Earth-abundant antimony trisulphide (Sb$_2$S$_3$), or simply antimonite, is a promising material for capturing natural energies like solar power and heat flux. The layered structure, held up by weak van-der Waals forces, induces anisotropic behaviors in carrier transportation and thermal expansion. Here, we used stress as mechanical stimuli to destabilize the layered structure and observed the structural phase transition to a three-dimensional (3D) structure. We combined in situ x-ray diffraction (XRD), Raman spectroscopy, ultraviolet-visible spectroscopy, and first-principles calculations to study the evolution of structure and bandgap width up to 20.1 GPa. The optical band gap energy of Sb$_2$S$_3$ followed a two-step hierarchical sequence at approximately 4 and 11 GPa. We also revealed that the first step of change is mainly caused by the redistribution of band states near the conduction band maximum. The second transition is controlled by an isostructural phase transition, with collapsed layers and the formation of a higher coordinated bulky structure. The band gap reduced from 1.73 eV at ambient to 0.68 eV at 15 GPa, making it a promising thermoelectric material under high pressure.
The needs for environmentally friendly and sustainable energy supplies are the prerequisites for achieving carbon neutrality. According to Renewables 2020 Global Status Report, renewable technologies like solar, geothermal, and wind power have provided 8.7% of the final world’s primary energy consumption. The development of solar cells has enjoyed its blossom since the last decade. However, their broad implications are still restricted by the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE)

### Results and discussion

#### Crystal structure of compressed Sb₂S₃

The layered structure of Sb₂S₃ was stabilized in a quasi-3D structural phase transition at similar pressures. Upon further compression, Sb₂S₃ becomes a substitutial alloy. Since the crystal structure strongly influences the electronic band gap of materials, it is necessary to conduct an updated study and figure out the underlying transition mechanisms.

#### Table 1 Resolved atomic positions for Sb₂S₃ at 1.7 and 11.1 GPa.

| Run | Sb₂S₃ (1.7 GPa) | Sb₂S₃ (11.1 GPa) |
|-----|----------------|-----------------|
| **Temperature** | 297 K | 297 K |
| **Space group** | Pnma (#62) | Pnma (#62) |
| **a (Å)** | 11.276 (4) | 10.531 (2) |
| **b (Å)** | 11.002 (2) | 10.501 (5) |
| **c (Å)** | 3.744 (1) | 3.751 (3) |
| **β (°)** | 90 | 90 |
| **Z** | 4 | 4 |
| **V/Å³** | 116.12 (4) | 103.7 (4) |
| **Atom position** | x, y, z | x, y, z |

At 1.7 GPa, Sb₂S₃ is the original layered structure. The sample undergoes an isostructural phase transition at ~10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials cost, reliability, and power conversion efficiency (PCE). Sb₂S₃ is a promising solar energy absorber with affordable cost, good Earth abundance and non-toxic composition. It features a large Seebeck coefficient at below 10 GPa, the materials content was previously extracted for it.
Supplementary Fig. 2 and the evolution of interlayer distance in Supplementary Fig. 3. A clear stiffening of lattice was observed near the isostructural transition point, where the $B_0$ of reconstructed 3D-Sb$_2$S$_3$ is 24% greater ($B_0 = 54.4$ GPa compared to 43.8 GPa for the low-pressure phase). Seeing from the evolution of structural parameters (Fig. 1c, d), the compression in low-pressure phase is mainly achieved by squeezing layers made of Sb–S polyhedral chains. Above the transition point, the material becomes less-compressible as the Sb$_2$S$_3$ features higher atomic coordination described in the 3D structure. A notable jump of the $c$ axis length is observed at 11 GPa, accompanying the shortening of $a$ and $b$ lattice axis and the isostructural transition. This compression anomaly is the signature for the formation of new chemical bonds, which may profoundly change the electronic structure of Sb$_2$S$_3$. Pressure-regulated dynamic stereochemistry has been reported in many layered materials.\textsuperscript{36–41} We also characterized the interlayer distance as a function of pressure force (Supplementary Fig. 3 and Supplementary Data 1), which suggest the layer is initially maintained by the van der Waals force and then by covalent bonding upon isostructural transition.

Our x-ray diffraction analysis indicate that the isostructural phase transition is achieved by the reconstruction of bonds and coordination environments. In light of this, we performed Raman spectroscopy which is more sensitive to the change of chemical bonds. The experimental results are summarized in Fig. 2 and compared with the first-principles simulation (Supplementary Fig. 4). The frequencies of modes in our experiments generally agree with the previous experiment by Dai et al.\textsuperscript{31} and Efthimiopoulos et al.\textsuperscript{32} Here, we identified each mode on the basis of first-principles calculations and classified them into two groups: interlayer modes (solid red circles in Fig. 2b) and other bulk-like inner-layer modes (open blue circles in Fig. 2b). The interlayer breathing mode ~100 cm$^{-1}$ was terminated soon after the transition, suggesting the completion of the layer to bulk isostructural phase transition. While both interlayer stretching modes were observed to be softened below ~14 GPa, they robustly shifted to higher frequencies upon the completion of the phase transition. The rest bulk-like inner-layer mode exhibit blueshift over the pressure region. It was also reported that a turning point of electronic conductivity was seen at ~5 GPa.\textsuperscript{31} However, our XRD and Raman experiments alone were unable to identify this phase transition. The electronic phase transition is unlikely due to the collapse of Sb$_2$S$_3$ layers, but may due to changes in the electronic band structures.

### Ultraviolet–Visible and bandgap analysis

Therefore, we are motivated to measure the electronic band-gap energy in compressed Sb$_2$S$_3$ single crystals. At ambient condition, bulk Sb$_2$S$_3$ has indirect band-gap energy of 1.73 eV, which is suitable for solar cell application, although its self-trapping states substantially inhibit its photon-energy conversion.\textsuperscript{6,14,42} Here, we obtained the ultraviolet–visible (UV–Vis) spectra and calculated the bandgap by the Kubelka–Munk (K–M) equation\textsuperscript{43} over the regime of phase transition (Fig. 3a, b and Supplementary Data 1). We also conducted the first-principles calculation on the basis of HSE06 hybrid functionals to find the mechanism. The calculated
band-structure confirmed that ambient Sb$_2$S$_3$ has an indirect semiconductor, with its valence band maximum located at Γ (0, 0, 0) and conduction band minimum (CBM) located near Z, at (0,0,0.375) (Fig. 3c). However, the CBM moved to the Γ (0, 0, 0) point of the Brillouin zone once pressure was increased to 5.2 GPa and Sb$_2$S$_3$ tuned into a direct bandgap semiconductor. Guided by our simulation results, the bandgap change induced the first discontinuity in our bandgap measurement. Such electronic phase transition was also predicted in layered structures like MoS$_2$ and was known to boost electrical conductivity. Similarly, the onset of direct band-gap type would be the principal reason of observed higher electrical conductivity in Sb$_2$S$_3$.

Once we pressurized the sample to the previously observed isostructural transition point, we observed a kink of band-gap...
energies (Fig. 3b). It is worth noting that the isostructural phase transition does not alter the direct bandgap, but only stagger the change of bandgap energies. The kink was verified by our first-principles simulation, where the closing of band gap slightly accelerated in between 11 and 13 GPa. It is worth noting that the narrowed bandgap at above 11 GPa is specifically useful for thermo-electrical materials \(^{30}\). We stopped our experiment at ~15 GPa because the band gap energy becomes greatly lowered and evolves towards full metallization \(^{31}\). A previous work on Sb\(_2\)S\(_3\) thin film reported a broad albeit weak photoluminescence peak from the states at ambient conditions \(^{14}\). We also closely monitored possible photoluminescence during the compression experiment through our optical window. However, throughout the pressure experiment, the photoluminescence has yet become visible and should keep weak due to the active self-trapping states.

**Collapsed layers and the bandgap transition.** On the basis of pioneering works, our results attempt to clarify two main points during the densification of Sb\(_2\)S\(_3\) crystals. First, the previously observed turning of electrical conductivity at ~4 GPa \(^{31}\) is due to the shift of CBM to the \(\Gamma\) point of Brillouin zone. At the same pressure, Sb\(_2\)S\(_3\) is still chained by Sb–S polyhedron and a well-defined layered structure. Also, our experiments demonstrate that compressed Sb\(_2\)S\(_3\) maintains the same crystal space group up to 20.1 GPa under room-temperature compression. Although under high pressure, the \(Pnma\) phase might not be the most energetically favored phase \(^{34}\), large-scale atomic movement or reconstructive structural transition was not observed in our single-crystal experiment most likely due to the high energy barrier, the bulky single-crystal sample and relatively fast compression rate. Transition kinetics and sample crystallinity should be taken into consideration for polymorphism in similar layered structures \(^{46,47}\).

Loading strain is well-known to influence the electrical conductivity of materials, and may reversely response to the Seebeck coefficient. Our experiment demonstrated that hydrostatic compression of Sb\(_2\)S\(_3\) single-crystals has greatly squeezed the interatomic spacing and reduced the bandgap to below 1.0 eV above 11 GPa, at which pressure normal strains of 5.89%, 6.11%, and 5.42% were applied along the \(x\), \(y\), and \(z\) axis, respectively. The improved electrical conductivity may partially offset the relatively low carrier concentration of Sb\(_2\)S\(_3\) which was measured on the order of 10\(^{12}\) at ambient conditions and enhanced the overall thermoelectric performance. However, it is still necessary to directly calibrate the Seebeck effect under pressure for more accurate description under pressure, which will be systematically studied in the future.

An interesting issue is the electronic topological transition in antimony chalcogenides like Sb\(_2\)S\(_3\) and Sb\(_2\)Se\(_3\). Those chalcogenides have the same layered structure at ambient conditions. Both of them were reported to undergo electronic topological transitions at a few GPa \(^{30,32,38,48}\) at which the atomic vibration and lattice compressibility exhibit sharp anomaly. The transition occurs when a band extreme associated with a Van Hove singularity passes through the Fermi level and causes a strong redistribution of the density of electronic states near the Fermi surface. The density of states as a function of pressure over the entire range of pressure is provided in Supplementary Fig. 5. Our work not only verified previous results on the compressibility and vibrational modes, but also, observed the onset of band gap energy discontinuity at ~4 GPa, along with the indirect-direct type of band gap. This is probably caused by the charge density redistribution from the electronic topological transition. The indirect-direct bandgap transition of Sb\(_2\)S\(_3\) was previous reported in Ibañez et al. \(^{35}\) and was verified by our hybrid function simulation. This bandgap transition was achieved by the opposite shifts of the conduction band minima at the \(Z\) and \(\Gamma\) points in the Brillouin zone. While the \(d\)-electrons are deep in the valence state of Sb\(_2\)S\(_3\) and the electronegativity of S atoms are stable in the pressure range of 0-11 GPa (Supplementary Fig. 6), the abnormal shifts in the conduction band is mainly a pressure effect, which reduces the interatomic distances and strengthens the atomic interactions, leading to the redistribution of energy bands. The critical transition pressure was then anchored to the formula used to calculate the band gap in our UV-Vis experiment.

We also conducted Bader charge analysis to confirm the transition at 11 GPa \(^{39}\). A sudden change of Sb and S charges was observed at the critical transition pressure. For example, charges of Sb\(_1\) increased from 2.0 to 2.5 while that of S\(_1\) dropped from 7.5 to 7.0. The transition came along with the disappearance of Sb\(_{1-}\) lone-electron pair and the formation of Sb\(_2\)S\(_3\) polyhedra in the bulk structure. Pressure has been previously used to engineer the band gap energies of insulators and semiconductors, which also alters their electronic structures. For example, insulators like Cs\(_2\)Au\(_3\) perovskite can even reach a rate of 0.2 eV/GPa in closing its band gap. Our UV-Vis experiment showed a normalized 0.07(1) eV/GPa decrease of band gap energy, and this trend generally reflected the shortening of bond-length with more overlapped charge density between atoms (Fig. 3).

**Conclusion**

In summary, the band gap engineering in Sb\(_2\)S\(_3\) is achieved through two-step transitions at 4 and 11 GPa. The first bandgap transition is mainly due to the redistribution of charge density near the CBM. The latter is controlled by an isostructural phase transition, which is the result of collapsing layers. The evolution of band gap energies in compressed Sb\(_2\)S\(_3\) is covered by this hierarchical electronic phase transition mechanism. Although compression alone could not overcome self-trapping or yield strong photoluminescence, future opportunities may lie in combined doping and pressurization methods to eliminate the harmful self-trapping states and optimize band structures \(^{14,50,51}\).

**Methods**

**Sb\(_2\)S\(_3\) single crystals.** We use natural antimony (III) sulfide (Sb\(_2\)S\(_3\)) single crystal collected from Xikuangshan mountain, Hunan province, China. The natural crystals were polished and the chemical composition was measured by electron probe micro-analysis coupled with a scanning electron microscope (SEM–EPMA) available at the Central South University (Supplementary Fig. 7 and Supplementary Table 1). By averaging 8 spots on the polished single-crystal facet, the natural single-crystal sample exceeds 99% purity and its deviated atomic ratio of S (Sb:S) value is below 0.08%. Single-crystal sample was then crushed into small pieces with typical size of 50 \(\times\) 20 \(\times\) 10 \(\mu\)m\(^2\) and arbitrary orientation before loading into the diamond anvil cell (DAC).

**X-ray diffraction experiments.** Single-crystal x-ray diffraction experiments were performed at 13BM-C station of GeoSoilEarthCARS (GSECARS) of the Advanced Photon Source, Argonne National Laboratory. The crushed natural stibnite (Sb\(_2\)S\(_3\)) single-crystal sample was loaded in between two diamond anvils of 400 \(\mu\)m culet size and was sealed with a T301 steel gasket. The sample chamber was a drilled hole of 200 \(\mu\)m diameter with neon gas as the pressure medium. Pressure was applied by increasing pressure in a gas membrane system that coupled with the DAC. The monochromatic beam wavelength used for data collection was 0.434 Å with a focus spot of 12 \(\times\) 18 \(\mu\)m\(^2\). Single-crystal diffraction patterns were collected on a Pilatus detector at each x-ray incident angle (1° per image) from ~30° to 30° for 10 s each. The orientation matrix, the diffraction data reduction, and crystal structure refinement were performed using the APEX3 program (Bruker). The lattice parameters from powder XRD patterns were initially reduced by the software Unitcell\(^{22}\). Then their atomic positions are refined by the program GSAS. Pressure is primarily determined by calibrating the ruby fluorescence line shift in an online Ruby system. The pressures are also compared to the equation of state of neon, from which measurement uncertainties <1 GPa are achieved throughout the experiment.

**Low-frequency Raman spectroscopy.** In situ high-pressure Raman measurements were conducted on a customized system available at Center for High Pressure Science and Technology Advanced Research (HPSTAR). Spectra are...
taken for the back-scattering geometry using an Argon laser (532 nm and power <1 mW) in the range 0.5–500 cm$^{-1}$ with a spectral resolution of 1.0 cm$^{-1}$, and the resolution of the laser spot is ~0.8 μm. The acquiring time for each spectrum was 60 s and each collection was repeated for 10 times to attenuate the effects of fluorescence and cosmic rays. Raman spectra were fitted by a Lorentzian-type function using Peakfit v4.12 software to determine the positions of each Raman mode.

**In situ high-pressure photoluminescence measurement.** In situ high-pressure photoluminescence measurements were conducted on a customized system available at the HPSTAR. To measure the high-pressure optical properties (e.g., UV-Vis absorption spectroscopy and photoluminescence) of Sb$_2$S$_3$ in an diamond anvil cells (DACs), we used low fluorescence type Ila diamonds with a culet size of 300 μm. Absorption spectra were collected using a Xenon light source between 320 and 1600 nm. The absorption spectra and optical images were measured in a home-designed spectroscopy system in a micro-region (Gora-UVN-FL, built by Ideaoptics, Shanghai, China). Silicone oil was used as the pressure transmitting medium.

**First-principles calculation.** First-principles calculations were performed under the framework of density functional theory through Vienna’s Ab Initio Package ver. 5.3.4. The generalized gradient approximation of Perdew, Burke, and Ernzerhof revised for solids was implemented to describe the exchange-correlation functions. Pseudopotentials were used with eight valence electrons for Sb atoms (4s$^2$4p$^3$) and six for S atoms (3s$^2$3p$^4$). We employed a 2 × 7 × 2 k point mesh. The structures were allowed to relax for cell variables, cell volume, and atomic positions. We applied a simple D2 method of Grimme with a 0.2 Å cutoff radius to calculate the long-distance van der Waals correction. A plane-wave basis set with a kinetic energy cutoff of 350 eV was found sufficient to converge the force between atoms less than 0.01 eV/Å. After structural relaxation, the density of states and a kinetic energy cutoff of 350 eV was found sufficient to converge the force between atoms less than 0.01 eV/Å. After structural relaxation, the density of states and a kinetic energy cutoff of 350 eV was found sufficient to converge the force between atoms less than 0.01 eV/Å.

**Data availability.** The authors declare that all data supporting the findings of this study are available within the paper and its supplementary files (Supplementary Information and Supplementary Data 1). The data supporting the findings of this study have been deposited at the 4TU Center for Research Data (https://doi.org/10.4121/151316655). Any additional data can be requested by e-mailing the corresponding author. Source data are provided with this paper.

Received: 26 March 2021; Accepted: 17 August 2021; Published online: 02 September 2021

**References**

1. De Castro, C., Medaillva, M., Miguel, L. J. & Frechoso, F. Global solar electric potential: a review of their technical and sustainable limits. *Renew. Sustain. Energy Rev.* 28, 824–835 (2013).

2. Keglevic, L., Liu, G., Gong, J., Mao, L. & Mao, H. K. Highly tunable properties in pressure-treated two-dimensional Dion-Jacobson perovskites. *Proc. Natl Acad. Sci. USA* 117, 16121–16126 (2020).

3. Righini, G. C. & Enrichi, F. Solar cells’ evolution and perspectives: a short review. *Solar Cells and Light Management* 4, 17533–17539 (2020).

4. Sorb, Y. A. et al. Pressure induced electronic topological transition in Sb$_2$S$_3$. *J. Phys. Condens. Matter* 28, 015602 (2016).

5. Dai, L. et al. Pressure-induced irreversible metallization accompanying the phase transitions in Sb$_2$S$_3$. *Phys. Rev. B* 97, 024103 (2018).

6. Effimiopeolou, L., Buchan, C. & Wang, Y. Structural properties of Sb$_2$S$_3$ under pressure: evidence of an electronic topological transition. *Sci. Rep.* 6, 24246 (2016).

7. Ibáñez, J. et al. Structural, vibrational, and electronic study of Sb$_2$S$_3$ at high pressure. *J. Phys. Chem. C* 120, 10547–10558 (2016).

8. Wang, Y. et al. Experimental observation of the high pressure induced substitutional solid solution and phase transformation in Sb$_2$S$_3$. *J. Phys. Chem. B* 120, 4795 (2018).

9. Birch, F. Finite elastic strain of cubic crystals. *Phys. Rev.* 71, 809–824 (1947).

10. Kejun, B., Luo, H., Guo, S., Li, M. & Lu, X. Pressure-regulated dynamic stereochemical role of lone-pair electrons in layered Bi$_2$O$_3$S. *J. Phys. Chem. Lett.* 11, 9702–9707 (2020).

11. Matsubh, K., Ishihara, T., Onari, S., Chang, Y. H. & Park, C. H. Optical properties and structural phase transitions of lead-halide based inorganic-organic 3D and 2D perovskite semiconductors under high pressure. *Phys. Status Solidi C* 241, 3328–3333 (2010).

12. Xiao, G. et al. Pressure-induced reversible phase transformation in nanostructured Bi$_2$Te$_3$ with reduced transition pressure. *J. Phys. Chem. C* 119, 1843–1848 (2015).

13. Wang, P. et al. Pressure-induced structural and electronic transitions, metallization, and enhanced visible-light responsiveness in layered rhenium disulphide. *Phys. Rev. B* 97, 235202 (2018).

14. Park, S., Rittman, D. R., Tracy, C. L., Chapman, K. W. & Ewing, R. C. A. TiO$_2$ thin film deposition on Cd$_x$Er$_{1-x}$Yb at 973 K. *Inorg. Chem.* 57, 2269–2277 (2018).

15. Radescu, S. et al. Study of the orpiment and anorpiment phases of As$_2$S$_3$ under pressure. *J. Phys. Conf. Ser.* 950, 042018 (2017).
Sheng-Cai, Z. et al. Structure-controlled oxygen concentration in Fe₂O₃ and FeO₂. Inorg. Chem. 58, 5476–5482 (2018).

Guo, Y. et al. Probing the dynamics of the metallic-to-semiconducting structural phase transformation in MoS₂ crystals. Nano Lett. 15, 5081–5088 (2015).

Eftimiopoulos, I., Kémichck, J., Zhou, X., Khare, S. V. & Wang, Y. High-pressure studies of Bi₅S₃. J. Phys. Chem. A 118, 1713–1720 (2014).

Zhao, K. et al. First principles study of isostructural phase transition in Sb₂Te₃ under high pressure. Phys. Status Solidi RRL 9, 379–383 (2015).

Lu, X. et al. Regulating off-centering distortion maximizes photoluminescence in halide perovskites. Natl. Rev. Sci. nwa288 (2020).

Lee, C., Kim, S., Son, W.-J., Shim J.-H. & Whangbo. M.-H. Ternary selenides A₂Sb₅Se₉ (A = K, Rb and Cs) as an n-type thermoelectric material with high power factor and low lattice thermal conductivity: importance of the conformationally flexible Sb–Se–Sb–Se bridges. RSC Adv. 10, 14415–14421 (2020).

Holland, T. J. B. & Redfern, S. A. T. Unit cell refinement from powder diffraction data; the use of regression diagnostics. Mineral. Mag. 61, 65–77 (1997).

Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).

Perdew, J. P. et al. Restoring the density-gradient expansion for exchange in solids and surfaces. Phys. Rev. Lett. 100, 246–249 (2008).

Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comp. Chem. 27, 1787–1799 (2006).

Krukau, A. V., Vydrov, O. A., Izmaylov, A. F. & Scuseria, G. E. Influence of the exchange screening parameter on the performance of screened hybrid functionals. J. Chem. Phys. 125, 3863 (2006).

Acknowledgements

We acknowledge the use of synchrotron X-ray diffraction at the 13BM-C of GSECARS, Advanced Photon Source, Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation – Earth Sciences (EAR – 1634415) and Department of Energy- GeoSciences (DE-FG02-94ER14466). 13BM-C is partially supported by COMPRES under NSF Cooperative Agreement EAR-1608856. Y.Z. is supported by the National Science Foundation of China (Grant No. 11974034). Operations of Center for High Pressure Science and Technology Advanced Research (HPSTAR) is partially supported by NSAF (Grant No. U1530002).

Author contributions

Z.C., K.B., Y.Z., M.-E.D., D.Z., P.D.-S., R.T.H., and J.Z. carried out the experiment. Z.C., D.Z., and Q.H. performed the experimental data analysis and interpretation. Q.H. performed the theoretical simulation. X.L. and Q.H. conceived and designed the project. Z.C. and Q.H. wrote the manuscript. All authors contributed to the discussion of the results and revision of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s42004-021-00565-4.

Correspondence

and requests for materials should be addressed to Q.H.

Peer review information Communications Chemistry thanks Zhi-Gang Chen, Shuo Chen and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

Reprints and permission information is available at http://www.nature.com/reprints

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2021
