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Band structure engineering of multiple bands degeneracy for enhanced thermoelectric power factors in *M*Te and *M*Se (*M*=Pb, Sn, Ge)

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The thermoelectric (TE) conversion efficiency is always limited by the low TE figure of merit (*ZT*). Improving *ZT* requires both a high power factor (*PF*) and a low thermal conductivity. So far, however, most works in improving the *ZT* have been made by reducing the thermal conductivity but less by maximizing the *PF*. Recently, band engineering which can effectively solve the paradox between the density-of-states effective mass and carrier mobility, has been treated as an efficient approach to improve *ZT* by maximizing the *PF*. In this paper, based on the first-principles and Boltzmann transport theory, we calculate the electronic structure and thermoelectric properties of classical IV-VI semiconductors *M*Te and *M*Se (M=Pb, Sn, Ge). We find that band engineering of multiple bands degeneracy induced by engineering the conduction bands near the Fermi level can increase the room temperature n-type *PF* about 3 to 8 times. The present work is useful in thermoelectrics and will attract more research interest in optimizing the TE performance by band engineering.

1. Introduction

Thermoelectric (TE) power generation devices, which directly convert heat into electricity, have long been regarded as the promising next energy revolution since the discovery of TE effect.¹ High-performance TE power generation devices require TE materials with high TE conversion efficiency which is proportional to the TE figure of merit ZT: $ZT = S^2 \sigma T / \kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, T the absolute temperature, and κ the thermal conductivity including the contributions from electrons (κ_{e}) and lattice $(\kappa_{l})^{2}$ These concepts indicate that increasing ZT requires both a large power factor $PF(PF=S^2\sigma)$ and a low κ . However, since the Bi₂Te₃ family were discovered as promising TE materials $(ZT\sim 1)^{3,4}$, very few bulk materials have been found with ZT greater than 1, because the phonon mean free path can not become shorter than the interatomic distance in bulk materials, which results in that there is a lower limit to the lattice thermal conductivity.⁵ Thus, the past advances in ZT are based on nanostructures by reducing the thermal conductivity, improving the ZT larger than 2.1,6-8 Unfortunately, ZT is also nearing a lower limit because the thermal conductivity can not be reduced below the amorphous limit.⁵ Recently, maximizing the PF has been regarded as another effective approach to realize a new breakthrough in ZT.⁹

For more than decades, improving ZT by maximizing the PF was believed to be a challenge due to the paradox between density-of-states effective mass (m_d^*) and carrier mobility (μ) , which induces a compromise between S and σ .^{6,10} For a degenerate semiconductor, S is given by:⁵

$$S = \frac{8\pi^2 k_B^2 T}{3eh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3},\tag{1}$$

and the density of states (DOS):

$$g(E) = \frac{(m_d^*)^{3/2} \sqrt{2E}}{\hbar^3 \pi^2} \,. \tag{2}$$

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For a given Fermi energy (carrier concentration n), a high overall DOS means a high effective mass (m_a^*) , leading to a high *S*. Here, the high total DOS can come from either a large number of conducting bands (N_v) or a high band effective mass (m_b^*) relating to flat bands, which can be related by $m_d^* = N_v^{2/3} m_b^{*.10,11}$ The number of conducting bands and the flatness of bands (high $m_b^*)$ usually have different effect on carrier mobility μ . In most cases, the number of conducting bands have little influence on μ unless there is a significant inter-valley scattering. However, μ is low for bands with heavy mass m_b^* , thus leading to the low electrical conductivity $(\sigma = ne\mu)$.^{10,11} Therefore, increasing band mass is not beneficial to optimize the *PF*. Band engineering, which can produce a large m_d^* without reducing μ by increasing the factor N_v , has been used to realize excellent TE performace by maximizing the *PF*.^{5,11-13} A doubling of *ZT* in PbTe above 1.5 was obtained by Heremans *et al.* in 2008 through distortion of electronic DOS.⁵ In 2011, Pei *et al.* realized a high *ZT* of 1.8 in doped PbTe_{1-x}Se_x by means of multiple valley degeneracy.¹¹ These breakthroughs indicate that it is feasible to optimize the TE performance by band engineering without using complex nanostructures.

Electronic resonance states and band degeneracy are the two kinds of widely used approaches of band engineering.^{1,10} Resonant states may occur when dopants have energy levels in band of host materials, which can distort the DOS and increase the effective mass, leading to an enhanced PF.¹ Band degeneracy includes orbital degeneracy (the band extrema of multiple bands have their energy within a few k_BT of each other) and valley degeneracy (separate pockets of Fermi surface with the same or similar energy).¹⁰ A highly degenerate bands lead to an effective increase in N_v , producing an enhanced m_d^* , and therefore the *PF*. However, previous improvements are mainly realized in low-dimensional materials. Extending this concept to bulk materials where already

exist highly band degenerate would be most useful for rapid integration with applications and has realistic significance. What's more, theoretical prediction and explanation are still lacking. In this work, we improve the room temperature PF of classical bulk thermoelectrics 3 to 8 times by engineering the conduction bands near the Fermi level (multiple bands degeneracy). This is achieved in IV-VI classical bulk semiconductors (PbTe family) without using nanostructures or inducing resonant states by doping. Our results provide an example of searching for optimal PF in classical bulk materials by the characteristic of band degeneracy, which will attract more research interest in optimizing the PF by similar approaches.

2. Computational details

We firstly study the electronic structure of IV-VI semiconductors (PbTe family) by using the full-potential linearized augmented plane-wave method with generalized gradient approximation (GGA) for the exchange-correlation potential, as implemented in the WIEN2K code.¹⁴ This method has been successfully used to deal with the electronic structure of various materials.^{15,16} The convergence results are determined by the cut-off $K_{max}R_{mt} = 9$ for the plane-wave and 60000 k points in the first Brillouin zone. The precision of the convergence is set as 10⁻⁵ Ry per formula unit. Spin-orbit coupling is included. Then, the electronic transport calculations are done by using the Boltzmann transport theory and relaxation time approximation implemented in the BoltzTraP code.¹⁸ Within this approximation, *S* is independent of relaxation time τ , whereas σ and *PF* depend linearly on τ . Calculating τ in bulk materials is trivial, which is treated as a constant in the present work. This method has been used for a long time and shows reliable results for TE properties of semiconductors.^{16,17,19} The classical IV-VI semiconductors belong to the fcc crystal

system (rocksalt structure) with the space group Fm3-m, and two atoms in the primitive cell individually locate in 4a (Pb) and 4b (Te) sites.^{20,21}

3. Results and discussion

We firstly consider our research for traditional PbTe as shown in Figs. 1(a) and 2(a). Bulk PbTe is known as a traditional *p*-type TE material.²² Our calculated direct band gap at L point is 0.1eV, which is smaller than the experimental value of 0.19eV^{23} due to the gap underestimation in GGA. The conduction bands near the Fermi level are dominated by Pb p states, while valence bands are the Te p states. These states are highly hybridized, and the minimum direct gap appears at L point where the Pb p states shift down due to hybridization with Te d states while the Te p states shift up due to interaction with Pb s states.²⁰ Here, we name the conduction and valence bands near the Fermi level as Pb p-like and Te p-like bands, respectively. The calculated room temperature PFs are $\sim 1.6 \times 10^{11}$ W/mK²s for *n*-type PbTe and $\sim 7 \times 10^{11}$ W/mK²s for *p*-type PbTe, respectively (the Fermi level shifts up for *n*-type, while down for *p*-type). It is thus demonstrated that PbTe is an intrinsic *p*-type TE material and the *p*-type $PF \sim 7 \times 10^{11}$ W/mK²s is comparable to $\sim 6 \times 10^{11}$ W/mK²s for p-type Bi₂Te₃.¹⁹ Interestingly, PbTe intrinsically exhibits a trend of multiple bands degeneracy at L point due to the orbits hybridization. However, the degeneracy level is not strong. For example, the energy difference between the band extrema of the first and the second conduction bands near the Fermi level at L point is 1.2eV, which is far beyond the degeneracy condition (little or even no significant energy difference between the band extrema¹⁰). If one can increase the degenerate level of these Pb p-like bands or Te p-like bands, enhanced DOS near the Fermi level will be obtained, and therefore the PF.

Instead of using complex low-dimensions approach, we try atomic substitutions on PbTe in order to check whether an enhanced band degeneracy at L point would be achieved. As shown in Fig. 1(a), we consider atomic substitution at 4a(Pb) site, replacing atom Pb by the atoms in the same group. We represent this first set of materials as MTe (M=Pb, Sn, Ge). As M site going from heavy-mass element to light one, the lattice parameters decrease (6.464Å for PbTe, 6.327Å for SnTe and 6.012 for GeTe)²⁴⁻²⁶, resulting in an increase of interaction between atomic layers and the hybridization of atomic orbits. Consequently, although the Te p-like bands has little changes for we haven't substitute the Te site, we surprisingly find the degeneracy of the M p-like bands at L point is greatly enhanced as going to light-mass element at M site. This increases the room temperature *n*-type *PF* from $\sim 1.6 \times 10^{11}$ W/mK²s for PbTe to $\sim 7.7 \times 10^{11}$ W/mK²s for SnTe and $\sim 12 \times 10^{11}$ W/mK²s for GeTe, which enhance about 5 to 8 times. DOS analysis for these compounds indicates that the enhanced *PF* mostly comes from the increased *M p* states. We consider in Fig. 2(a) the total and partial DOS of MTe (M=Pb, Sn, Ge), and only s and p states are listed because other states have little contribution to the DOS around the Fermi level. The first conduction band with energy between 0eV and 1eV mostly consists of M p states. Although there is an increase of Te p states in the second and third bands, the M p states also make the main contributions (1-3eV). Thus, the M p states are enhanced as the M p-like bands tend to degenerate at L point, and therefore the DOS and PF. This is achieved without changing the shape of the band structure (band effective mass).

We also consider the second set of materials $MSe (M=Pb, Sn, Ge)^{24,27,28}$ as shown in Figs. 1(b) and 2(b). Similar enhanced band degeneracy for M p-like bands at L point are found. The room temperature n-type PFs also increase from $\sim 1.2 \times 10^{11} W/mK^2s$ for PbSe to $\sim 4 \times 10^{11} W/mK^2s$ for

SnSe and $\sim 8 \times 10^{11}$ W/mK²s for GeSe, and the *M p* states also contribute to most of the *PF*. The *PF* is increased about 3 to 7 times. However, in comparison with the first set, we find atomic substitution on 4b(Te) site shows opposite effect. Firstly, the energy difference between the band extrema of the first and second Se p like bands at L point is larger than those of Te. And also, the degenerate level of M p like bands is weak this time, leading to a depressed M p states near the Fermi level, and therefore the *PF*. This is caused by the subdued hybridization of atomic orbits. For example, we have made clear before that the valence Te p states or Se p states shift up at L point due to hybridization with M s states.²⁰ However, as seen in Fig. 2, the energy difference between these two states is expanded as going from Te to Se at 4b site, which results in subdued hybridization and therefore the decreased degenerate level. In both of the two sets, except a sharp DOS for conduction band at around 1eV, there are also other peaks at higher energies. However, we are willing to realize a low doping level with a carrier concentration about $\sim 10^{19}$ cm⁻³ in order to give consideration to S and σ .⁶ In this respect, the paradox between S and σ would usually be represented as carrier concentration.

The two sets of materials we researched both exhibit an enhanced *n*-type *PF* by engineering the conduction bands at L point. These bands like small pockets centered at L and mainly associated with *M p* states, containing electrons for TE transport. The increased degeneracy of *M p*-like bands leads to an enhanced DOS, and thereby the *PF*. This is an effective demonstration of the concept of optimizing the *PF* by band engineering, where the compromise between *S* and σ is solved, realizing large *PF* without depressing the carrier concentration and mobility.

We further plot in Fig. 3 the room temperature S, σ , and PFs for the first set of materials MTe (M=Pb, Sn, Ge) as a function of chemical potential, in which we can clearly see how these

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coefficients vary with different *M* members. For *p*-type, these coefficients show little changes for different compounds because of the little change in valence bands dominated by Te *p* states. The *n*-type *PF*s are gradually enhanced as *M* going from Pb to Ge due to the increased degenerate level in *M p*-like bands. The enhanced region probably locates in 0.25eV-0.75eV, in which the *S* and σ are simultaneously increased instead of compromising with each other. It is demonstrated that the converged multiple *M p*-like bands increase the *S* without overshadowing its σ , and thus realizing in large *PF*s. Also, as the *n*-type *PF*s enhanced, the properties of these thermoelectric materials are changed from *p*-type to *n*-type.

4. Conclusions

Motivated by the recent studies that band engineering can solve the paradox between density of states effective mass and carrier mobility, resulting in the increase of the Seebeck coefficient without overshadowing the electrical conductivity, we use the first-principles combined with the Boltzmann transport theory to investigate the electronic structure, Seebeck coefficients S, and power factors PF for traditional semiconductors MTe and MSe. It is found that the room temperature n-type PF of classical thermoelectrics can be increased about 3 to 8 times by engineering the band degeneracy through atom substitution instead of complex low-dimensions approach. This is explained in detain by the calculated band structure and DOS. The present work will inspire further interest in optimizing the TE performance by band engineering.

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Figures and captions



Fig. 1 Calculated band structures and power factors for (a) MTe (M=Pb, Sn, Ge), and (b) MSe (M=Pb, Sn, Ge). Red lines for M=Pb, bule for M=Sn, and magenta for M=Ge. The Fermi level is set at 0 eV. Calculated power factors with n-type above the Fermi-level while p-type under the Fermi-level. Note here that n-type power factors are mainly concerned as the conduction bands are engineered in the substitution.



Fig. 2 Calculated total density of states (DOS) and partial DOS for (a) MTe (M=Pb, Sn, Ge), and (b) MSe (M=Pb, Sn, Ge). Only contributions from s and p states for different atoms are given. Black lines denotes the total DOS, and the partial DOS are represented by the red lines for s states of M, blue lines for p states of M, dark cyan lines for s states of Te and Se, and magenta lines for p states of Te and Se.



Fig. 3 Calculated room temperature Seebeck coefficients, electrical conductivities, and power factors as a function of chemical potential for the first set of materials MTe (M=Pb, Sn, Ge). For n-type, it is found that the Seebeck coefficient and electrical conductivity simultaneously increase instead of compromising with each other, which leads to the enhanced power factors.