Experimental report

10/05/2023

Proposal: TEST-3279 **Council:** 4/2023

Title: QENS study of super-uionic compounds Ag2TeSeS

Research area: Materials

This proposal is a new proposal

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Samples: Ag2TeSeS

Instrument	Requested days	Allocated days	From	To
IN16B Si 111 BATS	2	2	13/04/2023	14/04/2023

Abstract:

Ag2Te/Se/S compounds are promising thermoelectric materials for room temperature applications. They show very low energy vibrational excitations (~2.5meV) which soften upon heating. Their detailed energy depends on the composition and thus the Te, Se, and S content. In addition to the soft phonon modes Ag2Te/Se/S exhibit fast ionic diffusion of Ag. The onset T of the fast diffusion is as well dependent on the composition and can be as low as 200K for Ag2Te.
This Ag diffusion has not been characterized yet for their microscopic mechanism. Geometry of the diffusion and energy scale are not known. We request the IN16/BATS beam to close this information gap by measurements of the QENS signal on 1-500 microeV scale at a few temperatures.

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QENS study of super-ionic compounds Ag2TeSeS

Instrument: IN16B in BATS mode
Incident wavelength: Si(111) analysers with ~6Å
Sample Environment: standard cryofurnace
Samples: $Ag_2Te_ySe_xS_{1-x-y}$ with (x,y) = (0,0);(.3,0),(.4,0);(0,.3) of ~10 g each
Sample can: Al-foil, slab geometry

Scientific background: Ag_2S doped with Se and Te ($Ag_2Te_ySe_xS_{1-x-y}$ with x+y<1) are promising materials for thermoelectric applications. Depending on the composition they take on different structures and undergo phase transitions between those structures upon temperature variation. In the regime of low doping grades $Ag_2Te_ySe_xS_{1-x-y}$ take on a monoclinic P21/c structure at low T and transform into a cubic Im-3m phase upon heating. The idiosyncratic property of the cubic phase is its high degree of Ag disorder facilitated by a high number of symmetry-equivalent positions for the Ag atoms. Each of this positions is occupied with only 10% probability by Ag atoms. As a result, Ag is highly mobile in the cubic phase setting ground for super-ionic conductivity.
With high enough Te doping $Ag_2Te_ySe_xS_{1-x-y}$ remain in the cubic phase down to base temperature. The high degree of dynamic disorder in the Ag sublattice can be thus frozen in to a glass-like state at low enough temperatures. This transition is reminiscent of a glass-transition of super-cooled liquids and associated with a characteristic temperature of the melting of the Ag matrix.

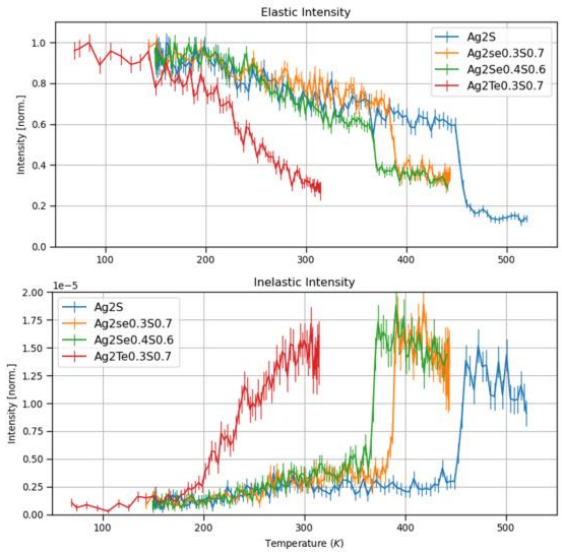

Figure 1: Elastic (top) and inelastic (bottom) signals derived from temperature dependent QENS scans with four different $Ag_2Te_ySe_xS_{1-x-y}$ compounds. Step-like loss of elastic intensity and gain of inelastic intensity in the binary and the two Se-doped compounds mark their phase changes from monoclinic to cubic structures. High mobility of Ag and a strong QENS signal are observed above this phase transition. Note the strong T-dependence of this transition upon Se doping. The Te-doped compound is in cubic phase throughout the sampled temperature range. The loss of elastic and gain of inelastic signal signify the melting of the amorphous Ag sublattice reminiscent of a glass transition behavior of super-cooled liquids. Note that similar however subtle intensity changes are detectable in signals of the binary and Se-doped compounds starting at about 200 K in their monoclinic structures.

To shed light on the translational relaxation processes of Ag we have carried out a measurement on four different compositions of $Ag_2Te_ySe_xS_{1-x-y}$ at the spectrometer IN16B/BATS (see **Fig. 1** and **Samples** description above for stoichiometries). The primary goal was to follow the transition behavior from monoclinic to cubic phases as well as the melting of the Ag matrix in a bulk cubic phase in order to trace a possible onset of quasi-elastic neutron scattering (QENS) signal as the fingerprint of enhanced Ag mobility. Fast temperature scans were carried out over temperature ranges adapted to the compounds' phase behavior. Elastic and inelastic intensities computed from the recorded QENS data are reported in **Fig. 1**. Any of the compounds give evidence of a high mobility of Ag in the cubic phase at sufficiently high T. However, Ag is already mobile on the time scale of the experiment in the monoclinic structures above about 200 K. See caption of **Fig. 1** for more details.

To estimate the time scale of the Ag diffusion process we have carried out 2 hours QENS measurements with one of the compounds at three different T. Measured spectra are reported in **Fig. 2**. Fits accounting for an elastic and a Lorentzian shaped QENS signal result in a half width at half maximum (HWHM) of 0.01 meV (~60 psec) at 275 K and of 0.02 meV (~30 psec) at 400 K. Signal recorded at 150 K reflects the resolution of the IN16B/BATS spectrometer and was taken into account for the QENS fitting.

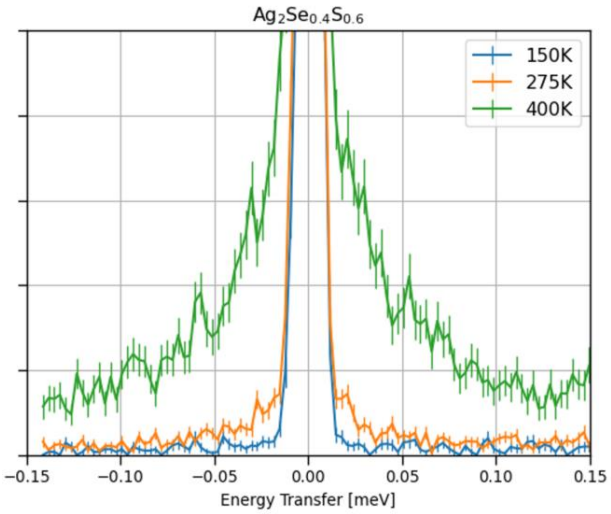

Figure 2: QENS spectra on a linear scale with arbitrary units. Data were recorded with $Ag_2Se_{0.4}S_{0.6}$ at the temperatures 150, 275 and 400 K. At 150 K the compound is in the monoclinic phase and Ag atoms are immobile on the time scale of the experiment. Spectrum reflects the resolution of the spectrometer. At 275 K the compound is in the monoclinic phase, Ag diffusion is detectable by a weak QENS signal on a time scale of ~60 psec (HWHM = 0.01 meV). At 400 K the compound is in the super-ionic cubic phase with highly mobile Ag atoms evidenced by the strong QENS signal on a time scale of ~30 psec (HWHM = 0.02 meV).