Monolayer SnP$_3$: an excellent p-type thermoelectric material†

Xue-Liang Zhu,$^{a,b,c}$ Peng-Fei Liu,$^{d}$ Junrong Zhang,$^{c,d}$ Ping Zhang,$^e$ Wu-Xing Zhou,$^{a,f}$ Guofeng Xie$^{d}$ $^{*}$ and Bao-Tian Wang$^{d}$ $^{*}$

Monolayer SnP$_3$ is a novel two-dimensional (2D) semiconductor material with high carrier mobility and large optical absorption coefficient, implying its potential applications in the photovoltaic and thermoelectric (TE) fields. Herein, we report on the TE properties of monolayer SnP$_3$ utilizing first principles density functional theory (DFT) together with semiclassical Boltzmann transport theory. Results indicate that it exhibits a low lattice thermal conductivity of $\sim$4.97 W m$^{-1}$ K$^{-1}$ at room temperature, mainly originating from its small average acoustic group velocity ($\sim$1.18 km s$^{-1}$), large Grüneisen parameters ($\sim$7.09), strong dipole–dipole interactions, and strong phonon–phonon scattering. A large in-plane charge transfer is observed, which results in a non-ignorable bipolar effect on the lattice thermal conductivity. The exhibited mixed mode between in-plane and out-of-plane vibrations enhances the complexity of the phonon phase space, which enhances the possibility of phonon scattering processes and results in suppression of thermal conductivity. A highly twofold degeneracy appearing at the K point gives a high Seebeck coefficient. Our calculated figure of merit (ZT) for optimal p-type doping at 500 K can approach 3.46 along the armchair direction, which is better than a theoretical value of 1.94 reported in the well-known TE material SnSe. Our studies here shed light on monolayer SnP$_3$ in use as a TE material and supply insights to further optimize the TE properties in similar systems.

1. Introduction

Along with the development of human society, a huge demand in energy has followed. Thus, techniques and materials in relation to producing and converting energy are important. With the depletion of fossil energy resources, which give rise to many problems such as air pollution and the greenhouse effect, exploiting renewable energy resources as well as related materials is urgently in demand. In particular, TE materials that could directly and reversibly convert waste heat and electrical power have attracted much attention.$^{1,2}$ Generally, the conversion efficiency of a TE material can be well quantified by ZT$^3$

$$ZT = \frac{S^2\sigma T}{\kappa},$$

where $S$, $T$, $\sigma$, and $\kappa$ are the Seebeck coefficient, absolute temperature, electric conductivity, and total thermal conductivity, respectively. The total thermal conductivity is the sum of the lattice thermal conductivity $\kappa_l$, unipolar electronic thermal conductivity $\kappa_e$ and the bipolar thermal conductivity $\kappa_b$. For commercial applications of a TE material, its ZT value should be greater than 1.0. Normally, a good TE material should exhibit both low thermal conductivity and a high Seebeck coefficient.$^4$ Although it is very difficult to regulate the transport coefficients independently because of their strong interaction, TE performance has been improved time and time again by new concepts or mechanisms. Several common approaches to enhance ZT are mainly devoted to optimizing the electrical transport property by band structure engineering,$^5,6$ and/or suppressing the material’s heat conductivity ability via low-dimensional technologies$^7$–$^9$ and phononic crystal patterning.$^{10,11}$

Since the experimental acquisition of graphene by the mechanical cleavage method in 2004,$^{12}$ 2D materials have

---

$^a$School of Materials Science and Engineering, Hunan University of Science and Technology, 411201 Xiangtan, China. E-mail: gfxie@xtu.edu.cn
$^b$School of Physics and Optoelectronics, Xiangtan University, Hunan 411105, P. R. China
$^c$Institute of High Energy Physics, Chinese Academy of Sciences (CAS), Beijing 100049, China. E-mail: wangbt@ihep.ac.cn
$^d$Dongguan Neutron Science Center, Dongguan 523803, China
$^e$Institute of Applied Physics and Computational Mathematics, Beijing 100088, China
$^f$Hunan Provincial Key Lab of Advanced Materials for New Energy Storage and Conversion, 411201 Xiangtan, China

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9nr04726c
become the hottest topic in the scientific community due to their wonderful optical, thermal, electronic, and mechanical properties. Various 2D materials, such as silicene, phosphorene, borophene, and a series of layered transition metal dichalcogenides, have been predicted theoretically and/or synthesized experimentally. Monolayer semi-conducting materials with a narrow band gap have been systematically studied in recent years due to their favourable combination of electrical and thermal transport properties, which can lead to a significantly large figure-of-merit. For example, by employing first-principles methods Huang et al. found that the unique crystal structure and electronic properties of Mg$_2$Sb$_2$ monolayer can result in a low lattice thermal conductivity and high power factor, and consequently a high $ZT$ ($>2$ at 600 K) for the n-type sample.

Very recently, a 2D layered material, SnP$_3$, which can be extracted from its bulk structure by using mechanical exfoliation approaches, has been theoretically proposed by Sun et al. Note that the layered bulk SnP$_3$ has been synthesized since 1970 experimentally and exhibits metallic properties. It is reported that the monolayer SnP$_3$ possesses an indirect band gap ($\sim$0.82 eV) with high electron mobility of 228 cm$^2$ V$^{-1}$ s$^{-1}$. Meanwhile, its excellent electrical properties, large optical absorption coefficient ($\sim$10$^6$ cm$^{-1}$) and tunable band gap offer diverse perspectives for applications in Na-ion batteries, nanophotonics, and photovoltaic solar cells. Based on these intrinsic properties, it probably has a good TE performance. In this paper, we systematically study the TE properties of monolayer SnP$_3$ by using first-principles calculations and a Boltzmann transport approach. We find that it shows a good combination of electrical and thermal transport properties. Detailed analyses of the phonon spectra, lattice vibration mode, Born effective charge, phonon velocity, and Grüneisen parameters are provided to explain its good macroscopic properties. The maximum $ZT$ value of 3.46 can be achieved by the optimal p-type doping at 500 K. These results indicate that SnP$_3$ exhibits an extraordinary TE response and could be an ideal material for TE applications.

2. Computational methods

In this paper, first-principles calculations were carried out based on DFT as implemented in the Vienna $ab$ initio simulation package (VASP). The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form for the exchange–correlation functional was used. The valence electrons included Sn: 5s$^2$5p$^2$ and P: 5s$^2$5p$^3$. The cutoff energy of the plane wave was set as 500 eV on a $7 \times 7 \times 1$ Monkhorst–Pack $k$-mesh. To avoid interlayer interactions, the length of the unit cell of 20 Å was used along the $z$ direction. The van der Waals (vdW) interactions were corrected by using the DFT approach. The geometric structure was fully relaxed until the residual forces on atoms were less than 0.01 eV Å$^{-1}$. The criterion of convergence for total energy was set as $10^{-6}$ eV Å$^{-1}$. To obtain a more accurate band gap, the Heyd–Scuseria–Ernzerhof (HSE06) screened hybrid functional was employed.

The phonon transport properties were evaluated by the Boltzmann transport equation as implemented in ShengBTE code. The harmonic second-order interaction force constants (2$^{nd}$ IFCs) were obtained by the VASP and Phonopy packages using a $3 \times 3 \times 1$ supercell with a $3 \times 3 \times 1$ k-mesh. The anharmonic third-order IFCs (3$^{rd}$ IFCs) were obtained using the same supercells with the finite-difference method. Interactions including the sixth-nearest-neighbor atoms were considered for the 3$^{rd}$ IFCs. Here, the convergence of the $k_i$ with respect to the $k$-grids was carefully tested. A dense $35 \times 35 \times 1$ k-mesh was used for the calculation of the lattice thermal conductivity (see Fig. S1, ESI†).

On the basis of Boltzmann transport theory and the rigid band approach, the electronic transport properties were acquired, implemented in the BoltzTraP code. The constant relaxation time does not vary strongly within the energy scale of $k_BT$. This method has accurately predicted TE properties of many materials. In order to obtain an accurate Fourier interpolation of the Kohn–Sham eigenvalues, a dense $45 \times 45 \times 1$ k-mesh was used in the Brillouin zone (BZ).

3. Results and discussion

3.1. Atomic and electronic structures

Monolayer SnP$_3$ crystallizes in a hexagonal lattice with space group $P\bar{3}m1$ (164) as shown in Fig. 1. The optimized lattice parameter $a$ equals 7.37 Å, which is consistent with the previous report. This structure has a puckered configuration along the zigzag direction, analogous to that of blue phosphorene. Interestingly, it looks like a graphene type honeycomb from the top view. Compared with bulk SnP$_3$, the plicated configuration of monolayer SnP$_3$ is more conspicuous, resulting in strong lattice vibrations.

In Fig. 1(d), we present the electronic band structures obtained from the PBE as well as the HSE06 hybrid functional potentials. It can be seen that the two approaches exhibit analogous band structures. Our calculations show that monolayer SnP$_3$ is a semiconductor with the valence band maximum (VBM) and conduction band minimum (CBM) locating at the K and $\Gamma$ points, respectively. Based on the PBE functional, the calculated band gap is 0.53 eV. The more accurate band gap of 0.82 eV obtained from HSE06 is between that of the monolayer GeP$_3$ (0.55 eV) and InP$_3$ (1.14 eV). A twofold degeneracy could be observed at the K point. This kind of band degeneracy has been verified to be critical for achieving high $ZT$ and can be realized through proper band engineering. Such intrinsic twofold degeneracy mainly appears in the valence band (VB) along the $\Gamma$–K direction (zigzag) and primarily originates from the p-orbitals. This gives rise to outstanding p-type electronic properties along the zigzag direction.
Interestingly, this degenerated electronic state is relatively flat at the VB edge, which is beneficial for good Seebeck coefficients and has been verified in many materials.\(^{50}\) Several sharp peaks in the electronic density of states (DOSs) are observed at the VB, a signal of a dramatic increase in Seebeck coefficients. Thus, an intrinsic VB degeneracy and a peaky DOS appear together in the monolayer SnP\(_3\). These features are good electronic characteristics for high-performance TE devices.

Based on DFT calculations, the Born effective charge and dielectric constant could be obtained, as shown in Table 1. It is noted that the dielectric constant of in-plane (xz and yz direction) is much higher than that of out-of-plane (zz direction), which is a characteristic behavior for all 2D layered materials. The calculated Born effective charge is \(Z_{\text{Sn,xx}}^* = Z_{\text{Sn,yy}}^* = 2.27\) and \(Z_{\text{Sn,zz}}^* = 0.37\). We find that the charge transfer in the xz and yz directions is 6 times larger than that along the zz direction, which indicates that the dipole–dipole interactions have marked anisotropy in the in-plane and out-of-plane directions. Here, we present the corresponding parameters of MoS\(_2\).\(^{51,52}\) The dielectric constants of MoS\(_2\) are slightly higher than that of SnP\(_3\) in the in-plane direction, while the dielectric constants are almost equal along the zz direction. Additionally, we can also see clearly that the Born effective charge of SnP\(_3\) is much larger than that of MoS\(_2\), which implies that SnP\(_3\) has a stronger dipole–dipole interaction than MoS\(_2\). A recent report indicates that the strong dipole–dipole interaction is beneficial to the stability of acoustic vibrations and leads to the low thermal conductivity.\(^{53}\)

### 3.2. Electrical transport properties

The electronic properties can be characterized on the basis of carrier mobilities for monolayer SnP\(_3\), along both the armchair and zigzag directions. We calculate them using the deformation potential (DP) theory.\(^{53}\) The formula of carrier mobility in 2D systems can be written as follows:\(^{54,55}\)

\[
\mu_{\text{2D}} = \frac{e\hbar C^{\text{2D}}}{k_B T m^* E_1^2},
\]

where \(m^*\), \(m^*_d\), \(k_B\), \(E_1\) and \(C^{\text{2D}}\) are the effective mass, average effective mass \(m^*_d = \sqrt{m^*_x m^*_y}\), \(x\) and \(y\) are armchair and zigzag directions, the Boltzmann constant, the DP constant and the 2D elastic constants, respectively. The calculated effective mass, carrier mobility and scattering time \(\tau = \mu n_0/e\) are shown in Table 2. Clearly, the mobilities of the electrons are highly isotropic, while the mobilities of the holes are strongly anisotropic, agreeing with the previous theoretical report.\(^{29}\) Noticeably, it shows a high hole mobility (703.47 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) along the armchair direction at room temperature, which is much higher than that of MoS\(_2\) (~200.52 cm\(^2\) V\(^{-1}\) s\(^{-1}\)).\(^{55}\) The high mobility in monolayer SnP\(_3\) is associated with the ideal band gap, which is beneficial to its electrical transport.

The Seebeck coefficients \(S\), electrical conductivity \(\sigma\), and electronic thermal conductivity \(\kappa\) are indispensable for evaluating the TE performance of materials. Here, using the Boltzmann transport theory based on the rigid band approach, we systematically research these electronic transport coefficients. The negative and positive chemical potentials \(\mu\) correspond to p- and n-type doping, respectively. The transport coefficients as functions of \(T\) and \(\mu\) can be defined by\(^{41}\)

\[
S_{\text{eff}}(T, \mu) = \frac{1}{eTV}\sigma_{\text{eff}}(T, \mu) \int \Sigma_{\text{eff}}(\epsilon)(\epsilon - \mu) \left[ -\frac{\partial f_{\text{B}}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon, \quad (3)
\]

\[
\sigma_{\text{eff}}(T, \mu) = \frac{1}{V} \int \Sigma_{\text{eff}}(\epsilon) \left[ -\frac{\partial f_{\text{B}}(T, \epsilon)}{\partial \epsilon} \right] d\epsilon, \quad (4)
\]

### Table 2: DP constant \(E_1\), elastic constant \(C^{\text{2D}}\), effective mass \(m^*\), carrier mobility \(\mu\), and scattering time \(\tau\) for electrons and holes along the zigzag and armchair directions in monolayer SnP\(_3\) at 300 K

<table>
<thead>
<tr>
<th>Direction</th>
<th>Carrier type</th>
<th>(E_1) (eV)</th>
<th>(C^{\text{2D}}) (N m(^{-1}))</th>
<th>(m^*) (m(_0))</th>
<th>(\mu) (cm(^2) V(^{-1}) s(^{-1}))</th>
<th>(\tau) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zigzag</td>
<td>Electron</td>
<td>1.87</td>
<td>31.72</td>
<td>0.98</td>
<td>201.67</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Hole</td>
<td>1.08</td>
<td>31.72</td>
<td>1.67</td>
<td>302.73</td>
<td>0.28</td>
</tr>
<tr>
<td>Armchair</td>
<td>Electron</td>
<td>1.81</td>
<td>31.16</td>
<td>0.97</td>
<td>215.85</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Hole</td>
<td>1.02</td>
<td>31.16</td>
<td>0.79</td>
<td>703.47</td>
<td>0.31</td>
</tr>
</tbody>
</table>
where \( \alpha \) and \( \beta \) are Cartesian indices, \( \Sigma_{\alpha\beta}(\varepsilon) \) is the transport distribution function, and \( V \) is the volume of the unit cell. As shown in Fig. 1(b), the distance between the top-Sn and bottom-Sn of monolayer SnP\(_3\) is 2.82 Å, and the van der Waals radius of Sn is 2.25 Å.\(^{56}\) Therefore in our calculations the effective thickness of monolayer SnP\(_3\), \( h_{\text{eff}} = 2.25 \times 2 + 2.82 = 7.32 \) Å is chosen to convert the conductance of monolayer SnP\(_3\) to conductivity. It should be pointed out that the results of the thermoelectric figure of merit \( ZT \) is independent of the choice of \( h_{\text{eff}} \) because we use the same effective thickness for both electrical and phonon transport property calculations. As shown in Fig. 2, the monolayer SnP\(_3\) exhibits relatively large values of the Seebeck coefficients. Obviously, the Seebeck coefficient for p-type doping is visibly higher than that of the n-type due to the larger \( \mu \) and degenerate VBs. At room temperature, the maximum Seebeck coefficients along the armchair and zigzag directions can reach to 907 and 900 \( \mu V \) K\(^{-1}\), respectively. The temperature-dependent decreasing behavior of the Seebeck coefficients is slowing down with increasing temperature. This phenomenon is typical for TE materials. At low chemical potentials, we can see that the Seebeck coefficients appear as peaks due to the sharp energy dependence of

![Fig. 2](image-url)
the total DOS, i.e., large $\frac{dn(\varepsilon)}{d\varepsilon}$, as shown in Fig. 1. Actually, the Seebeck coefficients and the electronic DOS have the following Mott relation\textsuperscript{57}

$$S = \frac{e^2 k_B T}{3e} \left( \frac{1}{n} \frac{dn(\varepsilon)}{d\varepsilon} + \frac{1}{\mu} \frac{dn(\varepsilon)}{d\varepsilon} \right)_{\varepsilon = \mu}. \tag{5}$$

The formula implies that the Seebeck coefficient can be further improved by regulating the carrier concentration.

Fig. 2(c) and (d) show the electrical conductivity $\sigma/\tau$ as a function of chemical potential. One can see that the $\sigma/\tau$ of monolayer SnP\textsubscript{3} exhibits an evidently anisotropic behavior. The $\sigma/\tau$ along the zigzag direction is obviously larger than that along the armchair direction. In addition, we can also find that the p-type doping has larger $\sigma/\tau$ than that of the n-type ones. Meanwhile, the slopes of the $\sigma/\tau$ around the VBM and CBM are flattened with increasing temperature because the electrons obey the Fermi–Dirac distribution. As shown in Fig. 2(e) and (f), the $\kappa_e$ of monolayer SnP\textsubscript{3} can be defined by solving the Wiedemann–Franz law\textsuperscript{58}

$$\kappa_e = L_0 T, \tag{6}$$

where $L$ is the Lorenz number. To provide accurate calculation of the TE performance, here we use electron transport modeling, and calculate the Lorenz numbers by $L = 1.5 + \exp\left(-\frac{|S|}{116}\right)$\textsuperscript{59,60} based on the Seebeck coefficients.

The Lorenz numbers are presented in Fig. S2.\textsuperscript{†} Similar to the $\sigma/\tau$, the $\kappa_e/\tau$ is highly anisotropic as well. The large electrical transport coefficients along the zigzag direction may lead to high TE values along it. Based on the Seebeck coefficients and the electrical conductivity, we calculate the power factor with respect to the scattering time as shown in Fig. 2(g) and (h). No matter what kinds of directions, the $S^2\sigma\tau$ of the p-type is always higher than that of the n-type, which implies it can be categorized as a p-type TE material.

Based on the Boltzmann transport equation, the calculated Seebeck coefficients and electrical conductivities are the sum of the contributions from both the majority and minority carriers, which already include the bipolar effect.\textsuperscript{61} However, the bipolar part of the thermal conductivity needs to be additively considered in the case of a small band gap and high temperature,\textsuperscript{62} which is given by $\kappa_b = \sigma_p\sigma_n(S_p - S_n)^2 T (\sigma_p + \sigma_n)$. In the next section, we discuss the bipolar effect on the thermal conductivity and TE performance of monolayer SnP\textsubscript{3}.

### 3.3. Phonon transport properties

The phonon dispersions as well as the partial atomic phonon density of states (PhDOS) of monolayer SnP\textsubscript{3} are shown in Fig. 3. The phonon dispersion curves with their color weighted by the contributions of Sn and P atoms are calculated to guarantee the optimized structure locating at the minimum on the potential energy surface. No imaginary frequency is observed, indicating the dynamical stability of monolayer SnP\textsubscript{3} at ambient pressure. The maximum frequency of the optical mode can approach 13.08 THz, comparable to those of MoS\textsubscript{2} (14.83 THz)\textsuperscript{63} and phosphorene (13.35 THz).\textsuperscript{64} Similar to the well-known TE material SnSe,\textsuperscript{65} the lowest optical mode frequency of monolayer SnP\textsubscript{3} is 1.91 THz, which is a sign for good TE performance. In the low-frequency region, we find that the partial PhDOSs of Sn and P atoms are evenly distributed, which further proves its stable nature. Note that the relatively flat phonon dispersion curves and spiculate PhDOS are responsible for small phonon velocities and low thermal conductivities.

The vibration modes can be carefully analyzed by investigating the atomic motions for each mode of the phonon spectrum, especially near/at the high symmetry points. Here, some typical lattice vibrations of monolayer SnP\textsubscript{3} near/at the $\Gamma$ point are presented in Fig. 3(c). One can see that the vibrations of the acoustic phonon branches are strictly along the in-plane (TA and LA) or out-of-plane (ZA), which belong to an intrinsic

---

**Fig. 3** (a) Phonon dispersion and (b) total and partial phonon density of states (PhDOS) of monolayer SnP\textsubscript{3}. (c) The corresponding vibrational modes of the acoustic phonon branches (ZA, TA, and LA) and the lowest optical branch (Opt\textsubscript{1}) near and at the $\Gamma$ point.
vibration property. Interestingly, disordered off phase phonon vibrations are observed for the lowest optical branch. One of the Sn atoms moves in-plane in the opposite direction to the other, while the P atoms vibrate out-of-plane. These in-plane and out-of-plane mixed mode vibrations will significantly suppress phonon thermal transport via phonon–phonon scattering and give rise to the low thermal conductivity.\textsuperscript{66}

The expression for the thermal conductivity of a phonon in the i direction, which is obtained by solving the Boltzmann transport equation under the relaxation time, is given as:\textsuperscript{67}

\[ \kappa_{ii} = \sum_{\lambda} \sum_{q} \epsilon_{\text{ph}} v_{g,i}^2(q,\lambda) \tau(q,\lambda). \] (7)

The summation is over all phonon modes with wave vector \( q \) and dispersion branch \( \lambda \), \( \epsilon_{\text{ph}} \) is the mode volumetric specific heat, \( v_{g,i}(q,\lambda) \) is the i component of the group velocity vector, and \( \tau(q,\lambda) \) is the relaxation time of the phonon mode with wave vector \( q \) and dispersion branch \( \lambda \). The \( \kappa_{i} \) values of monolayer SnP\(_3\), at temperatures from 300 to 800 K, are presented in Fig. 4(a). Obviously, the \( \kappa_{i} \) exhibits temperature dependence and is proportional to \( 1/T \), due to inherent enhancement in phonon–phonon scattering with respect to the temperature. This is a common behavior demonstrated in some classical TE materials.\textsuperscript{68–70} It is demonstrated in the inset of Fig. 4(a) that the bipolar thermal conductivity increases exponentially with increasing temperature. The values of bipolar thermal conductivity \( \kappa_{b} \) reach \( \sim 0.1 \text{ W m}^{-1} \text{ K}^{-1} \) at 700 K, which are clearly smaller than the values of lattice thermal conductivity \( \sim 2 \text{ W m}^{-1} \text{ K}^{-1} \). Therefore, the influence of bipolar thermal conductivity on the thermoelectric performance is non-negligible in the temperature range concerned \((300 \leq T \leq 700 \text{ K})\). However, at higher temperature \((T > 700 \text{ K})\), because the bipolar thermal conductivity increases sharply with increasing temperature, and the lattice thermal conductivity obeys \( T^{-1} \), the effect of bipolar thermal conductivity becomes non-negligible. Unlike its electrical transport properties, the \( \kappa_{i} \) of monolayer SnP\(_3\) exhibits weak anisotropy. As shown in Fig. 4(a), the \( \kappa_{i} \) values at room temperature are calculated to be 4.97 and 5.41 W m\(^{-1}\) K\(^{-1}\) along the armchair and zigzag directions, which are much lower than that of stanene (11.9 W m\(^{-1}\)).

![Fig. 4](image)

Fig. 4  (a) Calculated lattice thermal conductivity with respect to temperature for monolayer SnP\(_3\). (b) Phonon group velocity, (c) Grüneisen parameters, and (d) phonon relaxation time with respect to frequency for monolayer SnP\(_3\). The inset of (a) is the bipolar thermal conductivity. The insets of (b) and (c) are the phonon group velocity and Grüneisen parameters of the three acoustic modes along the \( \Gamma \rightarrow M \rightarrow K \rightarrow \Gamma \) high-symmetry lines. The inset of (d) is the total three phonon scattering phase space.
K$^{-1}$)\(^7\) and phosphorene (78 W m$^{-1}$ K$^{-1}$).\(^2\) Such low $\kappa_l$ implies that it might be a promising candidate for TE applications.

The phonon velocity is a closely related physical parameter for the thermal transportation. Using our calculated phonon dispersion, it can be calculated by

$$v_{\lambda, q} = \frac{\partial \omega_{\lambda, q}}{\partial q},$$  

where $\omega_{\lambda, q}$ is the phonon frequency, and is plotted in Fig. 4(b). We find that the phonon velocities for TA and LA branches at the $\Gamma$ point are 2.53, and 4.04 km s$^{-1}$, respectively. Compared with the bulk phosphorene,\(^6\) monolayer SnP$_3$ possesses lower phonon group velocities, due to the flat phonon dispersions and low cutoff frequency. Additionally, it is evident that the group velocities have small differences along the $\Gamma$–M (armchair) and $\Gamma$–K (zigzag) high-symmetry directions, shown in the inset in Fig. 4(b), further demonstrating the weak anisotropy of the $\kappa_l$. To obtain more insights for the phonon transport properties, the Grüneisen parameters $\gamma$ and phonon relaxation time of each phonon branch are introduced, as shown in Fig. 4(c) and (d). The $\gamma$ can qualitatively analyze the anharmonic interactions. It can be obtained according to

$$\gamma_{\lambda, q} = -\frac{V}{\omega_{\lambda, q}} \frac{\partial \omega_{\lambda, q}}{\partial V}.$$  

Generally, large $|\gamma|$ indicates that it has a strong phonon–phonon anharmonic scattering\(^7\) and is responsible for low $\kappa_l$, especially under high temperature. Obviously, a large $\gamma$ of about $-7$ for ZA can be observed, implying strong anharmonicity. The large $\gamma$ mainly exists in the low-frequency region, which greatly suppresses the thermal transport and leads to low $\kappa_l$. In general, for materials containing lone-pair electrons, the nonbonding electrons will interact with the valence electrons of the adjacent neighboring atoms, causing increased anharmonicity at limited temperature. This is the common origin for high Grüneisen parameters.\(^7\)\(^4\),\(^7\)\(^5\) The negative values of the $\gamma$ indicate that this material may have the property of negative thermal expansion. The phonon relaxation time can be acquired by the summation of various scattering processes.\(^7\)\(^6\) From Fig. 4(d), we find that the phonon relaxation

---

**Fig. 5** $ZT$ with respect to chemical potential and carrier concentration for monolayer SnP$_3$ along the (a) and (c) armchair and (b) and (d) zigzag directions.
time of the LA mode is the longest, then the TA and ZA modes, and then the optical modes. Compared with the bulk phosphorene and stanene, monolayer SnP₃ exhibits a shorter phonon relaxation time, which is also a significant driven force for its low κₜ. The three phonon scattering phase space (P₃) can further provide insight into the phonon relaxation time and is shown in the inset of Fig. 4(d). We can see clearly that the monolayer SnP₃ has a larger P₃ in the whole frequency region than that of the bulk phosphorene.⁷⁷ This fact indicates that it possesses a large P₃ allowing phonon–phonon scattering and will hinder the thermal transport.

3.4. Thermoelectric figure of merit

By combining the phonon and electron transport coefficients, we calculate the ZT of monolayer SnP₃ and plot it in Fig. 5. The electronic scattering time τ is obtained by the DP theory as shown in Table 2. Similar to SnSe₂,⁷⁸ an anisotropic TE response is observed in monolayer SnP₃. One can see that the ZT of the p-type doping is obviously superior to that of the n-type doping, which can be attributed to the difference in the carrier mobility in electrons and holes. No matter what type of doping, the ZT of monolayer SnP₃ along the zigzag direction is always larger than that along the armchair direction, which originates mainly from the different electronic relaxation times. We find that the thermal stability of monolayer SnP₃ can be retained at 700 K by performing ab initio molecular dynamic (AIMD) simulations (see Fig. S3, ESI†). Therefore, we only consider the value of ZT below 700 K. As shown in Fig. 5, the ZT at 500 K can approach 3.46 and 2.97 along the armchair and zigzag directions, respectively. Unlike the isotopic advantages of monolayer SnP₃ for converting heat energy with high efficiency at moderate temperatures ranging from 300 K to 500 K.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The calculations were performed at the Supercomputer Centre in the China Spallation Neutron Source. This work was financially supported by National Natural Science Foundation of China (NSFC) (Grant No. 11874145) and the PhD Start-up Fund of National Science Foundation of Guangdong Province, China, (No. 2018A0303100013).

References