Experimental report

07/09/2022

Proposal: 7-01-568 **Council:** 4/2021

Title: Phonon properties of materials forwearable thermoelectric generators

Research area: Materials

This proposal is a new proposal

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Samples: ¿-Ag2S
Ag2S0.5Se0.45Te0.05

Instrument	Requested days	Allocated days	From	To
PANTHER	4	4	24/06/2021	28/06/2021

Abstract:

Wearable renewable energy generators are an attractive alternative to battery-based systems and can generate power up to a few Watts for portable electronic equipment. Although the most inorganic semiconductor materials are brittle at room temperature the Ag2(SeTeS)1 shows exceptional plastic deformability and high thermoelectric performance making it very interesting material for wearable power generator. Ag2S based compounds shows a remarkebly low lattice thermal conductivity of less than 0.6 Wm¿1K¿1. Phonon dispersion calculations indicates that the weak chemical bonding between Ag and S(SeTe) and their mass difference are responsible for the low lattice thermal conductivity resulting in clear separation between lower energy acoustic region (under 16 meV) and high energy optic band (around 40 meV). We aim to study the phonon DOS of master alloy ¿-Ag2S, and Te; Se alloyed Ag2S0.5Se0.45Te0.05 exhibiting the highest ZT parameter, in 2 states: in highly disordered and well relaxed. The Ag2S0.5Se0.45Te0.05 after casting is amorphous, while after annealing is fully crystalline. We plan to measure 4 samples at two incident neutron energies (19 and 50 meV) at the PANTHER spectrometer.

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Instrument: thermal time-of-flight spectrometer PANTHER
Incident energy: 12.5, 30 and 50 meV
Temperatures: 1.5, 100, 200, 300 K with 12.5 and 30 meV; 1.5 and 100 K with 50 meV
Acq. time: 60 min. at stable T and any incident energy; 5 min. for cooling runs with 12.5 meV
Sample Environment: standard cryostat
Samples: $Ag_2Se_xTe_yS_{1-x-y}$ with (x,y) = (0,0);(.05,0),(.3,0),(.4,0);(0,4);(.4,.1),(.3,.2),(.1,.4) of ~10 g each
Sample can: Al-foil, slab geometry

Wearable renewable energy generators are an attractive alternative to battery-based systems and can generate power up to a few Watts for portable electronic equipment. Although the most inorganic semiconductor materials are brittle at room temperature the alloys $Ag_2Se_xTe_yS_{1-x-y}$ with $x+y<1$ show exceptional plastic deformability and high thermoelectric performance making it very interesting material for wearable power generation. Ag2S based compounds show a remarkably low lattice thermal conductivity of less than 0.6 W/m/K. Phonon dispersion calculations indicate that weak chemical bonding between Ag and S(SeTe) and the mass difference of the constituents are responsible for the low lattice thermal conductivity resulting in clear separation between lower energy acoustic region below 16 meV and high energy optic band around 40 meV. Apart from theoretical studies addressing the properties of phonons no detailed experimental work on the vibrational dynamics has been carried out, yet. The present inelastic neutron scattering (INS) measurements were intended to shed light on the complexity of the vibrational dynamics of a series of $Ag_2Se_xTe_yS_{1-x-y}$ compounds.

INS measurements were performed on the direct geometry thermal time-of-flight spectrometer PANTHER. Solid polycrystalline specimens of ~10 g were arranged to flat slabs of ~20x30 mm^2 cross section and ~1 mm thickness and oriented at ~45° face-normal to neutron beam. Three incident energies were applied to focus on the total inelastic response with 50 meV, in more detail on the Ag-dominated low-energy modes with 30 meV, and a soft mode and quasi-elastic signal (QENS) with 12.5 meV. Applied temperatures and acquisition periods are indicated above. In addition, 12.5 meV neutrons were used to follow the evolution of a QENS signal present in highly Te-doped samples upon cooling from room temperature to below a dynamic transition at which the QENS signal freezes out.

Depending on the composition the compounds undergo a set of phase transitions and structural modifications. Ag_2S as well as alloys with low Se and Te doping adopt a monoclinic (P121/c1) structure in the monitored *T* range. With increasing Se content an orthorhombic (P212121) structure is formed at base *T* transforming upon heating into a monoclinic or cubic (Im-3m) phase for quaternary compounds containing Te. For higher Te contents the cubic phase is stabilized down to the base *T*. See **Fig. 1** for examples. The cubic structures are accompanied by disorder in the Ag sublattice giving rise to an extensive amorphous formfactor.

The phonon properties are strongly modified by the alloying and temperature treatment. See **Fig. 2** for examples. Ag_2S shows well defined phonons only at base *T* with the first localized mode at ~2 meV. With alloying as well as heating peaks are broadened and the low-energy localized mode softens. This holds in particular for the cubic structures. For quaternary compounds showing the transition from orthorhombic to cubic phase (low Te content) diffusion of Ag atoms sets in at the transition giving rise to the amorphous formfactor. In high-Te alloys we observe a transition from the solid amorphous to a liquid amorphous structure. The transition temperatures, orthorhombic to cubic as well as glass to liquid, depend inversely on

the Te content. An example of the glass to liquid transition and QENS signal is shown in **Fig. 3**. Fits to data at 300 K with single Lorentzian indicate a QENS energy scale of 4 meV with visible De Gennes narrowing.

Figure 1: Elastic intensity of binary Ag_2S (left), a quaternary (middle), and Te-doped ternary (right) compounds. Note the structural and dynamic transitions of the different compounds. Left, The Ag2S shows a modification of the monoclinic structure below 50 K. Middle, the quaternary undergoes a transition from an orthorhombic to cubic structure with a strong amorphous formfactor indicating the high disorder in the Ag sublattice as well as high mobility of Ag. Right, the amorphous formfactor highlights that disorder is frozen in down to base temperature within the cubic structure of the Te-doped ternary compound.

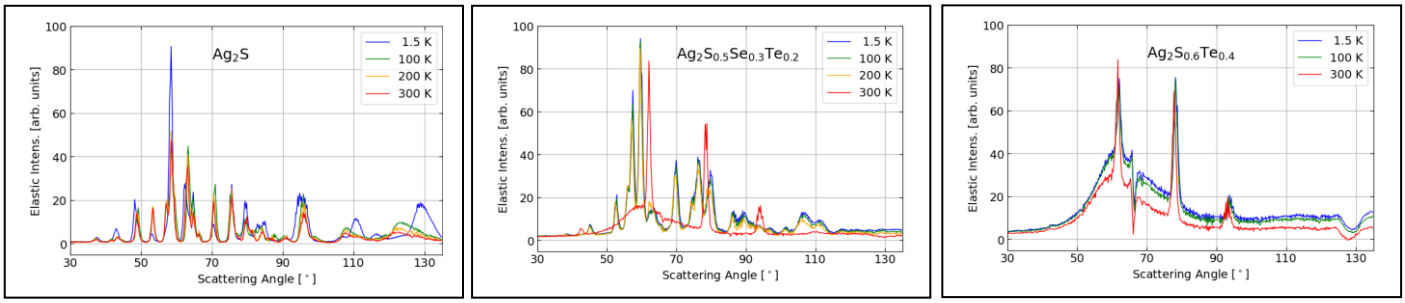

Figure 2: Generalized densities of states of binary Ag_2S (left), a quaternary (middle), and Te-doped ternary (right) compounds. Signals from 30 and 50 meV measurements are merged in the main figures, insets report the 12.5 meV data. Gray-shaded areas in the left and right figures report results from our DFT lattice dynamics and DFT-MD simulations, respectively. Left, note the presence of sharp, distinguished peaks in the GDOS at 1.5 K. They are well reproduced by the DFT lattice dynamics data.

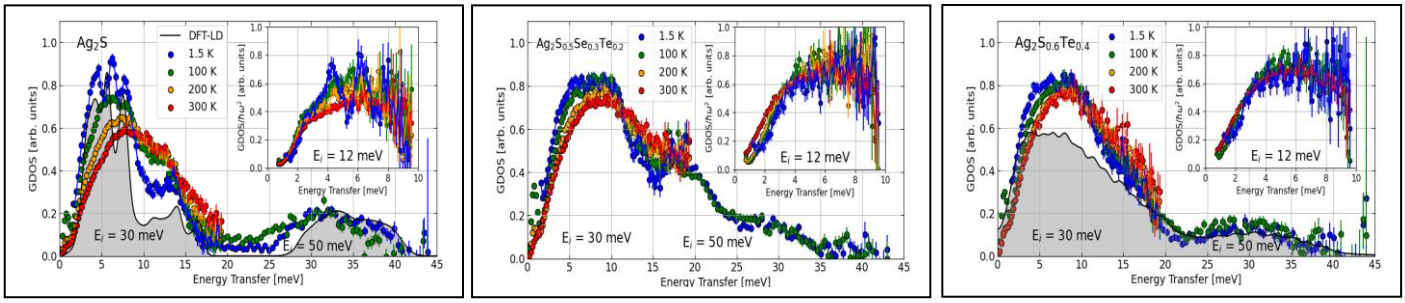

Figure 3: S(Q,E) spectra of the highly Te-doped ternary compound at 100 K (left) and 300 K (right). Note the distinguished mode at ~2 meV at 100 K. At 300 K a broad QENS signal is detectable highlighting the diffusion of Ag within the disordered sublattice. Lorentzian fits indicate an energy scale of 4 meV and De Gennes narrowing in accordance with the amorphous formfactor.