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Enhanced thermoelectric performance of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound from first-principles calculations

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The electronic properties of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound are examined by using the full-potential linearized augmented plane-wave method. The transport coefficients are then calculated within the semiclassical Boltzmann theory, and further evaluated as a function of chemical potential assuming a rigid band picture and constant relaxation time. The ZT value is thus estimated by inserting an averaged thermal conductivity. Our theoretical calculations give a valuable insight on how to enhance the thermoelectric performance of this compound, and many potential doping elements and their optimal concentrations are suggested. © 2010 American Institute of Physics.

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Owing to their great applications in cooling and power generation, thermoelectric materials have attracted much attention from the science community. The performance of thermoelectric material is given by a 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 thermal conductivity which includes contributions from both electrons (κ_e) and phonons (κ_l). A good thermoelectric material requires a high ZT value, one therefore must try to increase the power factor ($S^2\sigma$) and/or decrease the thermal conductivity. As these transport coefficients (S , σ , and κ) are coupled with each other, the effort to search for new compounds with large ZT value becomes extremely difficult.

Recently, $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound has been intensively investigated because of its excellent thermoelectric performance in the vicinity of room temperature. It was found experimentally that the Z value of the gas atomized Sb_2Te_3 -25% Bi_2Te_3 alloy with an excess of 4 wt % Te can be enhanced to $2.788 \times 10^{-3} \text{ K}^{-1}$.¹ By mechanical alloying for 12 h, single phase 25% Bi_2Te_3 -75% Sb_2Te_3 alloy can be obtained and has a maximum ZT value of 0.93 at room temperature.² Additionally, improved thermoelectric properties could be obtained in nanostructured³⁻⁶ or pressure-tuned⁷ $\text{Sb}_{1.5}\text{Bi}_{0.5}\text{Te}_3$ compound. On the other hand, chemical doping is found to be an effective way to enhance the thermoelectric performance of the compound. It was found that the ZT value of the In-doped compound $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_3$ can be substantially increased in the temperature range from 100 to 300 K.⁸ Cui *et al.*⁹ prepared the pseudobinary alloys $(\text{Al}_2\text{Te}_3)_x-(\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3)_{1-x}$ and found that the maximum ZT value can be enhanced to 0.86 for $x=0.1$ at 419 K, which is higher than that of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy prepared by the same fabrication technology. Using SPS technique, Cui *et al.*¹⁰ also prepared the

$(\text{Cu}_4\text{Te}_3)_x-(\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3)_{1-x}$ alloys and the maximum ZT value of 1.26 can be achieved with $x=0.025$ at 474 K. In addition, Ga (Ref. 11) were also introduced into the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ alloy to increase the thermoelectric performance. It should be mentioned that in most of the experimental works, there exists a certain degree of randomness to select doping elements. In order to theoretically predict the best candidates for doping, in this work we examine the electronic and thermoelectric properties of the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound by using first-principles band structure calculations and Boltzmann transport theory.¹² Our results may serve as a guide on how to optimize the thermoelectric properties of this compound.

Our calculations were performed using the full-potential linearized augmented plane-wave method¹³ within the density functional theory (DFT).^{14,15} The code is implemented in the WIEN2K package.¹⁶ The exchange-correlation potential is in the form of Perdew-Burke-Ernzerhof (PBE)¹⁷ with generalized gradient approximation. The plane-wave cutoff is determined by $\min(R_{\text{MT}})\max(k_n)=7.0$ and the muffin tin radii are chosen to be 2.5 a.u. for all the atoms involved. Self-consistent calculations are done with 144 \mathbf{k} points in the irreducible Brillouin zone (IBZ) and the total energy is converged to within 0.0001 Ry. Since Bi, Sb, and Te atoms are heavy elements, the effect of spin-orbit (SO) coupling is included in the calculations. The transport coefficients are derived from the electronic structure by using the semiclassical Boltzmann theory as implemented in the BOLTZTRAP code.¹² Doping is treated within the rigid-band picture¹⁸ and a constant relaxation time τ is used for the calculations of electrical conductivity and power factor.

We begin with the crystal structure of bulk Sb_2Te_3 shown in Fig. 1. The primitive cell contains five atoms and has a rhombohedral structure with space group $D_{3d}^5(R\bar{3}m)$. After geometry optimizations, we find that the calculated lattice constants are $a=4.32 \text{ \AA}$ and $c=30.10 \text{ \AA}$ (corresponding to the hexagonal unit cell), which are very close to those found experimentally.¹⁹ To simulate the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound, we construct a $1 \times 1 \times 2$ supercell with nominal

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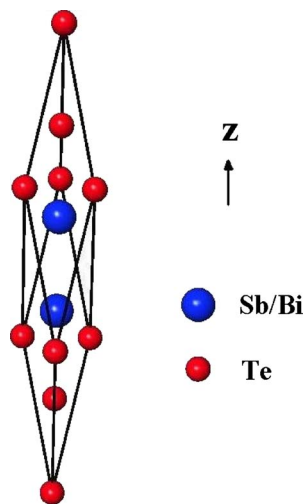


FIG. 1. (Color online) The primitive cell of Sb_2Te_3 compound. Note the Sb atom can be replaced by a Bi atom.

formula Sb_4Te_6 and replace one Sb atom with Bi atom. The optimized lattice constants are $a=4.34 \text{ \AA}$ and $c=30.22 \text{ \AA}$ which are slightly larger than those of the Sb_2Te_3 compound. The heat of formation, defined by $H=E(\text{Sb}_3\text{BiTe}_6)+E(\text{Sb})-2 \times E(\text{Sb}_2\text{Te}_3)-E(\text{Bi})$ is found to be -1.56 eV , which suggests that the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound is energetically stable and may be synthesized under appropriate experimental conditions.

Figure 2(a) shows the calculated band structure and density of states (DOS) for the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound. For comparison, the same plot for the pristine Sb_2Te_3 is also shown [Fig. 2(b)]. In both cases, a $1 \times 1 \times 2$ supercell containing ten atoms is used and the energy bands exhibit multivalley structures. This is believed to be caused by SO coupling and is responsible for the good thermoelectric properties. It should be mentioned that we have done additional calculation for the Sb_2Te_3 compound using primitive cell containing five atoms, and the results agree well with previous first-principles calculations^{20,21} which confirms the reliability of our calculations. The band gap of Sb_2Te_3 is found to be 0.14 eV , which is much smaller than the experimental value of 0.28 eV .²² The underestimation of energy gap is a well-known limit of DFT. By introducing a Bi atom into the Sb_2Te_3 compound, we see that the topology of Fig.

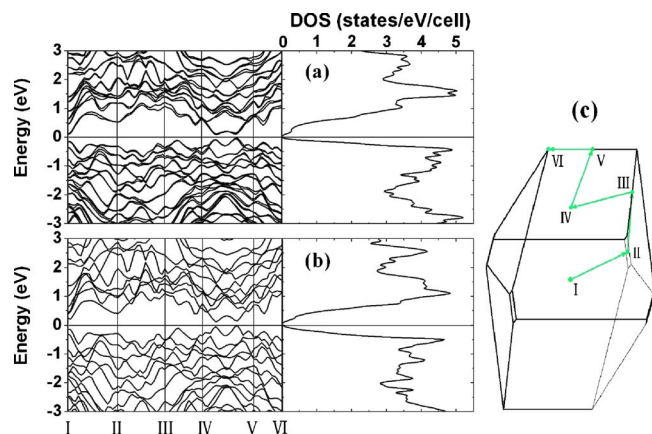


FIG. 2. (Color online) Calculated band structure and DOS for (a) $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ and (b) Sb_2Te_3 compounds with $1 \times 1 \times 2$ supercell. The high-symmetry directions in the first Brillouin zone are illustrated in (c). The Fermi level is at 0 eV .

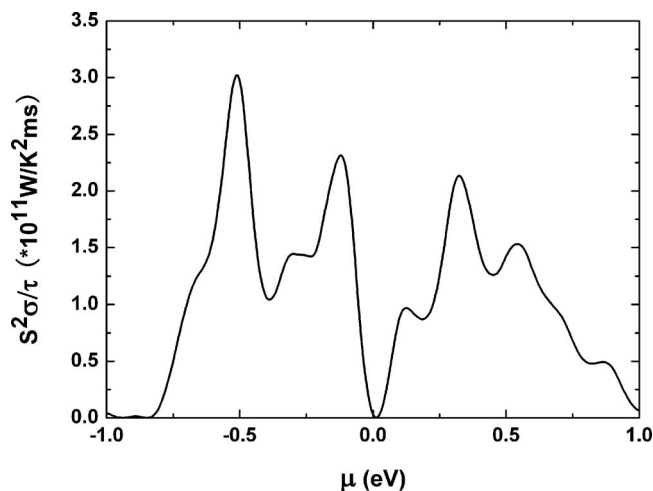


FIG. 3. Calculated power factor $S^2\sigma/\tau$ of the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound as a function of chemical potential μ at 300 K. Note here the relaxation time τ is included as a parameter.

2(a) is very similar to that of Fig. 2(b). However, the degenerate bands are now obviously separated due to symmetry breaking caused by Bi substitution. The electronic states are redistributed and the band gap becomes 0.11 eV , which is in excellent agreement with the experimentally measured value of 0.12 eV .²³ Considering the usual underestimation of energy gaps calculated by DFT, it is possible that such match is coincidental. The DOS of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ near the valence band maximum is steeper and higher than that near the conduction band minimum. As larger DOS in the vicinity of Fermi level often leads to higher Seebeck coefficient,^{24,25} this suggests that the compound may have better thermoelectric performance when it is p -type doped.²⁶

Based on the calculated electronic properties of the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound, we are able to evaluate the transport coefficients by using the Boltzmann theory and rigid-band approach. This method has been used to predict the optimal doping level of some known thermoelectric materials.^{20,27-29} As bismuth telluride based thermoelectric materials are usually performed in the vicinity of room temperature, we plot in Fig. 3 the calculated power factor $S^2\sigma/\tau$ at 300 K as a function of chemical potential μ for the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound. Note here the relaxation time τ is included as a parameter. Within the rigid-band approach, the chemical potential μ determines the doping level of the compound. The positive and negative μ correspond to n -type and p -type doping of the system, respectively. It should be noted that our conclusions are correct only when the chemical potential is not far away from the Fermi level where the rigid band approximation is still applicable. As can be seen from Fig. 3, there are several peaks within the chemical potential range considered, which suggests that the thermoelectric performance of the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound can be optimized by appropriate doping. In the vicinity of the Fermi level ($\mu=0$), we see that the peak at $\mu=-0.12 \text{ eV}$ and $\mu=0.32 \text{ eV}$ have obviously larger power factor. As mentioned before, the chemical potential indicates the doping level and by which we can obtain the number of electron (N) that should be added to (n -type doping) or withdrawn from (p -type doping) the system. For the two peaks located at $\mu=-0.12 \text{ eV}$ and $\mu=0.32 \text{ eV}$ in Fig. 3, the calculated values are $N=0.0172$ and $N=0.155$, respectively. In the

TABLE I. Optimal doping elements and doping concentrations of the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound at 300 K. Note the p -type and n -type doping corresponds to $\mu = -0.12$ eV and $\mu = 0.32$ eV in Fig. 3, respectively. The cited references indicate previously reported experimental works.

	p -type doping		n -type doping	
	Elements	Concentration	Elements	Concentration
$(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{A}_x\text{Te}_3$	C/Si/Ge/Sn/Pb	0.0086	O/S/Se/Te/Po	0.077
	B/Al ^a /Ga ^b /In ^c /Tl	0.0043	Cl/Br/I	0.039
	Be/Mg/Ca/Sr/Ba	0.0029		
$(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_{3-x}\text{B}_x$	N/P/As/Sb/Bi	0.0086	Cl/Br/I	0.077
	C/Si/Ge/Sn/Pb	0.0043		
	B/Al/Ga/In/Tl	0.0029		

^aReference 9.

^bReference 11.

^cReference 8.

$(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound, there are two different atomic sites, namely, the Bi/Sb site and the Te site (see Fig. 1). In principle, each one can be substituted by other atoms. The doping is p -type if the doped atom has less valence electron than that of the site atom. Otherwise, it is an n -type doping. To keep the doped system energetically stable, we should focus on those atoms in the periodic table which are neighbors of the site atoms. Our results are summarized in Table I, which gives the optimal doping concentrations and possible doping atoms for the left and right peaks marked in Fig. 3. Indeed, we see that some of the doping elements (Al, Ga, and In) have been reported experimentally.^{8,9,11} The many other possible doping atoms indicated in Table I suggest that there is still large room to further enhance the thermoelectric performance of the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound.

By fitting available experimental electrical conductivity (σ) (Refs. 8–10) with our calculated values (σ/τ), the relaxation time τ at 300 K is estimated to be 4.14×10^{-14} s and 3.04×10^{-14} s for the p -type and n -type doping, respectively. Inserting these values into the calculated power factor ($S^2\sigma/\tau$) and using an averaged thermal conductivity $\kappa = 1.59 \text{ W m}^{-1} \text{ K}^{-1}$,^{3,8,10} we can predict the ZT value of the doped $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound. The result indicates that p -type doping in the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ compound may be more favorable than n -type doping to enhance the thermoelectric performance. At the optimized doping concentrations mentioned above, the ZT value can be increased to 1.8 for the p -type doping. It should be emphasized that in our calculations we have assumed the scattering rate is the same as a function of doping by using a constant relaxation time and an averaged thermal conductivity. This may not be the case in the experiments. We expect that a proper treatment of these terms could give an improved prediction of the ZT value, which however depends on the exact doping atoms used in the experiments and the detailed scattering mechanism. On the other hand, the ZT value can be further improved in nanoscale compound where an even lower thermal conductivity is expected. Our theoretical calculations may provide a guide for future experimental investigations.

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