

Pressure Induced Topological Phase Transition in Layered Bi_2S_3

Supplementary Materials

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1. Electronic Structure of Orthorhombic Bi_2S_3

The ambient-condition stable structure of Bi_2S_3 is shown in Fig. S1, which has orthorhombic (OR) lattice consisted by 12 S and 8 Bi atoms in one unit cell and belongs to $Pnma$ space group. The OR- Bi_2S_3 unit cell is consisted by two B_4S_6 ribbons with weak van der Waals interaction between them, while within each ribbon the interaction between Bi-S bonds is dominated by strong covalent bonds.¹ The calculated lattice constant is $a=11.137$, $b=3.981$, and $c=11.297$ Å, respectively. The calculated bulk modulus B_0 for orthorhombic Bi_2S_3 is estimated to be 39.07, and B_0' is calculated to be 7.12. All these results are in good agreement with the previous

study.^{1,4}

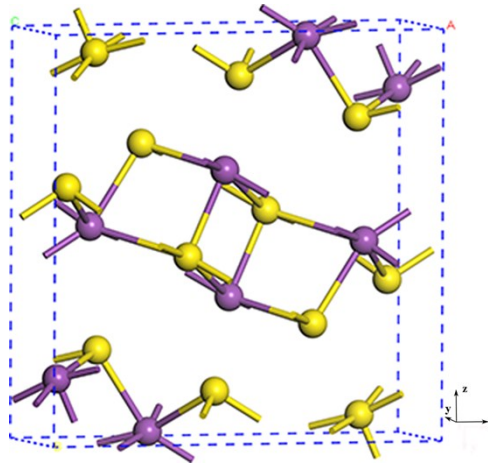


Figure S1: 3D crystal structure of orthorhombic Bi₂S₃

Figure S2 shows band structure of orthorhombic Bi₂S₃ with and without SOI. It is noted that orthorhombic Bi₂S₃ is an insulator with indirect PBE band gap about 1.27 eV, where the valence band maximum that locates between Γ and Y points are mainly consisted by the hybridization of p_x and p_y orbitals from S atoms and the conduction band minimum residing between Γ and X points are contributed by p_y orbitals of Bi atoms. All these results agree well with other studies.¹ When the SOI is applied, the band gap is reduced to 0.91 eV, but there is no band-inversion occurred. It is found that it is difficult to realize band-inversion in orthorhombic Bi₂S₃ as even a high pressure of about 36 GPa is applied, the orbital characters for the VBM and CBM remain the same, although the band gap is significantly decreased to 0.18 eV due to the pressure and SOI effects.

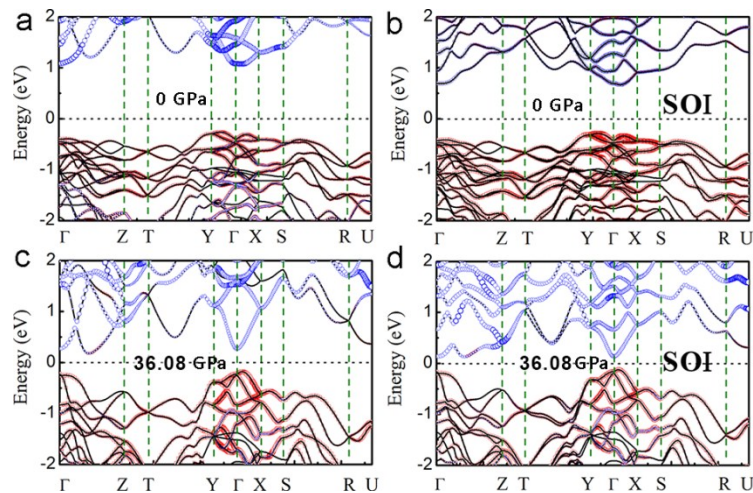


Figure S2: Band structures of pristine orthorhombic Bi₂S₃: (a) without SOI, (b) with

SOI, (c) with 36.08 GPa hydrostatical pressure, and (d) with 36.08 GPa hydrostatical pressure and SOI. The blue open circles denote contributions from p_y orbitals in Bi atoms, and the red open lattices show the contributions from p_x and p_y orbitals in S atoms. Fermi level is shifted to 0 eV.

2. Thermodynamical Properties of rhombohedral Bi_2S_3

To study the thermodynamical stability of rhombohedral Bi_2S_3 (RH- Bi_2S_3), we also performed molecular dynamics simulation for $3 \times 3 \times 1$ layered Bi_2S_3 supercell at the temperature of 300 K, which is shown in Fig. S3. It is noted that the maximum B-S bond oscillation is within 0.3 Å during 3 ps MD time steps at room temperature. From the snapshots in Fig. S3(c) taken from the maximum bond oscillation (0.27 Å), we can see that the layered hexagonal Bi_2S_3 structure is well kept. All these results suggest that rhombohedral Bi_2S_3 is thermodynamically metastable at room temperature. We also study the thermal stability at a higher temperature of 800 K. As Fig. S4 shows, we can see that the rhombohedral Bi_2S_3 is still stable at 800 K as the bond length variation is within 0.4 Å, and the rhombohedral Bi_2S_3 remains its essential lattice structure.

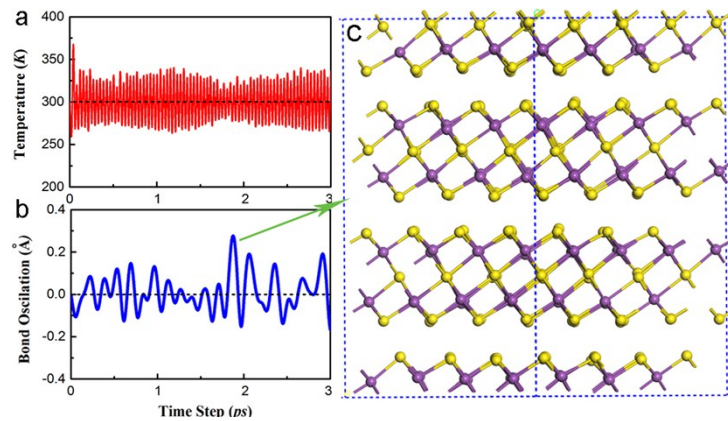


Figure S3: The temperature evolution (a) and Bi-S bond oscillation (b) of the rhombohedral Bi_2S_3 during the molecular dynamics simulation at the temperature of 300 K. (c) Side view of the rhombohedral Bi_2S_3 configuration with the maximum bond oscillation during the MD simulation.

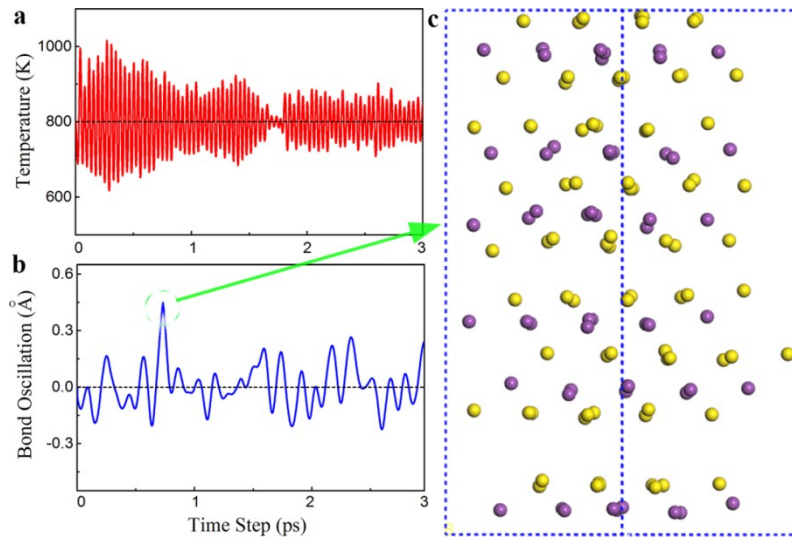


Figure S4: The temperature evolution (a) and Bi-S bond oscillation (b) of the rhombohedral Bi_2S_3 during the molecular dynamics simulation at the temperature of 800 K. (c) Side view of the rhombohedral Bi_2S_3 configuration with the maximum bond oscillation during the MD simulation.

3. Phonon Dispersion of rhombohedral Bi_2S_3 Under Pressure

The structural stability of rhombohedral Bi_2S_3 under pressure was also examined by its phonon dispersion. The phonon dispersion of Bi_2S_3 under 7.15 GPa and 30.87 GPa pressure is shown in Figs. S5(a) and (b), respectively. There is no imaginary frequency found in both cases, indicating that layered Bi_2S_3 remains stable even a high pressure of 30.87 GPa is applied.

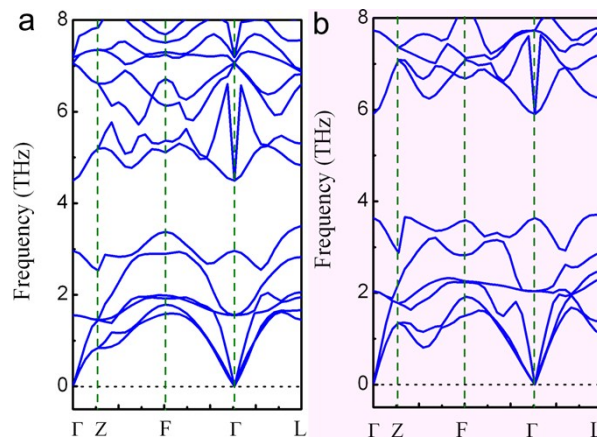


Figure S5: Phonon dispersion of layered Bi_2S_3 under (a) 7.15 GPa and (b) 30.87 GPa pressure.

4. Estimation of Critical Pressure for Topological Phase Transition in rhombohedral Bi₂S₃

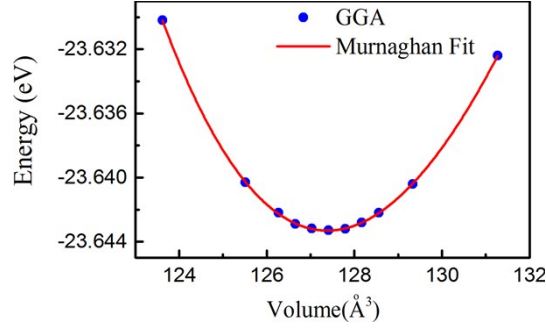


Figure S6: Volume dependent total-energy of rhombohedral Bi₂S₃ based on GGA calculation (blue solid dots), where the data is fitted to the Murnaghan equation of state (red solid line).

The GGA calculated volume dependent total-energy of layered Bi₂S₃ is shown in Fig. S6, which is fitted based on the Murnaghan equation of state²:

$$E(V) = E_0 + \frac{B_0 V}{B_0'} \left[\left(\frac{V_0}{V} \right)^{B_0'} + 1 \right] - \frac{B_0 V_0}{B_0' - 1}, \quad (1)$$

Where V_0 is the equilibrium lattice volume, V is the deformed lattice volume, B_0 is the bulk modulus, and B_0' is the pressure derivative of the bulk modulus. Thus, the bulk modulus B_0 for rhombohedral Bi₂S₃ is estimated to be 39.7, and B_0' is calculated to be 6.35, which are close to its orthorhombic phase.^{3,4}

From the previous study, we found that when the volume is compressed by 9.3%, layered Bi₂S₃ became a topological insulator. Following the below relation²

$$P(V) = \frac{B_0}{B_0'} \left[\left(\frac{V_0}{V} \right)^{B_0'} - 1 \right], \quad (2)$$

the critical pressure to realize the TI transition is estimated to be about 5.3 GPa. This pressure might be realized in the experiment, for example, by growing the Bi₂S₃ thin films on a substrate with a smaller lattice constant.

5. Pressure-dependent formation energy of RH-Bi₂S₃

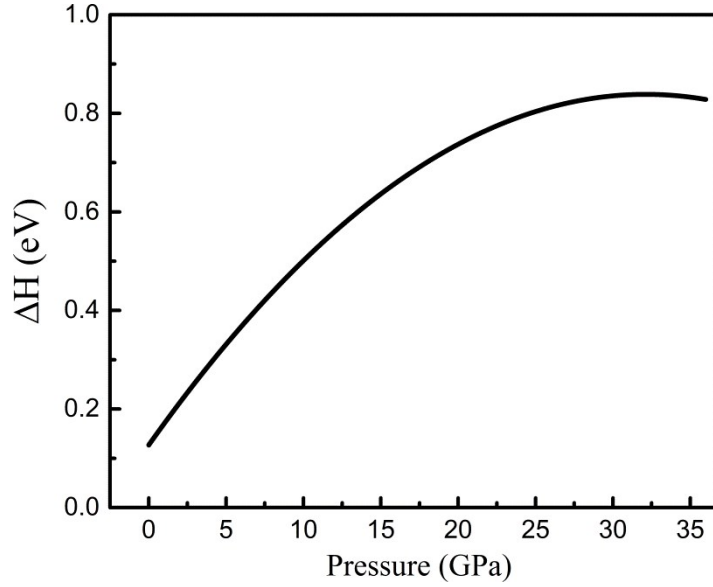


Figure S7: Pressure-dependent relative formation enthalpy ΔH between OR and Rh-Bi₂S₃ crystal, where $\Delta H = H(\text{RH}) - H(\text{OR})$.

The enthalpy (H) can be defined by:

$$H = U + PV,$$

In which U is the internal energy (total-energy in our calculation), P is the applied pressure, and V is the corresponding deformed volume.

The relative stability between OR-Bi₂S₃ and RH-Bi₂S₃ can be evaluated by the corresponding formation enthalpy:

$$E_f = E_{(\text{Bi}_2\text{S}_3)} - 2E_{\text{Bi}} - 3E_{\text{S}} \quad (3)$$

Where $E_{\text{Bi}_2\text{S}_3}$ is the total energy of the Bi₂S₃ per formula unit and E_{Bi} is the total energy of scalenohedral Bi metal per Bi atom. In this calculation, we use the total energy of S₂ molecule per S atom as E_{S} because S vapor is often used during the synthesis process. The calculated pressure dependent relative formation enthalpy between OR-Bi₂S₃ and RH-Bi₂S₃ is shown in Fig. S7, from which we can see that OR-Bi₂S₃ is more energetically stable than RH-Bi₂S₃ by about 0.15 eV per formula unit at the equilibrium state. With increasing the applied pressure, both the formation enthalpy of OR-Bi₂S₃ and RH-Bi₂S₃ increase, but OR-Bi₂S₃ remains more stable compared with

RH-Bi₂S₃ in term of the formation enthalpy. This is evidenced in experiment that it is difficult to realize the RH-Bi₂S₃ through applying pressure on OR-Bi₂S₃, as the phase transition was not observed even at a high pressure of about 50 GPa. Thus, a more feasible way to realize the RH-Bi₂S₃ is to grow the Bi₂S₃ on the substrate with hexagonal surface lattice using the MBE method.

Acknowledgement

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