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Revisiting the Electronic Structures and Phonon Properties of Thermoelectric Antimonide-Tellurides: Spin–Orbit Coupling Induced Gap Opening in ZrSbTe and HfSbTe

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Abstract: We report theoretical studies based on density functional theory within spin-orbit coupling to explore electronic structures, lattice dynamical properties of ZrSbTe and HfSbTe. With spin–orbit coupling included, our findings reveal that ZrSbTe and HfSbTe exhibit a semiconducting behavior with narrow indirect band gaps of 0.10 eV, and 0.15 eV, respectively. Besides, the lattice dynamical properties revealed that the explored materials based on antimonide–tellurides are dynamically stable. On the basis of electronic structures, the thermoelectric properties were computed using the Landauer–Buttiker formula by considering both electron and phonon contributions in the transport properties calculation. We employed Green’s-function method based on the Green–Kubo–Mori formula, where the thermoelectric properties such as the electrical conductivity σ and thermopower α were estimated in terms of the correlation functions. The present work could be viewed as a significant amendment of the electronic nature of ZrSbTe and HfSbTe that were reported to be metallic in literature.

Keywords: thermoelectric properties; spin-orbit coupling; vibrational properties; thermal conductance



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1. Introduction

Thermoelectric-based materials have received increasing attention due to the particular capability of such materials for converting thermal energy directly into electrical energy via a solid-state technology [1,2]. They have shown excellent promise for usage in the waste heat recuperation, clean energy and photon sensing devices [3–6]. Besides these characteristics, they can provide a substantial scalability, lightness, and even transform into micro/nano devices in order to achieve local cooling/heating or power generation. A main challenge for allowing multifunctional applications of thermoelectric materials is to enhance their thermoelectric features. The thermoelectric efficiency of a material can be estimated by the dimensionless figure of merit, ZT through relation $ZT = S^2\sigma T/\kappa$ where S , σ , T and κ are the Seebeck coefficient, the electrical conductivity, absolute temperature and the thermal conductivity, respectively [7,8]. The thermal conductivity is composed of two main contribution parts such as electronic (κ_e) and lattice (κ_l). To obtain good thermoelectric performances, a high figure of merit value needs a combination of a high S and σ together with a low κ simultaneously. Moreover, the major quality to design a thermoelectric material is to growth a semiconductor with a narrow band gap [2,9]. During the last several years, a large number of new compounds with narrow-band gap semiconducting have been identified exhibiting reasonably excellent thermoelectric properties [4,10–13].

Topological insulators have gained the greatest attention within the community of researchers in the field of materials science because of their controlling of gaped bulk states and gapless Dirac boundary states at the same time and keep time-reversal symmetry owing to spin–orbit coupling [14–16]. More importantly, several topological insulators are excellent thermoelectric materials at or below room temperature [17–21] which have many potential applications such as bismuth telluride (Bi_2Te_3) [22–26], antimony telluride (Sb_2Te_3) [22], CoSb [26], SnTe [23,27] and GeTe compounds [28]. In addition, interesting topological effects have been observed experimentally in chalcogenide materials such as TlBiQ_2 ($\text{Q} = \text{Se}, \text{Te}$), MTe_2 ($\text{M} = \text{W}, \text{Mo}$).

Various new topological materials with moderate thermoelectric efficiency have been established during the past several years. Ternary antimonide-tellurides form an essential category of such materials. Experimental report by Soheilnia et al. [13] shows that two new antimonide-tellurides based on ZrSbTe and HfSbTe were synthesized in the NbPS structure type. They also reported that ZrSbTe and HfSbTe exhibit a metallic conducting behavior with a weak Seebeck coefficient. Single-crystal and poly-crystal mechanical properties were studied by Deligoz et al. [29], where they have reported that these compounds are mechanically stable. Furthermore, Bradlyn et al. have predicted that ZrSbTe and HfSbTe compounds are promising family of topological materials in space group $P4/\text{mmm}$ [30].

Motivated by these findings, we concentrate our work on the layered antimonide-telluride compounds. We investigated the electronic structures and lattice dynamic characteristics of ZrSbTe and HfSbTe employing the first-principles calculations. Also, we computed the thermoelectric properties applying the Landauer-Buttiker formula in which the transport properties were determined using the Green's function method. Moreover, the spin–orbit coupling (SOC) is included in our calculations of the electronic structure where it has generated visible changes on the energy band structure.

2. Materials and Computational Methods

Relaxation of atomic positions and electronic structures were executed within the scheme of density functional theory (DFT) as implemented in the Vienna ab initio Simulation Package (VASP) [31]. The generalized gradient approximation (GGA) parameterized by form of Perdew, Burke, and Ernzerhof (PBE) is selected to characterize the exchange and correlation functional [32]. The kinetic energy cutoff of 450 eV was used for plane-wave expansion with a projector augmented wave method [33]. The first Brillouin-zone is sampled applying Monkhorst-Pack [34] grid with a k-point mesh of $13 \times 9 \times 4$ for all compounds. The geometry structures are relaxed until the values of Hellmann-Feynman forces on the atoms were less than 0.01 eV/Å. For the self-consistent field cycles, an energy convergence criterion of 10^{-6} eV per unit cell was set for all systems. The spin-orbit coupling was considered in calculations.

Besides, PHONON Software [35] based on the lattice dynamic theory [36] was adopted to compute the phonon spectra of ZrSbTe and HfSbTe. The amplitudes related to displacement were expressed as 0.03 Å to improve the accuracy and reduce the anharmonic effects. We used the Landauer-Buttiker formalism [37,38] for the calculation of the Seebeck coefficient, and transport properties. In addition, the transmission coefficient is computed by using the Green's function method [39]. Based on the Green-Kubo-Mori approach, the electrical conductivity (σ) and thermopower (α) are presented in forms of the correlation functions which are thus in turn shown as Green's functions [40]:

$$\sigma = \frac{2e^2}{\pi\Omega} \int d\omega_2 \left(-\frac{dn_f}{d\omega_2} \right) \times \int d\omega \sum_{n,k} [v_n(k) \Im m G_{n,n}(k, \omega_2)]^2 \delta[\omega - E_n(k)] \quad (1)$$

$$\alpha = \sum_{S=1}^2 (\sigma\alpha)^{(S)} \quad (2)$$

Using the linear response limit, the thermoelectric properties of investigated system can be obtained from the descriptions of the electrical and thermal currents [37,38]

$$I = \frac{2q}{h} \int dE T(E) [f_L(E) - f_R(E)] \quad (3)$$

$$I_Q = \frac{2q}{h} \int dE T(E) [f_L(E) - f_R(E)] (E - \mu) \quad (4)$$

where the factor of 2 is given for the spin, Q is the charge, $T(E)$ is the transmission coefficient of the device configuration, and f_L and f_R represent the distribution functions of the left and right reservoirs with chemical potentials μ_L and μ_R .

In the case of linear response of the system, it can be assumed that $\Delta\mu = \mu_L - \mu_R$ as well as $\Delta T = T_L - T_R$ are considered as infinitesimally small quantities in which the currents are linear. As a result, the average of the left and right chemical potentials can be defined by the chemical potential μ in the thermal current. Moreover, the thermoelectric response functions can be computed from the unperturbed ground state properties of the system.

Then Taylor expansion can be used in powers of ΔV and ΔT in Equation (3), the transport properties can be written in terms of the transmission coefficient $T(E)$ as below:

$$\text{Conductance: } G = -\frac{1}{\Delta V} \bigg|_{\Delta T=0} = q^2 K_0$$

$$\text{Peltier Coefficient: } \Pi = \frac{I_Q}{I} \bigg|_{\Delta T=0} = \frac{K_1}{qK_0}$$

$$\text{Thermopower (Seebeck Coefficient): } S = -\frac{\Delta V}{\Delta T} \bigg|_{I=0} = \frac{K_1}{qTK_0} = \frac{\Pi}{T}$$

$$\text{Thermal Conductance: } \kappa = -\frac{I_Q}{\Delta T} \bigg|_{I=0} = \frac{(K_2 - \frac{K_1^2}{K_0})}{T}$$

$$\text{where } K_n \text{ is the following integral: } K_n = \frac{2}{h} \int dE T(E) \left(-\frac{\partial f}{\partial E} \right) (E - \mu)^n$$

This integral depends strongly on the $T(E)$ properties near the Fermi level. Furthermore, our transmission coefficient $T(E)$, which is extracted from our transmission spectrum as

$$\text{calculated from DFT. The figure of merit will be deduced as follow: } ZT = \frac{GS^2T}{\kappa} = \frac{K_1^2}{K_2K_0 - K_1^2}.$$

Based on the definition of ZT , one can clearly conclude that high Seebeck coefficient, high electrical conductivity and low thermal conductivity are beneficial for high ZT [37,38].

3. Results and Discussion

3.1. Structural and Electronic Properties

ZrSbTe and HfSbTe adopt the orthorhombic NbPS structure type (space group Immm) with planar rectangular antimony layers. Moreover, Zr or Hf atoms are surrounded by four Sb and four Te atoms generating of a bi-capped trigonal prism, as illustrated in Figure 1. The calculated optimized lattice parameters are $a = 3.917 \text{ \AA}$, $b = 5.823 \text{ \AA}$, $c = 13.618 \text{ \AA}$ for ZrSbTe and $a = 3.910 \text{ \AA}$, $b = 5.805 \text{ \AA}$, $c = 13.517 \text{ \AA}$ for HfSbTe, which is in good agreement (error < 1.5%) with the experimental data [13].

The electronic band structures of ZrSbTe and HfSbTe are calculated without (red line) and with taking in consideration the SOC (blue line), as shown in Figure 2. Along the high-symmetry directions, it can be observed that there is a very similar behavior for band structures calculated with and without SOC contributions. It is also observed that the position of the conduction-band minimum (CBM) is shifted upwards whereas the valence-band maximum (VBM) is shifted downwards, showing an opening of the band gap, being a consequence of the presence of SOC. The upper valence band of both compounds presents a local maximum at the T-point, while the dispersion of the conduction band minimum leads to the characteristic of the band inversion along the Γ point. Moreover, the computed band structures for ZrSbTe and HfSbTe compounds exhibit a narrowing indirect band gap values of 0.10 eV, and 0.15 eV, respectively. Soheilnia et al. [13] were reported that ZrSbTe and HfSbTe compounds are metallic because of an overlap of metal d states with the Te p states. Conversely, we have predicted that ZrSbTe and HfSbTe compounds show

a semiconductor character with a narrow band gap with taken in consideration the SOC. The anticrossing between the conduction band minimum and valence band maximum, a typical identity of the SOC-induced formation of topological materials states [41].

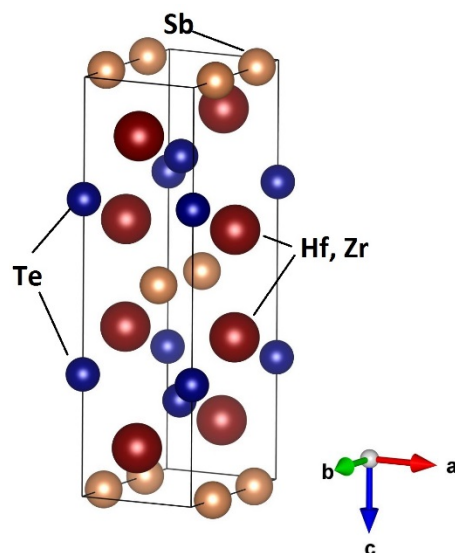


Figure 1. Crystal structure of ternary antimonide-tellurides: ZrSbTe and HfSbTe.

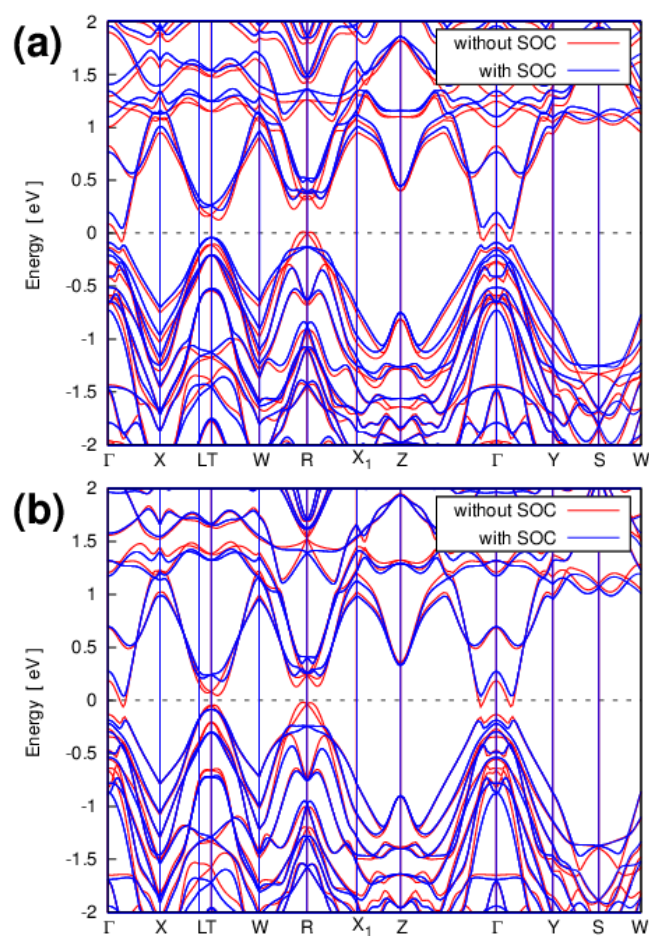


Figure 2. Electronic band structures (a) ZrSbTe (Without SOC (red line) and with SOC (blue line)), (b) HfSbTe (Without SOC (red line) and with SOC (blue line)).

3.2. Phonon Properties

To have a deep understanding of the vibrational character, we computed the phonon spectrum curves and the total and projected phonon density of states for ZrSbTe and HfSbTe, as plotted in Figure 3, respectively. The primitive unit cell of scrutinized systems consists of six atoms, which gives rise to a total number of 18 phonon modes. Three of the phonon modes are acoustic modes and the rest of the modes (15) represent optical phonon modes. The overall characteristics of the phonon dispersion curves show a similar trend for both compounds. It can be seen that no soft or imaginary phonon mode in the entire Brillouin has been observed which indicates that the investigated compounds are dynamically stable. It is found that there is no band gap between the acoustic and optical modes except for the highest optical branches, which have been separated from other optical phonon modes. This suggests that the highest optical phonons will be easily scattered with greatly limited thermal conductivity contribution. The highest frequency is observed at Γ -point for both compounds. Another case of interest is the fact that acoustic branches show similar dispersions in the Γ -Y and Γ -Z directions.

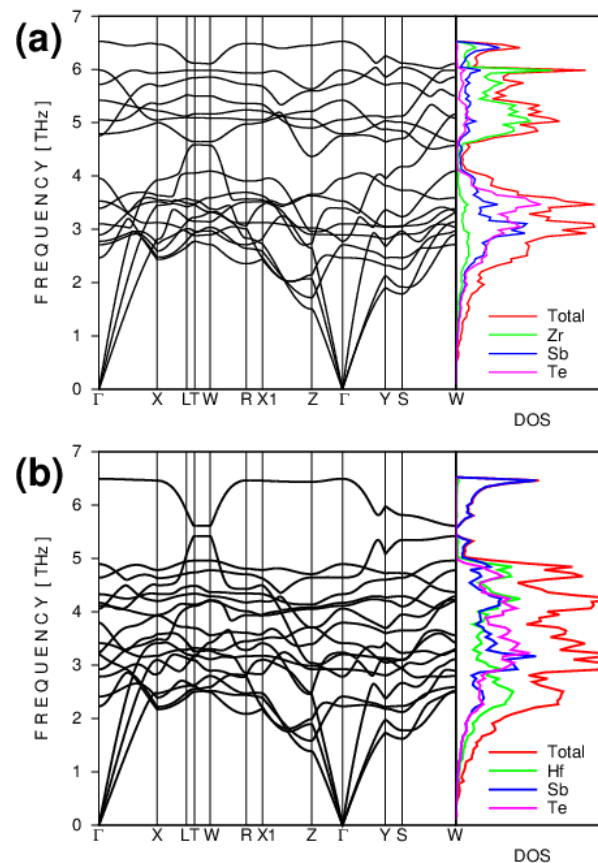


Figure 3. Phonon band structures and phonon densities of states (a) ZrSbTe, (b) HfSbTe.

It can be observed from Figure 3 that for higher frequency (above 3.5 THz), all the modes are optics. For the frequency between 3.5 and 2.5 THz, the modes correspond to both acoustic and optical modes while for lower frequency (below 2.5 THz), there are only acoustical modes.

In addition, our calculations indicated that a strong hybridization is noticed between the lower optic branches and the acoustic branches essentially far from the Γ point. Note that the hybridization in HfSbTe is stronger than that of ZrSbTe. This hybridization may conduct to the heat-carrying acoustic modes being scattered by low-frequency optical modes, which can also decrease the phonon velocity and hence thermal conductivity [42]. Moreover, the low optical phonon mode acts a crucial role in lowering the thermal conduc-

tivity [43]. Some optical modes are faintly dispersive, and these flat optical branches have a small contribution toward heat transport [42,43].

The Brillouin zone-center phonon modes corresponding to acoustic and optical modes are classified as follows:

$$\Gamma_{ac} = B_{1u}(I) + B_{2u}(I) + B_{3u}(I)$$

$$\Gamma_{op} = 2B_{2g}(R) + 3B_{3g}(R) + 2B_{2u}(I) + B_{1g}(R) + 2B_{3u}(I) + 3A_g(R) + 2B_{1u}(I)$$

In Table 1, Brillouin zone-center phonon frequencies with corresponding mode symmetries are listed for both materials. The Raman active modes are labeled by R while Infrared active by I. Generally, ZrSbTe has higher phonon energies than that of HfSbTe. It is known that, the phonon vibration modes have profound influences on the phonon thermal conductivity. If the phonon vibration frequency is lowered by doping of heavy atoms or substituting, the phonon thermal conductivity is reduced, meanwhile the electrical properties are also adjusted [44,45].

Table 1. Phonon frequencies (THz) at Γ point: * (R): Raman Active; (I): Infrared Active.

Symmetry *	ZrSbTe	HfSbTe
B_{2g}(R)	2.466	2.229
B_{3g}(R)	2.710	2.411
B_{2u}(I)	2.775	2.785
B_{1g}(R)	2.895	2.921
B_{3u}(I)	3.104	2.921
A_g(R)	3.395	3.235
B_{3g}(R)	3.529	3.412
B_{2g}(R)	4.756	3.793
B_{1u}(I)	3.957	4.060
B_{3g}(R)	4.790	4.114
B_{3u}(I)	5.055	4.169
B_{2u}(I)	5.419	4.331
A_g(R)	5.718	4.642
B_{1u}(I)	5.987	4.895
A_g(R)	6.525	6.495

On the right side of phonon curves, the corresponding the total and projected density of phonon states are also plotted for these compounds. The PDOS curves for ZrSbTe and HfSbTe can be divided into two distinct regions. For ZrSbTe, the main contribution phonon modes for the first region (<4 THz) come from the Te and Sb. Phonon modes for second region (>4 THz) is mostly due to the vibration of Zr atoms with only a small contribution of Sb and Te atoms. For HfSbTe, while the low-frequency phonon modes (<6 THz) are characterized by the motion of the Hf, Sb, and Te atoms, the high-frequency phonon modes (>6 THz) are primarily dominated by the motion of the Sb atoms.

3.3. Thermoelectric Properties

It is well known that the current important challenge of optimizing thermoelectric property is to balance a variety of conflicting parameters. In order to maximize the figure of merit (ZT), a large Seebeck coefficient, high electrical conductivity and low thermal conductivity are required. Figure 4 displays the Seebeck coefficients, ZT, thermal conductance and conductance of ZrSbTe and HfSbTe for a temperature variation from 100 to 800 K. According to the plot of Figure 4a,b, Seebeck coefficients of optimized ZrSbTe and HfSbTe are

27.84 $\mu\text{V/K}$ and 2.24 $\mu\text{V/K}$ respectively. Consequently, both investigated systems exhibit small Seebeck coefficients at 300 K, indicating that the *p*-type carriers dominate a common observation in tellurides [46]. In the other hand, these values are strongly enhanced to 4 and 5 times from 400 K and 800 K respectively. The behavior of the conductivity curves for both compounds shows that HfSbTe is reaching a room-temperature conductivity of $226 \Omega^{-1}\text{cm}^{-1}$ (Figure 4), while the conductivity ZrSbTe ($157 \Omega^{-1}\text{cm}^{-1}$) is independent of the temperature. Our calculations are also in good agreement with the predictions performed with LMTO method [14]. It can be seen that the change of ZT with temperature shows a linear increase for HfSbTe, while for ZrSbTe it almost did not change by about 500 K. This may be due to the stronger hybridization for HfSbTe than ZrSbTe in phonon dispersion curves. The ZT values at 800 K are around 1.2 and 1.5 for HfSbTe and ZrSbTe, respectively. Our theoretical study predicts these compounds are a possible potential thermoelectric material [47]. However the efficiency is very poor in the low temperature for ZrSbTe.

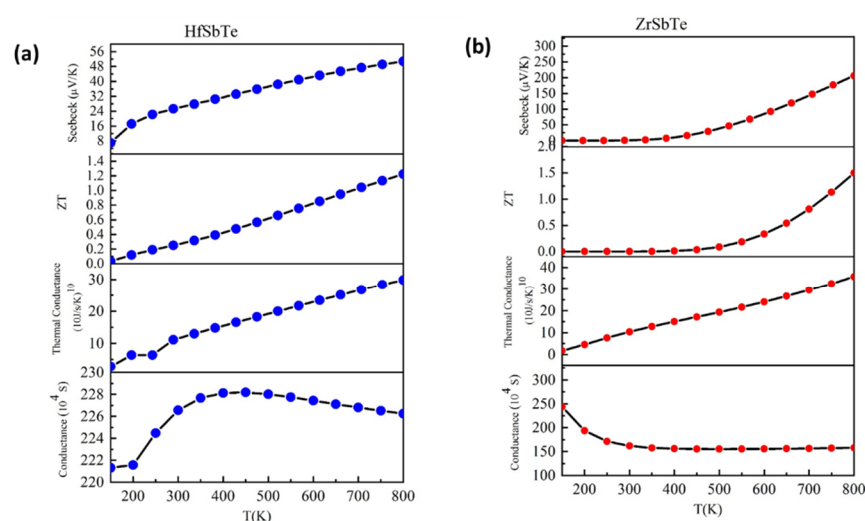


Figure 4. Thermoelectric properties of (a) HfSbTe, (b) ZrSbTe.

4. Conclusions

The first-principles calculation coupled to non-equilibrium scheme in the Landauer-Buttiker formalism based on Green's functions have been performed to investigate the structural, electronic, thermoelectric, and phonon properties of ZrSbTe and HfSbTe compounds. Without SOC, these compounds exhibit a metallic character, while both ZrSbTe and HfSbTe are semiconductors with indirect band gaps with SOC inclusion. The obtained phonon dispersion curves reveal the dynamic stability of both antimonides. A considerable mixing between the acoustic and optical branches is desirable to create phonon-phonon scattering which lead consequently to lower thermal conductivity. Both compounds are semiconductors with a relatively small Seebeck coefficient and high figure of merit increasing with the temperature. Thermoelectric properties indicate that of ZrSbTe and HfSbTe are suitable thermoelectric material for energy conversion at elevated temperatures.

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