# Supplementary information for "First-principles study on bilayer $SnP_3$ as a promising thermoelectric material"

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## **Section A:** Structural relaxation

According to the experimentally reported bulk structure of $SnP_3$[1], the crystal structure of bilayer $SnP_3$ is formed by stacking monolayers with the same sequence as the bulk $SnP_3$. Besides, a vacuum of 15 Å along the direction perpendicular to the plane is added to avoid interlayer interactions. We have provided the POSCAR file for bilayer $SnP_3$ in Table S1. And the in-plane lattice parameters, bond lengths and bond angles for the bilayer structure of $SnP_3$ compared with other reported results[2,3] are also shown in Table S2.

**Table S1.** POSCAR file for bilayer $SnP_3$ within PBE.

| | | |
|---|---|---|
| Bilayer $SnP_3$ | | |
| 1.00000000000000 | | |
| 7.4928002356999999 | 0.0000000000000000 | 0.0000000000000000 |
| -3.7464001178999999 | 6.4889553496000003 | 0.0000000000000000 |
| 0.0000000000000000 | 0.0000000000000000 | 25.1947002411000014 |
| Sn P | | |
| 4 12 | | |
| Direct | | |
| 0.3333340378201405 | 0.6666659911139337 | 0.5962731254556956 |
| 0.3333335719926248 | 0.6666664569414494 | 0.3947916345191211 |
| 0.0000002442793311 | -0.0000002442793311 | 0.5336783647504029 |
| 0.6666670327095947 | 0.3333330594678569 | 0.4573834525228213 |
| 0.7036700238728139 | 0.8518347278968561 | 0.4473065954476734 |
| 0.1481653850398975 | 0.8518345887314699 | 0.4473064010083572 |
| 0.1481652582200341 | 0.2963299745968899 | 0.4473065954476734 |
| 0.9629977031533816 | 0.4814979234708353 | 0.5437581703256403 |
| 0.5185024213025320 | 0.4814975893665447 | 0.5437581508961021 |
| 0.5185020673337262 | 0.0370022676592781 | 0.5437581703256403 |
| 0.3611558230697992 | 0.1805768796831098 | 0.5869021724370207 |
| 0.8194229101684515 | 0.1805770810808879 | 0.5869022344936056 |
| 0.8194230986555182 | 0.6388441742493373 | 0.5869021724370207 |
| 0.3055072929715626 | 0.1527534581127887 | 0.4041609067526607 |
| 0.8472465871337612 | 0.1527534503067388 | 0.4041610490461744 |
| 0.8472465534237467 | 0.6944927245510167 | 0.4041609067526607 |

**Table S2.** Comparison of in-plane lattice parameters, bond lengths, and bond angles between bilayer and bulk $SnP_3$.

| | Lattice parameter (Å) | $Bond_{Sn-P}$ (Å) | $Bond_{P-P}$ (Å) | $Angle_{P-Sn-P}$ (degree) | $Angle_{P-P-P}$ (degree) |
|---|---|---|---|---|---|
| Bulk $SnP_3$ (exp.)[2] | 7.38 | 2.66 | 2.22 | 97.30 | 99.05 |
| Bilayer $SnP_3$[3] | 7.49 | 2.72 | 2.26 | 94.25 | 98.43 |
| Bilayer $SnP_3$ | 7.49 | 2.74 | 2.24 | 97.47 | 98.33 |

As shown in Tables S1 and S2, we can see that our calculated bilayer $SnP_3$ structure exhibits almost the same lattice parameter, bond length, and bond angles with the previously reported work[3]. And the dynamical stability of the bilayer $SnP_3$ is further checked by our calculated phonon dispersion without no imaginary frequency shown in our manuscript.

## **Section B:** Electronic transport coefficients with respect to chemical potential

The temperature dependence of the chemical potential is considered by the formula: $dF=-pdV-SdT+\mu dN$, where $F$, $p$, $V$, $S$, $T$, $\mu$ and $N$ are Helmholtz free energy, pressure, volume, entropy, temperature, chemical potential and number of particles, respectively. Then we can make the more useful definitions: $\mu = (\partial F/\partial N)_{V,T}$. Calculated electronic transport coefficients as a function of the chemical potential at 300, 500 and 700 K are shown in Figure S1.

As shown in Figure S1, the relationship between electronic transport coefficients and $\mu$ shows similar trend at 300, 500, and 700 K to monolayer $SnP_3$ reported by Zhu *et al*[4].

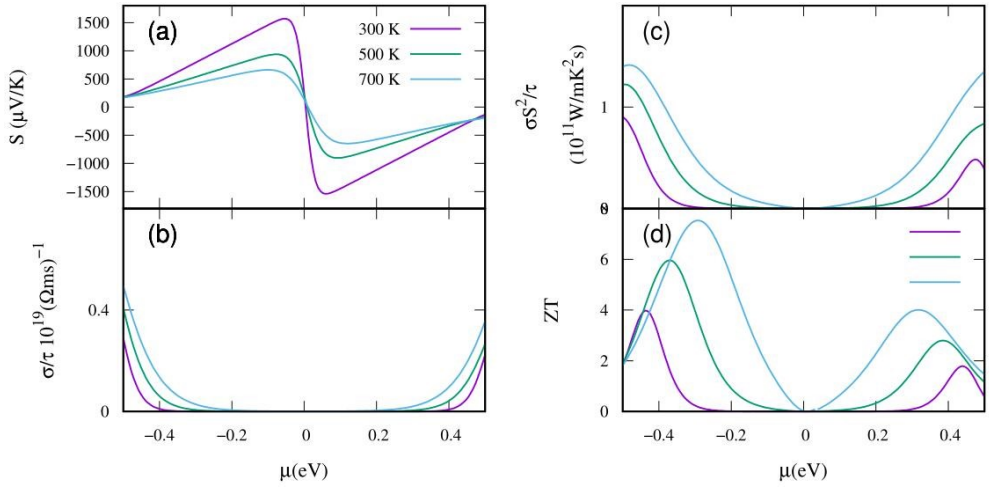


**Fig. S1.** Electronic transport coefficients of (a) $S$, (b) $\sigma/\tau$, (c) $\sigma S^2/\tau$ and (d) $ZT$ as functions of the chemical potential $\mu$.

## **Section C:** DP calculations

In order to evaluate $ZT$, the carrier relaxation time $\tau$ should be known. Here, we employ the deformation potential theory[5] based on the effective mass approximation to calculate $\tau$. Figure S2 (a) presents the maximum energy at the top of the valence band (VBM) and the minimum energy at the bottom of the conduction band (CBM) with respect to deformation $\Delta a/a_0$, which can estimate the deformation potential constant $E_l$. Figure S2 (b) shows the total energy as a function of deformation $\Delta a/a_0$, which can estimate the elastic constant $C_{2D}$.

After all parameters are obtained, according to equations 1 and 2 in the manuscript, the $\tau$ can be simplified as:

$$\tau = \frac{\hbar^3 C_{2D}}{k_B T m_d E_l^{\,2}} \tag{S1}$$

Here $\hbar = 1.05\times10^{-34}$ J·S, $k_B = 1.38\times10^{-23}$ J/K, T = 300 K, and $m_d = \sqrt{m^*_{\Gamma-X} m^*_{X-K}}$. Then with the relation of 1eV=$1.6\times10^{-19}$J and $m_e = 9.11\times10^{-31}$kg, put all the parameters

shown in Table 1 in our manuscript in the above equation S1， the $\tau$ for electrons and holes are:

$$\tau = \frac{(1.05\times10^{-34})^3 \times 98.77}{1.38\times10^{-23}\times300\times\sqrt{0.23\times0.26}\times9.11\times10^{-31}\times(4.48\times1.6\times10^{-19})^2}$$
$$= 2.4\times10^{-13}\,s$$

$$\tau = \frac{(1.05\times10^{-34})^3 \times 98.77}{1.38\times10^{-23}\times300\times\sqrt{0.66\times0.68}\times9.11\times10^{-31}\times(1.96\times1.6\times10^{-19})^2}$$
$$= 4.6\times10^{-13}\,s$$

Besides, we can obtain the temperature dependence of the relaxation time $\tau$, namely, $\tau = \frac{h^3 C_{2D}}{k_B T m_d E_l^2}$. Then the $\tau$ at 500 K and 700 K for electrons (holes) is about $1.4\times10^{-13}$ s ($2.8\times10^{-13}$ s) and $1.0\times10^{-13}$ s ($2.0\times10^{-13}$ s), respectively.

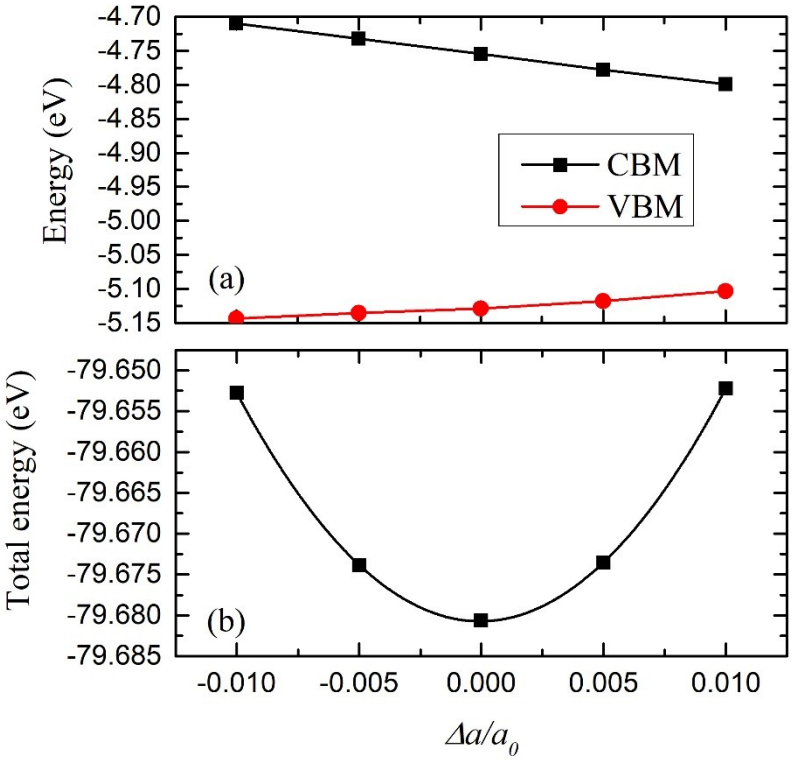


**Fig. S2.** (a) Maximum energy of the valence band (VBM) and minimum energy of the conduction band (CBM) as a function of deformation $\Delta a/a_0$. (b) The total energy as a function of deformation $\Delta a/a_0$.

## **Section D:** Electronic contribution to the figure of merit ($ZT_e$)

The electronic contribution to the figure of merit $ZT_e$ is calculated by $ZT_e = S^2\sigma T / \kappa_e$, and the value of $ZT_e$ as a function of the carrier concentration at 300, 500, and 700 K are presented in Figure S3.

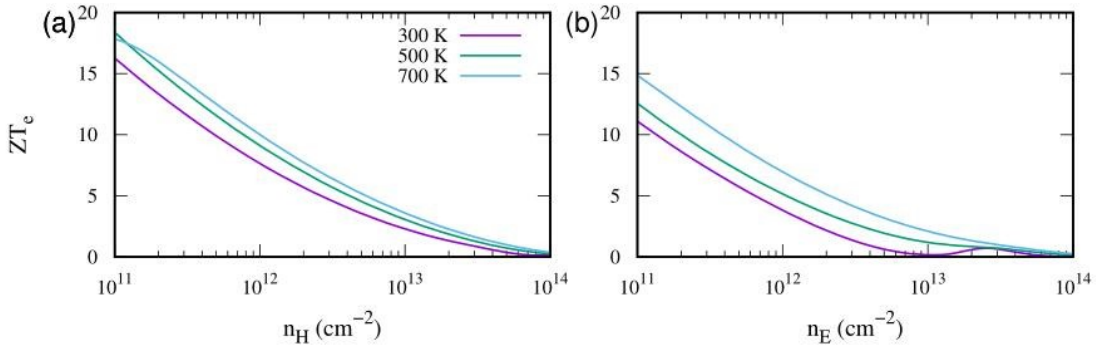


**Fig. S3.** Calculated $ZT_e$ as a function of the carrier concentration at 300, 500, and 700 K. The left panel is for hole doping and the right is for electron doping.

## Reference


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