MLF Experimental Report	提出日 Date of Report 2011/7/28
課題番号 Project No. 2010A0060 実験課題名 Title of experiment Crystal structure analysis of Thio-LISICONs - Super ionic conductor for 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.） SHRPD (BL No.8) 実施日 Date of Experiment 2010/6/25 - 6/26

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 $Li_{10}GeP_2S_{12}$ was synthesized at 500̃600 °C for 8 h in a quartz tube. $Li_{10}GeP_2S_{12}$ has a new crystal structure. Peak indexing of the synchrotron XRD pattern revealed that the new phase has a tetragonal unit cell with cell parameters of a = 8.71771(5) and c = 12.63452(10) Å and with the extinction rule $hk0$: $h+k = 2n$, hhl: $l = 2n$, $00l$: $l = 2n$, and $h00$: $h = 2n$, which is characteristic of the space group $P4_2/nmc$ (137). An *ab initio* structure analysis determined the arrangement of PS_4 and GeS_4 tetrahedra in the unit cell. Synchrotron X-ray Rietveld refinements obtained using the structural model determined by the *ab initio* method revealed low agreement factors. In this proposal, the positions of lithium ions and the lithium content were determined by neutron Rietveld analysis, based on the structural model obtained by synchrotron XRD data analysis.

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.

Fig. 1 shows Rietveld refinement results of $Li_{10}GeP_2S_{12}$. Table 1 summarizes the R factors, lattice parameters, and the final structure parameters determined by the refinement process. The unit cell has two tetrahedral sites: 4*d* and 2*b* sites. The 4*d* tetrahedral site is occupied by Ge and P ions with occupancy parameters of 0.515(5) and 0.485(5), respectively. The 2*b* tetrahedral site is occupied only by P with an occupancy parameter of 1.00(15). The Ge/P ratio is then 4.06:1.94, which is very close to the stoichiometric ratio of 2:1 and is consistent with the composition determined by ICP analysis. There are three lithium sites in the unit cell: 16*h*, 4*d*, and 8*f* sites with occupancy parameters of 0.691(5), 1.000(8), and 0.643(5), respectively. The number of lithium atoms in the unit cell is then calculated to be 20.200. Based on the ICP and neutron diffraction analyses, the composition of the new phase was determined to be $Li_{10}GeP_2S_{12}$.

$Li_{10}GeP_2S_{12}$ has a three-dimensional framework structure consisting of $(Ge_{0.5}P_{0.5})S_4$ tetrahedra, PS_4 tetrahedra,

LiS_4 tetrahedra, and LiS_6 octahedra. This framework structure has a one-dimensional lithium conduction pathway along the *c* axis. The framework is composed of $(Ge_{0.5}P_{0.5})S_4$ tetrahedra and LiS_6 octahedra, which share a common edge and form a one-dimensional chain along the *c* axis. These one-dimensional chains are connected to each other via PS_4 tetrahedra, which are connected to LiS_6 octahedra by a common corner. The one-dimensional conduction pathway is formed by LiS_4 tetrahedra in the 16*h* and 8*f* sites, which share a common edge and form a one-dimensional tetrahedra chain. These chains are connected by common corners of the LiS_4 tetrahedra. Neutron diffraction analysis indicates that the thermal vibration of lithium at the 16*h* and 8*f* sites is highly anisotropic. The anisotropic thermal displacements indicate that lithium is displaced from the 16*h* and 8*h* sites toward interstitial positions between two 16*h* sites and between 16*h* and 8*f* sites. This clearly indicates the existence of one-dimensional conduction pathways along the *c* axis. The occupancy parameters of 16*h* and 8*f* sites (determined respectively to be 0.691(5) and 0.643(5)) indicate partially occupied sites and show the average distribution of lithium ions along the conduction pathway, which is a characteristic of superionic conductors.

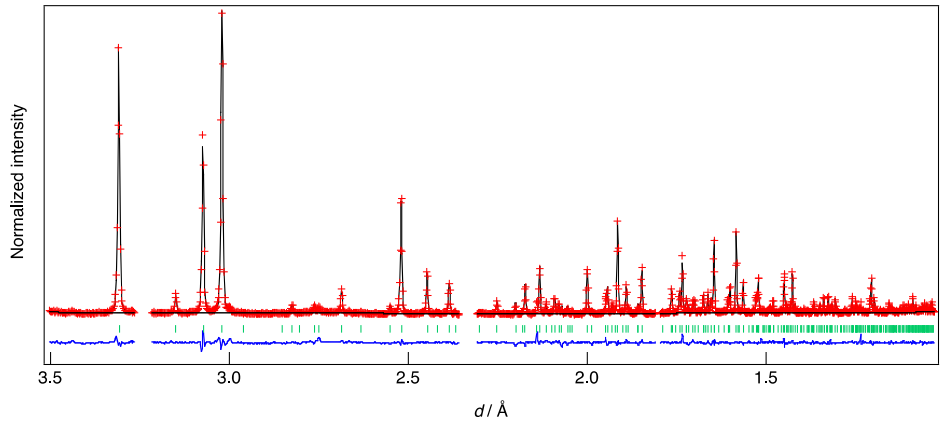

FIG. 1: Rietveld refinement of $Li_{10}GeP_2S_{12}$. Diffraction data were obtained using neutron radiation at room temperature. Red: observed intensities; black: calculated intensities; blue: difference plot; green makers indicate the position of the diffraction lines.

Table 1 Rietveld refinement result for neutron diffraction pattern of $Li_{10}GeP_2S_{12}$ at □□ °C.

Atom	Site	*g*	*x*	*y*	*z*
Li(1)	16*h*	0.691(5)	0.2563(5)	0.2718(3)	0.1832(3)
Li(2)	4*d*	1.000(8)	0	1/2	0.9446(2)
Li(3)	8*f*	0.643(5)	0.2463(3)	= *x*(Li(3))	0
Ge(1)	4*d*	0.515(5)	0	1/2	0.6907(6)
P(1)	4*d*	0.485(5)	= *x*(Ge(1))	= *y*(Ge(1))	= *z*(Ge(1))
Ge(2)	2*b*	0.00(15)	0	0	1/2
P(2)	2*b*	1.00(15)	= *x*(Ge(2))	= *y*(Ge(2))	= *z*(Ge(2))
S(1)	8*g*	1	0	0.1843(15)	0.4103(11)
S(2)	8*g*	1	0	0.2991(18)	0.0950(11)
S(3)	8*g*	1	0	0.6990(15)	0.7914(12)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li(1)	0.289(7)	0.093(3)	0.327(9)	0.049(3)	-0.023(6)	0.024(4)
Li(2)	0.061(2)	0.072(3)	0.008(16)	0	0	0
Li(3)	0.110(3)	$=U_{11}$(Li(2))	0.313(8)	-0.099(4)	0.158(4)	$=-U_{13}$(Li(3))
Ge(1)	0.0542(8)	0.0336(7)	0.0331(7)	0	0	0
P(1)	$=U_{11}$(Ge(1))	$=U_{22}$(Ge(1))	$=U_{33}$(Ge(1))	$=U_{12}$(Ge(1))	$=U_{13}$(Ge(1))	$=U_{23}$(Ge(1))
Ge(2)	0.0373(7)	$=U_{11}$(Ge(2))	0.045(12)	0	0	0
P(2)	$=U_{11}$(Ge(2))	$=U_{22}$(Ge(2))	$=U_{33}$(Ge(2))	$=U_{12}$(Ge(2))	$=U_{13}$(Ge(2))	$=U_{23}$(Ge(2))
S(1)	0.079(12)	0.037(12)	0.048(13)	0	0	0.0190(9)
S(2)	0.071(13)	0.060(14)	0.027(10)	0	0	0.0092(8)

Unit cell: tetragonal $P4_2/nmc$ (137); a = 8.69407(18) Å, c = 12.5994(4) Å, V = 952.349(6) Å^3;
R_{wp} = 4.25, R_e = 1.41, R_b = 5.36, R_F = 5.72, goodness of fit □^{2} = 9.08.