Structure and dynamics of solid electrolyte $(LiI)_{0.3}(LiPO_3)_{0.7}$

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ARTICLE INFO

ABSTRACT

Neutron scattering measurements have played important roles in not only the structural information study, but also the dynamical insight of solid state ionic materials in the form of polymer, crystalline and glassy materials. Quasielastic neutron scattering (QENS) measurement explores the diffusion mechanism of mobile ions, on the other hand, inelastic neutron scattering (INS) reveals the dynamical insight of solid ionic conductor materials. Here we present the neutron scattering study of superionic glass $(LiI)_{0.3}(LiPO_3)_{0.7}$ by using the inelastic neutron spectrometer AMATERAS at the Japan Proton Accelerator Research Complex (J-PARC). Simultaneous two dimensional maps of dynamical structure factor $S(Q,E)$ with the incident energy E_i 93.85, 23.59, 10.57 and 5.92 meV over a wide momentum transfer (Q)-range were observed for $(LiI)_{0.3}(LiPO_3)_{0.7}$. The first sharp diffraction peak appears at $Q \sim 1.8\ Å^{-1}$ in the elastic structure factor. From the inelastic scattering, low energy excitation or the Boson Peak appears at ~6.0–7.0 meV. The extra quasielastic scattering was observed in the energy range $1\ meV < E < 3\ meV$ at 285 K but not at 20 K. The Q dependence of the dynamical structure factor $S(Q,E)$ can be approximated to the long-wave acoustic like density fluctuation.

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1. Introduction

Research on solid electrolytes as a battery component has been rapidly growing due to the increasing demands of portable electronic devices [1]. Solid electrolytes based on superionic conducting glasses have several advantages compared with other solid electrolytes like polycrystals and ceramic based electrolytes; such as high ionic conductivity, no grain boundary, wide range composition, and ease of fabrication. Due to safety reason, it is important to replace the existing liquid electrolyte by the solid electrolyte, which exhibits high ionic conductivity at ambient temperature. Solid electrolyte AgI–AgPO₃ has been used as a model of superionic conducting glasses, and has been well studied by various techniques such as neutron scattering, X-ray diffraction, and Raman scattering [2–5]. The ionic conductivity of AgI–AgPO₃ is 10^{-3} S/cm, which is much higher compared with the conductivity of AgPO₃ glass at 10^{-7} S/cm [3]. The neutron scattering data shows the appearance of pre-peak on AgI–AgPO₃ at low momentum transfer ~0.8 Å^{-1}, but not in AgPO₃. This peak can be related to the intermediate range order ~10–20 Å [4]. The inelastic structure factor $S(Q,E)$ shows the existence of low energy excitation or Boson Peak (BP) at the energy of ~2.5 meV [5].

Similar to the silver phosphate glasses, the lithium based-glass LiI–LiPO₃ serves as an ideal model for examination of the ion dynamics and the transport phenomena in superionic conducting glasses. These materials are technologically important for solid electrochemical devices such as batteries, fuel cells and sensors. The ionic conductivity of LiPO₃ is ~10^{-8} S/cm and it increases to 10^{-6} S/cm for $(LiI)_{0.3}(LiPO_3)_{0.7}$ [6,7]. The neutron diffraction on LiPO₃ was studied by S. Beaufills et al. [8], but there is no inelastic neutron scattering reported so far on both LiPO₃ and LiI–LiPO₃. Therefore in order to elucidate the microscopic understanding of ion transport in disorder solid, it is important to perform inelastic neutron scattering experiment.

The neutron measurements have played important roles in not only the structural information study, but also the dynamical insight of solid state ionic materials. The Japan Proton Accelerator Research Complex (J-PARC) has shown the ability of its inelastic neutron spectrometers, such as 4SEASONS and AMATERAS [9]. This instrument is able to explore the dynamics through a two dimensional map of dynamical structure factor $S(Q,E)$ over a wide Q-range. In this study, the dynamical insight of superionic glass $(LiI)_{0.3}(LiPO_3)_{0.7}$ will be explored by the inelastic instrument AMATERAS at J-PARC. Our purpose is to observe the dynamical structure factor in this lithium system, including both elastic and inelastic scattering, in comparison to the silver system. Furthermore, a preliminary study of the quasielastic neutron scattering of $(LiI)_{0.3}(LiPO_3)_{0.7}$ at temperatures 285 K and 20 K will be briefly described.

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2. Experimental

Lithium phosphate glass $(LiI)_{0.3}(LiPO_3)_{0.7}$ was prepared by melt quenching technique (for further discussion, it is called LiI–LiPO₃). Raw materials LiI, Li_2CO_3, and $NH_4H_2PO_4$ were mixed together and melted at 850 °C. The molten mixture was quenched in liquid N_2 and it produced white transparent glasses. In order to avoid the water content or moistures, the glasses were kept under vacuum condition. The glass preparation was done at the laboratory in BATAN, Indonesia. Detail in preparation has been described elsewhere [5]. The amount of 30 g samples was wrapped in the aluminum foil with the thickness of 2 mm and was attached to the inner side of a cylindrical-hollow aluminum container. The inelastic neutron experiment was performed by using AMATERAS spectrometer at the Japan Proton Accelerator Research Complex (J-PARC). Two sets of experiments were conducted by utilizing different monochromatic chopper frequencies at 150 Hz and 300 Hz, for low resolution and high resolution measurements, respectively. The measurements on LiI–LiPO₃ were performed at room temperatures 285 K and 20 K, with the bottom loading cryostat. Detail of the spectrometer was described elsewhere [9].

3. Results and discussion

The dynamical structure factor S(Q,E) has a relation with generalized phonon density of states G(Q,E) as follows:

$$S(Q,E) \alpha e^{-2W(Q)}[n(E)+1]G(Q,E)Q^2/E \tag{1}$$

where W(Q) is the Debye Waller factor and n(E) is the Bose–Einstein population factor.

By utilizing the multiple incident energies of the AMATERAS spectrometer at J-PARC, with beam power of 217 kW, various two-dimensional maps of dynamical structure factors, S(Q,E) for $(LiI)_{0.3}(LiPO_3)_{0.7}$ with four incident neutron energies, $E_i \sim 5.92$ meV, 10.57 meV, 23.59 meV and 93.85 meV were simultaneously obtained as shown in Fig. 1. The horizontal axis shows the momentum transfer $(Q/Å^{-1})$ which varies depending on the incident energies from 0.3 Å^{-1} to 12 Å^{-1}. The vertical axis shows the energy transfer (E/meV) and the maximum is limited by the incident energy, E_i. The intensity is shown by gradation of color, with the strongest intensity is red (Fig. 1). A lot of valuable information can be extracted from the respective S(Q,E) maps. One can see an overall feature of the excitations from the data with high E_i, while the data with small E_i give precise information at low energy region.

In order to observe the quasielastic scattering, a high resolution measurement was applied. For example, the high-resolution measurement at the $E_i = 23.5$ meV was 2.8% corresponding to 0.66 meV of FWHM at the elastic peak. Fig. 2 shows the high resolution measurements of S(Q,E) map with E_i 23.59 meV at temperatures (a) 20 K and (b) 285 K. It appears that for the S(Q,E) map at 285 K there is an extra scattering that occurred at the energy transfer 1 meV < E < 3 meV, while this is not clearly shown at similar spectra at 20 K. With close

inspection, by taking the constant Q-slice at about 1.5 Å^{-1} and energy transfer at −3 meV < E < 3 meV, besides the strong elastic line corresponding to the instrumental resolution, the onset of quasielastic scattering was observed for the spectra at 285 K, while it is rather flat for spectra at 20 K (Fig. 3). Since such feature is not observed at the frozen state at 20 K, and the temperature at 285 K is too low compared with the glass transition temperature at 435 K of LiI–LiPO₃ [7], in which thermally activated viscous flow diffusion takes place. Therefore it is suggested that only the mobile ion motion can give rise to such extra quasielastic intensity. For comparison, the intensity was normalized at the elastic position. However, the quasielastic line broadening was not observed between these two temperatures, though high resolution measurement was applied.

Further analysis was needed on the inelastic spectra for constant Q at higher energy range. Fig. 4(a) shows the inelastic neutron scattering S(Q,E) of various glasses LiI–LiPO₃, LiPO₃, and SiO₂. All the data were measured by AMATERAS spectrometer at room temperature. The low energy excitation so-called Boson Peak (BP) appears significantly at the energy around 4.0–5.0 meV, 5.0–6.0 meV and 6.0–7.0 meV, for SiO₂, LiPO₃, and LiI–LiPO₃, respectively. By Raman scattering and neutron inelastic scattering experiments, a low energy broad response called a Boson Peak (BP) has generally been observed in various glasses and amorphous materials. Therefore, it is reasonable to conclude that BP is strongly related to the random structure of glass. Several models considered the physical origin of BP to be various kinds of localized modes, for example, mechanical resonance modes of sphere, vibration of ten or more atoms, and fractions [10]. Another model is based on soft potential, or soft mode which is responsible for the displacive phase transition of crystalline materials. However, among these, the origin of BP is still being discussed. Although the origin of BP has not been clarified, it is reasonable that it originates from some kind of a localized vibration, like a torsional resonance mode of some cluster, and the doped ions change the shear modulus but do not contribute to the mass of the oscillator. The contribution of Li ions into the phosphate network is distributed along the low-dimensional channels, leading through expansion of the phosphate network, in agreement with modified random network model by Greaves [11]. In this case, the doped ions Li and Ag will give different effects, due to their difference in ionic size, mass and also the average bond distance, such as Li–O and Ag–O, thus their frequency of BP is different [10]. In silver phosphate glasses AgI–AgPO₃ the BP was observed at the energy around 2.5 meV, while the position of BP of LiI–LiPO at energy ~6.0–7.0 meV (~0.1 ps). Fig. 4(b) shows the BP of LiI–LiPO₃ with various Q. The position does not change with Q, but the intensity approximately follows the S(Q) dependence.

Fig. 5 shows the constant E-slice of the dynamical structure factor S(Q,E) with the E_i was at 93.85 meV. The elastic structure factor S(Q,E ~0) shows several broad peaks at around 1.8, 2.8, 5.5, and 8.2 Å^{-1}. These peaks are rather similar to the structure factor S(Q) of LiPO₃ [8]. The pre-peak at low Q is not apparent in $(LiI)_{0.3}(LiPO_3)_{0.7}$, which is similar to LiPO₃. The structure factor of LiI–LiPO₃ reflects a homogeneity of the network and has no indication of the pronounced intermediate
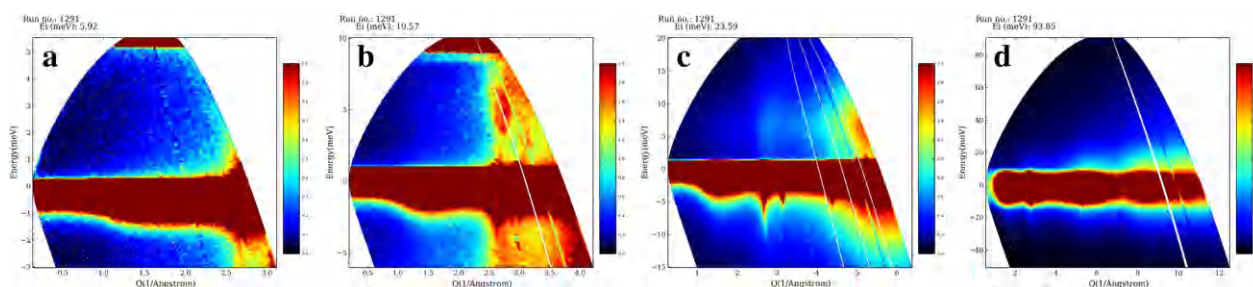

Fig. 1. S(Q,E) maps of LiI–LiPO₃ with multiple incident energies, E_i (a) 5.92 meV, (b) 10.57 meV, (c) 23.59 meV, and (d) 93.85 meV measured at room temperature by utilizing a lower resolution energy on AMATERAS, J-PARC, Japan.
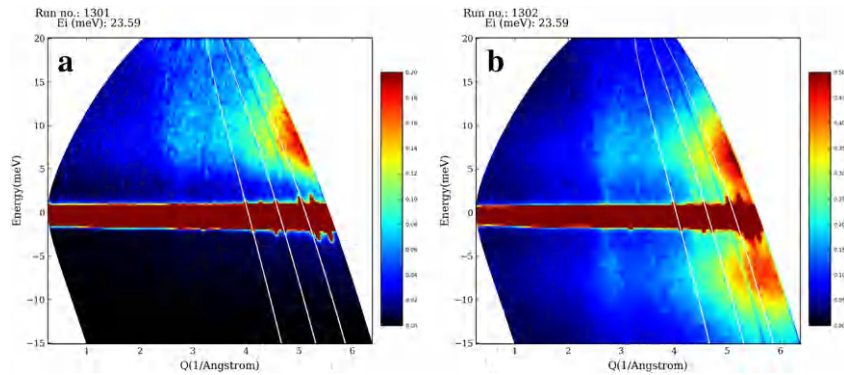
Fig. 2. S(Q,E) map of LiI–LiPO$_3$ at temperatures (a) 20 K and (b) 285 K, with incident energy, $E_i = 23.59$ meV measured by utilizing a higher resolution energy on AMATERAS, J-PARC, Japan. Extra quasielastic scattering is shown in the sub-energy range $-3 < E < 3$ meV for 285 K, but not for 20 K.

range order (IRO); no peaks were observed at very low Q values smaller than 1 Å^{-1}. The absence of IRO pre-peak is also reported for pure AgPO$_3$ glass. But the addition of AgI changes the structure dramatically, and a pronounced pre-peak appears in $(AgI)_{0.3}(AgPO_3)_{0.7}$ at Q$_p$ ~0.8 Å^{-1} [4], indicating some ordering in the corresponding length scale. The pre-peak as explained by the RMCA model was due to the expansion of the phosphate network or to the P–O distance from the radial distribution function. The predominant effect of doping salt is to expand the glass 'network' leading to an increase in the accessible free volume and conduction pathway, thus increase the ionic conductivity from AgPO$_3$ ~10^{-7} S/cm to AgI–AgPO$_3$ ~10^{-3} S/cm [12,13]. The structure of LiPO$_3$ is also assumed to be a homogenous network built of P–O chains, which are connected by Li–O bridges. However, the addition of LiI does not change the structure, and it has no indication of intermediate range order (IRO). Thus the ionic conductivities are still low for both LiPO$_3$ ~10^{-8} S/cm and $(LiI)_{0.3}(LiPO_3)_{0.7}$ ~10^{-6} S/cm.

Fig. 5(b) shows the dynamical structure factor S(Q,E) at two energy ranges, 9.2 meV < E < 15.6 meV and 22.8 meV < E < 30.0 meV. The four peaks observed in the inelastic structure factor are less pronounced, and the intensity increases towards higher Q. Further information is coming from the Q-dependence of the dynamical structure factor S(Q,E). In a plane wave approximation, S(Q,E) for an acoustic mode should oscillate in phase with S(Q), by approximately S(Q)Q^2 [14]. Since the structure factor S(Q) is rather similar to the elastic structure factor S(Q,0), therefore S(Q,0)Q^2 is used in this approximation, as shown by the dashed line in Fig. 5(b). The acoustic-like density fluctuations incorporate the structural correlations between the nearest neighbors, including the short-range order correlations between atoms
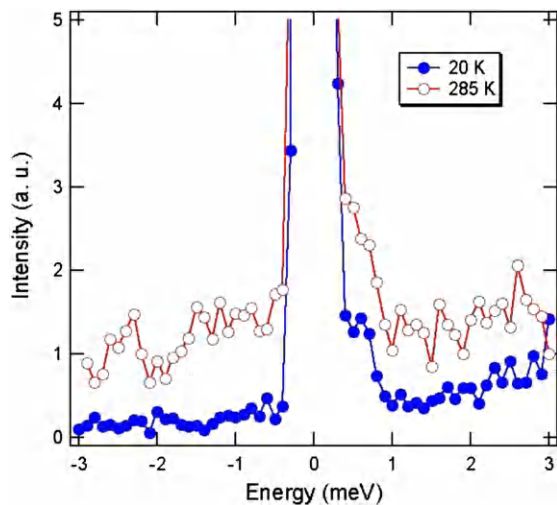
moving collectively together. The localized, not cooperative short range motion results in Q^2 term only [15]. Our results show that the spectra were fit to the model for sound wave for the low energy range. However, deviations from S(Q,0)Q^2 model appear in the Q
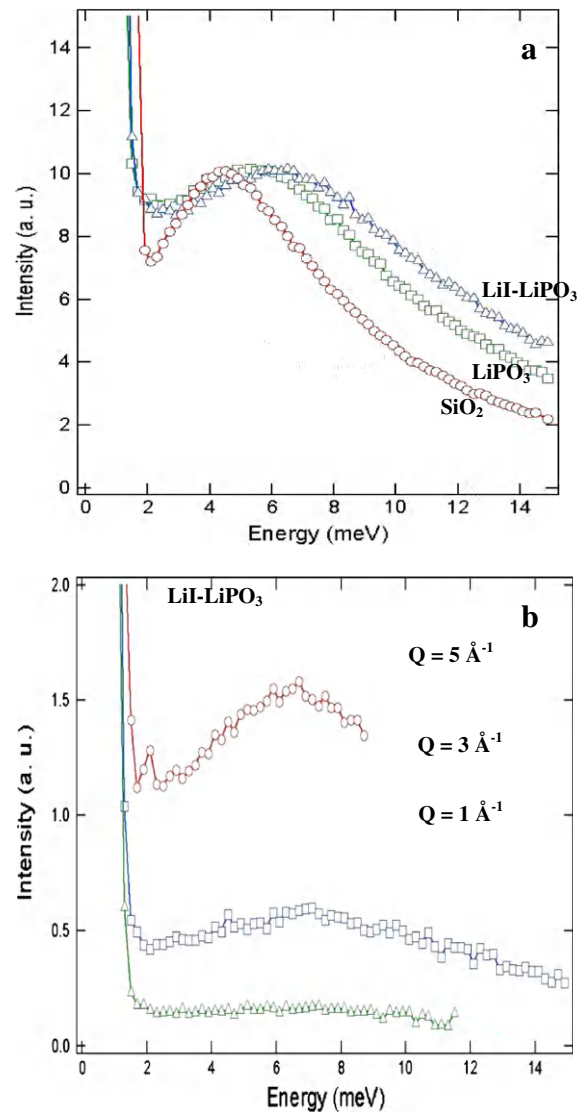

Fig. 4. Inelastic neutron scattering S(Q,E) of (a) various glasses LiI–LiPO$_3$, LiPO$_3$, and SiO$_2$ and (b) LiI–LiPO$_3$ with various Q, measured by AMATERAS spectrometer at room temperature. The Boson Peak (BP) appears significantly at the energy around 4.0–5.0, 5.0–6.0, and 6.0–7.0 meV, for SiO$_2$, LiPO$_3$, and LiI–LiPO$_3$, respectively. The peak-intensity changes following S(Q).
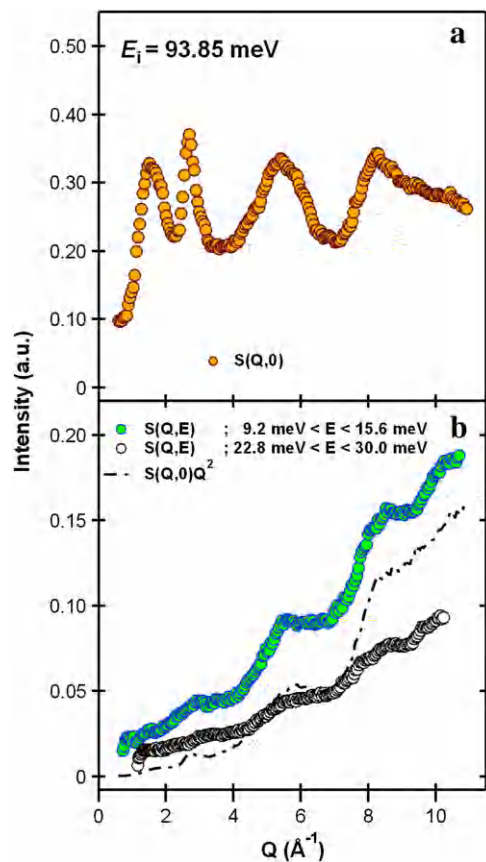

Fig. 3. Quasielastic neutron scattering, S(Q,E) of LiI–LiPO$_3$ at Q = 1.5 Å^{-1} measured with a high resolution at temperatures 285 K and 20 K.

Fig. 5. (a) Elastic structure factor S(Q,0) of LiI–LiPO$_3$; (b) dynamical structure factor S(Q,E); 9.2 meV < E < 15.6 meV and S(Q,E); 22.8 meV < E < 30.0 meV. It is shown that the inelastic spectra have similar tendencies with S(Q,0)Q^2 (dashed line).

range 7–10 Å^{-1} and are actually stronger if the energy is higher. This is a clear indication of the existence of another type of motion, such as the localized jumps of the single atoms from neighboring sites.

4. Conclusions

The structural and dynamical insight of $(LiI)_{0.3}(LiPO_3)_{0.7}$ has been observed by inelastic neutron scattering. Many valuable information can be extracted from the S(Q,E). In lithium phosphate glasses, no peaks observed at very low Q values smaller than 1 Å^{-1}, indicating that the structure factor of LiI–LiPO$_3$ reflects a homogeneity of the network with no indication of the pronounced intermediate range order (IRO). However, the indication of IRO was observed in $(AgI)_{0.3}(AgPO_3)_{0.7}$, but not in AgPO$_3$ glass. Though the origin is still not understandable, the reason of the pre-peak has been previously attributed to increase distances and voids, i.e. free volume between the P–O chains due to the introduction of I-ions. The existence of the pre-peak in AgI–AgPO$_3$ can be related to the expansion of glass network and the increase of ionic conductivity. In the lithium phosphate, the absence of the pre-peak shows that network expansion is limited, no IRO, and thus the ionic conductivity is still low. Our inelastic data shows the dynamics on the energy scale corresponding to the picosecond (>0.2 ps) at 285 K, far below the glass transition temperature. Since such motion does not occur for the quasielastic scattering at frozen temperature at 20 K, and the viscous flow at 285 K is many orders of magnitude slower, only motion from mobile ions can cause such extra quasielastic intensity. Recent computer simulation confirms the existence of such localized oscillating back and forth jumps [13]. The presence of the Boson Peak at higher energy range is also interesting to be further discussed [10]. At the Boson Peak position the motion is more correlated and cooperative, while on the low energy range corresponding to the longer time scale (0.4 meV–15 ps) the motion is more localized. In general, the inelastic intensity S(Q,E) increases with Q by approximately S(Q)Q^2, as expected for long wavelength sound waves. In order to elucidate the structural model of the LiI–LiPO$_3$, further neutron diffraction experiment needs to be performed by using a NOVA instrument at JPARC, Japan.

Acknowledgments

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