MLF Experimental Report	提出日 Date of Report 13/04/08
課題番号 Project No.2012B0110 実験課題名 Title of experiment Lithium conduction mechanism of lithium superionic conductors Li4-xGe1-xPxS4 for all-solid-state lithium batteries 実験責任者名 Name of principal investigator Ryoji Kanno 所属 Affiliation Tokyo Institute of Technology	装置責任者 Name of responsible person Takashi Kamiyama 装置名 Name of Instrument/(BL No.) Super HRPD (BL-08) 実施日 Date of Experiment 2013/01/18-20

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.

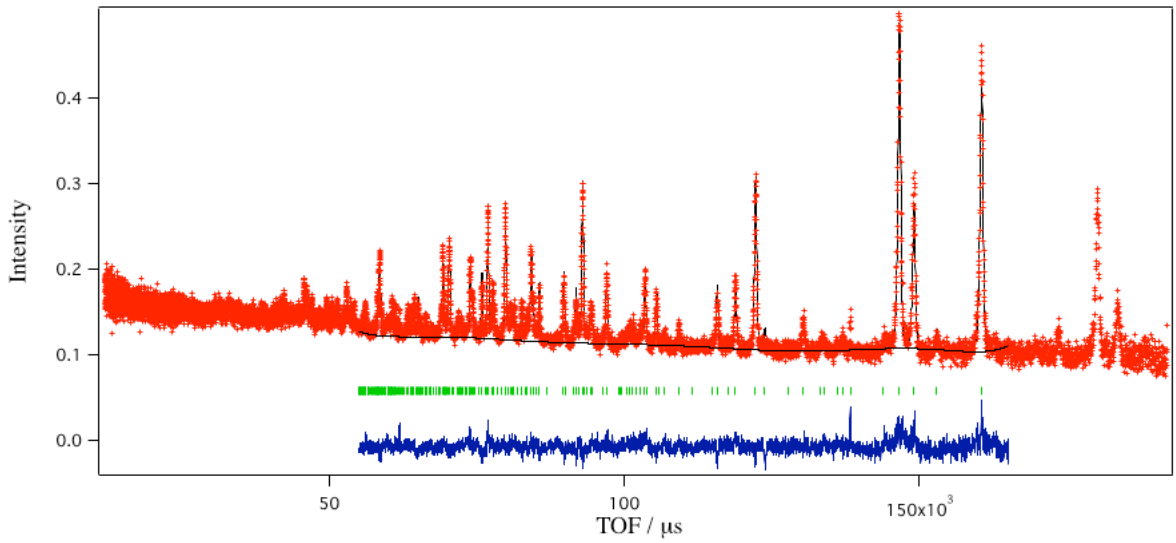
Powdered $Li_{4-x}Ge_{1-x}P_xS_4$(x = 0.55 and 0.65) were synthesized by a solid state reaction. We confirmed $Li_{4-x}Ge_{1-x}P_xS_4$ formed solid solution range from 0.55 to 0.65 using X-ray diffraction measurement. The structure of x = 0.5 - 0.65 were confirmed by the synchrotron X-ray diffraction Rietveld refinement. These compounds were iso-structural to $Li_{10}GeP_2S_{12}$. However, positions and occupancy values of lithium have not been clarified. These samples show high lithium ionic conductivity.

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.

Neutron diffraction data of $Li_{3.45}Ge_{0.45}P_{0.55}S_4$ and $Li_{0.335}Ge_{0.35}P_{0.65}S_4$ were taken at low temperatures on a time-of-flight (TOF) neutron powder diffractometer at Super HRPD (BL08) using the BS (Back Scattering) bank. Measurement temperatures were 5, 100, 135 and 200 K to determine lithium positions. The specimen of ca. 1.5 cc is contained in a cylindrical vanadium cell of dimensious 10 mm inradius, 20 mm in height. The data were analyzed by the Rietveld method using the Z-Rietveld program. Figure 1 shows a preliminary Rietveld analysis result using neutron diffraction data of $Li_{3.45}Ge_{0.45}P_{0.55}S_4$ measured at 200 K. Structural parameters are summarized in Table 1. The structure was refined based on the structure model with $Li_{10}GeP_2S_{12}$ type structure investigated by the X-ray Rietveld analysis. Li site(Li(4) site) was suggested from present refinement structure. Li(4) forms twisted octahedra with sulfide anion and links to $Li(1)S_6$ and $Li(3)S_6$ octahedra which form lithium conduction path in the structure, by face and edge sharing. Structural changes against temperatures have been investigated.

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

This can give better understanding of lithium conduction mechanism.



Cell parameter: a= 8.696036 Å, c= 12.620741 Å. Space group: $P4_2/nmc$. R_{wp} = 4.25 %, R_p = 3.54 %, R_e = 3.20 %, R_B = 13.06 %, R_F = 7.25 %, χ^2 = 1.76

Table 1 Rietveld refinement results for $Li_{3.45}Ge_{0.45}P_{0.55}S_4$ measured at 200 K.

Atom	Site	Occupancy	*x*	*y*	*z*	*B* / Å^2
Ge1	4d	0.675	0	0	0.6889 (9)	0.85
P1	4d	0.325	= *x*(Ge1)	= *y*(Ge1)	= *z*(Ge1)	0.85
P2	2b	1	0	0	0.5	0.93
S1	8g	1	0	0.1892 (7)	0.4081 (7)	0.64
S2	8g	1	0	0.2943 (7)	0.0982 (7)	0.75
S3	8g	1	0	0.6977 (8)	0.7885 (8)	0.09
Li1	16h	0.5771 (9)	0.2504 (9)	0.2504 (9)	0.2003 (9)	5.96
Li2	4d	1	0	0.5	0.9537 (9)	3.18
Li3	8f	0.5512 (9)	0.2473 (9)	0.2473 (9)	0	6.28
Li4	4d	0.7406 (3)	0	0	0.2644 (9)	2.46