Monolayer enhanced thermoelectric properties compared with bulk for BiTeBr

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It is believed that nanostructuring is an effective way to achieve excellent thermoelectric performance. In the work, by combining the first-principles calculations and semiclassical Boltzmann transport theory, we investigate the thermoelectric properties of bulk and monolayer BiTeBr including both the electron and phonon transports. The generalized gradient approximation (GGA) plus spin-orbit coupling (SOC) is employed for the electron part, and GGA for the phonon part. It is found that SOC has important effects on electronic transport coefficients because of SOC-induced obvious influences on energy band structures. In p-type doping, monolayer has larger Seebeck coefficient than bulk in wide doping range, which is beneficial to excellent thermoelectric performance. The calculated average lattice thermal conductivity of bulk is 1.71 Wm$^{-1}$K$^{-1}$ at room temperature, which is close to experimental value 1.3 Wm$^{-1}$K$^{-1}$. Calculated results show that monolayer has better $ZT_e$ and lower lattice thermal conductivity than bulk, which suggests that monolayer has better thermoelectric performance than bulk. The lower lattice thermal conductivity in monolayer than bulk is due to shorter phonon lifetimes. By comparing the experimental electrical conductivity of bulk with calculated value, the scattering time is determined for $3.3 \times 10^{-14}$ s. Based on electron and phonon transport coefficients, the thermoelectric figure of merit $ZT$ of bulk and monolayer are calculated. It is found that monolayer has higher peak $ZT$ than bulk, and the peak $ZT$ of monolayer can be as high as 0.55 in n-type doping and 0.75 in p-type doping at room temperature. These results imply that monolayer BiTeBr may be a potential two-dimensional (2D) thermoelectric material, which can stimulate further experimental works to synthesize monolayer BiTeBr.

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I. INTRODUCTION

Thermoelectric materials are of interest due to potential applications in energy conversion devices, and make essential contributions to the crisis of energy. The dimensionless figure of merit $ZT$, defined as $ZT = S^2 \sigma T / (\kappa_e + \kappa_L)$, can describe the performance of thermoelectric materials, where $S$, $\sigma$, $T$, $\kappa_e$ and $\kappa_L$ are the Seebeck coefficient, electrical conductivity, working temperature, the electronic and lattice thermal conductivities, respectively. According to expression of $ZT$, a potential thermoelectric material requires high power factor ($S^2\sigma$) and low thermal conductivity ($\kappa = \kappa_e + \kappa_L$). Unfortunately, Seebeck coefficient and electrical conductivity are oppositely proportional to carrier concentration. Therefore, searching for high-performance thermoelectric materials is interesting and challenging.

To improve $ZT$ of bulk materials, many strategies have been proposed, such as bands convergence to enhance the Seebeck coefficient by strain or doping and phonon engineering to reduce lattice thermal conductivity by alloying or introducing layered structures. To improve $ZT$, nanostructuring is another effective way, which is firstly proposed by Hicks and Dresselhaus in 1993. The low-dimensional materials can dramatically improve the power factor due to the sharp peaks in the electronic density of states (DOS) near the Fermi energy, which can induce asymmetry between holes and electrons transport and enhance electrical conductivity, and then can produce large Seebeck coefficient. Great progress by nanostructuring to enhance $ZT$ has been made, such as Bi$_2$Te$_3$/Sb$_2$Te$_3$, PbTe/Ag$_2$Te and silicon nanowires.

Due to noncentrosymmetric crystal structure and strong SOC, bulk BiTeX (X = Cl, Br, I) exhibit a giant Rashba-type spin splitting. Both in theory and in experiment, it is found that pressure can produce a topological transition in BiTeX (X = Br, I). The thermoelectric properties of BiTeI have been investigated both theoretically and experimentally, and the thermoelectric performance can be enhanced in Cu-intercalated BiTeX, through Br-substitution and by pressure. Experimentally, the thermoelectric properties of BiTeBr have also been studied, whose thermoelectric efficiency is better than that of BiTeI. Theoretically, monolayers BiTeX (X = Br, I) have been predicted based on the

FIG. 1. (Color online) The crystal structures of BiTeBr: the frame surrounded by a black box is bulk unit cell, and the monolayer is presented by a red box.
first-principles calculations, which can also produce a giant Rashba spin splitting\textsuperscript{25,26}. Recently, the thermoelectric properties of 2D materials, such as semiconducting transition-metal dichalcogenide monolayers, orthorhombic group IV-VI monolayers and group-VA elements (As, Sb, Bi) monolayers\textsuperscript{4,27–31}, have been widely investigated.

![Energy band structure of bulk (Left) and monolayer (Right) BiTeBr using GGA (Black lines) and GGA+SOC (Red lines).](image)

**FIG. 2.** (Color online) The energy band structures of bulk (Left) and monolayer (Right) BiTeBr using GGA (Black lines) and GGA+SOC (Red lines).

### TABLE I. The lattice constants $a$ and $c$ (Å); the calculated energy band gaps using GGA $G$ (eV) and GGA+SOC $G_{so}$ (eV); $G$-$G_{so}$ (eV); Rashba energy $E_R$ (meV).

| Name       | $a$  | $c$  | $G$  | $G_{so}$ | $E_R$ |
|------------|------|------|------|----------|-------|
| Bulk       | 4.27 | 6.46 | 1.09 | 0.28     | 0.81  | 63    |
| Monolayer  | 4.37 | -    | 1.57 | 0.84     | 0.73  | 19    |

Here, we investigate thermoelectric properties of bulk and monolayer BiTeBr by the first-principle calculations and Boltzmann transport theory. It is found that SOC has important effects on electronic transport coefficients, which has also been found in bulk BiTeBr\textsuperscript{24}. The predicted average room-temperature lattice thermal conductivity for bulk BiTeBr is 1.71 Wm\textsuperscript{-1}K\textsuperscript{-1}, being close to experimental value 1.3 Wm\textsuperscript{-1}K\textsuperscript{-1}\textsuperscript{19,20}. The room-temperature lattice thermal conductivity for monolayer BiTeBr is lower than one of bulk due to shorter phonon lifetimes. The scattering time can be attained by the comparison between experimental and theoretical electrical conductivity. Finally, the thermoelectric figure of merit $ZT$ of bulk and monolayer are calculated. It is found that monolayer has more higher peak value of $ZT$ than bulk due to better $ZT_e$ and lower lattice thermal conductivity, which shows monolayer can improve thermoelectric performance compared with bulk for BiTeBr.

The rest of the paper is organized as follows. In the next section, we shall describe computational details about the first-principle and transport coefficients calculations. In the third section, we shall present the electronic structures and thermoelectric properties of bulk and monolayer BiTeBr. Finally, we shall give our discussions and conclusion in the fourth section.
The conduction bands of both bulk and monolayer BiTeBr are shown in Figure 2. The band crossing point of conduction bands at high symmetry point, forming a significant Rashba spin splitting. The SOC can lead to a huge reduction in the band gap. The GGA and GGA+SOC gaps of bulk are 1.09 eV and 0.84 eV. The GGA+SOC gap of bulk agrees well with other theoretical value 0.31 eV\(^{50}\). It is clearly seen that monolayer has larger gap than bulk, which is similar to semiconducting transition-metal dichalcogenide compounds. The outlines of band structures are strongly modified due to spin-orbit splitting. The splitting makes the conduction band minimum (CBM) of the bulk (monolayer) BiTeBr deviate slightly from high symmetry A (Γ) point, forming a significant Rashba spin splitting. The Rashba energy \((E_R)\) of bulk (monolayer) BiTeBr, which is defined as the energy between the CBM and the band crossing point of conduction bands at high symmetry

III. MAIN CALCULATED RESULTS AND ANALYSIS

Bulk BiTeBr has a layered structure along c axis with space group being \(P3m1\), whose unit cell contains three atoms with Bi atom sandwiched between Te and Br atoms, forming a triple layer. Because of weak van der Waals interactions between the adjacent triple layers, monolayer BiTeBr can be exfoliated in experiment. The schematic crystal structures of bulk and monolayer BiTeBr are presented in Figure 1. In our calculations, the experimental values of lattice constants of bulk BiTeBr \((a=b=4.27 \text{ Å}, c=6.46 \text{ Å})\) are used\(^{49}\). The lattice constants of monolayer BiTeBr are optimized within GGA-PBE, and the optimized value is \(a=b=4.37 \text{ Å}\), which is less than one of monolayer BiTeI(4.42 Å)\(^{26}\). The unit cell of monolayer BiTeBr, containing one Bi, one Te and one Br atoms, is constructed with the vacuum region of larger than 15 Å to avoid spurious interaction. All the free atomic positions of both bulk and monolayer are optimized within GGA-PBE.

The energy band structures of bulk and monolayer BiTeBr using GGA and GGA+SOC are shown in Figure 2. The conduction bands of both bulk and monolayer are mainly composed of the 6p-states of Bi, while the valence bands are dominated by Te-p and Br-p states. The SOC can lead to a huge reduction in the band gap. The GGA and GGA+SOC gaps of bulk are 1.09 eV and 0.28 eV, respectively, while ones of monolayer are 1.57 eV and 0.84 eV. The GGA+SOC gap of bulk agrees well with other theoretical value 0.31 eV\(^ {50}\). It is clearly seen that monolayer has larger gap than bulk, which is similar to semiconducting transition-metal dichalcogenide compounds. The outlines of band structures are strongly modified due to spin-orbit splitting. The splitting makes the conduction band minimum (CBM) of the bulk (monolayer) BiTeBr deviate slightly from high symmetry A (Γ) point, forming a significant Rashba spin splitting. The Rashba energy \((E_R)\) of bulk (monolayer) BiTeBr, which is defined as the energy between the CBM and the band crossing point of conduction bands at high symmetry

FIG. 3. (Color online) At room temperature (300 K), transport coefficients of bulk (Top) and monolayer (Bottom) BiTeBr as a function of doping level (N), including Seebeck coefficient $S$, electrical conductivity with respect to scattering time $\sigma/\tau$ and power factor with respect to scattering time $S^2\sigma/\tau$ calculated with GGA and GGA+SOC.

FIG. 4. Phonon band structures of bulk (Left) and monolayer (Right) BiTeBr using GGA-PBE.
point A (Γ), is 63 meV (19 meV). The bulk Rashba energy is in agreement with previous calculated value 55 meV.  

Next, the electronic transport coefficients are performed using CSTA Boltzmann theory, Seebeck coefficient of which is independent of scattering time. The doping level, which is defined as electrons (minus value) or holes (positive value) per unit cell, can be simulated by simply shifting Fermi level into conduction (n-type doping) or valence (p-type doping) bands within the framework of rigid band approach. The n-type doping produces the negative Seebeck coefficient, while the p-type doping leads to the positive Seebeck coefficient. At room temperature, Seebeck coefficient S, electrical conductivity with respect to scattering time σ/τ and power factor with respect to scattering time S^2σ/τ of bulk and monolayer BiTeBr as a function of doping level using GGA and GGA+SOC are shown in Figure 3. Note: The electrical conductivity of monolayer has been normalized by multiplying L2/d, where d is the lattice constant c of bulk. For bulk BiTeBr, SOC has a reduced effect on Seebeck coefficient, which leads to SOC-reduced power factor. For monolayer BiTeBr, SOC has a slight effect on n-type Seebeck coefficient, but it has a obviously reduced effect on p-type Seebeck coefficient. The SOC influence on power factor of monolayer is the same with one on Seebeck coefficient. It is found that monolayer has larger p-type Seebeck coefficient than bulk, leading to larger power factor, if the scattering time τ is assumed to be the same. The p-type Seebeck coefficient of bulk is larger than 200 μV/K with doping level being less than 5.9×10^{-4}, while monolayer one with doping level being less than 2.9×10^{-2} is larger than 200 μV/K. That shows monolayer has more wider doping range than bulk for efficient thermoelectric application.  

Based on the harmonic IFCs, phonon band structures of bulk and monolayer BiTeBr are calculated, which are shown in Figure 4 along high-symmetry pathes. Due to three atoms per unit cell, the phonon dispersions of bulk and monolayer BiTeBr contain 3 acoustic and 6 optical phonon branches. It is found that three acoustic branches of bulk are linear near the Γ point. However, the longitudinal acoustic (LA) and transverse acoustic (TA) branches are linear near the Γ point, while the z-direction acoustic (ZA) branch is quadratic. Calculated results also show that the whole branches of monolayer move toward lower energy compared to ones of bulk. There is a phonon band gap of 0.19 THz between acoustic and optical branches for bulk, but ZO branch crosses with the LA branch for monolayer, which can lead to more scattering channel.

The lattice thermal conductivities of bulk and monolayer BiTeBr are calculated within the linearized phonon Boltzmann equation, and the lattice thermal conductivity is assumed to be independent of doping level, which is reasonable in many thermoelectric materials. Because of crystal symmetry of bulk, the lattice thermal conductivities along a and b axes (the in-plane direction) are equivalent, but they are different from one along c axis (the cross-plane direction). Therefore, the lattice thermal conductivities along a and c axes and the average one (κL(ax)=κL(ay)+κL(az))/3 as a function of temperature are plotted in Figure 5. Calculated results show that the lattice thermal conductivity exhibits obvious anisotropy, and the lattice thermal conductivity along c axis is lower than that along a axis. The corresponding lattice thermal conductivity at 300 K is 2.27 Wm^{-1}K^{-1} along a axis and 0.58 Wm^{-1}K^{-1} along c axis, respectively. The average room-temperature lattice thermal conductivity is 1.71 Wm^{-1}K^{-1}, which is larger than experimental value 1.3 Wm^{-1}K^{-1}. This difference may be due to defect in experimental sample, which leads to lower lattice thermal conductivity. The lattice thermal conductivity of monolayer along a axis (κL(ax)=κL(ay)=κL(ax)) as a function of temperature is also plotted in Figure 5 with the thickness d being lattice constant c of bulk. The room temperature lattice thermal conductivity of monolayer is 1.47 Wm^{-1}K^{-1}, which is lower than average one 1.71 Wm^{-1}K^{-1} of bulk. The phonon modes contributions of bulk (the in-plane and cross-plane directions) and monolayer BiTeBr to the
It is found that the acoustic phonon branches dominate lattice thermal conductivity, and the acoustic branches comprise around 88.46% for bulk along a direction, 96.25% for bulk along c direction and 84.00% for monolayer, respectively. Along the in-plane direction for bulk, the contribution from the first (17.00%) acoustic branch is the smallest in acoustic branches, and the eighth (2.75%) and ninth (5.56%) optical branches have obvious contributions. However, the second acoustic branch (19.71%) provides the smallest contribution in acoustic branches along the cross-plane direction for bulk. For monolayer, the ZA branch (7.77%) provides the smallest contribution in acoustic branches, and the fifth (5.50%), eighth (3.59%) and ninth (4.61%) optical branches have relatively large contributions.

To understand deeply phonon transports of bulk and monolayer BiTeBr, the mode level phonon group velocities and lifetimes are plotted in Figure 7. It is clearly seen that group velocities of bulk have the same order of magnitude with ones of monolayer, but the phonon lifetimes of monolayer are very shorter than ones of bulk, which leads to lower lattice thermal conductivity for monolayer than bulk. For both bulk and monolayer, the optical branches have relatively large group velocities, which leads to relatively large contributions from optical branches to total lattice thermal conductivity. Moreover, for the fifth optical branch of monolayer, the maximum group velocity is 2.58 kms^{-1}, which is larger than maximum group velocity of acoustic branches. This leads to the largest contribution from the fifth optical branch in optical branches, which is close to one of ZA branch. The most of phonon lifetimes of ZA branch for monolayer are very shorter than ones of LA and TA branches, which produces very little contributions to total lattice thermal conductivity.

Based on the power factor and electronic thermal conductivity, monolayer has more higher $ZT_e$ than bulk, where $ZT_e$ is defined as $S^2\sigma T/\kappa_e$. The $ZT$ is connected to $ZT_e$ by the relation $ZT=ZT_e\times\kappa_e/(\kappa_e + \kappa_L)$. Here, the $\kappa_e$ is calculated by the Wiedemann-Franz law with the Lorenz number of $2.4\times10^{-8}$ WΩK^{-2}. To attain the figure of merit $ZT$, only scattering time $\tau$ is unknown. Here, a range of reasonable relaxation time is used in our calculations from $1\times10^{-15}$ s to $1\times10^{-13}$ s. The $ZT$ values of bulk and monolayer BiTeBr as a function of doping level with temperature being 300 and 600 K are plotted in Figure 8 with the scattering time $\tau$ equaling $1\times10^{-15}$ s, $1\times10^{-14}$ s and $1\times10^{-13}$ s. As the scattering time $\tau$ increases, the $ZT$ moves toward its upper limit $ZT_e$. Calculated results show that monolayer has larger peak $ZT$ than bulk in both n- and p-type doping with the scattering time $\tau$ from $1\times10^{-15}$ s to $1\times10^{-13}$ s, which shows monolayer enhanced thermoelectric properties compared with bulk. It is found that the p-type doping has more excellent thermoelectric properties than n-type doping for both bulk and monolayer.

Due to the complexity of various carrier scattering mechanisms, calculating scattering time $\tau$ from the first principles is difficulty and challenging, but it can be calculated by comparing experimental value of electronic conductivity with the calculated value of $\sigma/\tau$. Experimentally, the electronic conductivity of bulk BiTeBr at room temperature is about $670$ Ω^{-1}cm^{-1} with n-type doping.
doping concentration $1.4 \times 10^{19} \text{cm}^{-3}$ \cite{319,20}. The scattering time $\tau$ is found to be $3.3 \times 10^{-14} \text{s}$. The calculated Seebeck coefficient with n-type doping concentration $1.4 \times 10^{19} \text{cm}^{-3}$ at 300 K is -89.5 $\mu \text{V/K}$, which is close to experimental value -115 $\mu \text{V/K}$ \cite{19,20}. The electronic thermal conductivity $\kappa_e$ with n-type doping concentration $1.4 \times 10^{19} \text{cm}^{-3}$ is calculated using $\tau=3.3 \times 10^{-14} \text{s}$, and the calculated value is 0.52 $\text{Wm}^{-1}\text{K}^{-1}$, which is in good agreement with experimental value 0.5 $\text{Wm}^{-1}\text{K}^{-1}$ \cite{119,20}. The scattering time $\tau$ attained from bulk BiTeBr is also used in monolayer BiTeBr, and the $ZT$ values of bulk and monolayer as a function of doping level at 300 and 600 K are plotted in Figure 9. It is found that the peak $ZT$ values of monolayer in both n- and p-type doping are larger than ones of bulk. The n- and p-type peak $ZT$ of monolayer is 0.55 and 0.75 at 300 K, and 1.95 and 2.56 at 600 K. These results imply that monolayer BiTeBr may be a potential two-dimensional (2D) thermoelectric material.

IV. DISCUSSIONS AND CONCLUSION

The SOC can produce a giant effect on energy band structures near the Fermi level by removing band degeneracy and modifying the outline of bands, which can lead to remarkable reduced effects on the Seebeck coefficient, and further can induce detrimental power factor. Similar detrimental effects on power factor are also found in MgS$_2$X (X = Si, Ge, Sn) \cite{53}, half-Heusler ANiB (A = Ti, Hf, Sc, Y; B = Sn, Sb, Bi) \cite{54} and semiconducting transition-metal dichalcogenide monolayers MX$_2$ (M=Zr, Hf, Mo and Pt; X=S, Se and Te) \cite{4,55,56}. However, the SOC also can lead to observably enhanced power factor in monolayers WX$_2$ (X=S, Se and Te) due to the bands converge induced by SOC \cite{56}. The maximum power factors (MPF) in unit of $\tau \times 10^{14} \mu \text{W}/(\text{cmK}^2)$ of bulk in n-type doping and monolayer in p-type doping are extracted with GGA and GGA+SOC at 300K, and the corresponding GGA and GGA+SOC values are 12.96 and 9.00 for bulk, 55.74 and 17.65 for monolayer. The MPF with SOC is predicted to be about 30.56% (bulk) and 68.34% (monolayer) smaller than that without SOC. So, it is very important for electronic transport coefficients of BiTeBr to include SOC.

Strain or pressure has been proved to be very effective to achieve enhanced thermoelectric properties in both bulk and 2D materials. Low-dimensional electronic structures can occur in Rashba semiconductor BiTeI \cite{21}, and pressure can lead to two-dimensional-like DOS in the conduction bands by tuning Rashba spin-splitting, which can induce significantly enhanced power factor in n-type doping by pressure \cite{24}. The bulk BiTeBr has similar energy band structures with bulk BiTeI, so it is possible to achieve improved power factor in bulk BiTeBr by pressure. Strain-enhanced power factor is observed in monolayer MoS$_2$ \cite{55}, PtSe$_2$ \cite{4} and ZrS$_2$ \cite{57} due to bands converge induced by strain. It has been proved that the Rashba spin-splitting can be modified significantly by the biaxial strain in monolayer BiTeBr \cite{25}, and it is possible to achieve enhanced power factor in monolayer BiTeBr by tuning Rashba spin-splitting.

The thermoelectric properties of many 2D materials have been investigated \cite{4,27–31}, and low lattice ther-
nential conductivity is very important to achieve potential thermoelectric materials. To compare the lattice thermal conductivities of various 2D materials, the same thickness should be used. Here, the same thickness of 3.35 Å is used, and the lattice thermal conductivity of monolayer BiTeBr is 2.84 Wm⁻¹K⁻¹, which is lower than that of orthorhombic group IV-VI monolayers (5.24∼15.80 Wm⁻¹K⁻¹), semiconducting transition-metal dichalcogenide monolayers (18.55∼261.0 Wm⁻¹K⁻¹), and group-VA elements (As, Sb, Bi) monolayers (4.78∼48.09 Wm⁻¹K⁻¹). Therefore, monolayer BiTeBr may be a potential 2D thermoelectric material due to lower lattice thermal conductivity compared to other well-studied 2D materials.

In summary, based mainly on the reliable first-principle calculations, the thermoelectric properties of bulk and monolayer BiTeBr are investigated. The electron part is performed using GGA+SOC, and phonon part is calculated using GGA. Calculated results show that SOC has important effects on electronic transport coefficients due to obvious SOC influences on electronic structures. The calculated average bulk lattice thermal conductivity at room temperature is 1.71 Wm⁻¹K⁻¹, being close to experimental value 1.3 Wm⁻¹K⁻¹. The monolayer lattice thermal conductivity (300 K) is 1.47 Wm⁻¹K⁻¹ with d being c of bulk, which is lower than that of bulk. The scattering time τ is determined by fitting the calculated electronic conductivity with experimental measurement, and the attained scattering time τ is 3.3 × 10⁻¹⁰ s. The monolayer has larger peak ZT in both n- and p-type doping than bulk due to higher ZTe and lower lattice thermal conductivity. The present work can encourage further experimental efforts to achieve monolayer BiTeBr, and then to investigate it’s thermoelectric performance.

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