Unveiling the Optoelectronic and Thermal Properties of SnSe Polycrystals via EELS

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Tin Selenide (SnSe) has become a globally focused research topic in the field of thermoelectricity thanks to its low thermal conductivity and high electrical transport performance, which combined result in remarkable thermoelectric efficiencies. In its crystalline form, SnSe suffers from poor mechanical properties, rigid controlled crystal growth conditions and high production costs [1]. This has led the research to focus instead on SnSe polycrystals which, although less performing with respect to their crystalline counterpart, have great potential for significant efficiency enhancement [2]. A potential strategy to overcome the performance degradation, mainly related to the higher thermal conductivity of Tin oxide (SnOx) which percolates in the material through the grain boundaries, is by selective doping [3]. Here, we prove the effectiveness of Na doping in limiting the formation of SnOx and substituting the oxide at the grain boundaries in form of coherent precipitates through Scanning transmission Electron Microscopy (STEM). The ultralow spatial resolution imaging (~1Å) achieved with the aberration corrected STEM Spectra 300, combined with EDX spectroscopy, allows to map the elemental distribution at the grain boundary with atomic resolution, highlighting the presence of Na confined within the boundary.

The effect of the Na inclusions on the electronic and vibrational properties of SnSe polycrystals is further investigated through Low-Loss EEL Spectroscopy. Monochromated operation on the beam accelerated at 60kV, combined with low beam currents (~70pA) and convergence and collection semi-angles of 30 and 20 mrad, respectively, allow to collect the forward-scattered and higher momentum transfer signals in the first Brillouin Zone. From here, the information on the bandgap together with the plasmonic and phonon signals can be extracted for each probe position. In the specific, bandgap fitting across the doped grain boundary is supported by a customized Python algorithm [4], which highlights the decrease in the pure SnSe bandgap value due to the Na inclusions, in accordance with the DFT calculations. Further investigation on the vibrational signals within the low range of the EELS spectrum is performed to evidence the phonon modes that appear when in proximity of the grain boundaries. The specific vibrational-modes mapping will in the future enable the acquisition of phonon dispersion at grain boundaries, interfaces, edges, and various nature defects unlocking a powerful tool for thermoelectric performance evaluation at the atomic scale.

Keywords:

Thermoelctricity, EELS, Bandgap, Phonon modes

Reference:

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