Preparation and thermoelectric properties of $\text{Cu}_{1.8}\text{S}/\text{CuSbS}_2$ composites

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Abstract: Chalcostibite (CuSbS_2) is composed of earth-abundant elements and has a proper band gap ($E_g = 1.05$ eV) as a thermoelectric (TE) material. Herein, we report the TE properties in the CuSbS_2 based composites with a mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$), which were prepared by mechanical alloying (MA) combined with spark plasma sintering (SPS). X-ray diffraction (XRD) and back-scattered electron image (BSE) results indicate that a single phase of CuSbS_2 is synthesized at $x = 0$ and the samples consist of CuSbS_2 , Cu_3SbS_4 , and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ at $0.1 \leq x \leq 0.3$. The correlation between the phase structure, microstructure, and TE transport properties of the bulk samples is established. The electrical conductivity increases from 0.14 to $50.66 \text{ S}\cdot\text{cm}^{-1}$ at 723 K and at $0 \leq x \leq 0.03$, while the Seebeck coefficient holds an appropriate value of $190.51 \mu\text{V}\cdot\text{K}^{-1}$. The highest ZT value of 0.17 is obtained at 723 K and at $x = 0.3$ owing to the combination of a high PF $183 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and a low κ $0.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

Keywords: CuSbS_2 ; phase structure; ZT ; thermoelectric

1 Introduction

Thermoelectric (TE) materials have caused extensive attention due to their potential applications in converting waste heat into electrical power and solid state refrigeration [1]. The conversion efficiency of TE materials is generally evaluated by the dimensionless figure of merit $ZT = \alpha^2 \sigma T / \kappa$, where α is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the total thermal conductivity (the sum of the electronic thermal conductivity (κ_e) and the lattice thermal conductivity (κ_L)). κ_L can be considered as an independent TE

parameter, while α , σ , and κ_e are interconnected closely by the carrier concentration (n). The outstanding performance of TE materials requires a large α , a high σ , as well as a low κ . Today, Bi_2Te_3 -based and PbTe -based TE materials have been applied in cooling devices and power generation. However, expensive (Te) and toxic (Pb) elements limit their market applications.

Chalcostibite (CuSbS_2) belongs to the compounds with the formula of ABX_2 , where A is Cu, Ag, or Au, B is As, Sb, or Bi, and X is S, Se, or Te. CuSbS_2 is more earth-abundant, less toxic, and cheaper compared with the compounds which include Ag, Au, Se, and Te elements [2]. In the orthorhombic crystal structure of CuSbS_2 , the Cu and Sb atoms occupy the cation sites and they are coordinated by four and three S atoms, respectively [3]. CuSbS_2 , Cu_3SbS_3 (skinnerite), Cu_3SbS_4

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(famatinnite), and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (tetrahedrite) are the four main crystalline phases in the Cu–Sb–S system. Three temperature-dependent crystal structures of Cu_3SbS_3 are orthorhombic with space group $P2_12_12_1$ below 263 K, monoclinic with space group $P2_1/c$ between 263 and 395 K, and orthorhombic with space group $Pnma$ above 395 K, respectively [4]. The low phase transition temperature for Cu_3SbS_3 may lead to micro-cracking during thermal cycling process, which is a potential problem for applications. Cu_3SbS_4 has a tetragonal structure with the space group $I42m$ and lattice parameters of $a = b = 5.3850 \text{ \AA}$ and $c = 10.7540 \text{ \AA}$, whose electrical resistance (ρ) and κ are as high as ca. $250 \text{ m}\Omega\cdot\text{cm}$ and $1.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which means a low TE performance [5,6]. $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ has a cubic structure with the space group $I\bar{4}3m$ and lattice parameters of $a = b = c = 10.3293 \text{ \AA}$. Many researches have shown that ZT value of intrinsic $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ lies in 0.3–0.5 [7–9]. Among the Cu–Sb–S system, Kumar *et al.* [10] report via a theoretic calculation that CuSbS_2 has a proper band gap ($E_g = 1.05 \text{ eV}$) and a large α , indicating CuSbS_2 may be a promising TE material, whose TE performance has rarely been reported until now. The σ of CuSbS_2 films was reported to be 0.03 [11], 10^{-4} – 10^{-3} [12], and $10^{-5} \text{ S}\cdot\text{cm}^{-1}$ [13], indicating the importance via obtaining a higher σ to enhance the TE performance of CuSbS_2 . Copper sulfides (Cu_{2-x}S , $0 \leq x \leq 1$) have recently attracted extensive attention as TE materials benefiting from the inexpensive, non-toxic, and earth-abundant elements of Cu and S [2,14]. Among Cu_{2-x}S compounds, $\text{Cu}_{1.8}\text{S}$ is considered to be a promising TE material due to the stable structure and the feature of the superionic conductor. Owing to the high mobility of Cu ions in the lattice, the σ of $\text{Cu}_{1.8}\text{S}$ was reported to be $3500 \text{ S}\cdot\text{cm}^{-1}$ at 373 K [15] and $2815 \text{ S}\cdot\text{cm}^{-1}$ at 323 K [16].

In the present work, the high-conductive $\text{Cu}_{1.8}\text{S}$ was composited with CuSbS_2 in the mole ratio of $(1-x)\text{CuSbS}_2$ – $x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$) to enhance the electrical transport properties of CuSbS_2 . The correlation between the phase structure, microstructure, and TE transport properties of the bulk samples was established.

2 Experimental

2.1 Preparation

CuSbS_2 powders were prepared by mechanical alloying

(MA) using a planetary ball mill (QM-1SP2, Nanjing University, China). The mixed Cu (99.7%), Sb (99.999%), and S (99.5%) raw powders were milled firstly at 425 rpm for 10 h in a mixed atmosphere of high-purity Ar (95%) and H_2 (5%) gases and then at 300 rpm for 2 h after adding 50 mL alcohol to the stainless steel vessel. The weight ratio of the stainless steel ball to powder was kept at 20:1. $\text{Cu}_{1.8}\text{S}$ was prepared by MA method described by Ref. [15]. $\text{Cu}_{1.8}\text{S}$ powder was mixed with CuSbS_2 powder in a mole ratio of $(1-x)\text{CuSbS}_2$ – $x\text{Cu}_{1.8}\text{S}$ at 200 rpm for 0.5 h, where x was fixed at 0, 0.1, 0.2, and 0.3. The corresponding powders were sintered at 723 K for 5 min in a $\Phi = 20 \text{ mm}$ graphite mould under an axial pressure of 50 MPa in a vacuum using SPS system (Sumitomo SPS1050, Japan) to obtain the bulk samples [17].

2.2 Characterization methods

The phase structure was identified by X-ray diffraction (XRD, Rigaku Dmax-RB, Japan) with a Cu K α radiation filtered through a Ni foil. The phase purity was refined by the Rietveld method using the Materials Studio (MS) software over the 2θ angular range of 20° – 60° . The microstructure and grain morphology of the bulk samples were observed by field emission scanning electron microscopy (FESEM, SUPRATM 55, Japan). The α and σ were simultaneously measured from 373 to 723 K in a helium atmosphere using a Seebeck coefficient/electrical resistance measurement system (ZEM-2, Ulvac-Riko, Japan). The κ was calculated by the formula of $\kappa = DC_p d$, where the thermal diffusivity (D) was measured by the laser flash method (NETZSCH, LFA457, Germany), the specific heat capacity (C_p) was measured via the thermal analysis device (NETZSCH DSC 404C, Germany), and the density (d) was measured by the Archimedes method.

3 Results and discussion

3.1 Phase structure

Figure 1(a) shows the XRD patterns of bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2$ – $x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$). All the diffraction peaks at $x = 0$ are consistent with the pattern of the orthorhombic CuSbS_2 ($\odot$, PDF#88-0822), whose space group and unit cell dimension are $Pnma$ (No. 62) and $6.0160 \text{ \AA} \times 3.7968 \text{ \AA} \times 14.4990 \text{ \AA}$ $<90^\circ \times 90^\circ \times 90^\circ>$, respectively, indicating

a formation of a single phase without any impurity phase within the detectable limit of the XRD spectrometer. To further confirm whether the pure CuSbS_2 phase was prepared, corresponding X-ray Rietveld refinement profiles achieved at $x = 0$ are shown in Fig. 1(b). The experimental pattern (observed) is well fitted with the theoretically simulated one (calculated). A high accuracy in the fitting is observed, where the differences provided at the middle of the patterns are almost linear except at the peak position, and the fitting accuracy converging to the acceptable Rietveld parameter R_{wp} is 12.97%. The lattice parameter values are $6.0231 \text{ \AA} \times 3.8033 \text{ \AA} \times 14.5036 \text{ \AA}$, which are similar to $6.0160 \text{ \AA} \times 3.7968 \text{ \AA} \times 14.4990 \text{ \AA}$ of the standard card (CuSbS_2 , PDF#88-0822). It is reasonable that a pure CuSbS_2 phase was synthesized by MA combining with SPS. As shown in Fig. 1(c), the diffraction peaks for $\text{Cu}_{1.8}\text{S}$ powder and bulk correspond well to the rhombohedral $\text{Cu}_{1.8}\text{S}$ (PDF#47-1748) without any second phases within the detectable limit of XRD. The corresponding X-ray Rietveld refinement profiles for $\text{Cu}_{1.8}\text{S}$ powder were also achieved.

When $0.1 \leq x \leq 0.3$, no $\text{Cu}_{1.8}\text{S}$ phase was detected, while some second phases identified to tetragonal Cu_3SbS_4 (◆, PDF#71-0555) and cubic $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (★, PDF#88-0282) were observed. The calculated formation energy from density functional theory (DFT) is in order of -0.200 , -0.359 , -0.377 , and -0.394 eV/atom for $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, Cu_3SbS_4 , and CuSbS_2 [18,19], respectively, which is also the sorting

of structural instability, where $\text{Cu}_{1.8}\text{S}$ is the most unstable compared with $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, Cu_3SbS_4 , and CuSbS_2 . In order to discuss the effect of x on the phase structure, some diffraction peaks of CuSbS_2 , Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ with the highest and/or higher intensities are highlighted in Figs. 2(a)–2(d), whose 2θ angle and diffraction intensity are abbreviated as $2\theta_{\text{phase}}^{(hkl)}$ and $I_{\text{phase}}^{(hkl)}$, respectively. The absent peaks at $2\theta_{\text{Cu}_3\text{SbS}_4}^{(200)}$ (Fig. 2(b)) and $2\theta_{\text{Cu}_{12}\text{Sb}_4\text{S}_{13}}^{(510)}$ (Fig. 2(d)) also confirm the formation of the pure CuSbS_2 phase at $x = 0$. Due to the increased Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, obviously increased $I_{\text{CuSbS}_2}^{(104)}$ and $I_{\text{CuSbS}_2}^{(013)}$ were observed because of the peak overlap between $2\theta_{\text{Cu}_3\text{SbS}_4}^{(112)}$ and $2\theta_{\text{CuSbS}_2}^{(104)}$, $2\theta_{\text{Cu}_{12}\text{Sb}_4\text{S}_{13}}^{(222)}$ and $2\theta_{\text{CuSbS}_2}^{(013)}$. Along with the variation of the phase structure, the diffraction peaks show a peak shifting apart from the varied $I_{\text{phase}}^{(hkl)}$. $2\theta_{\text{CuSbS}_2}^{(111)}$ and $2\theta_{\text{CuSbS}_2}^{(200)}$ at $x = 0$ in Figs. 2(a) and 2(c) are ca. 28.420° and 29.640° which are lower than those (28.448° and 29.675°) of the standard card (CuSbS_2 , PDF#88-0822) indicating an expanded CuSbS_2 lattice. A similar behavior was usually found in sulfur containing systems, which is attributed to the volatilization and/or loss of S in the MA and/or SPS process [14–16,20]. The shifting trend of $2\theta_{\text{CuSbS}_2}^{(111)}$ and $2\theta_{\text{CuSbS}_2}^{(200)}$ to high angle is observed at $x = 0.1$, but turns to weaken by further increasing x to 0.2 and even reversely shifts to low angle at $x = 0.3$, which reflects the shrinkage and enlargement of CuSbS_2 lattice.

Fig. 1 (a) XRD patterns of the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$), (b) Rietveld refinement of $x = 0$ bulk sample, and (c) XRD patterns and Rietveld refinement of $\text{Cu}_{1.8}\text{S}$.

Fig. 2 XRD patterns of the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$) at 2θ range of (a) 28° – 29° , (b) 32.8° – 33.8° , (c) 29.2° – 30.2° , and (d) 44.3° – 45.1° .

Because the Cu/S ratio of the $\text{Cu}_{1.8}\text{S}$ (Cu/S = 1.8 : 1) is far higher than that of CuSbS_2 (Cu/S = 1 : 2), the Cu-rich environment may be created by the addition of $\text{Cu}_{1.8}\text{S}$, which may lead to the formation of Cu_3SbS_4 , $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, and $\text{Cu}_{1+y}\text{SbS}_2$ (Cu-rich CuSbS_2 phase), where y increases with the increase of x and shows a doping effect. The effect of substitution solution on the lattice parameters is related to the ionic radius of dopants, while the interstitial solution would generally enlarge the lattice parameters. Because the ionic radius (r) of Cu^+ , Cu^{2+} , and Sb^{3+} is 0.60, 0.57, and 0.76 Å, respectively, the shrinkage of CuSbS_2 lattice is attributed to the substitution of Sb^{3+} ($r = 0.76$ Å) by Cu^+ ($r = 0.60$ Å) and/or Cu^{2+} ($r = 0.57$ Å) and the enlargement of CuSbS_2 lattice is attributed to the interstitial solution of rich Cu^+ and/or Cu^{2+} . When x increases from 0.2 to 0.3, the interstitial solution would weaken the effect of substitution solution on the lattice parameters and even play a dominant role. $I_{\text{Cu}_3\text{SbS}_4}^{(200)}$ increases when $0 \leq x \leq 0.2$ and then decreases at $x = 0.3$ in Fig. 2(b), while $I_{\text{Cu}_{12}\text{Sb}_4\text{S}_{13}}^{(510)}$ shows a continuous enhancement when $0 \leq x \leq 0.3$ in Fig. 2(d). Hence, Eqs. (1)–(6) related to the above behaviors should be as follows:

where, z is the content of volatilization and/or loss S during the MA and/or SPS process which depends on the preparation condition, y is the content of Cu rich in $\text{Cu}_{1+y}\text{SbS}_2$ and the sum of y_1 to y_4 . Equation (1) indicates that the vacancy $V_{\text{S}}^{\bullet\bullet}$ and two electrons (e') would generate when S is lacking [14,16,20]. Equation (2) indicates the formation of $\text{Cu}_{1+y}\text{SbS}_2$, Cu_3SbS_4 , and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. The substitution of Sb^{3+} by Cu^+ and/or Cu^{2+} in Eqs. (3) and (4) would introduce one and/or two holes ($h^\bullet$) and shrink the CuSbS_2 lattice, while the interstitial solution of Cu^+ and/or Cu^{2+} in Eqs. (5) and (6) would introduce one and/or two e' and enlarge the CuSbS_2 lattice.

The actual mole ratio of CuSbS_2 , Cu_3SbS_4 , and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ was calculated by Eqs. (7) and (8) [21] according to the XRD peak differentiating analysis in Fig. 3, where $A_{\text{phase}}^{(hkl)}$ is the peak area and the results are listed in Table 1. The volume ratio of CuSbS_2 : Cu_3SbS_4 : $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ changes from 0.7919:0.0407:0.1674 at $x = 0.1$ to 0.2968:0.0854:0.6178 at $x = 0.3$ when x increases. The significantly increased second phases would greatly impact on the TE performance of the matrix which would be discussed in detail later.

$$\frac{\text{Cu}_3\text{SbS}_4}{\text{CuSbS}_2} = \frac{A_{\text{Cu}_3\text{SbS}_4}^{(112)} + A_{\text{Cu}_3\text{SbS}_4}^{(220)} + A_{\text{Cu}_3\text{SbS}_4}^{(312)}}{A_{\text{CuSbS}_2}^{(111)} + A_{\text{CuSbS}_2}^{(104)} + A_{\text{CuSbS}_2}^{(013)}} \quad (7)$$

$$\frac{\text{Cu}_{12}\text{Sb}_4\text{S}_{13}}{\text{CuSbS}_2} = \frac{A_{\text{Cu}_{12}\text{Sb}_4\text{S}_{13}}^{(222)} + A_{\text{Cu}_{12}\text{Sb}_4\text{S}_{13}}^{(400)} + A_{\text{Cu}_{12}\text{Sb}_4\text{S}_{13}}^{(440)}}{A_{\text{CuSbS}_2}^{(111)} + A_{\text{CuSbS}_2}^{(104)} + A_{\text{CuSbS}_2}^{(013)}} \quad (8)$$

3.2 Microstructure

Figures 4(a) and 4(b) show the back-scattered electron (BSE) images of bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0.2, 0.3$). The second phases distribute evenly in the matrix along with an increased content when x increases from 0.2 to 0.3, which corresponds well to the XRD results (Figs. 1(a), 2(b), and 2(d)). Figures 4(c)–4(g) show the enlarged BSE

Fig. 3 XRD patterns of the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$) at 2θ range of (a) 28.2° – 29.0° , (b) 47.5° – 48.1° , (c) 56.4° – 57.1° , (d) 29.4° – 30.2° , (e) 34.5° – 34.9° , and (f) 49.6° – 50.2° .

Table 1 Actual ratio of $\text{CuSbS}_2:\text{Cu}_3\text{SbS}_4:\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ at room temperature

Sample	$\text{CuSbS}_2:\text{Cu}_3\text{SbS}_4:\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$		Theory density (g/cm^3)	Test density (g/cm^3)	Relative density (%)
	Mole ratio	Volume ratio			
$x = 0$	1:0:0	1:0:0	5.0010	4.1270	82.52
$x = 0.1$	1:0.0273:0.0324	0.7919:0.0407:0.1674	4.9917	4.1740	83.62
$x = 0.2$	1:0.0620:0.0969	0.5717:0.0668:0.3615	4.9876	4.4140	88.59
$x = 0.3$	1:0.1528:0.3189	0.2968:0.0854:0.6178	4.9870	4.2125	84.47

Fig. 4 BSE images and energy dispersive X-ray spectroscopy (EDX) data of the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0.2, 0.3$). (a) $x = 0.2$, (b, c) $x = 0.3$, (d) atomic ratio of Cu/Sb/S, and (e)–(g) EDX spectra.

images of $x = 0.3$ (Fig. 4(c)), in which the atomic ratio of Cu, Sb, and S at different positions (Fig. 4(d)), and EDX spectra are selected from the second phases (positions 1 and 2) and the matrix (position 3) (Figs. 4(e)–4(g)). Three elements Cu, Sb, and S were found both in the matrix (position 3) and the second phases (positions 1 and 2), but the composition of the matrix and the second phases is different. The atomic ratio of Cu, Sb, and S in the matrix (position 3) in Fig. 4(d) is almost similar around 1.25:1:2.16, which is consistent with the composition of CuSbS_2 . The atomic ratio of Cu, Sb, and S for the second phases shows different values at different positions, which is about 3.43:1:4.68 (position 1) and 2.78:1:3.41 (position 2) corresponding to the composition of Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, respectively.

Figure 5 shows the FESEM images of the fractured surfaces for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$). The grain sizes are refined from $0.72\ \mu\text{m}$ for $x = 0$ to $0.62\ \mu\text{m}$ for $0.1 \leq x \leq 0.2$, and further reduce to $0.47\ \mu\text{m}$ as x increasing to 0.3. The refined grains are owing to the pinning effect of Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ which would inhibit the grain growth. All samples have a porous microstructure, whose relative density increases from 82.52% to 88.59% when x ranges from 0 to 0.2, and then decreases to 84.47% at $x = 0.3$ as shown in Table 1 and Fig. 5(e). The similar grain sizes and increased density at $0.1 \leq x \leq 0.2$ may lead to a higher κ , while the obvious refined grains and decreased density would probably reduce the κ which would be clearly addressed later.

3.3 TE transport properties

Figure 6 shows the temperature dependence of electrical transport properties for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$). The highest σ in the whole measured temperature ranges from 373 to 723 K is almost the same which is located at ca. 0.54 and $0.68\ \text{S}\cdot\text{cm}^{-1}$ at $x = 0$ and 0.1 . The low σ of $x = 0$ may be attributed to a low hole carrier concentration (n). What's more, the lack of S in Eq. (1) would also reduce n and leads to a lower σ . When x increases to 0.1, the formation of Cu-rich CuSbS_2 phase would introduce the substitution of Sb^{3+} by Cu^+ and/or Cu^{2+} as shown in Eqs. (3) and (4) which would increase n . Although the interstice solution of Cu^+ and/or Cu^{2+} in Eqs. (5) and (6) would introduce e' and reduce n as x further increasing to 0.2 and 0.3, the σ value at 373 K is significantly enhanced to $6.78\ \text{S}\cdot\text{cm}^{-1}$ ($x = 0.2$) and $76.41\ \text{S}\cdot\text{cm}^{-1}$ ($x = 0.3$). The significantly enhanced σ in Fig. 6 is not only because of the increased relative density from 82.52% to 88.59% as x ranging from 0 to 0.2. What's more, the σ continues to increase while the relative density decreases to 84.47% at $x = 0.3$, indicating the TE performance of the second phases may play a dominant role at $x \geq 0.2$. According to the electrical conductivity law of mixtures [22], the logarithm of the total σ can be expressed as follows:

$$\ln \sigma_T = V_M \ln \sigma_M + V_S \ln \sigma_S \quad (9)$$

where σ_T , V_M , σ_M , V_S , and σ_S are the total σ , volume fraction and σ of the matrix and the second phase,

Fig. 5 FESEM images of the fractured surfaces and relative densities for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$): (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, and (e) grain size and relative density.

Fig. 6 Temperature dependence of electrical transport properties for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$). (a) Electrical conductivity (σ), (b) Seebeck coefficient (α), and (c) power factor (PF).

respectively. The increased V_S of the high-conductive second phases and the decreased V_M of low-conductive CuSbS_2 in Table 1 would lead to the enhancement of σ_T according to Eq. (9). Chen *et al.* [6] reported that the σ of Cu_3SbS_4 was ca. $2.01 \text{ S}\cdot\text{cm}^{-1}$ at 373 K, while $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ which was synthesized by the solid-state reaction at 723 K for 3 weeks and sintered at 723 K under 10 MPa pressure showed a high σ of $706.16 \text{ S}\cdot\text{cm}^{-1}$ [7], along with a metal like P-type conductivity calculated by DFT [8]. It is reasonable that the slightly increased σ at $x = 0.1$ is attributed to the formation of a little of the second phases whose σ is higher than CuSbS_2 ($\sim 0.01 \text{ S}\cdot\text{cm}^{-1}$). The remarkably enhanced σ at $0.2 \leq x \leq 0.3$ should be attributed to the additional appearance of high-conductive $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (shown in Figs. 2(d), 3(d), 3(f), and Eq. (2)). Table 2 shows the electrical and thermal transport properties at 373 K for all the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$), the Cu_3SbS_4 and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ second phases as well as the raw $\text{Cu}_{1.8}\text{S}$. The high σ of $\text{Cu}_{1.8}\text{S}$ up to $3353 \text{ S}\cdot\text{cm}^{-1}$ still indicates a great potential to enhance the electrical transport properties of CuSbS_2 , although the raw $\text{Cu}_{1.8}\text{S}$ phase is absent in the final bulk samples by applying

MA combined with SPS. How to composite $\text{Cu}_{1.8}\text{S}$ with CuSbS_2 is still a big challenge in the future.

The positive α value for all samples in Fig. 6(b) confirms the P-type semi conductive behavior, whose values all decrease with raising x from 0 to 0.3 in the whole measured temperature range from 373 to 723 K, which is contrary to the variation of σ . The second phases show a higher σ associated with a lower α in Table 2. The gradually reduced α value is mainly attributed to the low α of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ($\sim 82.26 \mu\text{V}\cdot\text{K}^{-1}$) and Cu_3SbS_4 ($\sim 641.88 \mu\text{V}\cdot\text{K}^{-1}$) second phases compared with CuSbS_2 ($\sim 930.5 \mu\text{V}\cdot\text{K}^{-1}$). Due to the high σ and the appropriate α value, the power factor ($PF = \alpha^2 \sigma$) in Fig. 6(c) peaks at $183 \mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and at 723 K when $x = 0.3$.

Figure 7(a) shows the temperature dependence of κ for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$). The κ of CuSbS_2 is $1.27 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 373 K which is little higher than $1.06 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ reported by Du *et al.* [5]. The increased κ as x ranging from 0 to 0.2 is attributed to the increased density and the high κ of Cu_3SbS_4 ($\sim 1.80 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) shown in Tables 1 and 2 [6]. However, the κ still increases above 473 K when the

Table 2 TE transport properties of bulk samples and second phases at 373 K

Sample	Phase	Crystal structure	σ ($\text{S}\cdot\text{cm}^{-1}$)	α ($\mu\text{V}\cdot\text{K}^{-1}$)	κ ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	ZT
$x = 0$	CuSbS_2	Orthorhombic	0.01	930.50	1.27	0.0001
$x = 0.1$	$\text{CuSbS}_2 + \text{Cu}_3\text{SbS}_4 + \text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	—	0.08	470.57	0.90	0.0007
$x = 0.2$	$\text{CuSbS}_2 + \text{Cu}_3\text{SbS}_4 + \text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	—	6.78	122.00	1.31	0.0028
$x = 0.3$	$\text{CuSbS}_2 + \text{Cu}_3\text{SbS}_4 + \text{Cu}_{12}\text{Sb}_4\text{S}_{13}$	—	76.41	88.36	1.27	0.0175
—	Cu_3SbS_4 [6]	Tetragonal	2.01	641.88	1.80	0.0171
—	$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ [7]	Cubic	706.16	82.26	1.09	0.1635
—	$\text{Cu}_{1.8}\text{S}$ [16]	Rhombohedral	3353.05	22.64	2.26	0.0284

density decreases to 4.21 g/cm^3 at $x = 0.3$, which may be due to the formation of a large amount of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ with a high κ above 473 K. The lowest κ $0.47 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for CuSbS_2 is achieved at 723 K. The κ_e could be estimated by the Wiedemann–Franz relation: $\kappa_e = L\sigma T$, where L is the Lorenz number, T is the absolute temperature. For nondegenerate semiconductor, L was calculated to be $1.485 \times 10^{-8} \text{ W}\cdot\Omega\cdot\text{K}^{-2}$ based on the assumption of $r = -1/2$ for acoustic phonon scattering according to Eq. (10) where k_B is the Boltzmann constant, e is the electron charge, and r is the scattering factor [23,24].

$$L = \left(\frac{k_B}{e} \right)^2 \left(r + \frac{5}{2} \right) \quad (10)$$

Figures 7(b) and 7(c) show the temperature dependence of κ_e and κ_L . The κ_L plays a dominant role in the thermal transport performance owing to the low σ resulting in an almost negligible κ_e . The increased κ_L as x ranging from 0 to 0.2 is attributed to the high κ_L of Cu_3SbS_4 which plays a dominated role compared to the contribution of increased alloy scattering and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$. When $x = 0.3$, the amount of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ is further increased as shown in Table 1 and the κ_L shows a slight reduction in Fig. 7(c). The decreased κ_L of $x =$

0.3 may be owing to the lower κ_L of $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ rather than the further increased alloy scattering. Moreover, the refined grain shown in Figs. 5(d) and 5(e) could also enhance the grain boundary scattering and lower the κ_L .

Figure 7(d) shows temperature dependence of ZT for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$). Significantly enhanced PF and slightly deteriorated κ for $0.2 \leq x \leq 0.3$ result in a higher ZT compared with CuSbS_2 . The highest ZT value of 0.17 at 723 K was obtained when $x = 0.3$.

4 Conclusions

P-type CuSbS_2 based TE composites with a mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$) were fabricated by MA combined with SPS. The correlation between the phase structure, microstructure, and TE transport properties of the bulk samples is systematically investigated. A single phase of CuSbS_2 is synthesized at $x = 0$ and the samples consist of CuSbS_2 , Cu_3SbS_4 , and $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ at $0.1 \leq x \leq 0.3$. The σ significantly increases from 0.14 to $50.66 \text{ S}\cdot\text{cm}^{-1}$ at 723 K when $0 \leq x \leq 0.03$, while the α holds an appropriate value of

Fig. 7 Temperature dependence of thermal transport properties and ZT value for the bulk samples with the mole ratio of $(1-x)\text{CuSbS}_2-x\text{Cu}_{1.8}\text{S}$ ($x = 0, 0.1, 0.2, 0.3$): (a) thermal conductivity (κ), (b) electronic thermal conductivity (κ_e), (c) lattice thermal conductivity (κ_L), and (d) ZT value.

190.51 $\mu\text{V}\cdot\text{K}^{-1}$. The highest ZT value of 0.17 is obtained at 723 K for $x = 0.3$ bulk sample owing to the combination of a high PF 183 $\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ and a low κ 0.8 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

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