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Are Cu$_2$Te-Based Compounds Excellent Thermoelectric Materials?

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Most of the state-of-the-art thermoelectric (TE) materials exhibit high crystal symmetry, multiple valleys near the Fermi level, heavy constituent elements with small electronegativity differences, or complex crystal structure. Typically, such general features have been well observed in those well-known TE materials such as Bi$_2$X$_3$, SnX$_2$, and PbX-based compounds (X = S, Se, and Te). The performance is usually high in the materials with heavy constituent elements such as Te and Se, but it is low for light constituent elements such as S. However, there is a great abnormality in Cu$_2$X-based compounds in which Cu$_2$Te has much lower TE figure of merit (zT) than Cu$_2$S and Cu$_2$Se.

It is demonstrated that the Cu$_2$Te-based compounds are also excellent TE materials if Cu deficiency is sufficiently suppressed. By introducing Ag$_2$Te into Cu$_2$Te, the carrier concentration is substantially reduced to significantly improve the zT with a record-high value of 1.8, 323% improvement over Cu$_2$Te and outperforms any other Cu$_2$Te-based materials. The single parabolic band model is used to further prove that all Cu$_2$X-based compounds are excellent TE materials. Such finding makes Cu$_2$X-based compounds the only type of material composed of three sequent main group elements that all possess very high zTs above 1.5.

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Cu₂Se. This is in contradiction with the general trend observed according to the literatures. Our XRD data show that it transitions from its melting point to room temperature. Although to control material’s quality, especially it has at least five phase transitions around 1.1, which is much smaller than those in Cu₂S and the other hand, Cu₂Te has too complex phase diagram to constitute excellent TE materials when their lattice defects and phase transition features are well tuned and optimized.

Cu₂Te has too large hole concentrations (pH) due to the presence of large amount of intrinsic Cu deficiency. Improving Cu amount can lower the Cu deficiency within a certain range but such reduction is very limited. Previous study showed that the vacancy formation energies of Ag₂Te are gradually decreased after the substitution of Cu at Ag sites. As a result, the carrier concentration of Ag₂₋₆Cu₂Te is gradually increased upon increasing the Cu contents. Since Ag₂Te has the similar cubic structure as Cu₂Te at high temperature, we thus expect the carrier concentration of Cu₂Te can be reduced by alloying Ag at Cu sites. Thus, herein we try to choose Ag to replace Cu to balance the Cu deficiency. The room temperature X-ray diffraction (XRD) patterns measured on powder Cu₂Te + x% Ag₂Te (x = 0, 15, 35, 40, 50, and 55) are depicted in Figure 2a. The phase compositions of pristine Cu₂Te are very complicated according to the literatures. Our XRD data show that it consists of multiple phases, including hexagonal, monoclinic, and orthorhombic phases (Figure S1, Supporting Information). After introducing Ag₂Te into Cu₂Te, some new diffraction peaks appear in the XRD patterns, which are mainly indexed to the hexagonal CuAgTe phase. These data show that it is inclined to form secondary phase rather than forming solid-solutions at room temperature for Cu₂Te + x% Ag₂Te. Similar phenomenon was also observed in Cu₂Se-Ag₂Se and Cu₂S-Ag₂S systems. However, pure phase is observed after going through the phase transitions at high temperatures. As demonstrated in Figure 2b, nearly all the diffraction peaks at 900 K can be indexed to the Cu₂Te cubic structure (PDF#053116) with the space group of F43m. This suggests that all the samples transform into single cubic phase at high temperatures and the second phase at room temperature dissolve into the matrix after the final structural transition. Besides, the diffraction peaks are shifted to a lower angle upon increasing the Ag₂Te content, indicating that the lattice constants increase with the increase of Ag₂Te content.

Figure 2c plots the measured differential scanning calorimetry (DSC) curves for Cu₂Te + x% Ag₂Te (x = 0, 15, 35, 50, and 55). For Cu₂Te, five successive phase transitions are observed with the transition temperatures somewhat different from the literatures due to its complex phase compositions. The number and temperature of phase transition, and peak intensity of DSC curves are all changed when adding Ag into Cu₂Te. Specifically, the temperature of the last phase transition between hexagonal phase and cubic phase is weakened and lowered from 815 K in Cu₂Te to 720 K in Cu₂Te + 15% Ag₂Te, and finally disappears in Cu₂Te + 55% Ag₂Te (see Figure 2d). This is also consistent with that Ag is dissolved into the Cu₂Te matrix with increasing the temperature. Such reduced phase transition temperature Tc is mainly attributed to the decreased ratio of the enthalpy change ΔH to the entropy change ΔS.

Figure 3 displays the temperature dependence of TE properties for Cu₂Te + x% Ag₂Te (x = 0, 15, 35, 40, 50, and 55). When x is less than 50, the electrical conductivity σ decreases in the entire temperature range as the content of Ag₂Te increases. Specifically, the room temperature σ decreases significantly from 4.2 × 10⁵ S m⁻¹ for Cu₂Te to 1.0 × 10⁵ S m⁻¹ for Cu₂Te + 50% Ag₂Te. The reverse trend at around x = 55 may be related to the decreased band gap Eg since CuAgTe has a much lower Eg than that of Cu₂Te. As the temperature increases, the electrical conductivity is roughly decreased except for the phase transition regions, behaving as a highly degenerate semiconductor. In contrast, the Seebeck coefficient S of Cu₂Te + x% Ag₂Te is roughly increased with increasing temperature. At room temperature, S is scarcely changed or even decreased when the Ag₂Te content is larger than 15%. The reason for this should be that Cu₂Te is a p-type semiconductor while CuAgTe is an n-type semiconductor at room temperature, thus the total Seebeck coefficients are partly counterbalanced. However, at high temperatures, all the samples have single cubic phases with one dominant type of carriers, i.e., holes. Therefore, the Seebeck coefficient increases significantly with increasing the Ag₂Te content. The increased Seebeck coefficient coupled with the decreased electrical conductivity implies that the hole concentration is reduced at high temperatures. We have tried to corroborate our speculation by measuring the carrier concentrations at different temperature. Unfortunately, no reliable data are obtained at high temperature.
We thus performed defect formation energy ($E_{\text{form}}$) calculations by using the high temperature cubic structures for Cu$_2$Te and CuAgTe (see Figure S3, Supporting Information). The $E_{\text{form}}$ values for Cu vacancy ($V_{\text{Cu}}$) or/and Ag vacancy ($V_{\text{Ag}}$) are calculated according to the equation

$$E_{\text{form}} = E_{\text{tot}[\text{defected}]} - E_{\text{tot}[\text{perfect}]} + \sum_i n_i \mu_i + qE_f + E_{\text{corr}}$$  \hspace{1cm} (1)$$

where $E_{\text{tot}[\text{defected}]}$ and $E_{\text{tot}[\text{perfect}]}$ are the total energy of defected and perfect structures, respectively; $\sum_i n_i \mu_i$ is the summation over the atomic chemical potentials; $q$ is the charge of defect; $E_f$ is the fermi energy; and $E_{\text{corr}}$ is the correction due to spurious electrostatic interaction of charged cell in periodic boundary calculation. The generalized gradient approximation (GGA) level band gap is zero for Cu$_2$Te and CuAgTe, leading to negligible $E_{\text{corr}}$. The atomic chemical potentials were calculated from the ternary phase diagram for Cu-Ag-Te, constructed by using the Pymatgen code based on density functional theory ground state energies from the Materials Project database. The calculation results based on the $2 \times 2 \times 2$ supercell are shown in Figure 4. The slanting lines with negative slope represent the defect formation energies for negatively charged $V_{\text{Cu}}$ and $V_{\text{Ag}}$ defects. The Cu vacancy formation energy in Cu$_2$Te is very low, suggesting that $V_{\text{Cu}}$ defects are prone to be formed during the fabrication processes. Thus, severe copper precipitation and quite high hole carrier concentration are expected in Cu$_2$Te, which is consistent with the experiment observation. The carrier concentration of Cu$_2$Te should be scarcely changed from room temperature to high temperatures although it experiences complex phase transitions. With the addition of Ag, the $V_{\text{Cu}}$ formation energy is increased within all the Fermi level range, implying that the formation of $V_{\text{Cu}}$ is suppressed. Besides, we also take into account the possible formation of $V_{\text{Ag}}$, whose formation energy is higher than that of Cu vacancy (see Figure 4). This indicates that $V_{\text{Ag}}$ is more difficult to be created in CuAgTe as compared with $V_{\text{Cu}}$. Furthermore, the convergence tests of the size effects on defect formation energies have been also performed for Cu$_2$Te and CuAgTe. Three different supercells, i.e., $1 \times 1 \times 1$, $2 \times 2 \times 2$, and $3 \times 3 \times 3$ were tested. As shown in Figure S4 in the Supporting Information, the calculated energies between the $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells are very close. The trends for energy variation of Cu vacancy or Ag vacancy in different supercells are also the same. Therefore, the substitution of Ag for Cu can decrease...
the formation of cation vacancies, resulting in much lower hole concentrations.

The power factors calculated from the formula \( PF = S^2 \sigma \) are shown in Figure 3c. The PF for pristine \( \text{Cu}_2\text{Te} \) is around 2.8 \( \mu \text{W cm}^{-1} \text{K}^{-2} \) below 600 K and subsequently increases with increasing temperature. A maximum PF of 9.5 \( \mu \text{W cm}^{-1} \text{K}^{-2} \) is obtained at 1000 K for \( \text{Cu}_2\text{Te} \). After introducing \( \text{Ag}_2\text{Te} \) into \( \text{Cu}_2\text{Te} \), the PFs increase in the entire temperature range except for \( \text{Cu}_2\text{Te} + 55\% \text{Ag}_2\text{Te} \), which shows a low PF near room temperature because of the influence of minor carriers (i.e., electrons). Nevertheless, in the middle temperature range, the PFs are greatly improved due to the suppression of phase transition temperature and the reduction of hole concentration. For instance, a high PF value of 9 \( \mu \text{W cm}^{-1} \text{K}^{-2} \) is achieved at 600 K for \( \text{Cu}_2\text{Te} + 50\% \text{Ag}_2\text{Te} \), which is five times higher than that for pristine \( \text{Cu}_2\text{Te} \) at the same temperature.

Figure 3d displays the total thermal conductivity \( \kappa \) as a function of temperature for \( \text{Cu}_2\text{Te} + x\% \text{Ag}_2\text{Te} \) (\( x = 0, 15, 35, 40, 50, \) and 55). They show complicated temperature dependencies in the temperature range from 300 to 1000 K due to the existence of multiple phase transitions. The \( \kappa \) is significantly decreased with increasing \( \text{Ag}_2\text{Te} \) content, which is mainly attributed to the decreased contribution of charge carriers to thermal transport. The lattice thermal conductivity \( \kappa_L \) for \( \text{Cu}_2\text{Te} + x\% \text{Ag}_2\text{Te} \) is calculated and shown in Figure S5 in the Supporting Information. All the samples exhibit ultralow lattice thermal conductivity with the values around 0.3 \( \text{W m}^{-1} \text{K}^{-1} \) at 900 K, which is even lower than the minimum lattice thermal conductivity \( (\kappa_{\text{min}}) \) estimated by Cahill’s model (see the details in the Supporting Information).

Figure 3e presents the temperature dependence of \( zT \) for \( \text{Cu}_2\text{Te} + x\% \text{Ag}_2\text{Te} \) (\( x = 0, 15, 35, 40, 50, \) and 55). At low temperature, both holes and electrons are involved in transport, resulting in relatively low \( zT \) values. However, at high temperature, the TE performance is greatly improved over a large temperature range, which can be traced to the suppressed phase transition temperatures and the reduction of hole concentrations.
transition temperature and the reduced carrier concentration. Specifically, the maximum $zT$ value for pristine Cu$_2$Te is only 0.4 and it is remarkably boosted to 1.8 for Cu$_2$Te + 50% Ag$_2$Te at 1000 K. This is a 323% improvement over Cu$_2$Te itself and outperforms any other Cu$_2$Te-based material reported so far (Figure 3f).

To further elucidate on the high TE performance of Cu$_2$Te, we modeled their TE properties using a single parabolic band (SPB) model with the carrier mobility limited by acoustic phonon scattering. In comparison, the data of Cu$_2$S and Cu$_2$Se are also modeled. The experimental data at 900 K are selected because all materials have same cubic structures at this temperature. Thus, the effect of different crystal structures on TE properties can be excluded. The model details are shown in the Supporting Information. Because the Hall data at 900 K is absent, we do not have the exact drift mobility $\mu_0$ or effective mass $m^*$. However, we can fit the $S$–$\sigma$ (Seebeck coefficient vs electrical conductivity) curves by taking the weighted mobility ($\mu_0 m^{3/2}$) as a single parameter (see Equation (56), Supporting Information). As shown in Figure 5a, the red dashed line is calculated by using a weighted mobility $\mu_0 m^{3/2}$ of 19.6 $m_e^{3/2}$ cm$^2$ V$^{-1}$ s$^{-1}$. All the experimental $S$ data for three different types of materials fall around on this derived line. This strongly suggests that Cu$_2$Te-, Cu$_2$Se-, and Cu$_2$S-based compounds have comparable weighted mobility parameter $\mu_0 m^{3/2}$ at high temperature. Thus, Cu$_2$Te-, Cu$_2$Se-, and Cu$_2$S-based compounds may have similar good electrical transport properties, which is further supported by the calculated power factors (see Figure 5b). All the data for Cu$_2$S, Cu$_2$Se, and Cu$_2$Te show a very nice agreement with the calculated curve. The only difference among Cu$_2$S, Cu$_2$Se, and Cu$_2$Te is the position of Fermi level. It is near the top of valence band for Cu$_2$S, in the deep covalent band for Cu$_2$Te, and in the middle for Cu$_2$Se. Thus, the electrical conductivity is low in Cu$_2$S, in the middle in Cu$_2$Se, and very high in Cu$_2$Te. According to Figure 5b,
the optimal electrical conductivity $\sigma_{\text{opt}}$ for maximized PF is around $5 \times 10^8$ S m$^{-1}$, which can be easily achieved in Cu$_2$Se. Due to the severe copper deficiency, Cu$_2$Te-based compounds have quite high electrical conductivity ($=10^8$ S m$^{-1}$) that greatly exceeds the $\sigma_{\text{opt}}$ value. Thus, its PF is relatively low. On the contrary, Cu$_2$S-based compound has very low electrical conductivity ($=10^5$ S m$^{-1}$) that is much less than the $\sigma_{\text{opt}}$ value, thus its PF is also very low. The electrical conductivity for Cu$_2$Se-based compound lies between that of Cu$_2$Te and Cu$_2$S. Nevertheless, according to our analysis, the PFs for all the Cu$_2$X compounds can be tuned to the optimal range when their electrical conductivity and carrier concentration are optimized.

The $\kappa$-$\sigma$ (total thermal conductivity vs electrical conductivity) relation is calculated under the assumption that $\kappa_\ell$ is 0.3 W m$^{-1}$ K$^{-1}$ for all materials. This is an acceptable assumption for these liquid-like materials with ultralow lattice thermal conductivity. As plotted in Figure 5c, the experimental data agree well with the calculated curve, indicating that the total thermal conductivity is dominated by carrier thermal conductivity in Cu$_2$X-based compounds. When increasing electrical conductivity, the total thermal conductivity is greatly improved. Thus, Cu$_2$S-based compounds generally have very low $\kappa$, whereas Cu$_2$Te-based compounds have quite high $\kappa$.

The $zT$ value as a function of $\sigma$ is then calculated based on the PF and $\kappa$ derived above, which is plotted in Figure 5d. The optimal electrical conductivity range for the maximized $zT$ is around $(1–3) \times 10^5$ S m$^{-1}$, which is slightly lower than that for PF because of the contribution from electronic thermal conductivity. Apparently, the electrical conductivity for Cu$_2$Se is close to the optimal value, thus high $zT$s are easily achieved in Cu$_2$Se. Whereas the $\sigma$ values in Cu$_2$S and Cu$_2$Te are either less or larger than the optimal value, resulting in low $zT$ values. Increasing the $\sigma$ in Cu$_2$S and decreasing the $\sigma$ in Cu$_2$Te can approach the optimal range for high $zT$s. In this study, when adding Ag into Cu$_2$Te, the $\sigma$ is greatly reduced and its TE performance is significantly improved. The above data and analysis clearly demonstrate that Cu$_2$Te is also an excellent TE material. It is not against the general trend shown in Figure 1. Furthermore, due to the ultralow $\kappa_\ell$ in these liquid-like materials, all Cu$_2$S, Cu$_2$Se, and Cu$_2$Te possess very high $zT$s when their electrical properties are optimized. This is beyond the other TE materials. Currently, it is the only material system that possesses very high $zT$s above 1.5 in the materials with all three constituent elements in the same group such as S, Se, and Te.

While Cu$_2$X-based liquid-like compounds are promising TE materials with high $zT$ values, the migration of Cu ions causes long-term stability problems under electric field and/or temperature gradient. Such stability issue has been well studied recently, which is determined by the critical voltage of Cu ions. Even Cu/Ag moves fast, the liquid-like materials can still be stable if the critical voltage is large enough. The critical voltage for Cu$_2$X-based materials is around 0.1 V, which is a few orders of higher than the voltage (0.0001 V) used for TE property measurements. To validate the sample stability under small voltage/current, repeatability measurements are performed on Cu$_2$Te $+$ 35% Ag$_2$Te for six cycles with different cycling temperatures. As presented in Figure S6 in the Supporting Information, both the $\sigma$ and $S$ show quite good reproducibility up to 1000 K with just a little change below the phase transition temperatures ($<500$ K) because of the presence of mixed phases.

To sum up, by introducing Ag$_2$Te into Cu$_2$Te, the high carrier concentration in pristine Cu$_2$Te is substantially reduced to an optimal range, resulting in much reduced thermal conductivity and enhanced power factors over the entire temperature range. Furthermore, the temperature of last phase transition is significantly lowered when increasing Ag content, which benefits to maintain the good TE properties of cubic phase at low temperatures. A maximum $zT$ of 1.8 is achieved at 1000 K in Cu$_2$Te $+$ 50% Ag$_2$Te, which is the highest reported value for Cu$_2$Te-based TE materials. An effective SPB model was used to model the transport properties of Cu$_2$S-, Cu$_2$Se-, and Cu$_2$Te-based compounds and it was found that they are all outstanding TE materials. This conclusion is beyond the general trend observed in other TE materials in which very high $zT$s cannot be achieved in all the sulfides, selenides, and tellurides.

**Experimental Section**

Synthesis: A series of samples with nominal compositions of Cu$_2$Te $+$ x% Ag$_2$Te ($x$ = 0, 15, 35, 40, 50, and 55) was synthesized by vacuum melting combined with the spark plasma sintering (SPS) process. High purity Cu (Sigma Aldrich, 99.999%), Ag (Sigma Aldrich, 99.999%), and Te (Sigma Aldrich, 99.999%) were weighed out and loaded into boron nitride crucibles that were sealed in a fused silica tube under vacuum. The loaded tubes were slowly heated to 1403 K in 12 h and soaked at this temperature for 6–12 h, then rapidly quenched to room temperature in water. Next, the sealed tubes were heated to 973 K in 8 h, dwelled at this temperature for 6 days, and subsequently cooled to room temperature by turning off the furnace power. The obtained ingots were hand-ground into fine powders using a mortar and a pestle. Then the powders were loaded into a graphite die with a diameter of 10 mm and then consolidated via SPS (Sumitomo SPS-2040) at 773–873 K under a pressure of 50–60 MPa for 5 min. Electrically insulating but thermally conducting boron nitride layers were coated on the carbon foils and the inner sides of the graphite died before the SPS process. Highly dense (>98% of theoretical density) disk-shaped pellets with dimensions of 10 mm in diameter and about 5 mm in thickness were obtained.

Characterization: Room-temperature powder X-ray diffraction (RT-PXRD) analysis was performed on Rigaku Rint 2000 with a Cu-K$_\alpha$ source. High-temperature PXRD patterns were collected at 900 K on a powder X-ray diffractometer (Bruker D8 Advance) with high temperature accessory operating at 45 kV and 200 mA. The sample compositions were measured by field emission scanning electron microscopy (Magellan-400) equipped with energy dispersive X-ray analysis (Horiba 250). The sound speed data were obtained by an ultrasonic measurement system UMS-100 with shear wave transducers of 5 MHz and longitudinal wave transducers of 10 MHz. DSC measurement was carried out using a Netzsch DSC 404FE instrument. The electrical conductivity ($\sigma$) and Seebeck coefficient (S) were measured simultaneously in a helium atmosphere using a commercial apparatus (ULVAC ZEM-3). Thermal diffusivity ($D$) was measured via the laser flash method using a Netzsch LFA-457. The pellet density ($d$) was measured by the Archimedes method. The $C_p$ for Cu$_2$Te $+$ 55% Ag$_2$Te sample was measured by using the commercial DSC equipment (see Figure S7, Supporting Information). The total thermal conductivity was calculated via the equation $\kappa = d \times C_p \times D$. The measurement errors for the electrical conductivity, the Seebeck coefficient, and the thermal conductivity were 5%, 7%, and 5%, respectively.

Defect Formation Energy Calculation: The present calculations were performed using the Perdew–Burke–Ernzerhof-GGA/75,76 with projector-augmented wave method, as implemented in the Vienna Ab Initio
The high temperature cubic structures for Cu$_2$Te and CuAgTe with ordered Cu and Ag distribution were adopted for all the calculations (see Figure S3, Supporting Information). Besides, a special quasi-random structure for CuAgTe to mimic a random distribution of Cu and Ag was also used for comparison based on "mcsga" code of the Alloy Theoretic Automated Toolkit (ATAT).[79] The obtained defect formation energy in the special quasi-random structure was close to that in the ordered structure (see Figure S8, Supporting Information). For simplicity, only the 8c sites were taken into account since the 32f formation energy in the special quasi-random structure was close to the relative value was quoteworthy and the conclusions were reasonable. 

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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