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

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Abstract: Cu$_{1.8}$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 Cu$_{1.8}$S$_{1-x}$Te$_x$ (0 ≤ x ≤ 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 Cu$_{1.8}$S was obtained at x = 0, and a second Cu$_{1.96}$S phase formed in all Cu$_{1.8}$S$_{1-x}$Te$_x$ samples when 0.05 ≤ x ≤ 0.125. With further increasing x to 0.15 ≤ x ≤ 0.2, the Cu$_{2-x}$Te phase was detected and the samples consisted of Cu$_{1.8}$S, Cu$_{1.96}$S, and Cu$_{2-x}$Te phases. Benefiting from a modified band structure and the coexisted phases of Cu$_{1.96}$S and Cu$_{2-x}$Te, the power factor is enhanced in all Cu$_{1.8}$S$_{1-x}$Te$_x$ (0.05 ≤ x ≤ 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 Cu$_{1.8}$S$_{0.875}$Te$_{0.125}$, which is 171% higher than that of Cu$_{1.8}$S (0.130). The study demonstrates that doping Te is an effective strategy to improve the TE performance of Cu$_{1.8}$S based materials and the proposed facile method combing MA and RT-HPS is a potential way to fabricate nanostructured bulks.

Keywords: Cu$_{1.8}$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$_{\text{carrier}}$) and lattice thermal conductivity (κ$_{\text{l}}$), simultaneously. However, these TE parameters are strongly coupled with each other, making high ZT difficult to obtain in a straightforward way [3,4]. Enhancing power factor (PF, PF = α$^2$σ) by optimizing carrier concentration (n)
and band structure [5–8], and reducing $\kappa$ 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$_2$S$_x$, the intermediate phases including Cu$_{1.8}$S, Cu$_{1.96}$S, Cu$_{1.97}$S, and Cu$_2$S 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 Cu$_{1.8}$S is regarded as the most potential one because of its stable electrical and thermal properties according to Dennler et al. [21]. Cu$_{1.8}$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, Cu$_{1.8}$S possesses high $\sigma$ ($\sim$ 3000 S·cm$^{-1}$) due to the high mobility of copper ions in the lattice [16]. The main challenges for enhancing the TE properties of Cu$_{1.8}$S-based materials are to improve the $\alpha$ and reduce the $\kappa$. Element doping or alloying in Cu$_{1.8}$S such as Ti doping, In doping, Sb/Sn co-doping, and Bi$_2$S$_3$ compoising 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 Cu$_{1.8}$S$_{1–x}$Te$_x$ system due to greatly enhanced PF and significantly reduced $\kappa$ [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 Cu$_{1.8}$S is desirable and high TE performance can be expected based on the potential effect of band structure modification and $\kappa$ 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 Mg$_2$Si$_{1–x}$Sb$_x$ samples show significantly enhanced TE performance due to the improved PF and greatly suppressed $\kappa$ 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$_x$X ($X = S/Se$) bulk samples with depressed $\kappa_\parallel$ 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 Cu$_{1.8}$S$_{1–x}$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 Cu$_{1.96}$S and Cu$_{2–x}$Te with Te doping, the PF is enhanced in all Cu$_{1.8}$S$_{1–x}$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 Cu$_{1.8}$S$_{0.875}$Te$_{0.125}$, which is 171% higher than that of Cu$_{1.8}$S (0.130).

## 2 Experimental

Stoichiometric Cu$_{1.8}$S$_{1–x}$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 Kα radiation and the average grain size of Cu₁.₈S was calculated by the Scherrer equation. Field-emission scanning electron microscopy (FESEM, SUPRA55, 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 (Cₚ) 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 κ = DCgd, and the ZT value was determined via ZT = D²σT/κ (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 μ = σR_H, where e is the elementary charge. Longitudinal (ν₁) and transverse (ν₂) sound velocities of Cu₁.₈S₁-xTeX 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 Cu₁.₈S₁-xTeX 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 (ahv)² to 0 as a function of photon energy (hv) for the direct band-gap semiconductor of Cu₁.₈S (a, h, and v 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 Cu₁.₈S₁-xTeX (0 ≤ x ≤ 0.2) after MA. All the diffraction peaks of x = 0 powders in Fig. 1(a1) are well matched to rhombohedral Cu₁.₈S (PDF#47-1748), suggesting the formation of single-phase Cu₁.₈S without any detectable impurity phase. All the Cu₁.₈S₁-xTeX (0.05 ≤ x ≤ 0.2) powders consist of Cu₁.₈S host phase and tetragonal Cu₁.₉₆S (●, PDF#29-0578) phase, while the diffraction intensity of Cu₁.₉₆S increases at 0.05 ≤ x ≤ 0.1 and then maintains similar at 0.1 ≤ x ≤ 0.2 as shown in Fig. 1(a2). Apart from Cu₁.₈S and Cu₁.₉₆S, some peaks of hexagonal Cu₂-xTeX (●, PDF#06-0661) phase in Fig. 1(a2) are detected with an increased intensity at 0.15 ≤ x ≤ 0.2, which attributes to the excessive addition of Te. Along with
the variation of the phase structure, a peak shift in Fig. 1(a3) is observed in the Cu1.8S host phase but absent in Cu1.96S and Cu2−zTe. The enlarged (0120)Cu1.8S peaks in Fig. 1(a3) at 0.05 ≤ x ≤ 0.2 shift toward a low diffraction angle with increasing x, suggesting an enlarged lattice of the Cu1.8S host phase, which is ascribed to the larger ionic radius of Te2− (2.21 Å) compared with that of S2− (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 ≤ x ≤ 0.2, which can be mainly ascribed to the peak superposition of the Cu1.96S with Cu1.8S host phase.

Figure 1(b) shows the XRD patterns of Cu1.8S1−xTex bulks and the reported Cu1.8S synthesized by SPS (SPS-Cu1.8S) [8], in which all Cu1.8S1−xTex 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):

\[ xTe \rightarrow Cu_{1.8}S \rightarrow Cu_{1.8}Cu + (1 - x)S_x + xTe_x \]  
\[ xTe \rightarrow Cu_{1.8}S \rightarrow \alpha Cu_{1.96}S + \beta Cu_{1.8-y}S_{1-x}Te_x \]  
\[ Cu_{1.8-y}S_{1-x}Te_x \rightarrow Cu_{1.8}S \rightarrow (1.8 - y)Cu_{1.8}S + (1 - x)S_x + xTe_x + yV_{Cu} + yh^* \]  
\[ xTe \rightarrow Cu_{1.8}S \rightarrow \alpha Cu_{1.96}S + \beta Cu_{1.8-y}S_{1-x}Te_x + \gamma Cu_{2-z}Te \]  

where x is the added Te content based on the stoichiometric ratio of Cu1.8S1−xTex (x = 0, 0.05, 0.10, 0.125, 0.15, and 0.2), y is the content of Cu-deficiency in Cu1.8−yS1−xTex. Equation (1) describes the substitution of Te for S in the Cu1.8S lattice. With further increasing x, Cu-rich Cu1.96S second phase and the Cu-poor Cu1.8−yS1−xTex matrix phase would be formed as shown in Eq. (2). The formation of Cu1.8−yS1−xTex would generate holes (h*) and vacancies (V_{Cu}*) in Cu1.8S lattice as shown in Eq. (3). Equation (4) describes the formation of coexisted Cu1.8−yS1−xTex, Cu1.96S, and Cu2−zTe phases when 0.15 ≤ x ≤ 0.2. Considering the different intrinsic n of the coexisted phases and the introduced h* 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 Cu1.8S, Cu1.8S0.8Te0.2, and previously synthesized SPS-Cu1.8S [29] bulks, along with insets showing the corresponding SEM images of the fractured surface. Both Cu1.8S and Cu1.8S0.8Te0.2 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 g·cm−3 (relative densities are over 98%),

![Fig. 2](image-url)
respectively. The SPS-Cu1.8S 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 Cu1.8S from XRD data. Comparing with the large average grain size of porous SPS-Cu1.8S (3.45 μm), denser Cu1.8S and Cu1.8S0.8Te0.2 possess smaller average grain size of 25.5 and 25.1 nm, respectively. The calculated grain size of nanostructured Cu1.8S 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 Cu1.8S₁₋ₓTex samples.

Figure 3 shows the electrical transport properties of Cu1.8S₁₋ₓTex (0 ≤ x ≤ 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 Cu1.8S but pushed to 473 K when 0.05 ≤ x ≤ 0.2. The turning behavior is caused by the phase transition of Cu1.8S 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 Cu1.96S phase with higher phase-transition temperature according to the Cu–S phase diagram [30]. The Cu1.8S 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 σ = neμ, the decreased σ is dominated by the decreased n 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* as the main carrier. The α of Cu1.8S increases from 16 to 54 μV·K⁻¹ upon raising temperature from 307 to 623 K. Doping Te significantly enhances the α to 90 μV·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 μW·m⁻¹·K⁻² for Cu1.8S0.95Te0.05 at 623 K.

Figure 4(a) shows the n and μ of Cu1.8S₁₋ₓTex bulk samples. The n decreases firstly from 4.87 × 10²³ to 3.02 × 10²³ cm⁻³ at 0 ≤ x ≤ 0.125, and then increases to 4.24 × 10²³ cm⁻³ when increasing x to 0.2. The initial decreased n is attributed to the increased Cu1.96S phase with lower intrinsic n due to its lower Cu-deficiency than that of Cu1.8S [18], whereas the latter increased n at x ≥ 0.15 is caused by the formation of high n phase Cu2–zTe [25,40] in Eq. (4). Thereby, the n of bulk samples is not determined by the introduced h* in p-type Cu1.8S (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 Cu1.8S₁₋ₓTex 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]:

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

(5)
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 Cu$_{1.8}$S alloys. Correspondingly, the $\mu$ in Fig. 4(a) decreases with increasing $x$ according to $\mu \propto 1/ m^* \ [37,43]$, which leads to a decreased $\sigma$ as $\sigma = ne\mu$. It is reasonable that both increased $m^*$ and decreased $n$ would enhance the $\alpha$ as shown in Fig. 3(b).

Figure 4(c) plots the optical absorption spectra of Cu$_{1.8}$S$_{1-x}$Te$_x$ bulks. The plot $(a\nu)^2$ vs. $\nu$ can be used to evaluate the $E_g$ by extrapolating the straight-line to $(a\nu)^2 = 0 \ [37]$. Cu$_{1.8}$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 Cu$_{1.8}$S$_{1-x}$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 Cu$_{1.8}$S$_{1-x}$Te$_x$ bulks will undoubtedly contribute to a smaller $E_g$. Similarly decreased $E_g$ in Te doped Cu$_2$S \ [25] also gives a good verification. Besides, the coexisted Cu$_{1.96}$S phase also contributes to the reduced $E_g$ owning to its smaller $E_g$ (1.4 eV) \ [46].

Figures 5(a) and 5(b) show the temperature-dependent $D$ and $\kappa$ of the Cu$_{1.8}$S$_{1-x}$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 Cu$_{1.8}$S from a low-temperature rhombohedral symmetry to a high-temperature cubic one, which is consistent with the nanostructured Cu$_{1.8}$S reported by Ref. \ [16]. The higher $D$ turning point at 523 K is ascribed to the coexisted phase of Cu$_{1.96}$S with higher phase-transition temperature. The $\kappa$ in Fig. 5(b) shows the same trend as $D$ and the Cu$_{1.8}$S possesses higher $\kappa$ ranging in 2.13–2.67 W·m$^{-1}$·K$^{-1}$ in 307–623 K. Undoubtedly, nano-grain boundaries in the Cu$_{1.8}$S$_{1-x}$Te$_x$ bulks will strengthen phonon scatterings and contribute to a lower $\kappa$. However, the highly-dense structure of Cu$_{1.8}$S leads to a slightly higher $\kappa$ compared to the SPS-Cu$_{1.8}$S with widely dispersed pores as shown in Fig. 2. Doping Te dramatically decreases the $\kappa$ to the
lowest value of 0.82 W·m⁻¹·K⁻¹ at room temperature when \( x = 0.2 \). The reduced \( \kappa \) with increasing \( x \) is reasonable because of the decreased contribution of the \( \kappa_{\text{carrier}} \) in the total \( \kappa \) due to the decreased \( \sigma \) in Fig. 3(a) according to the amended Wiedemann–Franz law \( (\kappa_{\text{carrier}} = L(\sigma - \sigma_i)T) \) [19,25], where \( L \) and \( \sigma_i \) denote the Lorenz number and ion conductivity, respectively). Generally, the \( \kappa_l \) can be obtained by subtracting the \( \kappa_{\text{carrier}} \) from the measured \( \kappa \), but it is difficult in the ionic conductors, because the calculation of \( \sigma_i \) and ion thermal conductivity is still a challenge [30]. Herein, we just give an estimation about the \( \kappa_l \) according to the following expression [47–49]:

\[
\kappa_l = \frac{1}{3} C_v v_{\text{avg}} l
\]

where \( C_v \) is the specific heat derived from the Dulong–Petit limit, \( v_{\text{avg}} \) is the average sound velocity calculated by \( v_{\text{avg}}^3 = (v_1^{-3} + 2v_1^{-3})/3 \), and \( l \) is the phonon mean free path. The \( \kappa_l \) 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 \( v_1, v_1, \) and \( v_{\text{avg}} \) 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 \( \kappa \). 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 \( \kappa_l \) [51,52]. It is reasonable that the decreased \( C_v, v_{\text{avg}}, \) and \( l \) with increasing \( x \) lead to a decreased \( \kappa_l \) 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 \( \kappa \) 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 \( \kappa \) 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).

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

Nanostructured Cu$_{1.8}$S$_{1-x}$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 Cu$_{1.8}$S to a coexisted Cu$_{1.96}$S, Cu$_{1.8}$S$_{1-x}$Te$_x$, and Cu$_{2-x}$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 me, resulting in an overall improved PF. Owning to the enhanced phonon scatterings introduced via Te doping, the room-temperature κ decreases significantly from 2.13 to 0.82 W·m$^{-1}$·K$^{-1}$ when x is increased from 0 to 0.2. A maximum ZT of 0.352 is obtained at 623 K for Cu$_{1.8}$S$_{0.875}$Te$_{0.125}$, demonstrating that Te doping is a convenient and effective way to enhance the TE properties of the Cu$_{1.8}$S based materials.

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