Experimental report

04/08/2016

Proposal: **5-22-736** **Council:** 10/2014

Title: Crystal chemistry and ionic conductivity within the LISICON-type Li_4SiO_4/Li_3PO_4, Li_4SiO_4/Li_5BO_4 and Li_4SiO_4/Li_5AlO_4 systems

Research area: Materials

This proposal is a new proposal

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Samples:
$Li_{3.25}Si_{0.25}P_{0.75}O_4$
$Li_{4.75}Si_{0.25}Al_{0.75}O_4$
Li_4SiO_4
$Li_{3.75}Si_{0.75}P_{0.25}O_4$
$Li_{3.5}Si_{0.5}P_{0.5}O_4$
$Li_{4.25}Si_{0.75}Al_{0.25}O_4$
$Li_{4.5}Si_{0.5}Al_{0.5}O_4$

Instrument	Requested days	Allocated days	From	To
D2B	3	3	17/07/2015	20/07/2015
			10/09/2015	11/09/2015
D20	1	1	07/07/2015	08/07/2015

Abstract:

The search for highly ionic conductive and chemically stable solid electrolytes is vital for all solid state batteries. Our interest is to develop solid electrolytes and to reinvestigate their crystal chemistry and physical properties. Key interests lie in the solid solution systems as Li_4SiO_4/Li_3PO_4, Li_4SiO_4/Li_5BO_4 and Li_4SiO_4/Li_5AlO_4. Our previous laboratory powder X-ray diffraction and single crystal diffraction measurements give out their structural information. Furthur investigation by both the D2B high resolution and the D20 high intensity powder diffractometers will help us to understand lithium conductivity mechanism and dynamics of diffusion. We therefore wish to use 3 days of D2B and 1 day of D20.

Crystal chemistry and ionic conductivity within the LISICON-type Li_4SiO_4/Li_3PO_4, Li_4SiO_4/Li_5BO_4 and Li_4SiO_4/Li_5AlO_4 systems

Context of the study

All **S**olid **S**tate **B**attery (ASSB) systems, comparing with **L**ithium **I**on **B**atteries (LIBs), show significant promise for scale-up and guaranteed safety, avoiding the use of flammable and toxic organic liquid electrolytes[1]. The search for highly ionic conductive and chemically stable solid electrolytes is vital for the ASSB technology[2,3,4,5].

We believe that the LISICON-type solid solutions around **Li_4SiO_4** and **Li_3PO_4**, originally investigated by A.R. West, deserve further investigation thanks to their chemical stability and light weight (important criteria for ASSBs). Indeed, varying the amounts of vacancies and/or interstitial sites within the $Li_{4-x}Si_{1-x}P_xO_4$ ($0 \leq x \leq 0.4$) or $Li_{3+y}P_{1-y}Si_yO_4$ ($0 \leq y \leq 0.5$) solid solutions results in a remarkable increase of three orders of magnitude of the ionic conductivity [6,7]. Our interest is to develop ASSBs using such kind of solid electrolytes (as we succeeded for Na-based NASICON compositions recently[8]) and to reinvestigate their crystal chemistry and physical properties by modern experimental (X-ray and neutron diffraction, impedance spectroscopy) and modeling (MD and DFT) techniques within a combined PhD project shared between LRCS Amiens (France) and Univ. of Bath. (UK).

Complex Li^+ order-disorder transitions within the LISICON structure

We recently succeeded in preparing high-purity and well-crystallized single-phase compositions in the (1-z) Li_4SiO_4 – (z) Li_3PO_4 system (z = 0, 0.25, 0.5, 0.75 and 1). Lab. XRD data show agreement with the literature: for z smaller than 0.5, the Li_4SiO_4-based solid solution is obtained (monoclinic *P*2_1/m); for $z \geq 0.5$, the Li_3PO_4-based solid solution is obtained (orthorhombic *P*nma). Interestingly, the XRD pattern of Li_4SiO_4 shows the existence of additional diffraction peaks related with a superstructure previously described by Tranqui[9]. Single crystal analysis revealed long range Li^+ ion ordering at 298 K, most likely responsible for the poor ionic conductivity. This ordering disappears (and hence the ionic conductivity is increased) when substituting Si by P ($Li_{4-z}Si_{1-z}P_zO_4$) or by elevating the temperature. Several high-purity samples were sent to the 11-BM beam line of APS at Argonne (USA) for high resolution synchrotron measurements. In the same time, the drastic increase in ionic conductivity is also observed for the Li_4SiO_4/Li_5BO_4 and Li_4SiO_4/Li_5AlO_4 systems[10]. It is of great interest to study the crystal structures of these solid solution compositions, with the aim of providing atomic scale understanding of the ion transport properties.

Experimental details

In this experiment, four samples have been measured: three samples within the (1-z) Li_4SiO_4 – (z) Li_3PO_4 system (z = 0.25, 0.5 and 0.75) have been measured at D20 ($\lambda = 1.54300$ Å) and

D2B (λ = 1.594644 Å); one composition within the (1-x) Li_4SiO_4 – (x) Li_5AlO_4 system (x = 0.25) has been measured at D2B (λ = 1.594644 Å).

Results

The crystal structure of the (1-z) Li_4SiO_4 – (z) Li_3PO_4 system (z = 0.25, 0.5 and 0.75) have been solved for the first time. The refined crystal structures have been compared with the values obtained from potentials based energy minimization calculations. The cell parameters and bond lengths from the two methods show good agreement (Table 1).

Table 1 : Comparison of cell parameters and bond lengths obtained from Rietveld refinement and energy minimization calculation for (1-z) Li_4SiO_4 – (z) Li_3PO_4

		a (Å)	*b* (Å)	*c* (Å)	*β* (°)	Si/P – O (Å)	Li-O (Å)
z = 0.25	Rietveld	5.105	6.112	5.297	90.37	1.612	2.110
	calculated	5.248	6.065	5.255	88.03	1.584	2.064
z = 0.5	Rietveld	10.589	6.115	5.006	90	1.587	2.080
	calculated	10.636	6.119	5.072	90	1.563	1.974
z = 0.75	Rietveld	10.526	6.115	4.970	90	1.566	2.080
	calculated	10.636	6.151	5.054	90	1.542	2.073

The collected diffraction patterns and Rietveld refinement results are shown in Figure 1. With these results, we have carried out molecular dynamics calculations to simulate the Li^+ ion diffusion within the materials. An interstitialcy knock-on like mechanism has been proposed to explain the high ionic conductivity of these solid solution compositions. More details can be found in our recently published article:

Y. Deng, C. Eames, J.-N. Chotard, F. Lalère, V. Seznec, S. Emge, O. Pecher, C. P. Grey, C. Masquelier, M. S. Islam. Structural and mechanistic insights into fast lithium-ion conduction in Li_4SiO_4-Li_3PO_4 solid electrolytes. *J. Am. Chem. Soc.* **2015**, *137*, 9136-9145. (DOI: 10.1021/jacs.5b04444)

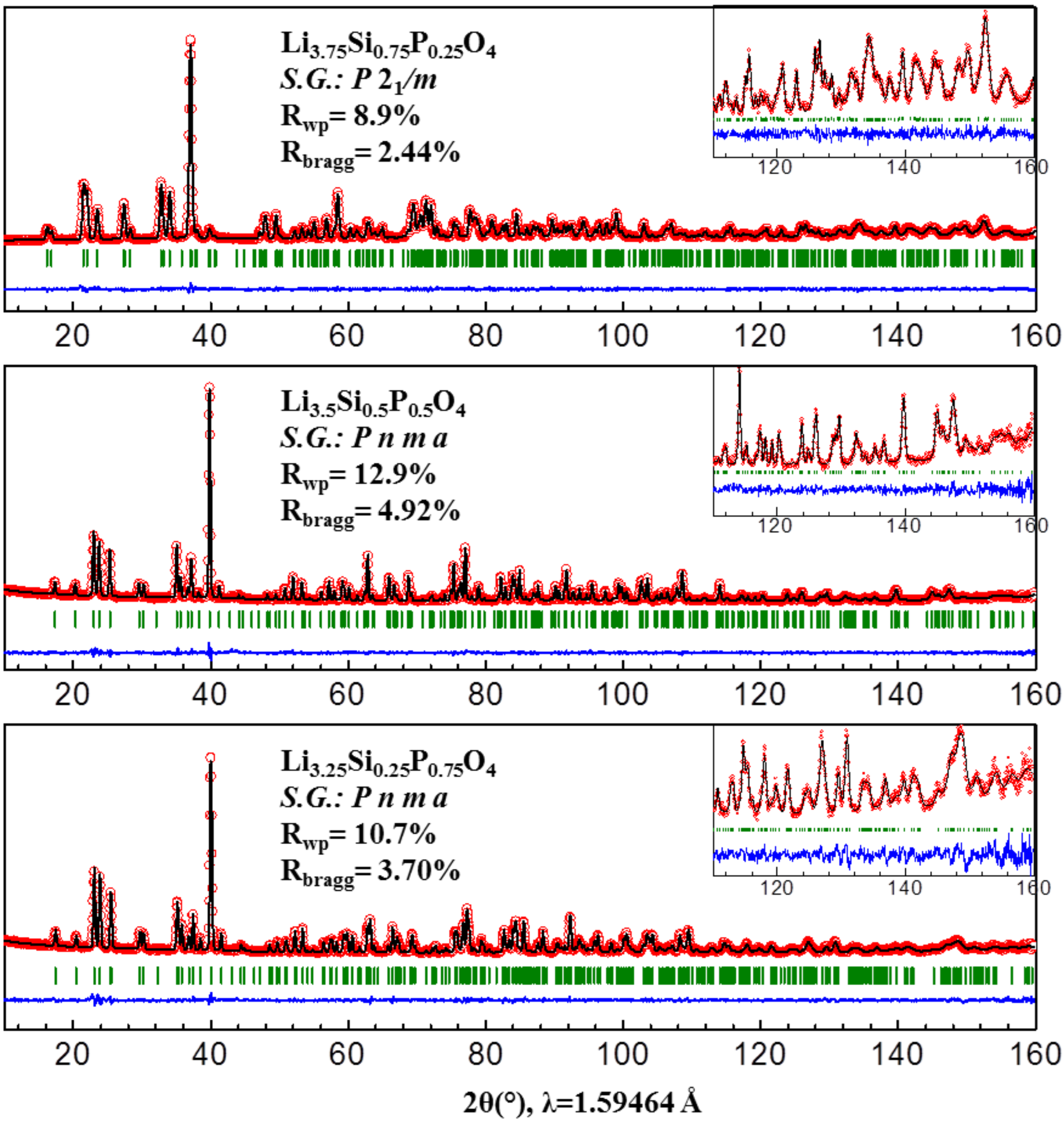

Figure 1 : Powder neutron diffraction patterns and Rietveld refinement results for $Li_{3.75}Si_{0.75}P_{0.25}O_4$ (top), $Li_{3.5}Si_{0.5}P_{0.5}O_4$ (middle) and $Li_{3.25}Si_{0.25}P_{0.75}O_4$ (bottom).

References

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