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Anisotropic thermoelectric properties of layered compounds in SnX₂ (X = S, Se): A promising thermoelectric

Bao-Zhen Sun, Zuju Ma, Chao He and Kechen Wu

Thermoelectrics interconvert heat to electricity and are of great interest in waste heat recovery, solid-state cooling and so on. Here we assessed the potential of SnS₂ and SnSe₂ as a thermoelectric material at the temperature gradient from 300 to 800 K. Reflecting the crystal structure, the transport coefficients are highly anisotropic between a and c directions, in particular for the electrical conductivity. The preferred direction for both materials is a direction in TE application. Most strikingly, when 800 K is reached, SnS₂ can show a peak power factor (PF) of 15.50 µW·cm⁻¹·K⁻² along the a direction, while a relatively lower value (11.72 µW·cm⁻¹·K⁻²) is obtained in the same direction of SnSe₂. These values are comparable to those observed in thermoelectrics such as SnSe and SnS. At 300 K, the minimum lattice thermal conductivity (κₘᵢₙ) along the a direction is estimated to be about 0.67 and 0.55 W·m⁻¹·K⁻¹ for SnS₂ and SnSe₂, respectively, even lower than the measured lattice thermal conductivity of Bi₂Te₃ (1.28 W·m⁻¹·K⁻¹ at 300 K). The reasonable PF and κₘᵢₙ suggest that both SnS₂ and SnSe₂ are potential thermoelectric materials. Indeed, the estimated peak ZT can approach 0.88 for SnSe₂ and a higher value of 0.96 for SnS₂ along the a direction at a carrier concentration of 1.94×10¹⁹ (SnSe₂) vs. 2.87×10¹⁹ cm⁻³ (SnS₂). The best ZT values in SnX₂ (X = S, Se) are comparable to that in Bi₂Te₃ (0.8), a typical thermoelectric material. We hope this theoretical investigation will
provide useful information for further experimental and theoretical studies on optimizing the thermoelectric properties of SnX$_2$ materials.
Introduction

The use of thermoelectric (TE) materials to harvest electricity from waste heat via the Seebeck effect has become increasingly important, because of the global need for energy production and conservation.\textsuperscript{1-3} The TE efficiency of a material used in TE devices is determined by the dimensionless figure of merit, \( ZT = S^2 \sigma T / \kappa \), where \( S \) is the Seebeck coefficient or thermopower, \( \sigma \) the electrical conductivity, \( T \) the absolute temperature, and \( \kappa \) the thermal conductivity (\( \kappa = \kappa_L + \kappa_E \), where \( \kappa_L \) and \( \kappa_E \) are the lattice and electronic contributions, respectively). By definition, we see that a large Seebeck coefficient, a high electrical conductivity, and a low thermal conductivity are needed to achieve a high \( ZT \). In the past few years, pursuing high \( ZT \) has been the focus of TE studies. However, for practical applications, efficiency is not the only concern, and toxicity, price and density of the material are issues that must also be taken into account. Thus, one of the current main interests is to develop new, non-toxic and cheap thermoelectric materials.

Because of their anisotropic character, layered compounds appear to be attractive targets in the quest for TE materials. Indeed, some of them (for example \( A_2^V B_3^{VI} \), \textsuperscript{4,6} \( A^{IV} B^{VII} \), \textsuperscript{7-10} and layered Co oxides\textsuperscript{11-13}) display interesting thermoelectric properties. This holds especially true for SnSe which exhibits an outstanding \( ZT \) value of \( \sim 2.6 \) at 923 K.\textsuperscript{7} This is also well evidenced in the layered Bi\textsubscript{2}Te\textsubscript{3}-based materials which are the best TE materials around room temperature.\textsuperscript{14} In layered structure, an interesting feature is that the layer and the interlayer spacing can often be modified independently,
and hence leading to the possibility of tuning the electronic and thermal transport properties adequately. This is an advantageous situation for thermoelectrics. What’s more, the bonds between the layers are extremely weak (due to weak van der Waal’s forces). It is beneficial to the low thermal conductivity. For instance, this has been proven in the layered compounds such as (Na, Ca)Co$_2$O$_4$, AgCrSe$_2$, and SnSe.$^{7, 17}$ For these reasons, the TE potential of layered metal dichalcogenides MX$_2$ (M is a metal atom like Sn, Ti, Zr, or Hf and X is a chalcogen like S, Se, or Te) has increasingly attracted attention.

The family of MX$_2$ have been investigated for a long period and are known to exhibit several interesting physical properties as well as find innovative practical applications, such as solid lubricant, photovoltaics, electrochemical fuel cells, etc.$^{18-20}$ MX$_2$ compounds typically grow in layered crystals similar to graphite and the interaction between the layers is weak van der Waals type and, therefore, they can be easily intercalated by various guest species. This will greatly affect their structural and electronic properties, which in turn means that the TE properties of these materials can be optimized by controlling the type and the concentration of the dopants.$^{21}$ Recently, several studies have demonstrated the great TE potential of MX$_2$ compounds.$^{16, 22-24}$ Typical examples include the dichalcogenides MX$_2$ (M = Mo, W, Ti; X = S, Se, Te), which are good candidates for thermoelectric applications because of their high Seebeck coefficients and low thermal conductivity.$^{23, 25, 26}$ For example, Guilmeau E. et al.$^{24}$ reported that TiS$_2$ exhibits high power factor value of 1.7 mW·m$^{-1}$·K$^{-2}$ at 325 K. Most recently, Nunna R. et al.$^{27}$ further proposed that the ZT
value increases with temperature and reaches a maximum value of 0.54 at 700 K for
Cu$_{0.05}$TiS$_{1.5}$Se$_{0.5}$, the highest value so far observed in layered titanium chalcogenides.
Naidu A. et al.$^{28}$ also interestingly found that WS$_2$ is an excellent high-temperature
thermoelectric material. The maximal $ZT$ values of 0.90 and 0.77 for $n$-type and
$p$-type WS$_2$, respectively, are obtained at 1500 K and are comparable to the best
thermoelectric materials currently used in devices.$^{29}$ Further enhancement to $ZT$ is
anticipated for these materials in future research.

SnS$_2$ and SnSe$_2$ are another interesting MX$_2$ compounds, and both crystallize in
hexagonal close-packed CdI$_2$-type layered structure, hence, it may be of interest to
study the TE properties of SnS$_2$ and SnSe$_2$. In addition, SnS$_2$ and SnSe$_2$ offer several
advantages for practical applications, such as non-toxicity, low cost. However, only
limited information is now available concerning the TE properties of SnS$_2$ and
SnSe$_2$.$^{30, 31}$ The optimal temperature and doping concentration have not been
determined experimentally and theoretically. In either case, thermal conductivity data
are lacking because of difficulties in the handling the lattice thermal conductivity. To
access the potential of SnS$_2$ and SnSe$_2$ as a thermoelectric material, in this work, we
theoretically examine the doping and temperature dependence of TE properties of
SnX$_2$ (X=S, Se) by using first-principles band structure calculations and Boltzmann
transport theory.$^{32}$ In particular, the anisotropy of transport coefficients is discussed
and the lattice thermal conductivity is evaluated using the approach developed by
Cahill.$^{33}$ Our results may serve as a guide on how to optimize the thermoelectric
properties of these compounds.
Computational detail

Density functional theory (DFT) based on the Vienna ab-initio Simulation Package (VASP)\textsuperscript{34} is used with plane wave energy up to 400 eV in the expansion of the electronic wave function. For the structure optimization and the electronic structure calculations we employ the Heyd-Scuseria-Ernzerhof (HSE03) hybrid functional.\textsuperscript{35} This methodology has been shown to provide good band structure predictions. The valence electron configurations considered in this calculation are Sn(4d\textsuperscript{10}5s\textsuperscript{2}5p\textsuperscript{2}), S(3s\textsuperscript{2}3p\textsuperscript{4}), and Se(4s\textsuperscript{2}4p\textsuperscript{4}), respectively. The lattice vectors and atomic positions are fully relaxed by minimizing the quantum mechanical stresses and forces. The convergence for energy is chosen as 10\textsuperscript{-6} eV between two steps. The structural optimization is obtained until the Hellman-Feynman forces acting on each atom are less than 0.01 eV/Å. A Monkhorst-Pack k-point mesh of 6\times6\times4 are used to sample the Brillouin zones in the structural optimization and self-consistent calculation.

Transport calculations are performed through solving the Boltzmann Transport Equations within the rigid band and constant relaxation-time (τ) approximations as implemented in BOLTZTRAP program.\textsuperscript{32} Rigid band approximation (RBA) is the assumption that the band structure of the host is unchanged by doping, only the chemical potential changes with doping concentration and of course temperature. RBA usually overestimates the Seebeck coefficient and the power factor.\textsuperscript{36} The constant relaxation-time approximation assumes τ as energy-independent. The advantage of using this approximation is that the Seebeck coefficient can be calculated without adjustable parameters. τ has a complex T dependence depending
on the scattering mechanism. Sources of scattering in semiconductors are ionized
impurities, neutral impurities, and electron-phonon interaction (acoustic phonon
scattering, optical phonon scattering, and piezoelectric scattering), etc. $\tau$ is directly
proportional to the temperature in ionized impurity scattering whereas independent of
the temperature in neutral impurity scattering. $\tau$ will decrease with temperature if the
scattering is dominated by an electron-phonon interaction (the primary scattering
mechanism in heavily doped semiconductors). In Boltzmann method, all kinds of
scattering processes can be simply introduced by relaxation time approximation. Its
prime advantage is that detailed assumptions about the nature of the scattering are not
necessary. The calculation of $\tau$ is a very difficult task. Typically, $\tau$ is treated as a
constant for simplicity and convenience.\textsuperscript{37-39} Choosing a constant for $\tau$ is an
approximation for the real scattering mechanism. This approximation might result in
the overestimations in the electrical conductivity and therefore in $ZT$ predictions. It is
difficult to reliably predict the temperature dependence of transport coefficients under
this assumption. However to obtain the electrical conductivity and $ZT$ the constant
relaxation-time approximation is more feasible. Nevertheless, this \textit{ab initio} approach
has been successfully used in rationalizing and predicting the optimal doping level of
known compounds and recently has been used to screen potential candidates for TE
materials.

A more dense $k$-point grid of $12\times12\times8$ is used for transport calculations to
guarantee convergence and to obtain accurate carrier group velocities, which are
essential for determining the transport properties. $ZT$ can be evaluated by
\[ ZT = \frac{S^2 \sigma T}{\kappa_E + \kappa_L} = \frac{S^2}{L_0 + \frac{\kappa_L}{\sigma T}} \quad (1) \]

where \( L_0 = 2.45 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2} \) is the Lorentz number. Here, \( \kappa_L \) adopted the value of the minimum lattice thermal conductivity, which can be calculated by Cahill’s model:\(^3\)

\[ \kappa_{\text{min}} = \left( \frac{\pi}{6} \right)^{1/3} \kappa_0 n^{2/3} \sum_i v_i \left( \frac{T}{\Theta} \right)^2 \frac{x^3 e^x}{(e^x - 1)^2} \int_0^{\frac{T}{\Theta}} \mathrm{d}x \quad (2) \]

where \( v, \Theta \) and \( n \) are the phonon velocity, Debye temperature and the number density of atoms, respectively. The values of \( v \) and \( \Theta \) are calculated from the phonon dispersion. This approach has been successfully applied to estimate the \( \kappa_{\text{min}} \) of several materials, such as SnSe\(^7\), SrTiO\(_3\)\(^{40}\), In\(_2\)O\(_3\)-based compounds\(^{41}\).

Phonon dispersion is calculated using the supercell (192 atoms in the SnS\(_2\) supercell and 240 atoms in the SnSe\(_2\) supercell) force constant method. The harmonic second order interatomic force constants (IFCs) were obtained within the linear response framework by employing the density functional perturbation theory (DFPT)\(^{42}\) as implemented in the VASP code. Then we could get the phonon dispersion of SnS\(_2\) and SnSe\(_2\) using the PHONOPY package\(^{43}\) based on the harmonic second order IFCs.

**Results and discussion**

**3.1 Geometrical structure**

SnS\(_2\) and SnSe\(_2\) often crystallize in different polytypes. The usual and stable polytype
is 2H, *i.e.* a hexagonal unit cell consisting of two layers.\textsuperscript{44} Therefore, type 2H was chosen to model the SnX\textsubscript{2} (X = S, Se) crystals in our calculations. It has an anisotropic structure with a trigonal space group, $P\overline{3}m1$. Within one layer, a plane of Sn atoms is sandwiched between two S/Se planes with strong covalent metal-anion bonds in the $a$-$b$ plane. The formed S(Se)-Sn-S(Se) layers are stacked by weak van der Waals interactions along the $c$ axis. Fig. 1 shows the optimized SnX\textsubscript{2} structures. In the crystal structure of SnX\textsubscript{2}, Sn atoms occupy the 1a (0 0 0) site, S atoms at 2d (0.333 0.667 0.224) site, and Se atoms at the 2d (0.333 0.667 0.234) site. The bond length of Sn-S vs. Sn-Se is calculated to be 2.58 vs. 2.73 Å, which matches the corresponding experimental value (2.57 vs. 2.69 Å)\textsuperscript{45}. Clearly, the Sn-S bond length is smaller than that of Sn-Se, as S has a smaller atomic radius. It brings about the corresponding weaker intra-layer bonding for SnSe\textsubscript{2}. As is known, weaker bonding leads to lower thermal conductivity.\textsuperscript{46} Thus, lower thermal conductivity along the $a$ axis could be anticipated for SnSe\textsubscript{2}. In addition, the optimized interlayer separations for SnS\textsubscript{2} and SnSe\textsubscript{2} are approximately identical and significantly exceeds 3 Å, suggestive of weak bonding and hence soft phonons, favorable for TE performance.
Fig. 1 Crystal structures of SnX$_2$ (space group P-3m1). (a) SnS$_2$; (b) SnSe$_2$. The unit of interatomic distance is in Å. Here, grey, yellow and green colors represent Sn, S and Se atoms, respectively.

### 3.2 Electronic structure

To study the TE properties, an accurate electronic structure is required. We calculated the band gap of SnS$_2$ and SnSe$_2$ with PBE, HSE03, and HSE06 functionals, listed in Table 1. From the PBE calculations, SnS$_2$ (SnSe$_2$) is found to have an indirect band gap of 1.55 (0.71) eV. However, the band gap calculated through the HSE03 functional is found to be 2.04 (1.09) eV, which is closer to the experimental value compared with the corresponding gap from HSE06 functional (2.53 and 1.48 eV, respectively). Hence, here onward we will discuss only the HSE03 results. The band dispersion plots of SnS$_2$ and SnSe$_2$ calculated through the HSE03 method are shown in Fig. S1. The band gap for SnSe$_2$ is smaller than that for SnS$_2$, which is consistent with our common expectation that the selenides have smaller band gaps than the
corresponding sulfides.

Table 1 Calculated band gap results of SnX\(_2\) (X = S, Se) systems using PBE, HSE03, and HSE06 methods

<table>
<thead>
<tr>
<th>System</th>
<th>PBE</th>
<th>HSE03</th>
<th>HSE06</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnS(_2)</td>
<td>1.55</td>
<td>2.04</td>
<td>2.53</td>
<td>2.07 (ref. 47)</td>
</tr>
<tr>
<td>SnSe(_2)</td>
<td>0.71</td>
<td>1.09</td>
<td>1.48</td>
<td>0.97 (ref. 47)</td>
</tr>
</tbody>
</table>

In addition, we also calculated the electron effective masses (\(m^*\)) for SnS\(_2\) and SnSe\(_2\) in two different directions of the reciprocal space by fitting the band structure around the CBM using the equation \(m^* = \hbar^2 / (d^2E/dk^2)\). In the \(G \rightarrow A\) direction (\(c\) axis), the calculated effective masses are 0.43 \(m_0\) (\(m_0\) is the electron mass) for SnS\(_2\) and 0.28 \(m_0\) for SnSe\(_2\), while in the \(G \rightarrow K\) direction (\(a\) axis), values of 0.61 \(m_0\) and 0.52 \(m_0\) were found for SnS\(_2\) and SnSe\(_2\), respectively. The electron effective mass of SnSe\(_2\) along the \(a\) axis is estimated as 0.4±0.2 \(m_0\) by Lee et al.,\(^{48}\) in agreement with our predicted value for SnSe\(_2\) in the \(a\) direction. A high effective mass translates to larger Seebeck coefficient. For both materials, the higher value for \(m^*\) in the \(G \rightarrow K\) direction compared to that in the \(G \rightarrow A\) direction indicates improved Seebeck coefficient from \(c\) to \(a\) direction. Likewise, in both directions, the Seebeck coefficient can be increased by replacing Se by S.

Since the electron states around the Fermi level have an important effect on the TE transport properties of SnS\(_2\) and SnSe\(_2\), we calculated their total and partial density of states (TDOS and PDOS) and draw them in Fig. 2. Due to the similar crystalline structure and bonding nature, the total DOS of SnS\(_2\) and SnSe\(_2\) has similar shape.
From Fig. 2(a1) and (b1), we can see that the conduction band (CB) is much delocalized than the valence band (VB) near the Fermi level, which is indicative of a higher electrical conductivity for \( n \)-type doping. Moreover, experimental studies\(^{47-50} \) revealed that both SnS\(_2\) and SnSe\(_2\) usually exhibit \( n \)-type conduction and so only \( n \)-type doping was considered in the following TE properties. From the partial DOS, it is found that for both compounds the VB from -5 eV to Fermi level is composed of p orbital of the chalcogen (S or Se), while the CB near the Fermi level is mainly dominated by Sn 5s state and chalcogen p states. This means the electrical conductivity and Seebeck coefficient for \( n \)-type are primarily determined by Sn 5s and chalcogen p electrons. Generally, large Seebeck coefficients are usually associated with a large DOS peak. As seen in Fig. 2, moving from SnS\(_2\) to SnSe\(_2\), the peaks becomes lower in the CB near Fermi level, which will make the Seebeck coefficient decrease from SnS\(_2\) to SnSe\(_2\) for \( n \)-type doping. In the CB of both materials, we also note the increase of the chalcogen p-orbital contribution from \( p_z \) to \( p_x \), which is probably related to the increase in the Seebeck coefficient from \( p_z \) to \( p_x \). In other words, \( a \) direction has a higher Seebeck coefficient than \( c \) direction for \( n \)-type doping of both materials. These observations support the above results obtained by analyzing electron effective mass. We will observe these points in the following section.
Fig. 2 Calculated total DOS and partial DOS for (a) SnS$_2$ and (b) SnSe$_2$ within the energy range -8 to 8 eV. Top of the valence band is set to zero.
3.3 Thermoelectric properties

Since, as mentioned previously, the anisotropy and anharmonicity is a significant issue for layered materials. The anisotropic transport properties of SnS$_2$ and SnSe$_2$ are calculated based on the calculated electronic structure using the Boltzmann theory. The carrier concentration greatly affects $S$ and $\sigma$, so we simulated doping using the rigid band approximation. The Seebeck coefficients along the $a$ and $c$ directions are shown in Fig. 3. Fig. 3(a) and (c) shows the anisotropy of $S$ of SnS$_2$ at different carrier concentrations and at different temperatures. Clearly, the $S$ shows a near linear decrease with increasing carrier concentration but exhibits an increasing trend with temperature. Also, the values of $S$ are very different along the $a$ and $c$ directions. The values along the $a$ direction are larger than those along the $c$ direction, which confirms the conclusion obtained from DOS and effective mass analysis. Such anisotropy is affected by temperature and carrier concentration in different ways (see Fig. 3(c)). At high carrier concentration, for example, the anisotropy at $n = 10^{20}$ cm$^{-3}$ nearly keeps unchanged with temperature. While at mid-and-low carrier concentrations, the anisotropy becomes larger and larger with rising temperature.
Fig. 3 Seebeck coefficients of SnS$_2$ and SnSe$_2$ along the $a$ ($S_a$) and $c$ ($S_c$) directions as a function of carrier concentration and temperature ranging from 300 K to 800 K.

For SnSe$_2$ (see Fig. 3(b)), due to smaller band gap, the bipolar conduction starts to play a role below $\sim 2 \times 10^{17}$ cm$^{-3}$ for 800 K and above $\sim 4 \times 10^{19}$ cm$^{-3}$ for 300 K and 400 K. However, they do not enter into the regime of probable optimal doping. Optimal doping ranges are given as $8.61 \times 10^{18} – 2.03 \times 10^{19}$ cm$^{-3}$ for $a$ direction while $1.71 \times 10^{19} – 2.47 \times 10^{19}$ cm$^{-3}$ for $c$ direction (see Fig. 7(b)). Therefore, the $ZT$ values for SnSe$_2$ will not be affected by the bipolar effect in the optimal doping range. The big difference between SnSe$_2$ and SnS$_2$ is that SnSe$_2$ shows a smaller anisotropy in the Seebeck coefficient. As seen in Fig. 3(d), at mid-and-low carrier concentration, the anisotropy almost disappears below 500 K and becomes larger above 500 K. Specially, the $S$ at $n = 10^{17}$ cm$^{-3}$ increases with temperature below 700 K and suddenly turns to
decrease at 800 K due to the bipolar effect. At high doping levels, the anisotropy of $S$
shows an overall increase with increasing temperature up to 800 K.

The calculated result $\sigma/\tau$ includes the scattering rate $\tau^{-1}$. To obtain the particular value
of $\sigma$, we used the experimental data in ref. 47 to derive the value of $\tau$. Comparing the
calculated electrical conductivities (per relaxation time) at room temperature with the
reported experimental conductivities of SnS$_2$ and SnSe$_2$ samples ($2.38 \times 10^{-3}$ and 100
$\Omega^{-1}\cdot m^{-1}$, respectively) yields relaxation times of about 1.37 and 1.28 fs, respectively,
which agree with the typical relaxation time values for semiconductors. We then
calculated $\sigma$ by $\sigma/\tau \times \tau$. For SnS$_2$, the calculated $\sigma$ is $15.33 \Omega^{-1}\cdot m^{-1}$ at 300 K and at a
carrier concentration of $3.2 \times 10^{16}$ cm$^{-3}$. Agreement between calculated value and
experiment ($16.56 \Omega^{-1}\cdot m^{-1}$)$^{52}$ is quite good. The resulting electrical conductivities
along the $a$ and $c$ directions are shown in Fig. 4. For both materials, the value of $\sigma$ is
little affected by temperature in both directions. For example, for SnS$_2$ at $n = 10^{19}$
cm$^{-3}$, the $\sigma$ along the $c$ direction reduces slightly from 493.65 to 305.30 $\Omega^{-1}\cdot m^{-1}$ for
the temperature from 300 K up to 800 K. However, the doping dependence of $\sigma$ is
more pronounced. The values of $\sigma$ in both directions increase greatly with the
increase in carrier concentration. Taking SnS$_2$ as an example, as the carrier
concentration increases from $10^{17}$ to $10^{20}$ cm$^{-3}$, the $\sigma$ at 800 K varies rapidly from
68.38 to $66.20 \times 10^{3}$ $\Omega^{-1}\cdot m^{-1}$ for $a$ direction while from $2.97$ to $2.10 \times 10^{3}$ $\Omega^{-1}\cdot m^{-1}$ for
$c$ direction. For SnS$_2$, Madelung$^{53}$ and Julier$^{51}$ also reported that the electrical
conductivities at 300 K increase from $2.38 \times 10^{-3}$ to 90 $\Omega^{-1}\cdot m^{-1}$ with carrier
concentrations from $10^{13}$ to $2 \times 10^{17}$ cm$^{-3}$. 

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Fig. 4 Electrical conductivities of SnS$_2$ and SnSe$_2$ along the $a$ ($\sigma_a$) and $c$ ($\sigma_c$) directions as a function of carrier concentration in the temperature range of 300-800 K.
Compared to the anisotropy of Seebeck coefficient, the electrical conductivity anisotropy tends to be larger. At a given temperature and carrier concentration, the value of $\sigma$ along the $a$ direction is much greater than that along the $c$ direction due to the weaker interactions between layers in the $c$ direction. For example, for SnS$_2$ at $T = 300$ K and $n = 10^{19}$ cm$^{-3}$, the $\sigma$ along the $a$ and $c$ directions is $7.62 \times 10^3$ and $4.94 \times 10^2 \Omega^{-1}\text{m}^{-1}$, respectively. Experimental measurements$^{54-56}$ also showed $a$ axis is more conducting than $c$ axis. The anisotropy ratio $\sigma_a/\sigma_c$ is found to be greater for SnS$_2$ than that for SnSe$_2$, which agrees with our results. In our case, it is found that the anisotropy ratio $\sigma_a/\sigma_c$ is 12.80 for SnS$_2$ and 6.92 for SnSe$_2$ when the carrier concentration is $10^{17}$ cm$^{-3}$ and the temperature is 300 K. This means SnS$_2$ has larger electrical conductivity anisotropy than SnSe$_2$. However, the temperature has little effect on the electrical conductivity anisotropy (see Fig. S2). For SnS$_2$, compared with SnSe$_2$, it has lower values of $\sigma$ but higher Seebeck coefficients in both directions at a given temperature and carrier concentration. The trend can be explained by the fact that SnS$_2$ has larger electron effective masses than SnSe$_2$ in both directions.

Under a given temperature difference, the ability of a material to produce useful electrical power is quantified by its power factor ($PF$): $PF = S^2 \sigma$. We have calculated this parameter as a function of the carrier concentration and temperature and plotted the results in Fig. 5. As shown in Fig. 5, for both materials, the $PF$ along the $a$ direction is much greater than that along the $c$ direction. This behavior agrees reasonably well with the magnitude of $S$ and $\sigma$ in $a$ and $c$ directions. As a consequence, the TE properties of SnX$_2$ are dominated by the $PF$ along the $a$
direction. In both directions, there is an optimal carrier concentration to yield the peak $PF$, which grows with rising temperature mainly because of larger Seebeck coefficient at higher temperature. At 800 K, this parameter along the $a$ axis reaches the values $15.50 \times 10^{-4}$ and $11.72 \times 10^{-4}$ W·m$^{-1}$·K$^{-2}$ at the carrier concentrations of $8.59 \times 10^{19}$ and $7.21 \times 10^{19}$ cm$^{-3}$ for SnS$_2$ and SnSe$_2$, respectively. Compared to typical TE material Bi$_2$Te$_3$ ($40 \times 10^{-4}$ W·m$^{-1}$·K$^{-2}$ in the $ab$ plane)\cite{12}, the power factors obtained in SnS$_2$ and SnSe$_2$ crystals are lower, but are comparable to those found in other thermoelectrics with layered structure (for example, SnSe\cite{7} and SnS\cite{8,46}). On the other hand, Fig. 5 shows that as the temperature increases, the difference of peak $PF$ values between the two directions grows.
Fig. 5 Power factors ($\sigma^2$) of SnS$_2$ and SnSe$_2$ along the $a$ ($PF_a$) and $c$ ($PF_c$) directions as a function of carrier concentration in the temperature range of 300-800 K.

The minimum lattice thermal conductivities can be evaluated using the approach developed by Cahill, as illustrated by Eqs. (2). This model assumes that the conductivity is not limited by phonon-phonon scattering but by a temperature-independent structural scattering mechanism. In this treatment, the predicted thermal conductivity shows a weak temperature-dependence. Because the structures of SnS$_2$ and SnSe$_2$ are similar to WSe$_2$, it might be more appropriate to calculate the thermal conductivity by the methods used in WSe$_2$-type systems. At present, molecular dynamics (MD) simulation and ShengBTE methods are applied to calculate the thermal conductivities of WSe$_2$-type systems.$^{28, 57, 58}$ However, the approach of MD simulation suffers from problems of low accuracy and lack of
transferability, since an appropriate potential for each compound must be developed. ShengBTE can be applied to pursue the accurate prediction of the lattice thermal conductivity without any assumption about phonon lifetimes, including the dependence on the phonon mean free path. The more accurate prediction for thermal conductivity is favorite. In our next work, we will apply the available computational code for the prediction of the lattice thermal conductivity. Nevertheless, the minimum lattice thermal conductivity is an important and useful referenced parameter for experiments even it might be not able to be fully obtained by the experiments.

The temperature-dependent of theoretically predicted minimal lattice thermal conductivity ($\kappa_{\text{min}}$) of SnS$_2$ and SnSe$_2$ is depicted in Fig. 6. For both materials, the lattice thermal conductivity is obviously anisotropic that the trend of $\kappa_{\text{min}}$ in the two directions is always in the order: $\kappa_{\text{min}}^a > \kappa_{\text{min}}^c$. Such anisotropy could be attributed to the anisotropic structures of the two materials. The acoustic modes along the $G \rightarrow A$ Brillouin zone direction ($c$ axis) are significantly softer (with lower Debye temperatures and smaller phonon velocities; see Fig. S3 and Table S1) than those along $G \rightarrow K$ Brillouin zone direction ($a$ axis). These softer modes along the $c$ axis lead to smaller lattice thermal conductivity in this direction. For both directions, SnSe$_2$ has lower values of $\kappa_{\text{min}}$ than SnS$_2$, also determined by softer acoustic modes in SnSe$_2$ than in SnS$_2$. Similar trend is also found in a comparison between SnSe and SnS. At 300 K, for SnS$_2$, the values of $\kappa_{\text{min}}$ are (in W·m$^{-1}$·K$^{-1}$) ~0.67 and ~0.47 along the $a$ and $c$ axis directions, respectively; for SnSe$_2$, the values decrease separately to 0.55 and 0.42 W·m$^{-1}$·K$^{-1}$. Unfortunately, we cannot find the corresponding
experimental data for a comparison. However, these values are comparable to the measured $\kappa_L$ in SnSe (about 0.7 W·m$^{-1}$·K$^{-1}$ at 300 K)$^7$ and even lower than that in Bi$_2$Te$_3$ (about 1.28 W·m$^{-1}$·K$^{-1}$ at 300 K)$^{59}$. For both SnS$_2$ and SnSe$_2$, the $\kappa_{\min}$ increases slowly with increasing temperature along the $a$ direction whereas almost hold the same values along the $c$ directions. Considering SnX$_2$ possesses large power factor and low thermal conductivity, SnX$_2$ may serve as a new potential candidate for TE applications.

![Graph showing calculated minimum lattice thermal conductivities for $a$ and $c$ directions in SnX$_2$ (X = S, Se) as a function of temperature ranging from 300 K to 800 K.](image)

**Fig. 6** Calculated minimum lattice thermal conductivities for $a$ and $c$ directions in SnX$_2$ (X = S, Se) as a function of temperature ranging from 300 K to 800 K.

Using the above calculated minimum lattice thermal conductivity of SnX$_2$, we were able to make an estimate of $ZT$ (see Fig. 7). Fig. 7(a) and (b) shows the
dependence of $ZT$ on the carrier concentration for SnS$_2$ and SnSe$_2$. The anisotropy of $S$, $\sigma$, $\kappa_E$ and $\kappa_L$ in SnX$_2$ crystals inevitably results in the anisotropy of $ZT$. Indeed, $ZT$ exhibits a strong anisotropy for both materials. As mentioned above, the electronic conductivity along the $a$ axis can be substantially greater than that along the $c$ axis. This is enough to compensate for a lattice thermal conductivity along the $c$ axis that is about 0.2 W·m$^{-1}$·K$^{-1}$ lower than that along the $a$ axis. It induces remarkably higher $ZT$ values in the $a$ direction. In Fig. 7(a) and (b) it is easily found that the $ZT$ value can be highly influenced by carrier concentration. The $ZT$ value first increases with the carrier concentration, reaches an optimal value, and then decreases. For SnS$_2$, the peak $ZT$ value increases from 0.19 to 0.96 along the $a$ axis while rises from 0.02 to 0.05 along the $c$ axis for temperature from 300 K up to 800 K. For SnSe$_2$, compared with SnS$_2$, the optimal $ZT$ value is slightly lower in the $a$ direction whereas slightly higher in the $c$ direction, which ranges from 0.15 to 0.88 for the former and varies from 0.04 to 0.17 for the latter in the 300-800 K temperature range. The $ZT$ values along the $c$ axis are much lower than those along the $a$ axis, in particularly for SnS$_2$. Therefore, $a$ direction of both materials is a preferred direction for TE application. In the preferred direction, the highest peak $ZT$ value is predicted to be 0.96 for SnS$_2$ and 0.88 for SnSe$_2$ when $n = 2.87 \times 10^{19}$ cm$^{-3}$ and $n = 1.94 \times 10^{19}$ cm$^{-3}$, respectively. Such doping concentration is probably experimentally controllable.
Fig. 7 (a) and (b): $ZT$ values for $a$ ($ZT_a$) and $c$ ($ZT_c$) directions in SnX$_2$ as a function of carrier concentration, (a) is for SnS$_2$ and (b) for SnSe$_2$; (c) and (d): $ZT$ values for $a$ ($ZT_a$) and $c$ ($ZT_c$) directions in SnX$_2$ as a function of temperature ranging from 300 to 800 K, (c) is for SnS$_2$ and (d) for SnSe$_2$. 
The temperature dependence of $ZT$ for SnS$_2$ and SnSe$_2$ at four different carrier concentrations i.e. $10^{17}$, $10^{18}$, $10^{19}$ and $10^{20}$ cm$^{-3}$, respectively, is plotted in Fig. 7(c) and (d). As shown in Fig. 7(c) and (d), at the same carrier concentration, the $ZT$ values for both materials in both directions exhibit a linear climb as temperature increases in the 300-800 K temperature range. For example, the $ZT$ value of SnS$_2$ at $n = 10^{19}$ cm$^{-3}$ increases from 0.18 for 300 K to 0.79 for 800 K. Also, its anisotropy becomes stronger and stronger with temperature. Most interestingly, as temperature increases, the $ZT$ and its anisotropy increases at a faster rate at mid carrier concentration and a slower rate at high carrier concentration. For instance, the $ZT$ value at $n = 10^{19}$ cm$^{-3}$ increases faster with temperature than that at $n = 10^{20}$ cm$^{-3}$. All above-mentioned results undoubtedly reveal that the $ZT$ value for SnX$_2$ compound can be improved by tuning temperature and carrier concentration.

The predicted $ZT$ values in SnX$_2$ are comparable to that of the commercial TE material Bi$_2$Te$_3$ (about 0.8). Compared with reported MX$_2$ compounds, the $ZT$ value in SnX$_2$ is remarkably lower than those found in $n$-type 1TL-MoS$_2$ and 2TL-WSe$_2$ (about 1.6 and 2.1, respectively$^{60}$) but higher than other MX$_2$ compounds such as TiS$_2$, TiSe$_2$, and ZrSe$_2$. For example, The $ZT$ reaches a maximum value of 0.54 at 700 K for Cu$_{0.05}$TiS$_{1.5}$Se$_{0.5}$, the highest value so far observed in layered titanium chalcogenides.$^{27}$ However, the best $ZT$ value is only 0.25 for Li-intercalated ZrSe$_2$.61

**Conclusions**

In conclusion, we have systematically investigated the crystal structure, electronic structure and anisotropic thermoelectric properties of SnX$_2$ ($X = S$ or Se) via
first-principles method. The results reveal that the anisotropic structure of layered SnX$_2$ compound brings about the anisotropy of transport coefficients, which behaves in different ways. For SnS$_2$, the anisotropy of Seebeck coefficient is little affected by temperature at high carrier concentration whereas becomes larger and larger at mid-and-low carrier concentrations. For SnSe$_2$, differently, at high doping levels, the Seebeck coefficient anisotropy shows an overall increase with increasing temperature up to 800 K. At mid-and-low carrier concentration, it almost disappears below 500 K and tends to be higher above 500 K. Our calculations also suggest the temperature has little effect on the electrical conductivity and hence its anisotropy. The remarkably greater electrical conductivity in the $a$ direction along with the corresponding higher Seebeck coefficient induces larger power factor in this direction. In the $a$ direction, the peak $PF$ can reach $15.50 \times 10^{-4}$ and $11.72 \times 10^{-4}$ W m$^{-1}$ K$^{-2}$ for SnS$_2$ and SnSe$_2$, respectively. The values are almost equal to those found in SnSe and SnS. At 300 K, the predicted minimum lattice thermal conductivities along the $a$ axis are (in W m$^{-1}$ K$^{-1}$) about 0.67 and 0.55 for SnS$_2$ and SnSe$_2$, respectively. Moreover, for both materials, the parameter only increases slowly with temperature. The large peak $PF$ and low lattice thermal conductivity are favorable for producing good thermoelectric performance along the $a$ direction. In this direction, SnSe$_2$ can show a peak $ZT$ value of 0.88 at 800 K when the carrier concentration reaches $1.94 \times 10^{19}$ cm$^{-3}$. For SnS$_2$, an even higher $ZT$ value of 0.96 can be obtained at the same temperature when the carrier concentration approaches $2.87 \times 10^{19}$ cm$^{-3}$. The values of this parameter in SnX$_2$ (X = S, Se) are comparable to the typical $ZT$ values 0.8 of Bi$_2$Te$_3$. Therefore, these layered
metal dichalcogenides would have promising prospects for thermoelectric applications. Further deeper theoretical and experimental studies are required to explore this class of materials.

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