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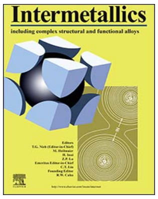

Thermoelectric performance of polycrystalline $Sn_{1-x}Cu_xSe$ ($x = 0–0.03$) prepared by high pressure method

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A B S T R A C T

P-type $Sn_{1-x}Cu_xSe$ ($x = 0–0.03$) polycrystal was prepared through melting synthesis and high pressure (6.0 GPa) sintering (HPS) method. The composition and microstructure of the samples was analyzed, and the thermoelectric transport properties were investigated in the temperature range of 303 K–823 K. The results indicate that the electrical conductivity increases as Cu content increases. An observable improvement is found for the Seebeck coefficient when x is 0.01. In addition, the total thermal conductivities (κ_{tot}) of all samples decrease with rising temperature, and reach its minimum values at 773 K. As a result, the maximum power factor (*PF*) and ZT_{max} value are 378 μW m^{-1} K^{-2} and 0.79 for $Sn_{0.97}Cu_{0.03}Se$ at 823 K, respectively.

1. Introduction

In today's society, the increasingly serious environmental pollution and energy crisis caused by excessive development are the two major challenges our world currently faces. Research and development of no pollution, no noise and high efficiency of thermoelectric material have always been the goal of the researchers. Thermoelectric (TE) material is a kind of functional materials, which can directly affect the thermoelectric conversion and has wide application prospects, such as low-temperature refrigeration and thermoelectric power generation, etc. Dimensionless quality factor *ZT* (*T* is the absolute temperature) is used to measure the pros and cons of thermoelectric performance. It can be expressed by the equation: $ZT = \frac{\alpha^2\sigma T}{\kappa}$, where α, σ, and κ are Seebeck coefficient, electric conductivity, and thermal conductivity respectively. The greater the value of *ZT* is, the higher the thermoelectric conversion efficiency is. Obviously, for the high quality factor, the material must possess high Seebeck coefficient (α), high conductivity (σ) and low thermal conductivity (κ). In order to search for high *ZT* value TE materials, one feasible strategy is that the materials possess intrinsically low thermal conductivity [1,2].

SnSe is a binary IV-VI group semiconductor compound. It adopts a layered structure crystallized in the orthorhombic *Pnma* space group at room temperature and it is derived from the NaCl-type structure. The tin atoms and selenium atoms form a zig-zag structure, which is a distorted octahedron [3–7]. Around 750 K, a phase transition is undergone from *Pnma* space group to *Cmcm* space group in SnSe [4–7]. It was revealed that such compound has extremely low thermal conductivity. Zhao reported that the thermal conductivity of single crystal SnSe decrease with rising temperature, and its value achieves the range of 0.23–0.34 W m^{-1} K^{-1} at 973 K in the decline [4]. Thus pure SnSe shows excellent thermoelectric properties in the high temperature ranges.

Very recently, due to its low mechanical properties in single crystal SnSe [8], thermoelectric properties of polycrystalline SnSe have stimulated interest of scientific researchers. In undoped polycrystalline SnSe samples, the performance of the samples has not yet reached the level of a single crystal, where *ZT* values reach 1.1 at 873 K [9]. However, different doping elements in this compound have generated some optimization for its thermoelectric property. As candidates, Ag, Na, I, Al, K, Zn et al. can increase the defect concentration, finally improving the *ZT* value of polycrystalline SnSe [10–15]. For instance, the ZT_{max} of 1.1 was obtained for $Sn_{0.99}K_{0.01}Se$ at 773 K, and the ZT_{max} of 0.96 was reached for $Sn_{0.99}Zn_{0.01}Se$ at 873 K [14,15].

It is well known that the valence state for Cu in Cu_2Se is +1, Sn is +2 in SnSe. Therefore, the former has lesser valence electrons than the latter. When the element Cu is used as a substitute for Sn within the SnSe lattice, the hole concentration will be increased. In addition, as a thermoelectric material, Cu_2Se has intrinsic low thermal conductivity at high temperature range [16–18]. As a result, Cu doping in SnSe compounds might be an effective way to improve hole conductivity and decrease thermal conductivity. Furthermore, high pressure sintering (HPS) method can not only improve the TE property of SnSe by modulating the band structure [19,20], improve the mechanical property by increasing the density, but also improve prepared effi-

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ciency. For example, it only needs 6–10 min for the entire high pressing sintering processing per sample. Therefore, in this work, $Sn_xCu_{1-x}Se$ ($x = 0, 0.01, 0.02, 0.03$) was prepared by melting synthesis and high pressure sintering (HPS) method. The effect of Cu content on transport properties was investigated. It is found that the doping of Cu can increase the power factor and *ZT* value.

2. Experiment section

The starting materials used elements Sn, Se and Cu powders of 99.99%. These powders were mixed well in an agate mortar, and were synthesized for 2 h in vacuumed and sealed quartz tubes at 1203 K. The obtained ingot was smashed to fine powders, and then the powders were cold compacted and loaded into cubic press. Dense samples of Φ16 mm were formed by HPS at 1073 K for 3 min under high pressure (6.0 GPa).

The actual phase composition of samples was investigated using X-ray diffraction (XRD, Rigaku D/MAX-2550P diffractometer, Cu-Kα). The lattice constants were obtained from diffraction data using Rietveld refinement. The field-emission scanning electron microscopy (FE-SEM, FEI, Quanta FEG 450, America) was used for observing the microstructures of HPS sample. The electrical conductivity (σ) and Seebeck coefficient (α) were measured by self-made equipment in argon atmosphere from 303 K to 823 K. Four probes were attached to the samples by silver conductive adhesive paste. The standard four-probe method was used to measure the electrical conductivity. When a temperature gradient (5 K) was applied to the two ends of the specimen, the voltage between these two ends of sample was measured through the probes. The Seebeck coefficient (α) was determined by the equation: $\alpha = \frac{dU}{dT}$, where dU is Seebeck voltage difference under the temperature difference of dT between the two ends of sample. The thermal properties (thermal diffusivity (λ) and specific heat (C_p)) were meticulously measured by laser flash instrument (NETZSCH, LFA427, Germany) in the temperature range from room temperature (303 K) to 823 K. The Archimedes method was employed for estimating the volumetric density (d). Thermal conductivity (κ) is the product of the three physical parameters: $\kappa = \lambda C_p d$. The Hall coefficient R_H was measured for the HPS $Sn_{1-x}Cu_xSe$ ($x = 0, 0.01, 0.02, 0.03$) samples at 300 K and the HPS $Sn_{0.97}Cu_{0.03}Se$ sample from 300 to 400 K by a physical properties measurement system (Quantum Design, PPMS-9, America), the Hall carrier concentration n and the Hall mobility μ were obtained from R_H based on the formulas $n = 1/(eR_H)$ and $\mu = \sigma R_H$.

3. Results and discussion

3.1. XRD and FE-SEM analysis

Fig. 1 (a) exhibits the XRD patterns of the $Sn_{1-x}Cu_xSe$ ($x = 0, 0.01, 0.02, 0.03$) before and after HPS. The position of all characteristic peaks are consistent with the standard peaks of SnSe with orthorhombic structure (JCPDS No. 48-1224); second phase was not found in the samples, and an obvious orientation along (400) directions was exhibited in the XRD patterns. It can be clearly seen that the peaks move toward a higher angle with increasing Cu content for HPS samples (Fig. 1 (b)). This result indicates that Cu atoms are incorporated into the lattice of SnSe.

The lattice constants were determined from the X-ray diffraction peaks. Fig. 2 shows the composition (x) dependence of lattice constants and crystal cell volume of the HPS samples. An obvious decrease can be observed when the cell volumes of pure and doped SnSe were compared. Indeed, the lattice constants and crystal cell volume of the HPS $Sn_{1-x}Cu_xSe$ samples decrease with increasing substituted Cu. This is due to the fact that the ion radius of Cu^{1+} (0.077 nm) is smaller than that of Sn^{2+} (0.112 nm).

Table 1 lists the density and percentage of relative density for $Sn_{1-x}Cu_xSe$ ($x = 0, 0.01, 0.02, 0.03$) before and after HPS. It can be found that the densities of samples were obviously improved after High Pressure Sintering (6.0 Gpa, 1073 K for 3 min), during which the samples were rapidly densified in a short time. The result testifies that the HPS technology is an excellent way to boost the mechanical intensity of SnSe.

Fig. 3 shows the FE-SEM morphologies of fractured surfaces for HPS $Sn_{0.97}Cu_{0.03}Se$ sample. It can be seen that the obvious layered structure distributes in the sample. This structure results from the preferred orientation along (400) direction as shown in Fig. 1.

3.2. The effects of Cu doping on electrical transport performances

The electrical conductivities for HPS samples are exhibited in Fig. 4 (a). The σ-T curve of undoped SnSe displays semiconducting characteristics as the data shows that the electrical conductivity increases with increasing temperature. Dopant can indeed increase electrical conductivity with increasing Cu content in the entirety of the temperature range measured. For the doped samples, the electrical conductivity increases with temperature from 303 K to 473 K initially, then decreases slightly from 473 K to 623 K, and finally increases substantially with further increases in temperature. It reaches the maximum 3513 S m^{-1} for $Sn_{0.97}Cu_{0.03}Se$ at 823 K.

Fig. 4 (b) displays the α-T curve for HPS samples. The compound $Sn_{1-x}Cu_xSe$ ($x = 0, 0.01, 0.02, 0.03$) obtained is p type. Due to the fact that the minority carriers are excited, the mutation of α occur around 650 K. The values of Seebeck coefficient decrease with increasing dopant content before mutation temperature for doped sample. It is noteworthy that an observable improvement can be found when comparing the Seebeck coefficients of $Sn_{0.09}Cu_{0.01}Se$ with that of SnSe before 723 K. The maximal value of 493.5 μV K^{-1} is reached for $Sn_{0.09}Cu_{0.01}Se$ at 623 K. However, with Cu content further increasing, the Seebeck coefficients decrease evidently before 723 K. This result suggests that the value of Seebeck coefficients for Cu doped samples with $x = 0.02, 0.03$ are lower than undoped SnSe before 723 K.

Noteworthy, the Seebeck coefficient exists a maximum value at the temperature between 600 and 700 K, thus the energy gap E_g can be estimated from the equation [21]: $E_g \approx 2e|\alpha_{\max}|T_{\max}$, where e is the electron charge. The calculated energy gap E_g are 0.51 eV, 0.62 eV, 0.58 eV and 0.5 eV for SnSe, $Sn_{0.99}Cu_{0.01}Se$, $Sn_{0.98}Cu_{0.02}Se$ and $Sn_{0.97}Cu_{0.03}Se$, respectively. An obvious phenomenon is the E_g for all samples are much smaller than 0.9 eV for SnSe as reported in literature [22]. The reason is small cell volume contributed by HPS leads to narrow energy band gap [19,20]. As of such, the HPS dramatically decreases the E_g of SnSe. It indicates that the samples here have a different electron structure from normal SnSe reported, although they have similar crystal structure to normal SnSe. High pressure induces electronic phase transition has been found for many materials [23]. This result also shows that HPS can be a way to intercept the high pressure state or property of materials to normal pressure.

Fig. 4 (c) shows composition (x) dependence of the carrier concentration (n) and carrier mobility (μ) for HPS samples at room temperature. The carrier concentration and carrier mobility present an inversed trend in the measure process. When carrier concentration increases with increasing Cu content, the decrease of carrier mobility may be the result of carrier scattering enhancement. Dopant Cu is capable of improving carrier concentration from 3.65 × 10^{16} cm^{-3} for SnSe to 15.72 × 10^{16} cm^{-3} for $Sn_{0.97}Cu_{0.03}Se$ at room temperature. However, the carrier concentration is not found improvement with the energy gap decreasing when comparing the data (3.65 × 10^{16} cm^{-3}) for present SnSe with 16.88 × 10^{16} cm^{-3} for single crystal SnSe along the b axis reported. The reason is the hole carrier concentration is proportional to the Sn vacancy or V_{Sn} that decreases with the high pressure. This result is consistent with reports [19,20]. This phenomenon is very similar to the behavior of $Bi_{0.5}Sb_{1.5}Te_{2.7}Se_{0.3}$ preparing by high pressure sintering method [19], and demonstrate that SnSe can be