MLF Experimental Report	提出日 Date of Report 2020/03/16
課題番号 Project No. 2014PM0001 実験課題名 Title of experiment Development of visualization technique for ion conducting pathway 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 Toru Ishigaki 装置名 Name of Instrument/(BL No.) iMATERIA /(BL 20) 実施日 Date of Experiment 2014/12/6-7

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.

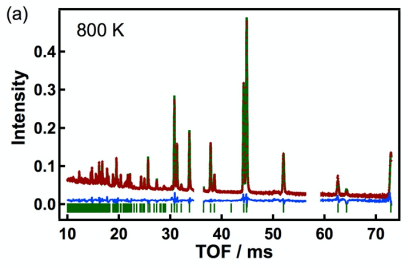
1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

Polycrystalline $Li_{9.81}Sn_{0.81}P_{2.19}S_{12}$ (LSPS) powder was prepared via a solid-state reaction using a carbon-coated quarts tube at 823 K for 72 h. X-ray diffraction measurement confirmed that the diffraction pattern of the LSPS could be indexed using space group of $P4_2/nmc$ (137), which is iso-structure to the $Li_{10}GeP_2S_{12}$ (*Nat. Mat.* 2011). Lithium ionic conductivity was evaluated by ac-impedance method using cold-pressed LSPS powders. High ionic conductivity over 10^{-3} S cm^{-1} was confirmed at room temperature measurement.

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.

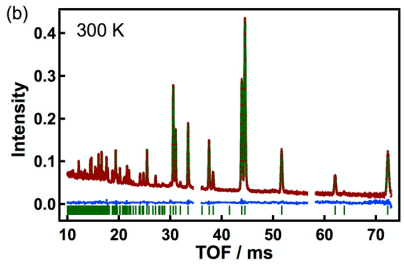
Time-of-flight (TOF) powder neutron diffraction data were collected for the LSPS contained within a 6-mm-diameter vanadium sample holder at 12, 300 and 800 K. Diffraction profiles were obtained using the iMATERIA (BL20) neutron powder diffractometer. Rietveld refinements for the diffraction patterns were carried out using the Z-Rietveld program. The diffraction data from 10 to 73 ms in TOF was analyzed using pseudo-Voigt function. Diffraction data around 35 and 57 ms were excluded from analysis because small diffraction peaks due to impurity phase appeared in these regions. Figure 1 shows a preliminary refinement results with tables indicating obtained parameters at each temperature. Structural parameters of $Li_{10}GeP_2S_{12}$ (LGPS) with space group $P4_2/nmc$ (a = 8.69440(2) Å, c = 12.60025(5) Å) [1,2] were applied as the initial structural model for fitting. The analysis results at 300 K were used for further analysis at other temperature data. Occupancies of all the atomic sites, which form the framework structure for lithium migration pathway, were fixed at 1.0. At first, each structural parameter was separately refined, then multi-parameters were refined together to obtain better fitting. Finally, all the parameters were refined at the same time.

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



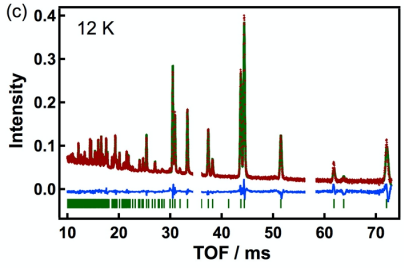
Atom	Site	g	x	y	z	U_{iso} /Å^2
Li(1)	16*h*	0.476(3)	0.2555(5)	0.2715(4)	0.1889(3)	0.117(3)
Li(2)	4*d*	1	0	0.5	-0.0420(3)	0.1148(16)
Li(3)	8*f*	0.759(7)	0.2447(4)	0.2447(4)	0	0.200(5)
Li(4)	4*c*	0.483(3)	0	0	0.2301(4)	0.005(2)
Sn	4*d*	0.405	0	0.5	0.68923(8)	0.0228(3)
P(1)	4*d*	=1-Sn(1)	=Sn(1)	=Sn(1)	=Sn(1)	=Sn(1)
P(2)	2*b*	1	0	0	0.5	0.0355(5)
S(1)	8*g*	1	0	0	0.5	0.0355(5)
S(2)	8*g*	1	0	0.18860(13)	0.41091(10)	0.0380(6)
S(3)	8*g*	1	0	0.29233(14)	0.10560(12)	0.0501(5)

Note: space group $P4_2/nmc$ (137), a = 8.81040 (3) Å, c = 12.79321 (7) Å, R_{wp} = 4.40 %, R_p = 3.59 %, $S = R_{wp}/R_e$ = 3.04, R_B = 7.45 %, R_F = 6.20 %.



Atom	Site	g	x	y	z	U_{iso} /Å^2
Li(1)	16*h*	0.493(3)	0.2495(4)	0.2709(3)	0.1888(2)	0.084(2)
Li(2)	4*d*	1	0	0.5	-0.0454(3)	0.1315(16)
Li(3)	8*f*	0.693(6)	0.2418(4)	0.2418(4)	0	0.154(4)
Li(4)	4*c*	0.546(3)	0	0	0.2384(3)	0.0089(17)
Sn	4*d*	0.405	0	0.5	0.68801(8)	0.0253(3)
P(1)	4*d*	=1-Sn(1)	=Sn(1)	=Sn(1)	=Sn(1)	=Sn(1)
P(2)	2*b*	1	0	0	0.5	0.0293(4)
S(1)	8*g*	1	0	0.18825(12)	0.40924(9)	0.0232(4)
S(2)	8*g*	1	0	0.29165(13)	0.10396(11)	0.0401(4)
S(3)	8*g*	1	0	0.69792(13)	0.78720(9)	0.0256(4)

Note: space group $P4_2/nmc$ (137), a = 8.73762 (12) Å, c = 12.71622 (7) Å, R_{wp} = 3.79 %, R_p = 3.26 %, $S = R_{wp}/R_e$ = 2.75, R_B = 6.63 %, R_F = 6.36 %.



Atom	Site	g	x	y	z	U_{iso} /Å^2
Li(1)	16*h*	0.494(3)	0.2477(4)	0.2721(3)	0.1838(3)	0.067(2)
Li(2)	4*d*	1	0	0.5	-0.0485(3)	0.1216(16)
Li(3)	8*f*	0.686(7)	0.2421(4)	0.2421(4)	0	0.138(4)
Li(4)	4*c*	0.556(3)	0	0	0.2431(4)	0.00628
Sn	4*d*	0.405	0	0.5	0.68708(8)	0.0223(3)
P(1)	4*d*	=1-Sn(1)	=Sn(1)	=Sn(1)	=Sn(1)	=Sn(1)
P(2)	2*b*	1	0	0	0.5	0.0228(4)
S(1)	8*g*	1	0	0.18817(12)	0.40872(9)	0.0153(4)
S(2)	8*g*	1	0	0.29064(13)	0.10168(12)	0.0316(4)
S(3)	8*g*	1	0	0.69877(14)	0.78583(10)	0.0211(4)

Note: space group $P4_2/nmc$ (137), a = 8.70071 (3) Å, c = 12.68619 (8) Å, R_{wp} = 4.26 %, R_p = 3.73 %, $S = R_{wp}/R_e$ = 2.75, R_B = 7.43 %, R_F = 6.38 %.

Figure 1. Rietveld refinement results for the neutron diffraction patterns of $Li_{9.81}Sn_{0.81}P_{2.19}S_{12}$ obtained at (a) 800 K, (b) 300 K and (c) 12 K. Obtained structure parameters are summarized in the tables at right side of the fitting patterns.

All the R_{wp} values were lower than 5.0, indicating that good fitting results were obtained for all conditions. Although lattice expansion with an increase in temperature was confirmed, no significant change in the structure parameters was observed. This fact indicates that the LSPS phase with the LGPS-type structure is thermodynamically stable in the temperature range from 12 to 800 K. The Si atom occupies 4*d* site, where Ge exists in the LGPS, and forms (P/S)S_4 tetrahedra. Thermal parameter of U_{iso} of Li(2) showed smaller increase compared to those of Li(1) and Li(3) sites. One dimensional lithium diffusion along *c* axis through Li(1) and Li(3) sites was indicated. Further analytical study with Maximum Entropy Method (MEM) is expected to provide detailed lithium diffusion mechanism in the LSPS structure and its temperature dependences.

Reference 1）N. Kamaya, *et al.*, *Nat. Mater.* (2011). 2) O. Kwon *et al.*, *J. Mater. Chem. A* (2015).

以下は、MLFで内部資料として使用します。(日本語可)
The following sheet is for internal use only.　Description in Japanese is acceptable.

○論文等による成果発表の予定 (Your publication plan)

a) 発表形式(*1) Publication style(*1)	b) 発表先(誌名、講演先)(*2) Publication/Meeting information(*2) (Name of journal/book or meeting)	c)投稿/発表時期(*3) Date of paper submission or presentation(*3)
Refereed journal	*Acta Crystallographica Section B*	S. Hori, S. Taminato, K. Suzuki, M. Hirayama, Y. Kato and R. Kanno, *Acta Crystallographica Section B*, 2015, **71**, 727–736. doi:10.1107/S2052520615022283

【記入要領】(Instructions)

(*1)　原著論文、総説、プロシーディングス、単行本、特許、招待講演(国際会議)、その他口頭発表等、具体的な発表方法を示して下さい。
Please describe planned publication and/or presentation style; *ex.* refereed journal, review article, conference proceedings, book, patent, invited talk, oral presentation *etc.*

(*2)　成果を発表する誌名、講演先を示して下さい。
Please describe the name of journal or book you are planning to submit, or name of meeting you will make a presentation.

(*3) およその発表予定時期を示して下さい。(3月以内、6月以内、1年以内、2年以内、2年以上先、等)
Please describe the estimated date of paper submission or presentation; *ex.* within 3 months, within 6 months, within 1 year, within 2 years, beyond 2 years, *etc.*

○成果になる予定が立たない場合の理由と今後の計画を記述してください。
In case you can not publish your results, please describe reasons and future plan.

(例:「論文になる十分な結果が得られなかった」、「複数回の実験が必要で次回の課題終了後に発表予定」、等)