Thermoelectric Properties of Cubic SnSe Phase from First Principles Calculation

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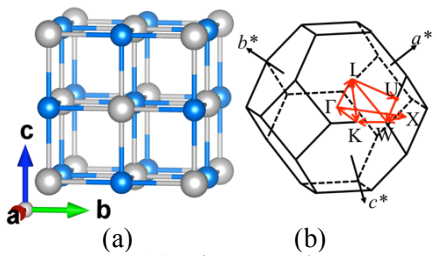
I. INTRODUCTION Aiming to practically utilize thermoelectric materials as power generators, we should find a material which has a high thermoelectric figure of merit $ZT > 1$. Presently, many studies have been performed on the orthorhombic SnSe that showed a high ZT about 2.6 along b-axis at 950 K with the ultralow thermal conductivity of 0.35 $W/m^{-1}K^{-1}$ at 900 K [1]. SnSe shows a phase transition from low-temperature *Pnma* phase to high-temperature *Cmcm* phase in the range of 750 ~ 800 K that the *Cmcm* phase has higher symmetry than the *Pnma* phase. Similarly, the high-symmetry cubic (*Fm-3m*) phase of SnSe (**FIG. 1** (a)) has been proved to be stable from the early experiments [2-4]. However, thermoelectric properties of the cubic phase have not been reported yet. We focus on the cubic SnSe phase and study its thermoelectric properties based on the combination of first principles density functional calculation and semi-classical Boltzmann transport theory.

II. METHODS We studied thermoelectric properties of the cubic SnSe phase by using the density functional theory (DFT) within the generalized gradient approximation (GGA) with Perdew-Berke-Ernzerhof (PBE) exchange-correlation functional as implemented in the *WIEN2k* package [5]. We used the full-potential augmented plane-wave (FLAPW) and local orbitals method to optimize crystal structure and then calculated electronic structure. The whole Brillouin zone was sampled with a Monk-Horst-pack grid of 3×3×3 and a much denser grid of 50,000 k-points was used for thermoelectric property calculation based on the Boltzmann transport theory, as implemented in *BoltzTraP* code [6]. We obtained the electrical conductivity σ and Seebeck coefficient S within the constant relaxation time approximation. Meanwhile we calculated the phonon spectrum of cubic SnSe phase based on the Parlinski-Li-Kawazoe method using a real-space superlattice approach with the finite displacement within the *phonopy* code [7]. The calculation and symmetrization of force constants on 2×2×2 supercell are executed by using singular-value decomposition (pseudo-inverse) from *WIEN2k*. We also did a comparative study by using *QUANTUM ESPRESSO* (*QE*) [8] using pseudo-potentials to represent electron-ion interactions.

III. RESULTS & CONCLUSIONS The optimized lattice parameter (5.99 Å) agrees with previous experimental data [4]. An indirect band gap along LW (**FIG. 1** (b)) line is 0.204eV. **FIG. 2** shows that ZT_{max} could be reached up to 0.8 at room temperature level. ZT_{max} decreases with increasing temperature in the low doping region. High thermoelectric properties of n-type and p-type in cubic SnSe phase could be obtained simultaneously. **FIG. 3** shows phonon dispersion relation of cubic SnSe phase. No imaginary frequencies are found, suggesting cubic SnSe phase is thermodynamically stable. Low values of both group velocity v_g and highest frequency ω_{max} show a potentially low thermal conductivity κ_L in such phase. Further, detailed analysis on thermoelectric properties of the phase will be shown in presentation.



(a) (b)

FIG. 1 (a) The crystal structure and (b) the path in the first Brillouin zone of cubic SnSe phase.

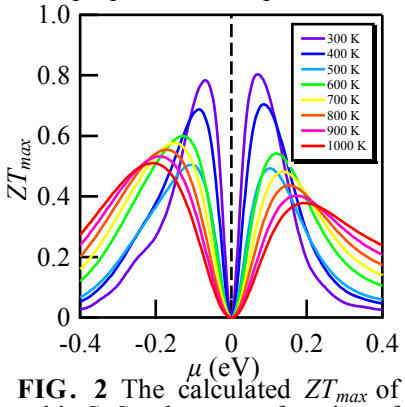


FIG. 2 The calculated ZT_{max} of cubic SnSe phase as a function of T and chemical potential μ.

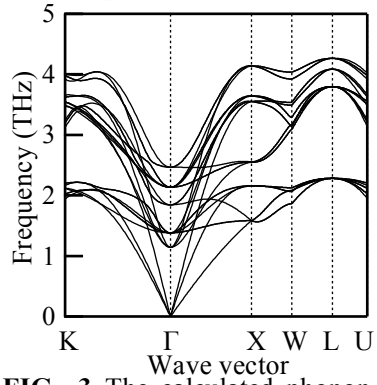


FIG. 3 The calculated phonon band structure of cubic SnSe phase.

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