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Enhancing thermoelectric performance of Cu$_3$SnS$_4$-based solid solutions through coordination of the Seebeck coefficient and carrier concentration

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To improve the thermoelectric (TE) performance of Cu$_3$SnS$_4$ is challenging because it exhibits a metallic behavior, therefore, a strategy should be envisaged to coordinate the carrier concentration ($n_H$) and Seebeck coefficient ($\alpha$). The coordination in this work has been realized through the Fermi level ($E_f$) unpinning and shifting towards the conduction band (CB) via an addition of excess Sn in Cu$_3$SnS$_4$. As a result, the solid solution Cu$_{x}$Sn$_{1-x}$S$_4$ ($x=0.2$) has the moderate $\alpha$ (178.0 $\mu$V/K) at 790 K and high $n_H$ (1.54 $\times$ 10$^{14}$ cm$^{-3}$) values. Along with the lowest lattice thermal conductivity $\kappa_l$ (0.39 WK$^{-1}$m$^{-1}$) caused by the increased phonon scattering by carriers, the highest ZT value of 0.75 is attained at ~790 K. This value is 2.8 times that of the stoichiometric Cu$_3$SnS$_4$, and stands among the tops for the ternary Cu$_x$Sn$_y$S$_z$ sulfide thermoelectrics at the corresponding temperatures. More importantly, this approach used in the ternary Cu$_3$SnS$_4$ provides a guidance or reference to improve the TE performance of other materials.

1. Introduction

Ternary chalcogenides Cu-Sn-S based compounds$^{1,3}$ or oxide ceramics$^{4,5}$ have attracted much attention in thermoelectrics in recent years, due to earth-abundance of constituent elements or thermal stability in air. Therefore, the development of these materials is crucial if thermoelectrics is to supply a significant fraction of the world’s energy needs. In the Cu-Sn-S system, several ternary compounds have extensively been investigated as candidates for photovoltaic absorbers, including Cu$_3$SnS$_4$, Cu$_2$SnS$_6$, Cu$_2$SnSe$_6$, Cu$_4$Sn$_2$S$_7$, Cu$_2$Sn$_3$S$_8$, Cu$_2$Sn$_3$S$_9$, Cu$_2$Sn$_3$S$_{10,11}$ etc. However, limited attention, to our knowledge, has been paid as TE candidates so far.$^{1,3}$ The reported ternary Cu-Sn-S TE families mostly are on Cu$_4$Sn$_2$S$_6$ (ZT$\sim$0.30 at 600 K,$^1$ and 0.41 at 863 K$^{12}$), Zn(In)-doped Cu$_2$SnS$_3$ (ZT$\sim$0.58 at 723-773 K)$^{2,13}$ and a mixture of CuS and CuSn (ZT = 0.60 at 370-570 K)$^{14}$ Hence, it is urgent either to develop new Cu-Sn-S alternatives or significantly improve the TE performance of existing Cu-Sn-S ternary compounds.

The main drawback of restricting the applications of Cu-Sn-S compounds in thermoelectrics is their low electrical conductivities ($\sigma$) likely due to their wide bandgap (0.93-1.35 eV for Cu$_3$SnS$_4$, 1.0-1.80 eV for Cu$_4$Sn$_2$S$_6$,$^{15,17}$ and 0.8 eV for Cu$_2$Sn$_3$S$_7$,$^3$), and inharmonious relation of the Seebeck coefficient ($\alpha$) and carrier concentration ($n_H$). Hence it is challenging to significantly improve their TE performance, which is described by the dimensionless figure of merit (ZT), $ZT = T\alpha^2\sigma / \kappa = T\alpha^2\sigma / (\kappa_l+\kappa_v)$. Here $T$ is the absolute temperature, and $\kappa$, $\kappa_l$, and $\kappa_v$ are the total, electronic and lattice thermal conductivity respectively.

Cu$_3$SnS$_4$ is a p-type semiconductor with the bandgap $E_g$ ranging from 1.0 eV to 1.8 eV.$^{15,17}$ This compound is easy to be synthesized because it has a wide thermodynamic stability window due to a large chemical potential phase space.$^{18,19}$ However, differing from Cu$_3$SnS$_4$ that contains only two Cu(I) ions, the Cu$_3$Sn$_2$S$_4$ compound formally contains two Cu(I) and one Cu(II) ions per formula unit. Since every formal Cu(II) ion creates one free hole,$^{18,19}$ the Cu$_3$Sn$_2$S$_4$ is usually a degenerate p-type semiconductor with a high carrier concentration ($-6\times10^{21}$ cm$^{-3}$)$^{18,19}$ and low electrical resistivity (3.5-7.4$\times$10$^4$ $\Omega$ cm)$^{15,20}$.

Owing to its inherent carrier concentration ($-6\times10^{21}$ cm$^{-3}$) higher than the optimal one ($10^{19}-10^{21}$ cm$^{-3}$)$^{21}$ the compound Cu$_3$Sn$_2$S$_4$ exceptionally exhibits the metallic behavior with low Seebeck coefficient, hence the pristine Cu$_3$Sn$_2$S$_4$ is never a good TE candidate. In order to improve its TE performance, it is strongly suggested to harmonize the Seebeck coefficient and carrier concentration. This strategy is feasible as the unpinning of the Fermi level ($E_f$) via the movement of the $E_f$ towards the conduction band minimum (CBM) enables the adjustment of
both the carrier concentration and local density of states (DOS) over a narrow energy range, leading to the increasing of the Seebeck coefficient. While the unpinning of the $E_f$ can be realized by the creation of the antisite defect Sn$_{Cu}$ in Cu$_3$Sn$_4$, as the defect Sn$_{Cu}$, acting as a dopant, has deep states with the transition from +1 to +3 located 0.2 eV below the CBM, and is energetically favorable in Cu$_3$Sn$_4$. Therefore, the band structure engineering via the creation of defect Sn$_{Cu}$ species can coordinate the carrier concentration and Seebeck coefficient, then improve the TE performance.

2. Experimental

2.1 Sample preparation

The mixtures, consisting of three elements Cu, Sn and S according to the formula Cu$_3$Sn$_{1-x}$S$_x$ ($x=0, 0.1, 0.2, 0.3$), were loaded into four different vacuum silica tubes, and then heated to 723 K in 4.5 h followed by holding for 2 h. The subsequent heating from 723 K to 1223 K was carried out in ~7 h, and holding at 1223 K for ~3.5 h. Afterwards, the melted mixtures were cooled to 1073 K in 2 h with the holding time at this temperature for 48 h. Finally, the melts were cooled to room temperature (RT) in the furnace for the synthesis of the solid solutions. The ingots were subsequently ball milled for 5 h, prior to consolidation using spark plasma sintering (SPS) at the highest sintering temperature of 923 K and pressure of 60 MPa. The holding time at 923 K is about 2 min. The densities of the sintered samples were measured by using Archimedes' method. Each sample was cut into 3 mm slices measuring 2.5 × 12 mm$^2$ out of the sintered block with the size of φ 20 × 2.5 mm$^2$ for electrical property measurements. After polishing the surfaces of the two sides, coin-shaped blocks with the size of φ10 × 1.5 mm$^2$ were prepared for thermal diffusivity measurements.

2.2 Physical property Measurements

The electrical properties including Seebeck coefficient ($\alpha$) and electrical conductivity ($\sigma$) were measured using a ULVAC ZEM-3 instrument system under a helium atmosphere from RT to ~800 K, with measurement uncertainties of ~5.0% for both of them. During the measurement of Seebeck coefficient, a temperature difference of around 5°C was applied to the two terminals of each sample, while the measurement of the electrical conductivity was conducted using a four-probe method. The thermal diffusivities ($\lambda$) were measured by using TC-1200RH apparatus, with uncertainties of about 10%. The heat capacities ($C_p$) were estimated using the Dulong–Petit rule. The total thermal conductivities ($\kappa$) were determined according to the formula $\kappa = \frac{dc_p\lambda}{d}$, here $d$ is the material density. The three physical parameters ($\alpha$, $\sigma$, and $\kappa$) were finalized by measuring three times each. The total uncertainty of the ZT value is estimated as 18%.

The lattice contributions ($\kappa_L$) were calculated by subtracting the electronic contribution ($\kappa_e$) from the total $\kappa$, i.e., $\kappa_L = \kappa - \kappa_e$. Here $\kappa_e$ is expressed by the Wiedemann–Franz law, $\kappa_e = L_0\sigma T$, where $L_0$ is the Lorenz number, estimated as $2.0\times10^{-8}$ WΩK$^{-2}$ for the current semiconductors, close to the value $2.2\times10^{-8}$ WΩK$^{-2}$ reported in ref.[24]. The Hall coefficient ($R_H$) measurements at RT were conducted with a Hall effect measurement system (PPMS, Model9) using a four-probe configuration with a magnetic field sweeping between ±5.0 T. The rectangular samples with the size of 2×2×7 mm$^3$ were prepared for measurement. The Hall mobility ($\mu$) and carrier concentration ($n_H$) were subsequently determined according to the relationships $\mu = |R_H|\sigma$ and $n_H = 1/(eR_H)$, respectively, where $e$ is the electron charge.

2.3 Chemical compositions and structural analyses

The chemical compositions were determined using an electron probe micro-analyzer (EPMA) (S-4800, Hitachi, Japan) with an accuracy of >97%.

The powder X-ray diffraction patterns of the samples were analyzed using an X-ray powder diffractometer (XRD) (D8 Advance) operated at 50 kV and 40 mA. Cu Ka radiation ($\lambda = 0.15406$ nm) and a scan rate of 4° min$^{-1}$ were used to record the patterns in the range of 10° to 100°. The lattice constants $a$ and $c$ were obtained from the refinement of the X-ray patterns using Jade software.

2.4 Electronic structure calculations

The electronic structures were calculated using spin-polarized density functional theory (DFT) with the generalized approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) implemented in the Vienna ab initio software package (VASP, version 5.2.12). The DFT+U methodology with a value of $U = 5.0$ eV was used in this work. The valence electronic states were expanded in the plane wave basis set, with the core–valence interaction represented using the scalar relativistic projector augmented wave (PAW) approach and a cut-off of 400 eV.

In the real material system Cu$_3$Sn$_{1-x}$S$_x$, there are two incorporations of extra Sn in the crystal lattice, (1): Occupation in the Cu sites, and (2): In the interstitial sites. In the present calculations the arrangement of Sn is randomized, therefore the most stable structures are used for calculation. Considering the large cell volume and calculation burden, the density of states of Cu$_3$Sn$_{2-y}$S$_y$ ($y=0,1.2$) (Sn is in the interstitial sites) and Cu$_{3-y}$Sn$_y$S$_{1.5}$ ($y=0,1,2,3,4$) (Sn occupying Cu sites) have been calculated using HSE06 functional with a more accurate single point electronic structure calculation. The detailed arrangements of Sn in the unit cell are described in the section 3.3.

3. Results and discussions

3.1 XRD and composition analyses

Fig.S1 is the EMPA mappings (Fig.S1a-c) of three elements Cu, S and Sn along with the energy dispersive spectrum (EDS) (Fig.S1d) for the sample at $x=0.2$. The chemical compositions of stoichiometric Cu$_3$Sn$_4$ and Cu$_3$Sn$_{2.5}$ are shown in Table S1, where the number of S moles is normalized to 4. Generally, the three elements are distributed uniformly in the matrix without much segregation observed. The relative molar fractions shown in

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Table S1 are close to those of the nominal ones, except for a slight excess in Cu and Sn, which might be resulted from the evaporation of S during the material processing.

The XRD patterns of the powders are presented in Fig.1a, where a single Cu₃SnS₄ phase has been identified at ≤0.2 with tetragonal structure (space group: I-42m) (PDF: 330501), in agreement with the result reported in ref. [7], instead of the orthorhombic one (Pmn21). At x=0.3 trace impurity phase Sn₂S₃ (PDF:14-0619) is visible, indicating that the solubility of excess Sn (x value) in ternary CuₓSn₁₋ₓS₄ is less than 0.3. Look at the main peaks in the regions of 26°-34° and 40°-60°, one can see these peaks shift toward low diffraction angles with Sn content increasing (see Fig.1b). This suggests that the lattice structure suffers dilation. In other hand, the lattice constants a and c increases linearly with x value increasing, and follow the Vegard’s law, as shown in Fig.1c, indicating that the excess Sn has already incorporated into the crystal lattice. The a and c values for the pristine Cu₃SnS₄ are 5.40 and 10.83 Å respectively.

Since the excess Sn is incorporated into the Cu₃SnS₄ crystal lattice, the band structure should be modified. To better understand the band structure alterations, we have calculated the density of states (DOS) and formation energies (dₓ) of CuₓSn₁₋ₓS₄ (y=0,1,2) and Cu₂₄SnₓSi₁₋ₓS₄ (y=0,1,2,3,4). The results are shown in Fig.4 and 5. The panel A in Fig.4, arranging in sequence from y=0 to y=2 from left to right, represents the crystal structures upon different Sn incorporations into the interstitial sites, and the blue balls circled using wine color represent incorporated Sn atoms. The panel B is the DOS of different materials, where the Fermi level (Eᵥ) uppins and gradually moves toward the conduction band (CB) with

3.2 Microstructure observations

In order to further confirm the synthesis of Cu₃SnS₄-based ternary compounds, the microstructures have been examined by using high resolution TEM (HRTEM) for the samples at x=0 and 0.2, shown in Fig.2 and 3. Fig.2a is the TEM image of the sample with x=0, and Fig.2b is the corresponding HRTEM image. The inset in Fig.2b is its magnified image, showing the d spacing between (112) crystal planes is about 0.31 nm. Fig.2c is its corresponding selected area electron diffraction (SAED) pattern and Fig.2d is showing the EDS measurement results. These observations confirm the structure of the synthesized Cu₃SnS₄ solid solution.

Fig.3a,b are the TEM image and its corresponding SAED pattern for the sample at x=0.2. Fig.3c is the HRTEM image and Fig.3d is an enlarged image, which shows that the d spacing between (220) crystal planes is ~0.20 nm. This spacing is in good agreement with that in the XRD pattern.

3.3 First principle calculations

![Image](https://example.com/image1.png)

**Fig.1** (a) X-ray diffraction patterns of CuₓSn₁₋ₓS₄ (x=0, 0.1, 0.2, 0.3) powders; (b) Two close-up views with the 2θ ranging between 26°-34°, and 40°-60°; (c) Lattice constants a and c, which increase with x value increasing, follow the Vegard’s law.

![Image](https://example.com/image2.png)

**Fig.2** High resolution transmission electron microscopy (HRTEM) image observed in Cu₃SnS₄. (a) TEM image; (b) The corresponding high resolution TEM image, the inset is the magnified high resolution TEM image, which shows that the spacing between (112) crystal planes is about 0.31 nm. (c) The selected area electron diffraction (SAED) pattern; (d) Chemical compositions analyses.

![Image](https://example.com/image3.png)

**Fig.3** High resolution transmission electron microscopy (HRTEM) image observed in CuₓSn₁₋ₓS₄. (a) TEM image; (b) The selected area electron diffraction (SAED) pattern; (c) The corresponding high resolution TEM image; (d) Magnified high resolution TEM image, which shows that the spacing between (220) crystal planes is about ~0.20 nm.
Sn content increasing, although the calculated bandgap ($E_g$) ($E_g = \sim1.25$ eV) remains almost constant. The calculated $E_g$ values are lower than those reported (1.5-1.6 eV),\textsuperscript{17} which might be due to the GGA problem.\textsuperscript{30,31} However, the impurity levels gradually creates within the gap as $y$ value increases, see the magnified pattern as an inset in panel B(c) is the close-up view of the impurity levels labeled by blue lines); (c) Panel C is the overall total-formation energy ($d_H$) profile when the different Sn is incorporated.

The results for Cu$_{2+y}$Sn$_{2+y}$S$_8$ ($y=0,1,2,3,4$) from the first principle calculation are shown in Fig.5. Similarly, the Fermi level ($E_f$) unpins and gradually moves toward the conduction band (CB) with Sn content increasing. The negative formation energies ($d_H$) suggest that Sn is energetically favorable to the Cu sites either. The above results indicate that the extra Sn in current materials, whether it occupies the interstitial or Cu sites, is inclined to stabilize the structure, creating the defect species Sn$_{i}$, or Sn$_{Cu}^{3+}$ and Sn$_{Cu}^{2+}$. However, it still remains a challenge to figure out how much defect Sn$_{i}$ or Sn$_{Cu}^{3+}$ and Sn$_{Cu}^{2+}$ in the defect clusters in the synthesized samples. These calculations are beyond the current limit of the investigations. Besides, the Sn content incorporated into the lattices should be limited due to limited solubility, that is why we have observed the increased formation energy at $y=4$.  

Fig. 4. The results from the first principle calculation. (a) Panel A, arranging in sequence from $y=0$ to $y=2$ from left to right, presents the tetragonal structures with different arrangements of Sn in the interstitial sites in Cu$_{6}$Sn$_{2+y}$S$_8$ ($y=0,1,2$). The enclosed balls represent incorporated Sn atoms into the interstitial sites; (b) Panel B are the density of States (DOS) for different Sn incorporations, indicating that the Fermi level ($E_f$) unpins and moves towards the conduction band. However, the deep impurity levels creates near the middle of the bandgap (an inset in panel B(c) is the close-up view of the impurity levels labeled by blue lines); (c) Panel C is the overall total-formation energy ($d_H$) profile when the different Sn is incorporated.

3.4 Transport properties

In order to better understand the effects of band structure engineering on the transport properties, we have specially measured the Hall coefficients ($R_{H}$) of Cu$_{x}$Sn$_{1-y}$S$_{y}$ (x=0, 0.1, 0.2, 0.3) at RT, and then attained the Hall carrier concentrations ($n_{H}$) and mobility ($\mu$). The results are shown in Fig. 6. We observed that $n_{H}$ value at x=0 is $4.25\times10^{21}$ cm$^{-3}$, and that at x=0.3 is $4.27\times10^{18}$ cm$^{-3}$, reducing by 3 orders of magnitude. While the mobility ($\mu$) increases from $13.47$ cm$^{2}$V$^{-1}$s$^{-1}$ (x=0) to $94.79$ cm$^{2}$V$^{-1}$s$^{-1}$ (x=0.3) with Sn content increasing. Although the creation of the defect species Sn$_p$, Sn$_{p}^{2-}$ or Sn$_{p}^{3-}$ neutralizes the $p$-type holes to some extent, we believe that the significantly decreased $n_{H}$ value with Sn content increasing is mainly due to the unpinning of the Fermi level, followed by its movement toward the conduction band. Besides, the associated impurity levels, acting as an annihilation center for electrons and holes, plays a role in reducing the $n_{H}$ value. The precipitated Sn$_2$S$_3$ at x=0.3 identified using XRD, which is a n-type semiconductor, might have a negative effect on the carrier concentration, however, we do not know its correlation with the impurity level yet.

3.5 TE performance

The reduction in $n_{H}$ should have a profound impact on the TE performance, which was summarized in Fig. 7. Fig. 7a presents the positive Seebeck coefficients ($\alpha$), indicating $p$-type semiconducting behavior of the materials. In addition, the $\alpha$ value increases with the measuring temperature increasing for all the samples, indicating the extrinsic conducting behavior. With Sn content increasing from x=0 to 0.3, the $\alpha$ value increases from $103.0 \mu$VK$^{-1}$ to $504.0 \mu$VK$^{-1}$ at ~790 K, while the electrical conductivity ($\sigma$) decreases from $1.3\times10^{2}$ $\Omega^{-1}$cm$^{-1}$ to $2.9\times10^{2}$ $\Omega^{-1}$cm$^{-1}$, as shown in Fig. 7b, decreasing by ~3 orders of magnitude. At x=0.2 and 790 K the electrical conductivity is $2.0\times10^{4}$ $\Omega^{-1}$cm$^{-1}$.

![Fig. 5. The results from the first principle calculation.](image)

![Fig. 6. Measured Hall carrier concentration ($n_{H}$) and Mobility ($\mu$) against x value in Cu$_{x}$Sn$_{1-y}$S$_{y}$](image)
Combined with the above three physical parameters, we have attained the TE figure of merit (ZT), as shown in Fig.7d. Because of high electrical and low thermal conductivities at x=0.2, the highest ZT value is 0.75 at ~790 K, while that at x=0 is only 0.27. Although this ZT value is still lower than those of state-of-the-art mid temperature TE materials, like elemental tellurium (ZT=1.0 at 773 K) alloys, PbTe- (ZT=2.5 at 923 K) and SnSe-based (ZT=1.7 at 873 K) alloys, it stands among the tops for ternary Cu-Sn-S sulﬁdes at the corresponding temperatures.

The increasing of a and c values indicate the expansion of the unit cell, which has a potential to modify the band structure and improve the TE performance, as those indicated in the CoSbS surfide. In order to better understand the band structure alterations, we present the Pisarenko plots in Fig.8a, assuming m∗ = 0.2, 3.5, and 4.5 m∗ at RT, in which the measured Seebeck coefficients (α) for the Sn-incorporated samples (labeled by ★ symbol) are roughly between the lines with m∗ = 3.5 m∗ and 4.5 m∗, decreasing slightly with increasing nH. However, if we carefully fit the measured α values as a function of carrier concentration nH, a α ~ nH−1/3 dependence is obtained, instead of the Pisarenko relationship (α ~ nH−2/3). This suggests that the α ~ nH relation does not exactly follow the single parabolic model (SPB). Although there are many defects in Cu2Sn1−xSb, such as Sn, SnSe, Cu in the interstitial sites, and possibly created p-type compensating defects CuSn, VSn and VCu only SnSe is energetically favorable in the Cu-Sn-S material system. This implies that the compensating defects (CuSn, VSn and VCu) in the current materials should have little impact on the Fermi level (Ef).

The lattice thermal conductivity (κ(L)), shown in Fig.7c, reduces from 1.93 WK−1m−1 (x=0) to 0.39 WK−1m−1 at ~790 K as Sn content increases to x=0.2, and above x=0.2 the sample gives the enhanced κ(L) value (0.57 WK−1m−1). This might be due to the reduced scattering of phonons by carriers, because the nH values at x=0.3 is rather lower than those at x=0.2. However, the temperature dependence of κ(L) for the samples at x=0 and 0.1 is quite abnormal. The κ(L) values for these two samples increase rapidly with temperature increasing above ~700 K, whereas the total thermal conductivities (κ) reduce linearly with temperature increasing, see the inset in Fig.7c. The abnormally increased κ(L) values were confirmed by repeated measurements, and might involve the contribution of peripheral phonons, which increases with the measuring temperature increasing, especially, when the donor levels merge with the conduction band (see Fig.4 and 5), although the contribution of peripheral phonons is usually realized at the very low temperatures. Alternatively, the enhanced κ(L) values at high temperatures might also involve the contribution of photon conduction, κp, described below:

\[
κ_p = \frac{16π}{3} στ δ r
\]

where r is the refractive index in the medium, τ is the mean free path of photons. Based on the equation (1), the κp value is proportional to T3. However, the photon conduction may usually be observed in some polycrystalline oxides, such as BaO and SrO, Al2O3 and BeO, and in single crystals of Al2O3, MgO, CaF2 and TiO2. Therefore, the abnormally increased κ(L) values at high temperatures requires further investigations.
unpinning (Fig.5b). It is the preferential occupation of Sn in the interstitial or Cu sites that engineers the band structure, and then reduces the \( n_{H} \) value significantly. Besides, the extra electrons provided by the dopants Sn\(_{Cu}^{2+}\) or Sn\(_{Sn}^{3+}\) themselves have a limited contribution in reducing \( n_{H} \) either. This conclusion is not in agreement with that reported by Fan et al.,\(^\text{44}\) who suggests that in the Ga and In co-doped Cu\(_{2}\)SnS\(_{3}\) system the defects have a dominant effect on the carrier concentration.\(^\text{44}\)

In order to confirm our hypothesis, we have calculated the carrier density in Sn-incorporated Cu\(_2\)SnS\(_3\) environment using the valence counting rule,\(^\text{45-47}\) based on the following descriptions without taking into account the creation of the compensating defects,

\[
n_{\text{cal}}=(1-3x/8)n_{100}, \quad \text{for Sn}_{Cu}^{3+} \text{ species (2)}
\]

or,

\[
n_{\text{cal}}=(1-2x/8)n_{300}, \quad \text{for Sn}_{Sn}^{3+} \text{ species (3)}
\]

Here \( n_{100} \) is the experimentally measured Hall carrier concentration for the pristine Cu\(_2\)SnS\(_3\), \( n_{100}=4.25\times10^{17} \text{ m}^{-3} \). The calculated results are presented in Fig.8b. It is apparent that there is no agreement between the measured Hall carrier concentrations \( n_{H} \) and the calculated \( n_{\text{cal}} \) values. The theoretically calculated \( n_{\text{cal}} \) values are almost unchanged. If the compensating defects with an opposite charge are taken into account, the estimated \( n_{\text{cal}} \) values should be a little higher than those from the equation (2) and (3). But it is obvious that such estimations could not change the tendency described in Fig.8(b). The slightly decreased \( \alpha \) value with carrier concentration increasing, as shown in Fig.8a, suggests that the coordination between the carrier concentration and Seebeck coefficient has been realized in the current Cu\(_2\)Sn\(_{1.1}\)S\(_4\) solid solutions. Besides, owing to the reduction in \( n_{H} \) with Sn content increasing, the mobility \( \mu \) increases, as shown in Fig.6, caused by the increasing of the carrier scattering time (\( \tau \)), according to the equation (4):

\[
\mu = e \nu / m^* \quad (4)
\]

here \( e \) is the electron charge.

Since at \( x=0.2 \) the ternary Cu\(_2\)Sn\(_{1.1}\)S\(_4\) compound has the lowest lattice contribution (\( \kappa_{L} \)) and relatively high effective mass \( m^* \), therefore, we estimate that it has a high quality factor \( B \), according to the following relation,\(^\text{23}\)

\[
B = (m^*/m_e)^{3/2} T^{1/2}/\kappa_{L} \quad (5)
\]

The detailed \( B \) value is plotted in Fig.9, in which the effective mass \( m^*/m_e \) is also shown. As \( x \) value increases both the \( m^*/m_e \) and \( B \) values increase up to \( x=0.2 \), then rapidly decrease. These results further confirms that \( x=0.2 \) is a critical Sn content in Cu\(_2\)Sn\(_{1.1}\)S\(_4\) at which the highest TE performance can be expected.

Fig. 9 The relatively effective mass \( (m^*/m_e) \) (A) and quality factor \( B \) (●) at RT, defined by \( B = (m^*/m_e)^{3/2} T^{1/2}/\kappa_{L} \), as a function of \( x \). At \( x = 0.2 \) both the effective mass \( m^*/m_e \) and quality factor \( B \) value reach the highest.

4. Conclusions

Ternary Cu\(_2\)Sn\(_{1.1}\)S\(_4\) solid solutions with an excess of Sn have been synthesized and their thermoelectric properties have been examined. The first principle calculations reveal that the Fermi level (\( E_F \)) uppins and moves towards the conduction band (CB) with Sn content (\( x \) value) increasing, which effectively harmonizes the Seebeck coefficient and carrier concentration. Combined with the lowest lattice thermal conductivity \( \kappa_{L} \) (0.39 W K\(^{-1}\) m\(^{-1}\) at 790 K) at \( x=0.2 \) caused by the increased phonon scattering for carriers, a significant improvement in TE performance has been achieved with the ZT value of 0.75 at 790 K, about 2.8 times that of the stoichiometric Cu\(_2\)SnS\(_3\). This value stands among the highest in the ternary sulfide thermoelectric materials.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references


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