Enhanced thermoelectric performance of $\beta$-Zn$_4$Sb$_3$ based nanocomposites through combined effects of density of states resonance and carrier energy filtering

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It is a major challenge to elevate the thermoelectric figure of merit $ZT$ of materials through enhancing their power factor (PF) and reducing the thermal conductivity at the same time. Experience has shown that engineering of the electronic density of states (eDOS) and the energy filtering mechanism (EFM) are two different effective approaches to improve the PF. However, the successful combination of these two methods is elusive. Here we show that the PF of $\beta$-Zn$_4$Sb$_3$ can greatly benefit from both effects. Simultaneous resonant distortion in eDOS via Pb-doping and energy filtering via introduction of interface potentials result in a ~40% increase of PF and an approximately twofold reduction of the lattice thermal conductivity due to interface scattering. Accordingly, the $ZT$ of $\beta$-Pb$_{0.02}$Zn$_{3.98}$Sb$_3$ with 3 vol.% of Cu$_3$SbSe$_4$ nanoinclusions reaches a value of 1.4 at 648 K. The combination of eDOS engineering and EFM would potentially facilitate the development of high-performance thermoelectric materials.

Thermoelectric materials play an important role in cooling of electric devices and power generation from waste heat$^1$–$^7$. The conversion efficiency of a thermoelectric material is characterized by the figure of merit, $ZT$, defined as: $ZT = (S^2/\rho \kappa)T$, where $S$, $\rho$, $\kappa$ are the thermopower, electrical resistivity, and thermal conductivity, respectively. Typically, there are two ways to improve the $ZT$ of thermoelectric materials: one is to lower the thermal conductivity $\kappa$$^8$–$^{12}$ and the other is to boost the power factor PF $= S^2/\rho$$^{13}$–$^{16}$. While a variety of techniques is available to reduce the thermal conductivity, such as embedding nanostructures in bulk materials$^{10,11}$, the fundamental challenge is to boost PF, for instance by increasing the thermopower $S$. According to the Mott equation, the thermopower $S$ of a degenerate semiconductor can be expressed as:

$S = \frac{e}{4\pi^2} \sqrt{\frac{2\alpha}{\hbar}}$.
Our results show that appropriate Pb-doping and Cu3SbSe4 nanoinclusions both increase PF owing to an improved thermoelectric performance of β-Zn4Sb3. As it is known, β-Zn4Sb3 is one of the most promising thermoelectric materials on account of its low glasslike thermal conductivity and good electrical properties at moderate temperatures. Cu3SbSe4 is another important thermoelectric material with a narrow band gap and EFM have been used separately to enhance the thermopower S of a specific material, a successful application of both effects at the same time has not been reported so far.

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In order to induce resonant distortion of the eDOS, we substituted Pb for Zn in β-ZnSb to form β-(Zn1-xPbx)Sb3, where x = 0, 0.01, 0.02, and 0.03. On the other hand, we synthesized β-(Zn1-xPbx)Sb3-based composites with Cu3SbSe4 nanoinclusions to enhance energy filtering by creating interface potentials. Our results show that appropriate Pb-doping and Cu3SbSe4 nanoinclusions both increase PF owing to an increased thermopower and significantly reduce (approx. 2-fold) the thermal conductivity of β-ZnSb3. This results in a large ZT of up to 1.4 at 648K of the nanocomposite f(Cu3SbSe4)/β-Pb0.02Zn1.98Sb3 with f = 3 vol.% (where f is the volumetric percentage of Cu3SbSe4).

Results and Discussion
Thermoelectric properties. The temperature dependences of the electrical resistivity ρ of β-ZnSb3, β-(Zn1-xPbx)Sb3 (x = 0.01, 0.02, and 0.03) and f(Cu3SbSe4)/β-Pb0.02Zn1.98Sb3 (f = 2, 3 and 4 vol.%) nanocomposite samples are shown in Fig. 1(a). The resistivity of each sample increases with temperature and reaches a maximum at around 550 K. Further increasing temperature leads to a decrease of ρ. This reduction might be mainly ascribed to the onset of mixed conduction or thermal excitation of minority carriers. Moreover, it can be noticed that the resistivities of both Pb-doped β-ZnSb3 [β-(Zn1-xPbx)Sb3 (x = 0, 0.01, 0.02, and 0.03)] and the nanocomposite compounds [f(Cu3SbSe4)/β-Pb0.02Zn1.98Sb3 (f = 2, 3 and 4 vol.%)] are much smaller compared to pristine β-ZnSb3.

The carrier concentrations determined by Hall coefficient measurements are given in Table 1. It can be seen that with x increasing from 0 to 0.01 and 0.02, the hole concentration of β-(Zn1-xPbx)Sb3 increases from 12.1 to 13.6 and 16.9 × 1019 cm−3, respectively (see Table 1). With further increase of x to 0.03, the hole concentration slightly decreases to 15.2 × 1019 cm−3. As for the Cu3SbSe4 containing composites f(Cu3SbSe4)/β-Pb0.02Zn1.98Sb3 (f = 2, 3,4 vol.%) (Table 1), the carrier concentration varies from 18.4 to 22.4 and 20.2 × 1019 cm−3 as the Cu3SbSe4 content increases from 2 to 3 and 4 vol.%, respectively. In addition, the mobility μ decreases moderately from 17.4 cm2/Vs to 15.1 cm2/Vs as f increases from 2 to 4 vol.%. These results indicate that the decrease of the resistivity with increasing inclusion content (see Fig.1 (a)) originates from the increased carrier concentration. Besides, the increase of the carrier concentration significantly exceeds the decrease of the mobility. The carrier concentration of f(Cu3SbSe4)/β-Pb0.02Zn1.98Sb3 for various values of x and f agrees with the resistivity trend in Fig.1 (a), indicating

\[ S = \pi k_B^2 T \left( \frac{\partial \ln (\sigma (E))}{\partial E} \right)_{E=E_f} \]

\[ = \pi k_B^2 T \left( \frac{1}{p} \frac{\partial \rho (E)}{\partial E} + \frac{1}{\mu} \frac{\partial \mu (E)}{\partial E} \right)_{E=E_f} \]

with the carrier mobility \( \mu = q/\tau m^* \), where \( \sigma \) is the electrical conductivity, \( q \) the carrier charge, \( E \) the energy, \( \rho (E) \) and \( \mu (E) \) energy dependent carrier density and mobility, \( \lambda \) the scattering parameter, \( k_B \) the Boltzmann constant, \( m^* \) the effective mass and \( E_f \) the Fermi energy. With the approximation of a free-electron gas and assuming an exponential dependence of the scattering parameter \( \lambda \) on the relaxation time \( \tau \), i.e. \( \tau = \tau_0 e^{-\lambda/2} \) (here \( \tau_0 \) is an energy-independent constant), Eq.(1) can be written as:

\[ S \approx \pi k_B^2 T \left( \frac{N(E)}{p} + \frac{\lambda - \frac{1}{\tau}}{E} \right)_{E=E_f} \]

where \( N(E) \) is the electronic density of states (eDOS). Eq(2) implies that at a given carrier concentration, \( S \) can be enhanced by either increasing \( N(E) \), i.e. the eDOS at the Fermi level, or the scattering parameter \( \lambda \), which corresponds to the energy filtering mechanism (EFM). Heremans et al. showed that after Ti-doping of PbTe, its ZT is doubled due to the enhancement of the thermopower. This is attributed to the resonant distortion of the eDOS. Accordingly, the recently observed enhanced thermopower of Pr and Sm doped \( \beta \)-Zn3Sb can also be ascribed to the eDOS distortion of the host.
Figure 1. Temperature dependences of (a) electrical resistivity, (b) thermopower, (c) power factor, (d) total thermal conductivity, (e) lattice thermal conductivity, and (f) figure of merit ZT of $\beta$-Zn$_4$Sb$_3$, $\beta$-(Zn$_{1-x}$Pb$_x$)$_4$Sb$_3$ ($x = 0.01$, 0.02, and 0.03) and f(Cu$_3$SbSe$_4$)/$\beta$-Pb$_{0.02}$Zn$_{3.98}$Sb$_3$ ($f = 2$, 3 and 4 vol.%) composite samples.

Table 1. Physical parameters of $\beta$-Zn$_4$Sb$_3$, $\beta$-(Zn$_{1-x}$Pb$_x$)$_4$Sb$_3$ ($x = 0.01$, 0.02, and 0.03) and f(Cu$_3$SbSe$_4$)/$\beta$-Pb$_{0.02}$Zn$_{3.98}$Sb$_3$ ($f = 2$, 3 and 4 vol.%) at room temperature (300K). $^a$ and $^c$ are the lattice parameters. $^b$ is the hole concentration. $^d\mu$ is the Hall mobility. $^e\frac{m_e}{m_e}$ is the ratio of the effective mass and the mass of the free electron. $^f$ is the scattering parameter.
that the decrease of the resistivity with increasing doping and inclusion content originates from the changes of carrier concentration.

Figure 1(b) shows the temperature dependences of thermopower of \( \beta \)-Zn\(_4\)Sb\(_3\), \( \beta \)-(Zn\(_{1-x}\)Pb\(_x\))\(_4\)Sb\(_3\) (x = 0.01, 0.02, and 0.03) and \( \overline{f} \)/(Cu\(_{1/2}\)SbSe\(_{3/2}\)) of \( \beta \)-(Pb\(_{0.02}\)Zn\(_{0.98}\))Sb\(_3\) (f = 2, 3 and 4 vol.%) nanocomposite samples. Two points are particularly interesting: (1) Unlike the resistivity (Fig. 1(a)), the thermopower of all nanocomposite samples is nearly independent of the Pb and CuSbSe\(_3\) content; (2) From the observed increased carrier concentration (Fig. 1(a)), a lower thermopower S of the Pb-doped samples and nanocomposite samples compared to pristine \( \beta \)-Zn\(_4\)Sb\(_3\) would be expected. Instead, we find that the thermopower of these samples obviously increases in the whole temperature range implying an increase of N(E) or/and \( \lambda \) (energy filtering effect) according to Eq. 2 (see below). Because of the enhanced thermopower and decreased resistivity, all \( \beta \)-(Zn\(_{1-x}\)Pb\(_x\))\(_4\)Sb\(_3\) (x = 0.01, 0.02, and 0.03) and \( \overline{f} \)/(Cu\(_{1/2}\)SbSe\(_{3/2}\)) of \( \beta \)-(Pb\(_{0.02}\)Zn\(_{0.98}\))Sb\(_3\) (f = 2, 3 and 4 vol.%) samples have a higher power factor PF (=\( S^2/\rho \)) than \( \beta \)-Zn\(_4\)Sb\(_3\) in the whole temperature range (Fig. 1(c)). \( \overline{f} \)/(Cu\(_{1/2}\)SbSe\(_{3/2}\)) of \( \beta \)-(Pb\(_{0.02}\)Zn\(_{0.98}\))Sb\(_3\) with \( \lambda = 3 \) vol% shows the largest value with PF = 1.55 W/mK\(^2\) at 650 K, which is around 51% higher than that of pristine \( \beta \)-Zn\(_4\)Sb\(_3\).

**Enhanced S by the resonant distortion of eDOS in Pb-doped \( \beta \)-(Zn\(_{1-x}\)Pb\(_x\))\(_4\)Sb\(_3\).** From these results we assume that the anomalously enhanced thermopower [Fig. 1(b)] of the nanocomposite samples is due to resonant distortion of the eDOS and the EFM, respectively. Evidence of the resonant distortion of the eDOS will be provided by means of the Pb-doped samples. Based on the measured values of carrier concentration \( p \) and thermopower S, the effective mass \( m^*_d \) is calculated. In the single parabolic band model, \( m^*_d \) and S can be approximated by:\(^{33,34}\)

\[
m^*_d = \frac{\hbar^2}{2k_B T} \left[ \frac{p}{4\pi F_{1/2}(\xi_F)} \right]^{2/3}
\]

\[
S = \frac{k_B T}{e} \left[ \frac{(\lambda + 2) F_{\lambda+1}(\xi_F)}{(\lambda + 1) F_{\lambda}(\xi_F)} - \xi_F \right]
\]

where \( h \) is the Planck constant, \( \xi_F \) is the reduced Fermi level \( F/(k_B T) \) and \( \lambda \) is the scattering parameter. As mentioned by Heremans et al., the scattering parameter \( \lambda \) of doped systems without inclusions (or secondary phase) is dominated by the acoustic modes and can be zeroed\(^{17}\). Table 1 summarizes the resulting effective mass \( m^*_d/m_e \) (where \( m_e \) is the free electron mass). At 300 K, \( m^*_d \) of un-doped \( \beta \)-Zn\(_4\)Sb\(_3\) is around 1.51 \( m_e \). The \( m^*_d \) of Pb-doped \( \beta \)-(Zn\(_{1-x}\)Pb\(_x\))\(_4\)Sb\(_3\) (x = 0.01, 0.02, and 0.03) reaches 1.91 \( m_e \), 2.14 \( m_e \), and 2.04 \( m_e \), respectively, which is 1.26, 1.42, and 1.35 times larger than that of the un-doped sample. The large effective mass indicates the strong resonant distortion of the eDOS around the Fermi level, since the eDOS is directly related to effective mass \( m^*_d \) (for instance, \( N(E) = \frac{4\pi (2m^*_d)^{3/2} e^{1/2}}{h^2} \) for a free-electron gas)\(^{35}\).

Using formulae (3) and (4) and \( m^*_d = 1.51 m_e \) for the un-doped \( \beta \)-Zn\(_4\)Sb\(_3\), we can plot the dependence of S on carrier concentration at 300K (black solid line in Fig. 2). Without resonant distortion of the eDOS Pb-doping, the thermopower S would be the same irrespective of the Pb-content and result in the same line. However, we find that S of \( \beta \)-(Zn\(_{1-x}\)Pb\(_x\))\(_4\)Sb\(_3\) (x = 0.01, 0.02, and 0.03) is ~23, 31 and 29 \( \mu \)V/K higher than the values of the black line, respectively (at 300K in Fig. 1(b)), indicating strong eDOS resonant distortion effects.

The origin of the resonant eDOS distortion caused by Pb substitution is determined by first principle calculations of the energy bands of pristine \( \beta \)-Zn\(_4\)Sb\(_3\) and Pb-doped \( \beta \)-Zn\(_4\)Sb\(_3\) (Fig. 3). The calculated result indicates that Pb-doping induces a strong sharp resonant peak near the Fermi level, which is mainly dominated by the Pb s orbitals (bottom of Fig. 3). The Pb p orbitals contribute little to the peak, which is due to the transfer of the outmost p electrons from Pb to Sb. The sharp peak indicates a larger effective mass \( m^*_d \) and thermopower S of the Pb-doped system compared to pristine \( \beta \)-Zn\(_4\)Sb\(_3\).

Furthermore, the resonant distortion of the eDOS of \( \beta \)-(Zn\(_{1-x}\)Pb\(_x\))\(_4\)Sb\(_3\) can also be quantified using the low-temperature heat capacity \( C_p \) of the samples. However, there are two temperature-dependent Zn\(_4\)Sb\(_3\) modifications, i.e. \( \beta \)-Zn\(_4\)Sb\(_3\) (T \( > \) 260 K) and \( \alpha \)-Zn\(_4\)Sb\(_3\) (T \( < \) 260 K), meaning that below ~260 K the \( \beta \) phase will transform to the \( \alpha \)-phase. As a result, one can only measure low-temperature heat capacity \( C_p \) of \( \alpha \)-Zn\(_4\)Sb\(_3\). Nevertheless, previous work\(^{38}\) showed that the eDOS patterns of the two Zn\(_4\)Sb\(_3\) modifications (\( \beta \) and \( \alpha \)) are similar. Thus, it is appropriate to deduce the heat capacity (eDOS) of \( \beta \)-Zn\(_4\)Sb\(_3\) from the \( \alpha \)-Zn\(_4\)Sb\(_3\) measurements. The temperature dependence of the low temperature (<4 K) heat capacity...
Cp of a solid is expressed by
\[ C_p = \gamma T + bT^3, \]
where the term \( bT^3 \) stands for the lattice contribution and \( \gamma \) for the charge carrier contribution with \( \gamma \) being related to \( N(E_F) \) (eDOS at the Fermi level) \(^{37}\):

\[ \gamma = \pi^2 k_B^2 N(E_F). \] (6)

Hence, the slope of a \( C_p/T^3 \) vs. \( 1/T^2 \) plot gives \( \gamma \), which is directly proportional to the eDOS at the Fermi level. Figure 4 shows the \( C_p/T^3 \) vs. \( 1/T^2 \) plots of un-doped Zn\(_4\)Sb\(_3\) (\( \alpha \) phase) and a typical doped compound \((Zn_{1-x}Pb_x)\)\(_4\)Sb\(_3\) (\( x = 0.02 \) (\( \alpha \) phase)). The slope (\( \gamma \)) of the plot of doped \((Zn_{1-x}Pb_x)\)\(_4\)Sb\(_3\) is substantially larger than that of un-doped Zn\(_4\)Sb\(_3\). Linear fitting in the low temperature regime yields the ratio \( \gamma_{\text{dop}}/\gamma_{\text{un-dop}} = N(E_F)_{\text{dop}}/N(E_F)_{\text{un-dop}} \approx 3.5 \) (see Fig. 4) revealing that Pb-doping indeed significantly increases the eDOS at Fermi level. This is in agreement with the first principle calculation result shown in Fig. 3.

Energy filtering effect induced by Cu\(_3\)SbSe\(_4\) nanoinclusions in f(Cu\(_3\)SbSe\(_4\))/\( \beta \)-Pb\(_{0.02}\)Zn\(_{3.98}\)Sb\(_3\).

We calculated the scattering parameters \( \lambda \) (Table 1) of the nanocomposites using the effective mass.
md* = 2.14 me and the measured thermopower S values. The results are comparable to those obtained by Heremans et al. with Ag/PbTe nanocomposites20. Scattering parameters of the composite samples are throughout larger than that of β-Pb0.02Zn3.98Sb3 (see Table 1) suggesting a higher thermopower of the nanocomposite samples. The carrier concentration dependence of the thermopower S of β-Pb0.02Zn3.98Sb3 (λ = 0) at 300 K can be evaluated using formulae (3) and (4) yielding the pink dashed line in Fig. 2 (Pisarenko plot). Without energy filtering effect thermopower values of nanocomposites should lie on this pink line. Interestingly, the thermopower values of the f(Cu3SbSe4)/β-Pb0.02Zn3.98Sb3 (f = 2, 3 and 4 vol.%) nanocomposites at 300 K are above the line (~10, 15 and 12 μV/K, respectively) proving the enhanced energy filtering effect.

The above results indicate that the incorporation of nanophase Cu3SbSe4 in the Pb-doped β-Zn4Sb3 contributes to the large enhancement of S through the EFM. Microstructure analysis using high-resolution transmission electron microscopy (HRTEM) reveals the underlying mechanism. As shown in Fig.5(b), the Pb-doped β-Zn4Sb3 matrix and the dispersed Cu3SbSe4 particles are incoherently jointed at the phase boundary. Moreover, at room temperature the band gaps Eg of Cu3SbSe4 and Pb-doped β-Zn4Sb3 are 0.3–0.4 eV31,38 and 0.26 eV39, respectively, leading to a valence band offset and the formation of p-p-type heterojunction barriers at the phase boundary. It is reasonable to assume that these potential barriers act as scattering centers giving rise to the EFM23. Hence, the enhanced thermopower of f(Cu3SbSe4)/β-Pb0.02Zn3.98Sb3 results from the two effects: the resonant distortion of the eDOS in the Pb-doped β-Pb0.02Zn3.98Sb3 matrix and the energy filtering effect at the phase boundaries confirming that it is feasible to combine both effects in one system.

The temperature dependence of κ of β-Zn4Sb3, β-(Zn1-xPbx)4Sb3 (x = 0.01, 0.02, and 0.03) and f(Cu3SbSe4)/β-Pb0.02Zn3.98Sb3 (f = 2, 3 and 4 vol.%) nanocomposite samples is shown in Fig.1(d). It can be seen that in the range of 300K to 500–550K, κ decreases with increasing temperature and then gradually increases as the temperature is further increased. κ includes the lattice thermal conductivity κL and the carrier contribution κc: κ = κL + κc. Thus, κL can be obtained by subtracting κc evaluated by the Wiedemann-Franz relation: κc = LT/ρ, where L is the Lorenz number. It is known that for heavily doped semiconductors, L is far below the Sommerfeld value L0 = 2.45 × 10−8 ΩK−2, but depends on the reduced chemical potential ξ, the band structure and the scattering process. In the single parabolic band model the Lorenz number is expressed as33:
plane wave expansion was 450 eV. The Brillouin zones were sampled by Monkhorst-Pack k-point meshes and Ernzerhof (GGA-PBE) for the electronic exchange-correlation functional. The energy cutoff for the Archimedes method was 450 eV.

Due to phonon scattering at both the doped sites and the bound-aries, ξ_f is obtained by fitting the measured S data using Eq.(4). The evaluated L(T) curve is plotted in Fig. S4 (Supplementary Information). To obtain Cu_3SbSe_4 powders, constituent elements CuCl (99%, powder), SbCl_3 (99.999%, powder) and Se (99.999%, powder) in stoichiometric proportions. The elements were sealed in quartz tubes under vacuum (~10^-2 Pa). The tubes were heated to 1023 K for 12 h and then quenched in cool water. The β-(Zn_{1-x}Pb_x)_{4}Sb_3 (x = 0, 0.01, 0.02, and 0.03) ingots were ground to powders by an agate mortar. To obtain Cu_SbSe_4 powders, constituent elements CuCl (99%, powder), SbCl_3 (99.9%, powder) and Se (99%, powder) were put into a glass beaker containing ethylenediamine. Then the collected powder was filtered, washed and dried in a vacuum oven. The nanometer-sized Cu_SbSe_4 and β-(Zn_1-xPb_x)_{4}Sb_3 (x = 0, 0.01, 0.02, and 0.03) powders were mixed for 4 h in a volume ratio of 2:98, 3:97, 4:96 in a planetary mill. The disk-shaped bulk nanocomposites were obtained by hot-pressing the blended powders at 600MPa in vacuum at 650 K for 1 h.

X-ray diffraction (Philips-X PERT PRO) with Cu Kα radiation was used to check the phase constitu-tions. Scanning electron microscopy (SEM) (Hitachi S4800) equipped with an energy dispersive X-ray spectroscopy (EDS) was used to analyze the microstructures of the composite samples. Moreover, micro-structure investigations were also carried out using high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2010) operating at a 200 kV accelerating voltage. Hall coefficients were measured by using a physical property measurement system (PPMS, Quantum Design). Low temperature heat capacity measurements were performed on the same instrument in the range of 2 K to 4 K. Electrical resistivity and thermopower were measured simultaneously by the standard four-probe method (ULVAC-RIKO: ZEM-3) in helium atmosphere from 300 K to 650 K. The thermal diffusivity α was measured with a NETZSCH LFA-457 instrument in the temperature range of 300 K to 650 K. The thermal conductivity κ was calculated according to κ = DC_pα_p, where C_p is the specific thermal capacity obtained by differential scanning calorimetry (DSC, perkin-Elmer) and D is the sample density measured by the Archimedes method.

DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP) with the projector augmented wave (PAW) scheme and the generalized gradient approximation of Perdew, Burke and Ernzerhof (GGA-PBE) for the electronic exchange-correlation functional. The energy cutoff for the plane wave expansion was 450 eV. The Brillouin zones were sampled by Monkhorst-Pack k-point meshes (3 × 3 × 2). Atomic positions and unit cell vectors were relaxed until all forces and components of the stress tensor were below 0.01 eV/Å and 0.2 kbar, respectively.

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Author Contributions
T.Z. wrote the main manuscript text. X.Q. designed the experiments and analyzed data. X.L. was responsible for measuring the low-temperature heat capacity. Y.Z and Z.Z. contributed to the first-principles calculation. D.L., J.Z., H.X., W.X. and A.W. revised the manuscript. All authors reviewed the manuscript.

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