MLF Experimental Report	提出日 Date of Report 2012/12/04
課題番号 Project No.2012A0107 実験課題名 Title of experiment Crystal structure analysis of new 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 2012/06/18−21

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=0.5, 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 0.5 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, lithium positions 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 $Li_{3.5}Ge_{0.5}P_{0.5}S_4$, $Li_{3.45}Ge_{0.45}P_{0.55}S_4$ and $Li_{0.335}Ge_{0.35}P_{0.65}S_4$ were taken at room temperature on a time-of-flight (TOF) neutron powder diffractometer at Super HRPD (BL08) using the BS (Back Scattering) bank. Low temperature data of $Li_{3.45}Ge_{0.45}P_{0.55}S_4$ were taken at 4 and 135 K to determine lithium position. 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 $Li_{3.45}Ge_{0.45}P_{0.55}S_4$. Structural parameters are summarized in Table 1. The structure was refined based on the structure model with $Li_{1o}GeP_2S_{12}$ type structure investigated by the X-ray Rietveld analysis. A new 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.

This can give better understanding of lithium conduction mechanism.

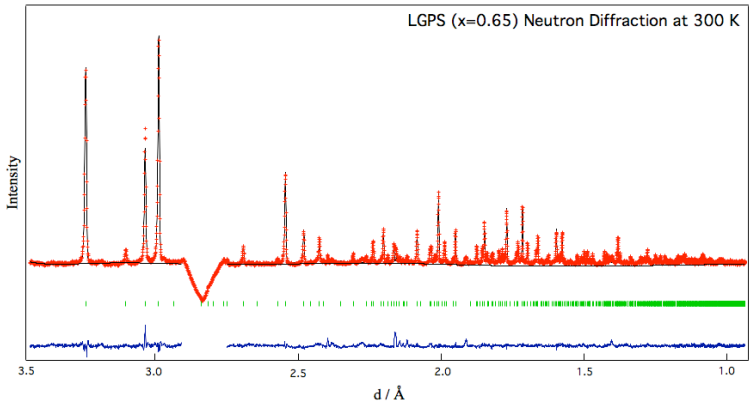

Fig. 1 Observed (plus marks), calculated (solid line), and difference (bottom) patterns for the Rietveld refinement from neutron diffraction data for $Li_{3.45}Ge_{0.45}P_{0.55}S_4$.

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

Atom	Site	Occupancy	*x*	*y*	*z*
Ge1	4d	0.515	0	0	0.6913
P1	4d	0.485	$=U_{33}$(Ge1)	$=U_{12}$(Ge1)	$=U_{13}$(Ge1)
P2	2b	1	$=U_{33}$(Ge2)	$=U_{12}$(Ge2)	$=U_{13}$(Ge2)
S1	8g	1	0	0.1867	0.4087
S2	8g	1	0	0.2982	0.1010
S3	8g	1	0	0.6967	0.7921
Li1	16h	0.592	0.2636	0.2700	0.1923
Li2	4d	0.810	0	0.5	0.9456
Li3	8f	0.547	0.2390	0.2390	0
Li4	4c	0.752	0	0	0.2561

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ge1	0.0351 (1)	0.0318 (1)	0.0113 (1)	0	0	0
P1	$=U_{11}$(Ge1)	$=U_{22}$(Ge1)	$=U_{33}$(Ge1)	$=U_{12}$(Ge1)	$=U_{13}$(Ge1)	$=U_{23}$(Ge1)
Ge2	0.0234	$=U_{11}$(Ge2)	0.0278	0	0	0
P2	$=U_{11}$(Ge2)	$=U_{22}$(Ge2)	$=U_{33}$(Ge2)	$=U_{12}$(Ge2)	$=U_{13}$(Ge2)	$=U_{23}$(Ge2)
S1	0.0369 (2)	0.0265	0.0361 (2)	0	0	-0.0067
S2	0.0337 (1)	0.0350 (1)	0.0340	0	0	-0.0070
S3	0.0289 (1)	0.0375 (2)	0.0325	0	0	-0.0112
Li1	0.0415 (3)	0.0317 (4)	0.3063 (3)	0.0190 (2)	-0.0332	-0.0241 (2)
Li2	0.0727 (1)	0.0607 (1)	0.3079 (2)	0	0	0
Li3	$=U_{22}$(Li3)	0.0587 (6)	0.3079 (5)	-0.0407 (2)	$=U_{23}$(Li3)	-0.1211 (1)
Li4	0.0463 (2)	0.0438 (2)	0.0318 (2)	0	0	0