Electron and phonon transport properties of layered Bi$_2$O$_2$Se and Bi$_2$O$_2$Te from first-principles calculations

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Abstract

Recent experiments indicated that both layered Bi$_2$O$_2$Se and Bi$_2$O$_2$Te are promising thermoelectric materials with low thermal conductivities. However, theoretical study on the thermoelectric properties, especially the phonon transport properties, is rare. In order to understand the thermoelectric transport mechanism, we here investigate the electron and phonon transport properties by using the first-principles calculations combined with the Boltzmann transport theory. Our results indicate that both Bi$_2$O$_2$Se and Bi$_2$O$_2$Te are semiconductors with indirect energy gaps of 0.87 eV and 0.21 eV within spin–orbit coupling, respectively. Large Seebeck coefficient and power factor are found in the p-type than the n-type for both compounds. Low lattice thermal conductivities at room temperature are obtained, 1.14 W m$^{-1}$ K$^{-1}$ for Bi$_2$O$_2$Se and 0.58 W m$^{-1}$ K$^{-1}$ for Bi$_2$O$_2$Te, which are close to the experimental values. It is found that the low-frequency optical phonon branches with higher group velocity and longer lifetime also make a main contribution to the lattice thermal conductivity. Interestingly, the lattice thermal conductivity exhibits obvious anisotropy especially for Bi$_2$O$_2$Te. These results are helpful for the understanding and optimization of thermoelectric performance of layered Bi$_2$O$_2$Se and Bi$_2$O$_2$Te.

1. Introduction

Thermoelectric materials, which possess of the characteristic to transform waste heat into electric power, have been extensively studied for new sustainable energy technology [1–3]. The efficiency of thermoelectric conversion is governed by the figure of merit $ZT = S^2\sigma T/\kappa$, where $S$, $\sigma$, $T$ and $\kappa$ are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively. The thermal conductivity $\kappa$ includes electronic $\kappa_e$ and phonon (or lattice) $\kappa_p$ parts. As for high $ZT$ materials, they typically have a high power factor ($PF = S^2\sigma$) and a low $\kappa$. Nevertheless, this does not mean we can limitless increase the power factor and reduce the thermal conductivity, because these parameters are always coupled with each other. Therefore, different strategies have been taken to improve the $ZT$ value, including doping [4, 5], band engineering [6, 7] and low dimensional structure [8, 9], etc.

As we all know, the Bi-based thermoelectric materials firstly reported were the layered Bi$_2$Se$_3$ and Bi$_2$Te$_3$, which have been widely studied in both experiments and theories [10–12]. The measured thermal conductivities are low, 3.1 W m$^{-1}$ K$^{-1}$ for Bi$_2$Se$_3$ [13] and 2.0 W m$^{-1}$ K$^{-1}$ for Bi$_2$Te$_3$ [14]. By the solid state reaction of Bi$_2$Se$_3$ with Bi$_2$O$_2$ and Bi$_2$Te$_3$ with Bi$_2$O$_2$, the ordered ternary layered bismuth oxide crystalline compounds of Bi$_2$O$_2$Se and Bi$_2$O$_2$Te have been synthesized experimentally [15–17], and they exhibit a tetragonal structure with I4/mmm space group and make up of Se/Te atomic layers sandwiched between Bi$_2$O$_2$ layers with weak electrostatic interactions. Ruleova et al [17] experimentally observed that Bi$_2$O$_2$Se has a low thermal conductivity with 1.1 W m$^{-1}$ K$^{-1}$ at room temperature and 0.7–0.75 W m$^{-1}$ K$^{-1}$ at $T = 800$ K. However, the $ZT$ value is only about 0.2 at 800 K due to the low electrical conductivity. Fu et al [18] have performed experimental and theoretical studies on the electronic and transport properties of Bi$_2$O$_2$Se. It was found that the Se vacancies (V$_{Se}$)
and the Se–Bi antisites (S_{Bi}) are crucial donors for electron carriers in Bi₂O₂Se. To improve the thermoelectric performance, some strategies have been implemented. For instance, the large ZT value 1.42 of p-type doping Bi₂O₂Se under tensile strain at 800 K was predicted by Guo et al., but they adopted the experimental thermal conductivity for ZT prediction and did not consider the change with strain [19]. The Cl doping can significantly improve the electrical conductivity and the ZT can reach 0.23 at $T = 823$ K for Bi₂O₂Se [20]. The recently measured Bi₂O₂Te is also a n-type semiconductor with a band gap of 0.23 eV and a low thermal conductivity of 0.91 W m⁻¹ K⁻¹ at room temperature [21]. Based on this experimental thermal conductivity, Tran et al. theoretically predicted that the ZT value of Bi₂O₂Te is 1.27 at about 600 K for the p-type doping [22]. As far as we know, however, there is no theoretical study on the phonon transport properties for Bi₂O₂X. What’s more, the previous theoretical reports on electron transport properties almost did not consider the effect of spin–orbit coupling (SOC), which may not be neglected due to the heavy elements Bi and Te in Bi₂O₂X.

For layered Bi₂O₂X, what is the origin of the low lattice thermal conductivity? How about the anisotropy of the lattice thermal conductivity? How about the p-type thermoelectric performance compared to the n-type? How about the effect of SOC on the thermoelectric performance? With these questions, in this work, we use the first-principles calculations combined with the Boltzmann transport theory to investigate the electron and phonon transport properties. It is found that the p-type thermoelectric performance is better than the n-type, and thus the thermoelectric performance can be enhanced by reasonable p-type doping. The obtained lattice thermal conductivities, 1.14 W m⁻¹ K⁻¹ for Bi₂O₂Se and 0.58 W m⁻¹ K⁻¹ for Bi₂O₂Te at 300 K, are close to the experimental values, and the main contribution is also from the low-frequency optical phonon branches in addition to the acoustic phonon branches. The lattice thermal conductivities exhibit obvious anisotropy especially for Bi₂O₂Te. We also find that the SOC has a considerable effect on the thermoelectric performance, and the optimized ZT values decrease from 0.74 to 0.53 for Bi₂O₂Se, and 0.87 to 0.62 for Bi₂O₂Te within SOC.

2. Computational methods

The structural optimization of Bi₂O₂X (X = Se, Te) is performed within the framework of density functional theory using the projector-augmented-wave [23] pseudopotential and the Perdew–Burke–Ernzerhof [24] exchange correlation functional as implemented in the VASP [25]. The energy cutoff for the plane-wave expansion is set to 550 eV, and a Monkhorst–Pack $k$-mesh of $13 \times 13 \times 13$ is used in the Brillouin zone. The energy convergence threshold is $10^{-6}$ eV and the force $10^{-7}$ eV Å⁻¹ in the structural optimization. In order to overcome the underestimation of energy gap from the generalized gradient approximation (GGA), we use the recently developed GGA plus Tran–Blaha modified Becke–Johnson (TB-mBJ-GGA) potential [26] to calculate the electronic transport properties, and the SOC is also considered. A $33 \times 33 \times 13$ Monkhorst–Pack $k$ point grid is used for the calculations of the electronic transport properties by utilizing the Boltzmann transport theory and the relaxation time approximation as implemented in the BoltzTraP code [27], from which we can obtain the $S$ and $\sigma/\tau$. The electrical thermal conductivity is calculated by the Wiedemann–Franz law: $\kappa_e = L\sigma T$, where $L = 2.4 \times 10^{-8}$ W K⁻¹ is the Lorenz number [28].

The lattice thermal conductivity is calculated based on the phonon Boltzmann transport equation as implemented in the ShengBTE [29]. We use a $4 \times 4 \times 4$ supercell to calculate the second and third-order force constants. The second-order force constants are calculated by the Phonopy package [30], and the third-order force constants are obtained by the thirdorder.py script in the ShengBTE [29]. A cutoff of 0.57 nm for the calculation of anharmonic force constants is employed. Finally, a $19 \times 19 \times 11$ $q$-mesh is selected to sample the corresponding phonon wave-vector mesh in the ShengBTE calculations. The present computational methods of electron and phonon transport properties have been successfully used in bulk and two-dimensional thermoelectric materials [7, 31, 32].

3. Results and discussion

3.1. Electronic structure and electronic transport

Both Bi₂O₂Se and Bi₂O₂Te belong to the tetragonal structure with $I4/mmm$ space group (figure 1(a)). Our optimized equilibrium lattice constants shown in table 1 are consistent with the experimental values [17, 21] and other theoretical values [33]. Based on the equilibrium structures, we firstly calculate the band structure of Bi₂O₂X, as shown in figures 1(b) and (c). It is clear that both Bi₂O₂Se and Bi₂O₂Te are semiconductors with indirect energy gaps of 0.87 eV and 0.21 eV, respectively, which are in agreement with the previous experimental and theoretical values [21, 35] (see table 1). Furthermore, we calculate the total and atomic partial density of states (DOS) near the Fermi level. It can be extracted from figure 2 that the conduction bands around the Fermi level are mostly contributed by Bi 6$p$ states, and the valence bands originate from the hybridized states of Se (Te) $p$ states and O 2$p$ states. At the same time, the valence bands exhibit much higher DOS than the conduction
bands, and thus one can expect that the Seebeck coefficient of $p$-type is much larger than that of $n$-type by reasonable doping.

Next, we calculate the electronic transport properties by the semiclassical Boltzmann transport theory. With so-called constant relaxation time approximation, the Seebeck coefficient $S$ is independent of the relaxation time $\tau$, while the electrical conductivity $\sigma$ is dependent on $\tau$. In the present work, by fitting the calculated Seebeck coefficient and electrical conductivity with the experimental results for Bi$_2$O$_2$X at 300 and 500 K [17, 21], we obtain the carrier concentration $n$ and the relaxation time $\tau$. For Bi$_2$O$_2$Se, $n$ is $2.85 \times 10^{-18}$ cm$^{-3}$ at 300 K and

|                | $a$ (Å) | $c$ (Å) | $E_g$ (eV) |
|----------------|---------|---------|------------|
| Bi$_2$O$_2$Se  | 3.92    | 12.41   | 0.87       |
| 3.89[17]       | 12.20[17]| —       |            |
| 3.90[33]       | 12.39[33]| 0.09[33]|            |
| Bi$_2$O$_2$Te  | 4.02    | 12.90   | 0.21       |
| 3.98[21]       | 12.77[21]| 0.23[21]|            |
| 4.01[33]       | 12.90[33]| 0.16[33]|            |

Figure 1. The crystal structure of bulk Bi$_2$O$_2$X ($X = $ Se, Te) (a) and the calculated electronic band structures of Bi$_2$O$_2$Se (b) and Bi$_2$O$_2$Te (c).

Figure 2. The calculated total and atomic partial density of states for Bi$_2$O$_2$Se (a) and Bi$_2$O$_2$Te (b).
The calculated Seebeck coefficient $S$, electrical conductivity $\sigma$ and electrical thermal conductivity $K_e$ as a function of carrier concentration at 300 K for Bi$_2$O$_2$X (X = Se, Te). Note that the fitted relaxation times are $1.35 \times 10^{-15}$ s at 300 K for Bi$_2$O$_2$Se and $2.5 \times 10^{-15}$ s at 300 K for Bi$_2$O$_2$Te.

Figure 3.

The calculated power factor as a function of carrier concentration at different temperatures of 300 and 500 K for Bi$_2$O$_2$Se (a) and Bi$_2$O$_2$Te (b). Note that the fitted relaxation times are $1.35 \times 10^{-15}$ s at 300 K and $1.91 \times 10^{-15}$ s at 500 K for Bi$_2$O$_2$Se, and $2.5 \times 10^{-15}$ s at 300 K and $3.43 \times 10^{-15}$ s at 500 K for Bi$_2$O$_2$Te.

Figure 4.

$2.34 \times 10^{-18}$ cm$^{-3}$ at 500 K, and $\tau$ is $1.35 \times 10^{-15}$ s at 300 K and $1.91 \times 10^{-15}$ s at 500 K. For Bi$_2$O$_2$Te, $n$ is $1.06 \times 10^{-18}$ cm$^{-3}$ at 300 K and $6.15 \times 10^{-18}$ cm$^{-3}$ at 500 K, and $\tau$ is $2.51 \times 10^{-15}$ s at 300 K and $3.43 \times 10^{-15}$ s at 500 K. The obtained carrier concentrations are in agreement with the experimental values $\sim 10^{-18}$ cm$^{-3}$ [21, 34], and their changes with temperature are slight [34]. The fitted $\tau$ values at 300 K are close to the previous theoretical results of $1.2 \times 10^{-15}$ s for Bi$_2$O$_2$Se [35] and $4.4 \times 10^{-15}$ s for Bi$_2$O$_2$Te [22]. Figures 3(a) and (b) show the calculated $S$ and $\sigma$ as a function of carrier concentration at 300 K. It is noticed that the Seebeck coefficient of $p$-type doping is larger than the $n$-type doping, and this characteristic is consistent with the DOS that the valence bands exhibit much higher DOS than the conduction bands. Both $p$-type Seebeck coefficients of Bi$_2$O$_2$Se and Bi$_2$O$_2$Te can reach about 450 $\mu$V K$^{-1}$ at an appropriate carrier concentration. We note that the previous theoretical $S$ of $-95 \, \mu$V K$^{-1}$ at the $n$-type carrier concentration of $1.5 \times 10^{19}$ cm$^{-3}$ and 400 $\mu$V K$^{-1}$ at the $p$-type carrier concentration of $2.0 \times 10^{19}$ cm$^{-3}$ [35] are close to our present results of $-85 \, \mu$V K$^{-1}$ and $370 \, \mu$V K$^{-1}$, respectively (see figure 3(a)).

Figure 3(b) indicates that, compared with Bi$_2$O$_2$Se, the electrical conductivity of Bi$_2$O$_2$Te is higher due to the small band gap. The electrical conductivity rapidly increases as the increasing carrier concentration, while the change is reverse for the Seebeck coefficient, and thus it is natural to obtain the maximum power factor by fitting a balanced value of the carrier concentration between the Seebeck coefficient and the electrical conductivity. Indeed, It can be clearly seen from figure 4 that Bi$_2$O$_2$Se shows the best power factor of 1.39 mW mK$^{-2}$ at a concentration of $1.05 \times 10^{21}$ cm$^{-3}$ for $p$-type doping at 500 K, while the maximum power factor of Bi$_2$O$_2$Te is about 1.13 mW mK$^{-2}$ with the concentration of $3.08 \times 10^{20}$ cm$^{-3}$ for $p$-type doping at 500 K. As for Bi$_2$O$_2$Te, the power factor of $n$-type doping increases with the increase of temperature, which is consistent with the experimental results [21]. The calculated electrical thermal conductivity $\kappa_e$ is shown in figure 3(c). One can see that the $p$-type value is clearly lower than the $n$-type value at the same carrier concentration. Overall, all these
results indicate that the thermoelectric performance of the \( p \)-type doping is more favorable than the \( n \)-type doping. The electronic transport performance can be enhanced by reasonable \( p \)-type doping.

### 3.2. Phonon transport and figure of merit

The calculated phonon spectra of Bi\(_2\)O\(_2\)X are plotted along high-symmetry paths in figure 5(a). As the primitive cells of Bi\(_2\)O\(_2\)X (\( X = \text{Se, Te} \)) have five atoms, fifteen phonon branches can be observed. There are significant frequency gaps between the high-frequency and low-frequency modes of optical branches, and they are about 3.03 THz and 3.12 THz for Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te, respectively. Meanwhile, we find some special features from the phonon spectra. One point of interest is the fact that compared with acoustic branches and low-frequency optical branches, the high-frequency optical branches show distinct dispersion, indicating their higher group velocity. What’s more, acoustic branches and some optical branches show different dispersions along the cross-plane (\( \Gamma \)-Z) and in-plane (\( \Gamma \)-X) directions, which suggests a strong phonon anisotropy as discussed in detail below. It can also be seen that all the phonon branches moves toward lower frequency for Bi\(_2\)O\(_2\)Te compared to Bi\(_2\)O\(_2\)Se, which implies the phonon spectra become more localized, namely the coupling strength between low-frequency optical branches and acoustic branches is enhanced. We also present in figure 5(b) the calculated total and partial phonon DOS. The optical modes with high frequency of Bi\(_2\)O\(_2\)X are dominated by O atoms, while doping. The electronic transport performance can be enhanced by reasonable \( p \)-type doping.

The calculated phonon group velocity with respect to frequency is shown in figure 6. It can be seen that the optical phonon branches also show remarkable dispersion, which points to higher group velocities of these optical modes, and their contributions to lattice thermal conductivity cannot be ignored. In addition, as for Bi\(_2\)O\(_2\)Se, the group velocities of transverse acoustic (TA) branches and longitudinal acoustic (LA) branch along \( \Gamma \)-X are about 1.54 km s\(^{-1}\), 1.34 km s\(^{-1}\), and 4.02 km s\(^{-1}\), respectively, while the group velocities of TA and LA along \( \Gamma \)-Z are about 1.22 km s\(^{-1}\), 2.32 km s\(^{-1}\), and 4.2 km s\(^{-1}\). As for high-frequency optical branches, the maximum group velocity along \( \Gamma \)-X reaches 7.51 km s\(^{-1}\), whereas it is only 0.57 km s\(^{-1}\) along \( \Gamma \)-Z. Likewise, the group velocities along \( \Gamma \)-X and \( \Gamma \)-Z for Bi\(_2\)O\(_2\)Te also show large difference. Thus, the group velocities along in-plane are much different from those along cross-plane direction, which will lead to a strong anisotropy of lattice thermal conductivity. In addition, compared with Bi\(_2\)O\(_2\)Se, Bi\(_2\)O\(_2\)Te possessing of heavier atomic mass has smaller group velocities.

The calculated lattice thermal conductivity of Bi\(_2\)O\(_2\)X as a function of temperature is shown in figure 7. Both Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te exhibit fairly low lattice thermal conductivities. The room temperature lattice thermal conductivities are 1.14 W m\(^{-1}\) K\(^{-1}\) for Bi\(_2\)O\(_2\)Se and 0.58 W m\(^{-1}\) K\(^{-1}\) for Bi\(_2\)O\(_2\)Te, which are lower than those of 1.6 W m\(^{-1}\) K\(^{-1}\) for PbTe [36] and 0.97 W m\(^{-1}\) K\(^{-1}\) for SnSe [37], respectively. They are also close to the experimental values of 1.1 W m\(^{-1}\) K\(^{-1}\) for Bi\(_2\)O\(_2\)Se [17] and 0.91 W m\(^{-1}\) K\(^{-1}\) for Bi\(_2\)O\(_2\)Te [21]. When the temperature is raised to 800 K, the lattice thermal conductivities are merely 0.45 W m\(^{-1}\) K\(^{-1}\) and 0.22 W m\(^{-1}\) K\(^{-1}\) for Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te, respectively. The lattice thermal conductivity of Bi\(_2\)O\(_2\)Te is lower
than that of Bi$_2$O$_2$Se due to the lower group velocity induced by heavier Te atom in Bi$_2$O$_2$Te than Se atom in Bi$_2$O$_2$Se. Interestingly, both lattice thermal conductivities exhibit strong anisotropy. For example, the in-plane and cross-plane room temperature lattice thermal conductivities are 1.31 and 0.82 W m$^{-1}$ K$^{-1}$ for Bi$_2$O$_2$Se, and 0.83 and 0.09 W m$^{-1}$ K$^{-1}$ for Bi$_2$O$_2$Te. The origin of the anisotropic lattice thermal conductivity can be explained from two aspects. On the one hand, as mentioned above, the acoustic branches and some optical branches show different dispersions along the cross-plane ($\Gamma$–Z) and in-plane ($\Gamma$–X) directions, which results in different group velocities along the cross-plane and in-plane directions. On the other hand, the atomic interactions along the cross-plane (weak electrostatic interactions) and in-plane directions (strong covalent bonding interactions) are different [38]. The weak electrostatic interactions along the cross-plane direction limit the phonon transport and yield low $\kappa_l$.

To further reveal the thermal transport mechanism, we show in figure 8 the calculated total relaxation time for all phonon modes as a function of frequency. Here, the phonon relaxation time $\tau_\lambda$ can be obtained from the phonon linewidth $2\Gamma_\lambda(\omega_\lambda)$ of the phonon mode $\lambda$:

$$\tau_\lambda = \frac{1}{2\Gamma_\lambda(\omega_\lambda)}.$$  

(1)
The $\Gamma_\lambda(\omega)$ takes a form analogous to the Fermi golden rule:

$$\Gamma_\lambda(\omega) = \frac{18}{\hbar^2} \sum_{XX'} |\Phi_{\lambda XX'}|^2 \left[ (f'_\lambda + f''_\lambda + 1) \delta(\omega - \omega'_\lambda - \omega''_\lambda) + (f'_\lambda - f''_\lambda) \delta(\omega + \omega'_\lambda - \omega''_\lambda) - \delta(\omega - \omega'_\lambda + \omega''_\lambda) \right],$$

where $f_\lambda$ is the phonon equilibrium occupancy, and $\Phi_{\lambda XX'}$ is the strength of interaction among the three phonons, $\lambda$, $\lambda'$, and $\lambda''$, involved in the scattering. Please see [39] about the more detailed description of these calculations. From figure 8, one can see that the average relaxation times are 1.3 ps for Bi$_2$O$_2$Se and 2.1 ps for Bi$_2$O$_2$Te for the acoustic branches and low-frequency optical branches (below 6 THz), and 0.41 ps for Bi$_2$O$_2$Se and 0.23 ps for Bi$_2$O$_2$Te for the high-frequency optical branches (above 6 THz), these values have the same magnitude to that of PbTe [40] which has a very dispersive transverse optical branch. Therefore, like PbTe, such low relaxation times in Bi$_2$O$_2$X are mainly attributed to the large phonon scattering. Importantly, the low-frequency optical phonon modes, as coupled with acoustic modes, possess comparable relaxation times with acoustic phonon modes, in contrast the high-frequency optical modes exhibit lower relaxation times. This means that the low-frequency optical phonons also make a dominate contribution to the lattice thermal conductivity.

We have also calculated the cumulative thermal conductivity as a function of phonon maximum mean-free path (MFP) to study the size dependence of $\kappa_s$. From figure 9, one can see that the total accumulation keeps increasing as MFPs increases, until reaching the plateau after MFPs increase to 64 nm and 38 nm for Bi$_2$O$_2$Se and Bi$_2$O$_2$Te, respectively. The maximum MFPs in Bi$_2$O$_2$Se and Bi$_2$O$_2$Te are much shorter than that of PbTe (about 300 nm) [40]. Furthermore, phonons with MFPs contributed about 80% of the total $\kappa_s$ are 17 nm for Bi$_2$O$_2$Se and 8.9 nm for Bi$_2$O$_2$Te. This means that the nanostructures with the length of 17 and 8.9 nm would
reduce \( \kappa_l \) by 20% for both Bi\(_2\)O\(_2\)X. That is to say, to consequentially reduce lattice thermal conductivity of Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te, the size of nanostructures should be below 17 nm and 8.9 nm, respectively.

Based on above results of electronic and phonon transport coefficients, we can obtain the \( ZT \) value of Bi\(_2\)O\(_2\)X as shown in figure 10. The calculated \( ZT \) values are close to the available experimental ones, e.g. the calculated \( ZT \) values for \( n \)-type Bi\(_2\)O\(_2\)Se are 0.006 at 300 K with the carrier concentration \( 2.85 \times 10^{18} \) cm\(^{-3}\), and 0.042 at 500 K with the carrier concentration \( 2.34 \times 10^{18} \) cm\(^{-3}\), which are in agreement with the experiment values of 0.007 and 0.034, respectively [17]. Figure 10 also indicates that the \( p \)-type doping is superior to the \( n \)-type doping, and the maximum of \( ZT \) value increases with increasing temperature. At 500 K, the \( p \)-type optimal \( ZT \) values can reach 0.53 and 0.62 for Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te, respectively. Therefore, the \( p \)-type doping is more favorable for the improvement of thermoelectric performance of Bi\(_2\)O\(_2\)X.

### 3.3. The comparison of thermoelectric properties with and without SOC

Above results are all based on the SOC. Now we discuss the difference of thermoelectric performance with and without SOC. We firstly present in figure S1 (see the supplementary materials available online at stacks.iop.org/NJP/20/123014/mmedia) the calculated electronic band structure of Bi\(_2\)O\(_2\)X using the TB-mBJ potential with and without SOC. One can see that both conduction band and valence band within SOC obviously move to low energy compared to those without SOC. The SOC reduces the energy gap, from 1.15 eV to 0.87 eV for Bi\(_2\)O\(_2\)Se, and 0.36 eV to 0.21 eV for Bi\(_2\)O\(_2\)Te. Without SOC, the energy gap of 1.15 eV is close to the previous theoretical value of 1.28 eV for Bi\(_2\)O\(_2\)Se [18]. For the conduction band, the shift toward low energy is obvious. For the valence band, we compare the energy difference between the first and the second valence band valleys for Bi\(_2\)O\(_2\)Se as shown in figure S1. The energy difference \( \Delta_1 \) at the X point within SOC is larger than \( \Delta_1 \) without SOC for Bi\(_2\)O\(_2\)Se. There is a big energy gap \( \Delta_2 \) at the Z point for Bi\(_2\)O\(_2\)Te due to the SOC. Therefore, the effect of SOC on the electronic band structure of Bi\(_2\)O\(_2\)X is obvious, and in turn, the thermoelectric performance will also be affected by the SOC.

We further calculate and compare the \( S, \sigma, S^2 \sigma \) and \( ZT \) with and without SOC. Figure S2 (see the supplementary materials) indicates that the SOC has an obvious influence on the \( p \)-type \( S \) of Bi\(_2\)O\(_2\)X (X = Se, Te) at 300 K for low doping concentration. When the temperature is raised to 500 K, both \( p \)-type and \( n \)-type \( S \) decrease at the low doping concentration due to the effect of SOC on the electronic structure. The calculated electrical conductivity \( \sigma \) in figure S3 (see the supplementary materials) shows that the values within SOC are smaller than those without SOC at the same carrier concentration. We further give in figure S4 (see the supplementary materials) the calculated power factor \( S^2 \sigma \) with and without SOC. It can be seen that the difference is small at 300 K but obvious at 500 K, especially for the \( p \)-type doping the \( S^2 \sigma \) decreases greatly. Finally, we present in figure S5 (see the supplementary materials) the calculated \( ZT \) values with and without SOC as a function of carrier concentration. The SOC has a considerable effect on the \( ZT \) values for both \( p \)-type Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te at 500 K, and the optimized \( ZT \) values decrease from 0.74 to 0.53 for Bi\(_2\)O\(_2\)Se, and from 0.87 to 0.62 for Bi\(_2\)O\(_2\)Te within SOC.

### 4. Conclusion

In summary, by utilizing the first-principle calculations and Boltzmann transport equation, we investigate the electronic structure and thermoelectric properties of layered Bi\(_2\)O\(_2\)X. Both Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te are
semiconductors with moderate indirect gaps of 0.87 eV and 0.21 eV within SOC, respectively. The Seebeck coefficient and power factor in the \( p \)-type are higher than those in the \( n \)-type. Ultra-low phonon thermal conductivities of 1.14 Wm\(^{-1}\) K\(^{-1}\) for Bi\(_2\)O\(_2\)Se and 0.58 Wm\(^{-1}\) K\(^{-1}\) for Bi\(_2\)O\(_2\)Te at 300 K are found, which are in agreement with the experimental values. The low-frequency optical phonons also make a dominate contribution to the lattice thermal conductivity. The lattice thermal conductivity shows strong anisotropy between the in-plane and the cross-plane. The optimal \( ZT \) values of \( p \)-type doping at 300 K reach 0.53 and 0.62 for Bi\(_2\)O\(_2\)Se and Bi\(_2\)O\(_2\)Te, respectively, due to the lower phonon thermal conductivity and the higher power factor. We also find that the effect of SOC on the thermoelectric performance is not negligible, and the SOC reduces the thermoelectric performance. The present work, especially the theoretical study on phonon transport properties for the first time, is helpful for the understanding and the optimization of thermoelectric properties of layered Bi\(_2\)O\(_2\)X.

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