Experimental report

22/02/2021

Proposal: 7-03-178 **Council:** 10/2018

Title: Elucidation of ion dynamics in Li3PS4 solid electrolytes for all solid state batteries by means of inelastic neutron scattering

Research area: Materials

This proposal is a new proposal

Main proposer: Theodosios FAMPRIKIS

Experimental team: Mohamed ZBIRI
Theodosios FAMPRIKIS

Local contacts: Mohamed ZBIRI

Samples: Li3PS4
ceramic Li3PS4

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	6	3	28/01/2020	31/01/2020

Abstract:

All-solid-state batteries are one of the main contenders for the batteries of the future due to their potential advantages in terms of safety, cycle-life and energy density. Li3PS4 has emerged as one of the candidate solid electrolyte materials at the heart of the solid-state battery concept. Nevertheless, the reasons for its high ionic conductivity and its variance depending on the synthesis method are poorly understood. We have synthesized Li3PS4 utilizing all the prominent synthesis routes in the literature (ceramic, quenching, mechanochemical, soft-chemistry) and propose to perform a comprehensive series of inelastic neutron scattering experiments to elucidate the dynamical effects of atomic structure, microstructure and composition as pertains to Li ion transport in Li3PS4.

Experimental report for proposal 7-03-178

Title: Elucidation of ion dynamics in Li_3PS_4 solid electrolytes for all solid state batteries by means of inelastic neutron scattering

Proposers : T. Famprikis, M. Zbiri, C. Masquelier

Instrument : IN6

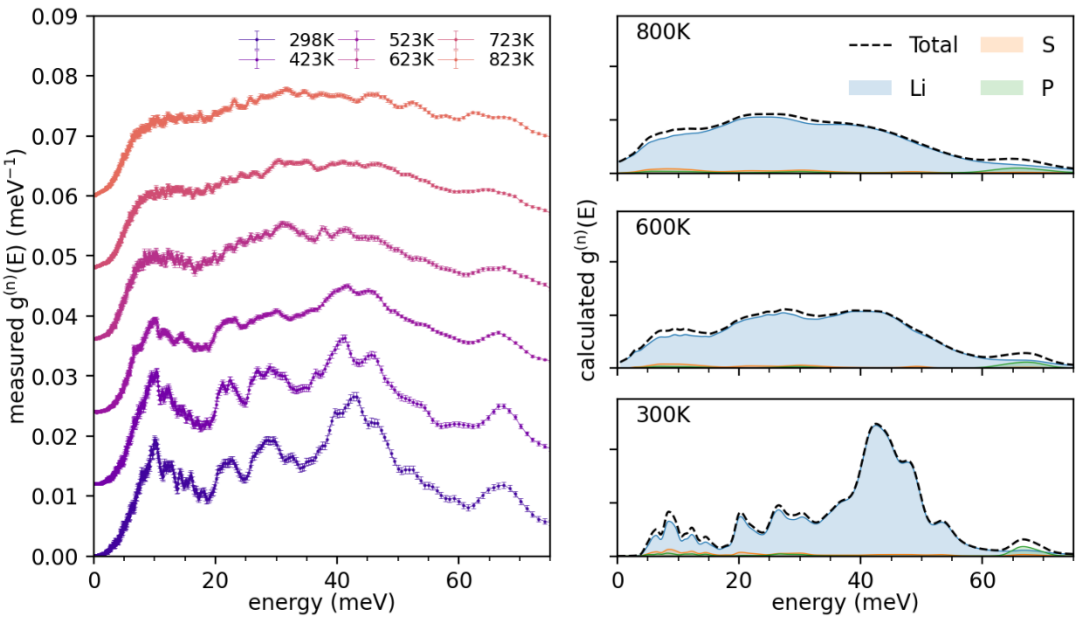
Beamtime : 3 days allocated (out of 6 requested)

Experiments were carried out in accordance with the proposal and accounting for the limited granted time (half of requested). It was deemed necessary to limit the scope of the experiments to the accurate determination of the temperature response of a single, well-crystallized sample, rather than try to squeeze in all the experiments at half the time with limited temperature points and lower counting times.

Additionally, to enhance the quality of the data, significant efforts were made to synthesize an isotropically enriched sample of $^{7}Li_3PS_4$ to eliminate the highly absorbing ^{6}Li nuclide in natural lithium.

The analysis of the results is separated into (1) the phonon DOS and (2) the quasi elastic signal to be published separately.

1) The evolution of the generalized phonon density of state with temperature are discussed in the context of the crystallographic phase transformations in an article to be submitted (in preparation). In this context, the analysis of the neutron spectra was combined with ab-initio molecular dynamics simulations performed by M. Zbiri (ILL, FR) and J.A. Dawson (Newcastle University, UK). The relevant figure from the working manuscript is reproduced below:



The signal is visibly dominated by the Li displacements of interest. Moving from the room temperature γ-phase of interest to the superionic β- and α-phases the GDOS visibly broadens and the phonon band centers shift to much lower energies (soften). This is in accord with Raman- and impedance-spectroscopy results and will be published soon™.

2) The quasi-elastic signal (QENS), characteristic of Na diffusivity, will be included in a second publication in combined analysis with in-depth Raman and NMR spectroscopies, currently in preparation.