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Effect of high pressure on thermoelectric performance and electronic structure of SnSe via HPHT

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ABSTRACT

Polycrystalline SnSe bulks were synthesized by a simple and rapid High Pressure and High Temperature (HPHT) method in pressure range of 1–5 GPa, and the thermoelectric performances were assessed after high pressure was released. HPHT can not only sharply shorten synthetic time to 25 min, but also tune thermoelectric properties in a broad range. More importantly, the beneficial thermoelectric properties under high pressure are effectively retained to ambient conditions via “quenching” procedure. The intrinsically high electrical resistivity of SnSe is remarkably reduced by HPHT, which is ascribed to pressure-induced band gap narrowing. A minimum electrical resistivity of 0.1 Ω cm at 5 GPa and maximum power factor of 1×10^{-4} $\mathrm{Wm^{-1}K^{-2}}$ at 3 GPa for $SnSe_{0.98}Te_{0.02}$ are achieved at ambient conditions. Besides, the first principle calculations reveal that high pressure can fundamentally shrink interatomic distances and lattice parameters, which thus lead to a decreased band gap. The pressure coefficient of band gap $dE_g/dP = -0.074$ eV/GPa is obtained. The variations of electronic structure under high pressure are in accordance with the trend in measured thermoelectric properties.

1. Introduction

Thermoelectric (TE) materials can achieve the transformation between temperature gradient and voltage directly. Recently, a variety of TE materials and applications emerge rapidly to reduce energy consumption and alleviate negative environmental influences. The primary issue in practical implementation is the conversion efficiency, characterized by the dimensionless figure of merit ($ZT = S^2\sigma T/\kappa$, where S, σ and κ are Seebeck coefficient, electrical conductivity and thermal conductivity, respectively) [1]. Due to the interdependency and confliction of the three factors (S, σ and κ), it is challenging to optimize them synergistically. Currently, both guiding conceptions and precise instruments accelerate the research of TE materials. One feasible approach is nanostructuring to fabricate all-scale hierarchical architecturing, which can achieve phonon blocking efficiently [2,3]. Another is band engineering to enhance thermopower, such as electron energy barrier filtering and density-of-states distortion [4–6].

Conventional alloys such as Bi_2Te_3 and PbTe have exhibited outstanding TE performance enough for commercial production. However, the toxicity and rarity of these elements severely hinder their widespread applications. In contrast, a binary alloy SnSe not only eliminates the above mentioned disadvantages, but also is relative thermal stable at high temperature. SnSe has a typical layered and anisotropic crystal structure, with weak Sn–Se bonding connecting two-atom slabs along a axis (Fig. S1a). SnSe shows an orthorhombic structure (Pnma, #62) at room temperature, which will undergo a displacive phase transition at around 800 K. The high-temperature phase of SnSe (Cmcm, #63) reveals a higher symmetry and smaller band gap [7,8]. Initially, SnSe is intensively studied as solar cells and phase change memory alloys. Recently, a record ZT value of 2.6 at 923 K was realized for SnSe single crystal along b axis, which makes SnSe promising candidate at high temperature range [9]. Moreover, hole-doped SnSe single crystals exhibit ultrahigh power factor and broad temperature plateau with high ZT [10,11]. However, single crystals usually exhibit weak mechanical property and anisotropic transport features. Besides, the synthetic process is time consumption and complexity. Hence, extensive investigations are performed to pursue performance optimization in polycrystals. Nevertheless, due to the intrinsically high electrical resistivity of SnSe, little achievement is obtained and no ZT value exceeding 1 has been reported so

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far [12–18]. Therefore, how to effectively decrease the high electrical resistivity of SnSe is a key issue.

Pressure tuning can yield multifold enhancements in TE performance, which has been verified by many materials [19,20]. Unfortunately, it is impossible to obtain the enhanced TE performance at ambient pressure, due to the severe reversibility after high pressure is released. In contrast, High Pressure and High Temperature (HPHT) method provides an alternative route. HPHT combines the rapid synthesis process (directly from elements to bulks) and pressure tuning process simultaneously. What's more, HPHT is capable of retaining high pressure features to ambient conditions via “quenching” procedure (see below in sample synthesis section) [21,22]. However, high pressure experiments are seldom conducted to tune TE performance on SnSe bulks.

In this paper polycrystalline $SnSe_{1-x}Te_x$ bulks are successfully synthesized by HPHT method as fast as 25 min. The microstructures of SnSe bulks are described in HRTEM analysis. HPHT shows an apparent advantage in decreasing electrical resistivity, and the high pressure effects are retained to ambient conditions without reversibility after the pressure is released. Afterwards, the band structure variations under pressure by first principle calculations are exhibited to verify the trends in experimental results.

This paper is organized as follows. Experimental and computational procedures are revealed in Section 2. In Section 3 thermoelectric performances at ambient conditions are presented. Section 4 describes the theoretical outcomes of band structure variations under pressure. Compared the experimental results with computational data, the pressure dependence of TE performance is examined qualitatively, and then we draw a conclusion in Section 5.

2. Experimental section and computational details

2.1. Sample synthesis and characterization

Bulk polycrystalline $SnSe_{1-x}Te_x$ ($x = 0.02$, 0.03, and 0.05) samples were synthesized by HPHT at 1–5 GPa. Stoichiometric amounts of commercial Sn (4 N), Se (4 N), and Te (4 N) powders were grinded in Ar-protective atmosphere and then loaded into a die to cold press. The cold-pressed cylinder (φ 10.5 × 4 mm) was subjected to synthetic chamber in China-type large volume cubic high-pressure apparatus (CHPA) (SPD-6 × 1200) (Fig. 1). The samples were prepared at different synthetic pressure for 25 min. Before the pressure was released, the sample chamber was “quenched” from synthetic temperature to room temperature at a high cooling rate of at least 400 K/min. The temperature was measured with type Pt-RH/Pt-Rh thermocouple junction at the surface of sample chamber. The pressure was calibrated by the resistance change of standard materials.

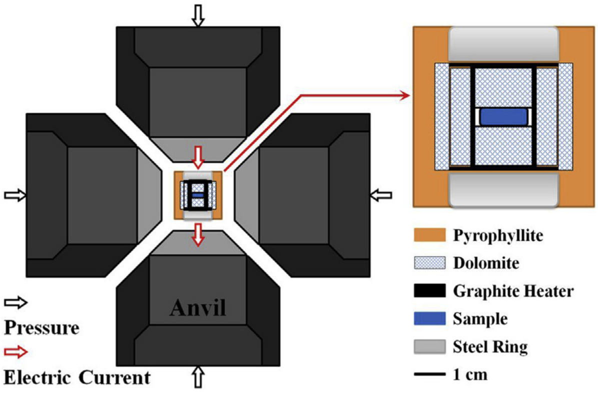

Fig. 1. Diagrams of (a) front view of China-type large volume cubic high-pressure apparatus (another two anvils are not drawn) and (b) the sample assembly for HPHT synthesis.

The X-ray diffraction (D/MAX-RA) was performed to obtain phase structure. Field emission scanning electron microscopy (JEOL JSM-6700F) was used to probe morphology, and the microstructures were revealed by high-resolution transmission electron microscopy (JEOL JEM-2200FS). To avoid the anisotropy, the transport properties were measured along the same direction at ambient conditions. The Seebeck coefficient was calculated from the relationship of electromotive voltage and temperature difference between two ends of sample (computer-assisted device monitored by program from NI-company), and the uncertainty was within 5% compared with commercial ZEM-3 (Ulvac-Riko). The electrical resistivity was measured by a typical dc four-point technique. Optical spectra were recorded on bulks with a UV-3150 double-beam spectrophotometer at room temperature. Absorption data were obtained from reflectance by $\alpha/s = (1-R)^2/(2R)$, and then the band gap was derived from linear extrapolation from absorption coefficient.

2.2. Computational details

The first principle calculations about conventional 8-atom cell Pnma structure of SnSe were performed on CASTEP package, based on density functional theory (DFT) with ultrasoft pseudopotential calculation method [23]. The generalized gradient approximation (GGA) in scheme of Perdew–Burke–Eruzerhof (PBE) was employed to describe the exchange and correlation potential. The geometric optimization of unit cell was carried out by the BFGS minimization algorithm. The force, stress component and tolerance in self-consistent field (SCF) were 0.03 eV/Å, 0.05 GPa and 10^{-6} eV/atom respectively. The energy cutoff for plane wave expansion of 600 eV and Monkhorst-Pack k-point meshes of 4 × 12 × 12 mesh parameter grids were used. The lattice constants used for geometric optimization were $a = 11.502$ Å, $b = 4.153$ Å, and $c = 4.45$ Å [8]. Besides, electronic band structures and density of states (DOS) spectra were calculated.

3. Results and discussion

3.1. XRD spectra, morphology and microstructure

The crystallographic structure of the synthesized bulks was determined by XRD analysis (Fig. 2a). All samples crystallize in orthorhombic structure (Pnma), and all the diffraction peaks are indexed to SnSe (PDF#48-1224). The peak positions shift to higher angle with increasing synthetic pressure (Fig. 2b), because high pressure compression can reduce interatomic distances, lattice constants, and interplanar distances. Meanwhile, it means that the high pressure effects by HPHT are captured and retained to ambient conditions after the release of applied pressure, which is unavailable for in situ pressure tuning. In short, polycrystalline SnSe bulks have been successfully synthesized in 25 min by HPHT. Furthermore, high pressure has the ability to adjust the fundamental factor, interatomic distance, which determines band structure and transport properties.

FESEM images (Fig. 3) are displayed to analyze morphology. Typical laminar grains exhibit several ten um in size, and no distinct pores and cracks are observed. The magnified image clearly shows that the laminar grains stack together closely. According to two-dimensional nucleation theory, the typical laminar feature can be ascribed to the layered crystal structure with weak bonding connecting between Sn–Se atom slabs. The occurrence of relative slippage along the laminar grain surface is generated by high