Experimental report

22/02/2021

Proposal: 7-03-179 **Council:** 4/2019

Title: Lattice Dynamics and Ion Migrationin Na3PS4 for solid state sodium batteries.

Research area: Materials

This proposal is a resubmission of 7-03-177

Main proposer: Theodosios FAMPRIKIS

Experimental team: Mohamed ZBIRI
Theodosios FAMPRIKIS

Local contacts: Mohamed ZBIRI

Samples: Na3PS4
Na3PS4 (ball-milled)

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	5	3	12/07/2019	15/07/2019

Abstract:

Na3PS4 is a promising Na+ solid electrolyte to be used in solid-state sodium batteries. We have recently brought to light a previously unknown phase of this conductor which exhibits superionic conductivity up to 1 S/cm. We suspect the high ionic conductivity is linked to rotational disorder of the PS4 anionic moieties that comprise the new crystalline structure. We propose neutron inelastic scattering experiments to assess this hypothesis and examine its effect on the Na+ dynamics.

Experimental report for proposal 7-03-179

Title: Lattice Dynamics and Ion Migration in Na_3PS_4 for solid state sodium batteries

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

Instrument : IN6

Beamtime : 3 days allocated (out of 5 requested)

Experiments were carried out in accordance with the proposal and accounting for the limited granted time. Two Na_3PS_4 samples have been measured, denoted in the following HT- (for high-temperature synthesis) and BM- (for ball-milling synthesis).

The results are disseminated in three separate publications:

1) The comparison between the HT- and BM- samples has already been published in the Journal of the American Chemical Society (JACS).

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Article

Under Pressure: Mechanochemical Effects on Structure and Ion Conduction in the Sodium-Ion Solid Electrolyte Na_3PS_4

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Cite This: https://dx.doi.org/10.1021/jacs.0c06668

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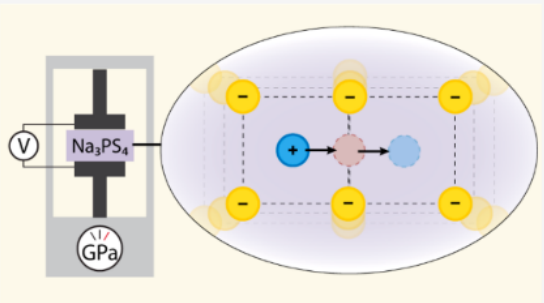
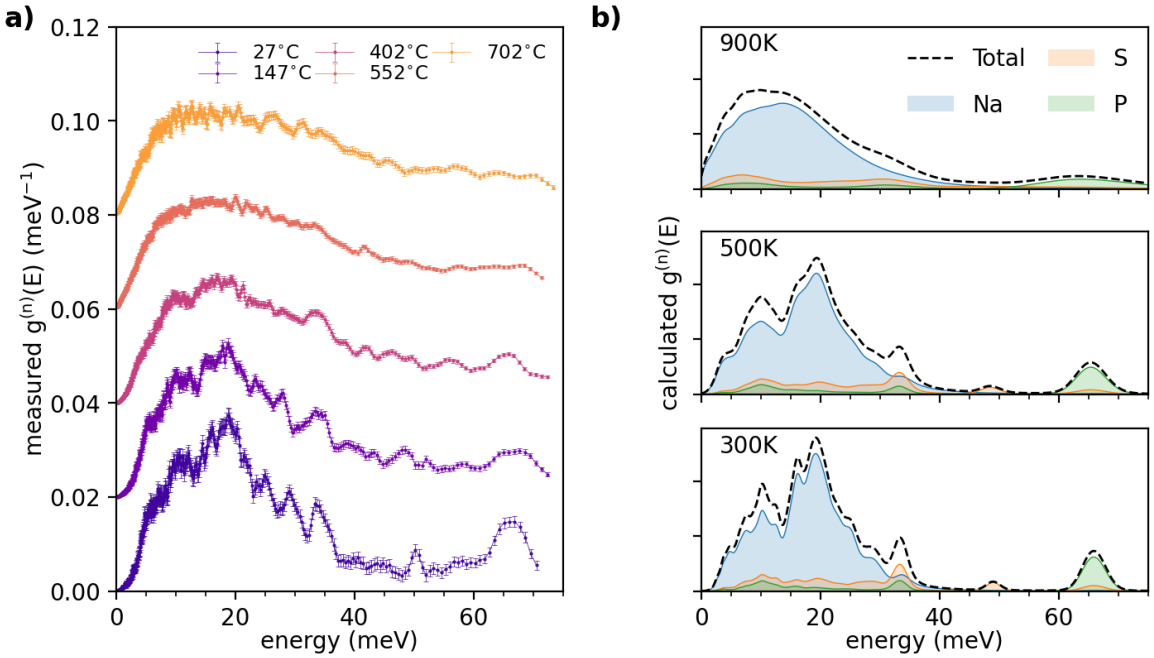
ABSTRACT: Fast-ion conductors are critical to the development of solid-state batteries. The effects of mechanochemical synthesis that lead to increased ionic conductivity in an archetypical sodium-ion conductor Na_3PS_4 are not fully understood. We present here a comprehensive analysis based on diffraction (Bragg and pair distribution function), spectroscopy (impedance, Raman, NMR and INS), and *ab initio* simulations aimed at elucidating the synthesis–property relationships in Na_3PS_4. We consolidate previously reported interpretations regarding the local structure of ball-milled samples, underlining the sodium disorder and showing that a local tetragonal framework more accurately describes the structure than the originally proposed cubic one. Through variable-pressure impedance spectroscopy measurements, we report for the first time the activation volume for Na^+ migration in Na_3PS_4, which is ~30% higher for the ball-milled samples. Moreover, we show that the effect of ball-milling on increasing the ionic conductivity of Na_3PS_4 to ~10^{-4} S/cm can be reproduced by applying external pressure on a sample from conventional high-temperature ceramic synthesis. We conclude that the key effects of mechanochemical synthesis on the properties of solid electrolytes can be analyzed and understood in terms of pressure, strain, and activation volume.



2) The evolution of the spectra of the HT- sample with temperature are discussed in the context of the crystallographic phase transformations in an article submitted to ACS Chemistry of Materials. A preprint of said article is already available on ChemRxiv.

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 manuscript is reproduced below:



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