Experimental report

28/05/2019

Proposal: 5-22-753 **Council:** 4/2017

Title: Crystal chemistry and ionic conductivity of novel, oxysulfide, LISICON-type Li3PO4-xSx ionic conductors for All-Solid-State Batteries

Research area: Materials

This proposal is a new proposal

Main proposer: **Theodosios FAMPRIKIS**

Experimental team: Theodosios FAMPRIKIS
Jean Noel CHOTARD
Adolfo URRUTIA
Omer Ulas KUDU

Local contacts: Emmanuelle SUARD

Samples: Li3PO4
Li3POS3
Li3PS4
Li3PO2S2
Li3PO3S

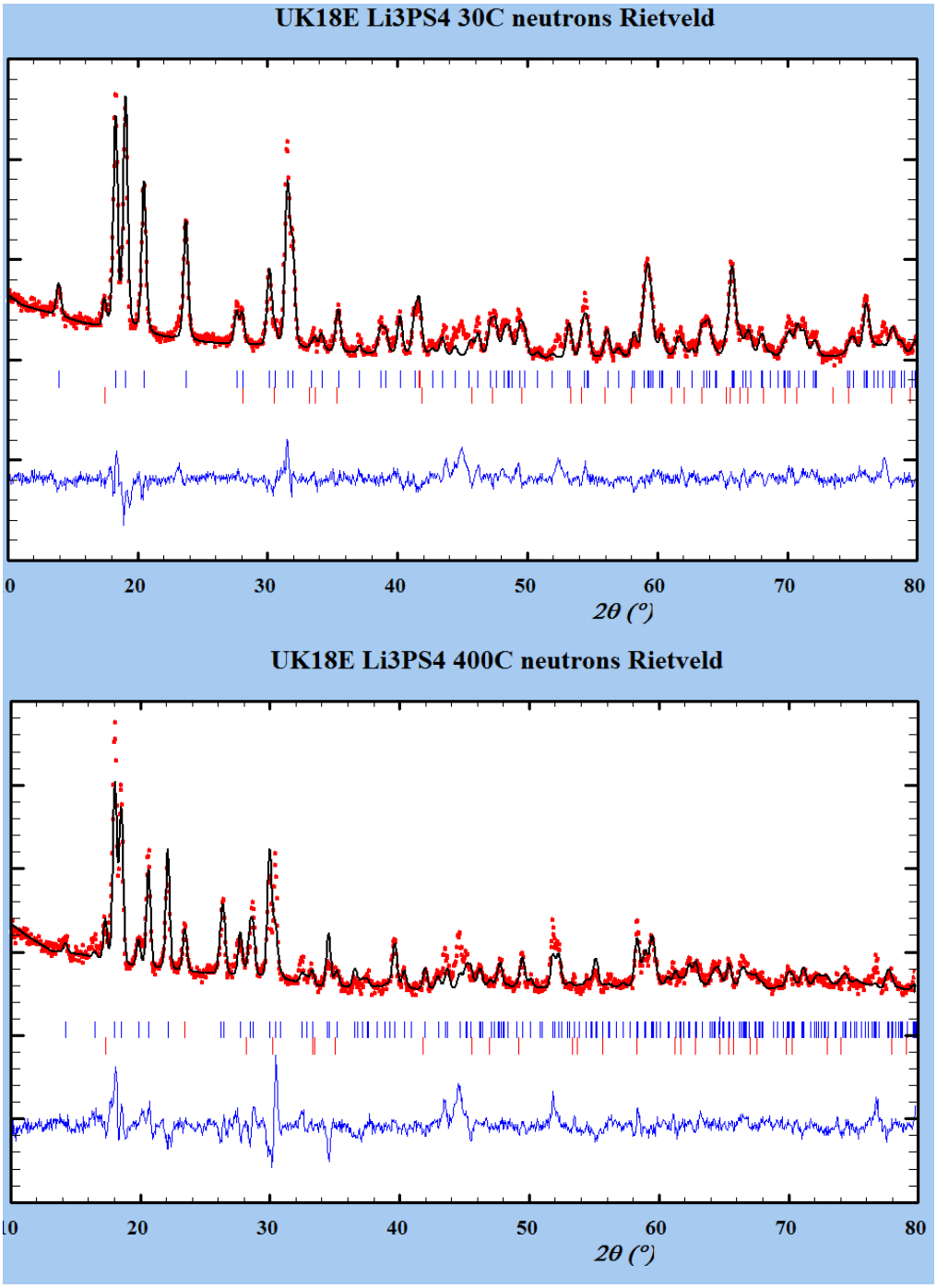
Instrument	Requested days	Allocated days	From	To
D2B	6	6	29/06/2018	02/07/2018
			02/07/2018	05/07/2018

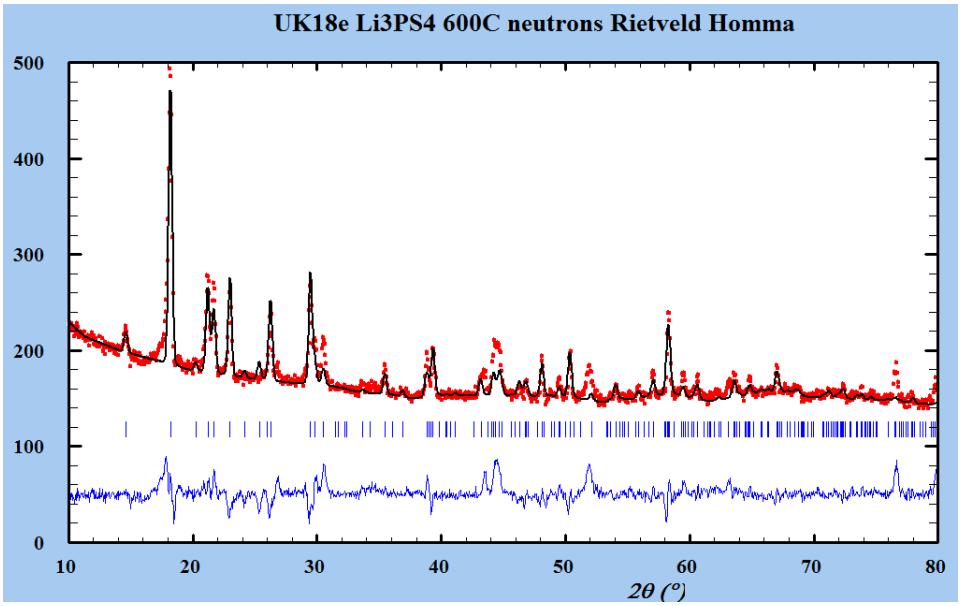
Abstract:

All-Solid-State Batteries (ASSBs) are regarded as the most promising candidate for the next generation of energy storage systems for both stationary and mobile applications, especially with regards to potentially vastly improved safety, energy- and power density compared to current Lithium Ion Batteries. Our group follows a comprehensive approach to predict (first principles simulations), synthesize and physically (X-ray and Neutron Diffraction, NMR, Impedance Spectroscopy etc.) and computationally (Molecular Dynamics) characterise Solid Electrolyte materials for ASSB applications. We now utilize this validated methodology to investigate novel materials on the interface of oxides and sulfides in order to obtain (electro-)chemically stable, easily formable, highly conductive electrolytes for ASSBs.

Following the acceptance of our proposal (submitted Feb 14th 2017, accepted May 29th 2017) we proceeded to perform neutron diffraction experiments in the D2B beamline between June 29th and July 4th 2018.

A significant part of the experiment was devoted to elucidation of the phase behavior of Li_3PS_4 in temperature. In preparation for the neutron diffraction experiments we had constituted an irreversible behavior with 3 phases observable on heating but only 2 on cooling. This was confirmed with neutron diffractograms. The state of the art in the literature regarding the crystal chemistry of Li_3PS_4 was established by Homma et al. through analogous temperature-controlled powder diffraction with x-ray radiation [1]. We show below our fits of our data using the models of Homma et al. for the three phases: γ-Li_3PS_4 (*Pmn*2_1) at 30 °C, β- Li_3PS_4 (*Pnma*) at 400 °C α- Li_3PS_4 (*Pbcn*) at 600 °C.





The Li_3PS_4 samples all exhibit a small amount of $Li_4P_2S_6$ impurity phase which can be modelled well using a *P*6$_3$/*mcm* space group. Further, a distinct asymmetry is noted which could be due to strain. Finally, the broadening could be anisotropic (dependent on hkl). Refinements using an instrumental resolution file will be attempted. The peak intensity and sharpness fall off drastically after ~80 ° possibly indicating high thermal motion and or strain in the sample.

While the fit for γ-Li_3PS_4 is reasonable; there's distinct difference plots for those of the medium- and high-temperature forms β- and α-, respectively. The structure of the α-form remains unsolved as the localization of the light Li atoms proved impossible using x-ray data. Our goal is to use the neutron data to complete the structure.

Especially the structure of β- is quite pertinent to solve accurately due to its practical interest for solid-state-batteries (it is already being used quite widely for such application on the laboratory and start-up scale). Apart from the model derived by Homma from high temperature XRD [1], there's two models derived at room temperature: one by Mercier et al. from a single crystal measurement [2] and one from Stoeffler et al. from powder XRD and ND on a sample stabilized by soft chemistry [3]. We aim to assess all models and weigh in on the debate for this very pertinent structure.

We have also measured several oxysulfide orthophosphate samples, most notably Li_3POS_3. This is a metastable material synthesized by quenching and presenting very interesting properties of high ionic conductivity and possibly high electrochemical stability due to the inclusion of oxygen. The structure of the material is still unkown, but a reasonable profile fit can be obtained with a tetragonal (*P*4$_2$/*nmc*) cell. Very interestingly this is the same space group as the famous $Li_{10}GeP_2S_{12}$ ion conductor which remains the fastest RT Li^+ conductor and extremely interesting for applications.

References: [1] K. Homma, M. Yonemura, T. Kobayashi, M. Nagao, M. Hirayama, R. Kanno, Crystal structure and phase transitions of the lithium ionic conductor Li3PS4, Solid State Ionics. 182 (2011) 53–58. doi:10.1016/j.ssi.2010.10.001. **[2]** R. Mercier, J. Malugani, B. Fahys, R. Guy, Structure du Tetrathiophosphate de Lithium, Acta Crystallogr. Sect. B. (1982) 1887–1990. doi:doi:10.1107/S0567740882007535. **[3]** H. Stöffler, T. Zinkevich, M. Yavuz, A. Senyshyn, J. Kulisch, P. Hartmann, T. Adermann, S. Randau, F.H. Richter, J. Janek, S. Indris, H. Ehrenberg, Li + -Ion Dynamics in β-Li 3 PS 4 Observed by NMR: Local Hopping and Long-Range Transport, J. Phys. Chem. C. 122 (2018) 15954–15965. doi:10.1021/acs.jpcc.8b05431.