



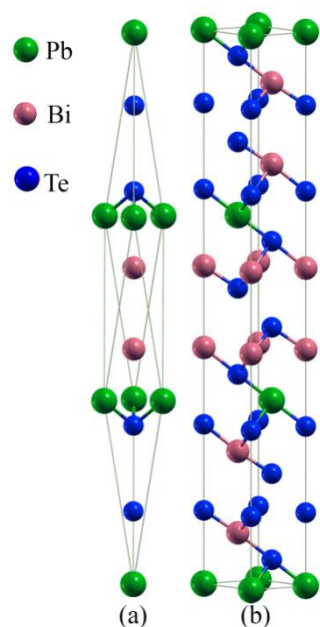
# First-Principle Investigations on the Electronic and Transport Properties of $\text{PbBi}_2\text{Te}_2\text{X}_2$ ( $\text{X}=\text{S}/\text{Se}/\text{Te}$ ) Monolayers

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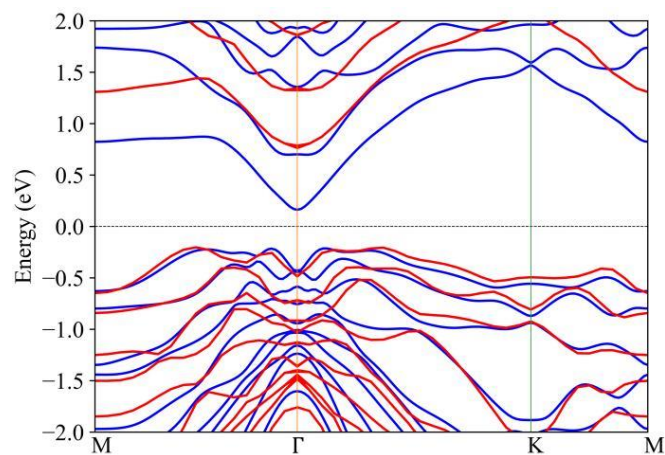
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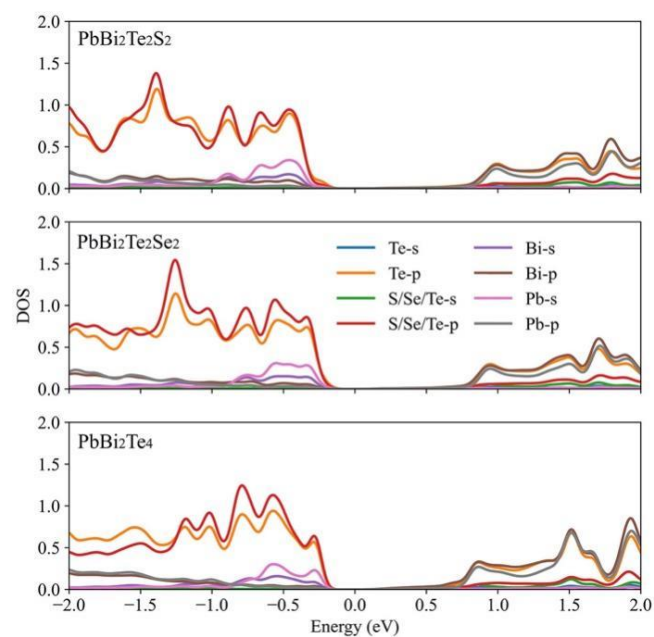
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**Figure S1.** Primitive (a) and conventional (b) cell of bulk  $\text{PbBi}_2\text{Te}_4$ .



**Figure S2.** Calculated electronic band structures of  $\text{PbBi}_2\text{Te}_4$  with the WC GGA (blue lines) and HSE06 hybrid (red lines) functionals.



**Figure S3.** Calculated partial DOS of  $\text{PbBi}_2\text{Te}_2\text{S}_2$ ,  $\text{PbBi}_2\text{Te}_2\text{Se}_2$  and  $\text{PbBi}_2\text{Te}_4$  with the WC functional.

**Table S1.** Born effective charges  $Z^*$  (e) and dielectric constants  $\epsilon_\infty$  in the in-layer and cross-layer directions  $[xx, zz]$  of  $\text{PbBi}_2\text{Te}_2\text{S}_2$ ,  $\text{PbBi}_2\text{Te}_2\text{Se}_2$  and  $\text{PbBi}_2\text{Te}_4$  calculated with the LDA (Ceperley-Alder) functional.

	$Z_{\text{Pb}}^*$	$Z_{\text{Bi}}^*$	$Z_{\text{Te}}^*$	$Z_{\text{S/Se/Te}}^*$	$\epsilon_\infty$
$\text{Pb}_2\text{Bi}_2\text{Te}_2\text{S}_2$	[4.88, 0.81]	[5.76, 0.59]	[-5.27, -0.80]	[-2.93, -0.21]	[12.73, 9.43]
$\text{Pb}_2\text{Bi}_2\text{Te}_2\text{Se}_2$	[5.05, 0.85]	[6.17, 0.61]	[-5.25, -0.83]	[-3.45, -0.21]	[13.32, 11.00]
$\text{Pb}_2\text{Bi}_2\text{Te}_4$	[5.34, 0.98]	[7.08, 0.65]	[-5.28, -0.93]	[-4.48, -0.22]	[16.09, 13.59]

#### Thermodynamic stability of the $\text{PbBi}_2\text{Te}_2\text{S}_2$ , $\text{PbBi}_2\text{Te}_2\text{Se}_2$ and $\text{PbBi}_2\text{Te}_4$ compounds:

To evaluate the thermodynamic stability of our compounds, we have calculated the Gibbs energy using the quasi-harmonic approximation (QHA) approach [1] in which the phonons are harmonic, but they depend on volume. The Gibbs free energy  $G(T, P)$  is given as:

$$G(T, P) = F(T, V) + PV$$

where  $F(T, V)$  is the Helmholtz free energy at temperature  $T$  and volume  $V$ , and  $P$  is the pressure. The free energy of a crystalline material  $F(T, V)$  can be expressed as follows [2]:

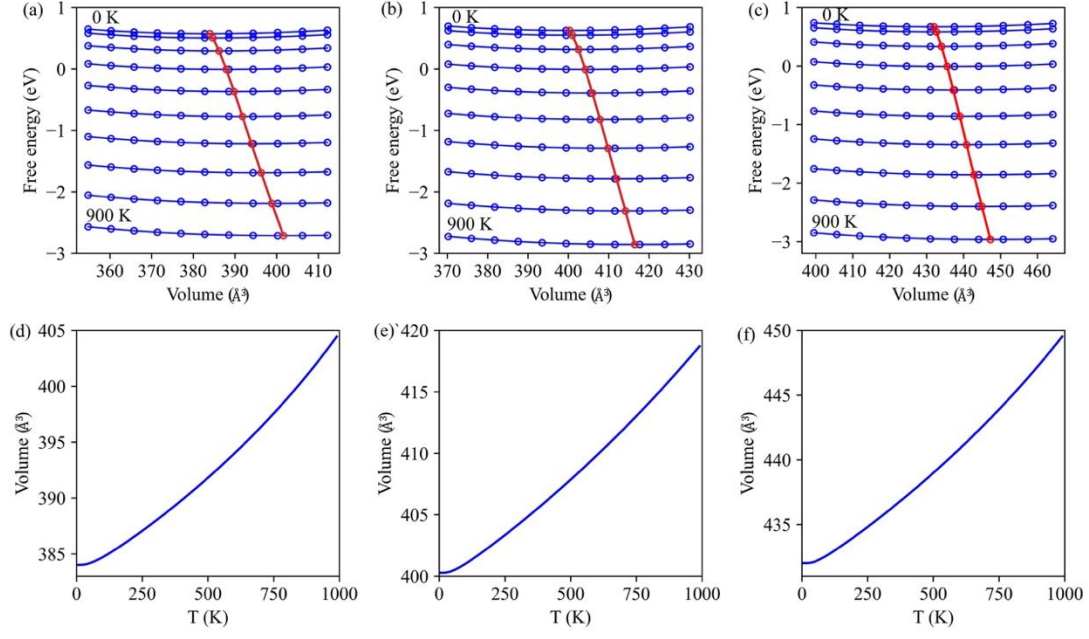
$$F(T, V) = E(V)_{0K} + F_{\text{vib}}(T) + F_{\text{el}}(T, V)$$

where  $E(V)_{0K}$  is the energy at 0K,  $F_{\text{vib}}(T, V)$  is the vibrational free energy and  $F_{\text{el}}(T, V)$  is the electronic free energy. The vibrational free energy reads [2]

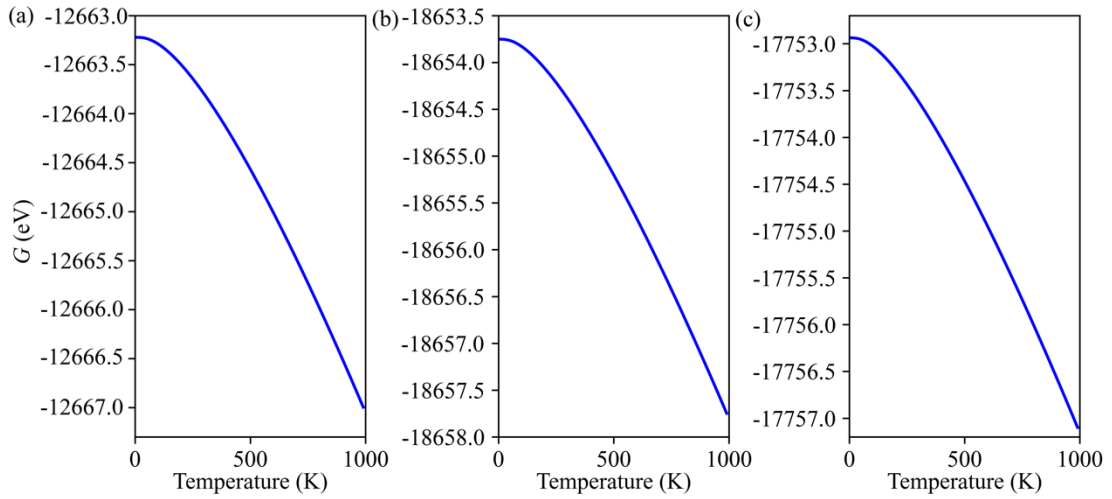
$$F_{\text{vib}}(T) = \frac{1}{2} \sum_{k,v} \hbar \omega(k, v) + k_B T \sum_{k,v} \ln \left( 1 - \exp \left( -\frac{\hbar \omega(k, v)}{k_B T} \right) \right)$$

where  $\omega(k, v)$  is the phonon frequency of the  $k^{\text{th}}$  band and  $v^{\text{th}}$  vector. In the following, the electronic part is neglected as this contribution is usually small.

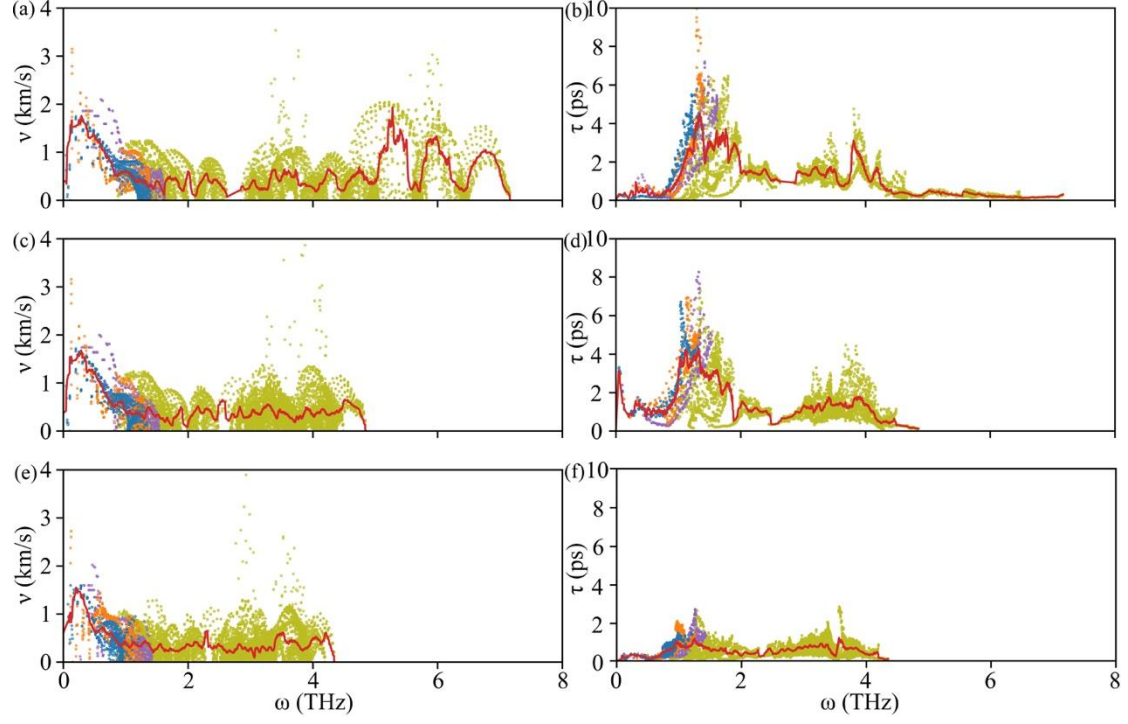
The Gibbs energy  $G(T, P)$  has been calculated at constant pressure and temperature by selecting the minimum value for each volume change (red line in Fig. S4). Then, the Gibbs energy is plotted as a function of temperature as shown in Fig. S5. Negative  $G$  is found for the investigated monolayers, suggesting that they are all stable.



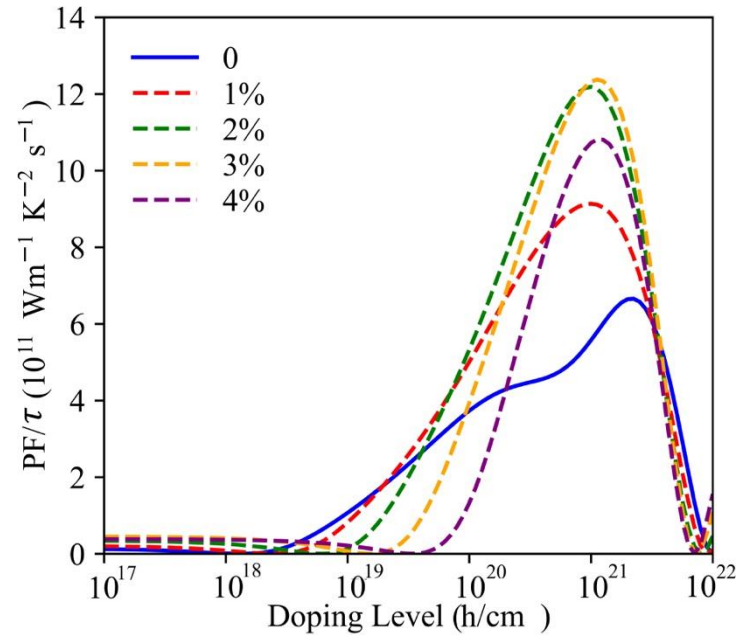
**Figure S4.** (a,b,c) Volume dependence of the free energy from 0K to 900K with a temperature step of 100K, and (d,e,f) temperature dependence of the crystal volume.  $\text{PbBi}_2\text{Te}_2\text{S}_2$  (a, d),  $\text{PbBi}_2\text{Te}_2\text{Se}_2$  (b, e) and  $\text{PbBi}_2\text{Te}_4$  (c, f).



**Figure S5.** Calculated Gibbs energy as a function of temperature for  $\text{PbBi}_2\text{Te}_2\text{S}_2$  (a),  $\text{PbBi}_2\text{Te}_2\text{Se}_2$  (b) and  $\text{PbBi}_2\text{Te}_4$  (c).

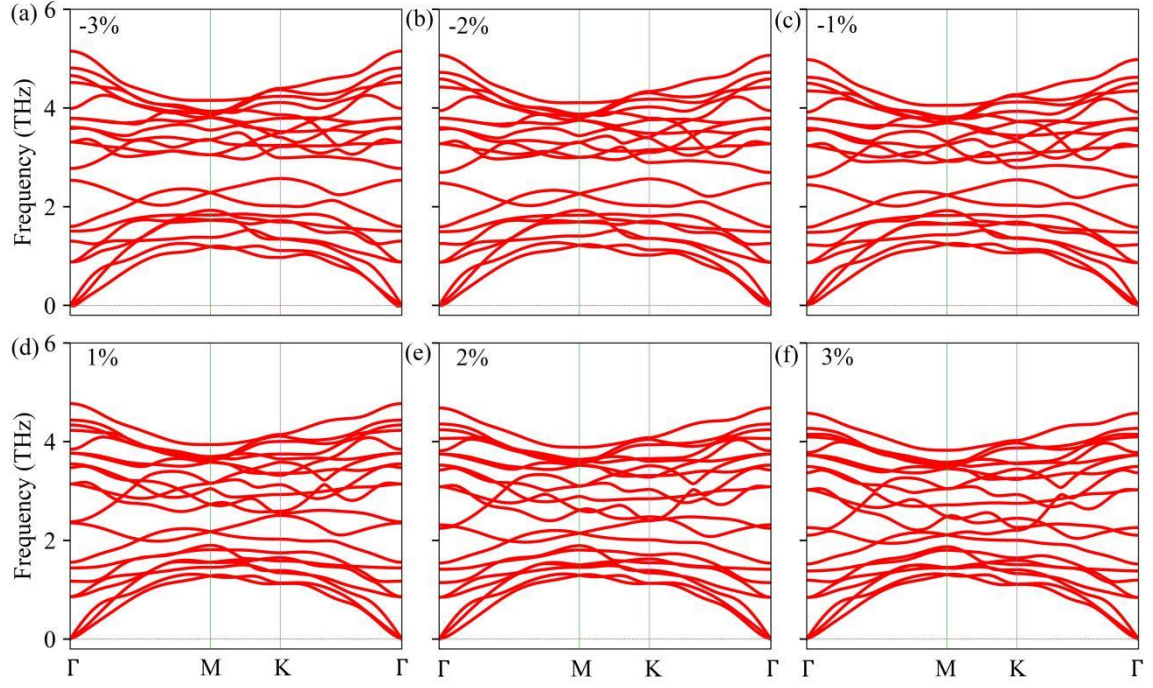


**Figure S6.** Group velocities (left panel) and phonon lifetimes (right panel) in the xx direction at 300K for PbBi<sub>2</sub>Te<sub>2</sub>S<sub>2</sub> (top row), PbBi<sub>2</sub>Te<sub>2</sub>Se<sub>2</sub> (middle row), and PbBi<sub>2</sub>Te<sub>4</sub> (bottom row). Contribution from phonon mode ZA (blue circles), TA (orange circles), LA (purple circles), optical (olive circles) branches and averaged value over a small frequency window of 0.04 THz (red lines).

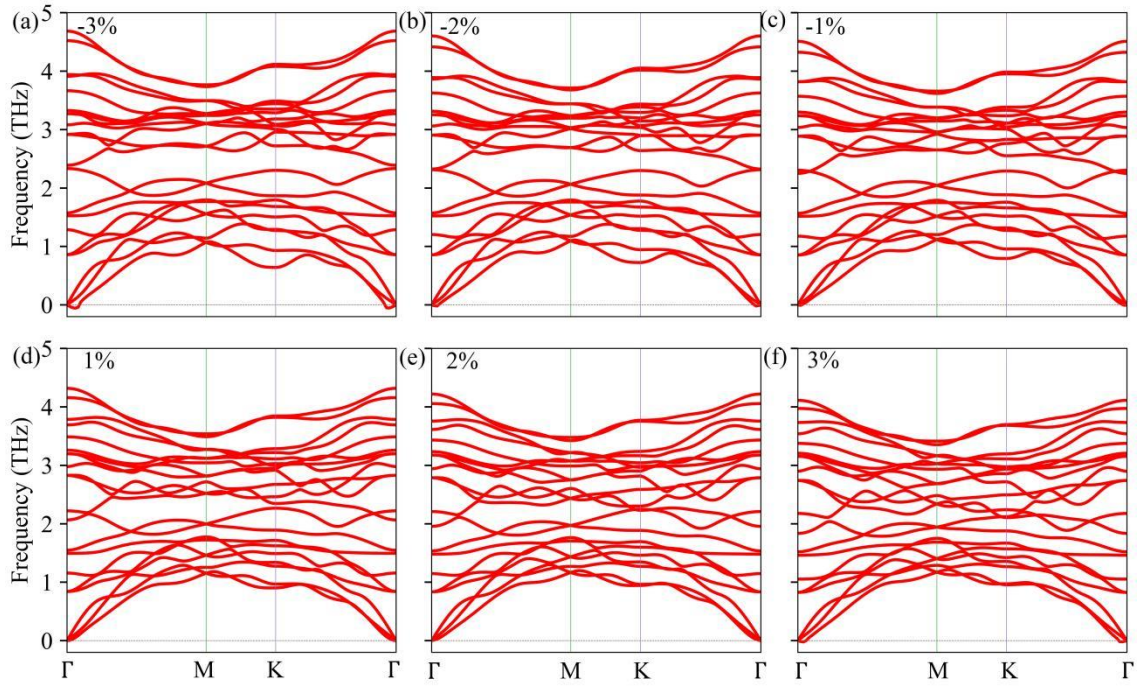


**Figure S7.**  $\tau$ -scaled power factor of PbBi<sub>2</sub>Te<sub>2</sub>S<sub>2</sub> monolayer versus p-type doping level for various compressive and tensile strains in a-axis direction at 500K.





**Figure S8.** Phonon spectrum curves of  $\text{PbBi}_2\text{Te}_2\text{Se}_2$  monolayer under strains.



**Figure S9.** Phonon spectrum curves of  $\text{PbBi}_2\text{Te}_4$  monolayer under strains.