Low temperature thermoelectric properties of p-type copper selenide with Ni, Te and Zn dopants

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Thermoelectric figure of merit (ZT) of 0.14 at 200 K is achieved in p-type α -phase copper selenide (Cu₂Se) parent compound made by a ball milling and hot pressing process which exhibits layered structure material. This figure of merit is higher than the conventional p-type TE material bismuth antimony at this temperature range. The broad maxima in the electrical resistivity data around 100 K indicates a possible charge density wave (CDW) transition and Peierls distortion, however, such kind of anomalies were not observed in other transport properties. These features suggest that p-type α -Cu₂Se could be a promising thermoelectric material at low temperatures.

I. Introduction

During the past several decades, physicists and engineers have devoted much effort to improving the conversion efficiency of thermoelectric (TE) materials, which are able to convert industrial waste heat into electricity. These solid-state materials have the potential to provide a renewable source of carbon free energy for our future [1,2]. The efficiency of the thermoelectric materials is characterized by the dimensionless quantity ZT called the figure of merit, defined by $S^2T/(\rho\kappa_{tot})$, where S , T , ρ and κ_{tot} are Seebeck coefficient, absolute temperature, electrical resistivity and total thermal conductivity, respectively. At low temperatures the total thermal conductivity κ_{tot} can be separated into two parts: the carrier (electrons, holes, etc.) part κ_e and phonon (or lattice) part κ_{ph} . Generally speaking, increasing the Seebeck coefficient and reducing the total thermal conductivity are the main methods to improve the value of figure of merit. In recent years reducing the phonon thermal conductivity κ_{ph} through the nanostructuring technique has proved to be the easiest and most straightforward approach [3-5]. The crucial point of the nanocomposite method is to introduce grain boundaries at the nanoscale whose sizes are larger than the mean free path of electrons but smaller than the one of phonons, as a result κ_{ph} would be significantly decreased while leaving other quantities unchanged or slightly altered. Besides employing a fabrication technique, the intrinsic properties of the material itself are also important in order to ensure a low thermal conductivity. For example, skutterudites and clathrates are shown to have complex

structures with strong phonon scattering centers and have low thermal conductivity [6,7]; layered structure materials also are demonstrated to have high ZT values due to their high Seebeck coefficient and low thermal conductivity resulting from their low dimensionality [8-11].

Cu₂Se is a layered compound which exhibits a second order structural phase transition at 130 °C from low temperature monoclinic α -Cu₂Se phase to high temperature anti-fluorite cubic β -Cu₂Se phase [10,11], and is shown to have a peak in the temperature dependent ZT curve at this transition temperature and can be tuned by iodine doping [12]. Cu₂Se has been extensively studied for its TE performance at temperatures above 300 K, which includes the phase transition at ~ 430 K. This higher temperature regime reflects the presence of a phonon-glass electron-crystal, considered to be the origin of the high ZT value determined for this material [21-24]. A charge density wave (CDW) is a periodic modulation of the electronic charge density with an accompanying lattice structure distortion, which results from the formation of electron-hole pair at the Fermi surface due to the instability of the lattice structure, and is usually induced by a perfect nesting on the Fermi surface [19]. α -Cu₂Se is said to exhibit a CDW transition with Peierls distortion below 125 K according to its local maxima in the electrical resistivity measurements in that temperature regime [13-15], and may benefit its thermoelectric performance, where the enhancement from the Peierls distortion was reported in In₄Se_{3- δ} crystals from CDW state [8]. Motivated by the above facts, α -Cu₂Se could very likely have a low thermal conductivity and a high figure of merit, and can be also tuned by different dopants.

II. Experimental Details

The bulk nanocomposite α -Cu₂Se samples with different dopants (2% Zn, 10% Ni, 10% Te) were synthesized by mechanical ball milling (BM) and hot pressing (HP) at 700 °C. This synthesis technique is similar to our previous work on Cu₂Se at $T \geq 300$ K [11,13]. The typical grain size of the as-fabricated sample is on the order of 1-2 μ m. A LR-700 AC resistivity bridge was used to perform the electrical resistivity and Hall coefficient measurements from 5 to 300 K using a standard 4-probe method. The thermal conductivity and Seebeck coefficient were measured by the thermal transport option (TTO) from Quantum Design - PPMS with a 2-probe method. The errors for the measurements were calculated from the standard deviation and propagation of errors, and were determined to be 4% for thermal conductivity, 5% for Seebeck coefficient, and 11% for figure of merit ZT.

III. Results

Fig. 1(a) shows the powder XRD patterns of the nanocomposite Cu₂Se parent compound and with 2% Zn, 10% Ni, and 10% Te doped samples, which were made by a ball milling and hot pressing fabrication process. The XRD measurements were performed on a Bruker D2 PHASER system at room temperature and the experimental details can

be found in our previous work [11,13]. The XRD patterns and subsequent refinements show that the α -Cu₂Se exhibits a layered and monoclinic structure where the structure maintains unaffected by different dopants. Research on the crystal structure of Cu₂Se has shown that several crystallographic structures may be present depending on the temperature [25]. Our XRD refinement calculation shows a monoclinic structure of Cu₂Se [13]. Fig. 1(b) shows a typical SEM image of the Cu₂Se hot pressed (HP) parent compound measured by JEOL JSM-6340F Field Emission Scanning Electron Microscope, and the dimensions of the grain sizes are on the order of several microns and are comparable with the grain dimensions for other doped samples.

Fig. 2 shows the transport properties of these Cu₂Se samples, where some of the electrical transport results are adopted from our previous work [13]. In Fig. 2(a), the electrical resistivity curves of Cu₂Se, Cu_{1.98}Zn_{0.02}Se and Cu_{1.9}Ni_{0.1}Se show a significant broad maxima around 100 K, which may be attributed to the possible formation of CDW [13-15], however the phenomenon is not visible in Cu₂Se_{0.9}Te_{0.1} sample (further discussed in sect. IV). Compared with the electrical resistivity results of single crystals during CDW transitions, nanostructuring broadens the peak and extends the phase transition to a wider temperature range [16-18]. The occurrence of a CDW and the accompanying Peierls distortion result from the perfect nesting on the Fermi surface and the subsequent partial disappearance of the Fermi surface, as a result the carrier concentration should have a decrease during the transition, and the scattering mechanism will be different from those outside the transition range [19]. Fig. 2(c) and Fig. 2(e) show the temperature dependence of mobility and Hall carrier concentration from the Hall measurements. As seen in Fig. 2(c), the slope of the curves has a significant decrease in the transition range, while maintaining nearly the same character outside of it. We conclude that the scattering originates from the same mechanism outside of the transition, but is altered by the formation of a CDW during the transition. Fig. 2(e) further confirms the transition by revealing the decrease of carrier concentration at this temperature range.

FIG. 1. Structural characterization and microstructure images of as-prepared Cu₂Se hot pressed samples with different dopants. (a) Room temperature XRD patterns. (b) A SEM image of Cu₂Se parent compound reveals the typical grain

size.

Fig. 2(b) and Fig. 2(d) show the total thermal conductivity and Seebeck coefficient vs. temperature, unlike the broad maxima revealed in the electrical resistivity data, there are no similar anomalies observed in thermal conductivity and Seebeck data. As reported in the literature, Cu_2Se is a p-type electrical conductor with a Cu deficiency in the lattice which results in an equivalent concentration of holes [10,14]. The 10% Ni doped sample shows evidence of similar hole doping behavior to the Cu deficiency because the Ni doping promotes an increased hole concentration due to the number of valence electrons available in Ni. By the Ni doping the carrier concentration is increased and, as a result, $\text{Cu}_{1.9}\text{Ni}_{0.1}\text{Se}$ has a lower electrical resistivity and higher thermal conductivity compared with other samples. While 2% Zn and 10% Te dopings more behave as scattering centers, thus these two doped samples have higher electrical resistivity and lower thermal conductivity. Fig. 2(f) and Fig. 2(h) show the temperature dependence of the power factor and figure of merit (ZT), and the best thermoelectric performance is from the parent compound, which has a ZT value of 0.14 at 200 K. Fig. 2(g) shows the comparison between Cu_2Se parent compound and p-type bismuth antimony single crystal [20], which is a conventional low temperature p-type TE material, and we can see that Cu_2Se has a better performance at low temperature.

FIG. 2. Temperature dependent behaviors of thermoelectric transport properties. (a) Electrical resistivity. (b) Total thermal conductivity. (c) Mobility plotted in $\log$ scale. (d) Seebeck coefficient. (e) Hall carrier concentration. (f) Power factor. (g) Comparison of ZT between Cu_2Se nanocomposite parent compound and conventional low temperature p-type bismuth antimony single crystal. (h) Figure of merit. Except (g) all other figures have the same legend. The

bismuth antimony data is taken as a comparison from ref. [20].

IV. Discussion

The good thermoelectric performance of α -Cu₂Se is due to its low dimensional layered structure combine with a ball milling and hot press fabrication process. This results in low thermal conductivity across a wide temperature range $T < 300$ K. The broad anomaly associated with a CDW transition at 90-150 K is observed in the electrical resistivity measurements of the Ni and Zn doped samples but does not occur in the Cu₂Se_{0.9}Te_{0.1} sample. The suppression of the CDW behavior may be due to the fact that Te is isoelectronic with Se where Te can easily replace Se in the crystal lattice. The electronic and lattice changes alter the band structure of the compound significantly and destroy the perfect nesting of the Fermi surface thereby eliminating the CDW phenomenon. This is supported by the mobility and carrier concentration data of Cu₂Se_{0.9}Te_{0.1} sample, which shows a smooth monotonic behavior in contrast to the sudden decrease at ~ 150 K in carrier concentration and mobility of the Ni and Zn doped samples.

Unlike the structural transition from α -Cu₂Se phase to β -Cu₂Se phase, which appears at ~ 130 °C in single crystals, the Peierls distortion manifests as a broad peak in both doped and undoped nanocomposite materials and looks like a “weak” phase transition compared with the higher temperature structural transition. Evidence of the Peierls distortion comes from the collective behavior of the many nanocomposite grains and is influenced by the grain size distribution. Our data from thermal conductivity and Seebeck coefficient does not show evidence of a Peierls distortion because this is a weak transition, however this is not the case for such anomalies observed in the structural transition at higher temperatures [12].

V. Conclusions

A CDW transition and the Peierls distortion are observed in Cu₂Se nanocomposite parent compound, which are confirmed by its electrical resistivity, mobility and carrier concentration measurements. Similar transitions are also observed in both Zn and Ni doped Cu₂Se, but eliminated by Te dopants, this reveals that the transition could be tuned by different dopants. The best ZT value of 0.14 at 200 K is achieved from the parent compound due to its unique structure and the distinctive fabrication processes, which is higher than the performance of the conventional low temperature p-type bismuth antimony single crystals. This confirms the potential applications of α -Cu₂Se as a p-type thermoelectric material in the low temperature field.

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