MLF Experimental Report	提出日 Date of Report January 9, 2015
課題番号 Project No. 2014A0212 実験課題名 Title of experiment Visualization of conduction pathways of lithium ions in Li_2S–GeS_2 and Li_2S–SiS_2 glasses 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 responsible person Toshiya OTOMO 装置名 Name of Instrument/(BL No.) NOVA / BL 21 実施日 Date of Experiment November 10–12, 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. $(Li_2S)_{40}(GeS_2)_{60}$ glass
2. $(Li_2S)_{50}(GeS_2)_{50}$ glass
3. $(Li_2S)_{60}(GeS_2)_{40}$ glass
4. $(Li_2S)_{40}(SiS_2)_{60}$ glass
5. $(Li_2S)_{50}(SiS_2)_{50}$ glass
6. $(Li_2S)_{60}(SiS_2)_{40}$ 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.

Li_2S–GeS_2 and Li_2S–SiS_2 glasses have attracted much attention as a solid electrolyte in all-solid-state lithium-ion batteries because of their high ionic conductivities at room temperature (10^{-4} S/cm). In order to understand the conduction mechanism for Li ions in Li_2S–GeS_2 and Li_2S–SiS_2 glasses, detailed information on the atomic structure is required. In this work, we synthesized $(^7Li_2S)_x(GeS_2)_{100-x}$ and $(^7Li_2S)_x(SiS_2)_{100-x}$ glasses by mechanical alloying (MA) and performed time-of-flight neutron diffraction (TOF-ND) measurements. Use of the lithium isotope, ^7Li, allowed the precise determination of the positions of Li ions in the neutron diffraction analysis because the absorption cross section, σ_a, of the ^7Li nuclei (0.045 b) is considerably lower than that of naturally occurring Li nuclei (70.5 b). Reverse Monte Carlo (RMC) modeling has been conducted to clarify the local structures of the $(^7Li_2S)_x(GeS_2)_{100-x}$ and $(^7Li_2S)_x(SiS_2)_{100-x}$ glasses, particularly the atomic positions of the Li ions.

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

The $(^7Li_2S)_x(GeS_2)_{100-x}$ glasses (x = 40, 50, and 60) and $(^7Li_2S)_x(SiS_2)_{100-x}$ (x = 40, 50, and 60) glasses were synthesized by MA. The electrical conductivities at room temperature, σ_{RT}, were measured using four-probe ac impedance; it was confirmed that σ_{RT} increases with increasing Li content. The TOF-ND analyses were performed using the total scattering spectrometer NOVA at the BL21 beam line of the Materials and Life Science Experimental Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC) [1]. The samples were placed in a cylindrical vanadium holder (6 mm in diameter) under a high-purity argon gas atmosphere. The TOF-ND data were collected in the Q range of 0.76–23 $Å^{-1}$ using a 90° detector bank at RT, where Q is the magnitude of the scattering vector. To obtain the structure factor, $S(Q)$, appropriate corrections related to multiple scattering, absorption, and incoherent scattering were applied to the TOF-ND data.

We succeeded to collect TOF-ND data for the $(^7Li_2S)_x(GeS_2)_{100-x}$ glasses (x = 40, 50, and 60) and $(^7Li_2S)_x(SiS_2)_{100-x}$ (x = 40, 50, and 60) using the NOVA, and then derived the observed $S(Q)$ by the appropriate corrections. For the $(^7Li_2S)_x(GeS_2)_{100-x}$ glasses, the radial distribution function (RDF) analysis was performed and the coordination number of S atoms around a Ge atom, N_{Ge-S}, was estimated to be 4 (i.e., GeS_4 tetrahedron) regardless of Li content. In the RMC modeling using the computer program RMC++ [2], excellent fit between the observed and the calculated $S(Q)$ was obtained for each sample (see Fig. 1). The local structure of the $(^7Li_2S)_{60}(GeS_2)_{40}$ glass is illustrated in Fig. 2, which shows a three-dimensional network of corner-sharing GeS_4 tetrahedra together with Li ions. The structural investigations for the $(^7Li_2S)_x(SiS_2)_{100-x}$ (x = 40, 50, and 60) glasses and the visualization of conduction pathways of Li ions in glasses are now in progress [3].

References

[1] T. Otomo *et al.*: KENS REPORT XVIII 2011, KEK Progress Report (2012) 27.

[2] O. Gereben *et al.*: J. Opt. Adv. Mater. 9 (2007) 3021.

[3] K. Mori *et al.*: Chem. Phys. Lett. 584 (2013) 113.

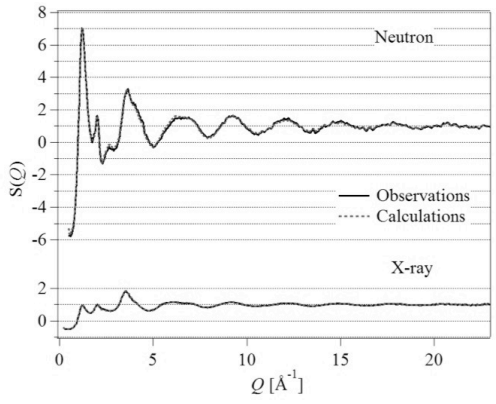

Fig. 1. RMC modeling of $(^7Li_2S)_{60}(GeS_2)_{40}$ glass using TOF-ND and synchrotron X-ray diffraction (SXRD) data at room temperature.

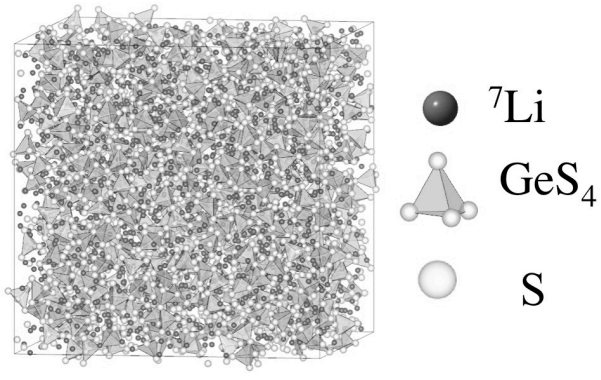

Fig. 2. The local structure of $(^7Li_2S)_{60}(GeS_2)_{40}$ glass obtained from the RMC modeling. The gray line indicates the cubic RMC unit with 4.5-nm-long edge.