Pronounced effect of ZnTe nanoinclusions on thermoelectric properties of Cu_{2-x}Se chalcogenides

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ABSTRACT Metal chalcogenides especially Cu_{2-x}Se has gained much attention in thermoelectric community due to its complex crystal structure and superionic behavior. Here, we report a facile method to improve the thermoelectric efficiency by introducing ZnTe nanoinclusions into the matrix of Cu_{2-x}Se . As a result, a substantial improvement of 32% in electrical conductivity of Cu_{2-x}Se -ZnTe composite is observed. The increase in electrical conductivity is at the expense of Seebeck coefficient, which slightly decreases the power factor of the composite samples than that of pure Cu_{2-x}Se . Furthermore, the introduction of secondary phase facilitates in declining the total thermal conductivity of Cu_{2-x}Se -ZnTe composite up to 34% by suppressing the lattice thermal contributions. Thus, the moderate power factor and lower thermal conductivity values result in an improved figure of merit (zT) value of ~ 0.40 in mid-range temperature (750 K) for Cu_{2-x}Se -ZnTe composite with 10 wt.% of ZnTe, which is about 40% higher than that of its pure counterpart. Hence, it is believed that the incorporation of ZnTe nanoinclusions in the matrix of Cu_{2-x}Se may be an important route to improve the thermoelectric properties of Cu_{2-x}Se based compounds.

Keywords: ZnTe nanoparticles, Cu_2S , thermoelectric materials, Cu_{2-x}Se -ZnTe composite, thermal conductivity

INTRODUCTION

Nowadays clean, highly efficient and environmental friendly sources of energy are crucial to overcome the depletion of fossil fuels. Green energy is now getting more attention because of environmental concerns and global warming issues associated with consumption of fossil fuels. One of the major issues associated with low efficiency of different

energy systems is the loss of energy such as heat production. However, thermoelectric materials have the ability to convert waste heat into electrical energy without making the system complex which makes these materials noiseless and environment friendly. The efficiency of thermoelectric materials can be characterized by the dimensionless figure of merit ($zT = S^2\sigma T/\kappa$), where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the total thermal conductivity comprised of lattice thermal (κ_l) and electronic thermal (κ_e) conductivities. Hence, the efficiency of a thermoelectric material can be enhanced by increasing the power factor and decreasing the total thermal. As S and k are interconnected to each other, the only possible way to enhance the efficiency of thermoelectric materials is to break the linkage between electronic and thermal transport properties. It has been experimentally proved that by reducing the particle size from their mean free path, thermal conductivity can be suppressed by breaking the linkage between electrical and thermal transport properties [1]. Meanwhile, the thermoelectric efficiency has also been enhanced by using various techniques such as growth of nanowires [2,3], nanocomposites [1,4–6], superlattices [7] and thin films [8]. Bulk nanocomposites has also been reported to reduce thermal conductivity without affecting the electronic transport [5]. Presently, copper chalcogenides are getting more attention due to their simple chemical formula but complex crystal structures [9–12]. Among the other copper chalcogenides, copper selenide has been investigated as a potential thermoelectric material due to the mixed electronic and ionic

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conduction mechanism, along with a unique phase transition from low temperature α to high temperature β phase near 400 K [13]. The α phase can be crystallized into cubic, monoclinic, orthorhombic or tetrahedral structure, while the β phase always exhibits cubic phase in which Cu atoms are distributed on tetrahedral sites due to high mobility and immobile Se atoms are located on face-centered cubic site which results in superionic behavior [14]. The increased ionic mobility with temperature causes phase transition and this transformation results in high efficiency of this material in the β phase [15]. Many efforts have been devoted to further enhancing the efficiency of Cu_{2-x}Se by ionic doping such as Te and I substitution at Se site [16–18], Ag substitution at Cu site [14], fabrication of Cu_2Se by high temperature self-propagating technique [19] single crystal synthesized by melt-quenched process [20] and by introducing nano dimensional defects [21]. The introduction of second phase is also considered as an efficient way to enhance zT by reducing thermal conductivity [22]. Recently, alloys of Cu_2Se with SnSe has been investigated in which high figure of merit is obtained by retaining the intrinsic properties of the materials [23]. The ZnTe is a p-type transport semiconductor with wide direct bandgap of 2.26 eV at room temperature, having zinc blend crystal structure and variety of application in the field of photovoltaic, electrochemical cells and energy devices. The nanoinclusion along with introduction of the second phase is found to be effective to enhance thermoelectric efficiency by improving electronic transport properties and reducing thermal conductivity by increasing phonon scattering with the expansion of grain boundaries and existence of defective centers [24,25]. Thus, the nanoinclusions of such a material having better intrinsic properties to break the phonon scattering will result in larger reduction in thermal and increase in electrical conductivities, leading to higher thermoelectric activity of the Cu_{2-x}Se bulks.

In this work, we developed a facile method to enhance the thermoelectric efficiency of Cu_{2-x}Se by introducing ZnTe nanoparticles (NPs) in the matrix of Cu_{2-x}Se by ball milling and spark plasma sintering (SPS) approach. The inclusion of ZnTe NPs in the Cu_{2-x}Se matrix results in the optimized values of electrical conductivities because of the increasing carrier concentration and reduced total thermal conductivity due to increased phonon scattering through point defects and larger number of grain boundaries. Engineering at nanoscale level in the Cu_{2-x}Se matrix by high energy ball milling and SPS technology helps with structure tuning at atomic level to alter the thermal and electrical variation of Cu_{2-x}Se -ZnTe composite. Therefore, the combined effects of all transport properties result in enhanced

zT values up to 0.40 for Cu_{2-x}Se -ZnTe composite that is almost 40% higher than that of pure Cu_{2-x}Se which proves this mesoscopic system as an efficient effort to enhance the efficiency of thermoelectric materials.

EXPERIMENTAL SECTION

Synthesis

The Cu_{2-x}Se and its composites Cu_{2-x}Se -ZnTe containing different weight percent (0, 5%, 10%, 15% and 20%) of ZnTe were synthesized using ball milling and SPS techniques. First, Cu_{2-x}Se was synthesized using pure Cu (99.5%) and Se (99.999%) powders. However, high purity Cu can also be achieved by dynamic decomposition process which may also contribute to the results [26]. The powdered materials were ball-milled at 425 rpm for 4 h under argon atmosphere in planetary ball mill. After the synthesis of pure Cu_{2-x}Se , high purity ZnTe (99.99, Alfa Aesar) powder was mixed in different ratios with Cu_{2-x}Se at 350 rpm for 6 h. The obtained series of composites Cu_{2-x}Se -ZnTe were compacted into bulk using SPS at 600°C for 6 min, under a uniaxial pressure of 50 MPa. The bulk samples were cut into rectangular bars having dimensions of 15 mm $\times$ 3 mm $\times$ 3 mm for simultaneous measurement of electrical conductivity and Seebeck coefficient. Further, the pellets having diameter of 10 mm with thickness of 2 mm were also cut from the sintered sample and used for thermal conductivity measurement.

Physical characterization

The crystal structure was investigated by X-ray diffraction (XRD) using a Rigaku X-Ray diffractometer with Cu-K α radiations ($\lambda = 0.15406$ nm) (Tokyo, Japan). The elemental distribution and grain morphologies were investigated by using scanning electron microscope (SEM, Zeiss Evo 18 Germany).

Thermoelectric transport properties

The rectangular specimens in the radial direction of the synthesized pellet were used to measure the Seebeck coefficient (S) and electrical conductivity by using LINSEIS LSR-3 (Seebeck & Electric Resistivity Unit) from room temperature to 750 K. The thermal diffusivity (D) and the heat capacity (C_n) were measured along the thickness direction of square pellet by Netzsch LFA 457. The total thermal conductivity (k) was calculated by the formula; $k = DC_n d$, where, d is the mass density measured by Archimedes principle. The carrier concentration, mobility and Hall coefficient were measured by Ecopia Hall Measurement System (HMS-3000) at room temperature.

RESULTS AND DISCUSSION

The schematic in Fig. 1a represents the phenomenon of the scattering of phonons of different wavelengths by the point defects, nanoinclusions, nanoporosity and the grain boundaries. In contrast to the previous report where inclusions of nanoporosity or atomic level defects caused the reduction in thermal conductivity, and affected the electrical conductivity, here the nanoinclusions of ZnTe were introduced to improve the electrical conductivity along with the reduction of thermal conductivity. The existence of a second phase of nanosized ZnTe NPs in the bulk of Cu_{2-x}Se facilitates to optimize the electrical conductivity via increasing carrier concentration as well as reducing the total thermal conductivity through lowering the lattice thermal conductivity by increasing the phonon scattering as shown in Fig. 1a. The increment of electrical conductivity is also based on the intrinsically higher conductivity of the ZnTe NPs, while they also help in phonon scattering due to their nanosize which converts low to high wavelength phonons resulting in lower thermal conductivity in Cu_{2-x}Se -ZnTe composite. In fact, the wide grain size distribution between NPs of ZnTe and micro sized Cu_{2-x}Se grains are responsible to scatter long wavelength phonons acting as additional scattering centers for the heat carrying phonons [27]. Further, high energy ball milling and SPS sintering result in structural defects which are also very helpful for low to high phonon conversion, and result in lower thermal conductivities. To determine the structural features of the pure Cu_{2-x}Se and composite phases, XRD was carried out as shown in Fig. 1b. The pure Cu_{2-x}Se is mainly crystallized into orthorhombic phase (indexed by PDF#47-1448) while the 5 wt.% ZnTe composite shifts the crystallization from purely orthorhombic phase to mixed

orthorhombic and cubic phases (indexed by PDF#47-1448 and PDF#15-0746) containing an additional cubic *Fm-3m* phase of ZnTe as shown in Fig. 1b. Interestingly, the composite with higher concentration of ZnTe nanoinclusions shows stronger diffraction peaks which belong to Cu_{2-x}Se exhibiting a phase change in which α -phase (orthorhombic) changes to β -phase (cubic) along with the cubic phase of ZnTe (indexed by PDF#71-0044 and PDF#15-0746).

To observe the distribution of ZnTe nanoinclusions in the matrix of Cu_{2-x}Se , SEM studies were carried out as shown in Fig. 2. The SEM studies of pure Cu_{2-x}Se and the composite show the freshly broken surface of as-synthesized pellet by SPS, which clearly indicates that ZnTe NPs are found in the matrix of Cu_{2-x}Se in the composite. The SEM image of pure Cu_{2-x}Se shows only the micro sized grains, as shown in Fig. 2a and for the composite phase Cu_{2-x}Se -ZnTe, the NPs of ZnTe (150–200 nm) can be seen clearly distributed over the grains of Cu_{2-x}Se , as shown in Fig. 2b. Further, SPS can achieve a density close to the theoretical one (99%) while maintaining the original nanostructural features grown by the high energy ball milling as shown in the inset of Fig. 2b. In order to further confirm the presence of ZnTe NPs in the matrix, the backscattered electron images along with the elemental mapping recorded from the polished surface were employed, as shown in Figs 3a–f. The elemental mapping confirms the presence of ZnTe NPs in the matrix of Cu_{2-x}Se . In Fig. 3b, it is obvious that ZnTe NPs have been successfully incorporated into the matrix of Cu_{2-x}Se .

The temperature dependent electrical conductivity, Seebeck coefficient and thermal conductivity from room temperature to 750 K were measured to determine the thermoelectric performance of the pure and composite samples.

Figure 1 (a) The schematic representing the phonon scattering mechanism of the Cu_{2-x}Se -ZnTe composites and (b) the XRD patterns of pure Cu_{2-x}Se and its Cu_{2-x}Se -ZnTe composites with different ratios (5 wt.%, 10 wt.% & 15 wt.%) of ZnTe NPs.

It is well-known that introducing NPs in the bulk matrix is very helpful for lowering the thermal conductivities by scattering the phonons. However, these defects might affect the electrical conductivity. It can be compensated by improving Seebeck coefficient and decreasing thermal conductivity, which results in significantly increased overall zT value. Thus, structural, morphological and compositional studies confirmed the introduction of ZnTe NPs into the matrix of Cu_{2-x}Se to boost its thermoelectric properties. To attain better thermoelectric properties and higher zT values, the density of the developed materials should be near the theoretical density. But it is well known that reduction of size to nanoscale or introduction of nanomaterials in the bulk results in poor packing density. Simple sintering to

get higher density will result in the formation of particles/grain boundaries which diminishes the nanoscale feature of ZnTe dopants. Thus, it is very essential to employ the sintering at high temperature using faster rate under pressure, and in this way the composite will spend less time in the low temperature regime preventing larger diffusion of NPs. The SPS technique is carried out in shorter time and at lower temperature, as it is a pressure assisted technique that uses spark plasma produced by the high amperage pulsed direct current. This facilitates to obtain higher density and maintains the nanofeature in the Cu_{2-x}Se -ZnTe composite. The SPS can achieve the densities close to the theoretical one (99%) as well as keeping the original nanostructural feature generated by the high energy ball mill-

Figure 2 The SEM images of (a) freshly broken surface of pure Cu_{2-x}Se and (b) Cu_{2-x}Se -ZnTe composite with 10 wt.% of ZnTe (the inset shows high magnification SEM image of Cu_{2-x}Se -ZnTe composite with 10 wt.% of ZnTe).

Figure 3 Microstructure of the polished cross section of Cu_{2-x}Se -ZnTe composite with 10 wt.% of ZnTe. (a) BSD image; (b) collective presentation of distribution of all the elements in the selected area; and (c) the distribution of Se (d) Te (e) Cu and (f) Zn.

ing, as shown in the XRD (Fig. 1) and SEM (Fig. 2) results. The electrical conductivities of all the samples including pure Cu_{2-x}Se and $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites decrease with increasing temperature which indicates intrinsic metallic behavior of Cu_{2-x}Se as shown in Fig. 4a. A prominent shift in the trend of electrical conductivities was observed near 400 K indicating the structural transformation by phase change from α to β for Cu_{2-x}Se [27]. On the other side, the electrical conductivities of all the composites are improved with increasing ZnTe contents and the maximum conductivity 959 S cm^{-1} is observed in the 15 wt.% sample at 750 K. The increased electrical conductivity can be associated with increased carrier concentration, as shown in Fig. 4b. The different composition leads to phase segregation rather than simple solid solution which can boost up the hole concentration to carry out the charges. The increased carrier concentration might be due to the small substitution of Cu^{+1} ($0.77 \text{ \AA}$) to Zn^{2+} ($0.74 \text{ \AA}$) site which facilitates the increase of the hole concentration. There is a direct relation between carrier concentration and electrical conductivity as given by the expression: $\sigma = ne\mu$, where n is the carrier concentration, e is the electronic charge and μ is the carrier mobility. It can be seen that μ decreases with increasing ZnTe contents but the increase in n is sufficient to increase the electrical conductivity overall. As the electrical conductivity of ZnTe increases directly with temperature [28] attributing to semiconducting behavior, the increased electrical conductivity of $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites can also be associated with semiconducting behavior of ZnTe NPs. Furthermore, the ZnTe NPs among the Cu_{2-x}Se grains behave like electrical contacts which can also be considered for the enhanced electrical conductivity. Temperature dependent Seebeck coefficient of all the specimens is shown in Fig. 4c, which exhibits positive values for pure Cu_{2-x}Se and all the $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites. The positive values of Seebeck coefficient indicate that holes are the major charge carriers confirming the p-type conduction behavior of the pure and composite samples. An obvious phase change near 400 K was also observed during Seebeck coefficient measurements in the pure Cu_{2-x}Se and all the $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites. Moreover, the Seebeck coefficient of all the specimens increases with increasing temperature in the pure Cu_{2-x}Se and all the $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites, therefore, this linear dependency of the Seebeck coefficient on temperature is in accordance with the picture of a degenerate semiconductors where the mean free path of carrier is almost equal to the inter atomic distance. An inverse relation is found among the ZnTe NPs concentration and Seebeck coefficient, as Seebeck coefficient decreases with increasing ZnTe contents due to increased carrier concen-

tration as defined by Equation (1):

$$S = \frac{8m^*K_B^2}{3eh^2} \left(\frac{\pi}{3n} \right)^{2/3} T, \quad (1)$$

where m^* is the carrier's effective mass, e is electronic charge, h is the planks constant, K_B is the Boltzmann constant, T is the working temperature and n is the carrier concentration. The above equation shows an inverse relation of Seebeck coefficient S with carrier concentration n and a direct relation with temperature. Fig. 4b clearly shows that carrier concentration of the composite phases increases with increasing ZnTe concentration which results in decreased Seebeck coefficient value. However, the intrinsically ZnTe inclusions have poor Seebeck coefficient values with increasing temperature [28] which might be another potential reason for the decreased Seebeck coefficient in the $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites. Meanwhile, the reduced Seebeck coefficient is compensated with the increased electrical conductivity and a moderate power factor (αS^2) of $806 \mu\text{W m}^{-1} \text{ K}^{-2}$ observed for the $\text{Cu}_{2-x}\text{Se-ZnTe}$ composite with 5 wt.% ZnTe NPs as shown in Fig. 4d and a linear increment is found with increasing temperature.

To explore the effect of nanoinclusions of ZnTe on the thermal conductivities of $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites, their total thermal conductivities were measured, which are the sum of electronic and lattice thermal conductivities. Interestingly, it is noted that the thermal conductivities of $\text{Cu}_{2-x}\text{Se-ZnTe}$ composites show a decreasing behavior with increasing temperature and ZnTe contents in the Cu_{2-x}Se matrix, as shown in Fig. 5a. The minimum thermal conductivity of $1.41 \text{ W m}^{-1} \text{ K}^{-1}$ is observed in the 15 wt.% specimen at 750 K. The electronic thermal conductivity was calculated using Wiedemann-Franz relation: $\kappa_e = L\sigma T$, where σ is the electrical conductivity, T is the working temperature and L is the Lorentz number. For semiconductors and metals, the Lorentz number strongly depends upon temperature, so in many semiconductors the actual L value is less than L_0 ($2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$) which can be estimated using the following equation:

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

where, k_B is the Boltzmann constant, r represents the scattering parameter and η is the reduced Fermi energy. The actual Lorentz number is used to calculate the electronic thermal conductivity as shown in Fig. 5b. The reduced total

Figure 4 (a) Temperature dependent electrical conductivities, (b) room temperature carrier mobility and carrier concentration, (c) temperature dependent Seebeck coefficient, and (d) power factor of the pure Cu_{2-x}Se and its Cu_{2-x}Se -ZnTe composites with different contents (5 wt.%, 10 wt.% and 15 wt.%) of ZnTe.

thermal conductivity can be associated with the suppressed lattice thermal conductivity which also shows a decreasing behavior with increased ZnTe contents in Cu_{2-x}Se -ZnTe composites as shown in Fig. 5c. The lowest lattice thermal conductivity ($k_{\min}$) value for Cu_2Se can be calculated by using Cahill's approximation [29]:

$$k_{\min} = \frac{1}{2}(\pi/6)^{1/3} k_B V^{-2/3} (2v_t + v_l), \quad (3)$$

where v_t (2320 m s^{-1}) and v_l (3350 m s^{-1}) [30] are the shear and longitudinal speed of sound, respectively, k_B is the Boltzmann constant and V represents the volume per unit atoms calculated for the orthorhombic phase of Cu_{2-x}Se . The predicted value of 0.70 is close to that of the pure Cu_2Se at 750 K, but it is further reduced to the lowest value of 0.13 for the Cu_{2-x}Se -ZnTe composite with 10 wt.% of ZnTe, as shown in Fig. 5c. The reason behind the lower thermal conductivity with increasing the ZnTe contents in Cu_{2-x}Se -ZnTe composites is the scattering of long wavelength pho-

nons from ZnTe nanoinclusions. As clearly shown in the SEM images, the Cu_{2-x}Se -ZnTe composites contain ZnTe NPs of 150–200 nm, and the mesoscopic grain size distribution can efficiently scatter the long wavelength phonons. Furthermore, there might be little substitution of Zn into the lattice of Cu_{2-x}Se , which may create point defects, resulting in the scattering of short wavelength phonons, hence, further reducing the lattice thermal conductivity. The high Grüneisen parameter (γ) leads to Umklapp scattering which decreases the lattice thermal conductivity due to the increased bond anharmonicity. Grüneisen parameter (γ) in ZnTe NPs (1.96) [1] is reported higher than that in bulk Cu_{2-x}Se (0.77) [2] and it is assumed that to increase the Grüneisen parameter of the Cu_{2-x}Se -ZnTe composite with the increased ZnTe contents, it might result in higher Umklapp scattering further reducing the lattice thermal conductivity of the composite.

Finally by combining the electrical and thermal conductivity transport properties, the figure of merit (zT) for

Figure 5 (a) Temperature dependent total thermal conductivity of the pure Cu_{2-x}Se and its Cu_{2-x}Se -ZnTe composites with different contents (5 wt.%, 10 wt.% and 15 wt.%) of ZnTe. (b) Temperature dependent lattice thermal conductivity of the pure Cu_{2-x}Se and its Cu_{2-x}Se -ZnTe composites with different contents (5 wt.%, 10 wt.% and 15 wt.%) of ZnTe. (c) Temperature dependent lattice thermal conductivity of the pure Cu_{2-x}Se and its Cu_{2-x}Se -ZnTe composites with different contents (5 wt.%, 10 wt.% and 15 wt.%) of ZnTe along with estimated for the pure Cu_{2-x}Se . (d) Temperature dependent figure of merit of the pure Cu_{2-x}Se and its Cu_{2-x}Se -ZnTe composites with different contents (5 wt.%, 10 wt.% and 15 wt.%) of ZnTe.

pure Cu_{2-x}Se and Cu_{2-x}Se -ZnTe composites can be calculated, as presented in Fig. 5d. The increased efficiency in case of Cu_{2-x}Se -ZnTe composite is the combined effect of enhanced electrical and reduced lattice thermal conductivities. It can be seen that the zT value shows an increasing trend with increased temperature for the pure Cu_{2-x}Se and its Cu_{2-x}Se -ZnTe composites. But the highest zT value of 0.40 is achieved at 750 K for the Cu_{2-x}Se -ZnTe composite with 10 wt.% ZnTe, which is about 40% higher than that of the pure Cu_{2-x}Se suggesting the significance of the developed method to improve the thermoelectric properties of the materials. The present zT value at the given temperature is even higher than some other reported values [31,32]. Therefore, the study presents a unique technology to improve the zT value through nano inclusions that can be extended to other systems by selecting better materials

which contain intrinsically good transport properties.

CONCLUSIONS

In summary, we synthesized a series of pure Cu_{2-x}Se and composite phases Cu_{2-x}Se -ZnTe with different weight percent (5%, 10% and 15%) of ZnTe NPs by high energy ball milling process followed by spark plasma sintering. The structural studies demonstrate that ZnTe NPs are distributed in the matrix of Cu_{2-x}Se . The enhancement in electrical conductivity is observed up to 32% with a subsequent decrease in the Seebeck coefficient, which results in the overall slight decrease in the power factor of the composite samples. Among all the pure and composite samples, the lowest value of total thermal conductivity is obtained for the sample containing 15% of ZnTe, which is about 34% less than that of the pure Cu_{2-x}Se . The enhanced zT value

of ~0.4 is observed for the Cu_{2-x}Se -ZnTe composite with 10% ZnTe at 750K, which is 40% higher than that of the pure Cu_{2-x}Se . Thus, it is suggested that the introduction of ZnTe nanoinclusions in the matrix of Cu_{2-x}Se is an effective strategy to improve the thermoelectric performance of Cu_{2-x}Se and other related compounds to be used for waste heat recovery.

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Author contributions Farooq MU, Gao K and Mahmood N planed the idea and designed the experiments. Farooq MU performed all the experiments and wrote the manuscript. Sun X helped with experiment and reviewed the structural part. Pang XL was involved in revising the transport properties. Butt S and Khan SU supported with Hall effect measurements. Mahmood A and Mahmood W worked with scanning electron microscope analysis. All the authors have their input in manuscript writing and revision.

Conflict of interest The authors declare that they have no conflict of interest

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纳米ZnTe插层对 Cu_{2-x}Se 硫属化合物热电性能的增强效应

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摘要 由于具有复杂的晶体结构和超离子导体行为, 金属硫属化合物特别是 Cu_{2-x}Se 在热电领域得到了广泛的关注. 本文报道了一种简单易行的提高热电效率的方法: 在基体材料 Cu_{2-x}Se 中添加纳米ZnTe插层, 用来提高 Cu_{2-x}Se 材料的热电性能. 实验结果表明, Cu_{2-x}Se -ZnTe复合材料的电导率提高了32%, 电导率的增加牺牲了塞贝克系数, 导致复合材料的功率因子稍微低于纯 Cu_{2-x}Se 基体材料; 第二相的引入抑制了晶格热扩散, 使得 Cu_{2-x}Se -ZnTe复合材料的热导率降低了34%. 由此可知, 适中的功率因子和较低的热导率致使含有10 wt.% ZnTe的 Cu_{2-x}Se -ZnTe复合材料在中温条件(750 K)下的 zT 值提高至0.40, 相比于纯 Cu_{2-x}Se 基体材料该数值提高了40%. 因此, 向 Cu_{2-x}Se 材料中添加纳米ZnTe插层, 是提高 Cu_{2-x}Se 基材料热电性能的一个有效途径.