

Supporting Information

BaPbSi₂O₆·BaSO₄: The first mixed anionic compound synthesized via BaSO₄ salt-inclusion

(Supporting Information: 17 pages)

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Experimental Section

Solid State Synthesis. Polycrystalline samples were synthesized by traditional solid-state reaction techniques. The starting chemicals were BaSO₄ (Tianjin Baishi Chemical Co., Ltd., 99.0%), BaCO₃ (Tianjin Damao Chemical Industry Co., Ltd., 98.0 %), PbO (Tianjin Damao Chemical Industry Co., Ltd., 99.5 %), and SiO₂ (Tianjin Hongyan Chemical Co., Ltd., 99.0%). A stoichiometric ratio of BaCO₃, PbO, and SiO₂ was mixed thoroughly in an agate mortar and packed into an alumina crucible. The mixture was heated to 650 °C at a rate of 5 °C/min, and dwelled at this temperature for 24 h. After that, the mixture was allowed to cool to room temperature and ground. Then, the reaction mixture with additional 20% PbO was heated to 845 °C, and calcined at 845 °C for 72 h with several intermediate grindings until a single-phase powder of BaPbSi₂O₆ was obtained. Stoichiometric mixtures of BaPbSi₂O₆ and BaSO₄ were initially ground thoroughly in an agate mortar and packed into an alumina crucible. The temperature was raised to 885 °C at a rate of 2 °C/min, and calcined at 885 °C for 72 h with several intermediate grindings until a single-phase powder of BaPbSi₂O₆·BaSO₄ was obtained.

Powder XRD. The powder XRD data were collected at room temperature in the angular range of $2\theta = 10\text{-}70^\circ$ with a scan step width of 0.02 and a fixed counting time of 1 s/step using an automated Bruker D2 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Single Crystal Growth. Single crystals of two compounds were obtained by high temperature solution method.

BaPbSi₂O₆. Reaction mixtures of BaF₂, PbO, SiO₂ and H₃BO₃ at a molar ratio of 1:6:1:2 were ground carefully to homogeneity in an agate mortar, and then transferred to a platinum crucible. The platinum crucible was put into a vertical, programmable temperature furnace under air, and then the furnace was heated up to 920 °C and kept at this temperature for 10 h. After then, the furnace was cooled down to 700 °C at a rate of 2 °C/h, and then cooled down to room temperature at a rate of 10 °C/h. Colorless and block-shaped crystals were found in the crucible.

BaPbSi₂O₆·BaSO₄. A mixture of BaPbSi₂O₆, BaSO₄, PbF₂ and H₃BO₃ at a molar ratio of 1:1:8:3 was ground carefully to homogeneity in an agate mortar, and then transferred to a platinum crucible. The platinum crucible was put into a vertical, programmable temperature furnace under air, and then the furnace was heated up to 980 °C and kept at this temperature for 10 h. After then, the furnace was cooled down to 700 °C at a rate of 2 °C/h, and then cooled down to room temperature at a rate of 10 °C/h. Colorless and block-shaped crystals were found in the crucible.

Single-crystal X-ray Diffraction. Transparent crystals (dimensions 0.054 mm × 0.091 mm × 0.096 mm for BaPbSi₂O₆ and 0.039 mm × 0.077 mm × 0.105 mm for BaPbSi₂O₆·BaSO₄) were selected under microscope, and then glued on an end of a glass fiber for single crystal X-ray determination study, respectively. The diffraction data were collected at room temperature on a Bruker Smart APEX II single crystal diffractometer equipped with a 4K CCD-detector (graphite Mo K α radiation, $\lambda = 0.71073$ Å). Data were collected and integrated with the *SAINTE-Plus* program.¹ The numerical absorption corrections were carried out using the SADABS program for area detector.² All refinements were completed with programs from the *SHELXTL-97* crystallographic software package.³ The structure was solved by direct methods, and all of the atoms were refined using full matrix least-squares techniques with anisotropic thermal parameters and final converged for $F_o^2 \geq 2\sigma(F_o^2)$. The structure was checked for missing symmetry elements with *PLATON*,⁴ and no additional symmetry was found. Relevant crystallographic data are listed in Table S1, the final atomic coordinates with equivalent isotropic displacements and bond valence analysis for both compounds are given in Table S2, and selected bond lengths are given in Table S3 in the Supporting Information.

Thermal Analysis. The thermal analyses of two compounds were carried out on NETZSCH STA 449C simultaneous analyser. The samples of BaPbSi₂O₆ and BaPbSi₂O₆·BaSO₄ were placed in a platinum crucible, and heated at a rate of 5 °C/min from room temperature to 1400 °C under flowing nitrogen, respectively.

Infrared Spectroscopy. The IR absorption spectra of BaPbSi₂O₆ and

BaPbSi₂O₆·BaSO₄ were recorded on the Shimadzu IRAffinity-1 FTIR spectrometer with a resolution of 2 cm⁻¹ in the range of 4000-400 cm⁻¹, respectively. The samples for this study were from ground polycrystalline materials that were pressed into discs with KBr (1 mg of the sample and 100 mg of KBr).

UV-Vis-NIR Diffuse Reflectance Spectroscopy. UV-Vis-NIR diffuse reflectance data for BaPbSi₂O₆ and BaPbSi₂O₆·BaSO₄ were collected using a SolidSpec-3700DUV spectrophotometer equipped with an integrating sphere over the spectral range 190-2600 nm, and reflectance spectra were converted to absorbance with the Kubelka-Munk function, respectively.

Electronic Structure. The energy band structure calculations were performed to give further understanding and interpretation of the electrical and optical properties of two compounds. The crystallographic data used were from the single crystal X-ray diffraction. The CASTEP module as implemented in Material Studio 5.5 was employed in our calculations. The total plane-wave pseudopotential method formed the basis of the CASTEP calculations.⁵ Norm-conserving pseudopotentials were chosen and the valence electrons were 5d¹⁰6s²6p² electrons for Pb, 5p⁶6s²6d electrons for Ba, 3s²3p⁴ electrons for S, 3s²3p² electrons for Si, and 2s²2p⁴ electrons for O. The exchange-correlation effects were treated within the Local-Density Approximation (LDA) using Ceperley and Alder-Perdew and Zunger (CA-PZ) functional.⁶ The plane-wave basis set energy cutoff was set at both 850.0 eV. The Monkhorst-Pack scheme *k*-point grid was set at 4 × 4 × 4 for the Brillouin zone. Total energy tolerance was 2 × 10⁻⁶ eV/atom.

Table S1 Crystal data and structure refinements for BaPbSi₂O₆ and BaPbSi₂O₆·BaSO₄.

Empirical formula	BaPbSi ₂ O ₆	BaPbSi ₂ O ₆ ·BaSO ₄
Formula weight	496.71	730.11
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, Space group	Orthorhombic, <i>Cmcm</i>	Orthorhombic, <i>Pnma</i>
<i>a</i> (Å)	5.5092(17)	7.2520(11)
<i>b</i> (Å)	15.450(5)	5.4841(8)
<i>c</i> (Å)	7.287(2)	24.352(4)
Volume (Å ³)	620.2(3)	968.5(2)
<i>Z</i> , Calculated density(Mg/m ³)	4, 5.319	4, 5.007
<i>F</i> (000)	856	1272
Cryst size (mm ³)	0.054×0.091×0.096	0.039×0.077×0.105
Limiting indices	-7≤ <i>h</i> ≤7, -20≤ <i>k</i> ≤9, -9≤ <i>l</i> ≤9	-9≤ <i>h</i> ≤6, -7≤ <i>k</i> ≤6, -29≤ <i>l</i> ≤31
Reflections collected / unique	1879/427	5705/1229
Completeness to θ (°, %)	27.55, 99.8	27.51, 99.8
Data / restraints / parameters	427/6/33	1229/18/89
Goodness-of-fit on F^2	1.061	1.029
Final <i>R</i> indices [$F_o^2 > 2\sigma(F_o^2)$] ^a	$R_1 = 0.0202$, $wR_2 = 0.0474$	$R_1 = 0.0297$, $wR_2 = 0.0566$
<i>R</i> indices (all data) ^a	$R_1 = 0.0238$, $wR_2 = 0.0494$	$R_1 = 0.0440$, $wR_2 = 0.0608$
Largest diff. peak, hole (e·Å ⁻³)	1.413 and -1.506	1.543 and -1.432

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ and } wR_2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w F_o^4}]^{1/2} \text{ for } F_o^2 > 2\sigma(F_o^2)$$

Table S2 Atomic coordinates, equivalent isotropic displacement parameters (\AA^2) and bond valence sum for $\text{BaPbSi}_2\text{O}_6$ and $\text{BaPbSi}_2\text{O}_6 \cdot \text{BaSO}_4$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyckoff positions	x	y	z	$U(eq)$	BVS
BaPbSi₂O₆						
Ba1	4 <i>c</i>	0	0.7808(1)	0.2500	0.010(1)	1.940
Pb1	4 <i>c</i>	0.5000	0.5737(1)	0.2500	0.011(1)	2.256
Si1	8 <i>f</i>	0	0.6036(1)	0.5303(3)	0.009(1)	4.125
O1	4 <i>c</i>	0	0.6232(6)	0.7500	0.034(2)	2.178
O2	16 <i>h</i>	0.7578(6)	0.6466(2)	0.4494(5)	0.016(1)	2.056
O3	4 <i>b</i>	0	0.5000	0.5000	0.024(2)	2.044
BaPbSi₂O₆ · BaSO₄						
Ba1	4 <i>c</i>	0.1391(1)	0.2500	0.1099(1)	0.012(1)	1.964
Ba2	4 <i>c</i>	0.6607(1)	0.7500	0.0710(1)	0.010(1)	2.052
Pb1	4 <i>c</i>	0.6451(1)	0.2500	0.2027(1)	0.012(1)	2.274
S1	4 <i>c</i>	0.2093(4)	0.7500	0.0141(1)	0.011(1)	6.109
Si1	4 <i>c</i>	0.8713(4)	0.7500	0.3177(2)	0.010(1)	4.250
Si2	4 <i>c</i>	0.9343(4)	0.7500	0.1864(1)	0.009(1)	4.210
O1	8 <i>d</i>	0.8508(8)	0.9901(9)	0.1593(2)	0.019(1)	2.111
O2	8 <i>d</i>	0.3160(7)	0.9682(9)	0.0296(2)	0.015(1)	2.098
O3	4 <i>c</i>	0.6539(12)	0.7500	0.3264(4)	0.041(3)	2.291
O4	4 <i>c</i>	0.1859(11)	0.7500	-0.0460(3)	0.021(2)	2.012
O5	4 <i>c</i>	0.0341(12)	0.7500	0.0425(4)	0.025(2)	1.999
O6	8 <i>d</i>	0.9491(8)	0.9928(8)	0.3456(2)	0.019(1)	2.049
O7	4 <i>c</i>	0.9122(11)	0.7500	0.2523(3)	0.023(2)	2.011

Table S3 Selected bond lengths (Å) of BaPbSi₂O₆ and BaPbSi₂O₆·BaSO₄.

Atom	Contact	Distance
BaPbSi ₂ O ₆		
Ba1	O1 ^{#7}	3.129(5)
	O1 ^{#11}	3.129(5)
	O2 ^{#1}	2.861(4)
	O2 ^{#2}	2.861(4)
	O2 ^{#5}	2.841(4)
	O2 ^{#6}	2.841(4)
	O2 ^{#7}	2.841(4)
	O2 ^{#8}	2.841(4)
	O2 ^{#9}	2.861(4)
	O2 ^{#10}	2.861(4)
Pb1	O2	2.324(4)
	O2 ^{#1}	2.324(4)
	O2 ^{#2}	2.324(4)
	O2 ^{#3}	2.324(4)
Si1	O1	1.629(3)
	O2	1.603(4)
	O2 ^{#12}	1.603(4)
	O3	1.616(2)
Symmetry: #1) -x+1,y,-z+1/2; #2) -x+1,y,z; #3) x,y,-z+1/2; #5) x-1/2,-y+3/2,-z+1; #6) -x+1/2,-y+3/2,z-1/2; #7) -x+1/2,-y+3/2,-z+1; #8) x-1/2,-y+3/2,z-1/2; #9) x-1,y,-z+1/2; #10) x-1,y,z; #11) -x+3/2,-y+3/2,-z+1; #12) -x+2,y,z.		
BaPbSi ₂ O ₆ ·BaSO ₄		
Ba1	O1	2.801(6)
	O1 ^{#1}	2.801(6)
	O2	2.803(5)
	O2 ^{#1}	2.803(5)
	O3 ^{#7}	3.153(5)
	O3 ^{#8}	3.153(5)
	O4 ^{#5}	2.823(8)
	O5	3.285(5)
	O5 ^{#4}	3.285(5)
	O6 ^{#6}	2.867(6)
O6 ^{#7}	2.867(6)	
Ba2	O1	2.874(6)
	O1 ^{#10}	2.342(11)
	O2 ^{#5}	2.901(5)
	O2 ^{#11}	2.901(5)
	O2 ^{#12}	2.949(5)
	O2 ^{#13}	2.949(5)

	O4 ^{#5}	3.021(3)
	O4 ^{#14}	3.021(3)
	O5	2.795(8)
	O6 ^{#2}	2.873(6)
	O6 ^{#9}	2.873(6)
Pb1	O1	2.234(11)
	O1 ^{#1}	2.300(12)
	O6 ^{#2}	2.520(13)
	O6 ^{#3}	2.714(12)
S1	O2	1.475(5)
	O2 ^{#10}	1.475(5)
	O4	1.473(9)
	O5	1.447(8)
Si1	O3	1.590(9)
	O6	1.598(5)
	O6 ^{#10}	1.598(5)
	O7	1.621(9)
Si2	O1	1.593(5)
	O1 ^{#10}	1.593(5)
	O3 ^{#7}	1.623(9)
	O7	1.612(9)

Symmetry: #1) $x, -y+5/2, z$; #2) $x-1/2, y, -z+1/2$; #3) $x-1/2, -y+5/2, -z+1/2$; #4) $x, y+1, z$; #5) $-x+2, -y+2, -z$; #6) $x+1/2, -y+5/2, -z+1/2$; #7) $x+1/2, y, -z+1/2$; #8) $x+1/2, y+1, -z+1/2$; #9) $x-1/2, -y+3/2, -z+1/2$; #10) $x, -y+3/2, z$; #11) $-x+2, y-1/2, -z$; #12) $x-1, -y+3/2, z$; #13) $x-1, y, z$; #14) $-x+2, -y+1, -z$.

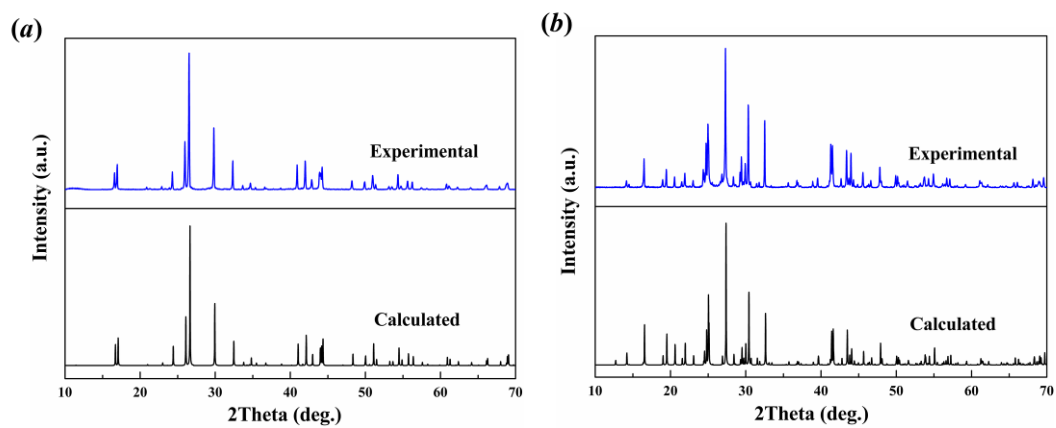


Fig. S1 Experimental and calculated XRD patterns of (a) BaPbSi₂O₆; and (b) BaPbSi₂O₆·BaSO₄.

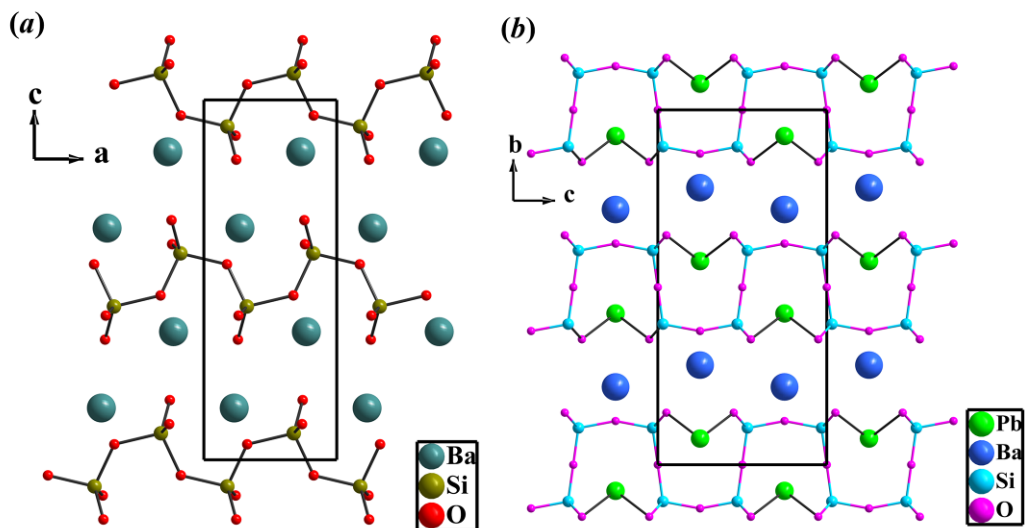


Fig. S2 The whole structures of (a) BaSiO₃ viewed along [010] direction; and (b) BaPbSi₂O₆ viewed along [100] direction.

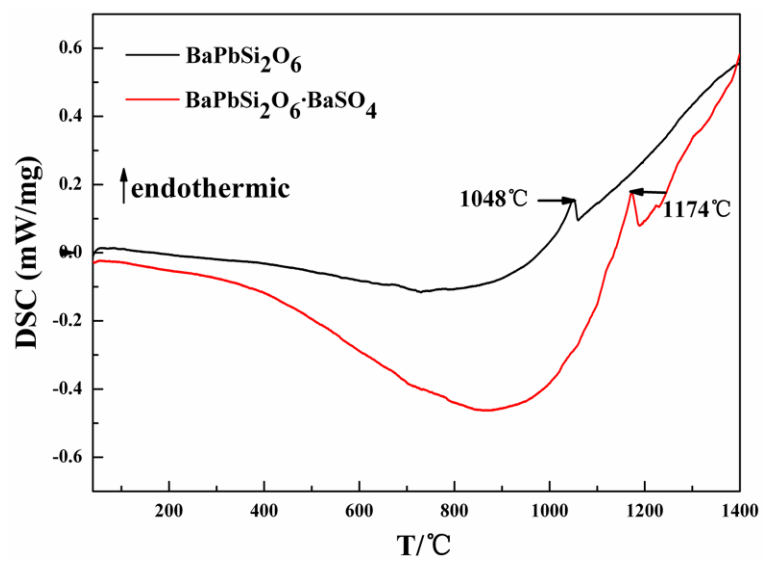


Fig. S3 DSC curves of BaPbSi₂O₆ and BaPbSi₂O₆·BaSO₄.

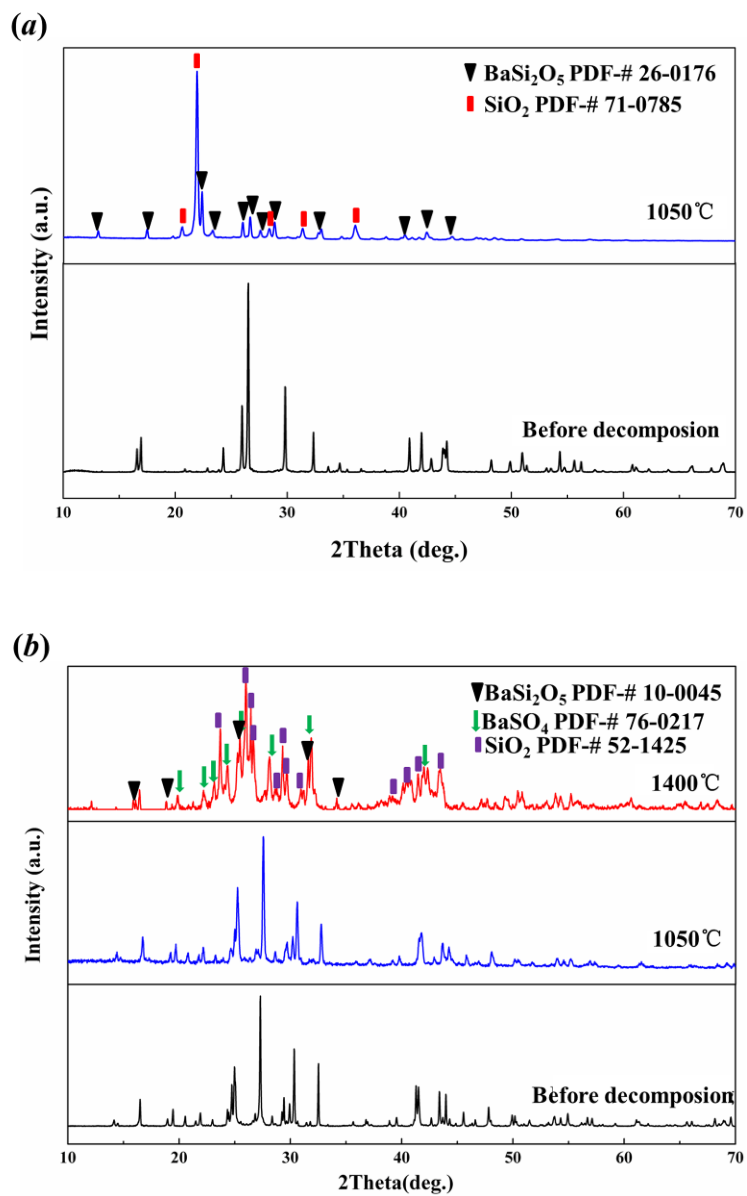


Fig. S4 The XRD patterns of (a) BaPbSi₂O₆; and (b) BaPbSi₂O₆·BaSO₄ before and after decomposition.

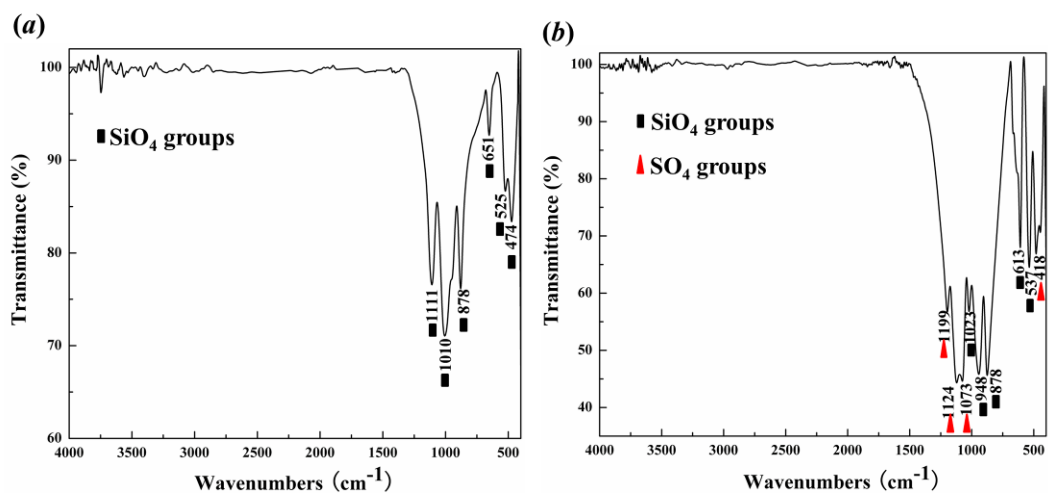


Fig. S5 IR spectra of (a) $\text{BaPbSi}_2\text{O}_6$ and (b) $\text{BaPbSi}_2\text{O}_6 \cdot \text{BaSO}_4$.

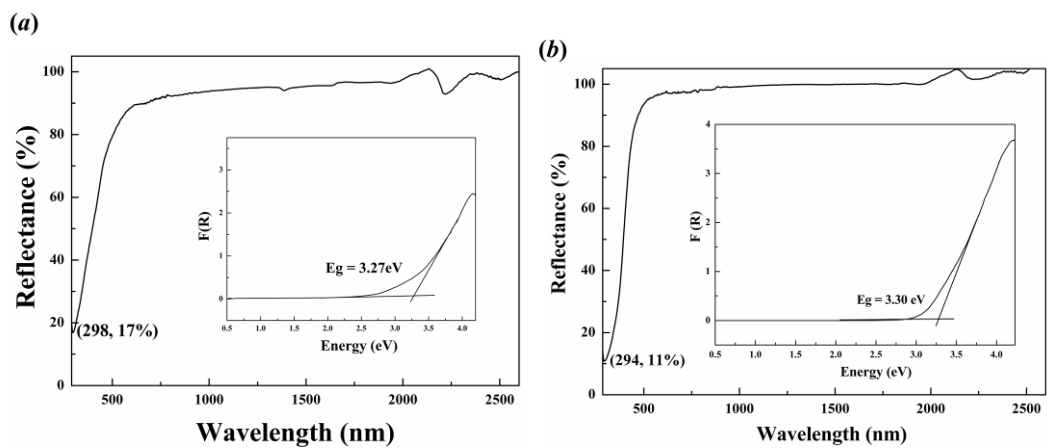


Fig. S6 UV-Vis-NIR diffuse reflectance spectra of (a) BaPbSi₂O₆; and (b) BaPbSi₂O₆·BaSO₄.

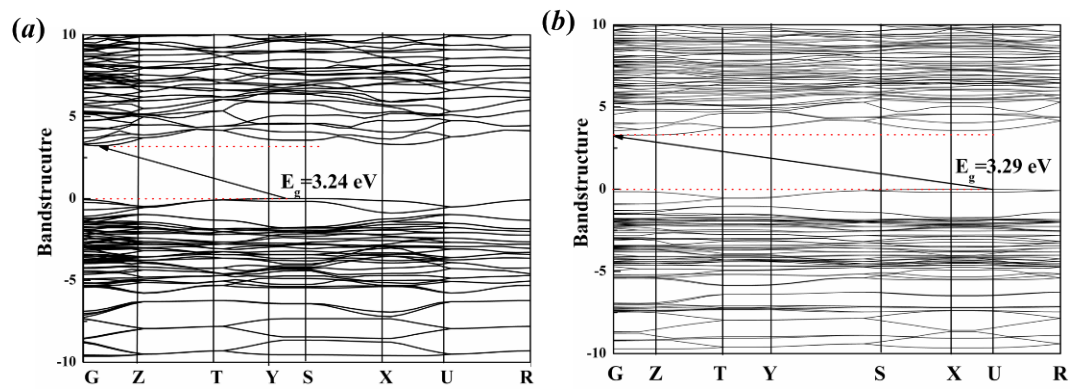


Fig. S7 Electronic band structures of (a) $\text{BaPbSi}_2\text{O}_6$; and (b) $\text{BaPbSi}_2\text{O}_6 \cdot \text{BaSO}_4$.

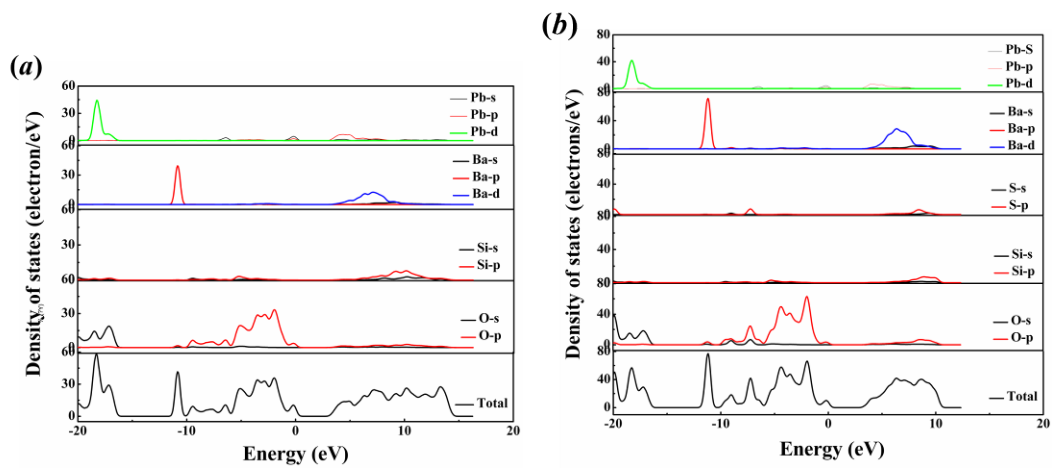


Fig. S8 Total and partial density of states of (a) BaPbSi₂O₆; and (b) BaPbSi₂O₆·BaSO₄.

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