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High electrical transport properties performance enhanced by anti-site defects in single crystalline SnSe

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ABSTRACT

Single crystalline tin selenide (SnSe) has attracted considerable attention due to its record high figure of merit value in medium temperature range. However, their large band gap restricts the electron transport. Herein, we tailor the carrier concentration by offering a variability of the Sn/Se ratio to fine-tune the electrical transport properties. Density functional theory demonstrated that the collaborative optimization of the Seebeck coefficient and the electrical conductivity through optimizing carrier concentration can improve significantly the power factor, and deviation from stoichiometry is an effective strategy to modulate the carrier concentration because anti-site defects Sn_{Se} lower the Fermi level and increases the number of carrier pockets in SnSe. Meanwhile, experimental observations confirm that the carrier concentration and electrical conductivity are changed with varied Sn/Se ratio. Through this work, a viable design principle for optimized carrier concentration for achieving high thermoelectric performance is provided.

1. Introduction

Thermoelectric devices enable a direct conversion between thermal and electrical energy, and provide a method for power generation from waste heat [1–5]. Effective thermoelectric devices depend on the high performance thermoelectric materials. Dimensionless figure of merit (ZT) is used to characterize the properties of thermoelectric materials, which defined as $ZT = (\alpha^2\sigma/\kappa)\,T$, where α, σ, κ and T are the Seebeck coefficient, electrical conductivity, total thermal conductivity (a sum of electron κ_{ele} and lattice κ_{lat} thermal conductivity), and absolute temperature, respectively [6–9]. As can be seen from the formula, high Seebeck coefficient (α), high electrical conductivity (σ) and low thermal conductivity (κ) were required at the same time to gain a higher ZT value. It is quite difficult to achieve this goal because of the complex intrinsic connection between the above parameters [10].

SnSe is a p-type semiconductor with a band gap of ~0.86 eV layered structure, and its constituent elements are abundant in the crust, non-toxic and non-polluting and the layered structure of SnSe derives from a distorted rock-salt structure [1,8,11,12]. In recent years, many studies have focus on the single crystal SnSe due to the advantage on conductivity compare to the polycrystallines [2,7,13–17]. The outstanding performance of SnSe single crystals is ascribed to ultralow thermal conductivities [18]. Single crystal SnSe prepared by vertical pulling method achieved a ZT value of 2.62 at $T = 923$ K [19].

The electrical conductivity and Seebeck coefficient play key role for a high power factor. The electrical conductivity is defined by the following formula:

$$\sigma = ne\mu_H \tag{1}$$

where e is the electron charge, μ is the carrier mobility and n is the carrier concentration. Electrical conductivity can be improved obviously through increasing carrier concentration. However, according to the Pisarenko relations, Seebeck coefficient α can be given by:

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$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} \quad (2)$$

where k_B is the Boltzmann constant, e is the electron charge, h is the Plank constant and m^* is the density of states effective mass of carriers [4], the Seebeck coefficient decreases with increasing carrier concentration. Thus carrier concentration is closely related to the electrical conduction characteristics of thermoelectric materials. Recently, Yasumitsu et al. [20] calculated the electrical conduction properties of SnSe with variation carrier concentration by using first-principle calculations, the results indicate that doping strategy is an effective method to improve the *ZT* value. Indeed, doped SnSe with various dopants have been performed to enhance the thermoelectric performance [9,13–15,21–26]. *ZT* value of Na-doped SnSe is 2.0 and Bi-doped SnSe achieve 2.2 [15]. Chang et al. [25] synthesized n-type Br-doped polycrystalline SnSe with high *ZT* value of ~1.2 at 773 K. Peng et al. [24]reported that the average *ZT* value is more than 1.17 along the crystallographic b-axis of Na-doped SnSe, with the maximum *ZT* value reaching a value of 2 at 800 K.

The relatively large band gap result in an excellent Seebeck coefficient but a low electrical conductivity compared to conventional thermoelectric material. Tuning carrier concentration by doping is an effective way to improve the thermoelectric properties of SnSe [27]. In this work, first-principles calculations coupled with the Boltzmann transport theory are used to calculate the influence of carrier concentration on the transport properties of thermoelectric materials. Based on the calculated results, we synthesized SnSe single crystals with different compositions by Sn self-flux method. Compare to traditional Bridgman method [1] and Spark Plasma Sintering [3,16,22], Sn self-flux method is a simple fabrication method and the carrier concentration can be effectively modulated by different Sn/Se ratio. Impressively, the fabricated single crystals SnSe can achieve excellent electrical properties by fine-tuning the Sn/Se ratio. Our work provides an insight into optimizing the carrier concentration for the development of highly efficient SnSe-based thermoelectric device.

2. Computational and experimental methods

2.1. Computational details

First-principles calculations were performed based on density functional theory (DFT) with Vienna ab initio simulation package (VASP) [28,29]. The exchange-correlation function are calculated using generalized gradient approximation (GGA) described by the Perdew, Burke and Ernzerhof (PBE) [30]. A $4 \times 12 \times 12$ k-point sampling grid and a cut-off energy of 500 eV are adopted [31]. Conjugated gradient method is used to the geometry optimization and all the atomic coordinates are fully relaxed until the maximal force on each atom was less than 0.01 eV/Å, and the convergence condition for energy is 10^{-6} eV. The anti-site defects Sn_{Se} is introduced by replacing one selenium atom in 3×3 supercell.

2.2. Boltzmann transport calculations

We have used Boltzmann theory to estimate semi-classical values of the Seebeck coefficient and electrical conductivity. The necessary crystal structure and Eigen-energies were obtained from the DFT-computed. All of the calculations of the transport properties were implemented in the BoltzTraP package. In order to obtain accurate transport properties, the Brillouin zones of the unit cells were represented by the Monkhorst_Pack special k-point scheme with $8 \times 24 \times 24$ grid meshes.

2.3. Experimental section

According to the results of theoretical calculations, in order to obtain predominant electrical transport properties of SnSe, carrier concentration must be optimized. In this work, we prepared single-crystal SnSe by the Sn self-flux method and adjust the carrier concentration by changing the solvent ratio in Sn self-flux method. High-purity elements Sn (99.999% ingot) and Se (99.99%, powder) were weighed in accordance with their atomic ratios as Sn: Se = 4.5, 5, 5.5 and 6, and denoted by S1, S2, S3, S4, respectively. Subsequently, the mixture was sealed in a vacuum quartz tube and heated to 1173 K at a heating rate of 180 K/h. Incubated at this temperature for 10 h, then cool down to 1023 K in 15 min and warm up to 1123 K in 5 min. After 1 h of incubation, slowly cool down to 773 K over 80 h. At this temperature, the single crystals were separated from the molten Sn flux by the centrifuge.

The crystal structures of the samples were analyzed by X-ray diffraction (XRD) with Cu *Kα* radiation (Ultima IV). The actual elemental compositions were measured by an electron probe microprobe analysis (EPMA, JXA-8230). In order to identify the chemical state of the samples, we performed X-ray Photoelectron Spectroscopy (XPS) measurement. The lattice structure of S3 is observed through high-resolution TEM and selected area electron diffraction (SAED). Electrical conductivity σ and Seebeck coefficient α were measured in the temperature range of 303–663 K in vacuum. Electrical conductivity σ was measured by a direct current (DC) four-probe method, and the DC current is kept at 10 mA. Seebeck coefficient was measured by a comparative method, and constantan (Ni: 40%) is used as a reference sample, of which α α in the measured temperature range is known. Hall coefficients (R_H) were measured by the Hall system (Nanometrics HL5500 Hall System) at room temperature (RT) in a magnetic field of 0.75 T.

3. Results and discussion

The low-temperature crystal structure of SnSe has a *Pnma* space group. Fig. 1 presents the geometrical structure and electronic band structure of SnSe. The calculated optimal lattice parameters of SnSe are a = 11.50 Å b = 4.16 Å and c = 4.45 Å, the results are in agreement with the previous theoretical values [32]. As we all know, fundamental band gaps are typically underestimated in DFT-PBE approach. The calculated band gap is 0.50 eV, and it is smaller than the experimental value of 0.86 eV reported by Zhao et al. [1] However, band gap is critical for the thermoelectric properties, and hence we adopt a scissor operator to rigidly shift the conduction bands such that the value of the band gap coincides with the experimental value of 0.86 eV.

As shown in Fig. 2, the calculated transport properties of SnSe crystal as a function of the carrier concentration at 300 and 450 K for each (a, b and c) axial direction. The positive value of the carrier concentration corresponds to the holes (p-type), and the negative corresponds to the electrons (n-type). Herein, we main focus on the tendency of thermoelectric properties upon carrier concentration and omitted the effect of relaxation time because that it is still a challenging task to estimate the relaxation time via first-principles calculations. It is obviously that carrier concentration can change the electrical transport properties of SnSe. The Seebeck coefficients decrease, meanwhile, σ/τ increases with increasing the level of carrier. In Fig. 2(e) and (f), it is obviously that anisotropic enhancements of the PF/τ occur with carrier. For n-type of SnSe, the higher values along a-axis, and a reduced value along b-axis while p-type gives the largest *PF/τ* along the b-axis. This anisotropic enhancement on the PF/τ is caused by different responses to σ by carrier. These results also agree well with the previous work [20].

Therefore, it is a suitable strategy to improve the thermoelectric