Optimal performance of $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ thermoelectric materials fabricated via high-pressure process at room temperature

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Abstract: $\text{Cu}_{1.8}\text{S}$ has been considered as a potential thermoelectric (TE) material for its stable electrical and thermal properties, environmental benignity, and low cost. Herein, the TE properties of nanostructured $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ ($0 \leq x \leq 0.2$) bulks fabricated by a facile process combining mechanical alloying (MA) and room-temperature high-pressure sintering (RT-HPS) technique were optimized via eliminating the volatilization of S element and suppressing grain growth. Experimentally, a single phase of $\text{Cu}_{1.8}\text{S}$ was obtained at $x = 0$, and a second $\text{Cu}_{1.96}\text{S}$ phase formed in all $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ samples when $0.05 \leq x \leq 0.125$. With further increasing x to $0.15 \leq x \leq 0.2$, the Cu_{2-z}Te phase was detected and the samples consisted of $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.96}\text{S}$, and Cu_{2-z}Te phases. Benefiting from a modified band structure and the coexisted phases of $\text{Cu}_{1.96}\text{S}$ and Cu_{2-z}Te , the power factor is enhanced in all $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ ($0.05 \leq x \leq 0.2$) alloys. Combining with a drastic decrease in the thermal conductivity due to the strengthened phonon scatterings from multiscale defects introduced by Te doping and nano-grain boundaries, a maximum figure of merit (ZT) of 0.352 is reached at 623 K for $\text{Cu}_{1.8}\text{S}_{0.875}\text{Te}_{0.125}$, which is 171% higher than that of $\text{Cu}_{1.8}\text{S}$ (0.130). The study demonstrates that doping Te is an effective strategy to improve the TE performance of $\text{Cu}_{1.8}\text{S}$ based materials and the proposed facile method combining MA and RT-HPS is a potential way to fabricate nanostructured bulks.

Keywords: $\text{Cu}_{1.8}\text{S}$; Te doping; nanostructure; high pressure; thermoelectric (TE)

1 Introduction

Thermoelectric (TE) technology can convert thermal energy directly into electricity and vice versa, which has been expected as a promising solution for the growing demands of green and renewable energy [1,2]. The practical applications of this technology have been

restricted by the generally low conversion efficiency, which is determined by the dimensionless figure of merit (ZT). A high-performance TE material with high ZT should possess high Seebeck coefficient (α), high electrical conductivity (σ), low total thermal conductivity (κ , the sum of the carrier thermal conductivity (κ_{carrier}) and lattice thermal conductivity (κ_l)), simultaneously. However, these TE parameters are strongly coupled with each other, making high ZT difficult to obtain in a straight forward way [3,4]. Enhancing power factor (PF , $PF = \alpha^2 \sigma$) by optimizing carrier concentration (n)

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and band structure [5–8], and reducing κ via multiscale defect scattering [9–13] by element doping or alloying are generally considered as more efficient strategies for TE performance enhancement.

Copper sulfides have attracted wide attention as promising TE materials for their tunable transport properties, high elemental abundance, nontoxicity, and environmental benignity [14–17]. In Cu_{2-x}S , the intermediate phases including $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.97}\text{S}$, and Cu_2S have been widely reported as promising TE materials with p-type transport character due to the copper vacancies in the lattice [18–20]. Among this, digenite $\text{Cu}_{1.8}\text{S}$ is regarded as the most potential one because of its stable electrical and thermal properties according to Dennler *et al.* [21]. $\text{Cu}_{1.8}\text{S}$ has two different crystal structures: low-temperature digenite (hexagonal phase, R3-MH) and high-temperature digenite (cubic phase, FM3-M) with a turning temperature of 360 K, in which the position of copper atom changes from ordered states to confused ones. As a superionic conductor, $\text{Cu}_{1.8}\text{S}$ possesses high σ ($\sim 3000 \text{ S}\cdot\text{cm}^{-1}$) due to the high mobility of copper ions in the lattice [16]. The main challenges for enhancing the TE properties of $\text{Cu}_{1.8}\text{S}$ -based materials are to improve the α and reduce the κ . Element doping or alloying in $\text{Cu}_{1.8}\text{S}$ such as Ti doping, In doping, Sb/Sn co-doping, and Bi_2S_3 compositing has been widely used as a simple and effective approach to enhance the ZT [19,22–24]. Recently, Te doping has been proven to be effective in enhancing ZT of $\text{Cu}_2\text{S}_{1-x}\text{Te}_x$ system due to greatly enhanced PF and significantly reduced κ [25]. In Ref. [26], Te doping can modulate the band structure and increase the density of states (DOS) of Cu_{2-x}Se due to its 5p electron contribution. Hence, investigation of Te doping in $\text{Cu}_{1.8}\text{S}$ is desirable and high TE performance can be expected based on the potential effect of band structure modification and κ reduction, which has rarely been reported so far.

It is well known that different preparation processes of TE materials can strongly affect the microstructure and TE properties of bulks. As previously reported, Cu–S–Te based materials can be synthesized through both liquid and solid phase routes, such as solvothermal process [27,28], hydrothermal synthesis [29], and mechanical alloying (MA) [8] combined with a follow-up procedure of hot pressing or spark plasma sintering (SPS) [30]. However, the large melting point difference between Cu and S, as well as the widely existed non-stoichiometry regions in the Cu_{2-x}S phase

diagram, makes the conventional high-temperature synthesis routes inadequate for accurate composition control and performance studies. It is desirable to develop a low-temperature fabrication method for Cu–S system.

High pressure can help lower the reaction temperature, promote the reaction, and shorten the reaction time, which are beneficial for inhibiting component element volatilization and suppressing grain growth [31]. Besides, a high-pressure process can be used as an effective avenue to change the crystal and electronic structures of TE materials for performance enhancement [32–34]. In Ref. [35], high-pressure synthesized $\text{Mg}_2\text{Si}_{1-x}\text{Sb}_x$ samples show significantly enhanced TE performance due to the improved PF and greatly suppressed κ compared with ambient-pressure synthesized ones [35]. Especially, high-pressure technology at room temperature has been proposed as a rapid and energy lean approach to synthesize dense, single-phase Cu_2X ($\text{X} = \text{S/Se}$) bulk samples with depressed κ due to the introduced high concentration of atomic-scale defects and amorphous regions in the samples [36].

In this study, a series of highly dense $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks with nanograins were prepared by a facile method combining MA and room-temperature high-pressure sintering (RT-HPS) technique, which can efficiently eliminate the volatilization of S element and suppress grain growth. The effect of Te doping on phase structure and TE properties were investigated. Benefiting from a modified band structure and coexisted phases of $\text{Cu}_{1.96}\text{S}$ and Cu_{2-x}Te with Te doping, the PF is enhanced in all $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ ($0.05 \leq x \leq 0.2$) alloys. Combining with a drastically decreased thermal conductivity due to strengthened phonon scatterings from multiscale defects introduced by Te doping and nano-grain boundaries, a maximum ZT of 0.352 is reached at 623 K for $\text{Cu}_{1.8}\text{S}_{0.875}\text{Te}_{0.125}$, which is 171% higher than that of $\text{Cu}_{1.8}\text{S}$ (0.130).

2 Experimental

Stoichiometric $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ ($x = 0, 0.05, 0.10, 0.125, 0.15$, and 0.2) samples were synthesized via MA combined with the RT-HPS process. High-purity powders of Cu (99.9%, Sinopharm Chemical Reagent Co., Ltd.), S (99.9%, Sinopharm Chemical Reagent Co., Ltd.), and Te (99.999%, ZhongNuo Advanced Material Technology Co., Ltd.) were used as raw

materials and weighed in stoichiometric proportions. These powders were put into stainless steel vessels and subjected to MA for 2 h at 450 rpm in a planetary ball milling machine (QM-3SP2, Nanjing University, China) under a protective atmosphere of mixed Ar (95 vol%) and H₂ (5 vol%). The weight ratio of grinding balls to mixed powders is 20:1. Ball-milled powders were subsequently cold pressed into a pellet of 28 mm diameter, inserted into a molybdenum crucible, and densified in a six-anvil high-pressure apparatus (CS-IV-D synthetic diamond hydraulic press) at room temperature under 3.5 GPa for 5 min. Disk-like bulks with a dimension of 28 mm × 3.5 mm were prepared. All samples possess high densities in the range of 5.557–5.882 g·cm⁻³, whose relative densities are above 98%.

Phase structure of the bulk materials was analyzed by X-ray diffraction (XRD) measurement (D8 Advance, Bruker, Germany) with Cu K α radiation and the average grain size of Cu_{1.8}S was calculated by the Scherrer equation. Field-emission scanning electron microscopy (FESEM, SUPRATM 55, Carl Zeiss, Germany) was conducted on the fractured surfaces of bulks for microstructure observation. The σ and α were simultaneously measured in the temperature range of 323–623 K using a Seebeck coefficient/electric resistance measuring apparatus (CTA-3, Cryoall, China) under a low-pressure helium atmosphere. The thermal diffusivity (D) was measured by a laser flash method on Netzsch LFA457 with an argon atmosphere. The heat capacity (C_p) was determined using the Dulong–Petit law. The density (d) of the sample was measured by the Archimedes method. The total κ was calculated using the equation $\kappa = DC_p d$, and the ZT value was determined via $ZT = \alpha^2 \sigma T / \kappa$ (T is the Kelvin temperature). The Hall coefficient (R_H) was directly measured at room temperature by the van der Pauw method using a Hall measurement system (ResiTest 8340DC, Toyo, Japan) with a magnetic field of 0.52 T. The n and mobility (μ) were respectively estimated by $n = 1/(eR_H)$ and $\mu = \sigma R_H$, where e is the elementary charge. Longitudinal (v_l) and transverse (v_t) sound velocities of Cu_{1.8}S_{1-x}Te_x bulks were determined through the ultrasonic pulse-echo measurement (5072PR, Olympus, Tokyo, Japan) with couplants applied between ultrasonic transducers and samples. Optical absorption measurements were performed on Cu_{1.8}S_{1-x}Te_x bulks at room temperature via a UV–Vis spectrophotometer (TU 1901). BaSO₄ powders were used as the standard sample with 100% optical reflectance. The optical band gap (E_g) was

estimated by extrapolating $(ah\nu)^2$ to 0 as a function of photon energy ($h\nu$) for the direct band-gap semiconductor of Cu_{1.8}S (a , h , and ν are the absorption coefficient, Plank constant, and light frequency, respectively) [8,37,38].

3 Results and discussion

Figure 1(a) presents the powder XRD patterns of Cu_{1.8}S_{1-x}Te_x ($0 \leq x \leq 0.2$) after MA. All the diffraction peaks of $x = 0$ powders in Fig. 1(a1) are well matched to rhombohedral Cu_{1.8}S (PDF#47-1748), suggesting the formation of single-phase Cu_{1.8}S without any detectable impurity phase. All the Cu_{1.8}S_{1-x}Te_x ($0.05 \leq x \leq 0.2$) powders consist of Cu_{1.8}S host phase and tetragonal Cu_{1.96}S (●, PDF#29-0578) phase, while the diffraction intensity of Cu_{1.96}S increases at $0.05 \leq x \leq 0.1$ and then maintains similar at $0.1 \leq x \leq 0.2$ as shown in Fig. 1(a2). Apart from Cu_{1.8}S and Cu_{1.96}S, some peaks of hexagonal Cu_{2-2x}Te (↓, PDF#06-0661) phase in Fig. 1(a2) are detected with an increased intensity at $0.15 \leq x \leq 0.2$, which attributes to the excessive addition of Te. Along with

Fig. 1 XRD patterns of (a1–a3) Cu_{1.8}S_{1-x}Te_x ($0 \leq x \leq 0.2$) powders, (b1–b3) Cu_{1.8}S_{1-x}Te_x ($0 \leq x \leq 0.2$) and SPS-Cu_{1.8}S bulks.

the variation of the phase structure, a peak shift in Fig. 1(a3) is observed in the $\text{Cu}_{1.8}\text{S}$ host phase but absent in $\text{Cu}_{1.96}\text{S}$ and Cu_{2-z}Te . The enlarged (0120) $_{\text{Cu}_{1.8}\text{S}}$ peaks in Fig. 1(a3) at $0.05 \leq x \leq 0.2$ shift toward a low diffraction angle with increasing x , suggesting an enlarged lattice of the $\text{Cu}_{1.8}\text{S}$ host phase, which is ascribed to the larger ionic radius of Te^{2-} (2.21 Å) compared with that of S^{2-} (1.84 Å). Besides, all the Te doped samples in Fig. 1(a3) show a wider full width at half maximum (FWHM) when $0.1 \leq x \leq 0.2$, which can be mainly ascribed to the peak superposition of the $\text{Cu}_{1.96}\text{S}$ with $\text{Cu}_{1.8}\text{S}$ host phase.

Figure 1(b) shows the XRD patterns of $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks and the reported $\text{Cu}_{1.8}\text{S}$ synthesized by SPS (SPS- $\text{Cu}_{1.8}\text{S}$) [8], in which all $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks in Figs. 1(b1)–1(b3) show similar diffraction patterns with powders in Figs. 1(a1)–1(a3), indicating the same phase structure and the same peak shifting behavior. The related equations can be described in Eqs. (1)–(4):

where x is the added Te content based on the stoichiometric ratio of $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ ($x = 0, 0.05, 0.10, 0.125, 0.15$, and 0.2), y is the content of Cu-deficiency in $\text{Cu}_{1.8-y}\text{S}_{1-x}\text{Te}_x$. Equation (1) describes the substitution of Te for S in the $\text{Cu}_{1.8}\text{S}$ lattice. With further increasing x , Cu-rich $\text{Cu}_{1.96}\text{S}$ second phase and the Cu-poor $\text{Cu}_{1.8-y}\text{S}_{1-x}\text{Te}_x$ matrix phase would be formed as shown in Eq. (2). The formation of $\text{Cu}_{1.8-y}\text{S}_{1-x}\text{Te}_x$ would generate holes ($h^{\bullet}$) and vacancies (V'_{Cu}) in $\text{Cu}_{1.8}\text{S}$ lattice as shown in Eq. (3). Equation (4) describes the formation of coexisted $\text{Cu}_{1.8-y}\text{S}_{1-x}\text{Te}_x$, $\text{Cu}_{1.96}\text{S}$, and Cu_{2-z}Te phases when $0.15 \leq x \leq 0.2$. Considering the different intrinsic n of the coexisted phases and the introduced $h^{\bullet}$ in Eq. (3), the n variation mechanism of bulk samples will be discussed later.

Figures 2(a)–2(c) show the grain size distribution of $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.8}\text{S}_{0.8}\text{Te}_{0.2}$, and previously synthesized SPS- $\text{Cu}_{1.8}\text{S}$ [29] bulks, along with insets showing the corresponding SEM images of the fractured surface. Both $\text{Cu}_{1.8}\text{S}$ and $\text{Cu}_{1.8}\text{S}_{0.8}\text{Te}_{0.2}$ in Figs. 2(a) and 2(b) possess similar nanoscale grains (20–40 nm) and dense microstructures, whose densities are about 5.557 and 5.882 $\text{g}\cdot\text{cm}^{-3}$ (relative densities are over 98%),

Fig. 2 Grain size distribution of (a) $\text{Cu}_{1.8}\text{S}$, (b) $\text{Cu}_{1.8}\text{S}_{0.8}\text{Te}_{0.2}$, and (c) SPS- $\text{Cu}_{1.8}\text{S}$ bulks with SEM images of the fractured surface in the inset. (d) Average grain size from SEM and the calculated one for $\text{Cu}_{1.8}\text{S}$ bulk from XRD.

respectively. The SPS-Cu_{1.8}S bulk in Fig. 2(c) shows microscale grains (2.5–6.5 μm) and the high porosity caused by the volatilization of S during the SPS process, leading to a relatively lower density of 5.424 g·cm⁻³. Figure 2(d) presents the measured average grain size of these three bulks from SEM as well as the calculated grain size for nanostructured Cu_{1.8}S from XRD data. Comparing with the large average grain size of porous SPS-Cu_{1.8}S (3.45 μm), denser Cu_{1.8}S and Cu_{1.8}S_{0.8}Te_{0.2} possess smaller average grain size of 25.5 and 25.1 nm, respectively. The calculated grain size of nanostructured Cu_{1.8}S by the Scherrer equation is about 20.1 nm, which is in reasonable agreement with the SEM results. It is demonstrated that the facile method combining MA and RT-HPS proposed in this study can effectively suppress the grain growth and obtain highly dense nanostructured Cu_{1.8}S_{1-x}Te_x samples.

Figure 3 shows the electrical transport properties of Cu_{1.8}S_{1-x}Te_x ($0 \leq x \leq 0.2$) bulks as a function of temperature. The σ in Fig. 3(a) increases initially and then decreases as increasing the measuring temperature to 623 K, showing a turning point at 423 K for Cu_{1.8}S but pushed to 473 K when $0.05 \leq x \leq 0.2$. The turning behavior is caused by the phase transition of Cu_{1.8}S from a low-temperature rhombohedral symmetry to a high-temperature cubic one, where Cu ion positions are changed [39]. The higher σ turning temperature (473 K) is attributed to the appearance of Cu_{1.96}S phase with higher phase-transition temperature according to the Cu–S phase diagram [30]. The Cu_{1.8}S bulk has the largest room-temperature σ about 2400 S·cm⁻¹ and decreases to 300 S·cm⁻¹ when x is increased to 0.2. Because $\sigma = ne\mu$, the decreased σ is dominated by the decreased $n\mu$ of the samples, which is further verified by the Hall measurement results in Fig. 4(a). The α of all the samples in Fig. 3(b) is positive, indicating a p-type transport property with $h^\bullet$ as the main carrier. The α of Cu_{1.8}S increases from 16 to 54 $\mu\text{V}\cdot\text{K}^{-1}$ upon raising temperature from 307 to 623 K. Doping Te significantly enhances the α to 90 $\mu\text{V}\cdot\text{K}^{-1}$ when x is increased to 0.2, showing an inverse varying tendency to the σ . Due to the increased α , the PF in Fig. 3(c) gets an overall enhancement with a maximum PF of 630 $\mu\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-2}$ for Cu_{1.8}S_{0.95}Te_{0.05} at 623 K.

Figure 4(a) shows the n and μ of Cu_{1.8}S_{1-x}Te_x bulk samples. The n decreases firstly from 4.87×10^{23} to 3.02×10^{23} cm⁻³ at $0 \leq x \leq 0.125$, and then increases to 4.24×10^{23} cm⁻³ when increasing x to 0.2. The initial decreased n is attributed to the increased Cu_{1.96}S

Fig. 3 Temperature dependence of electrical transport properties for Cu_{1.8}S_{1-x}Te_x bulks and the SPS-Cu_{1.8}S bulk from: (a) σ , (b) α , and (c) PF . Reproduced with permission from Ref. [8], © The Royal Society of Chemistry 2018.

phase with lower intrinsic n due to its lower Cu-deficiency than that of Cu_{1.8}S [18], whereas the latter increased n at $x \geq 0.15$ is caused by the formation of high n phase Cu_{2-z}Te [25,40] in Eq. (4). Thereby, the n of bulk samples is not determined by the introduced $h^\bullet$ in p-type Cu_{1.8}S (Eq. (3)). The monotonically decreased μ is predominantly associated with its DOS effective mass (m^*) deduced from the Hall measurements as follows.

Figure 4(b) shows the Pisarenko relationship of Cu_{1.8}S_{1-x}Te_x using a single parabolic band (SPB) model and assuming a dominated acoustic phonon scattering mechanism. The α and the n can be connected by the following equation [41,42]:

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} \left(\frac{\pi}{3n} \right)^{2/3} m^* T \quad (5)$$

Fig. 4 (a) Variation of n and μ as a function of x . (b) Pisarenko plot shows the room-temperature relationship of α and n . (c) Room-temperature optical absorption spectra of $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ indicate the decreasing E_g with increasing x . (d) Schematic representation of the band structure, including conduction band (CB) and valence band (VB).

where k_B is the Boltzmann constant, h is the Planck constant, and e is the electron charge. The result in Fig. 4(b) illustrates that the m^* is dramatically enhanced from 2.4 to 6.3 m_e when x is increased to 0.2, suggesting a modified band structure for the Te doped $\text{Cu}_{1.8}\text{S}$ alloys. Correspondingly, the μ in Fig. 4(a) decreases with increasing x according to $\mu \propto 1/m^*$ [37,43], which leads to a decreased σ as $\sigma = ne\mu$. It is reasonable that both increased m^* and decreased n would enhance the α as shown in Fig. 3(b).

Figure 4(c) plots the optical absorption spectra of $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks. The plot $(ah\nu)^2$ vs. $h\nu$ can be used to evaluate the E_g by extrapolating the straight-line to $(ah\nu)^2 = 0$ [37]. $\text{Cu}_{1.8}\text{S}$ exhibits a direct transition character with an observed E_g of 1.71 eV, which is close to the reported value of 1.75 eV [44]. When increasing x to 0.2, the E_g monotonically decreases to 1.63 eV for the $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks, whose band structure variation is simply illustrated in Fig. 4(d). Zeier *et al.* [45] proposed that larger electronegativity difference between the cationic and anionic elements in a compound leads to larger E_g . Because of the smaller electronegativity of Te (2.10) than S (2.58), the substitution of S by Te in $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks will undoubtedly contribute to a smaller E_g . Similarly

decreased E_g in Te doped Cu_2S [25] also gives a good verification. Besides, the coexisted $\text{Cu}_{1.96}\text{S}$ phase also contributes to the reduced E_g owing to its smaller E_g (1.4 eV) [46].

Figures 5(a) and 5(b) show the temperature-dependent D and κ of the $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks. The D in Fig. 5(a) increases firstly and then decreases with rising measuring temperature, whose turning behavior is at about 473 K when $0 \leq x \leq 0.1$ and becomes higher at about 523 K when $0.125 \leq x \leq 0.2$. The turning behavior at 473 K is mainly caused by the phase transition of $\text{Cu}_{1.8}\text{S}$ from a low-temperature rhombohedral symmetry to a high-temperature cubic one, which is consistent with the nanostructured $\text{Cu}_{1.8}\text{S}$ reported by Ref. [16]. The higher D turning point at 523 K is ascribed to the coexisted phase of $\text{Cu}_{1.96}\text{S}$ with higher phase-transition temperature. The κ in Fig. 5(b) shows the same trend as D and the $\text{Cu}_{1.8}\text{S}$ possesses higher κ ranging in $2.13\text{--}2.67 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ in 307–623 K. Undoubtedly, nano-grain boundaries in the $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks will strengthen phonon scatterings and contribute to a lower κ . However, the highly-dense structure of $\text{Cu}_{1.8}\text{S}$ leads to a slightly higher κ compared to the SPS- $\text{Cu}_{1.8}\text{S}$ with widely dispersed pores as shown in Fig. 2. Doping Te dramatically decreases the κ to the

lowest value of $0.82 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room temperature when $x = 0.2$. The reduced κ with increasing x is reasonable because of the decreased contribution of the κ_{carrier} in the total κ due to the decreased σ in Fig. 3(a) according to the amended Wiedemann–Franz law ($\kappa_{\text{carrier}} = L(\sigma - \sigma_i)T$ [19,25], where L and σ_i denote the Lorenz number and ion conductivity, respectively). Generally, the κ_l can be obtained by subtracting the κ_{carrier} from the measured κ , but it is difficult in the ionic conductors, because the calculation of σ_i and ion thermal conductivity is still a challenge [30]. Herein, we just give an estimation about the κ_l according to the following expression [47–49]:

$$\kappa_l = \frac{1}{3} C_v v_{\text{avg}} l \quad (6)$$

where C_v is the specific heat derived from the Dulong–Petit limit, v_{avg} is the average sound velocity calculated by $v_{\text{avg}}^{-3} = (v_l^{-3} + 2v_t^{-3})/3$, and l is the phonon mean free path. The C_v for $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ should be reduced with increasing x due to the heavier atomic weight of Te (127.6) than that of S (32.06). Figure 5(c) presents the room temperature v_l , v_t , and v_{avg} values of

$\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ and all sound velocities exhibit a decreasing trend with increasing x , which contributes to a low κ_l . Because Te is less electronegative than S, the weaker interatomic bonding between Cu and Te compared with Cu–S determines the decreasing sound velocities [45,50]. Meanwhile, multiscale defects introduced by point-defects from Te/S substitution, nano-grain boundaries, and secondary phases in the $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ also reduce l and contribute to lower κ_l [51,52]. It is reasonable that the decreased C_v , v_{avg} , and l with increasing x lead to a decreased κ_l for the $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ samples.

Figure 5(d) shows the temperature-dependent ZT of $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ and SPS- $\text{Cu}_{1.8}\text{S}$ [8] bulks. The improved PF and reduced κ produce enhanced ZT for the RT-HPSed samples at $0.05 \leq x \leq 0.2$. The room-temperature ZT is improved from 0.009 for $\text{Cu}_{1.8}\text{S}$ to 0.042 when $x = 0.2$. The slightly lower ZT of $\text{Cu}_{1.8}\text{S}$ than that of SPS- $\text{Cu}_{1.8}\text{S}$ is due to its higher κ deriving from its denser structure. The enhanced ZT ranging in 0.042–0.342 is obtained in the $x = 0.2$ sample in the whole temperature range. A maximum ZT of 0.352 is reached at 623 K for $\text{Cu}_{1.8}\text{S}_{0.875}\text{Te}_{0.125}$, which is 171% higher than that of $\text{Cu}_{1.8}\text{S}$ (0.130).

Fig. 5 Temperature dependence of thermal transport properties, sound velocities, and ZT values for $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ bulks and the SPS- $\text{Cu}_{1.8}\text{S}$ bulk from: (a) D , (b) κ , (c) sound velocity, and (d) ZT value. Reproduced with permission from Ref. [8], © The Royal Society of Chemistry 2018.

4 Conclusions

Nanostructured $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$ ($x = 0.000, 0.050, 0.100, 0.125, 0.150, 0.200$) samples with high densities were successfully fabricated by combining MA and RT-HPS, which can effectively inhibit the S element volatilization and suppress the grain growth. The phase composition varies from pure $\text{Cu}_{1.8}\text{S}$ to a coexisted $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.8}\text{S}_{1-x}\text{Te}_x$, and Cu_{2-z}Te solid solution with increasing x . The α for all the Te doped samples are dramatically enhanced due to the increased m^* from 2.4 to 6.3 m_e , resulting in an overall improved PF . Owing to the enhanced phonon scatterings introduced via Te doping, the room-temperature κ decreases significantly from 2.13 to 0.82 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ when x is increased from 0 to 0.2. A maximum ZT of 0.352 is obtained at 623 K for $\text{Cu}_{1.8}\text{S}_{0.875}\text{Te}_{0.125}$, demonstrating that Te doping is a convenient and effective way to enhance the TE properties of the $\text{Cu}_{1.8}\text{S}$ based materials.

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