Experimental report

12/09/2024

Proposal: 7-03-229 **Council:** 4/2023

Title: Understanding the ionic transport in the thermoelectric, mixed-conducting argyrodites Ag8+xMSe6 (M = Ge,Ga)

Research area: Chemistry

This proposal is a new proposal

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Samples: Ag9GaSe6
Ag8GeSe6
Ag8.5Ga0.5Ge0.5Se6
Na1+2xTa1-xlnxCl6 (x= 0, 0.125 and 0.25)

Instrument	Requested days	Allocated days	From	To
IN16B	4	4	30/10/2023	03/11/2023

Abstract:

The silver conducting argyrodites with the general formula Ag8+xMSe6 (M = Si, Ge, Sn, Ga) have attracted significant attention because of their intrinsically low lattice thermal conductivity, believed to originate from their superionic conduction and strong local structural disorder. Recently, it was shown that the low thermal transport cannot be correlated directly with the magnitude of the macroscopic ionic conduction, but the fundamental mechanism and potential interplay on a microscopic scale remains elusive. We propose an experimental study of the silver dynamics in the argyrodites, to assess ionic diffusion, residence times and jump lengths in a wide temperature range. We believe the proposed experiments, in combination with local structural characterizations and NMR spectroscopy, will give the necessary insights to uncover potential interrelations of thermal and ionic transport on a microscopic scale, while guiding the understanding of ionic transport in the material class.

Understanding the ionic transport in the thermoelectric, mixed-conducting argyrodites $Ag_{8+x}MSe_6$ (M = Ge,Ga)

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The initial aim of the proposal 7-03-229 was to determine the diffusion dynamics and mechanisms of Ag in the mixed-conducting argyrodites with nominal composition $Ag_{8+x}MSe_6$ (M = Ge,Ga). However, the results collected at that time on the $Na_{3-2x}In_{1-x}Ta_xCl_6$ substitution series including nuclear magnetic resonance, impedance results as well as an in-depth structural characterization changed the aim of the experiment. QENS on these materials could greatly improve our understanding and help publish a high-quality manuscript* on these materials within a short time frame post-beamtime. Thus, the final aim of the present proposal was to investigate the sodium diffusion in the $Na_{3-2x}In_{1-x}Ta_xCl_6$ substitution series by QENS measurements on the backscattering spectrometer IN16b. The three end members (x = 0.75, 0.875 and 1) were chosen due to their higher ionic conductivity and the less content in indium, a high absorbent of inelastic scattered neutrons. Quasi-elastic neutron scattering data were collected using an incident neutron wavelength of 6.271 Å and instrument resolution of ≈ 0.8 μeV (FWHM. The energy transfer window used for all QENS measurements was ± 30 μeV. Elastic (E = 0 μeV) and inelastic (E = 3 μeV) scattered intensities were measured, so called elastic and inelastic fixed window scans (EFWS, IFWS). Samples of (5-6 g) were filled under inert conditions into aluminium (1 mm-spaced double wall cylinder) and sealed mechanically with lead as a gasket. The sample holder was mounted in the spectrometer where a standard orange cryofurnace was used to measure at 150 K, 300 K, 350 K and 400 K for 4 h, respectively. ***Figure a*** shows the inelastic fixed window scans (IFWS) and the QENS spectra at 400 K for the members x = 0.75, 0.875 and 1 of $Na_{3-2x}In_{1-x}Ta_xCl_6$. The IFWS for $NaTaCl_6$ shows an onset of the inelastic signal below 250 K, indicative of the starting point of the local Na^+ diffusion in the material. Interestingly, this temperature is below the observed temperature at which the Na^+ start diffusing in a long range-order in the nuclear magnetic resonance spectra. IFWS for the other two members shows a similar transition temperature with an increase in the signal with respect to $NaTaCl_6$. It is worth mentioning that the maximum is not reached at 400 K. In turn, an increase in the broadening of the QENS spectra are observed as the Ta content decreases, which indicates a higher Na^+ diffusion coefficientas it is shown in ***Figure b***. This observation clearly matches with the tendency observed in the ionic transport properties of this system. The analyses of the spatial distribution to determine the actual values of the activation energies and diffusion coefficients was restricted by the limitations of the technique when the materials show diffusion coefficients below 10^{-10} m^2s^{-1}; the analysis of the broadening as a function of wave vector Q could not be performed in order to apply the Chudley-Elliott model due to the limited broadening in the present system.

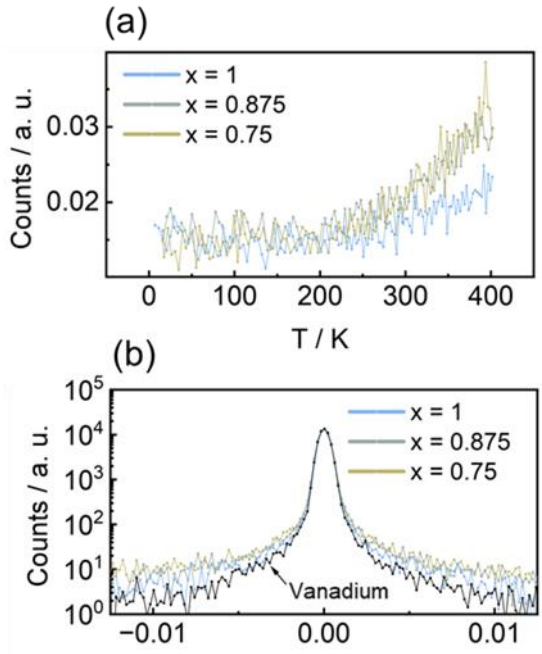

Figure 1. (a) IFWS intensity for $Na_{3-2x}In_{1-x}Ta_xCl_6$ (x = 0.75, 0.875 and 1) measured at 3 μeV and summed over all measured Q as a function of temperature. (b) Plots of the QENS spectra for $Na_{3-2x}In_{1-x}Ta_xCl_6$ (x = 0.75, 0.875 and 1) summed over all measured Q at 400K. Vanadium sample is also included for a better comparison.

**The results here obtained are going to be publish in a paper; X. Martínez de Irujo-Labalde, T. Zhao, B. Samanta, T. Bernges, V. Faka, A.N. Sobolev, O. Maus, M. Appel, M. A. Kraft, M. R. Hansen, W.G. Zeier. How crystal structure and microstructure can influence the sodium-ion conductivity in halide perovskites. J. Mater. Chem. A, 2024, under review.*