NF Electronic Instruments 2340 LCZ meter. Electrodes were prepared as silver films by depositing silver vapour on each side of the plate sample with a thickness of 0.2–0.3 mm obtained by the rapid-press quenching method⁴. For the flake sample with the thickness of ~ 20 μm obtained by the twin-roller quenching method, silver paste was painted on both sides of the sample as the electrodes and the sample with the electrodes was stiffened with an epoxy resin to prevent the sample from breaking during the measurements. The difference of the electrodes was confirmed not to affect the

⁴ Vapour-deposited gold electrodes were employed only for the $(\text{AgI})_{0.10}(\text{AgPO}_3)_{0.90}$ glass sample.

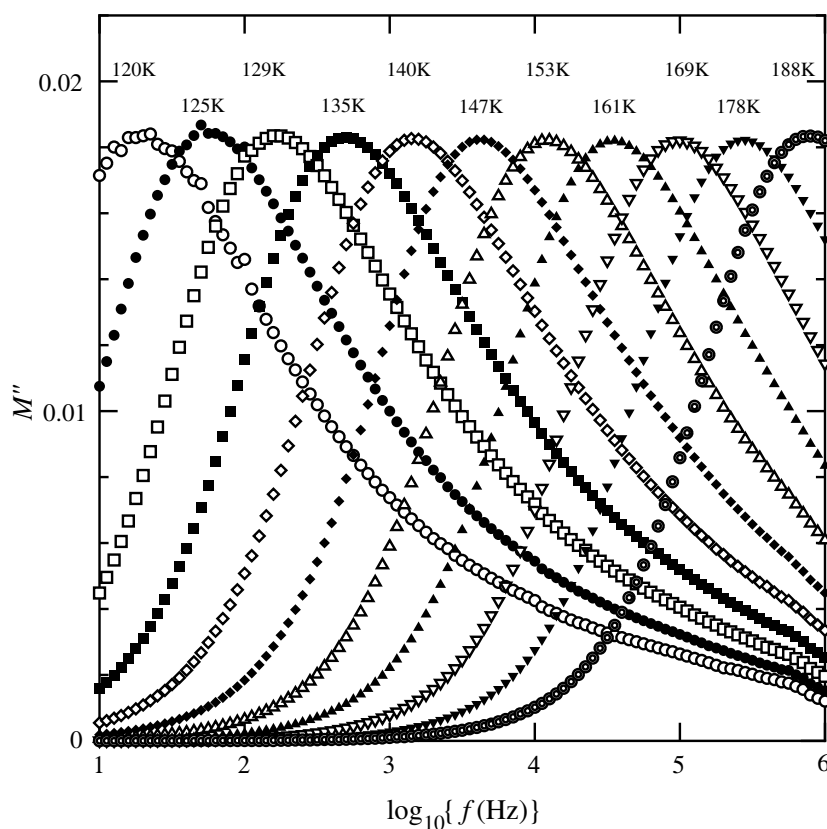


Figure 1. Isothermal M'' -spectra for an $(\text{AgI})_{0.50}(\text{AgPO}_3)_{0.50}$ glass at different temperatures: \circ , 120 K; \bullet , 125 K; \square , 129 K; \blacksquare , 135 K; \diamond , 140 K; \blacklozenge , 147 K; \triangle , 153 K; \blacktriangle , 161 K; ∇ , 169 K; \blacktriangledown , 178 K; \odot , 188 K.

results by making measurements for $(\text{AgI})_{0.65}(\text{AgPO}_3)_{0.35}$ glass samples. The results of the ac dielectric measurements were analysed according to the electric modulus M^* -formalism, which has been employed for analysing the ac response of FIC glasses [13, 14], to investigate precisely the relaxation of conductive Ag⁺ ions and its dependence on temperature.

3. Results

The imaginary component of the complex electrical modulus, M'' , measured at several different temperatures for $(\text{AgI})_{0.50}(\text{AgPO}_3)_{0.50}$ glass is plotted against the common logarithm of frequency in figure 1. The plot shows features typical of the M'' -spectra for all glasses studied here. The frequency of the M'' -peak, $f_{M''}$, was observed to increase with increasing temperature in the spectra, without changes of peak height and spectral shape. $f_{M''}$ is considered as the mean frequency of the fluctuational motion of conductive Ag⁺ ions in the glasses at the specific temperature, and thus the relaxation time, τ , associated with the diffusional motion of conductive Ag⁺ ions at that temperature was evaluated as $\tau = 1/(2\pi f_{M''})$.

Figures 2(a)–(c) show Arrhenius plots of the derived dielectric relaxation times for the glasses $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, and $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$, respectively. For all the glasses, the relaxation times are well on the respective straight lines, and the intercepts

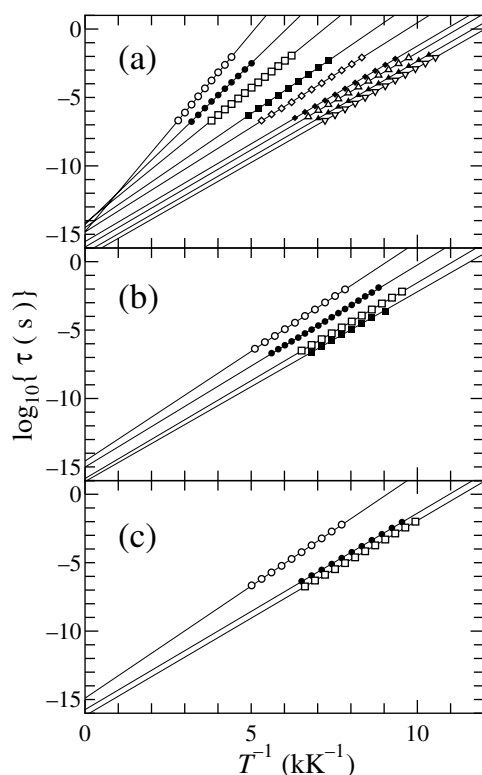


Figure 2. Arrhenius plots of the relaxation times, associated with the Ag^+ -ion migration in the AgI-based FIC glasses, evaluated from the results of the ac dielectric measurements: (a) $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$: \circ , $x = 0$; \bullet , $x = 0.10$; \square , $x = 0.25$; \blacksquare , $x = 0.40$; \diamond , $x = 0.50$; \blacklozenge , $x = 0.60$; \triangle , $x = 0.65$; \blacktriangle , $x = 0.75$; ∇ , $x = 0.80$; (b) $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$: \circ , $x = 0.55$; \bullet , $x = 0.65$; \square , $x = 0.75$; \blacksquare , $x = 0.80$; (c) $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$: \circ , $x = 0.65$; \bullet , $x = 0.80$; \square , $x = 0.83$. The solid line represents the result of least-squares fitting of a straight line to the relaxation time data for each glass.

at $T^{-1} (\text{K}^{-1}) = 0$, being at 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 glass transition temperatures. The activation energies, $\Delta\varepsilon_a$, of Ag^+ -ion migration in these glasses were calculated from the slope of the lines, and were plotted in figure 3 against the AgI composition, x , of the glasses. The $\Delta\varepsilon_a$ values estimated here for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses are in reasonable agreement with those estimated from the temperature dependence of the dielectric relaxation frequency [13] and of the dc conductivity [13, 15], as shown in figure 3 by plotting those literature data together.

4. Discussion

In this work, the activation energies, $\Delta\varepsilon_a$, of Ag^+ -ion migration in AgI– Ag_2O – P_2O_5 glasses were evaluated from the temperature dependence of the dielectric relaxation times. The dielectric relaxation frequency and the dc conductivity for FIC glasses have been correlated

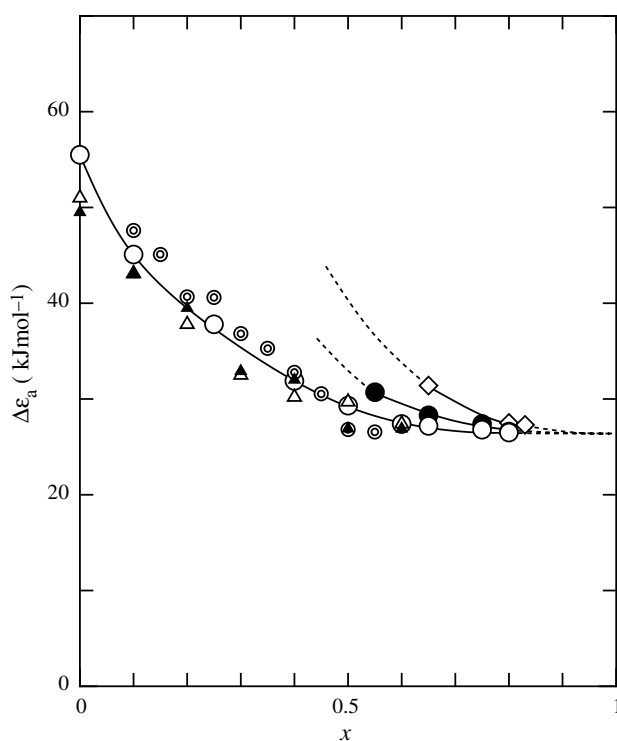


Figure 3. The dependence on the AgI composition, x , of the activation energy, $\Delta\epsilon_a$, for the Ag⁺-ion conduction in glasses: \circ , $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$; \bullet , $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$; \diamond , $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$. \triangle , \blacktriangle , and \odot represent the reported values of $\Delta\epsilon_a$ for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses: \triangle and \blacktriangle , from dielectric relaxation measurement and conductivity measurement, respectively [13]; \odot , from conductivity measurement [15].

using a linear function empirically, and the activation energy evaluated from the temperature dependence of the relaxation frequency has been reported to be essentially equal to that derived from the temperature dependence of the dc conductivity, indicating that the activation energies evaluated in the different ways originate from the same physical process [13]. Thus the $\Delta\epsilon_a$ evaluated here is considered as the activation energy for Ag⁺-ion conduction, and can be a good parameter to represent the conduction properties of Ag⁺ ions in the glasses [3, 15, 16].

In all the glasses of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, and $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$, the activation energies, $\Delta\epsilon_a$, of Ag⁺-ion conduction were observed to decrease with the AgI composition x as shown in figure 3. Phosphates in $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses exist mainly in the form of metaphosphate with one-dimensional chain structure, those in $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$ glasses are in the form of a pyrophosphate unit of $\text{Ag}_4\text{P}_2\text{O}_7$, and those in $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$ glasses are in the form of an orthophosphate unit of Ag_3PO_4 [17, 18]. The network structures have been reported for the glasses to be unchanged by addition of the dopant salt of AgI [18, 19], and the dopant salt was there interpreted as dissolving into the interstices between the network without altering the topological structure of the phosphate network. Therefore, the fact that $\Delta\epsilon_a$ decreases with increase of x indicates that the Ag⁺ ions introduced through addition of AgI into the glasses are interacting with I⁻ ions and contribute mainly to the fast-ionic conduction [7]. With the increase of AgI composition, AgI aggregate regions are formed naturally within the interstices between the glass network

formers of AgPO_3 , $\text{Ag}_2\text{PO}_{3.5}$, and Ag_3PO_4 , and the amorphous AgI aggregate regions develop with further increase of AgI composition resulting in higher Ag^+ -ion conductivity and lower $\Delta\varepsilon_a$ in the glasses.

When comparing $\Delta\varepsilon_a$ among the glasses $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{AgI})_x(\text{Ag}_2\text{PO}_{3.5})_{1-x}$, and $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$, $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glass shows the lowest value and $(\text{AgI})_x(\text{Ag}_3\text{PO}_4)_{1-x}$ glass exhibits the highest one at the same AgI composition x . This difference is reasonably considered to be due to the difference in the degree of the development of the AgI aggregate region; the development is hampered in the glasses by the more dispersed glass network in the order from AgPO_3 with one-dimensional chain structure to $\text{Ag}_2\text{PO}_{3.5}$ with dimer structure of $\text{Ag}_4\text{P}_2\text{O}_7$ to Ag_3PO_4 with monomer structure [8]. Thus, the Ag^+ ions relevant to the fast-ionic conduction are concluded to have the same energetic environment when the effective size of the AgI aggregate develops to the same degree, independently of the respective glass network structures.

At very high AgI composition, $\Delta\varepsilon_a$ shows a tendency to converge upon the same magnitude of $\sim 26 \text{ kJ mol}^{-1}$ irrespective of the species of the glass network formers at the limit of $x = 1$. Recently, the glass structure of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ system has been reported by Wicks *et al* [20] on the basis of the results of neutron, x-ray diffraction, and extended x-ray-absorption fine-structure spectroscopy with the help of reverse Monte Carlo modelling. They concluded that $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glass has an amorphous complex structure formed from the host glass of AgPO_3 and AgI, and that most Ag^+ ions are coordinated to both I and O anions without the existence of AgI ‘clusters’ by consideration of their size. However, they assumed that the AgI ‘clusters’ are of a crystalline type such as α -AgI crystallite, which is a typical crystalline FIC material, and their experiments were limited to glasses with the AgI composition with $x \leq 0.5$. The present result that $\Delta\varepsilon_a$ converges upon the same magnitude at $x = 1$ independently of the glass former network structure strongly suggests, for the high-AgI-content glasses, the formation of an AgI aggregate region in the interstices between the glass former phosphates. In the mechanical relaxation measurements for $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses, deviation has been reported for the glasses with high AgI compositions with $x > 0.4$ from the linear correlation between the AgI composition x and the Young’s modulus E' [21]. This is also considered reasonably to be due to the formation of an AgI aggregate region within the glasses in the high-AgI-content region. The AgI aggregate formed has an amorphous structure as indicated by x-ray diffraction patterns without any Bragg peak, and the properties of the amorphous AgI aggregate are expected to approach those proper to bulk amorphous AgI as the AgI composition increases.

The value of $\Delta\varepsilon_a = 26 \pm 1 \text{ kJ mol}^{-1}$ estimated at $x = 1$ is, therefore, considered to correspond to that in bulk amorphous AgI, which has never been obtained experimentally. In the amorphous AgI, the positions of I^- ions are virtually fixed and only Ag^+ ions are mobile—unlike for the case of liquid AgI, but as in the case of α -AgI crystal. However, the magnitude of $\Delta\varepsilon_a$ is much higher than $\sim 10 \text{ kJ mol}^{-1}$ reported for α -AgI [22]. This is not surprising when one considers the facts that the electrical conductivity decreases by about 12% when the crystalline α -AgI melts to liquid [23], and that the activation energy for the diffusion of Ag^+ ions in liquid AgI was estimated from a molecular dynamics simulation [24] to be 16 kJ mol^{-1} , higher than the 10 kJ mol^{-1} for α -AgI. The result obtained here suggests that the transformation of the amorphous AgI to α -AgI would increase the Ag^+ -ion conductivity in AgI-based glasses by of the order of 2–3 at the ambient temperature of 298 K.

The experimental technique used here for the estimation of Ag^+ -ion conduction properties of bulk amorphous AgI is also applicable to the other kinds of FIC glasses, and the ion conduction properties obtained for the constituents of the glasses in their bulk amorphous states would provide a more precise understanding of not only the structure of the glasses

but also the ion conduction mechanisms and the relation between them. The accumulation of knowledge on the materials in the amorphous states should give a useful guide for the realization of practically usable solid-state electrolytes.

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