Thermoelectric properties of S and Te-doped Cu₂SnSe₃ prepared by combustion synthesis

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ABSTRACT
S and Te-doped Cu₂SnSe₃ samples with chemical formula of Cu₂SnSe₃₊ₓSₓ and Cu₂SnSe₃₋ₓTeₓ (x = 0.05, 0.10, 0.15, 0.20) are prepared, and the effect of S and Te-doping on thermoelectric properties is investigated. In all the samples, the Cu₂SnSe₃ phase is synthesized as the major product, and its lattice parameters decrease with S-doping but increase with Te-doping. EDS analysis confirms the incorporation of S and Te dopants in the Cu₂SnSe₃ phase, and reveals an element segregation in the Te-doped samples. S- and Te-doping decreases the electrical conductivity, enhance the Seebeck coefficient, and reduce the thermal conductivity. S-doping is effective to improve the ZT of Cu₂SnSe₃, and the Cu₂SnSe₃₋ₓSₓ sample with x = 0.05 shows a ZT of 0.66 at 773 K, which is improved by more than 50% compared with that of the undoped sample. On the contrary, Te-doping leads to decreased ZT values owing to the significant reduction in electrical conductivity.

1. Introduction
Thermoelectric materials enable direct conversion between heat and electricity, and may be used for solar thermal energy conversion and waste heat recovery [1]. The efficiency of thermoelectric materials depends on the dimensionless figure of merit (ZT), defined as $ZT = (S^2\sigma/k)T$, where $S$, $\sigma$, $k$, and $T$ are Seebeck coefficient, electrical conductivity, thermal conductivity, and the absolute temperature, respectively. A larger ZT leads to a higher efficiency, and up to now most studies on thermoelectric materials have been focused on increasing ZT [2–7]. Besides ZT, however, the cost is also of great concern for industrial applications [8]. In order to reduce the cost, new thermoelectric materials composed of less expensive and nontoxic elements should be developed, in which Cu₂SnSe₃ is a good example that has drawn much interest recently [9–12].

Cu₂SnSe₃ is a p-type semiconductor with a narrow gap and can crystallize into a cubic or monoclinic phase depending on the synthesis conditions [13–18]. In Cu₂SnSe₃, the Cu-Se bonds stabilize the structure and form an electrically conductive framework, and Sn atoms reside in the framework and donate electrons to balance the structure [9]. Such a structure is similar to the phonon glass electron crystal (PGEC) [19] compounds and contributes to the intrinsic low thermal conductivity. The thermoelectric properties of Cu₂SnSe₃ can be improved by doping, and a ZT of 1.42 at 823 K has been realized by (Ag+In)-co-doping [20]. Up to now, most studies on Cu₂SnSe₃ are focused on doping at the cation sites [21–26], and doping at Se site is little reported.

This work makes an investigation on the effect of doping at Se site in Cu₂SnSe₃. S and Te-doped Cu₂SnSe₃ samples with chemical formula of Cu₂SnSe₃₊ₓSₓ and Cu₂SnSe₃₋ₓTeₓ are prepared, and the effects of S and Te-doping on the microstructure and thermoelectric properties of the samples are discussed.

2. Experimental
The element powders of Cu (99.9%, 300 mesh), Sn (99.99%, 200 mesh), Se (99.99%, 200 mesh), S (99.9%, 100 mesh), and Te (99.99%, 200 mesh) were weighed and mixed in an agate mortar according to the formula of Cu₂SnSe₃₊ₓSₓ and Cu₂SnSe₃₋ₓTeₓ (x = 0.05, 0.10, 0.15, 0.20), as shown in Table 1. Each batch of 200 g powder mixture was cold-pressed into a cylindrical compact with a diameter of 40 mm. The porosity of the compact was about 45%. The compact was loaded into a quartz crucible, and the crucible was placed into a steel reaction chamber and supported by a graphite substrate. A tungsten coil was fixed closely above the top of the reactant compact. The reaction chamber was closed and evacuated, and subsequently filled with Ar gas up to a pressure of 2 MPa. By passing an electric current of 10 A for 2 s through the tungsten coil, the reactant compact was ignited and then continued to burn in a self-sustained way, with the combustion front moving throughout the sample. After the reaction was over, the sample was naturally cooled down to room temperature.
Table 1. Bulk densities of the synthesized \( \text{Cu}_2\text{SnSe}_3\) and \( \text{Cu}_2\text{SnSe}_3\) samples.

| Chemical composition | Density (g/cm\(^3\)) |
|----------------------|----------------------|
| \( \text{Cu}_2\text{SnSe}_3\)     |                      |
| \( x = 0.05\)       | 5.72                 |
| \( x = 0.10\)       | 5.68                 |
| \( x = 0.15\)       | 5.67                 |
| \( x = 0.20\)       | 5.65                 |
| \( \text{Cu}_2\text{SnSe}_3\)     |                      |
| \( x = 0.05\)       | 5.72                 |
| \( x = 0.10\)       | 5.74                 |
| \( x = 0.15\)       | 5.75                 |
| \( x = 0.20\)       | 5.77                 |

in the reaction chamber, then taken out and machined for later characterizations and measurements.

The bulk density of the samples was measured according to the Archimedes principle by immersing the samples into deionized water at room temperature. The crystalline phase assemblage of the samples was identified by powder X-ray diffraction (XRD; D8 Focus, Bruker, Germany), using Cu-K\(\alpha\) radiation (\(\lambda = 1.5418\) Å) and with a scanning step of 0.02° and scanning rate of 6°/min. The microstructure for polished surface of samples was examined by scanning electron microscopy (SEM; S-4800, Hitachi, Japan), and energy dispersive spectroscopy (EDS; INCA, Oxford Instrument, UK) was used for chemical composition analysis. The electrical conductivity (\(\sigma\)) and the Seebeck coefficient (\(S\)) were measured using LSR-3 (Linseis, Germany) in a static He atmosphere using sample bars of 15 × 2 × 2 mm\(^3\). The electrical conductivity was measured by the standard DC four-probe method, and the Seebeck coefficient was determined from the slope of the thermoelectromotive force versus temperature gradient. The thermal diffusivity (\(\lambda\)) was measured by a laser flash method (LFA 457, Netzsch, Germany) using sample discs with a diameter of 10 mm and thickness of 1.5 mm, where the sample surface was coated with carbon before measurement. The thermal conductivity (\(\kappa\)) was calculated according to the relationship of \(\kappa = \lambda C_p \rho\), where \(C_p\) is the specific heat capacity referred to the Dulong–Petit approximation and \(\rho\) is the bulk density measured by the Archimedes method.

### 3. Results and discussion

After combustion synthesis, dense bulk samples were obtained for all the investigated compositions and the densities of the samples are listed in Table 1. The densities of the samples lie in the range of 5.65–5.77 g/cm\(^3\), which are close to the theoretical density of 5.82 g/cm\(^3\) for \( \text{Cu}_2\text{SnSe}_3 \) [17]. The densities of the S-doped samples (\( \text{Cu}_2\text{SnSe}_3\)\(_{3-x}\)\(\text{S}_x\)) are slightly lower and decrease with increasing content of S. On the contrary, the densities of the Te-doped samples (\( \text{Cu}_2\text{SnSe}_3\)\(_{3-x}\)\(\text{Te}_x\)) are higher and increase with increasing content of Te. The influence of S and Te-doping on sample densities can be explained by the difference in atomic weight of S (32.1), Te (127.6), and Se (79.0).

The XRD patterns of as-synthesized S and Te-doped \( \text{Cu}_2\text{SnSe}_3 \) samples are shown in Figure 1. In all the samples, the \( \text{Cu}_2\text{SnSe}_3 \) phase is synthesized as the major product, except for minor impurity phase of SnSe. For the S-doped samples (\( \text{Cu}_2\text{SnSe}_3\)\(_{3-x}\)\(\text{S}_x\)), a clear shift of diffraction peaks toward larger angles is observed with increasing \(x\) values, indicating that the substitution of Se with S leads to a decrease in lattice parameters. This is reasonable because the ionic radius of S\(^2\) is smaller than that of Se\(^2\). On the contrary, for the Te-doped samples (\( \text{Cu}_2\text{SnSe}_3\)\(_{3-x}\)\(\text{Te}_x\)), the diffraction peaks shift toward smaller angles with increasing \(x\) values, which implies that Te-doping results in an increase in lattice parameters, owing to the larger ionic radius of Te\(^2\) compared with that of Se\(^2\).

Figure 2 shows SEM images and EDS results of a S-doped sample with the nominal composition of \( \text{Cu}_2\text{SnSe}_{2.85}\text{S}_{0.15} \). In the back-scattered electron images, the presence of a secondary phase in bright contrast is clear. The EDS mapping reveals that the secondary phase is rich in Sn but does not contain Cu. From these results, the bright secondary phase...
should be SnSe, which agrees well with the phase assemblage of the sample identified by XRD analysis (Figure 1 (a)). In general, the thermal conductivity of SnSe is lower than Cu$_2$SnSe$_3$, and therefore the dispersion of SnSe inclusions in the Cu$_2$SnSe$_3$ matrix will reduce the thermal conductivity of the samples. The influence of SnSe on the electrical properties of the samples is complex, because SnSe usually shows a smaller electrical conductivity but larger Seebeck coefficient than Cu$_2$SnSe$_3$. In order to verify the existence of the doped S element in the sample, EDS analysis is carried out for five individual areas of larger than 3 × 2 mm$^2$ on well-polished surface, giving a result of S/(S+Se) = 0.040 ± 0.001 in atomic ratio. As a result, an EDS spectrum together with the selected area for analysis and a photo of the polished sample are shown in Figure 2 (d). From the EDS results, the doped S element is actually incorporated into the sample, and the S/(S+Se) ratio (0.04) is close to the nominal value of 0.05. The slight lower ratio of S/(S+Se) is probably caused by the evaporation loss of S during the synthesis because the reaction temperature [12] is usually much higher than the boiling point of S (718 K).

The SEM images and EDS results of a Te-doped sample with the nominal composition of Cu$_2$SnSe$_{2.85}$Te$_{0.15}$ is shown in Figure 3. Both the backscattered electron image and the EDS mapping reveal the presence of a secondary phase. From the EDS results and combining the XRD patterns, the secondary phase is SnSe or more exactly Te-doped SnSe that can be expressed as SnSe$_{1-x}$Te$_x$. It is noted that the segregation of Te element occurs in the sample. As shown in Figure 3 (d) and (e), in the Cu$_2$SnSe$_{3-x}$Te$_x$ matrix the atomic ratio Te/(Se+Te) is 0.053 and close to the nominal value of 0.05, but in the SnSe$_{1-x}$Te$_x$ secondary phase the Te/(Se +Te) ratio is much higher and reaches 0.212. It is interesting that even in the SnSe$_{1-x}$Te$_x$ phase itself element segregation still exists. From the EDS mapping, Te-rich and Se-rich regions with different contrast can be readily
distinguished in the SnSe$_{1-x}$Te$_x$ phase. The observed element segregation in the sample is possibly connected with the fast reaction characteristics of combustion synthesis, where the compositional homogenization by atomic diffusion is depressed because the dwelling time at high temperature is short.

The electrical and thermal transport properties of the Cu$_2$SnSe$_{3-x}$S$_x$ samples in a temperature range of 323–773 K are shown in Figure 4. In comparison with the un-doped Cu$_2$SnSe$_3$ sample, S-doping leads to decreased electrical conductivity and enhanced Seebeck coefficient. It is noteworthy that the dependence of electrical conductivity on the concentration of S (x) is not monotonic but complex, and the lowest electrical conductivity is observed for the sample with x = 0.10. In general, the electrical conductivities of the Cu$_2$SnSe$_{3-x}$S$_x$ samples lie in the range of 1.6–2.5 × 10$^4$ Sm$^{-1}$ at 323 K and 1.0–1.4 × 10$^4$ Sm$^{-1}$ at 773 K. The Seebeck coefficient of the Cu$_2$SnSe$_{3-x}$S$_x$ samples also shows a complex dependence on the x value, and the maximum Seebeck coefficient reaches 230 μVK$^{-1}$ at 773 K. Owing to the enhanced Seebeck coefficients, the Cu$_2$SnSe$_{3-x}$S$_x$ samples exhibit larger power factors than the un-doped sample, despite the lower electrical conductivities. The sample with x = 0.10 shows the largest power factor of 5.7 × 10$^{-4}$ Wm$^{-1}$K$^{-2}$ at 773 K, which is improved by nearly 20% compared with the un-doped sample.

The thermal conductivity of the samples decreases with increasing temperature. The thermal conductivities of the Cu$_2$SnSe$_{3-x}$S$_x$ samples are lower than the un-doped Cu$_2$SnSe$_3$ sample, indicating that S-doping helps to reduce the thermal conductivity. At 773 K, the thermal conductivity of the Cu$_2$SnSe$_{3-x}$S$_x$ sample with x = 0.05 is below 0.6 Wm$^{-1}$K$^{-1}$ and about 40% lower than that of the un-doped sample. The reduction of thermal conductivity by S-doping may be attributed to the distortion and diminished uniformity of the lattice structure, which will enhance the scattering of phonons. Because of the increase in power factor and decrease in thermal conductivity, the Cu$_2$SnSe$_{3-x}$S$_x$ samples show higher ZT values than that of the un-doped Cu$_2$SnSe$_3$ sample. The sample with x = 0.05 exhibits the maximum ZT of 0.66 at 773 K, which is improved by more than 50% compared with that of the un-doped sample. This means that S-doping is effective to improve the ZT of Cu$_2$SnSe$_3$ materials, and from the experimental data the optimum concentration of S-dopant (expressed as S/(S+Se) atomic ratio) is in the range of 0.05–0.10.

The electrical and thermal transport properties of the Cu$_2$SnSe$_{3-x}$Te$_x$ samples in a temperature range of 323–773 K are shown in Figure 5. Similar to S-doping, Te-doping results in a decrease in electrical conductivity and increase in Seebeck coefficient. The electrical conductivity of the Cu$_2$SnSe$_{3-x}$Te$_x$ samples decreases with increasing x values, and for the samples with x ≥ 0.15 the electrical conductivity is below 0.5 × 10$^4$ Sm$^{-1}$ in the whole temperature range of 323–773 K. The Seebeck coefficient of the Cu$_2$SnSe$_{3-x}$Te$_x$ samples increases with increasing x values, and reaches the maximum of

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**Figure 3.** SEM images and EDS results for the polished surface of the Cu$_2$SnSe$_{2.85}$Te$_{0.15}$ sample: (a) SEM image in back-scattered electron mode; (b) and (c) EDS mapping; (d) and (e) EDS spectra of the matrix (grey) and the secondary phase (bright), respectively.

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288 μVK−1 at 723 K, which is more than twice that of the un-doped sample. With reduced electrical conductivities and enhanced Seebeck coefficients, the Cu₂SnSe₃₋ₓTeₓ samples show power factors larger at lower temperatures but smaller at higher temperatures than those of the un-doped sample.

The thermal conductivities of the Cu₂SnSe₃₋ₓTeₓ samples are lower than that of the un-doped Cu₂SnSe₃ sample, indicating that Te-doping reduces the thermal conductivity. The lowest thermal conductivity of the Cu₂SnSe₃₋ₓTeₓ samples at 773 K is 0.66 Wm⁻¹K⁻¹ and about 20% lower than that of the un-doped sample. The effect of reducing thermal conductivity by Te-doping is analogous to that by S-doping, and should be connected with enhanced scattering of phonons because of the distortion and diminished uniformity of the lattice structure. The ZT values of the Cu₂SnSe₃₋ₓTeₓ samples are higher at lower temperatures but lower at higher temperatures than those of the un-doped sample, similar to the trend of power factor. The maximum ZT values of the Cu₂SnSe₃₋ₓTeₓ samples at 773 K are all lower than that of the un-doped sample. From the experimental data, Te-doping is not effective to improve the ZT of Cu₂SnSe₃, and the major drawback of Te-doping is the much-reduced electrical conductivity. Nevertheless, Te-doping still remains a possible way to the tailoring of thermoelectric properties of Cu₂SnSe₃ if it can be combined with other methods (e.g., In-doping) that can greatly increase the electrical conductivity, which will be investigated in detail in our future work.

4. Conclusion

S and Te-doped Cu₂SnSe₃ samples with chemical formula of Cu₂SnSe₃₋ₓSₓ and Cu₂SnSe₃₋ₓTeₓ (x = 0.05, 0.10, 0.15, 0.20) are prepared by combustion synthesis. In all the samples, the Cu₂SnSe₃ phase is synthesized as the major product, and its lattice parameters decrease with S-doping but increase with Te-doping. EDS analysis confirms that S and Te dopants are actually

Figure 4. Temperature dependence of the electrical resistivity (σ), Seebeck coefficient (S), power factor (PF), thermal conductivity (κ), and ZT of the Cu₂SnSe₃₋ₓSₓ samples.
incorporated into the Cu$_2$SnSe$_3$ phase, and reveals the existence of element segregation in the Te-doped samples. The thermoelectric properties of the samples are measured in a temperature range of 323–773 K, and the effect of S and Te-doping is investigated. It is found that S and Te-doping decrease the electrical conductivity, enhance the Seebeck coefficient, and reduce the thermal conductivity. S-doping is effective to improve the ZT of Cu$_2$SnSe$_3$, where the Cu$_2$SnSe$_3$$_x$S$_{1-x}$ sample with $x = 0.05$ shows a ZT of 0.66 at 773 K, which is improved by about 50% compared with that of the un-doped sample. On the contrary, Te-doping leads to a decrease in ZT because it causes a significant reduction in electrical conductivity.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**References**

1. Snyder GJ, Toberer ES. Complex thermoelectric materials. Nature Mater. 2008;7:105–114.
2. Du B, Zhang R, Chen K, et al. The impact of lone-pair electrons on the lattice thermal conductivity of the
thermoelectric compound CuSbS$_2$. J Mater Chem A. 2017;5:3249–3259.
3. Zhang R, Chen K, Du B, et al. Screening for Cu–S based thermoelectric materials using crystal structure features. J Mater Chem A. 2017;5:5013–5019.
4. Zhang Q, Xin A, Wang L, et al. Improved thermoelectric performance of silver nanoparticles-dispersed Bi$_2$Te$_3$ composites deriving from hierarchical two-phased heterostructure. Adv Funct Mater. 2015;25:966–976.
5. Yu GH, Xu YL, Liu ZH, et al. Recent progress in Heusler-type magnetic shape memory alloys. Rare Metals. 2015;34:527–539.
6. Zhang Q, Wang W, Jianlin L, et al. Preparation and thermoelectric properties of multi-walled carbon nanotube/polyaniline hybrid nanocomposites. J Mater Chem A. 2013;1:12109–12114.
7. Zhang K, Zhang Q, Wang L, et al. Enhanced thermoelectric performance of Se-doped PbTe bulk materials via nanostructuring and multi-scale hierarchical architecture. J Alloy Compd. 2017;725:563–572.
8. Gaultois MW, Sparks TD, Borg CKH, et al. Data-driven review of thermoelectric materials: performance and resource considerations. Chem Mater. 2013;25:2911–2920.
9. Shi X, Xi L, Fan J, et al. Cu–Se bond network and thermoelectric compounds with complex diamondlike structure. Chem Mater. 2010;22:6029–6031.
10. Ibanez M, Cadavid D, Anselmi-Tamburini U, et al. Colloidal synthesis and thermoelectric properties of Cu$_2$SnSe$_3$ nanocrystals. J Mater Chem A. 2013;1:1421–1426.
11. Fan J, Carrillo-Cabrera W, Akselrud L, et al. New monochalcogenidic phase at the composition Cu$_2$SnSe$_3$ and its thermoelectric properties. Inorg Chem. 2013;52:11067–11074.
12. Liu G, Chen K, Jiangtao L, et al. Combustion synthesis of Cu$_2$SnSe$_3$ thermoelectric materials. J Eur Ceram Soc. 2016;36:1407–1415.
13. Scott W. Some properties of Cu$_2$SnSe$_3$, Cu$_2$GeSe$_3$, and other A$_2$Bi$_x$C$_y$ compounds. J Elec Mater. 1974;3:209–223.
14. Marcano G, Rincon C, Chalbaud LM, et al. Crystal growth and structure, electrical, and optical characterization of the semiconductor Cu$_2$SnSe$_3$. J Appl Phys. 2001;90:1847–1853.
15. Choi SG, Kang J, Li J, et al. Optical function spectra and bandgap energy of Cu$_2$SnSe$_3$. Appl Phys Lett. 2015;106:043902.
16. Marcano G, Chalbaud LM, Rincon C, et al. Crystal growth and structure of the semiconductor Cu$_2$SnSe$_3$, Mater Lett. 2002;53:151–154.
17. Delgado GE, Mora AJ, Marcano G, et al. Crystal structure refinement of the semiconducting compound Cu$_2$SnSe$_3$ from X-ray powder diffraction data. Mater Res Bull. 2003;38:1949–1955.
18. Gulay LD, Daszkiewicz M, Ostayuk TA, et al. Monoclinic Cu$_2$Se$_2$Sn. Acta Crystallogr C. 2010;66:158–160.
19. Slack GA. Chapter 34. New materials and performance limits for thermoelectric cooling. In: Rowe DM, editor. CRC handbook of thermoelectrics. Boca Raton: CRC Press; 1995. p. 407.
20. Yuyang L, Liu G, Cao T, et al. Enhanced thermoelectric properties of Cu$_2$SnTe$_3$ by (Ag, In)-co-doping. Adv Funct Mater. 2016;26:6025–6032.
21. Skoug EJ, Cain JD, Morelli DT. Thermoelectric properties of the Cu$_2$SnSe$_3$–Cu$_2$GeSe$_3$ solid solution. J Alloy Compd. 2010;506:18–21.
22. Lu X, Morelli D. Thermoelectric Properties of Mn-Doped Cu$_2$SnSe$_3$. J Electron Mater. 2012;41:1554–1558.
23. Fan J, Liu H, Shi X, et al. Investigation of thermoelectric properties of Cu$_2$Ga$_x$Sn$_{1-x}$Se$_3$ diamond-like compounds by hot pressing and spark plasma sintering. Acta Mater. 2013;61:4297–4304.
24. Raju C, Falmbigl M, Rogl P, et al. Thermoelectric properties of Zn doped Cu$_2$SnSe$_3$. Mater Chem Phys. 2014;147:1022–1028.
25. Zhang A, Chen Q, Yao W, et al. Large-scale colloidal synthesis of co-doped Cu$_2$SnSe$_3$ nanocrystals for thermoelectric applications. J Electron Mater. 2016;45:1935–1941.
26. Li Y, Liu G, Li J, et al. High thermoelectric performance of In-doped Cu$_2$SnSe$_3$ prepared by fast combustion synthesis. New J Chem. 2016;40:5394–5400.