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 <b>Experimental Report</b> 	承認日 Date of Approval 2015/2/20 承認者 Approver Kaoru SHIBATA 提出日 Date of Report <b>Feb. 19, 2015</b>
課題番号 Project No. <b>2014B0076</b> 実験課題名 Title of experiment Direct observation of lithium-ion dynamics in $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ lithium superionic conductors 実験責任者名 Name of principal investigator Kazuhiro MORI 所属 Affiliation Research Reactor Institute, Kyoto University	装置責任者 Name of Instrument scientist Kaoru SHIBATA 装置名 Name of Instrument/(BL No.) DNA / BL 02 実施日 Date of Experiment December 18-22, 2014

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)  
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.
1. ${}^7\text{Li}_7\text{P}_3\text{S}_{11}$ crystal 2. $({}^7\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}$ glass 3. $({}^7\text{Li}_2\text{S})_{60}(\text{P}_2\text{S}_5)_{40}$ glass

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.
<p> <math>\text{Li}_2\text{S}-\text{P}_2\text{S}_5</math> glasses are promising candidates as solid electrolytes in all-solid-state lithium-ion batteries, because they show high ionic conductivities (<math>\sim 10^{-4}</math> S/cm) at room temperature (RT) [1]. Furthermore, <math>\text{Li}_7\text{P}_3\text{S}_{11}</math> metastable crystal, which can be prepared by aging <math>(\text{Li}_2\text{S})_{70}(\text{P}_2\text{S}_5)_{30}</math> glass, shows more than <math>10^{-3}</math> S/cm at RT [2]. The aim of this study is to observe the motion of Li ions in the <math>{}^7\text{Li}_2\text{S}-\text{P}_2\text{S}_5</math> glasses and the <math>{}^7\text{Li}_7\text{P}_3\text{S}_{11}</math> metastable crystal. Quasi-elastic neutron scattering (QENS) is a powerful tool for directly observing the motion of ions in solids. Even though the incoherent scattering cross section for <math>{}^7\text{Li}</math> nucleus is relatively small (<math>\sigma_{\text{inc}}({}^7\text{Li}) = 0.78</math> barn), we can observe the QENS spectrum associated with the thermal self-diffusion for the <math>{}^7\text{Li}</math> ions due to the high flux of neutron beam generated by the 1-MW pulsed-spallation neutron source in the J-PARC/MLF. In this work, we performed QENS experiments using the DNA at the BL02 beam line: the energy resolution of the DNA is 3.6 <math>\mu\text{eV}</math> [3].                 </p>

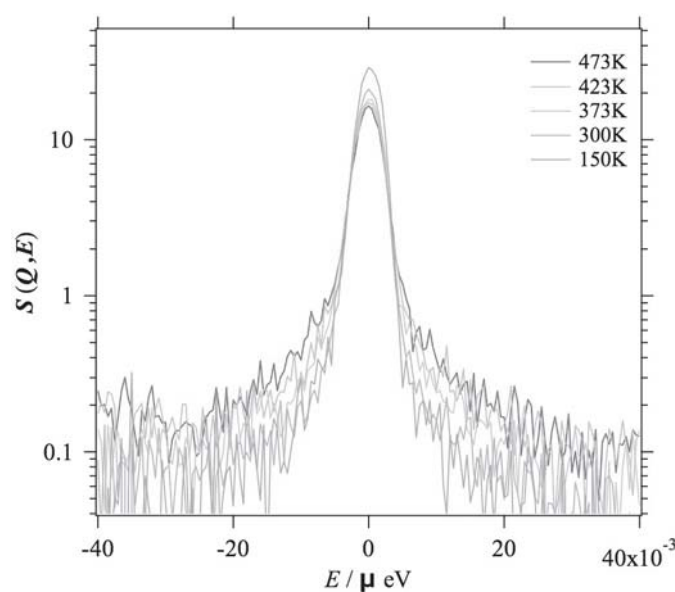
## 2. 実験方法及び結果(つづき) Experimental method and results (continued)

$({}^7\text{Li}_2\text{S})_x(\text{P}_2\text{S}_5)_{100-x}$  glasses ( $x = 60$  and  $70$ ) and  ${}^7\text{Li}_7\text{P}_3\text{S}_{11}$  metastable crystal were synthesized by mechanical alloying (MA). The three-dimensional structures and the predicted conduction pathways of Li ions in the  ${}^7\text{Li}_2\text{S}-\text{P}_2\text{S}_5$  glasses and the  ${}^7\text{Li}_7\text{P}_3\text{S}_{11}$  metastable crystal have been studied by combining the reverse Monte Carlo (RMC) modeling and the bond valence sum (BVS) approach using time-of-flight (TOF) neutron diffraction data (BL21 NOVA, J-PARC/MLF) [4]. The samples were placed in a cylindrical silica tube (12 mm in diameter and 0.5 mm in thickness), and then put into a cylindrical Al holder under a high-purity argon gas atmosphere. The QENS data were collected in the  $Q$  range of  $0.07-1.86 \text{ \AA}^{-1}$  at 150 K, 300 K, 373 K, 423 K, and 473 K, where  $Q$  is the magnitude of the scattering vector.

$S(Q, E)$  data for the  $({}^7\text{Li}_2\text{S})_x(\text{P}_2\text{S}_5)_{100-x}$  glasses ( $x = 60$  and  $70$ ) and the  ${}^7\text{Li}_7\text{P}_3\text{S}_{11}$  metastable crystal were collected using the DNA. Figure 1 shows the temperature dependence of  $S(Q = 0.35 \text{ \AA}^{-1}, E)$  spectrum for the  ${}^7\text{Li}_7\text{P}_3\text{S}_{11}$  metastable crystal. The QENS spectrum around the elastic peak ( $E = 0$ ) was clearly observed with increasing temperature. In order to get the dynamics information such as the jump distance,  $\langle l \rangle$ , and the residence time,  $\tau_0$ , for Li ions, further investigations are now in progress.

### References

- [1] A. Hayashi et al., J. Am. Ceram. Soc. 84 (2001) 477.
- [2] F. Mizuno et al., Electrochem. Solid-State Lett. 8 (2005) A603.
- [3] K. Shibata et al.: J. Opt. Adv. Mater., in press.
- [4] K. Mori et al., Chem. Phys. Lett. 584 (2013) 113.



**Fig. 1.** Temperature dependence of  $S(Q, E)$  spectrum for the  ${}^7\text{Li}_7\text{P}_3\text{S}_{11}$  metastable crystal ( $Q = 0.35 \text{ \AA}^{-1}$ ).