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ORIGINAL PAPER

Small angle neutron scattering experiments on solid electrolyte $(AgI)_x(AgPO_3)_{1-x}$

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Abstract Superionic conductor glasses have generated considerable technological interest in the applications such as batteries, fuel cell, sensors, etc. In $AgPO_3$ glass doped by AgI, $(AgI)_x(AgPO_3)_{1-x}$, small size of AgI clusters were formed and dispersed in the $AgPO_3$ glass. The size of clusters in the sample depends on the AgI content and influences the electrical properties of the sample. To understand the microscopic structure, in particular the shape and size of the clusters, a series of small angle neutron scattering experiment on $(AgI)_x(AgPO_3)_x$ with x= 0.0, 0.5, and 0.7 were performed at the Neutron Scattering Laboratory–National Nuclear Energy Agency, Indonesia. By assuming the clusters are spherical, a radius of gyration R_g of the clusters was determined from a Guinier plot. As there are different clusters sizes in the samples, a polydisperse model is also used to analyze the data. The results show that the average radius of clusters dispersed in $(AgI)_x(AgPO_3)_{1-x}$ samples with x=0.0, 0.5, and 0.7 are around 236.2, 252.6, and 257.5 Å, respectively.

Keywords SANS instrument · Radius of gyration · Superionic glass · Solid electrolyte

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Introduction

In the recent years, glassy superionic conductors have generated considerable technological interest not only in the applications such as batteries, sensors, and fuel cell but also in the scientific point of view, especially to understand the ionic conduction mechanism that occurs within rigid disordered matrix [1]. Among superionic glasses, silver phosphate $(AgI)_x(AgPO_3)_{1-x}$ glass is the most well-known samples and become of particular interest in this study. Superionic glass with high conductivity is obtained by dissolution of silver iodide (AgI) in the $AgPO_3$ glass. The ionic conductivity at ambient temperature increases by few orders of magnitudes in the mixture AgI–$AgPO_3$ up to 10^{-2} S/cm, while it is only 10^{-7} S/cm in $AgPO_3$ glass [2]. According to Brillouin scattering studies performed by Torell [3], there are two types of motions on the AgI–$AgPO_3$ glass associated with the motion of Ag^+ in the glass and in the PO_4^- matrix.

Several neutron scattering works on AgI–$AgPO_3$ have been performed by many group of scientists. The neutron diffraction study on AgI–$AgPO_3$ shows a pre-peak at anomalously low q value ~0.7 $Å^{-1}$. The peak can be related to the length scale (d=2π/q) at the intermediate range order ~12 Å [4, 5]. The pre-peak does not occur at the undoped glass $AgPO_3$, indicating that the expansion of PO_4^- occurs when the doping salt AgI is inserted into the glass matrix.

A small angle neutron scattering on AgI–$AgPO_3$ has also previously been performed by Dianoux et al. [6]. The results show that in the $(AgI)_x(AgPO_3)_{1-x}$ glass, independent clusters of AgI are formed and dispersed in the $AgPO_3$ matrix. It is found that the size of clusters plays an important role in conductivity of the superionic glass. However, the result is now still being debated whether the inhomogeneous cluster, i.e., α-AgI, occurs in the glass matrix or only a cluster of some ions that move together in the rigid disordered matrix. To have better understanding about this material and to complete the feature of the microscopic structure, in particular the shape and size of AgI clusters, in the $AgPO_3$ glass, we performed new series of small angle neutron experiments on various samples $(AgI)_x(AgPO_3)_{1-x}$ with x=0.0, 0.5, and 0.7.

Materials and methods

The basic process in small angle neutron scattering is a scattering involving small transfer of scattering vector $\boldsymbol{q}$. The transferred scattering vector $\boldsymbol{q}$ in this scattering process is described by

$$q = k_1 - k_0 \tag{1}$$

where $\boldsymbol{k}_0$ and $\boldsymbol{k}_1$ are the scattering vectors of the incident and scattered neutrons, respectively. In the case of elastic scattering, the magnitude of the transferred scattering vector $\boldsymbol{q}$ is expressed by the following equation [7],

$$q = \frac{4\pi}{\lambda}\mathrm{Sin}\left(\frac{\theta}{2}\right) \tag{2}$$

where λ is neutron wavelength and θ is the scattering angle.

This neutron beam is collimated to the sample by collimator and scattered by the sample. The angular distribution of the scattered neutrons are usually recorded using a two-dimensional position sensitive detector (2D-PSD). Figure 1 shows schematic drawing of a small angle neutron scattering (SANS) instrument used in this experiment.

Small angle neutron scattering is mainly decided by the coherent elastic scattering events. By assuming that the small angle neutron scattering is due to a mixture of independent particles of mean radius of gyration R_g dispersed in an host matrix, the scattering intensity can be expressed in Eq. 3,

$$I(q) = n\left(\rho_\mathrm{p} - \rho_\mathrm{m}\right)^2 V^2 P(q) \tag{3}$$

where ρ_p and ρ_m is scattering length density for particle and matrix, respectively, V is volume particle, and $P(q)$ is intra-particle scattering. In case of dilute system, the SANS experiment measures $P(q)$. For the globular particles, the scattering intensity can be expressed as

$$I(q) = \exp\left(-\frac{q^2R_g^2}{3}\right) \tag{4}$$

$$\ln I(q) = -\frac{Rg^2}{3}q^2 \tag{5}$$

For the spherical particle,

$$Rg = \left(\frac{3}{5}\right)^{1/2} R_\mathrm{s} \tag{6}$$

where R_s is the radius of sphere [8]. The radius of gyration can be obtained from the slope of ln(I) versus q^2 plot which is known as a Guinier plot.

The $AgPO_3$ and AgI–$AgPO_3$ glasses were prepared by melting together stoichiometric amounts of AgI, $AgNO_3$, and $NH_4H_2PO_4$ at ~650 °C for several hours until the gas evolution was ceased. The transparent melt was quenched in liquid nitrogen environment. The white transparent glasses were obtained for undoped glass $AgPO_3$, while the yellowish transparent and opaque glasses were obtained for the superionic glass of $(AgI)_{0.5}(AgPO_3)_{0.5}$ and $(AgI)_{0.7}(AgPO_3)_{0.3}$. Detail of sample preparation has been described elsewhere [9].

To measure the shape and size of the clusters, a series of SANS experiments were performed using a SANS instrument at the Neutron Scattering Laboratory BATAN. The SANS instrument at the NSL-PTBIN BATAN consisted of the following main parts: a mechanical-velocity selector, variable collimators, and a 2D-PSD having (128×128) pixels with a pixel size of 4.99×4.68 mm^2.

The quenched glasses were ground in a mortar to become a fine powder. This powder was mounted in an

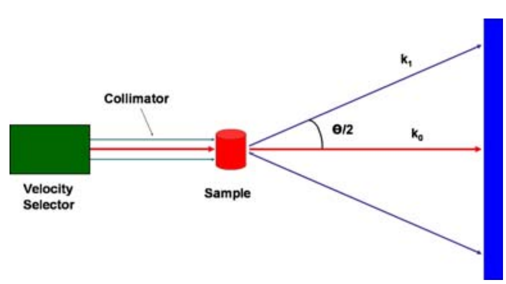

Fig. 1 Schematic drawing of a SANS method

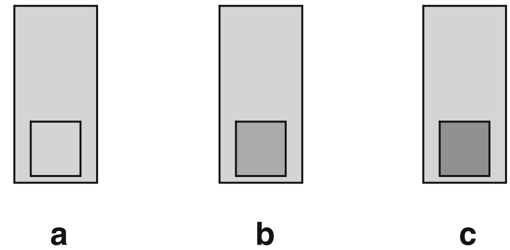

Fig. 2 SANS samples: **a** blank, **b** $AgPO_3$, **c** $(AgI)_x(AgPO_3)_{1-x}$

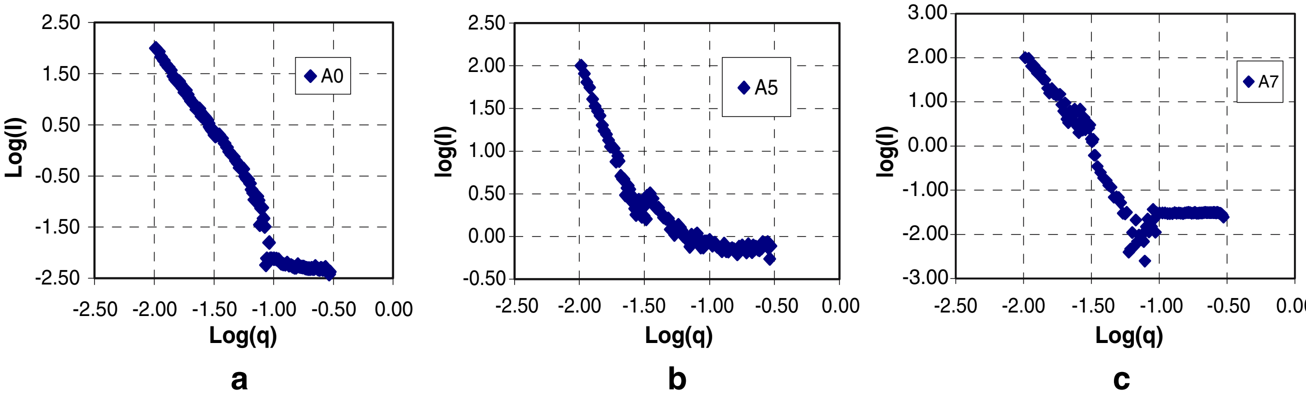

Fig. 3 Log-Log plot of $I(q)$ for three samples of $(AgI)_x(AgPO_3)_{1-x}$ **a** x=0.0 (A0), **b** x=0.5 (A5) and **c** x=0.7 (A7)

aluminum frame having a hole with cross-section of (10-mm width × 14-mm height) and 2-mm thickness shown as in Fig. 2.

Then, the sample was fixed on the SANS sample holder right before a sample slit of 10 mm in diameter which was set up to collimate the incident neutron beam coming to the sample.

The SANS experiment was carried out by the following experimental conditions: The mechanical-velocity selector was rotated at 5,000 rpm which results in the neutron wavelength of 3.9 Å, the collimator length was set up at 4 and 8 m, and the 2D-PSD was set up at the sample to detector distance (SDD) of 1.5, 4, and 13 m. The beam stop of 60 mm in diameter was set up right before the detector to protect the direct neutrons impinging on to the central region of the detector. By setting up the detector at the SDD of 1.5 to 13 m, it will cover $\boldsymbol{q}$ range from 0.007 up to 0.3 Å.

The measured data obtained from the small angle neutron scattering experiment show a distribution of neutron intensity versus channel number along the radius of the detector. The data correction was done by subtracting the raw intensity data by background, transmission of sample, and detector sensitivity using SANS BATAN Reduction software.

Results and discussions

The corrected intensity was plotted against the scattering vector $\boldsymbol{q}$, as shown in Fig. 3, for the glass samples $(AgI)_x(AgPO_3)_{1-x}$ with x=0.0 (A0), 0.5 (A5), and 0.7 (A7).

It is shown in general that the intensity versus $\boldsymbol{q}$ was nearly constant in the $\boldsymbol{q}$ range of $0.05<\boldsymbol{q}<0.3$ Å^{-1} for all samples with no clear peak observed. At lower $\boldsymbol{q}$, the log (I)–log(q) plots show slightly different slope, and the slope becomes larger at A5. This means that there was hardly inhomogenity observed in the $AgPO_3$ glass, as also observed by M. Tachez et al. [10]. By increasing the AgI into the $AgPO_3$ matrix, the intensity decreases faster as shown for A5 and A7 curves. This result suggested that the particle or cluster size formed in the matrix becomes larger as the AgI concentration is increased.

To determine the radius of gyration of independent clusters of AgI dispersed in the $AgPO_3$ matrix, a logarithmic neutron intensity was plotted against the square of scattering vector, $\boldsymbol{q}^2$. This plot is usually called as a Guinier plot, as shown in Fig. 4a–c for $AgPO_3$, $(AgI)_{0.5}(AgPO_3)_{0.5}$, and $(AgI)_{0.7}(AgPO_3)_{0.3}$, respectively.

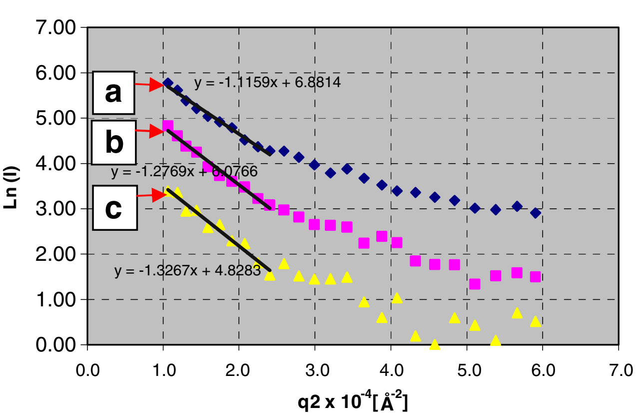

Fig. 4 Guinier plot for **a** $AgPO_3$, **b** $(AgI)_{0.5}(AgPO_3)_{0.5}$, **c** $(AgI)_{0.7}(AgPO_3)_{0.3}$

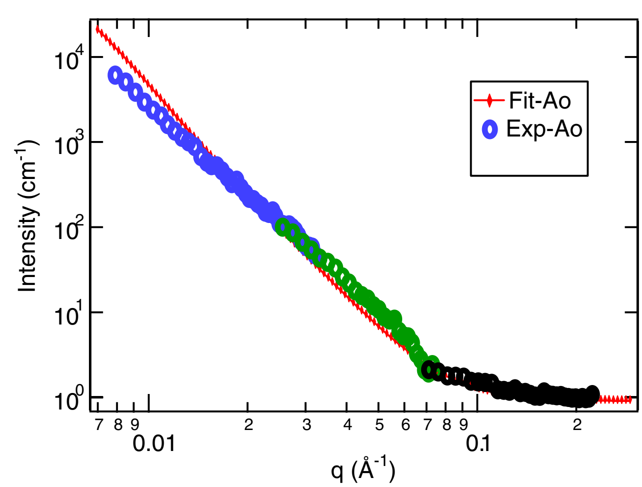

Fig. 5 Fit result for A0

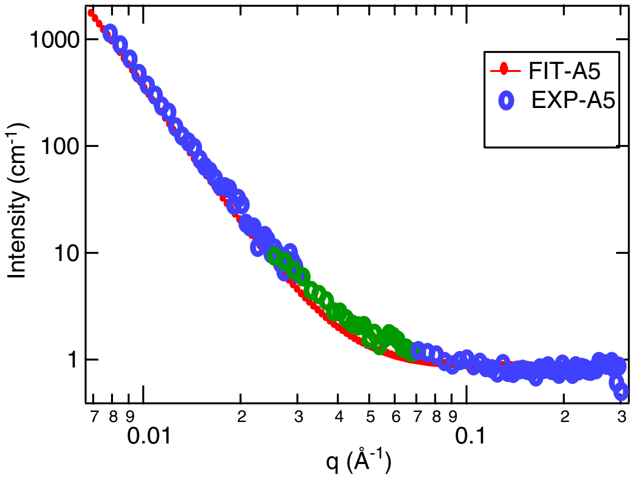

Fig. 6 Fit result for A5

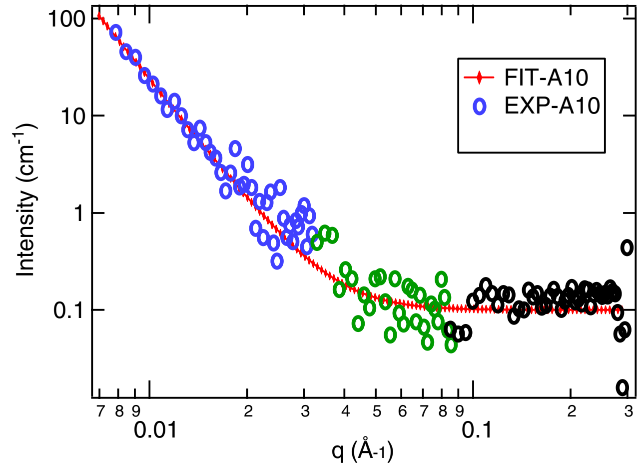

Fig. 8 Fit result for A10

A Guinear plot in Fig. 4 shows linear curves in the low ***q*** range. The radius of gyration, R_g, can be determined from the slope of the linear curve using Eqs. 5 and 6 as described in the previous section. The radius of gyrations (R_g) of particles are around 182.9, 195.7, and 199.5 Å for $AgPO_3$, $(AgI)_{0.5}$ $(AgPO_3)_{0.5}$, and $(AgI)_{0.7}$ $(AgPO_3)_{0.3}$, respectively, which correspond to the radius of spheres (R_s) around 236.2, 252.6, and 257.5 Å for $AgPO_3$, $(AgI)_{0.5}$ $(AgPO_3)_{0.5}$, and $(AgI)_{0.7}$ $(AgPO_3)_{0.3}$, respectively. The results show that the R_g for sample A7 with higher concentration is larger than the R_g for A5. This may be due to the fact that A7 is above the solubility limit, whereas the AgI cannot dissolve any more in the glass matrix so that the AgI clusters become larger.

As shown in Fig. 4, the Guinear plot of A0, A5, and A7 are rather similar at low ***q*** range. However, at higher ***q*** range, the statistical error of the particle size became larger. This suggests that a more complicated model than monodispersed spherical particles should be taken into account. For this reason, a model of polydisperse named PolyHSIntensity provided by NIST code [11] is also used to fit the SANS data. This function calculates the scattered intensity for a population of polydisperse spheres including hardsphere interaction between the particles. A Schultz distribution is used to describe the polydispersity of the diameter.

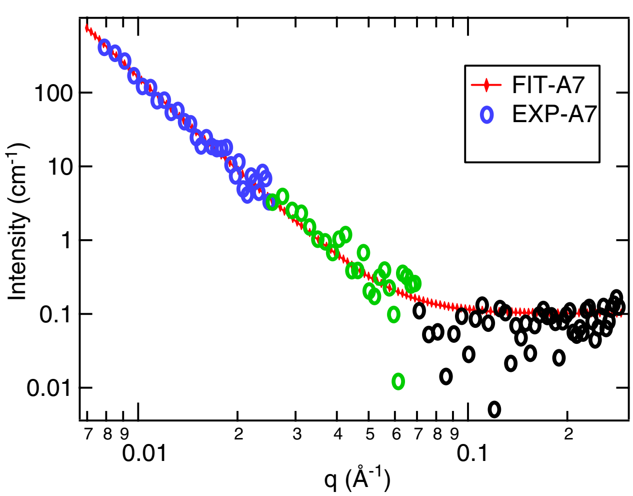

Fig. 7 Fit result for A7

The model explains that there are many different particle sizes observed in the matrix. To start with the model, several variables such as particles radius (*R*), polydispersity, scattering contrast, volume fraction, contrast, and background have to be given as an input parameters. The fit results are shown in Figs. 5, 6, and 7, respectively, for A0, A5, and A7. For comparison, the doppant salt AgI is also measured and fit by similar model as shown in Fig. 8. The average radius of particle for the AgI sample was around 235.0 Å with polydispersity of 0.8. The parameter data are summarized in Table 1.

The results show that in the superionic glasses $(AgI)_x$ $(AgPO_3)_{1-x}$, a nanoscale cluster, was formed. The size of cluster in the rigid disordered matrix increases with the amount of AgI concentration. As obtained from the fit results, the particle sizes are distributed from 236.2 to

Table 1 Variable input for curve fitting of A0, A5, A7, and A10 SANS data

No.	Parameter	A0	A5	A7	A10
1.	Radius (Å)	236.2	252.6	257.5	235.0
2.	Polydispersity	0.50	0.53	0.60	0.8
3.	Volume fraction	0.02	0.15	0.08	0.06
4.	Contrast ($Å^{-2}$)	1.85×10^{-05}	2.00×10^{-06}	2.00×10^{-06}	1.00×10^{-06}
5.	Background (cm^{-1})	0.9	0.8	0.1	0.1
6.	χ^2	0.982	0.988	0.984	0.971

257.5 Å for A0 to A7, with the polydispersity around 0.50–0.60. However, it is rather difficult to convince here whether the cluster is mainly the contribution of Ag^+ ions themselves or the AgI cluster that are not dissolved in the glass matrix. It may be possible that the different particle sizes are a combination from the phosphate network, silver, and iodine ions that disperse in the matrix, some cluster AgI, and the precipitate of AgI for high concentration.

There are also some correlation between the local structure and the ionic conductivity. According to the previous results, the ionic conductivity increases with the doping salt concentration, for example the conductivity for $AgPO_3$ is around 10^{-7} S/cm while for A5 is around 10^{-3} S/cm. However, by increasing the AgI above the solubility limit will decrease the ionic conductivity to around to 10^{-4} S/cm such as in A7. This result shows that there is an optimum size of particles that make the ions move easily.

Conclusions

Small angle neutron scattering experiments on the $(AgI)_x(AgPO_3)_{1-x}$ provide information about the existence of the clusters disperse in the glass matrix. The average radius of particle sizes can be deduced from the slope of the Guinier plot or from the curve fit of polyhardsphere model. The average radius of particles dispersed in $(AgI)_x(AgPO_3)_{1-x}$ samples with x=0.0, 0.5, and 0.7 are around 236.2, 252.6, and 257.5 Å with the polydispersity of around 0.50, 0.53, and 0.60. It is concluded that the particles sizes varies with the concentration of AgI in the glass matrix.

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