Phase transition and high temperature thermoelectric properties of copper selenide $Cu_{2-x}Se$ ($0 \leq x \leq 0.25$)*

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With good electrical properties and an inherently complex crystal structure, $Cu_{2-x}Se$ is a potential "phonon glass electron crystal" thermoelectric material that has previously not attracted much interest. In this study, $Cu_{2-x}Se$ ($0 \leq x \leq 0.25$) compounds were synthesized by a melting-quenching method, and then sintered by spark plasma sintering to obtain bulk material. The effect of Cu content on the phase transition and thermoelectric properties of $Cu_{2-x}Se$ were investigated in the temperature range of 300 K–750 K. The results of X-ray diffraction at room temperature show that $Cu_{2-x}Se$ compounds possess a cubic structure with a space group of $Fm3m$ (#225) when $0.15 < x \leq 0.25$, whereas they adopt a composite of monoclinic and cubic phases when $0 \leq x \leq 0.15$. The thermoelectric property measurements show that with increasing Cu content, the electrical conductivity decreases, the Seebeck coefficient increases and the thermal conductivity decreases. Due to the relatively good power factor and low thermal conductivity, the nearly stoichiometric Cu_2Se compound achieves the highest ZT of 0.38 at 750 K. It is expected that the thermoelectric performance can be further optimized by doping appropriate elements and/or via a nanostructuring approach.

Keywords: copper selenide, phase transition, thermoelectric properties

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1. Introduction

In recent years, due to a drastic reduction in fossil fuel supplies and their impact on the environment, the development of sustainable and environmentally friendly energy sources and energy conversion technologies has become a key topic of scientific research. Thermoelectric energy conversion, which is the simplest technology to achieve a direct energy conversion between heat and electricity, is expected to play a progressively more important role as an alternative energy technology. Therefore, it is of vital importance to develop high efficiency thermoelectric (TE) materials for large-scale applications of thermoelectric energy conversion.[1−5] The efficiency of a thermoelectric material is related to the dimensionless figure of merit ZT, which is expressed as $ZT = \alpha^2\sigma T/\kappa$, where α, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Currently, the ZT values of commercial and state of the art thermoelectric materials, such as Bi_2Te_3 alloys and PbTe compounds, are between 1 and 2, which is much lower than the efficiency of the counterpart mechanical systems. After performance, the fabrication cost of TE materials is a major concern for any large scale application of TE energy conversion. In this regard, those commercial and novel thermoelectric materials are based on Te-containing compounds. As the ninth least abundant element, Te (1 ppb by weight in the earth's crust) is too scarce to support usage on this scale.[6,7] Therefore, it is necessary to develop novel thermoelectric materials that contain less Te or are Te-free for large scale commercial application.

$Cu_{2-x}Se$ ($x = 0$–0.25) is a mixed ionic-electronic conductor (or superionic conductor),[8] and it exists in two allotropes: the low-temperature α-phase (monoclinic) with Se at% of 33.3%–33.8%, and the high-temperature β-phase (cubic) with Se at% of 35.3%–36.4%.[9−11] The Hall coefficient and Seebeck coefficient measurements showed that $Cu_{2-x}Se$ is a degenerate p-type semiconductor, where the holes originate from the Cu deficiency.[12−14] Danilkin *et al.*[15] and Skomorokhov *et al.*[16] studied the crystal structure of

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Cu_2Se by neutron scattering and synchrotron powder diffraction, respectively. It is found that in the copper selenide, selenium atoms form a "rigid framework" of the crystal lattice, and Cu ions are distributed on the different interstitial sites, but the precise distribution of the Cu cations is still a considerable discrepancy in the literature. The ordering of Cu cations in the β-phase results in a complicated superstructure that is very sensitive to the composition and preparation technique.[17,18]

To the best of our knowledge, Junod[19] first reported the temperature dependences of the Seebeck coefficient and electrical resistivity for Cu_2Se in 1959. In 1971, Okamoto[20] further confirmed Junod's work and pointed out that the anomalies in the Seebeck coefficient and resistivity were related to the α–β phase transition. These results show that the electronic conduction of Cu_2Se is about $\sim 3.3\times10^4$ S/m and the Seebeck coefficient is about ~ 200 μV/K at a temperature of 400 K. When the temperature is higher than the α–β phase transition temperature, the electronic resistivity practically retains the same value whereas the Seebeck coefficient increases as the temperature increases. Due to the fact that Cu_2Se compound possesses a complicated crystal structure and good electrical properties, it can be a potential TE material in the view of the "PGEC" approach. In addition, compared with the other p-type Ti(FeCo)Sb-based half-Heusler[21] and the BaGaGe-based clathrates,[22–24] Cu_2Se compounds not only have good electrical transport properties but also contain the low cost elements Cu and Se, which have high percentage abundance in the earth.[25] Therefore, the $Cu_{2-x}Se$ compound may be a potential candidate as a medium-temperature thermoelectric material.

As yet, the effect of Cu content on the thermoelectric transport properties of copper selenide has rarely been investigated in the high temperature range. In this paper, $Cu_{2-x}Se$ ($0 \le x \le 0.25$) bulk materials were prepared by the melt-quenching method combined with spark plasma sintering; the phase transition and effect of varying Cu content on the thermoelectric transport properties of $Cu_{2-x}Se$ compounds were investigated in the temperature range of 300 K–750 K.

2. Experiment

High purity Cu powder (99.99%) and Se powder (99.95%) as starting materials were weighed in the desired ratios and sealed in quartz tubes under vacuum ($p < 10^{-3}$ Pa). The tubes were placed in the furnace and slowly heated up to 1403 K at a heating rate of 2 K/min and held at this temperature for 10 h, and then cooled slowly down to 1173 K and held at this temperature for another 10 h, then quenched in cold salt water. In order to obtain high density samples for the following measurement, the obtained ingots were pulverized into powder and then sintered by a spark-plasma sintering (SPS) technique at 873 K under a pressure of 35 MPa for 7 min. The relative densities of these samples were 95%–98% of the theoretical density.

The phase compositions of the samples were characterized by X-ray diffraction (XRD) (PANalytical: X'Pert PRO, CuKa). Using high temperature XRD (X'Pert PRO, Cu Ka, DY2198), we detected the phase transition during heating in a vacuum of 8.2 Pa. Samples were heated in Pt crucibles at a heating rate of 10 K/min in the temperature range of 298 K–723 K, and each test temperature point was held for 15 min. The differential scanning calorimetry curves and specific heat (C_p) of all samples were carried out using a differential scanning calorimeter (DSC, Q20) at a heating rate of 10 K/min. The actual chemical compositions of the samples were determined by electron probe microanalysis (JXA-8800R). The Hall coefficient R_H, carrier concentration n, and carrier mobility μ of the samples at room temperature were measured by an Accent HL5500PC Hall system using the van der Pauw method under a magnetic field strength of 0.513 T. The electrical conductivity and Seebeck coefficient were measured simultaneously by the standard four-probe method (Sinkuriko: ZEM-1) in an inert gas (Ar) atmosphere from 300 K to 750 K. The thermal diffusivity (D) was measured by the laser flash method using the Netzsch LFA457 system, and the thermal conductivity κ was calculated from the measured D, C_p, and ρ according to the relationship $\kappa = DC_\mathrm{p}\rho$. Uncertainties in the electrical conductivity, Seebeck coefficient, and thermal conductivity measurements were ±5%, ±5%, and ±7%, respectively. In the present work, the thermoelectric properties of $Cu_{2-x}Se$ compounds were measured several times in the temperature range of 300 K–750 K, and the samples did not deform and decompose. This indicates that the prepared samples are stable during the measurements and the transport properties are repeatable and suffer no deterioration.

3. Results and discussion

3.1. Structure and composition analysis

Figure 1 presents the X-ray diffraction (XRD) patterns taken for the melt-quenched $Cu_{2-x}Se$ ($0 \leq x \leq 0.25$) compounds at room temperature. In order to facilitate the expression, we use the nominal composition as the sample name due to the fact that the actual composition is very close to the nominal composition, which is shown in Table 1. According to the XRD results shown in Fig. 1(a), $Cu_{2-x}Se$ compounds possess a β-phase structure for $0.15 \leq x < 0.25$, whereas $Cu_{2-x}Se$ consists of a mixture of β- and α-phase structures in the range of $0 \leq x \leq 0.15$. This is consistent with that in Refs. [16] and [26]. As shown in Fig. 1(b), with the increase in x, the high-angle peak of β-$Cu_{2-x}Se$ shift to higher angle, indicating that the absence of Cu leads to a decrease in the lattice parameter for β-$Cu_{2-x}Se$.

In order to check the phase transitions of $Cu_{2-x}Se$ ($0 \leq x \leq 0.25$) compounds, DSC measurements are adopted to obtain the information of thermal effects, and all results of DSC are in good agreement with those of the XRD. As shown in Fig. 2(a), the DSC curves of the $Cu_{1.75}Se$ and $Cu_{1.80}Se$ do not show any sign of phase transition. Combination of XRD and DSC results confirms that only β-phase exists in the obtained $Cu_{1.75}Se$ and $Cu_{1.80}Se$ compounds. On the other hand, the DSC curves of $Cu_{2-x}Se$ compounds with $0 \leq x \leq 0.15$ show endothermic peaks during the heating process. In addition, with an increase in Cu content, a gradual shift in the onset of the peak towards higher temperatures is observed. For $Cu_{1.85}Se$

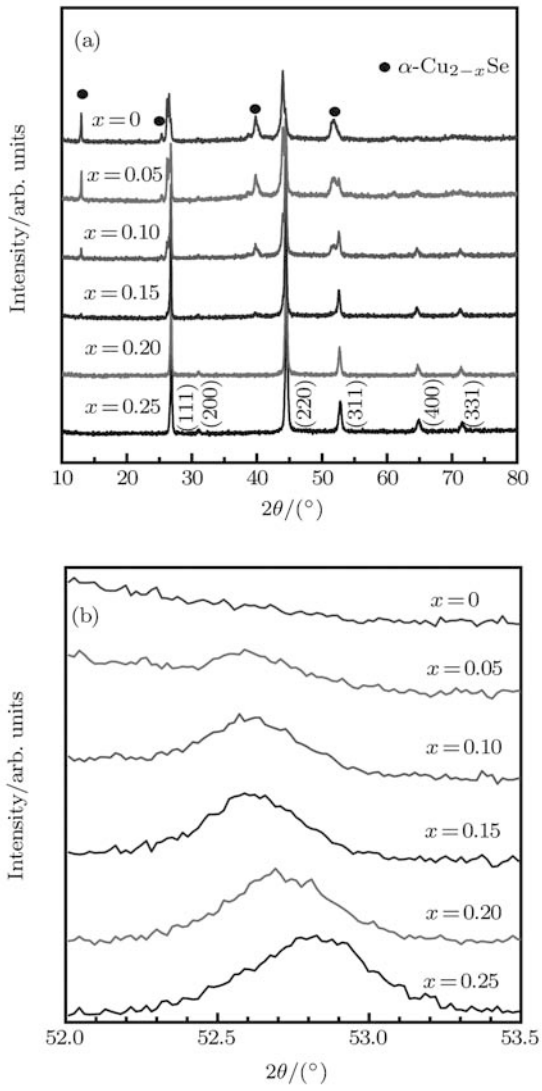


Fig. 1. (a) XRD patterns of as-prepared $Cu_{2-x}Se$ ($x = 0 \sim 0.25$) compounds; (b) peak shift in XRD for $Cu_{2-x}Se$ ($x = 0 \sim 0.25$) compounds.

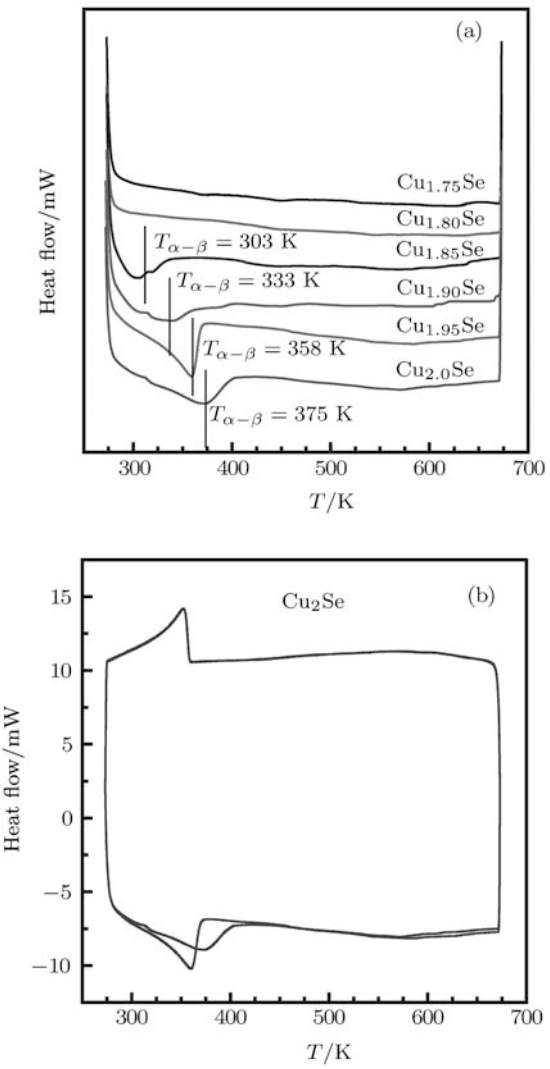


Fig. 2. DSC curves for $Cu_{2-x}Se$ ($x = 0 \sim 0.25$) (a); and the curves for Cu_2Se compound show the two heating-cooling cycles (b).

and Cu_2Se compounds, the peak temperature (T_p) is about 303 K and 375 K, respectively. In addition, according to the twice heating-cooling cycles of Cu_2Se compound (shown in Fig. 2(b)), it is shown that the α–β transition is the first-order reversible phase transition.

To further verify the phase transition and phase structure of the $Cu_{2-x}Se$ compounds in the high temperature range, high temperature X-ray diffraction was performed, and the results are shown in Fig. 3. For the $Cu_{1.75}Se$ compound (Fig. 3(a)), there is no sign of phase transition during the heating process in the temperature range from 298 K to 723 K. There are three diffraction peaks of Pt belong to the Pt crucible. Whereas for the Cu_2Se compound the intensity of the diffraction peak at $2\theta = 13.04°$, which is a distinct diffraction peak between the α-Cu_2Se and β-Cu_2Se, is gradually weaker with increasing temperature, and disappears when the temperature is higher than 393 K. This indicates that the low-temperature α-phase structure transforms to the β-phase structure when the temperature is higher than 393 K. However, the appearance of weak diffraction peaks from Cu_2O can be clearly seen when the temperature is higher than 673 K, which is consistent with the previous report by Skomorokhov *et al.*[16] The oxidation of Cu may be related to the low vacuum during the high temperature XRD testing. Combining the results of high-temperature XRD and DSC analysis, it can be concluded that $Cu_{2-x}Se$ compounds possess a β-phase structure when the temperature is higher than the phase-transition temperature.

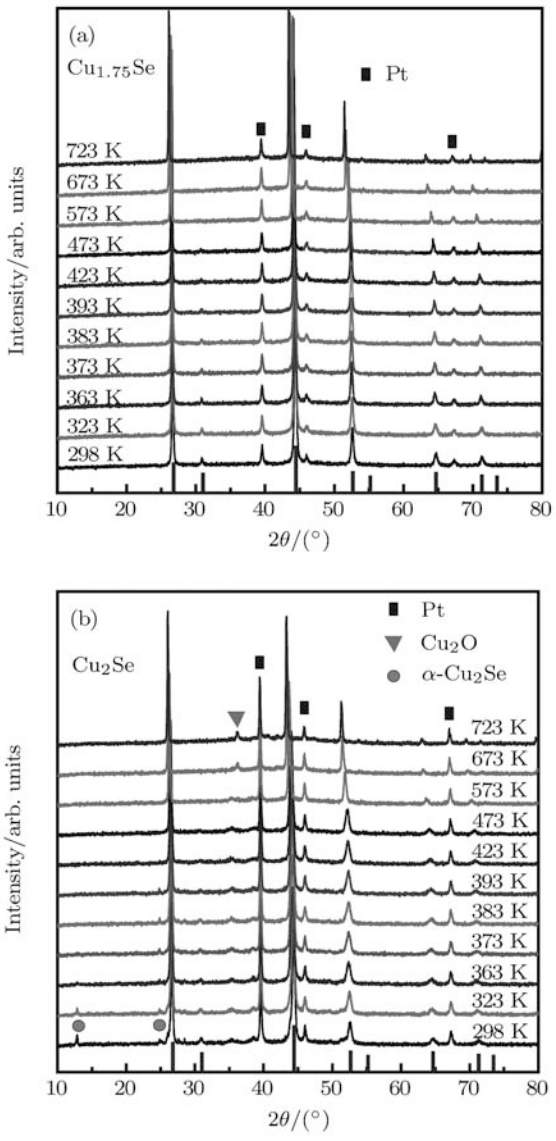


Fig. 3. XRD patterns for $Cu_{1.75}Se$ (a) and Cu_2Se (b) compounds at high temperatures.

3.2. Electrical transport properties

Temperature and Cu content dependences of electrical conductivity of $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds are plotted in Fig. 4. Over the entire temperature range, $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds show high electrical conductivity, which decreases with increasing temperature. At the same temperature, with an increase in x, the electrical conductivity of $Cu_{2-x}Se$ increases significantly. At 300 K, the electrical conductivity of $Cu_{1.75}Se$ is about 7.8×10^5 S/m, which is two times higher than that of Cu_2Se. The Hall coefficient and carrier concentration of $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds at room temperature are shown in Table 1. According to the Hall coefficient measurements, with a decrease in Cu content, the carrier concentration of $Cu_{2-x}Se$ increases

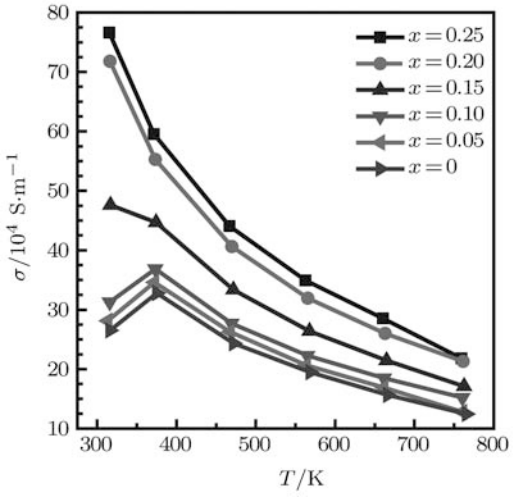


Fig. 4. The temperature dependence of electrical conductivity for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds.

significantly. This means more Cu vacancies will induce a greater carrier concentration, resulting in the enhancement of electrical conductivity. On the other hand, Cu vacancies will generate more point defects and dislocations, which will increase the scattering factors and diminish the carrier mobility. The Hall coefficient and electronic resistivity measurements showed the same trend in Ref. [17], which also pointed out that the deficiency of copper atoms would result in a higher electronic conductivity. When $x < 0.15$, the electrical conductivity of $Cu_{2-x}Se$ shows an anomaly behaviour at about 380 K. According to the XRD, DSC measurements and Ref. [27], the anomaly is due to the α–β phase transition.

Table 1. Actual composition, Hall coefficient (R_H), carrier concentration (n), carrier mobility (μ), and density (ρ) of the bulk materials for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) samples at room temperature.

Nominal composition	Actual composition	R_H /10^{-8} $m^3 \cdot C^{-1}$	n_p /10^{20} cm^{-3}	μ /$cm^{-2} \cdot V^{-1} \cdot s^{-1}$	ρ /$g \cdot cm^{-3}$
$Cu_{1.75}Se$	$Cu_{1.74}Se$	+1.4	4.3	67	6.48
$Cu_{1.80}Se$	$Cu_{1.78}Se$	+1.8	3.3	97	6.53
$Cu_{1.85}Se$	$Cu_{1.83}Se$	+2.3	2.6	123	6.54
$Cu_{1.90}Se$	$Cu_{1.89}Se$	+5.2	1.2	170	6.54
$Cu_{1.95}Se$	$Cu_{1.94}Se$	+6.0	1.0	199	6.58
$Cu_{2.00}Se$	$Cu_{1.97}Se$	+12.6	0.5	251	6.56

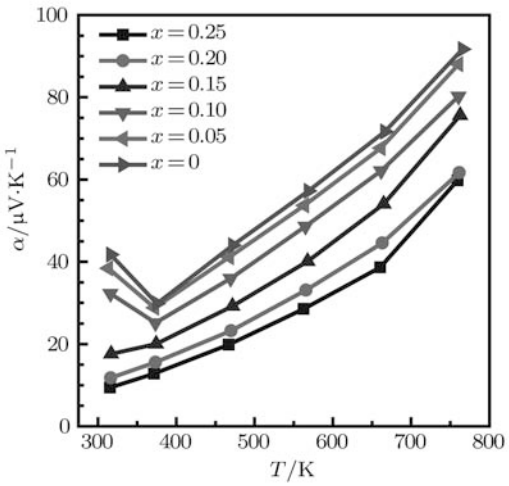


Fig. 5. The temperature dependence of the Seebeck coefficient for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds.

Figure 5 shows the temperature dependence of the Seebeck coefficient for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds. All $Cu_{2-x}Se$ compounds possess a positive Seebeck coefficient. This means that the $Cu_{2-x}Se$ compounds are p-type conduction and majority carriers are holes, which is consistent with the Hall measurements. At the same temperature, the Seebeck coefficient of $Cu_{2-x}Se$ compounds increases with the decrease of x, which means that Cu vacancies and the carrier concentration increase, compatible with the Hall measurements and the variation in electrical conductivity, as mentioned above. Owing to the α–β phase transition in $Cu_{2-x}Se$ compounds with $0 \le x \le 0.15$, both the Seebeck coefficient and the electrical conductivity show an anomaly transition near 373 K. The Seebeck coefficient of $Cu_{2-x}Se$ compounds increases with increasing temperature above 373 K, which indicates semi-metal or degenerate semiconductor behaviour. The Seebeck coefficient of Cu_2Se is about 90 μV/K at 750 K, and it increases by 50% compared with that of $Cu_{1.75}Se$.

Based on the results of electrical conductivity and the Seebeck coefficient, the power factor (PF) of all samples can be calculated according to the equation $PF = \sigma\alpha^2$. As shown in Fig. 6, the power factor increases as x decreases. Because of the high Seebeck coefficient, the sample Cu_2Se has a maximum power factor 1.0×10^{-3} W/mK^2, which increases by nearly 30% compared with $Cu_{1.75}Se$ at 750 K.

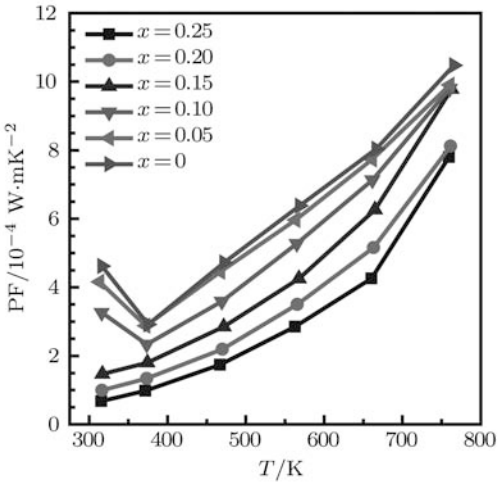


Fig. 6. The temperature dependence of the power factor for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds.

3.3. Thermal transport properties

Figure 7 shows the temperature dependence of the total thermal conductivity and lattice thermal conductivity for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds. The thermal conductivity for the $Cu_{1.75}Se$ and $Cu_{1.80}Se$ samples decreases gradually with increasing temperature and Cu content, and the thermal conductivity of $Cu_{1.75}Se$ is about 3.4 W/mK at 750 K. Whereas the samples of $Cu_{2-x}Se$ ($0 \le x \le 0.15$) are a mixture of β- and α-phases below 400 K, anomaly behaviour is observed near 373 K, which is related to the α–β phase transition and is consistent with the electrical conductivity and Seebeck coefficient results. With an increase in Cu content, the thermal conductivity decreases gradually at the same temperature above 400 K. The sample of Cu_2Se exhibits a minimum thermal conductivity of about 2 W/mK at 750 K.

The thermal conductivity can be expressed as the sum of a carrier component (κ_e) and a lattice component (κ_L). The carrier component (κ_e) can be estimated by the Wiedemann–Franz relationship, $\kappa_e = L\sigma T$, where L is the Lorenz number, σ is the electrical conductivity and T is the absolute temperature. In this study, we take $L = 1.5 \times 10^{-8}$ $V^2 \cdot K^{-2}$ to estimate κ_e. The lattice thermal conductivity κ_L is then deduced from the simple relation $\kappa = \kappa_e + \kappa_L$. Due to the fact that $Cu_{2-x}Se$ compounds with $x \le 0.15$ exhibit an α–β phase transition in the temperature range of 300 K–400 K, in order to facilitate discussion, we just calculate the κ_L of $Cu_{2-x}Se$ compounds at the temperature range of 400 K–750 K. At high temperatures, κ_L is presumably governed by the phonon–phonon interactions (the "Umklapp processes"), leading to a $(1/T)$ dependence, as is clearly shown in Fig. 7(b). Furthermore, with an increase in Cu content, the lattice thermal conductivity of $Cu_{2-x}Se$ compounds decreases, which may be related to the degree of disorder in the $Cu_{2-x}Se$ system and the strong scattering of short-wavelength phonons by short-range disorders. When $x < 0.15$, the $Cu_{2-x}Se$ compounds possess α and β mixed phase structure, and the content of α-phase increases with a decrease in x. Once the temperature is higher than 400 K, the α-phase will gradually transit to the β-phase. Besides, according to the literature, the structure of α- and β-phases is basically of the antifluorite-type with Se atoms in fcc positions and Cu atoms distributed over the large number tetrahedral, trigonal, and octahedral sites, many of which are vacant.[28–31] At low temperatures, α-$Cu_{2-x}Se$ and Cu cations form an ordered structure in the distorted fluorite unit cell. When the temperature is higher than the phase-transition temperature, the α-phase with ordered Cu cations will transit to the β-phase. Such an α–β phase transition will increase the degree of structure disorder, which will enhance the phonon scattering.

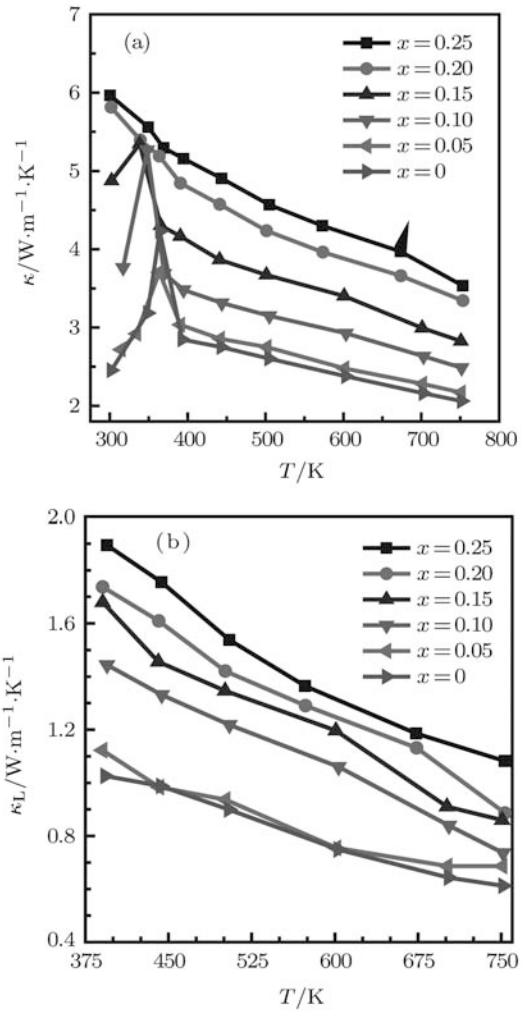


Fig. 7. The temperature dependence of the total thermal conductivity (a) and lattice thermal conductivity (b) for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds.

3.4. Dimensionless thermoelectric figure of merit *ZT*

According to the above measured results of electrical conductivities, the Seebeck coefficient, the thermal conductivity and the dimensionless thermoelectric figure of merit can be calculated using the formula

$ZT = \alpha^2\sigma T/\kappa$, as shown in Fig. 8. It can be seen that the ZT value of all samples increases with increasing temperature, and it also increases with increasing Cu content. The maximum ZT value of $\sim$0.38 was obtained at $\sim$750 K for a Cu_2Se sample because of the largest power factor and lowest thermal conductivity at high temperatures, nearly 125% improvement over the $Cu_{1.75}Se$ sample.

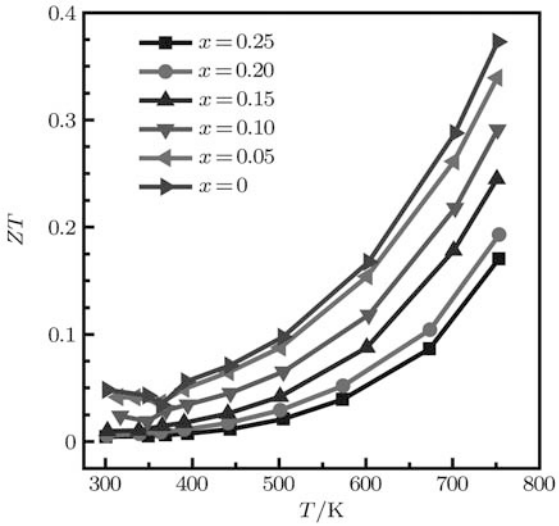


Fig. 8. The temperature dependence of the ZT value for $Cu_{2-x}Se$ ($0 \le x \le 0.25$) compounds.

4. Conclusion

The p-type $Cu_{2-x}Se$ compounds ($0 \le x \le 0.25$) were prepared by the melt-quenching method combined with the SPS technique. The phase structures and thermal transport properties of different compositions were investigated in the temperature range 300 K–750 K. The results show that $Cu_{2-x}Se$ ($0 \le x \le 0.15$) can exist in two modifications of the α- and β-phases at room temperature, whereas when $0.15 \le x < 0.25$, the samples consist only of single-phase β-$Cu_{2-x}Se$. The mixed phase of $Cu_{2-x}Se$ displays anomalous changes in the electrical and thermal transport properties accompanying the α–β phase transformation below 400 K. When the temperature is higher than 400 K, the mixture of α- and β-$Cu_{2-x}Se$ transforms to the single-phased β-$Cu_{2-x}Se$. With the increase in Cu content, the power factor of all samples increases but the thermal conductivity decreases in the whole temperature range. The largest ZT value of $\sim$0.38 was obtained at 750 K for Cu_2Se. A nearly stoichiometric Cu_2Se compound may be a potential candidate of the p-type thermoelectric materials at a medium temperature due to the good electrical properties and a relatively low thermal conductivity, although the Seebeck coefficient is not very high. In future research, the thermoelectric performance of Cu_2Se compound should be optimized by means of doping appropriate elements and/or nanostructuring for a tuning carrier concentration and diminishing thermal conductivity further.

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