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Enhanced thermoelectric performance through carrier scattering at heterojunction potentials in BiSbTe based composites with Cu$_3$SbSe$_4$ nanoinclusions

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Abstract

Thermoelectric materials with thermoelectric figure of merit, ZT, being much larger than unit at near room temperatures is vital for power generation by using low-grade waste heat. Here we show that by incorporating very small proportion (1 vol.%) of Cu$_3$SbSe$_4$ nanoparticles into BiSbTe matrix to form nanocomposites, besides large (~50%) reduction of lattice thermal conductivity, both enhanced thermopower through energy-dependent scattering and alleviated reduction of carrier mobility via carrier scattering at heterojunction potentials occur at elevated temperatures, which allow thermoelectric power factor of the composite material to reach ~37 µW/(cm·K) at 467 K. Consequently, a largest value of ZT = 1.6 is achieved at 476 K. Moreover, it has excellent performance in broad temperature range (say, ZT=1.0 at 300 K and ZT=1.5 at 500 K), which makes this material attractive for cooling and power generation.

In present work, Bi$_{0.3}$Sb$_{1.4}$Te$_{3}$ (BiSbTe) based composites incorporated with nanophase Cu$_3$SbSe$_4$ was fabricated. BiSbTe alloys are the state-of-the-art thermoelectric materials at near room temperatures with a band gap of ~0.13-0.15 eV. Cu$_3$SbSe$_4$ is a p-type semiconductor with good thermoelectric performance at moderate temperatures and has a wider band gap of ~0.3-0.4 eV. Hence, as they contact each other, p-p type heterojunction potentials at the interfaces will form, which could bring about enhanced EFE and elevated S at high temperatures. Indeed, our results indicate that the incorporation of 1 vol.% of Cu$_3$SbSe$_4$ results in ~5% increase in PF and ~50% decrease in κ at 467 K, leading to a largest ZT = 1.6. Moreover, the obtained material have high ZT (>1.4) in temperature range from 375 K to 500 K, which makes them suitable for cooling and low-grade waste heat recovery applications.

1. Introduction

Thermoelectric (TE) materials can convert electrical power and heat energy reversely. The efficiency of a TE material is evaluated by the thermoelectric figure of merit (ZT), expressed as ZT = (S$^2$ T)/($\rho$κ + κ$_L$), where $\rho$, S, κ$_C$, κ$_L$, and T are the electrical resistivity, Seebeck coefficient, carrier thermal conductivity, lattice thermal conductivity and absolute temperature, respectively. Obviously, one can enhance ZT by maximizing power factor (PF = $S^2$/ρ) and/or minimizing total thermal conductivity (κ = κ$_C$ + κ$_L$). Recent researches indicate that nanostructuring or nanocompositing in bulk materials can dramatically reduce κ$_C$, but PF is seldom elevated simultaneously. Clearly, if one wants to obtain a ZT value much larger than unit, one has to elevate PF simultaneously. Previous studies showed that introduction of resonance distortion of electronic density of states (DOS) by doping to increase S can increase PF (such as in PbTe doped with Tl), but no obvious reduction in κ$_L$ was observed. Furthermore, an excellent alternative way to increase PF is to incorporate nanoinclusions into matrices to form nanocomposites in which energy filtering effect (EFE) would be enhanced through carrier scattering at the interface potentials, leading to increase in S. But, in this case PF sometime declines due to large reduction in carrier mobility $\mu$. Hence, whether one can introduce in nanocomposites a proper heterojunction potentials that can not only bring about strong EFE but also give rise to increased $\mu_n$ (here $\mu_n$ is carrier mobility corresponding to carriers scattering at the interface potentials) and inhibit transport of minority carriers at elevated temperatures, in addition to enhancing phonon blocking, is greatly challenging, for this will result in large improvement of PF and ZT.

In present work, Bi$_{0.3}$Sb$_{1.4}$Te$_3$ (BiSbTe) based composites incorporated with nanophase Cu$_3$SbSe$_4$ was fabricated. BiSbTe alloys are the state-of-the-art thermoelectric materials at near room temperatures with a band gap of ~0.13-0.15 eV. Cu$_3$SbSe$_4$ is a p-type semiconductor with good thermoelectric performance at moderate temperatures and has a wider band gap of ~0.3-0.4 eV. Hence, as they contact each other, p-p type heterojunction potentials at the interfaces will form, which could bring about enhanced EFE and elevated S at high temperatures. Indeed, our results indicate that the incorporation of 1 vol.% of Cu$_3$SbSe$_4$ results in ~5% increase in PF and ~50% decrease in κ at 467 K, leading to a largest ZT = 1.6. Moreover, the obtained material have high ZT (>1.4) in temperature range from 375 K to 500 K, which makes them suitable for cooling and low-grade waste heat recovery applications.

2. Experimental

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Elemental Bi (99.99%, Alfa Aesar), Sb (99.5%, Sigma Aldrich), and Te (99.999%, Alfa Aesar) powders were weighed as starting materials. The powder mixture was loaded into quartz ampoule pumped under vacuum of 10⁻² Pa and then heated to 1073 K for 10 h. Then the ingot was grinded into powders. To prepare nanophase Cu₃SbSe₄ inclusions, 10 mmol SbCl₅ (99%, powder) and 40 mmol Se (99%, powder) and 400 mL ethylenediamine were put into a 800 mL glass beaker to react. After mixing uniformly, 30 mmol CuCl (99%, powder) was then put into the beaker. After about two hours, a large quantity of powders was precipitated. Then the nanometer-sized Cu₃SbSe₄ solution was stirred by a magnetic stirrer at the speed of 1700 r/s about two hours, a large quantity of powders was precipitated. The nanophase Cu₃SbSe₄ was then put into the beaker. After maintaining a temperature of 150°C during the synthesis. After about two hours, a large quantity of powders was precipitated. The collected powder was filtered, washed with anhydrous ethanol and distilled water until a PH value close to 7, and then dried under vacuum at 60 ºC for nearly 6 h. The nanometer-sized Cu₃SbSe₄ and BiSbTe powders were mixed in a planetary mill for 2 h in accordance with the volume ratios of 1:99, 2:98 and 3:97. Then the bulk nanocomposite samples were obtained by hot-pressing the blended powders under a pressure of 600 MPa in vacuum at 673 K for 1 h.

The phase structure of the obtained samples was studied by X-ray diffraction (Philips diffractometer, Cu Kα radiation) at room temperature. The morphology and fractographs were observed by field emission scanning electron microscopy (FE-SEM). Electrical resistivity and Seebeck coefficient were measured by the ZEM-3 system from ULVAC under Helium atmosphere from 293 to 493 K. The thermal diffusivity D was measured using the laser flash method (Netzsch, LFA-457). It should be pointed out that due to the anisotropic characteristic of BiSbTe alloys, D is measured in the perpendicular direction to the pressing direction, ensuring that the thermal and electrical properties are measured in the same direction. The specific heat, Cₚ, was determined by differential scanning calorimetry (DSC Pyris Diamond). The density d was measured by the Archimedes’ method. The resulting total thermal conductivity was calculated from the measured thermal diffusivity D, specific heat Cₚ, and density d according to the relationship κ = DdCₚ. Hall coefficient was measured at 300 K by the Physical Property Measurement System (PPMS). The accuracies in measurements of resistivity, Seebeck coefficient and thermal conductivity are around ±2%, ±5% and ±5%, respectively. The uncertainty of ZT is around ±10%.

3. Results and discussions

The XRD patterns of BiSbTe, Cu₃SbSe₄ and f(Cu₃SbSe₄)/BiSbTe composite samples (f = 1, 2, and 3 vol.%) are shown in Figure 1. The main diffraction peaks correspond well to the standard ICPODS cards (Bi₅Sb₄Te₃: No. 72-1836, Cu₃SbSe₄: No. 85-0003), as shown in Figure 1 (curves (a) and (b)). Moreover, apart from the peaks of BiSbTe, there is an additional small peak at 2θ°=27.3° in patterns from (c) to (e), which corresponds to (112) peak of Cu₃SbSe₄, indicating that there are two phases BiSbTe and Cu₃SbSe₄ in the composite samples, no obvious impurity phase being detected. In addition, the average grain size for Cu₃SbSe₄ is 42 nm that is determined from peak broadening of the XRD pattern for Cu₃SbSe₄ (curve (b) in Figure 1) based on Scherrer formula.

Figure 2(a) and (b) shows the FE-SEM images of BiSbTe (a) and Cu₃SbSe₄ (b) powders. One can observe that the average particle size of BiSbTe powders is around 500-1000 nm, while the average particle size of Cu₃SbSe₄ powders is around 200 nm. The fractographs of Cu₃SbSe₄/BiSbTe composite bulk samples are shown in Figure 2(c). It can be seen from Figure 2(c) that some white spots with sizes of 40-60 nm distribute in the big gray grains (see the inset in Figure 2(c)). By careful inspection with energy dispersive X-ray spectroscopy (EDX), one finds that the areas with white spots contain element Cu (Figure 2(d)), indicating that the white spots are actually Cu₃SbSe₄ grains, in agreement with XRD measurements. Present result indicates that nanophase Cu₃SbSe₄ are successfully incorporated in BiSbTe matrix, forming (Cu₃SbSe₄)/BiSbTe bulk nanocomposites. Fig. 3(a) gives the low magnification bright-field TEM image of Cu₃SbSe₄/BiSbTe, which shows that there are Cu₃SbSe₄ nanoparticles embedded in the BiSbTe matrix. Fig. 3(b) shows the lattice image (corresponding to the rectangle area in Fig. 3(a)) of BiSbTe matrix (lower-right), Cu₃SbSe₄ inclusion (upper-left), and a typical phase boundary (between the matrix and the dispersed phase), as shown by the two arrows.

The thermoelectric properties (ρ and S) of composites f(Cu₃SbSe₄)/BiSbTe (f = 0, 1, 2, and 3 vol.%) are shown in Figure 4 (the corresponding data of nanocrystalline (NC) BiSbTe bulk samples reported by Poudel et al.11 are also depicted there for comparison). It can be seen from Figure 4(a) that ρ for all the composite samples f(Cu₃SbSe₄)/BiSbTe (f = 0, 1, 2, and 3 vol.%) (samples 0°, 1°, 2° and 3°) increases with increasing temperature, indicating that they all exhibit a degenerate semiconductor behavior. On the other hand, ρ increases significantly with increasing f from 1 to 2 vol.% and then to 3 vol.% However, ρ for sample 1° is smaller than that of sample 0° in whole temperature range investigated (ρ decreases from 0.69 to 0.63 x 10⁻⁸ Ωm at 304 K and from 1.30 to 1.11 x 10⁻⁸ Ωm at 490 K as f increases from 0 to 1 vol.%, for instance). Moreover, it is found that the slopes (dρ/dT) of the ρ-T curves for samples with different f as well as NC BiSbTe differ obviously,11 which are 3.34 x 10⁻⁸, 2.61 x 10⁻⁸, 4.12 x 10⁻⁸ and 4.36 x 10⁻⁸ Ωm/K for f = 0, 1, 2 and 3 vol.%, respectively. Specially, it is noted that the (dρ/dT) for the sample 1° is obviously smaller than that of sample 0°, which could involve significant scattering mechanism (see following discussion). Similar phenomena can be found in other material systems, such as (Bi₅Sb₃Te₃)Bi₃SbTe₂/α-SiO₂,12 Bi₅Sb₃Te₃/Ge₆,13 and β-ZnSb₃/Cu₃SbSe₄ nanocomposites. The temperature dependences of S are shown in Figure 4(b). S values for all of the samples are positive, indicating that they belong to p-type semiconductors. The temperature behaviors of S for the sample 0° and NC BiSbTe are similar: S increases first with increasing temperature at T = 450 K.11 Then it decreases with
Further increase in temperature, which can be ascribed to the excitation of minority carriers (i.e. electrons) at high temperatures. In contrast, $S$ values of the composite samples with $f = 1, 2$ and $3$ vol.% increase almost monotonically with temperature in the whole temperature range investigated here. In addition, $S$ decreases obviously with increasing nanoinclusion content $f$ (except $f = 3$ vol.%).

In order to understand better the behavior of $p$ and $S$, carrier concentrations $p$ for all the samples are determined at room temperature, as listed in Table 1. One can see that $p$ increase from $4.52 \times 10^{19} \text{cm}^{-3}$ to $5.50 \times 10^{19} \text{cm}^{-3}$, $7.41 \times 10^{19} \text{cm}^{-3}$ and $8.98 \times 10^{19} \text{cm}^{-3}$, as $f$ increase from 0 to 1 vol.% 2 vol.% and 3 vol.%, respectively. Therefore, the decrease in $p$ of sample 1$^9$ results largely from the increase in $p$ due to the relation $p=(pe\mu)^{-1}$. In contrast, that $p$ of samples 2$^8$ and 3$^8$ are larger than that of sample 1$^8$ can be attributed to the substantial decline of $\mu$ caused by the enhanced interface scattering. On the other hand, the thermopower of a degenerate semiconductor can be expressed by Mott formula:16

$$S = \frac{\pi^2 k_B^2 T}{3q} \left( \frac{\partial \ln(\sigma(E))}{\partial E} \right)_{E=E_F}$$

$$= \frac{\pi^2 k_B^2 T}{3q} \left[ \frac{1}{p} \frac{\partial p(E)}{\partial E} + \frac{\partial \mu(E)}{\partial E} \right]_{E=E_F}$$

where $q$, $k_B$, $E_F$ are the carrier charge, the Boltzmann constant, and the Fermi energy, respectively. Formula (1) indicates that $S$ decreases with increasing $p$ which can explain qualitatively why $S$ of composite samples decrease with increasing $f$.

As mentioned above, the slopes of the $p$-$T$ curves are different among the samples. Especially the slope of sample 1$^9$ is smaller than that of sample 0$^9$. We assume here that $p$ do not change substantially (which is true for a degenerate semiconductor at the temperatures below intrinsic excitation$^{17,18}$) in the temperature range (300 K<T<450 K) investigated here. Then total $\mu$ can be estimated from values of $p$ at different temperatures $T$, as shown in Figure 5(a). If we assume that the scattering events are independent with each other, then one has:19

$$\frac{1}{\mu_T} = \frac{1}{\mu_m} + \frac{1}{\mu_p}$$

where $\mu_T$, $\mu_m$, and $\mu_p$ are the total carrier mobility of the composite samples, the mobility of the matrix and the mobility being related to scattering of interface potentials. Based on the experimental data, one can extract $\mu_p$ by using formula (2), as shown in Figure 5(b). It can be seen that $\mu_p$ of sample 1$^9$ increases with increasing temperature, while $\mu_p$ of samples 2$^8$ and 3$^8$ decrease with increasing temperature. Similar to the scattering of grain boundary potentials, $\mu_p$, caused by interface scattering in nanocomposites can be approximately given by:20,21

$$\mu_p = \frac{Lq}{2\pi m_p^* k_B T} \left[ \frac{E_{sp}}{k_B T} \right]^{1/2} \exp \left( -\frac{E_{sp}}{k_B T} \right)$$

(3)

where $L$ is the mean spacing between two adjacent potential barriers, and $E_{sp}$ is the height of the potential barrier at the interfaces. A logarithmic plot of $\mu_{sp1}^{*T^{1/2}}$ ($\mu_{sp1}$ is $\mu_p$ of sample 1) versus $\mu_{sp1}$ is shown in the inset of Figure 5(b). From the slope the height of the potential barrier is extracted to be $E_{sp1} = 67.1$ meV. If we take $d\mu_p/dT = 0$, i.e.

$$\frac{d\mu_p}{dT} = \frac{Lq}{2\pi m_p^* k_B T} \left[ \frac{1}{T^{1/2}} \exp \left( -\frac{E_{sp1}}{k_B T} \right) \left( \frac{1}{2} \right) \right]$$

(4)

then we obtain a critical temperature $T_c = 2E_{sp1}/k_B$. Using $E_{sp1} = 67.1$ meV and $k_B = 1.38 \times 10^{-23}$ J/K, $T_c = 1556$ K is obtained, which means that when $T<T_c$, there exists $d\mu_p/dT>0$. In our experiment, the temperature range investigated is 300-500 K; hence $\mu_{sp1}$ increases with increasing temperature, which alleviates the increase rate in $\mu$ of sample 1$^9$ (Figure 4(a)). With increasing $f$ from 1 to 2 and then to 3 vol. %, $p$ increase from $5.50 \times 10^{19} \text{cm}^{-3}$ to $7.41 \times 10^{19} \text{cm}^{-3}$ and then to $8.98 \times 10^{19} \text{cm}^{-3}$, and the depletion layer becomes narrow. As a result, $E_{sp}$ becomes smaller. Nonetheless, the scattering probabilities increase owing to substantial increase in scatterers, which cause the carriers to be scattered much stronger, as reflected by large decline of $\mu_{sp1}$ and the much enhanced EFE for samples 2$^8$ and 3$^8$ (as shown in Figure 5(b)). We estimate $E_{sp2} = 12.9$ meV (When $T_c = 300$ K, $E_{sp} = 12.9$ meV) and $d\mu_p/dT<0$ at 300-500 K, for $\mu_{sp}$ of samples 2$^8$ and 3$^8$ decrease with increasing temperature as shown in Figure 5(b), which cause $p$ for samples 2$^8$ and 3$^8$ to increase more steeply (than that of sample 0$^9$) with increasing temperature.

On the other hand, it is worthwhile to notice that $S$ of sample 3$^9$ is slightly larger than that of sample 2$^8$ (as shown in Figure 4(b)), although $p$ of the former is larger than that of the later (as shown in Table 1). This phenomenon could be related to the EFE caused by the incorporation of Cu$_3$SbSe$_4$ nanoparticles. As we know, when two semiconductors (here BiSbTe and Cu$_3$SbSe$_4$) contact each other a (here p-p type) heterojunction potential (barrier) will form at the interfaces due to difference of the chemical potentials of the two semiconductors, which could cause energy-dependent scattering (or EFE) to occur,22 as manifested by the increase of scattering parameter $\lambda$, that is usually related to relaxation time $\tau$ by the relation: $\tau = \tau_0 E^{-1/2}$ (here $E$ is the energy of carriers and $\tau_0$ is energy-independent constant). By using a single parabolic band model, the density of state effective mass $m^*_p$ and $S$ can be expressed as:23

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where $h$ and $\xi_i$ are the Planck constant and the reduced Fermi level, respectively. Here, we assume that acoustic scattering is dominant in BiSbTe (i.e., $\lambda=0$ for sample 0), and one obtains $m^*_d = 1.38 m_0$ (T = 300 K) and $m^*_e = 1.22 m_0$ (T = 443 K) (where $m_0$ is the free electron mass) for sample 0. Moreover, by assuming that the density of state effective mass does not change in different samples at the corresponding temperatures then one can calculate $\lambda$ for samples 1, 2 and 3 at T = 300 K and 443 K, respectively, as shown in Table 1. One can see that $\lambda$ increases with increasing Cu$_{3}$Bi$_{2}$Se$_{4}$ content. This increase of $\lambda$ leads to $\sim$3, $\sim$7 and $\sim$18 $\mu$V/K rise at 300 K and $\sim$3, $\sim$15 and $\sim$26 $\mu$V/K rise at T = 443 K in S for samples 1, 2 and 3, respectively, as shown in Figure 6(a), where the two lines are the Pisarenko relation of BiSbTe at T = 300 K and 443 K, respectively, which shows the dependence of $S$ on $p$ calculated by using formulae (5) and (6).

Moreover, another interesting phenomenon is that although $S$ for sample 0 (and NC BiSbTe) declines at $T\sim$450 K due to excitation of minorities, $S$ for the composite samples 1, 2 and 3 do not show decrease up to 500 K (the highest temperature investigated here). This result suggests that the introduced heterojunction potential barriers scatter electrons more strongly than holes. Since in the case of mixing conduction $S$ can be written as following:

\[
S_T = \frac{\sigma_p S_p + \sigma_n S_n}{\sigma_p + \sigma_n} \quad (8)
\]

where the subscript T, p and n represent total (hole and electronic conduction), hole conduction and electronic conduction, respectively. If electrons are scattered more strongly than holes, $\sigma_p$ (or $\mu_p$) will become negligibly small, and the term $\sigma_p S_p$ (or $S_n$) in formula (8) can be neglected as compared to $\sigma_n S_n$. Then formula (8) becomes $S = \frac{S_n}{\sigma_p}$ which explains why $S$ of samples 1, 2 and 3 monotonically increases with increasing temperature. In other words, the introduced heterojunction potential barriers have an asymmetric shape (i.e. the barrier height $E_{th}$ for electrons is much higher than $E_{th}$ for holes) as depicted schematically in Figure 6(b).

Figure 7 shows PF of f(Cu$_{3}$Bi$_{2}$Se$_{4}$)/BiSbTe as functions of temperature. One can see that PF of the composite samples increases slightly at the beginning; then PF decreases with further increasing temperature. Although PF of all the heavily incorporated samples ($f = 2$, and 3 vol.%) is smaller than that of the sample 0, the PF of the lightly incorporated sample with $f = 1$ vol.% enhances obviously at $T\approx$428 K, reaching 37 $\mu W/cm^2K^2$, which is $\sim$5% larger than that of sample 0 and $\sim$48% larger than that of NC BiSbTe. This enhancement of PF for sample 1 at $T\approx$428 K comes from increased both $\mu_n$ and $S$ at elevated temperatures, which originates comprehensively from contributions of interface potentials: scattering with proper potential barriers for holes, asymmetric scattering to carriers (stronger scattering to electrons than to holes) and enhanced EFE.

The results of the specific heat, $C_p$ determined by DSC for BiSbTe and Cu$_3$Bi$_2$Se$_4$ from 300 K to 500 K are shown in Figure 8(a). One can see that the values of $C_p$ for BiSbTe range from 0.185 to 0.221 Jg$^{-1}$K$^{-1}$, while the values of $C_p$ for Cu$_3$Bi$_2$Se$_4$ range from 0.303 to 0.357 Jg$^{-1}$K$^{-1}$. Due to the small changes for the values of $C_p$ in the temperature range from 300 K to 500 K, the average value of $C_p$ is set here, i.e. $C_p$ for BiSbTe is 0.20 Jg$^{-1}$K$^{-1}$ and $C_p$ for Cu$_3$Bi$_2$Se$_4$ is 0.33 Jg$^{-1}$K$^{-1}$. For the composite sample, $C_p$ can be determined by the rule of mixture:

\[
C_{p,v} = (1 - \chi)C_{p,0} + \chi C_{p,1} \quad (9)
\]

with the mass fraction

\[
\chi = \frac{f}{(1 - f)\eta + f} \quad (10)
\]

where $C_{p,v}$, $C_{p,0}$, and $C_{p,1}$ are the specific heat for the composite sample, BiSbTe and Cu$_3$Bi$_2$Se$_4$, respectively, and $\eta = d_1/d_2$, where $d_1$ and $d_2$ are the theoretical density of BiSbTe and Cu$_3$Bi$_2$Se$_4$. Then we obtain the values of $C_p$ for the composite samples 1, 2 and 3, which are almost the same as the $C_p$ for BiSbTe matrix (due to small content of the nanoinclusions) and equal to 0.20 Jg$^{-1}$K$^{-1}$. The total thermal conductivity $\kappa$ for all the samples, which is calculated from the measured thermal diffusivity $\alpha$, specific heat $C_p$, and density $\rho$, is given in Figure 8(b) as a function of temperature. One can see that $\kappa$ for all the composite samples ($f$=0) is smaller than that of sample 0 in the whole temperature range investigated here. Moreover, $\kappa$ decreases monotonically with the increasing Cu$_3$Bi$_2$Se$_4$ content $f$ (except for the sample 3). For instance, at 420 K, $\kappa$ decreases from 1.3 to 1.1, 0.9 and then 1.0 $\mu W/cm^2K$ as $f$ increase from 0 to 1, 2 and 3 vol.% in addition, as compared to that of NC BiSbTe, $\kappa$ of all the composite samples decrease much faster with increasing temperature and becomes smaller at high temperature range (see Figure 8(b)). The total thermal conductivity $\kappa$ consists of lattice thermal conductivity $\kappa_L$ and the carrier thermal conductivity $\kappa_v$, i.e. $\kappa = \kappa_L + \kappa_v$, where $\kappa_v$ can be estimated by the Wiedemann-Franz relation ($\kappa_v = L\tau$, in which the Lorenz number $L$ is estimated using formula (10) with the assumption of transport dominated by acoustic scattering and a single parabolic band. $^{25}$
The obtained values of $L$ are $1.68 \times 10^{-4} \times 10^{-5} \times 10^{-6} \times 10^{-7}$, as listed in Table 1. As shown in the inset of Figure 8(b), the incorporation of 1 vol.% nanophase Cu$_3$SbSe$_4$ leads to 50% reduction of $\kappa_l$ as compared to that of sample 0. According to Callaway mode, the lattice thermal conductivity $\kappa_l$ can be expressed as: \[ \kappa_L = \frac{4\pi k_B T}{v^3 \hbar} \int_0^\infty d\xi \int_0^\infty \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{1}{\tau(q)} \left( \frac{\xi^2}{\xi^2 - 1} \right) \]

where $h$, $\theta_b$, $v$, $\xi$, and $\tau$ are planck constant, Debye temperature, phonon velocity, usual dimensionless variable and phonon relaxation time, respectively. Moreover, according to Matthiessen’s rule, $\tau$ is mainly related to scattering from multiple scattering centers in the materials and can be written as:

$$\tau^{-1} = \tau_{PD}^{-1} + \tau_{NP}^{-1} + \tau_{p-p}^{-1} + \tau_{IF}^{-1}$$

where $\tau_{PD}$, $\tau_{NP}$, $\tau_{p-p}$, and $\tau_{IF}$ are the relaxation times corresponding to scattering from point defect, nanoinclusions, phonon-phonon interactions and interfaces, respectively. Obviously, the reduction of $\kappa_l$ in the composite samples 1, 2, 3 and 4 should be attributed to the additional phonon scattering from nanoinclusion ($\tau_{np}$) and the formed phase boundaries ($\tau_p$). However, we notice that with increasing $f$ from 1 to 2 and 3 vol.%, $\kappa_l$ rises instead of continuing falling, which could be caused by the inherent large lattice thermal conductivity $\kappa_l$ of Cu$_3$SbSe$_4$, which means that large proportion of its existence will inevitably lead to the increase in the overall $\kappa_l$ of the composite system.

Figure 9 shows ZT for all the samples. One can see that ZT of sample 1 is larger than unit in the whole temperature range and even larger than that of NC BiSbTe at $T>375$ K, reaching 1.6 at 476 K, which is 22% larger than that of sample 0 ($ZT_{max}$ 1.3 at 418 K) and 15% larger than that of NC BiSbTe ($ZT_{max}$ 1.4 at 373 K). Clearly, such excellent thermoelectric performance result from both increased PF and reduced $\kappa_l$ through interface scattering of both carriers and phonons. With such ZT characteristics, the present composite material system is attractive for power generation applications.

4. Conclusions

In summary, the incorporation of 1vol.% Cu$_3$SbSe$_4$ particles into BiSbTe matrix can concurrently result in ~5% increase in PF and ~50% reduction of $\kappa_l$ at 467 K. The increases in PF result from both alleviated reduction of carrier mobility and enhanced EFE at elevated temperatures due to carrier scattering at interface potential barriers in the composite system; while the reduction of $\kappa_l$ in the composite samples is attributed to the enhanced phonon scattering at dispersed nanoparticles and the phase boundaries. Owing to increased PF and reduced $\kappa_l$, ZT = 1.6 is achieved at 476 K in the composite system with 1 vol.% of Cu$_3$SbSe$_4$. Present study demonstrates that the thermoelectric performance of BiSbTe can be effectively improved by incorporating proper amount of nanophase Cu$_3$SbSe$_4$.

Acknowledgements

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References

Table 1
List of Hall mobility $\mu$, carrier concentration $p$, the relative density $d_r$ and the Lorenz number $L$ at room temperature and scattering parameter $\lambda$ at 300 K and 443 K for $f$(Cu$_3$SbSe$_4$)/BiSbTe nanocomposite samples ($f$ = 0, 1, 2 and 3 vol.%).

<table>
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<tr>
<th>$f$(vol.%)</th>
<th>$\mu$(cm$^2$V$^{-1}$s$^{-1}$)$^a$</th>
<th>$p$(10$^{19}$ cm$^{-3}$)$^b$</th>
<th>$\lambda_{300K}$$^c$</th>
<th>$\lambda_{443K}$$^c$</th>
<th>$d_r$(%)$^d$</th>
<th>$L$(10$^{-8}$V$^2$K$^{-2}$)$^e$</th>
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</table>

$^a$ $\mu$ is Hall mobility.

$^b$ $p$ is carrier concentration.

$^c$ $\lambda$ is scattering parameter.

$^d$ $d_r$ is relative density, defined as $d_r = \frac{d}{d_0}$, where $d$ is measured density and $d_0$ (= 6.76 g/cm$^3$) is theoretical density of BiSbTe. For composite samples $f$(Cu$_3$SbSe$_4$)/BiSbTe, its theoretical density is modified as: $d_0 = (1-f)d_1+fd_2$, here $d_1$ = $d_0$ for BiSbTe and $d_2$ (= 5.86 g/cm$^3$) is theoretical density of Cu$_3$SbSe$_4$.

$^e$ $L$ is the Lorenz number.
Figure caption

Figure 1. XRD patterns at room temperature of (a) BiSbTe, (b) Cu$_3$SbSe$_4$ and (c-e) f(Cu$_3$SbSe$_4$)/BiSbTe (f = 1, 2 and 3 vol.%).

Figure 2. FE-SEM micrographs of (a) BiSbTe powders, (b) Cu$_3$SbSe$_4$ powders, (c) fracture surface of f(Cu$_3$SbSe$_4$)/BiSbTe bulk composite sample, (d) EDS pattern detected in the marked area in (c).

Figure 3. (a) TEM bright-field image of Cu$_3$SbSe$_4$/BiSbTe shows the BiSbTe matrix and incorporated nanophase Cu$_3$SbSe$_4$ and (b) HRTEM image of the selected rectangle area in (a).

Figure 4. Temperature dependences of (a) electrical resistivity and (b) Seebeck coefficient for composite samples f(Cu$_3$SbSe$_4$)/BiSbTe (f = 0, 1, 2 and 3 vol.%) and nanocrystalline BiSbTe bulk sample in Poudel’s work.

Figure 5. Temperature dependences of (a) total carrier mobility $\mu_t$ and (b) carrier mobility that corresponds to the scattering of carriers at the interfaces $\mu_n$ for composite samples f(Cu$_3$SbSe$_4$)/BiSbTe (f = 0, 1, 2 and 3 vol.%). The inset of (b) is a logarithmic plot of $\mu_n^* T^{-1/2} \text{ versus } 1/T (300 \text{ K} < T < 450 \text{ K})$, and from the slope the height of the potential barrier is extracted to be $E_B = 67.1$ meV.

Figure 6. (a) Variation of Seebeck coefficient with carrier concentration for f(Cu$_3$SbSe$_4$)/BiSbTe (f = 0, 1, 2 and 3 vol.%) at 300 K and 443 K. The violet solid line is Pisarenko relation for BiSbTe at 300 K, and the pink dash dot line is at 443 K. (b) Cross sectional schematics of the energy bands for Cu$_3$SbSe$_4$ (band gap $E_{g1}$) and BiSbTe matrix (band gap $E_{g0}$) and p-p type interface potential barriers with an effective barrier height $E_{Bp}$ and $E_{Bc}$ formed from band bending (where $E_{c0}$ and $E_{c1}$ are the conduction band bottoms; $E_{v0}$ and $E_{v1}$ are the valence band tops and $d_p$ is the grain size of Cu$_3$SbSe$_4$).

Figure 7. Temperature dependences of power factor for composite samples f(Cu$_3$SbSe$_4$)/BiSbTe (f = 0, 1, 2 and 3 vol.%) and nanocrystalline BiSbTe bulk sample in Poudel’s work.

Figure 8. (a) Temperature dependences of the specific heat for BiSbTe and Cu$_3$SbSe$_4$. (b) Temperature dependences of total thermal conductivity (lattice thermal conductivity in the inset) for composite samples f(Cu$_3$SbSe$_4$)/BiSbTe (f = 0, 1, 2 and 3 vol.%) and nanocrystalline BiSbTe bulk sample in Poudel’s work.

Figure 9. Temperature dependences of ZT for composite samples f(Cu$_3$SbSe$_4$)/BiSbTe (f = 0, 1, 2 and 3 vol.%) and nanocrystalline BiSbTe bulk sample in Poudel’s work.
Fig-1
155x179mm (96 x 96 DPI)
Fig-2
303x127mm (96 x 96 DPI)
Fig-4(a)
246x186mm (96 x 96 DPI)
Fig-5(a)
249x182mm (96 x 96 DPI)
Fig-5(b)

249x178mm (96 x 96 DPI)
Fig-6(a)
249x189mm (96 x 96 DPI)
Fig-7
241x186mm (96 x 96 DPI)
Fig-8(a)

$C_p$ for BiSbTe

$C_p$ for Cu$_3$SbSe$_4$
Fig-8(b)
242x185mm (96 x 96 DPI)
Fig-9
175x187mm (96 x 96 DPI)