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SPECIAL TOPIC — Recent advances in thermoelectric materials and devices

Se substitution and micro-nano-scale porosity enhancing thermoelectric Cu_2Te*

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Binary Cu-based chalcogenide thermoelectric materials have attracted a great deal of attention due to their outstanding physical properties and fascinating phase sequence. However, the relatively low figure of merit zT restricts their practical applications in power generation. A general approach to enhancing zT value is to produce nanostructured grains, while one disadvantage of such a method is the expansion of grain size in heating-up process. Here, we report a prominent improvement of zT in $Cu_2Te_{0.2}Se_{0.8}$, which is several times larger than that of the matrix. This significant enhancement in thermoelectric performance is attributed to the formation of abundant porosity via cold press. These pores with nano- to micrometer size can manipulate phonon transport simultaneously, resulting in an apparent suppression of thermal conductivity. Moreover, the Se substitution triggers a rapid promotion of power factor, which compensates for the reduction of electrical properties due to carriers scattering by pores. Our strategy of porosity engineering by phonon scattering can also be highly applicable in enhancing the performances of other thermoelectric systems.

Keywords: thermoelectrics, Cu_2Te, porosity, thermal conductivity

PACS: 72.20.Pa, 68.35.bg, 44.10.+i, 44.30.+v **DOI:** 10.1088/1674-1056/27/4/047204

1. Introduction

Increasing consumption and demand for energy promotes the prosperity of functional materials.[1] Due to the direct and reversible conversion between thermal and electrical energy, thermoelectric materials have potential applications in solid-state cooling, waste heat recovery, etc.[2–6] The capability of thermoelectrics is evaluated by the dimensionless figure of merit $zT = S^2\sigma T/(\kappa_{lat} + \kappa_{ele})$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, κ_{lat} and κ_{ele} are the lattice and electron thermal conductivity.[7,8] However, it is difficult to combine a high S with high σ and low κ, due to their strong coupling.[9–11] Several strategies,[12–17] that decouple these relationships or minimize the independent material property κ_{lat} to enhance zT, have emerged during the past decades. The power factor (PF) has been enhanced by optimizing the carrier concentration[18–20] or various band engineerings via resonant states[21,22] or band convergence.[23,24] As for the depression of κ_{lat}, diverse routes to strengthening phonon scattering, including substitution doping,[25] nanoprecipitations,[26] nanograins,[27] and dislocations,[28] have been reported.

Binary Cu-based chalcogenides $Cu_{2-\delta}X$ (X = S, Se, and Te) have gained a great deal of attention recently because of their excellent thermoelectric performances and interesting physical properties.[29] Liu *et al.*[17] have reported that the liquid-like behavior of Cu ions responsible for the ultralow thermal conductivity enables a high $zT \sim 1.5$ for Cu_2Se at 1000 K, and they further proposed a new concept named "phonon-liquid electron-crystal" (PLEC) to explain this abnormal physical property. After that, tremendous efforts have been devoted to the Cu-based systems to reveal their underlying mechanisms or improve their thermoelectric performances.

Among them, Cu_2Te with more complicated phase sequence has attracted a great interest. There are five successive phases (α_I-, α_{II}-, β-, γ-, δ-phase) transitions in the Cu_2Te between 300 K and 900 K. Only δ-phase crystallizes into hexagonal structure, while the rest are of the orthorhombic

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structure.[29,30] Some remarkable achievements have been realized via doping[31] or unique sintering techniques.[32] However, few researches have focused on the porosity, which can be utilized to lower thermal conductivity. Although they may moderately scatter carriers, pores with nano- to microstructures possess an ideal phonon-scattering source to hinder the full frequency spectrum heat-carrying phonon. Accordingly, the thermoelectric performance can be enhanced through the incorporation of porosity while maintaining a relatively high *PF* via doping.

In this work, we use a cold press process to induce the enrichment of pores in a bulk Cu_2Te-based system. The sizes of porosity vary from nano to micro scale which can be characterized by scanning electron microscope (SEM). By introducing the porous architecture, κ_{lat} is successfully suppressed in $Cu_2Te_{0.8}Se_{0.2}$ in the entire temperature range. In addition, we also incorporate Se to increase σ, and thus alleviating the *PF* reduction from carrier scattering by pores. The synergistic effect from the phonon scattering via porosity engineering and the improvement of *PF* through Se doping gives rise to a prominent enhancement of thermoelectric performance, which opens up a new route to manipulating the phonon transport by porosity engineering.

2. Experimental procedure

Pristine Cu_2Te, pristine Cu_2Se, substituted $Cu_2Te_{0.8}Se_{0.2}$, and substituted $Cu_2Te_{0.2}Se_{0.8}$ samples were fabricated by conventional solid-state reaction method. Element copper (99.9 wt%), telluride (99.99 wt%), and selenium (99.99 wt%), were mixed as a nominal composition and sealed in evacuated quartz tubes. The samples were heated to 1393 K for 7 h, maintained at this temperature for 3 h, and then naturally cooled to room temperature. The obtained Cu_2Te and Cu_2Se ingots were ground into powders then densified by spark plasma sintering (SPS) method (LABOX-325, Japan). Samples were then ground in a mortar, pressed in a cold isostatic press (CIP), sealed again in quartz under vacuum and annealed at 1073 K several times. Powder x-ray diffraction (PXRD) measurements with Cu–Kα radiation were performed by using an x-ray diffractometer (DX-2700). The crack morphology was characterized by an FEI inspect F50 SEM. The temperature-dependent electrical conductivity σ and Seebeck coefficient *S* were measured by using apparatus (LSR-3). The temperature-dependent thermal diffusivity and thermal conductivity κ were measured by the laser flash method (LFA 457, Netzsch).

3. Results and discussion

Figure 1(a) shows the powder XRD patterns for the four samples. Obviously, both Cu_2Te and $Cu_2Te_{0.8}Se_{0.2}$ crystallize into a hexagonal structure that belongs to the space group $P6/mmm$ at room temperature. However, abundant Se atoms in $Cu_2Te_{0.2}Se_{0.8}$ enable the formation of cubic crystal structure, which is in accordance with that of Cu_2Se.

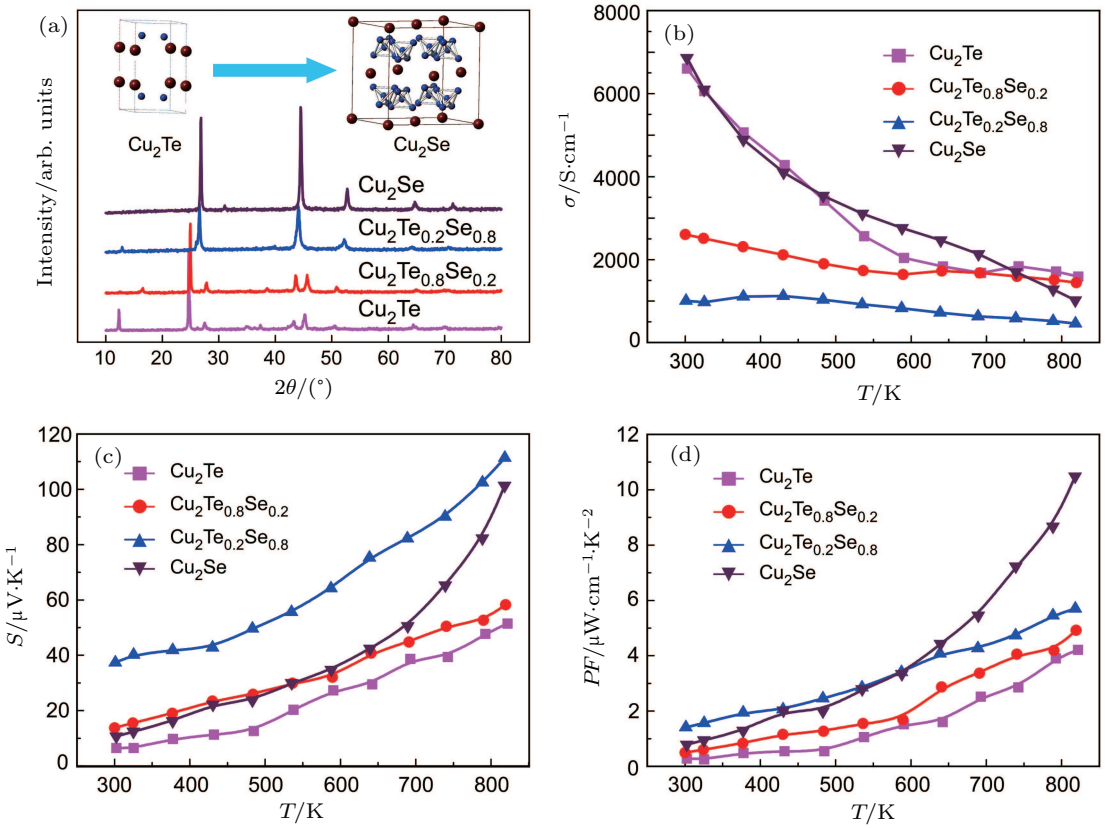


Fig. 1. (color online) (a) XRD patterns for Cu_2Te, Cu_2Se, $Cu_2Te_{0.8}Se_{0.2}$, and $Cu_2Te_{0.2}Se_{0.8}$. Temperature dependence of electrical properties for (b) electrical conductivity σ, (c) Seebeck coefficient *S*, and (d) power factor *PF*, respectively.

To examine the functional properties of the pristine Cu_2Te, Cu_2Se, $Cu_2Te_{0.8}Se_{0.2}$, and $Cu_2Te_{0.2}Se_{0.8}$ samples, we first measure the electrical conductivity σ as a function of temperature T (Fig. 1(b)). Magnitudes of σ for all samples are on the order of 10^3 S·cm^{-1}, which is comparable to the values reported previously.[32] One might have noticed that the behaviors of temperature-dependent electrical conductivity among the Cu_2Te, Cu_2Se matrix, and doped samples are totally different from each other. For Cu_2Te and Cu_2Se, σ decreases rapidly with temperature increasing in the entire temperature range, reflecting a typical behavior of degenerate semiconductor. In contrast, the trends of $Cu_2Te_{0.8}Se_{0.2}$ and $Cu_2Te_{0.2}Se_{0.8}$ seem to be independent of temperature. This phenomenon indicates that the charged carriers in the two sets of samples are scattered by the precipitates and nano- to micrometer size pores. The noticeable enhancement of S of $Cu_2Te_{0.8}Se_{0.2}$ may derive from the existence of porosity, which was observed in other thermoelectric systems,[33] resulting in the highest PF among these samples.

Figure 2(a) shows the temperature dependent heat capacities for Cu_2Te and Cu_2Se. Since the results of XRD can directly detect the structural variation from Cu_2Te to Cu_2Se with the number of Se atoms increasing, we therefore utilize a weighted average of the temperature-dependent C_p values of Cu_2Te and Cu_2Se for the three samples. To investigate the contribution of porosity to phonon scattering, we also measure thermal diffusivity coefficient D values of these samples as shown in Fig. 2(b). Accordingly, the total thermal conductivity can be calculated from a well-known formula $\kappa_{tot} = C_p \cdot D \cdot d$, where the density d is determined using the dimensions and mass of the sample (Fig. 2(c)). Apparently, Cu_2Te and $Cu_2Te_{0.8}Se_{0.2}$ have similar trends of temperature-dependent κ_{tot} due to the same crystal structure. Whereas, the trend of $Cu_2Te_{0.2}Se_{0.8}$ is more close to Cu_2Se, which also supports the results from XRD.

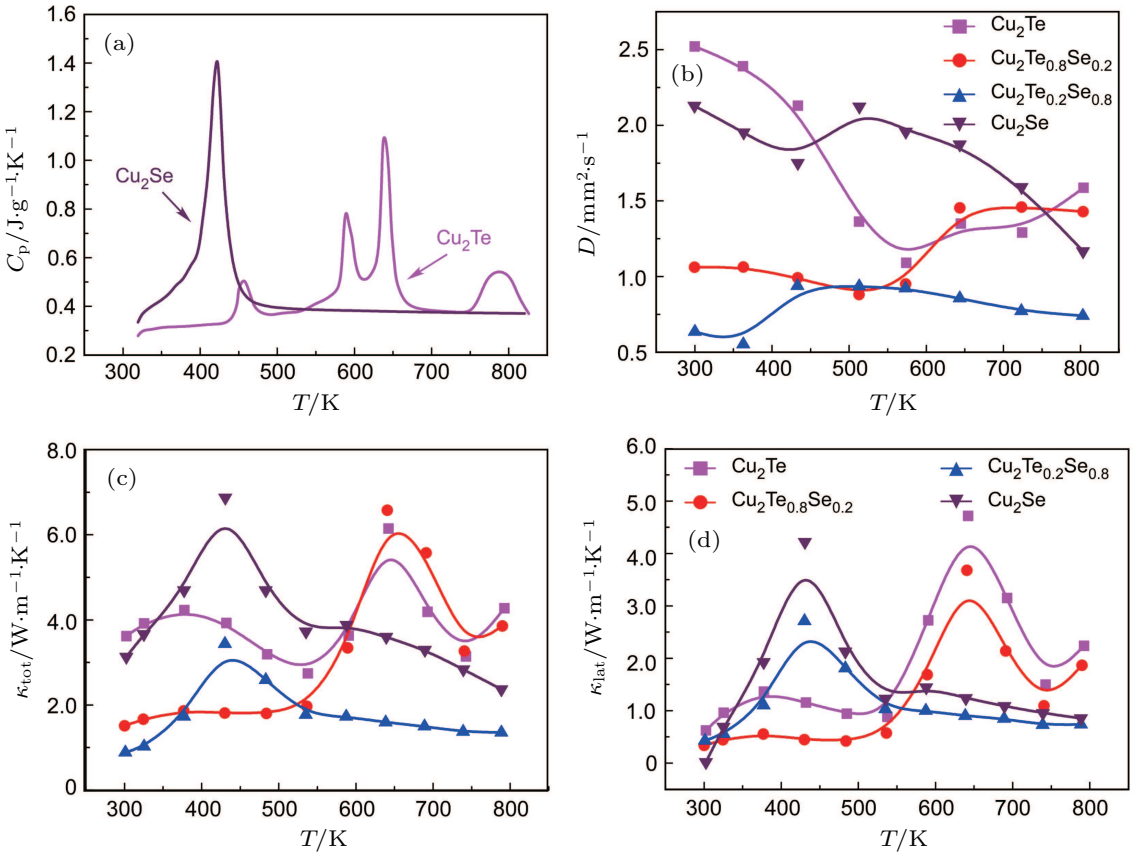


Fig. 2. (color online) Temperature dependence of physical properties for (a) heat capacity C_p, (b) thermal diffusivity coefficient D, (c) total thermal conductivity κ_{tot}, and (d) lattice thermal conductivity κ_{lat}, respectively.

It is noted that the total thermal conductivity κ_{tot} can be expressed by the sum of the two parts κ_{lat} and κ_{ele}. The electronic part κ_{ele} is directly proportional to the electrical conductivity σ through the floowing Wiedemann–Franz relation, i.e., $\kappa_{ele} = L\sigma T$, where L is the Lorenz number.[34] The Lorenz number for all compounds is calculated by using the following equations:

$$L = \left(\frac{k_B}{e}\right)^2 \times \left(\frac{(r+7/2)F_{r+5/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \left[\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)}\right]^2\right), \quad (1)$$

where r is the scattering parameter, k_B is the Boltzmann con-

stant, e is the electron charge, and $F_n(\eta)$ is the n-th order Fermi integral given by

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1+e^{\chi-\eta}} \mathrm{d}\chi, \tag{2}$$

$$\eta = \frac{E_\mathrm{f}}{k_\mathrm{B}T}. \tag{3}$$

Here, the calculation of η can be derived from the measured Seebeck coefficients by using the following relationship:

$$S = \pm\frac{k_\mathrm{B}}{e}\left(\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \eta\right). \tag{4}$$

Meanwhile, we assume that acoustic phonon scattering ($r=-1/2$) is the main carrier scattering mechanism.[34] Thus, the lattice thermal conductivity κ_lat can be estimated by directly subtracting κ_ele from κ_tot as shown in Fig. 2(d). It is found that the incorporation of Se into matrix triggers the formation of point defects and precipitates, leading to an intensive scattering of heat-carring phonon. Additionally, the abundant porosities in the Se doped samples also play an important role in κ_lat reduction. Therefore, with the synergistic effect of both Se doping and porosity, κ_lat of $Cu_2Te_{0.8}Se_{0.2}$ is much lower than that of matrix in the entire temperature range. As for $Cu_2Te_{0.2}Se_{0.8}$, the coexistence of strong anharmonicity in Cu_2Se crystal structure and massive porosity manipulates phonon transport simultaneously, resulting in a lower κ_lat than that of Cu_2Se. The slight upturn of $Cu_2Te_{0.2}Se_{0.8}$ near 450 K originates from α–β structural transition.

To further gain a direct insight into the tiny pores responsible for this apparent drop of thermal conductivity, we perform SEM on these samples in Fig. 3. Obviously, no porosities were observed in Cu_2Te nor Cu_2Se (Figs. 3(a) and 3(b)). Interestingly, a large number of pores with nano- to micrometer size appear in crack morphologies of $Cu_2Te_{0.8}Se_{0.2}$ and $Cu_2Te_{0.2}Se_{0.8}$ after cold press and annealing (Figs. 3(c) and 3(d)). The porosity of varying shapes and sizes breaks up the integrity of crystal structure, hindering the transport of phonon effectively.

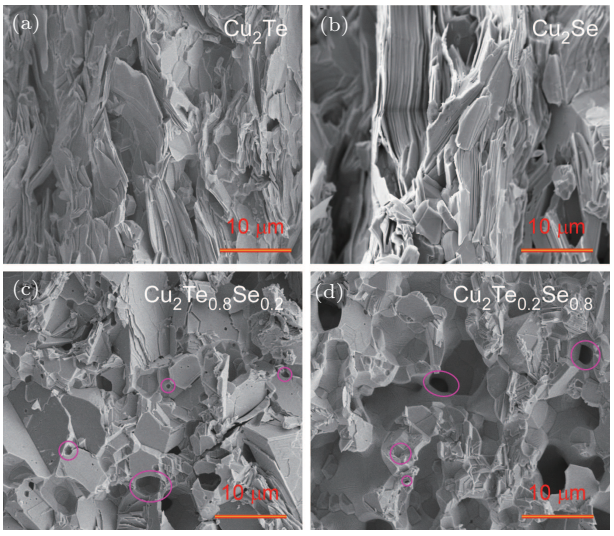


Fig. 3. (color online) Crack morphology characterized by SEM for (a) Cu_2Te, (b) Cu_2Se, (c) $Cu_2Te_{0.8}Se_{0.2}$, and (d) $Cu_2Te_{0.2}Se_{0.8}$, respectively.

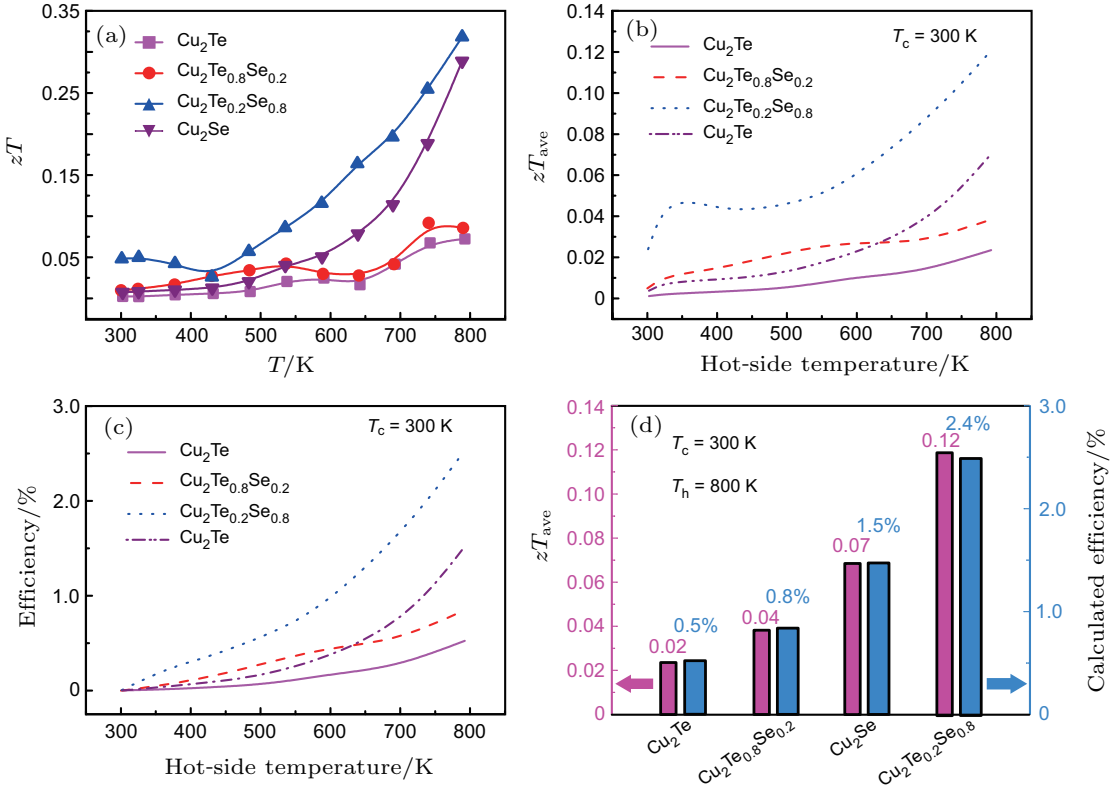


Fig. 4. (color online) Temperature dependence of (a) zT and (b) average zT_ave. (c) Conversion efficiency η for the samples. (d) Comparison of zT_ave and η in a wide temperature range.

Figure 4(a) shows the plots of figure-of-merit zT versus temperature. It is apparent that thermoelectric performance of $Cu_2Te_{0.8}Se_{0.2}$ has a promotion by comparing with those of the other samples. This phenomenon indicates that pores can largely enhance zT values even moderately reduce carrier mobility which is reflected by σ in Fig. 1(b). Moreover, the synergistic contributions from the improvement of Seebeck coefficient, and suppression of lattice thermal conductivity, caused by the appearance of porosity, drives the persistent enhancement of zT for $Cu_2Te_{0.2}Se_{0.8}$.

In addition, we also calculate average zT_{ave} and the thermoelectric conversion efficiency η which can be expressed as

$$ZT_{ave} = \frac{1}{T_h - T_c}\int_{T_c}^{T_h} zT\,dT, \tag{5}$$

$$\eta = \frac{T_h - T_c}{T_h}\frac{\sqrt{1+ZT_{ave}}-1}{\sqrt{1+ZT_{ave}}+T_c/T_h}, \tag{6}$$

where T_h and T_c are the hot-side and cold-side temperatures, respectively. The detailed results are depicted in Figs. 4(b) and 4(c) with different temperature ranges between the hot and cold side. The zT_{ave} and η are much larger than that of the previously reported pristine Cu_2Te ($zT_{ave} \approx 0.06$, $\eta \approx 1.4\%$).[31]

4. Conclusions

In conclusion, an extraordinary enhancement of zT merit in Se-substituted Cu_2Te derives from a simultaneous improvement in power factor and reduction in lattice thermal conductivity in the entire temperature range. The enhanced PF is attributed to the significantly increased absolute Seebeck coefficient via Se doping. And the reduced lattice thermal conductivity can be understood via phonon scattering by incorporated porosity. We believe that this strategy that constructing porous architecture could also be highly applicable in enhancing the performances of other state-of-the-art thermoelectric systems.

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