

Supporting Information

A Novel Two-Dimensional Oxysulfide $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$: Synthesis, Crystal Structure, and Photoelectric Properties

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List of contents:

- 1. Experimental section**
- 2. Supplementary figures**
- 3. Supplementary tables**

1. Experimental section.

Synthesis of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$. All the reagents were purchased and used as obtained. Polycrystalline $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ was synthesized as follow: SrO (0.1813 g, 1.75 mmol), PbO (0.1674 g, 0.75 mmol), Sb_2S_3 (0.5096 g, 1.50 mmol) and PbS (0.1196 g, 0.50 mmol) were mixed and fully ground. The mixture was loaded into a carbon-coated silica tube ($\phi = 10$ mm), then the tube was frame-sealed under vacuum (10^{-3} mbar). The tube was heated to 650 °C in 10 h, held for 48 h, and slowly cooled to 400 °C in 3 days. Black polycrystalline product was obtained with a yield of ~ 99% based on the Sb element. Black rod-shape single crystals of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ were grown by heating the reagents to 650 °C, held for 3 days and cooled to 300 °C in 4 days.

Single Crystal X-ray Crystallography. Single crystal X-ray diffraction measurement was performed at 180 K on a Rigaku XtaALB PRO 007HF single crystal X-ray diffractometer equipped with mirror-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) and Oxford Cryo stream (80-500 K). The crystal structure was solved via direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.¹ The crystallographic and structure refinement data are shown in **Table S1**, and the selected bond lengths are shown in **Table S2**. Atomic coordinates, equivalent isotropic displacement parameters and anisotropic displacement parameters are shown in **Table S3-S4**.

Powder X-ray Diffraction (PXRD) and Scanning Electron Microscopy (SEM). Polycrystalline sample was fully ground and the PXRD measurements were performed on a Bruker D2 phaser diffractometer equipped with a monochromatized source of Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) at 4 kW (40 kV, 100 mA). The pattern was collected with 2θ from 5° to 80° with a scan-rate of 1.2° min⁻¹. Single crystals were pick out and adhered on a double-sided carbon-aluminum tape on the aluminum substrate. The SEM images were acquired by a Phenom Pro scanning electron microscope equipped with a PGT energy-dispersive X-ray (EDS) analyzer. The EDS spectra and mapping analysis were conducted under the accelerating voltage of 15 keV with a 540 s accumulation time.

Ultraviolet-visible (UV-Vis) Light Diffuse Reflectance Spectroscopy. The UV-Vis light diffuse-reflectance spectrum was performed on a UV-4100 spectrophotometer operating in the range from 1500 nm to 400nm. BaSO₄ powder was compacted as the 100 % reflectance standard, with powder sample spread on it. The reflectance-wavelength curve was measured and converted to absorbance data using the Kubelka-Munk equation.²

Thermal Analysis. The thermostability of Sr_{3.5}Pb_{2.5}Sb₆O₅S₁₀ was probed by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) using a Thermal Analysis SDT2960 thermal analyzer under N₂ flow. A silica crucible containing 5.0 mg powder sample was placed on the sample side of the detector, with another empty crucible on the reference side. The sample were heated to 800 °C and cool down in the rate of ±15 °C/min with two cycles.

X-ray Photoelectron Spectroscopy (XPS). The oxidation states of Sr, Pb, Sb, O and S were determined by XPS using an Axis Ultra spectrometer. The spectra were collected for the Sr 3*d*, Sb 3*d*, Pb 4*f*, O 1*s* and S 2*p* regions, with the correction of binding energies by the reference C 1*s* (284.5 eV).

Electrical resistivity measurements. The fine powder sample was pressed into a pellet (ϕ = 5 mm) under a pressure of 15 MPa. Then the pellet was sealed into an evacuated quartz tube and sintered under 550 °C for 10 h. The electrical resistivity of the ceramic pellet was measured in the range of 2–300 K using the standard four-probe method on a Physical Properties Measurement System (PPMS).

Photoresponse measurement. The film device was fabricated by the drop casting method. The as-synthesized polycrystalline Sr_{3.5}Pb_{2.5}Sb₆O₅S₁₀ was well ground and dispersed in acetone by ultrasonic dispersion. The suspension was dropped on the glass substrate and dried. After repeating the above process, a film consisted only of Sr_{3.5}Pb_{2.5}Sb₆O₅S₁₀ was obtained. The film was stacked by small crystals, and the thickness was around 10 μm as shown in Figure S6. Most of the crystals were smaller than 500 nm. Current-voltage (*J-V*) measurements were performed by sweeping the voltage from the positive maximum to the negative minimum using a semiconductor characterization system (KEITHLEY 4200).

Theoretical Calculations. The electronic structure of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ was calculated under first principle using the Projected Augmented Wave Method (PAW)³ within the density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP).⁴ Generalized gradient approximation (GGA) and parameterized by Perdew-Burke-Ernzerhof (PBE)⁷ version were used to describe the exchange correlation functional. A $1 \times 2 \times 1$ supercell $\text{Sr}_7\text{Pb}_5\text{Sb}_{12}\text{O}_{10}\text{S}_{20}$ was constructed to describe the half-occupied O4 sites. The cutoff energy of plane wave basis was set to 560 eV. A Monkhorst-Pack k-point grid of $6 \times 6 \times 3$ was used for Brillouin zone (BZ) sampling. The lattice parameters were fixed as the diffraction data during structural optimization, while the positions of atoms could relax until the atomic forces on each atom reduce less than 0.01 eV/Å.

3. Supplementary figures.

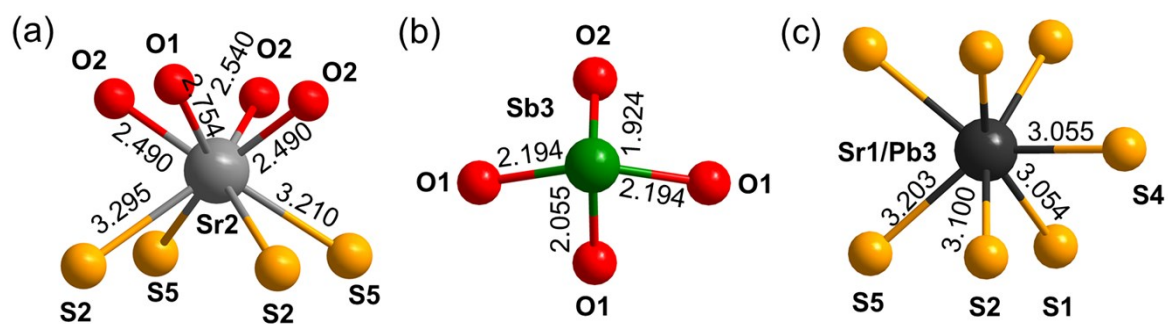


Figure S1. Coordination environments of (a) Sr2, (b) Sb3 and (c) Sr1/Pb3.

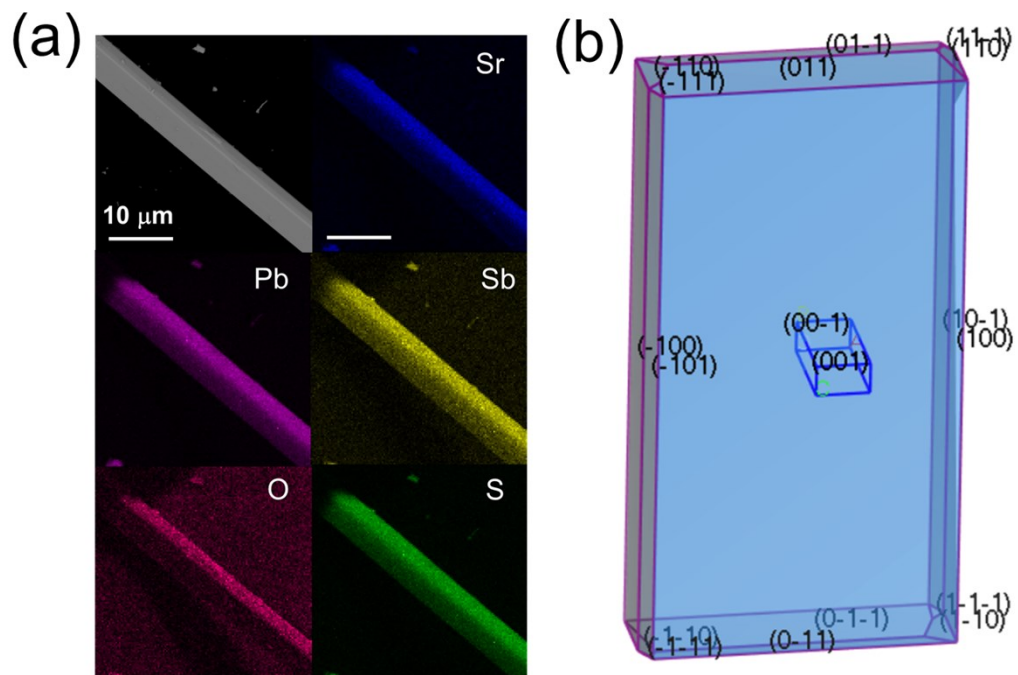


Figure S2 (a) The SEM image and EDS elemental distribution of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ crystal.

(b) Ideal morphology of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ crystal.

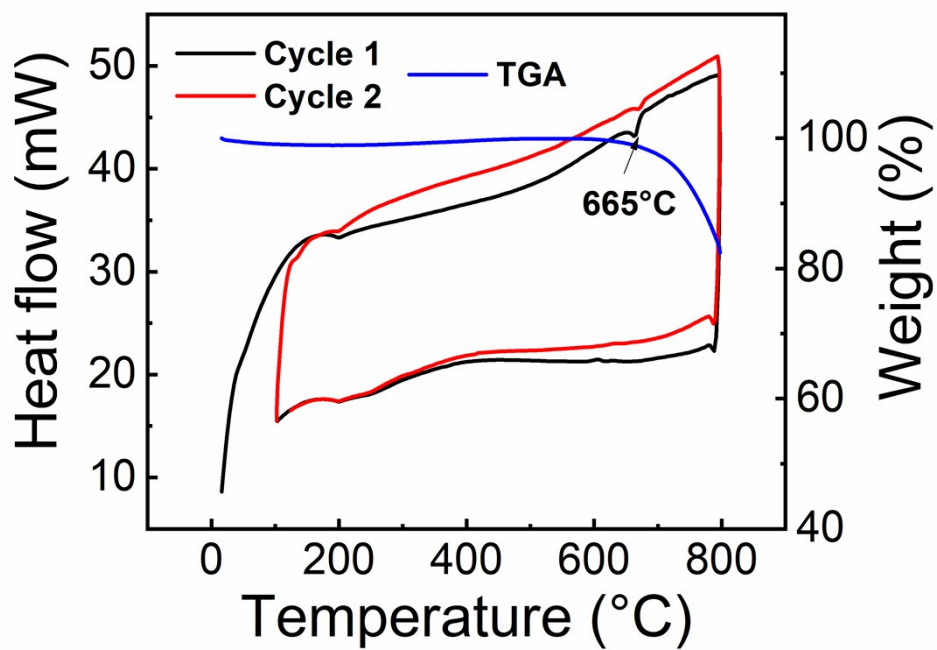


Figure S3 The DSC curve (first cycle: black, second cycle: red) and TGA curve (blue).

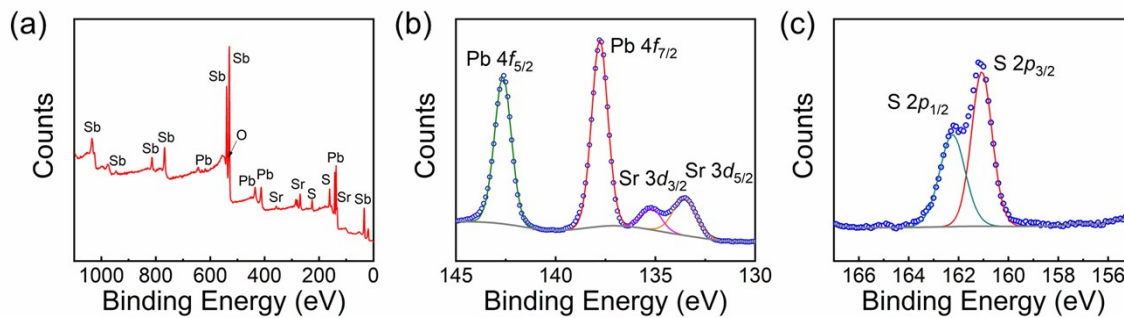


Figure S4. XPS of (a) the as-synthesized $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$, (b) Sr 3d and Pb 4f and (c) S 2p.

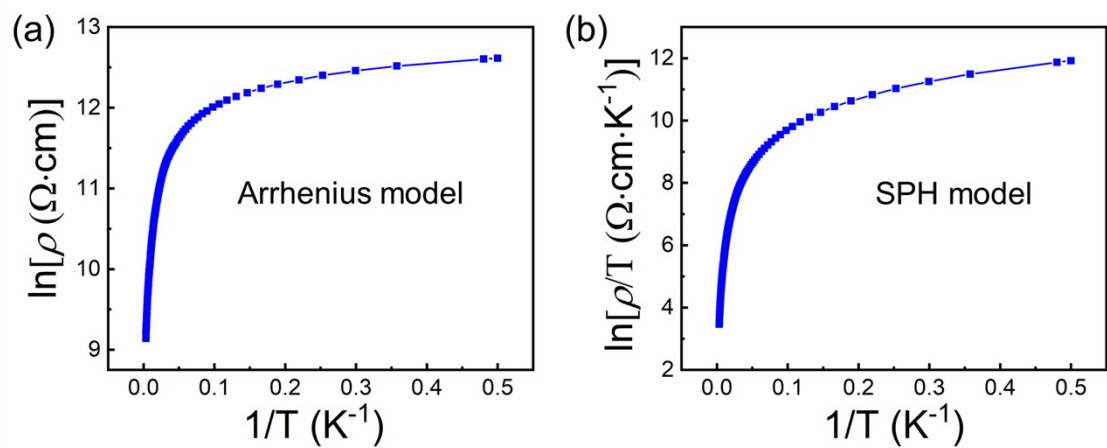


Figure S5. (a) $\ln(\rho/T)$ vs T^{-1} plot of the Arrhenius model. (b) $\ln(\rho/T)$ vs T^{-1} plot of the SPH model.

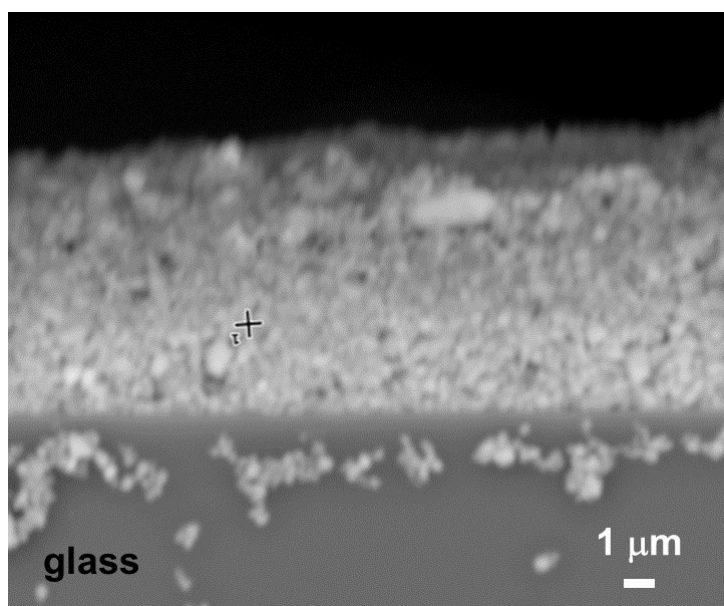


Figure S6. The SEM image of the cross-section of the drop-casting $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ film.

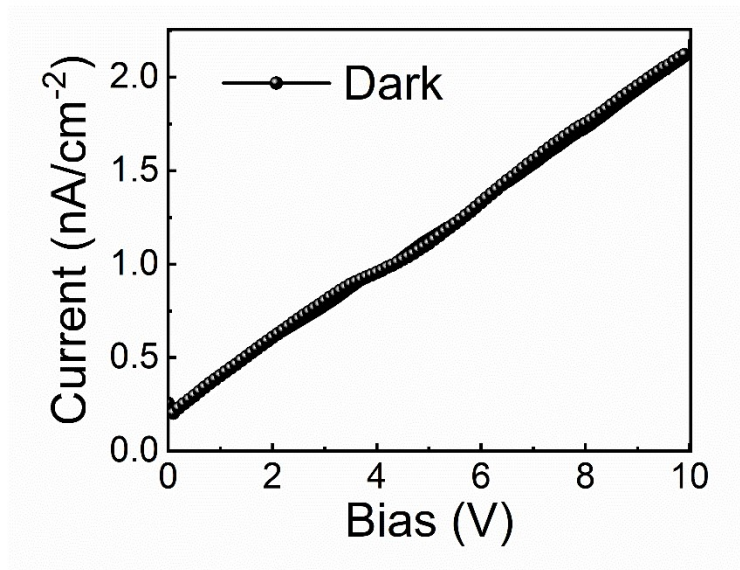


Figure S7. Current density vs voltage curve of Sr_{3.5}Pb_{2.5}Sb₆O₅S₁₀-based device in dark.

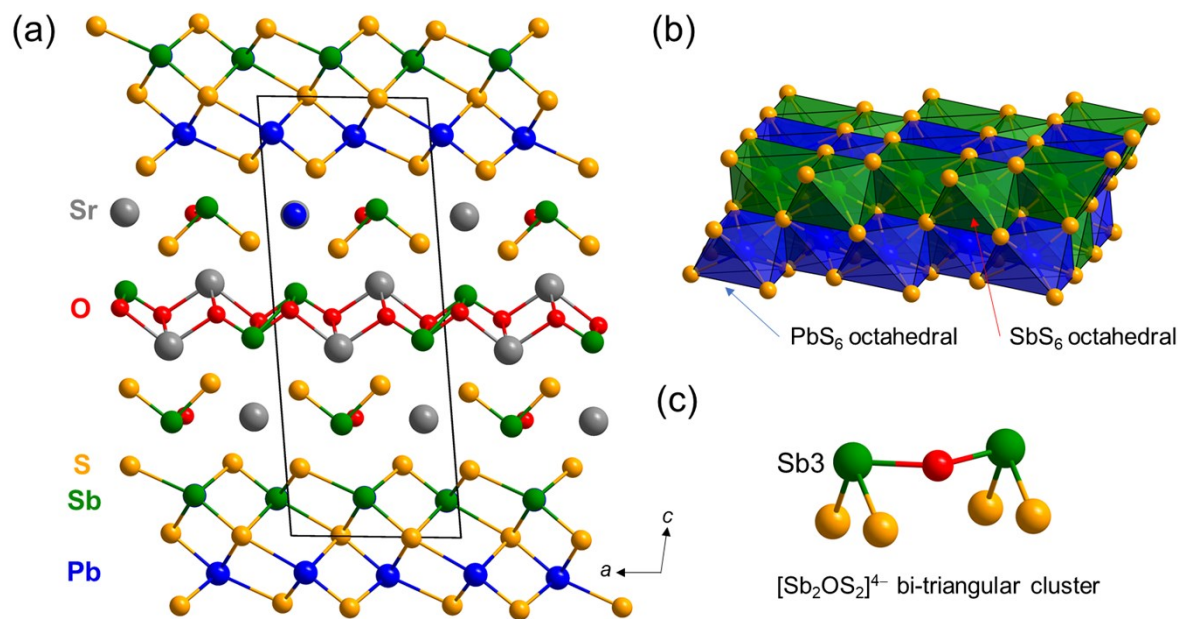


Figure S8. (a) Crystal structure of $\text{Sr}_7\text{Pb}_5\text{Sb}_{12}\text{O}_{10}\text{S}_{20}$ viewed along with b axis. (b) ordered arrangement of PbS_6 and SbS_6 octahedra in the Sb_2Se_3 -type $[\text{SbPbS}_3]^-$ layer. (c) $[\text{Sb}_2\text{OS}_2]^{4-}$ bi-triangular cluster.

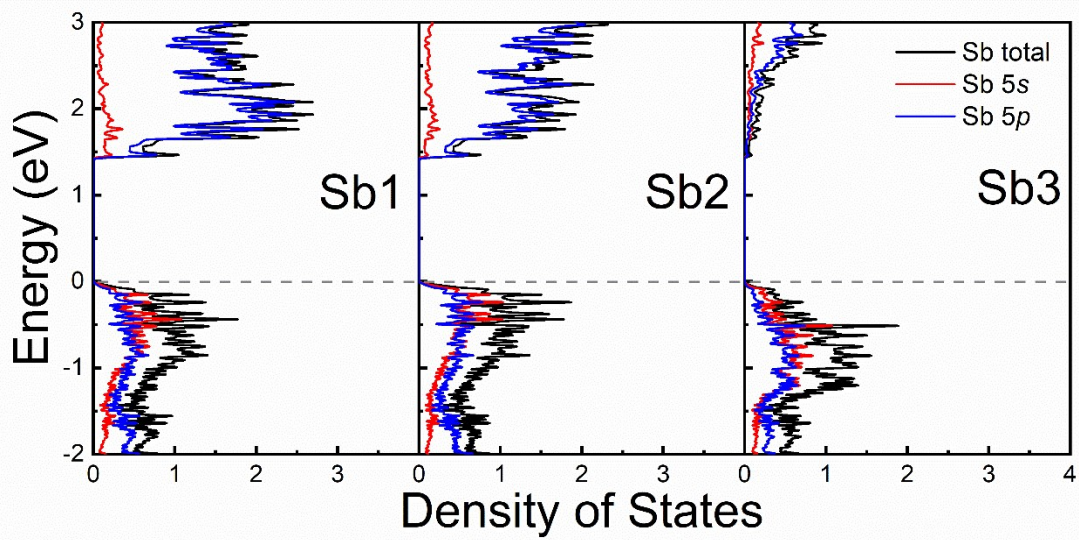


Figure S9. Partial DOS of Sb1, Sb2 and Sb3.

Supplementary tables.

Table S1. Crystallographic data and details of the structure refinement of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$

Formula	$\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$
Space group	$P2_1/m$
F_w (g·mol ⁻¹)	1955.66
a (Å)	7.5556(4)
b (Å)	4.1066(2)
c (Å)	19.575(2)
V (Å ³)	604.94(5)
β (°)	95.117(5)
Z	1
crystal color	black
μ (mm ⁻¹)	32.425
$F(000)$	844
data/parameters	1210/88
R_{int}	0.0266
$R1[I > 2\sigma(I)]$	0.0230
wR_2 (all data)	0.0525
GOF	1.044

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|, wR = \{ \sum [w(|F_o|^2 - |F_c|^2)^2] / \sum (w|F_o|^4) \}^{1/2} \text{ and calc } w = 1 / [\sigma^2(F_o^2) + (0.0182P)^2] \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

Table 2. Selected bond lengths of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$

bond type	distance (Å)	bond type	distance (Å)
Sb1/Pb1–S1×2	3.022(1)	Sr1/Pb3–S1×2	3.054(1)
Sb1/Pb1–S3×2	2.853(1)	Sr1/Pb3–S4	3.055(2)
Sb1/Pb1–S3	2.756(2)	Sr1/Pb3–S2×2	3.100(2)
Sb1/Pb1–S4	3.154(2)	Sr1/Pb3–S5×2	3.203(2)
Sb2/Pb2–S1	2.510(2)	Sr2–O2×2	2.490(3)
Sb2/Pb2–S3	3.281(2)	Sr2–O2	2.540(6)
Sb2/Pb2–S4×2	2.668(1)	Sr2–O1	2.754(5)
Sb2/Pb2–S3×2	3.063(1)	Sr2–S2×2	3.295(2)
Sb3–O1	2.055(6)	Sr2–S5×2	3.210(2)
Sb3–O1×2	2.194(1)		
Sb3–O2	1.924(5)		
Sb4–O3	2.156(6)		
Sb4–S2	2.427(2)		
Sb4–S5	2.427(2)		

Table S3. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ at 180 K

Label	x	y	z	Occupancy	U_{eq}^*
Sb1	0.55102(6)	0.75	0.91152(2)	0.308(4)	0.01946(17)
Pb1	0.55102(6)	0.75	0.91152(2)	0.692(4)	0.01946(17)
Sb2	0.06872(7)	0.25	0.91611(3)	0.693(4)	0.0214(2)
Pb2	0.06872(7)	0.25	0.91611(3)	0.307(4)	0.0214(2)
Sb3	0.86372(7)	1.25	0.44917(3)	1	0.00496(14)
Sb4	0.65187(9)	0.25	0.74451(3)	1	0.0294(2)
Sr1	0.83441(10)	0.25	0.26894(3)	0.7500(1)	0.02264(18)
Pb3	0.83441(10)	0.25	0.26894(3)	0.2500(1)	0.02264(18)
Sr2	0.63459(10)	0.75	0.57196(4)	1	0.00790(18)
S1	0.3123(3)	0.25	0.83687(11)	1	0.0125(4)
S2	0.8892(3)	0.25	0.66875(11)	1	0.0126(4)
S3	0.2917(3)	0.75	1.00199(12)	1	0.0217(5)
S4	-0.0824(3)	-0.25	0.84604(12)	1	0.0252(6)
S5	0.4077(3)	0.25	0.65512(12)	1	0.0312(7)
O1	0.9056(7)	0.75	0.4867(3)	1	0.0060(11)
O2	0.6600(7)	0.25	0.5015(3)	1	0.0066(11)
O3	0.570(2)	-0.25	0.7299(11)	0.5	0.051(5)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Anisotropic displacement parameters (\AA^2) of $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$ at 180 K

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb1	0.0170(3)	0.0147(3)	0.0266(3)	0	0.00196(18)	0
Pb1	0.0170(3)	0.0147(3)	0.0266(3)	0	0.00196(18)	0
Sb2	0.0172(3)	0.0237(3)	0.0238(3)	0	0.0053(2)	0
Pb2	0.0172(3)	0.0237(3)	0.0238(3)	0	0.0053(2)	0
Sb3	0.0033(3)	0.0057(3)	0.0061(3)	0	0.0013(2)	0
Sb4	0.0100(3)	0.0698(6)	0.0087(3)	0	0.0022(2)	0
Sr1	0.0381(4)	0.0125(3)	0.0159(3)	0	-0.0058(3)	0
Pb3	0.0381(4)	0.0125(3)	0.0159(3)	0	-0.0058(3)	0
Sr2	0.0063(4)	0.0065(4)	0.0108(4)	0	0.0003(3)	0
S1	0.0126(10)	0.0143(11)	0.0111(10)	0	0.0040(8)	0
S2	0.0092(10)	0.0187(12)	0.0104(9)	0	0.0028(8)	0
S3	0.0158(12)	0.0297(14)	0.0207(12)	0	0.0070(9)	0
S4	0.0140(12)	0.0460(17)	0.0158(11)	0	0.0028(9)	0
S5	0.0097(11)	0.072(2)	0.0124(11)	0	0.0026(9)	0
O1	0.006(3)	0.002(3)	0.010(3)	0	-0.001(2)	0
O2	0.003(3)	0.008(3)	0.009(3)	0	0.002(2)	0
O3	0.042(11)	0.011(8)	0.099(16)	0	-0.004(10)	0

Table S5. XPS binding energy of elements in $\text{Sr}_{3.5}\text{Pb}_{2.5}\text{Sb}_6\text{O}_5\text{S}_{10}$

Element	Binding energy (eV)
Sr	135.24 ($3d_{3/2}$) 133.51 ($3d_{5/2}$)
Pb	142.64 ($4f_{5/2}$), 137.78 ($4f_{7/2}$)
Sb	538.84 and 539.38 ($3d_{3/2}$), 529.45 and 530.12 ($3d_{5/2}$)
O	532.16 (1s)
S	162.24 ($2p_{1/2}$), 161.07 ($2p_{3/2}$)

Reference

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