Pressure Induced Topological Phase Transition in Layered Bi$_2$S$_3$

Supplementary Materials

Ming Yang $^{a,b,*}$, Yong Zheng Luo$^{c,*}$, Ming Gang Zeng$^c$, Lei Shen$^d$, Yun Hao Lu$^e$, Jun Zhou$^c$, Shi Jie Wang$^g$, Iam Keong Sou$^f$, and Yuan Ping Feng$^{b,c,*}$

a. Institute of Materials Research and Engineering, A*STAR, 2 Fusionopolis Way, Singapore 138634, Singapore
b. Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, 6 Science Drive 2, Singapore 117546, Singapore
c. Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117551, Singapore
d. Department of Mechanical Engineering, National University of Singapore, 5 Engineering Drive 1, Singapore 117608, Singapore
e. Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
f. Department of Physics, the Hong Kong University of Science and Technology, Hong Kong, China

† These authors contributed equally to this work.

* Correspondence and requests for materials should be addressed to Y. P. F (E-mail: phyfyp@nus.edu.sg)

1. Electronic Structure of Orthorhombic Bi$_2$S$_3$

The ambient-condition stable structure of Bi$_2$S$_3$ 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$_2$S$_3$ unit cell is consisted by two B$_4$S$_6$ 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$_2$S$_3$ 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
Figure S1: 3D crystal structure of orthorhombic Bi$_2$S$_3$

Figure S2 shows band structure of orthorhombic Bi$_2$S$_3$ with and without SOI. It is noted that orthorhombic Bi$_2$S$_3$ is an insulator with indirect PBE band gap about 1.27 eV, where the valence band maximum that locates between $\Gamma$ 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 $\Gamma$ and $X$ points are contributed by $p_y$ orbitals of Bi atoms. All these results agree well with other studies.\textsuperscript{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 Bi$_2$S$_3$ 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 Bi$_2$S$_3$: (a) without SOI, (b) with
SOI, (c) with 36.08 GPa hydrostical pressure, and (d) with 36.08 GPa hydrostical 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$_2$S$_3$

To study the thermodynamical stability of rhombohedral Bi$_2$S$_3$ (RH-Bi$_2$S$_3$), we also performed molecular dynamics simulation for 3×3×1 layered Bi$_2$S$_3$ 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$_2$S$_3$ structure is well kept. All these results suggest that rhombohedral Bi$_2$S$_3$ 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$_2$S$_3$ is still stable at 800 K as the bond length variation is within 0.4 Å, and the rhombohedral Bi$_2$S$_3$ remains its essential lattice structure.

Figure S3: The temperature evolution (a) and Bi-S bond oscillation (b) of the rhombohedral Bi$_2$S$_3$ during the molecular dynamics simulation at the temperature of 300 K. (c) Side view of the rhombohedral Bi$_2$S$_3$ 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$_2$S$_3$ during the molecular dynamics simulation at the temperature of 800 K. (c) Side view of the rhombohedral Bi$_2$S$_3$ Bi$_2$S$_3$ configuration with the maximum bond oscillation during the MD simulation.

3. Phonon Dispersion of rhombohedral Bi$_2$S$_3$ Under Pressure

The structural stability of rhombohedral Bi$_2$S$_3$ under pressure was also examined by its phonon dispersion. The phonon dispersion of Bi$_2$S$_3$ 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$_2$S$_3$ remains stable even a high pressure of 30.87 GPa is applied.

Figure S5: Phonon dispersion of layered Bi$_2$S$_3$ under (a) 7.15 GPa and (b) 30.87 GPa pressure.
4. Estimation of Critical Pressure for Topological Phase Transition in rhombohedral Bi$_2$S$_3$

Figure S6: Volume dependent total-energy of rhombohedral Bi$_2$S$_3$ 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 Bi$_2$S$_3$ is shown in Fig. S6, which is fitted based on the Murnaghan equation of state$^2$:

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[ \left( \frac{V_0}{V} \right)^{B'_0} - 1 \right] + \frac{B_0 V_0}{B'_0 - 1},$$

(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 Bi$_2$S$_3$ 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 Bi$_2$S$_3$ became a topological insulator. Following the below relation$^2$

$$P(V) = \frac{B_0}{B'_0} \left[ \left( \frac{V_0}{V} \right)^{B'_0} - 1 \right],$$

(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 Bi$_2$S$_3$ thin films on a substrate with a smaller lattice constant.
5. Pressure-dependent formation energy of RH-Bi$_2$S$_3$

Figure S7: Pressure-dependent relative formation enthalpy $\Delta H$ between OR and Rh-Bi$_2$S$_3$ 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-Bi$_2$S$_3$ and RH-Bi$_2$S$_3$ can be evaluated by the corresponding formation enthalpy:

$$E_f = E_{(Bi_2S_3)} - 2E_{Bi} - 3E_S \quad (3)$$

Where $E_{Bi_2S_3}$ is the total energy of the Bi$_2$S$_3$ 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 S$_2$ 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-Bi$_2$S$_3$ and RH-Bi$_2$S$_3$ is shown in Fig. S7, from which we can see that OR-Bi$_2$S$_3$ is more energetically stable than RH-Bi$_2$S$_3$ by about 0.15 eV per formula unit at the equilibrium state. With increasing the applied pressure, both the formation enthalpy of OR-Bi$_2$S$_3$ and RH-Bi$_2$S$_3$ increase, but OR-Bi$_2$S$_3$ remains more stable compared with
RH-Bi$_2$S$_3$ in term of the formation enthalpy. This is evidenced in experiment that it is difficult to realize the RH-Bi$_2$S$_3$ through applying pressure on OR-Bi$_2$S$_3$, 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-Bi$_2$S$_3$ is to grow the Bi$_2$S$_3$ on the substrate with hexagonal surface lattice using the MBE method.

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References

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