Thermoelectric property studies on $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ with nano-scale precipitates Bi_2S_3

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[Abstract] The microscopic mechanisms for higher thermoelectric performance of cost competitive rock salt compound Bi_2SeS_2 were investigated. A low doping of Cu as an *n*-type dopant was conducted in order to optimize the band structure and improve the electrical conductivity. It was revealed that this compound exhibits a Seebeck coefficient higher than $300 \mu\text{V K}^{-1}$, which sustains above $100 \mu\text{V K}^{-1}$ even with Cu doping, leading to a higher power factor. The microstructural characterizations revealed nano-scale Bi_2S_3 precipitates in the $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ matrix, beneficial to the lower lattice thermal conductivity that is insensitive to the Cu doping. A thermoelectric figure-of-merit factor *ZT* of ~ 0.7 at 450°C in accompanying with the power factor of $\sim 5.36 \mu\text{W cm}^{-1} \text{K}^{-2}$ was obtained under the optimized doping level, enabling this environmentally friendly compound interesting for thermoelectric power generation applications.

Keywords: thermoelectric, Bi_2SeS_2 , nano-scale Bi_2S_3 precipitates, Cu doping

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Introduction

The demand for energy is steadily rising and more fossil fuel energy resources are being consumed, leading to more emission of carbon dioxide [1]. Search for materials and technologies to obtain clean energy or make use of waste heat becomes urgent [2-6]. One of the research directions is to search for thermoelectric (TE) materials and devices which are environmentally friendly and can directly convert heat energy to electric energy and vice versa [7-12]. This direction poses substantial appeal for low and mid-temperature (T) TE materials and devices. So far, the most promising mid- T materials include PbTe [13], skutterudites [14, 15] and half-Heuslers [11]. However, Te is rare in the earth's crust and has been extensively used in solar cells [16, 17] and steel metallurgy [18] etc., while Pb is being forbidden in industries due to its toxicity. The thermal stability of skutterudites [15] and the price of half-Heuslers are also concerns [11]. Therefore, searching for materials that can maintain relatively higher ZT value is needed. A recent advance has been evidenced with the SnSe single crystals exhibiting ZT values of 2.6 and 2.2 along the b -axis and c -axis respectively [19], while polycrystalline SnSe also shows a relatively high ZT value of ~ 0.6 at about 500 °C [20].

Alternatively, alloy compounds formed from Bi_2Se_3 and Bi_2S_3 are Te-free and can have good ZT values above 250 °C [21-24]. It is noted that element Se is much more abundant than Te while S is one of the 16 highest abundant elements in the earth's crust [25]. However, the reported ZT of Bi_2Se_3 is below 0.2 due to low Seebeck coefficient (S) (less than $80 \mu\text{V K}^{-1}$) and high thermal conductivity (κ) ($>2 \text{ W m}^{-1} \text{ K}^{-1}$) [23]. By optimizing the nano-synthesis process and doping/substitution such as partially replacing Se by Te, these properties can be enhanced. The optimized S and κ values of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ are about $-220 \mu\text{V K}^{-1}$ and $1.1 \text{ W m}^{-1} \text{ K}^{-1}$, respectively [23]. For pristine Bi_2S_3 , so far the reported S value is as high as $300\sim 400 \mu\text{V K}^{-1}$, but the electric conductivity (σ) is less than 1500 S m^{-1} , with the ZT value below 0.2 at 500 °C [21, 22]. Through optimization by doping/substitution, the ZT value can be enhanced up to 0.55 [21, 22].

Interestingly, in addition to Bi_2S_3 and Bi_2Se_3 , compound Bi_2SeS_2 could be an attractive TE candidate, due to the following reasons. First, as known, the optimized band gap for a TE

semiconductor is $\sim 10k_B T$ where k_B is the Boltzmann constant, equivalent to ~ 0.7 eV for mid- T devices (~ 550 °C). In this case, an optimized power factor (PF) would be possibly obtained. However, Bi_2Se_3 has a gap of only ~ 0.3 eV, which is hard to be widened to 0.7 eV by doping, whereas Bi_2S_3 has a gap of ~ 1.35 eV much larger than 0.7 eV. Our electronic structure calculation (to be shown below) shows that a gap of ~ 1.0 eV is possible for Bi_2SeS_2 . Second, high carrier mobility and large S value are expected for semiconductors with multi-valley feature in the conduction bands [26]. It will be shown that Bi_2SeS_2 does have favored multi-valley feature. Third, a proper n -type dopant (such as Cu) seems to allow narrowing of the band gap down to a value close to ~ 0.7 eV. It is noted that the electronegativity values of Bi, Se, and S are 2.02, 2.55, and 2.58, respectively, implying the dominant covalent bonding between them in Bi_2SeS_2 . Since the electronegativity of Cu is only 1.9, and the effective atomic/ionic sizes of Cu, Cu^+ , and Cu^{2+} are $1.28\text{\AA}$, $0.77\text{\AA}$, and $0.73\text{\AA}$, respectively, one is allowed to argue that Cu in Bi_2SeS_2 most likely fills the lattice as interstitial and contributes its 4s electron to the lattice. Therefore, Cu doping is expected to produce Cu^+ or Cu^{2+} interstitials and highly hopping electrons, making Cu-doped Bi_2SeS_2 n -type semiconductor with a proper band gap for sufficient carrier density/mobility, large S , and relatively enhanced PF. In addition, if the microstructure accommodates ultrafine second phase precipitates upon proper synthesis procedure, one can reasonably expect a low thermal conductivity due to strong phonon scattering from these precipitates [27, 36].

These advantages make us further study the Bi_2SeS_2 system. Even though the earlier investigations demonstrated the ZT values of $\text{Cu}_{0.01}\text{Bi}_2\text{SeS}_2$ sample as high as 0.7 and 0.8 at 450 °C and 500 °C, respectively [23], the underlying physics for the enhanced ZT values remains to be explored. In this work, we intend to further study the Cu-doped Bi_2SeS_2 ($\text{Cu}_x\text{Bi}_2\text{SeS}_2$) compounds, focusing on the underlying mechanisms for the enhanced TE performances. A series of careful characterizations on the electronic structures, transport behaviors, microstructural features, and TE parameters of $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ suggest that Cu doping can effectively reduce the band gap and enhance the charge carrier concentration without sacrificing much the Seebeck coefficient. More importantly, it is revealed that the microstructure does accommodate nanosized Bi_2S_3 precipitates in the Bi_2SeS_2 matrix,

responsible for the low thermal conductivity. The optimized ZT value reached ~ 0.75 at 450 °C.

Experimental and computational details

Sample preparation & microstructural characterization

The sample preparation basically followed the procedure reported previously [27]. Bulk ingots of $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ ($0 \leq x \leq 0.025$) were synthesized by adding high-purity starting powder of Bi, Se, S, and Cu in appropriate ratios into quartz tubes in a N_2 -filled glove box. The tubes were sealed under vacuum (less than 10^{-2} Pa). Subsequently, the tubes were slowly heated up to 900 °C in 24 hours and maintained at it for 12 hours before cooling down to 500 °C in 6 hours and annealing at 500 °C for 48 hour. Finally, the as-grown ingots were cooled down to room temperature. The obtained ingots were crushed into powder in the N_2 -filled glove-box and the powder was loaded into two graphite dies with inner diameter of 12.7 mm in the glove-box. The graphite dies were taken out of the glove-box and immediately sintered by a home-made *dc* hot-press machine at 500 °C under a pressure of 60 MPa. The eventually obtained rods were 14 mm in height and 12.7 mm in diameter. These rods were cut into thin disks for thermal transport measurements and square-crossed long bars for electrical conductivity and Seebeck coefficient measurements. All the electrical and thermal transport measurements were performed along the press direction of the rods.

For structural characterization, the crystalline samples were ground into powder for X-ray diffraction (XRD) using the Bruker Advanced D8 machine with Cu K_α radiation in a reflection geometry operating at 40 kV and 40 mA. The EDS mapping associated with a scanning electron microscopy (SEM, Ultra 55, Zeiss) was obtained for probing the chemical composition inhomogeneity in sub-micrometer scale. The ultrafine precipitates and high-resolution lattice images were observed using transmission electron microscopy (TEM) with the JEOL 2100F microscope operating at 200 kV. The TEM specimens were prepared by standard cutting, grinding, dimpling, polishing, and Ar-ion milling procedures on liquid N_2 cooling stage. The sample density d was measured using an Archimedes method, and the results are shown in Table I.

Optical absorption and thermoelectric measurements

For detecting the optical band gap data of the samples, the optical reflectance spectra were collected in a vis-NIR range (600-2000 nm) using a Lambda 900 UV-VIS-NIR spectrometer with the BaSO₄ as the 100% reflectance standard. The gap was estimated by converting the reflectance into absorption ratio according to the Kubelka-Munk (K-M) relationship [27, 28]: $F(R) = (1-R)^2/2R$, where R is the reflectance. The measured $F(R)$ data as a function of photon energy E show a linearly decaying region. The band gap E_g can be obtained by extending the linear region to the intersection of $F(R)=0$ with the E -axis.

For thermal property measurements, both thermal diffusivity D and heat capacity C_p were measured on a commercial laser flash system (LFA 457, Netzsch) and differential scanning calorimeter (DSC 400 C, Netzsch), respectively. The total thermal conductivity κ_{tot} was calculated by $\kappa_{tot} = D \times C_p \times d$. The electrical resistivity ρ (conductivity $\sigma = 1/\rho$) and Seebeck coefficient S were measured using a commercial TE measuring unit (ZEM-3, ULVAC) in the standard procedure. κ_{tot} is the average from two measuring cycles under the same conditions and ρ and S are the averages of three consecutive measurements. The Hall coefficient R_H measurements were carried out on a Quantum Design physical properties measurement system (PPMS-9, Quantum Design) with the standard cross geometry, given an electrical current of 5 mA and varying magnetic field up to 2 T. The carrier density n was then obtained.

First-principles calculations

In order to clarify the electronic structure of Bi₂SeS₂ compound and the effect of Cu doping as interstitials, we performed the first-principles calculations using the projector augmented wave pseudo-potentials as implemented in the Vienna *ab initio* simulation package (VASP). For such calculations, the exchange correlation function was imported with generalized gradient approximation (GGA) and parameterized by Perdew-Burke-Ernzerhofer (PBE) formula. A cutoff energy at 500 eV and a mesh size of 7×15×7 were used for geometry optimization and electronic density of states (DOS) calculations. Using the block Davidson scheme, both the atomic positions and cell parameters were optimized until the residual forces

were below 0.01 eV/Å. The calculated band gap of pristine Bi₂SeS₂ is 1.1 eV, in good agreement with our experimental data (to be shown below). For the effect of Cu doping, we chose Cu_{0.25}Bi₂SeS₂ as the object of calculations while our doping experiments only dealt with the doping levels lower than 3%. The reason for this difference is the limitation of the computational capacity that is far from treating such low doping levels. Therefore, our calculation results can be discussed only in a qualitative sense.

In our calculation, we carefully considered the issue of Cu_{0.25} atom occupation in the lattice. For Bi₂SeS₂ lattice (space group *Pnma*), the Cu atom should occupy one of the (0.268, 0.75, 0.31658) sites and equivalent sites. The electronegativity values of Cu, S, and Se are 1.9, 2.58, and 2.55, respectively, suggesting that Cu prefers the site surrounded by S and Se. Second, this site has the biggest free space for impurity occupation. Cu, Se, and S constitutes a tetragonal unit and the separation between Cu and Se/S is larger than 0.22 nm, sufficient for Cu occupation.

Results and discussion

Structural characterizations & Bi₂S₃ precipitates

The as-prepared samples are dense and the measured density d is above 6.85 g cm⁻³, *i.e.*, over 95% of the theoretical density 7.14 g cm⁻³. We first examined the crystallinity of the as-prepared samples. The lattice structure of Bi₂SeS₂ compound is shown in Fig. 1a, and the θ -2 θ XRD spectra for all samples are plotted in Fig. 1b. Bi₂SeS₂ shows the lattice structure (space group *Pnma*), different from Bi₂Te₃ (space group *R-3m*) although species S is in the same column as Te in the Periodic Table [23]. It favors a highly anisotropic one-dimensional orthorhombic phase with unit cell parameters $a = 11.506$ Å, $b = 4.009$ Å, and $c = 11.304$ Å. The Bi₂SeS₂ infinite chains align along the b -axis. The XRD data indicated that all the as-prepared samples exhibit well-defined orthorhombic structure. The Cu doping as high as $x = 0.025$ does not induce identifiable peak shifting, suggesting the lattice is sufficiently empty for the occupations, associated with the argument that Cu atoms prefer to be in the lattice interstitials.

Here, it should be noted that there appears a very weak impurity peak at 2θ of $\sim 29.2^\circ$ for

all these samples, as seen from the inset in Fig. 1b, indicated by an arrow (red). The origin of this weak peak can't be identified by the XRD data since BiSe, Bi₈Se₉, and Bi₂S₃ compounds all have a weak peak around this position. In addition, this peak upon increasing x shows no shifting within the apparatus resolution limit, implying its irrelevance with the Cu doping. Subsequently, we consulted to the SEM and TEM characterizations in order to characterize the microstructure at lattice level, in particular to search for any phase possibly related to the impurity peak at 2θ of $\sim 29.2^\circ$.

The SEM images confirmed the very dense microstructures and one image for sample $x = 0.02$ is presented in Fig. 2 at sub-micrometer scale. The average grain size is above 1 μm and no visible defects or precipitates at such a scale are observed. We then selected several rectangles of $\sim 0.4 \times 0.3 \mu\text{m}^2$ for EDS compositional mapping. One set of mapped distributions for elements Bi, Se, and S are presented in Fig. 2. No clear inhomogeneous distributions for Bi, Se, and S can be seen, suggesting the spatial homogeneity of the three major elements in the sub-micrometer range.

The high-resolution TEM images did reveal nanoscale contrast in these samples. For excluding any potential relevance with doped Cu interstitials, we paid major attention to sample $x = 0.0$ shown in Fig. 3. One large-scale TEM image is given in Fig. 3a. We observed a high density of inhomogeneities (small contrast features) with a dimension around ~ 10 nm, as indicated by the white arrows. The dominant feature of these contrasts is short and bar-like precipitates in the homogeneous matrix. The inset in Fig. 3a shows an electron diffraction pattern with the selected area covering the precipitates, along the [010] direction of the Bi₂SeS₂ matrix. No well-defined Bragg spot splitting can be seen, indicating that these precipitates are minor in volume and very small in size.

We also analyzed the lattice structure on the contrast-free regions, as presented in Fig. 3b. The imaged lattice fringes over the whole region are uniform. The lattice spacing fits quite well with Bi₂SeS₂ phase. However, an image of the region containing the contrast difference, as presented in Fig. 3c, shows quite a few precipitates with twin-like feature and short-bar shape. The twin-like feature can be more clearly seen in the inset of Fig. 3c. The typical size for these precipitates is between 2 nm and 15 nm. No preferred orientation of these

precipitates was identified at this stage. We also performed local EDS probing on these precipitates. Qualitatively, the EDS revealed that the Bi and S are abundant and Se content is low, however, no accurate determination of the Bi/S ratio can be obtained considering the nanoscale and beam broadening effect [29], but the EDS analysis on the area with high density of such bar-like features gave a Bi/S molar ratio of $\sim 1:1$, and the Se content is below 5 at%. In combination with the imaging evidences, we believe that these precipitates are most likely the Bi_2S_3 phase. In fact, the d -spacing measurement on the image in Fig. 3c gives the fringe separations of 0.80 nm and 0.39 nm, corresponding to the (101) and (010) planes of Bi_2S_3 , respectively. Fig. 3d shows another region covering a grain boundary between the two grains. Typically these boundaries belong to the small-angle type, which may allow the electron transport to be well maintained, beneficial to good electrical conductivity.

The above structural features were also observed in the Cu-doped samples, suggesting no substantial impact of the Cu-doping on the formation of nanoscale Bi_2S_3 phase that seems to form spontaneously in the samples, given the synthesis procedure used in this work. The thermodynamic stability of Bi_2SeS_2 , Bi_2S_3 , and Bi_2Se_3 may be comparable, making the formation of these phases simultaneously possible. In fact, it was reported that both Bi_2Se_3 and Bi_2S_3 can be synthesized by hydrothermal method, while the mechanical alloying technique was used to successfully synthesize Bi_2SeS_2 , Bi_2Se_3 , and Bi_2S_3 [23]. This implies that tiny precipitates of one phase from another may be possible, such as Bi_2S_3 precipitates in Bi_2SeS_2 during the hot-press synthesis in the present work.

Density of states and band gap: effect of Cu doping

Given the relatively low Cu doping level ($x \leq 0.025$), the above characterization did not reveal substantial impact of the Cu doping on the microstructure at nanoscale. However, the impact on the electronic structure and electrical/thermal transport is significant. We present our first-principles calculation data on the density of states (DOS) in response to Cu doping. As mentioned earlier, the Slack criterion [30, 31] advised an energy gap around 0.70 eV for optimized TE performance at $T < 600$ °C. The calculated DOS profiles of Bi_2SeS_2 ($x = 0.0$) and $\text{Cu}_{0.025}\text{Bi}_2\text{SeS}_2$ are plotted in Fig. 4a, noting that the lattice super-cell for $\text{Cu}_{0.025}\text{Bi}_2\text{SeS}_2$ is

too big to be computable by the first-principles calculations. We then chose $\text{Cu}_{0.25}\text{Bi}_2\text{SeS}_2$ as the object of our calculations so that the effect of the Cu doping can be qualitatively predicted. First, the energy gap of Bi_2SeS_2 is ~ 1.1 eV. As expected, this gap falls down to ~ 0.7 eV at $x \sim 0.25$. In addition, the DOS of several $k_B T$ above the conduction band for $x = 0.25$ is higher than that of pure Bi_2SeS_2 , indicating enhanced density of carriers and then electrical conductivity. Instead, the gradient of the DOS right at the Fermi level seems to be suppressed slightly by the Cu doping, implying the possible degradation of the Seebeck coefficient [32]. Second, to confirm the above predictions, the measured optical absorption spectra for several samples are plotted in Fig. 4b, whereas Fig. 4c shows the curve by which the optical band gap E_g can be evaluated. The evaluated band gap as a function of x is shown in Fig. 4d. The gap for pure Bi_2SeS_2 is ~ 0.97 eV, roughly consistent with the calculated value. The Cu doping reduced the gap from 0.97 eV at $x = 0.0$ to 0.74 eV at $x = 0.03$, also roughly consistent with the first-principles predictions.

The third evidence with the predicted effect of Cu doping was given by the electrical conductivity $\sigma(T)$ of several samples. The data above room temperatures are plotted in Fig. 5a. All the samples showed metallic behavior. Nevertheless, a Cu doping as low as $x = 0.02$ allowed roughly 20 times enhancement of the conductivity. For example, σ increased from 1400 S m^{-1} and 900 S m^{-1} for $x = 0.0$ to 39500 S m^{-1} and 14600 S m^{-1} for $x = 0.02$ at 50°C and 450°C , respectively.

Seebeck coefficient & power factor

A natural effect of Cu-doping for increasing the DOS and reducing the band gap is that S decreases with increasing x . However, the extent of this decrease is not as big as that of the σ -enhancement, allowing an enhancement of PF. The measured $S(T)$ data for several samples are plotted in Fig. 5b. For pure Bi_2SeS_2 , the S displayed a maximum at 350°C above which the thermally activated holes reduced S . Following the relation $E_g \approx 2eS_{\max}T_{\max}$ [33, 34], where $S_{\max}$ is the maximum S value and $T_{\max}$ is the corresponding absolute temperature, the band gap accounting the intrinsic conduction is ~ 0.52 eV at 350°C . All the Cu-doped samples showed monotonously increasing S with increasing T , different from the n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$

which exhibited bipolar effects above 100 °C and thus deteriorated performance [23]. Such intrinsic conduction states are not reached in all of the Cu-doped samples until ~450 °C, implying even higher S values above 450 °C.

To present a quantitative understanding of the microscopic mechanism for the Seebeck coefficient in $\text{Cu}_x\text{Bi}_2\text{SeS}_2$, we used the single parabolic band (SPB) model [27, 35]. At 50 °C, the SPB model can be reasonably adapted. The measured carrier density n at room temperature as a function of x is plotted in Fig. 6a and then the measured $|S|$ as a function of n is plotted in Fig. 6b. The solid curve in Fig. 6b is the fitting from the SPB model. It is known that the Seebeck coefficient in this model can be simply written as:

$$S = \frac{k_B}{e} \left(\frac{(\lambda + 2)F_{\lambda+1}(\eta)}{(\lambda + 1)F_{\lambda}(\eta)} - \eta \right), \quad (3)$$

where e is the electron charge, k_B is Boltzmann constant, λ is a parameter related to the details of scattering mechanism, η is the reduced electrochemical potential, and $F_j(\eta)$ is the Fermi integrals which is written as:

$$F_j(\eta) = \int_0^{\infty} \frac{\xi^j d\xi}{1 + \exp(\xi - \eta)}, \quad (4)$$

where ξ is the reduced carrier energy. Any attempt to derive the value of S has to take into account the following relation between the carrier density n and function of $F_j(\eta)$:

$$n = 4\pi \left(\frac{2m^* k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta), \quad (5)$$

where h is the Planck constant, m^* is the effective carrier mass. In our fitting, we chose $\lambda = 0$ owing to the fact that the main scattering mechanism at high T is the acoustic phonon scattering [27]. The measured $S(n)$ data can be well-fitted using the above SPB model assuming $m^* = 2.9m_0$, where m_0 is the electron mass.

The good consistency between the data and the SPB model suggests there was no resonant-state scattering other than the acoustic phonon scattering [36] in the present samples. In addition, the SPB model with dominant acoustic phonon scattering allows us to evaluate the Lorenz number, so that we can estimate the thermal conduction behaviors (to be presented below). From the σ and S data, we calculated $PF = S^2 \sigma$, as a function of T for all the samples

and the data are plotted in Fig. 5c. It is seen that the PF values for sample $x = 0.0$ over the whole T range are less than $2.0 \mu\text{W cm}^{-1} \text{K}^{-2}$ due to the low σ ($\sim 1400 \text{ S m}^{-1}$ at 50°C and $\sim 900 \text{ S m}^{-1}$ at 450°C). The Cu doping resulted in substantial enhancement of the PF and the maximal value reached $\sim 5.3 \mu\text{W cm}^{-1} \text{K}^{-2}$ for sample $x = 0.02$ at 450°C . It should be noted that this enhancement by Cu doping was significant only in the low x cases and excessive doping decreased the PF , as shown by the case of $x = 0.025$. It is also worth pointing out that the PF is still low, leaving room for further improvement by alloying or doping.

Thermal conductivity

We are most concerned with the thermal conduction of the samples in response to the microstructural features, as discussed above, as well as the impact of the Cu-doping on the thermal conduction. It is expected that the precipitated nano Bi_2S_3 , if properly embedded in the $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ matrix, may be beneficial to the reduction of the lattice thermal conductivity (κ_L). Unfortunately, the electronic thermal conductivity (κ_e) may be unfavorably promoted by Cu-doping, and certainly more lattice interruption may be needed for minimizing the total thermal conductivity (κ_{tot}).

We compared the measured κ_{tot} data as a function of T for sample with $x = 0.01$ (squares) in Fig. 7a, in comparison with the earlier reported data on $\text{Cu}_{0.01}\text{Bi}_2\text{SeS}_2$ samples where no nano Bi_2S_3 precipitates (triangles) were observed due to different sample preparation method [23]. We observed a roughly 30% lower κ_{tot} over the whole T -range in our sample with $x = 0.01$ with the reported data [23]. The reason for such a big difference can be attributed to the existence of nano Bi_2S_3 precipitates embedded in the $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ matrix. Similar consequences of the nano-sized second phase were reported extensively and introduction of such phase has been proven to be an efficient approach to suppress the thermal conduction in TE materials [27, 35,36].

To provide further evidence with the effect of nano Bi_2S_3 precipitates in our samples, we started from the measured κ_{tot} data:

$$\kappa_{tot} = \kappa_e + \kappa_L, \quad (6)$$

where the κ_e was directly calculated by the Wiedemann-Franz relation, $\kappa_e = L\sigma T$, where L is

the Lorenz number [35]. It is known that for heavily doped semiconductors, L is usually far below the Sommerfeld value $L_0 = 2.45 \times 10^{-8} \Omega \text{ W K}^{-2}$, but dependent of the band structure, reduced chemical potential η , and details of the scattering process. We assumed that the SPB model applies to our case with the dominating acoustic phonon scattering ($\lambda = 0$). The Lorenz number is expressed as:

$$L = \frac{k^2}{e^2} \frac{(\lambda+1)(\lambda+3)F_\lambda(\eta)F_{\lambda+2}(\eta) - (\lambda+2)^2 F_{\lambda+1}(\eta)^2}{(\lambda+1)^2 F_\lambda(\eta)^2}, \quad (7)$$

where η is obtained by fitting the measured S data using Eq. (3). The evaluated $L(T)$ curve is plotted in Fig. 7b together with the $\kappa_e(T)$ curve in Fig. 7c.

It was revealed that over the whole T -range, the Lorenz numbers are indeed far below the L_0 that is marked by the top dotted line, obviously owing to the elastically scattered degenerate holes/electrons. The high- T values of L are very close to the non-degenerate limit as marked by the bottom dotted line in Fig. 7b. Second, the evaluated $\kappa_e(T)$ values are similar to the earlier reported data, indicating that the nano Bi_2S_3 precipitates don't degrade the electrical conductivity due to lattice coherence of these precipitates with the matrix. Eventually, as shown in Fig. 7d, the evaluated $\kappa_L(T)$ data are much lower than the reported values over the whole T -range [23], demonstrating the suppression of the lattice thermal conduction by the nano Bi_2S_3 precipitates embedded in the $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ matrix. However, different from the $\kappa_e(x)$, $\kappa_L(x)$ is not closely dependent on x , a quite reasonable outcome, since all the samples have the nano Bi_2S_3 precipitates embedded in the matrix and Cu only sits at the interstitial sites.

Figure of merit and discussion

Finally, the ZT data for the samples at different T are summarized in Fig. 8. Quite different from $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ compound that has peak ZT value at 100 °C [26], all the samples here exhibit linear T -dependences. The ZT value for sample $x = 0.0$ is 0.08 at 50 °C and 0.23 at 450 °C. This value is respectively enhanced to 0.19, 0.16 and 0.13 at 50 °C and 0.65, 0.75 and 0.66 at 450 °C for samples with $x = 0.01$, 0.02 and 0.025, respectively. The peak ZT value is 0.75 at 450 °C for samples with $x = 0.02$, which is ~3 times as high as that of sample with x

= 0.0. It seems that Cu is indeed a qualified *n*-type dopant, and the optimized doping level is $x = 0.01 \sim 0.02$.

Although the *ZT* values remain similar to the previously reported results [23], the present work found nano sized Bi₂S₃ phase precipitating from the matrix. We also have a better understanding of the underlying physics, including the Cu-doping induced variation of electronic structure, etc. Nevertheless, it is noted that the details of the physics for the thermodynamics of the nano Bi₂S₃ precipitates in the Cu_{*x*}Bi₂SeS₂ matrix remains to be an issue. The assigned occupation of Cu as interstitials in the lattice lacks direct structural evidence. The thermal conduction suppression by this microstructure deserves additional investigation in terms of the microscopic mechanism. Finally, our strategy is to introduce a tiny amount of Cu doping to improve the electrical conductivity without damaging too much the Seebeck coefficient. At the same time, the nano-sized Bi₂S₃ precipitates contribute to the low thermal conductivity. Along this line, one may expect that a tiny amount of Ag doping should have a similar benefit since Ag has similar electronegativity as Cu.

Conclusion

In conclusion, we have studied Cu-doped *n*-type Bi₂SeS₂ using hot press sintering technique, and carefully characterized the microstructure, electronic structure, and TE properties. It has been revealed that Cu doping can effectively reduce the optical band gap and enhance the electrical conductivity while the Seebeck coefficient remains relatively high. A higher power factor upon Cu doping is achieved. The nano-sized Bi₂S₃ precipitates embedded in the Cu_{*x*}Bi₂SeS₂ matrix are identified, which is believed to be responsible for the lower thermal conductivity. The lattice thermal conductivity reached as low as $\sim 0.36 \text{ W m}^{-1} \text{ K}^{-1}$. The highest peak *ZT* value of ~ 0.7 was achieved at 450°C in Cu_{0.02}Bi₂SeS₂ by optimizing the electrical and thermal transport properties.

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Table I. The measured density of the as-prepared $\text{Cu}_x\text{Bi}_2\text{SeS}_2$ samples ($0 \leq x \leq 0.025$)

x	0.0	0.005	0.01	0.02	0.025
$d \text{ (g cm}^{-3}\text{)}$	6.85	6.92	6.86	6.95	6.90

Figure Captions

Fig. 1. (color online) (a) Schematic of the room temperature crystal structure of Bi_2SeS_2 viewed along the b -axis. (b) Measured XRD θ - 2θ spectra for a series of samples with doping level x labeled numerically. These peaks are properly indexed and the standard spectrum is inserted as reference. The insert shows the locally amplified peak from the nano Bi_2S_3 precipitates (see text), as indicated by red arrow in the main panel.

Fig. 2. SEM image of the microstructure of sample $x = 0.02$, and the averaged grain size is bigger than $1\text{ }\mu\text{m}$. On the top row, the plane mappings of Bi, Se, and S distributions respectively, obtained by the EDS mapping over an area of $0.4\text{ }\mu\text{m} \times 0.3\text{ }\mu\text{m}$, are shown.

Fig. 3. TEM images of the as-prepared Bi_2SeS_2 sample. (a) A low-resolution image showing fine contrast features embedded in the matrix. The white arrows indicate those small particle-like contrast features. The inset shows the $[010]$ selected electron diffraction pattern. (b) A high-resolution lattice image of the homogeneous matrix region, clearly showing the lattice structure of Bi_2SeS_2 phase. The lattice spacings of 1.12 nm and 1.15 nm correspond to the (001) and (100) planes. (c) A high-resolution image of a region containing the contrast features, showing the Bi_2S_3 precipitates which are bar-like. The inset shows a magnified region where the 0.39 nm and 0.80 nm label the spacing values of the (010) and (101) planes, respectively. (d) A high-resolution image covering a grain boundary between two matrix grains, evidencing the small-angle boundary.

Fig. 4. (color online) (a) Calculated density of states (DOS) of samples $x = 0.0$ and $x = 0.25$. (b) Measured absorption spectra for a series of powdered samples. (c) An example to show how the band gap E_g is evaluated by best fitting the linearly decaying region using the Kubelka-Munk (K-M) function. (d) Evaluated optical band gap as a function of x using the K-M function, where the solid line is the fitted curve obtained using the B-spline model function with the Origin plot software.

Fig. 5. (color online) (a) Measured electrical conductivity σ , (b) Seebeck coefficient S , and (c) power factor (PF) as a function of T for a series of as-sintered samples. The error bars for ρ and S are $\pm 5\%$.

Fig. 6. (color online) (a) Measured carrier density n as a function of x from Hall measurements at 323K, where the solid line in (a) is the fitted curve obtained using the B-spline mode (model?) function with the Origin plot software. (b) The measured $|S|$ is as a function of n at 323K and the solid line represents the SPB model fitted $S(n)$ function. Here, $\lambda = 0$ and $m^* = 2.9m_0$ are assumed. The error bars for S are $\pm 5\%$.

Fig. 7. (color online) (a) Measured thermal conductivity κ_{tot} as a function of T for sample with $x = 0.01$ (square dots). The data from Ref. [23] are inserted for comparison (triangle dots). (b) The evaluated Lorenz number L , (c) electronic thermal conductivity κ_e , and (d) lattice thermal conductivity κ_L are plotted respectively. The gray dots are the reported data [23]. The double-head red arrows are for guidance of eyes, showing the difference between the present data and reported data [23]. The error bars for κ_{tot} are $\pm 5\%$.

Fig. 8. (color online) Evaluated figure of merit ZT as a function of T for a series of samples. The evaluated error bars for ZT are roughly $\pm 10\%$.

Figure 1a

Figure 1b

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8