$Na_2PbB_6O_{10}SO_4$ and $Ca_{2.58}Pb_{0.42}B_6O_{11}SO_4$: First Borate-Sulfates Featuring 3D Porous Borate Anionic Frameworks

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Characterization. Powder XRD data were collected with a Bruker D2 PHASER diffractometer (Cu Kα radiation with λ = 1.5418 Å, 2θ = 10 - 70 °). The single-crystal XRD data were collected on a Bruker SMART APEX II 4K CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at room temperature. Data integration, cell refinement, and absorption corrections were carried out with the SAINT program.[1] The structure was solved by direct method and refined using the SHELXTL program.[2] Thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out on a simultaneous NETZSCH STA 449 F3 thermal analyzer instrument in a flowing N_2 atmosphere. The sample was placed in a Pt crucible and was heated from 40 to 800 °C at a rate of 5 °C min^{-1}. Infrared spectroscopy was carried out on a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in the 400-4000 cm^{-1} range. UV-vis-NIR diffuse-reflectance spectroscopy data in the wavelength range of 270-1200 nm were recorded on a Shimadzu SolidSpec–3700DUV spectrophotometer.

Theoretical calculation. The plane-wave pseudopotential method was implemented through the CASTEP code[3] to solve the electronic structure of **I** and **II** with the Perdew-Burke-Ernzerhof (PBE) functional of generalized gradient approximation (GGA).[4] The

optimized norm-conserving pseudopotential (NCP)[5] was applied to simulate ion-electron interactions for all elements of Na, Pb, B, S, and O in **I** and Ca, Pb, B, S, and O in **II**. The valence electron configuration was set as Na $2s^2$ $2p^6$ $3s^1$, Pb $5d^{10}$ $6s^2$ $6p^2$, B $2s^2$ $2p^1$, S $2s^2$ $2p^4$ and O $2s^2$ $2p^4$ in **I** and Ca $3d^{10}$ $4s^2$, Pb $5d^{10}$ $6s^2$ $6p^2$, B $2s^2$ $2p^1$, S $2s^2$ $2p^4$ and O $2s^2$ $2p^4$ in **II**. The plane-wave energy cutoff was set as 900 eV and the Brillouin zone numerical integration was executed with 4 × 1 × 3. The pseudo-symmetric structure of **I** and **II** is structural relaxation, and the lattice constants are fixed in the corresponding experimental structure. We kept the default values of the CASTEP code on the aspect of the other calculation parameters and convergent criteria.

The calculations of the linear optical properties were described in terms of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega)$ was calculated from the momentum matrix elements between the occupied and unoccupied electronic states:

$$\varepsilon_2(\mathrm{h}\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{kcv}\left|\langle\psi_k^C|\hat{u}\cdot r|\psi_k^C\rangle\right|^2\delta\left[E_k^c - E_k^v - E\right]$$

Here Ω is the volume of the unit cell, and *v* and *c* represent the valence band (VB) and conduction band (CB), respectively. ω and $\hat{u}$ are the frequency and the unit vector in the polarization direction of the incident light. Under the periodic boundary condition, $\left|\langle\psi_k^C|\hat{u}\cdot r|\psi_k^C\rangle\right|$ is the transition matrix element between the VB and the CB at a specific *k* point in the first Brillouin zone. The real part $\varepsilon_1(\omega)$ can be obtained from the imaginary part $\varepsilon_2(\omega)$ using the Kramers–Kronig transformation. The refractive indexes *n* and birefringence Δn can be obtained from the complex dielectric function.

To balance the calculation efficiency and accuracy of the optical properties under a high-density k-mesh, the GGA and scissors-corrected methods were adopted. The number of empty bands required to achieve converging results for the optical properties was set at three times that of VBs.

Table S1. Study on Anhydrous Inorganic Borate-sulfates.

	Compounds	space group, crystal system	Units	FBBs	FBB Configuration Type and Anion Frame Dimension	Band gap/eV exp. band gaps[a]	GGA[b]	Δn (at 1064 nm)	Rfes.
1	**$Mg_3(OH)_2(SO_4)[B(OH)_4]_2$**	/	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[6]
2	**$Pb_6O_2(BO_3)_2(SO_4)$**	Orthoborate, *Pnma*	$[BO_3]$, and $[SO_4]$	$[BO_3]$, and $[SO_4]$	**isolated, 0**	/		/	[7]
3	**$Mg_3[B(OH)_4]_2(SO_4)(OH)F$**	/	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[8]
4	**$Ca_6(Al,Si)_2(SO_4)_2[B(OH)_4](OH,O)_{12}\cdot 26H_2O$**	hexagonal, *P*3l*c*	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[9]
5	**$La(SO_4)[B(OH)_4](H_2O)$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
6	**$Sm(SO_4)[B(OH)_4](H_2O)$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	4.66		/	[10]
7	**$Eu(SO_4)[B(OH)_4](H_2O)$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	4.53		/	[10]
8	**$Pr(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
9	**$Nd(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
10	**$Sm(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	4.62		/	[10]
11	**$Eu(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and	$[SO_4]$ and	**isolated, 0**	4.50 eV		/	[10]

12	**$Gd(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[B(OH)_4]$ $[SO_4]$ and $[B(OH)_4]$	$[B(OH)_4]$ $[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
13	**$Tb(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
14	**$Dy(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
15	**$Ho(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
16	**$Er(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
17	**$Tm(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
18	**$Yb(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[12]
19	**$Lu(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
20	**$Y(SO_4)[B(OH)_4](H_2O)_2$**	triclinic, $P\bar{1}$	$[SO_4]$ and $[B(OH)_4]$	$[SO_4]$ and $[B(OH)_4]$	**isolated, 0**	/		/	[10]
21	**$Pb_4(BO_3)_2(SO_4)$**	monoclinic, $P2_1/c$	$[BO_3]$, $[SO_4]$	$[BO_3]$, $[SO_4]$	**isolated, 0**	4.03	3.15	/	[11]
22	**$Pb_2[(BO_2)(OH)](SO_4)$**	monoclinic, $P2_1/m$	$[BO_3]$, $[SO_4]$	$[BO_3]$, $[SO_4]$	**isolated, 0**	4.08		/	[11]
23	**$La_2B_3O_4(OH)_3(SO_4)_2$**	orthorhombic, $Pna2_1$	$[BO_3]$, $[BO_3(OH)]$	$[B_3O_4(OH)_3]$, $[SO_4]$	**chain, 1D**		5.39	/	[12]
24	**$Ca_3Na_2Cl(SO_4)_2B_5O_8(OH)$**	monoclinic	$[BO_3]$, $[BO_4]$,	$[B_5O_8]$	**layered, 2**		/	/	[13]

	$_2$		$[BO_3(OH)]$, and $[SO_4]$					
25	**$Rb_3H(SO_4)_2(B_2O_3)_2$**	hexagonal	$[BO_3]$, $[SO_4]/[HSO_4]$	$[B_3O_6]$, $[SO_4]/[HSO_4]$	**layered, 2**	/	/	[14]
26	**$Cs_3H(SO_4)_2(B_2O_3)_2$**	hexagonal	$[BO_3]$, $[SO_4]/[HSO_4]$	$[B_3O_6]$, $[SO_4]/[HSO_4]$	**layered, 2**	/	/	[14]
27	**$Na_2PbB_6O_{10}SO_4$ (I)**	orthorhombic, *Pnma*	$[BO_3]$, $[BO_4]$, $[SO_4]$	$[B_6O_{13}]$, $[SO_4]$	**3D**	4.83	0.035	this work
28	**$Ca_{2.58}Pb_{0.42}B_6O_{11}SO_4$ (II)**	monoclinic, *P*121/*c*1	$[BO_3]$, $[BO_4]$, $[SO_4]$	$[B_7O_{17}]$, $[SO_4]$	**3D**	4.48	0.017	this work

/not mentioned in the article; 3D: three-dimensional framework; [a]experimental band gaps; [b]Calculated by using the generalized gradient approximation (GGA-PBE).

Table S2. Crystallographic data for *Pnma* and $P12_1/c1$ for **I**, and **II**.

Empirical formula	**I**	**II**
Formula weight	574.09	527.35
Wavelength (Å)	0.71073	0.71073
Temperature (K)	300.0	300.0
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma* (No. 62)	$P12_1/c1$ (No. 14)
a / Å	12.9566(8)	6.4716(2)
b / Å	9.9289(6)	17.2900(4)
c / Å	7.8800(5)	9.1455(3)
α / °	90	90
β / °	90	90.4110(10)
γ / °	90	90
Volume /Å^3	1013.72(11)	1023.30(5)
Z, ρ_{calcd} / g·cm^{-3}	4, 3.762	4, 3.423
μ / mm^{-1}	17.030	8.594
F(000)	1048	1008
Theta range for data collection	3.026 to 27.495	2.356 to 27.515
Limiting indices	$-16 \le h \le 16$, $-12 \le k \le 12$, $-10 \le l \le 9$	$-8 \le h \le 8$, $-22 \le k \le 22$, $-11 \le l \le 11$
Reflections collected / unique	8071 / 1240 [R_{int} = 0.0793]	15814 / 2321 [R_{int} = 0.0623]
Completeness / %	99.9 %	98.2 %
Data / restraints / parameters	1240 / 0 / 124	2321 / 0 / 227
Goodness-of-fit on F^2	1.068	1.080
Final R indices [I>2sigma(I)][a]	R_1 = 0.0275, wR_2 = 0.0558	R_1 = 0.0192, wR_2 = 0.0414
R indices (all data)[a]	R_1 = 0.0342, wR_2 = 0.0599	R_1 = 0.0204, wR_2 = 0.0419
Largest diff. peak and hole/ e·Å^{-3}	1.177 and -1.065	0.457 and -0.482

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

Table S3. The atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2× 10^3) for $Na_2PbB_6O_{10}SO_4$, and $Ca_{2.58}Pb_{0.42}B_6O_{11}SO_4$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the bond valence sum (BVS) for each atom in asymmetric unit.

Atom	Wyck. Site	x	y	z	S.O.F.	U_{eq} [a]	BVS[b]
			$Na_2PbB_6O_{10}SO_4$				
Na1	4*b*	10000	5000	5000		29(1)	0.9
Na2	4*a*	5000	5000	5000		34(1)	0.9
Pb1	4*c*	8003(1)	7500	6907(1)		13(1)	1.9
B1	8*d*	7366(5)	4808(6)	5185(8)		7(1)	3.1
B2	8*d*	6702(5)	6194(6)	2640(8)		7(1)	3.0
B3	4*c*	5063(7)	7500	2821(12)		8(2)	3.0
B4	4*c*	3191(7)	7500	3958(13)		10(2)	3.1
S1	4*c*	10568(2)	7500	7128(3)		12(1)	6.2
O1	8*d*	11211(4)	8707(4)	7068(7)		30(1)	1.9
O2	4*c*	9957(5)	7500	8681(9)		29(2)	1.7
O3	4*c*	9865(5)	7500	5660(9)		22(1)	2.0
O4	8*d*	8097(3)	4889(3)	6421(5)		9(1)	2.1
O5	8*d*	7220(3)	5953(3)	4257(5)		10(1)	2.0
O6	8*d*	6784(3)	3688(3)	4940(5)		10(1)	2.1
O7	8*d*	5596(3)	6300(4)	2801(5)		10(1)	2.2
O8	4*c*	4017(4)	7500	2761(8)		12(1)	1.9
O9	4*c*	2149(4)	7500	3064(7)		6(1)	2.0
			$Ca_{2.58}Pb_{0.42}B_6O_{11}SO_4$				
Ca(1)	4*e*	8749(1)	4922(1)	6836(1)		8(1)	2.0
Ca(2)	4*e*	1626(1)	2304(1)	7455(1)		11(1)	2.1
Ca(3)/ Pb(1)	4*e*	-3466(1)	3772(1)	336(1)	0.5798/0.4202	11(1)	1.8
B(1)	4*e*	3751(4)	4972(1)	6461(3)		8(1)	3.1
B(2)	4*e*	5154(4)	3623(1)	6579(3)		9(1)	3.1
B(3)	4*e*	1840(4)	3823(1)	5426(3)		9(1)	3.0

B(4)	4*e*	5053(4)	3609(1)	3705(3)	9(1)	3.0
B(5)	4*e*	-1750(4)	3052(1)	5116(3)	8(1)	3.1
B(6)	4*e*	-2921(4)	2481(1)	2615(3)	9(1)	3.0
S(1)	4*e*	11486(1)	4044(1)	10008(1)	14(1)	6.0
O(1)	4*e*	13095(3)	4642(1)	10003(3)	32(1)	1.8
O(2)	4*e*	12467(3)	3275(1)	9944(2)	21(1)	1.9
O(3)	4*e*	10327(3)	4087(1)	11403(2)	18(1)	2.0
O(4)	4*e*	10005(3)	4148(1)	8811(2)	19(1)	2.0
O(5)	4*e*	6328(2)	3311(1)	7757(2)	9(1)	2.0
O(6)	4*e*	6075(2)	3392(1)	5119(2)	9(1)	2.0
O(7)	4*e*	2993(2)	3418(1)	6526(2)	9(1)	2.1
O(8)	4*e*	5379(2)	4485(1)	6687(2)	11(1)	2.1
O(9)	4*e*	3897(3)	5712(1)	6934(2)	12(1)	1.9
O(10)	4*e*	1989(2)	4711(1)	5786(2)	10(1)	2.0
O(11)	4*e*	5258(2)	3007(1)	2619(2)	10(1)	2.0
O(12)	4*e*	2825(2)	3753(1)	3962(2)	10(1)	1.9
O(13)	4*e*	-340(2)	3690(1)	5433(2)	10(1)	1.8
O(14)	4*e*	-1408(2)	2695(1)	3734(2)	10(1)	2.1
O(15)	4*e*	-1760(3)	2561(1)	1232(2)	10(1)	2.0

[a] U_{eq} is defined as one-third of the trace of the orthogonalized Uij tensor.

[b] Bond valence sums (BVS) are calculated by using the bond-valence model ($S_i = \exp[(R_o - R_i)/B]$, where R_o and B are bond valence parameters, and R_i is the length of bond.

Table S4. Selected bond lengths (Å) and bond angles (°) for $Na_2PbB_6O_{10}SO_4$, and $Ca_{2.58}Pb_{0.42}B_6O_{11}SO_4$.[a]

$Na_2PbB_6O_{10}SO_4$			
Na(1)-O(3)	2.5422(15)	Pb(1)-O(1)$^{\#8}$	2.736(5)
Na(1)-O(3)$^{\#1}$	2.5422(15)	B(1)-O(6)	1.358(7)
Na(1)-O(1)$^{\#2}$	2.601(5)	B(1)-O(4)	1.360(7)
Na(1)-O(1)$^{\#3}$	2.601(5)	B(1)-O(5)	1.365(7)
Na(1)-O(7)$^{\#4}$	2.672(4)	B(2)-O(7)	1.442(7)
Na(1)-O(7)$^{\#5}$	2.672(4)	B(2)-O(5)	1.459(7)
Na(1)-O(4)	2.710(4)	B(2)-O(4)$^{\#6}$	1.465(7)
Na(1)-O(4)$^{\#1}$	2.710(4)	B(2)-O(9)$^{\#5}$	1.525(6)
Na(2)-O(7)$^{\#7}$	2.295(4)	B(3)-O(8)	1.356(10)
Na(2)-O(7)	2.295(4)	B(3)-O(7)	1.377(6)
Na(2)-O(6)	2.654(4)	B(3)-O(7)$^{\#2}$	1.377(6)
Na(2)-O(6)$^{\#7}$	2.654(4)	B(4)-O(8)	1.426(10)
Na(2)-O(2)$^{\#8}$	2.692(3)	B(4)-O(6)$^{\#11}$	1.465(7)
Na(2)-O(2)$^{\#6}$	2.692(3)	B(4)-O(6)$^{\#7}$	1.465(7)
Pb(1)-O(3)	2.604(6)	B(4)-O(9)	1.523(10)
Pb(1)-O(4)$^{\#2}$	2.624(3)	S(1)-O(2)	1.458(7)
Pb(1)-O(4)	2.624(3)	S(1)-O(1)	1.460(4)
Pb(1)-O(6)$^{\#9}$	2.679(4)	S(1)-O(1)$^{\#2}$	1.460(4)
Pb(1)-O(6)$^{\#4}$	2.679(4)	S(1)-O(3)	1.472(7)
Pb(1)-O(1)$^{\#10}$	2.736(5)		
O(3)-Na(1)-O(3)$^{\#1}$	180.0(3)	O(3)-Pb(1)-O(4)	84.38(9)
O(3)-Na(1)-O(1)$^{\#2}$	55.35(17)	O(4)$^{\#2}$-Pb(1)-O(4)	162.37(18)
O(3)$^{\#1}$-Na(1)-O(1)$^{\#2}$	124.65(17)	O(3)-Pb(1)-O(6)$^{\#9}$	103.96(15)
O(3)-Na(1)-O(1)$^{\#3}$	124.65(17)	O(4)$^{\#2}$-Pb(1)-O(6)$^{\#9}$	71.98(11)
O(3)$^{\#1}$-Na(1)-O(1)$^{\#3}$	55.35(17)	O(4)-Pb(1)-O(6)$^{\#9}$	124.10(12)
O(1)$^{\#2}$-Na(1)-O(1)$^{\#3}$	180	O(3)-Pb(1)-O(6)$^{\#4}$	103.96(15)
O(3)-Na(1)-O(7)$^{\#4}$	106.42(17)	O(4)$^{\#2}$-Pb(1)-O(6)$^{\#4}$	124.10(12)

O(3)$^{\#1}$-Na(1)-O(7)$^{\#4}$	73.58(17)	O(4)-Pb(1)-O(6)$^{\#4}$	71.98(11)
O(1)$^{\#2}$-Na(1)-O(7)$^{\#4}$	83.98(15)	O(6)$^{\#9}$-Pb(1)-O(6)$^{\#4}$	52.23(15)
O(1)$^{\#3}$-Na(1)-O(7)$^{\#4}$	96.02(15)	O(3)-Pb(1)-O(1)$^{\#10}$	153.85(9)
O(3)-Na(1)-O(7)$^{\#5}$	73.58(17)	O(4)$^{\#2}$-Pb(1)-O(1)$^{\#10}$	121.02(13)
O(3)$^{\#1}$-Na(1)-O(7)$^{\#5}$	106.42(17)	O(4)-Pb(1)-O(1)$^{\#10}$	69.47(13)
O(1)$^{\#2}$-Na(1)-O(7)$^{\#5}$	96.02(15)	O(6)$^{\#9}$-Pb(1)-O(1)$^{\#10}$	90.98(14)
O(1)$^{\#3}$-Na(1)-O(7)$^{\#5}$	83.98(15)	O(6)$^{\#4}$-Pb(1)-O(1)$^{\#10}$	68.37(14)
O(7)$^{\#4}$-Na(1)-O(7)$^{\#5}$	180	O(3)-Pb(1)-O(1)$^{\#8}$	153.85(9)
O(3)-Na(1)-O(4)	83.84(16)	O(4)$^{\#2}$-Pb(1)-O(1)$^{\#8}$	69.47(13)
O(3)$^{\#1}$-Na(1)-O(4)	96.16(16)	O(4)-Pb(1)-O(1)$^{\#8}$	121.02(13)
O(1)$^{\#2}$-Na(1)-O(4)	108.06(15)	O(6)$^{\#9}$-Pb(1)-O(1)$^{\#8}$	68.36(14)
O(1)$^{\#3}$-Na(1)-O(4)	71.94(15)	O(6)$^{\#4}$-Pb(1)-O(1)$^{\#8}$	90.98(14)
O(7)$^{\#4}$-Na(1)-O(4)	51.37(11)	O(1)$^{\#10}$-Pb(1)-O(1)$^{\#8}$	51.98(18)
O(7)$^{\#5}$-Na(1)-O(4)	128.63(11)	O(6)-B(1)-O(4)	122.5(5)
O(3)-Na(1)-O(4)$^{\#1}$	96.17(16)	O(6)-B(1)-O(5)	121.9(5)
O(3)$^{\#1}$-Na(1)-O(4)$^{\#1}$	83.83(16)	O(4)-B(1)-O(5)	115.5(5)
O(1)$^{\#2}$-Na(1)-O(4)$^{\#1}$	71.94(15)	O(7)-B(2)-O(5)	113.1(5)
O(1)$^{\#3}$-Na(1)-O(4)$^{\#1}$	108.06(15)	O(7)-B(2)-O(4)$^{\#6}$	106.7(5)
O(7)$^{\#4}$-Na(1)-O(4)$^{\#1}$	128.63(11)	O(5)-B(2)-O(4)$^{\#6}$	111.7(4)
O(7)$^{\#5}$-Na(1)-O(4)$^{\#1}$	51.37(11)	O(7)-B(2)-O(9)$^{\#5}$	110.3(4)
O(4)-Na(1)-O(4)$^{\#1}$	180	O(5)-B(2)-O(9)$^{\#5}$	106.4(5)
O(7)$^{\#7}$-Na(2)-O(7)	180	O(4)$^{\#6}$-B(2)-O(9)$^{\#5}$	108.5(5)
O(7)$^{\#7}$-Na(2)-O(6)	91.76(12)	O(8)-B(3)-O(7)	120.1(4)
O(7)-Na(2)-O(6)	88.24(12)	O(8)-B(3)-O(7)$^{\#2}$	120.1(4)
O(7)-Na(2)-O(6)$^{\#7}$	91.76(12)	O(7)-B(3)-O(7)$^{\#2}$	119.8(7)

O(6)-Na(2)-O(6)$^{\#7}$	180	O(8)-B(4)-O(6)$^{\#11}$	112.1(4)
O(7)$^{\#7}$-Na(2)-O(2)$^{\#8}$	102.73(17)	O(8)-B(4)-O(6)$^{\#7}$	112.1(4)
O(7)-Na(2)-O(2)$^{\#8}$	77.27(17)	O(6)$^{\#11}$-B(4)-O(6)$^{\#7}$	107.2(7)
O(6)-Na(2)-O(2)$^{\#8}$	118.54(16)	O(8)-B(4)-O(9)	111.1(8)
O(6)$^{\#7}$-Na(2)-O(2)$^{\#8}$	61.46(16)	O(6)$^{\#11}$-B(4)-O(9)	107.1(4)
O(7)$^{\#7}$-Na(2)-O(2)$^{\#6}$	77.27(17)	O(6)$^{\#7}$-B(4)-O(9)	107.1(4)
O(7)-Na(2)-O(2)$^{\#6}$	102.73(17)	O(2)-S(1)-O(1)	109.7(3)
O(6)-Na(2)-O(2)$^{\#6}$	61.46(16)	O(2)-S(1)-O(1)$^{\#2}$	109.7(3)
O(6)$^{\#7}$-Na(2)-O(2)$^{\#6}$	118.54(16)	O(1)-S(1)-O(1)$^{\#2}$	110.4(4)
O(2)$^{\#8}$-Na(2)-O(2)$^{\#6}$	180	O(2)-S(1)-O(3)	108.9(4)
O(7)$^{\#7}$-Na(2)-O(6)$^{\#7}$	88.24(12)	O(1)-S(1)-O(3)	109.1(3)
O(3)-Pb(1)-O(4)$^{\#2}$	84.38(9)	O(1)$^{\#2}$-S(1)-O(3)	109.1(3)

#1 -x+2, -y+1, -z+1; #2 x, -y+3/2, z;
#3 -x+2, y-1/2, -z+1; #4 -x+3/2, -y+1, z+1/2;
#5 x+1/2, y, -z+1/2; #6 -x+3/2, -y+1, z-1/2;
#7 -x+1, -y+1, -z+1; #8 x-1/2, y, -z+3/2;
#9 -x+3/2, y+1/2, z+1/2; #10 x-1/2, -y+3/2, -z+3/2;
#11 -x+1,y+1/2,-z+1;

$Ca_{2.58}Pb_{0.42}B_6O_{11}SO_4$

Ca(1)-O(8)	2.3112(16)	Pb(1)-O(4)$^{\#7}$	2.7306(19)
Ca(1)-O(10)$^{\#1}$	2.3408(17)	Pb(1)-O(1)$^{\#3}$	2.770(2)
Ca(1)-O(4)	2.3864(18)	Pb(1)-O(2)$^{\#9}$	2.7899(19)
Ca(1)-O(3)$^{\#2}$	2.4236(18)	B(1)-O(9)	1.353(3)
Ca(1)-O(10)$^{\#3}$	2.5232(17)	B(1)-O(8)	1.363(3)
Ca(1)-O(13)$^{\#1}$	2.5577(15)	B(1)-O(10)	1.369(3)
Ca(1)-O(12)$^{\#3}$	2.6093(15)	B(2)-O(5)	1.420(3)
Ca(2)-O(7)	2.2844(15)	B(2)-O(7)	1.444(3)
Ca(2)-O(14)$^{\#4}$	2.2929(17)	B(2)-O(8)	1.501(3)
Ca(2)-O(12)$^{\#4}$	2.4145(16)	B(2)-O(6)	1.520(3)
Ca(2)-O(11)$^{\#4}$	2.4146(16)	B(3)-O(13)	1.429(3)
Ca(2)-O(15)$^{\#4}$	2.4641(17)	B(3)-O(7)	1.431(3)
Ca(2)-O(2)$^{\#5}$	2.5667(19)	B(3)-O(12)	1.491(3)

Ca(2)-O(3)$^{\#5}$	2.7217(18)	B(3)-O(10)	1.574(3)
Ca(2)-O(2)$^{\#6}$	2.877(2)	B(4)-O(11)	1.446(3)
Ca(3)-O(5)$^{\#7}$	2.4921(16)	B(4)-O(9)$^{\#3}$	1.479(3)
Ca(3)-O(15)	2.5025(15)	B(4)-O(12)	1.483(3)
Ca(3)-O(11)$^{\#6}$	2.6108(16)	B(4)-O(6)	1.497(3)
Ca(3)-O(9)$^{\#8}$	2.6676(16)	B(5)-O(14)	1.426(3)
Ca(3)-O(3)$^{\#7}$	2.6903(19)	B(5)-O(13)	1.460(3)
Ca(3)-O(1)$^{\#9}$	2.702(2)	B(5)-O(15)$^{\#4}$	1.471(3)
Ca(3)-O(4)$^{\#7}$	2.7306(19)	B(5)-O(6)$^{\#6}$	1.525(3)
Ca(3)-O(1)$^{\#3}$	2.770(2)	B(6)-O(5)$^{\#5}$	1.459(3)
Ca(3)-O(2)$^{\#9}$	2.7899(19)	B(6)-O(14)	1.459(3)
Pb(1)-O(5)$^{\#7}$	2.4921(16)	B(6)-O(15)	1.483(3)
Pb(1)-O(15)	2.5025(15)	B(6)-O(11)$^{\#6}$	1.489(3)
Pb(1)-O(11)$^{\#6}$	2.6108(16)	S(1)-O(4)	1.4611(18)
Pb(1)-O(9)$^{\#8}$	2.6676(16)	S(1)-O(1)	1.4665(19)
Pb(1)-O(3)$^{\#7}$	2.6903(19)	S(1)-O(2)	1.4757(18)
Pb(1)-O(1)$^{\#9}$	2.702(2)	S(1)-O(3)	1.4861(19)

O(8)-Ca(1)-O(10)$^{\#1}$	140.56(6)	O(9)$^{\#8}$-Ca(3)-O(2)$^{\#9}$	96.81(5)
O(8)-Ca(1)-O(4)	100.22(6)	O(3)$^{\#7}$-Ca(3)-O(2)$^{\#9}$	165.11(5)
O(10)$^{\#1}$-Ca(1)-O(4)	85.51(6)	O(1)$^{\#9}$-Ca(3)-O(2)$^{\#9}$	51.78(5)
O(8)-Ca(1)-O(3)$^{\#2}$	119.92(6)	O(4)$^{\#7}$-Ca(3)-O(2)$^{\#9}$	141.86(6)
O(10)$^{\#1}$-Ca(1)-O(3)$^{\#2}$	99.51(6)	O(1)$^{\#3}$-Ca(3)-O(2)$^{\#9}$	111.93(6)
O(4)-Ca(1)-O(3)$^{\#2}$	79.18(6)	O(5)$^{\#7}$-Pb(1)-O(15)	93.59(5)
O(8)-Ca(1)-O(10)$^{\#3}$	81.61(6)	O(5)$^{\#7}$-Pb(1)-O(11)$^{\#6}$	125.41(5)
O(10)$^{\#1}$-Ca(1)-O(10)$^{\#3}$	79.24(6)	O(15)-Pb(1)-O(11)$^{\#6}$	57.00(5)
O(4)-Ca(1)-O(10)$^{\#3}$	157.19(6)	O(5)$^{\#7}$-Pb(1)-O(9)$^{\#8}$	170.88(5)
O(3)$^{\#2}$-Ca(1)-O(10)$^{\#3}$	119.86(5)	O(15)-Pb(1)-O(9)$^{\#8}$	91.29(5)

O(8)-Ca(1)-O(13)$^{\#1}$	85.35(5)	O(11)$^{\#6}$-Pb(1)-O(9)$^{\#8}$	52.09(5)
O(10)$^{\#1}$-Ca(1)-O(13)$^{\#1}$	56.90(5)	O(5)$^{\#7}$-Pb(1)-O(3)$^{\#7}$	116.76(5)
O(4)-Ca(1)-O(13)$^{\#1}$	80.46(6)	O(15)-Pb(1)-O(3)$^{\#7}$	69.59(5)
O(3)$^{\#2}$-Ca(1)-O(13)$^{\#1}$	149.93(6)	O(11)$^{\#6}$-Pb(1)-O(3)$^{\#7}$	96.06(5)
O(10)$^{\#3}$-Ca(1)-O(13)$^{\#1}$	77.02(5)	O(9)$^{\#8}$-Pb(1)-O(3)$^{\#7}$	72.19(5)
O(8)-Ca(1)-O(12)$^{\#3}$	84.50(5)	O(5)$^{\#7}$-Pb(1)-O(1)$^{\#9}$	91.88(6)
O(10)$^{\#1}$-Ca(1)-O(12)$^{\#3}$	111.79(5)	O(15)-Pb(1)-O(1)$^{\#9}$	149.75(6)
O(4)-Ca(1)-O(12)$^{\#3}$	146.56(6)	O(11)$^{\#6}$-Pb(1)-O(1)$^{\#9}$	96.15(6)
O(3)$^{\#2}$-Ca(1)-O(12)$^{\#3}$	70.08(6)	O(9)$^{\#8}$-Pb(1)-O(1)$^{\#9}$	80.08(6)
O(10)$^{\#3}$-Ca(1)-O(12)$^{\#3}$	56.10(5)	O(3)$^{\#7}$-Pb(1)-O(1)$^{\#9}$	132.62(6)
O(13)$^{\#1}$-Ca(1)-O(12)$^{\#3}$	132.98(5)	O(5)$^{\#7}$-Pb(1)-O(4)$^{\#7}$	68.37(5)
O(7)-Ca(2)-O(14)$^{\#4}$	121.63(6)	O(15)-Pb(1)-O(4)$^{\#7}$	90.21(5)
O(7)-Ca(2)-O(12)$^{\#4}$	136.60(6)	O(11)$^{\#6}$-Pb(1)-O(4)$^{\#7}$	142.66(5)
O(14)$^{\#4}$-Ca(2)-O(12)$^{\#4}$	88.95(6)	O(9)$^{\#8}$-Pb(1)-O(4)$^{\#7}$	119.35(5)
O(7)-Ca(2)-O(11)$^{\#4}$	80.31(5)	O(3)$^{\#7}$-Pb(1)-O(4)$^{\#7}$	52.08(5)
O(14)$^{\#4}$-Ca(2)-O(11)$^{\#4}$	143.62(6)	O(1)$^{\#9}$-Pb(1)-O(4)$^{\#7}$	119.35(6)
O(12)$^{\#4}$-Ca(2)-O(11)$^{\#4}$	59.15(5)	O(5)$^{\#7}$-Pb(1)-O(1)$^{\#3}$	102.41(6)
O(7)-Ca(2)-O(15)$^{\#4}$	95.57(5)	O(15)-Pb(1)-O(1)$^{\#3}$	145.74(6)
O(14)$^{\#4}$-Ca(2)-O(15)$^{\#4}$	57.96(5)	O(11)$^{\#6}$-Pb(1)-O(1)$^{\#3}$	128.27(6)
O(12)$^{\#4}$-Ca(2)-O(15)$^{\#4}$	127.71(5)	O(9)$^{\#8}$-Pb(1)-O(1)$^{\#3}$	77.48(6)
O(11)$^{\#4}$-Ca(2)-O(15)$^{\#4}$	155.68(6)	O(3)$^{\#7}$-Pb(1)-O(1)$^{\#3}$	76.16(6)
O(7)-Ca(2)-O(2)$^{\#5}$	84.89(6)	O(1)$^{\#9}$-Pb(1)-O(1)$^{\#3}$	60.57(7)
O(14)$^{\#4}$-Ca(2)-O(2)$^{\#5}$	130.12(6)	O(4)$^{\#7}$-Pb(1)-O(1)$^{\#3}$	68.59(6)
O(12)$^{\#4}$-Ca(2)-O(2)$^{\#5}$	98.42(6)	O(5)$^{\#7}$-Pb(1)-O(2)$^{\#9}$	74.68(5)

O(11)$^{\#4}$-Ca(2)-O(2)$^{\#5}$	75.89(6)	O(15)-Pb(1)-O(2)$^{\#9}$	101.40(5)
O(15)$^{\#4}$-Ca(2)-O(2)$^{\#5}$	79.88(6)	O(11)$^{\#6}$-Pb(1)-O(2)$^{\#9}$	69.08(5)
O(7)-Ca(2)-O(3)$^{\#5}$	137.12(6)	O(9)$^{\#8}$-Pb(1)-O(2)$^{\#9}$	96.81(5)
O(14)$^{\#4}$-Ca(2)-O(3)$^{\#5}$	85.25(6)	O(3)$^{\#7}$-Pb(1)-O(2)$^{\#9}$	165.11(5)
O(12)$^{\#4}$-Ca(2)-O(3)$^{\#5}$	68.28(5)	O(1)$^{\#9}$-Pb(1)-O(2)$^{\#9}$	51.78(5)
O(11)$^{\#4}$-Ca(2)-O(3)$^{\#5}$	97.08(5)	O(4)$^{\#7}$-Pb(1)-O(2)$^{\#9}$	141.86(6)
O(15)$^{\#4}$-Ca(2)-O(3)$^{\#5}$	69.60(5)	O(1)$^{\#3}$-Pb(1)-O(2)$^{\#9}$	111.93(6)
O(2)$^{\#5}$-Ca(2)-O(3)$^{\#5}$	53.57(5)	O(9)-B(1)-O(8)	118.9(2)
O(7)-Ca(2)-O(2)$^{\#6}$	74.42(5)	O(9)-B(1)-O(10)	120.8(2)
O(14)$^{\#4}$-Ca(2)-O(2)$^{\#6}$	75.74(6)	O(8)-B(1)-O(10)	120.35(19)
O(12)$^{\#4}$-Ca(2)-O(2)$^{\#6}$	86.06(5)	O(5)-B(2)-O(7)	116.43(19)
O(11)$^{\#4}$-Ca(2)-O(2)$^{\#6}$	84.39(5)	O(5)-B(2)-O(8)	106.02(18)
O(15)$^{\#4}$-Ca(2)-O(2)$^{\#6}$	117.82(5)	O(7)-B(2)-O(8)	109.88(17)
O(2)$^{\#5}$-Ca(2)-O(2)$^{\#6}$	153.55(7)	O(5)-B(2)-O(6)	110.83(18)
O(3)$^{\#5}$-Ca(2)-O(2)$^{\#6}$	148.35(5)	O(7)-B(2)-O(6)	106.96(18)
O(5)$^{\#7}$-Ca(3)-O(15)	93.59(5)	O(8)-B(2)-O(6)	106.31(17)
O(5)$^{\#7}$-Ca(3)-O(11)$^{\#6}$	125.41(5)	O(13)-B(3)-O(7)	115.33(19)
O(15)-Ca(3)-O(11)$^{\#6}$	57.00(5)	O(13)-B(3)-O(12)	114.8(2)
O(5)$^{\#7}$-Ca(3)-O(9)$^{\#8}$	170.88(5)	O(7)-B(3)-O(12)	111.56(18)
O(15)-Ca(3)-O(9)$^{\#8}$	91.29(5)	O(13)-B(3)-O(10)	102.36(17)
O(11)$^{\#6}$-Ca(3)-O(9)$^{\#8}$	52.09(5)	O(7)-B(3)-O(10)	107.41(18)
O(5)$^{\#7}$-Ca(3)-O(3)$^{\#7}$	116.76(5)	O(12)-B(3)-O(10)	103.95(16)
O(15)-Ca(3)-O(3)$^{\#7}$	69.59(5)	O(11)-B(4)-O(9)$^{\#3}$	104.80(18)
O(11)$^{\#6}$-Ca(3)-O(3)$^{\#7}$	96.06(5)	O(11)-B(4)-O(12)	108.89(18)
O(9)$^{\#8}$-Ca(3)-O(3)$^{\#7}$	72.19(5)	O(9)$^{\#3}$-B(4)-O(12)	112.34(18)
O(5)$^{\#7}$-Ca(3)-O(1)$^{\#9}$	91.88(6)	O(11)-B(4)-O(6)	111.71(18)
O(15)-Ca(3)-O(1)$^{\#9}$	149.75(6)	O(9)$^{\#3}$-B(4)-O(6)	109.86(18)
O(11)$^{\#6}$-Ca(3)-O(1)$^{\#9}$	96.15(6)	O(12)-B(4)-O(6)	109.21(18)

O(9)$^{\#8}$-Ca(3)-O(1)$^{\#9}$	80.08(6)	O(14)-B(5)-O(13)	113.72(19)
O(3)$^{\#7}$-Ca(3)-O(1)$^{\#9}$	132.62(6)	O(14)-B(5)-O(15)$^{\#4}$	107.72(17)
O(5)$^{\#7}$-Ca(3)-O(4)$^{\#7}$	68.37(5)	O(13)-B(5)-O(15)$^{\#4}$	114.39(19)
O(15)-Ca(3)-O(4)$^{\#7}$	90.21(5)	O(14)-B(5)-O(6)$^{\#6}$	108.51(18)
O(11)$^{\#6}$-Ca(3)-O(4)$^{\#7}$	142.66(5)	O(13)-B(5)-O(6)$^{\#6}$	106.53(17)
O(9)$^{\#8}$-Ca(3)-O(4)$^{\#7}$	119.35(5)	O(15)$^{\#4}$-B(5)-O(6)$^{\#6}$	105.54(18)
O(3)$^{\#7}$-Ca(3)-O(4)$^{\#7}$	52.08(5)	O(5)$^{\#5}$-B(6)-O(14)	113.44(18)
O(1)$^{\#9}$-Ca(3)-O(4)$^{\#7}$	119.35(6)	O(5)$^{\#5}$-B(6)-O(15)	109.57(17)
O(5)$^{\#7}$-Ca(3)-O(1)$^{\#3}$	102.41(6)	O(14)-B(6)-O(15)	103.45(18)
O(15)-Ca(3)-O(1)$^{\#3}$	145.74(6)	O(5)$^{\#5}$-B(6)-O(11)$^{\#6}$	108.01(18)
O(11)$^{\#6}$-Ca(3)-O(1)$^{\#3}$	128.27(6)	O(14)-B(6)-O(11)$^{\#6}$	111.77(17)
O(9)$^{\#8}$-Ca(3)-O(1)$^{\#3}$	77.48(6)	O(15)-B(6)-O(11)$^{\#6}$	110.54(18)
O(3)$^{\#7}$-Ca(3)-O(1)$^{\#3}$	76.16(6)	O(4)-S(1)-O(1)	111.89(12)
O(1)$^{\#9}$-Ca(3)-O(1)$^{\#3}$	60.57(7)	O(4)-S(1)-O(2)	111.15(11)
O(4)$^{\#7}$-Ca(3)-O(1)$^{\#3}$	68.59(6)	O(1)-S(1)-O(2)	109.25(12)
O(5)$^{\#7}$-Ca(3)-O(2)$^{\#9}$	74.68(5)	O(4)-S(1)-O(3)	107.71(11)
O(15)-Ca(3)-O(2)$^{\#9}$	101.40(5)	O(1)-S(1)-O(3)	109.32(12)
O(11)$^{\#6}$-Ca(3)-O(2)$^{\#9}$	69.08(5)	O(2)-S(1)-O(3)	107.40(10)

#1 x+1, y, z;
#2 -x+2, -y+1, -z+2;
#3 -x+1, -y+1, -z+1;
#4 x, -y+1/2, z+1/2;
#5 x-1, -y+1/2, z-1/2;
#6 x-1, y, z;
#7 x-1, y, z-1;
#8 -x, -y+1, -z+1;
#9 x-2, y, z-1;

Table S5. Assignments of IR absorption bands in **I** and **II**.

Assignment	**I** (cm^{-1})	**II** (cm^{-1})
Asymmetric stretching vibration of B−O in $[BO_3]$	1531−1315	1404−1300
Symmetric stretching vibration of B−O in $[BO_3]$	945−910	940−915
Out-of-plane bending vibration of B−O in $[BO_3]$	871−860, 574−528	815−805, 590−592
Asymmetric stretching vibration of B-O in $[BO_4]$	1103−1014	1130−1151
Symmetric stretching vibration of B-O in $[BO_4]$	648−551	670−540
Asymmetric stretching vibration of S-O in $[SO_4]$	1195	1200
Symmetric stretching vibration of S-O in $[SO_4]$	505	509

IR spectrum of **I**, and **II**. The IR spectrum confirms the presence of the structural $[BO_3]$, $[BO_4]$ and $[SO_4]$ units.

Table S6. Comparison of the structural and optical properties of **I** and **II**

compounds	space group	λ_{cutoff} (nm)	Δn[a]	spatial density($Å^{-3}$)[b]
$Na_2PbB_6O_{10}SO_4$ (**I**)	*Pnma*	< 270	cal. 0.035 (at 1064 nm)	8.88×10^{-2}
$Ca_{2.58}Pb_{0.42}B_6O_{11}SO_4$ (**II**)	*P*121/*c*1	< 300	cal. 0.017 (at 1064 nm)	3.91×10^{-2}

[a]birefringence; [b]spatial density of [BO_3].

Table S7. Bonding electron difference ($\Delta\rho$) and contribution percent w (%) of different units in **I**, and **II** calculated by the response electron distribution anisotropy (REDA) model.

I			**II**		
Units	$\Delta\rho$	w (%)	Units	$\Delta\rho$	w (%)
$[BO_3]$	0.001120141	77.0	$[BO_3]$	0.0012725	62.4
$[BO_4]$	-0.000177834	-12.2	$[BO_4]$	0.000274592	13.5
$[SO_4]$	4.40583E-05	3.0	$[SO_4]$	0.000196111	9.6
$[Na1O_8]$	0.000114421	7.9	$[Ca1O_7]$	0.00013057	6.4
$[Na2O_6]$	0.000155558	10.7	$[Ca2O_8]$	0.000275821	13.5
$[PbO_9]$	0.000198569	13.7	$[PbO_9]$	-0.000110198	-5.4

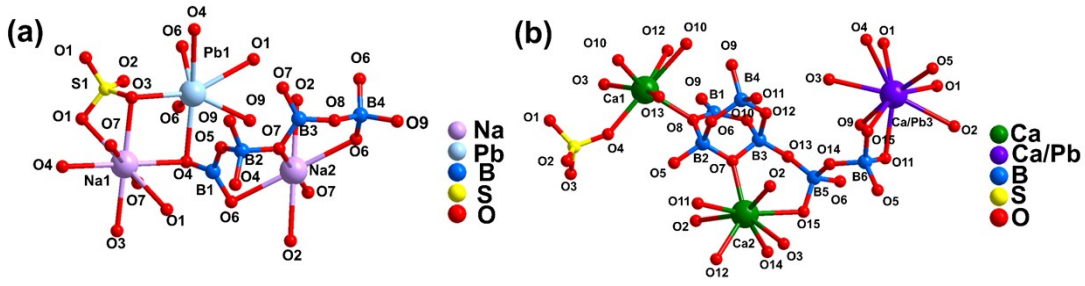

Figure S1. The asymmetric units of compounds **I** and **II**.

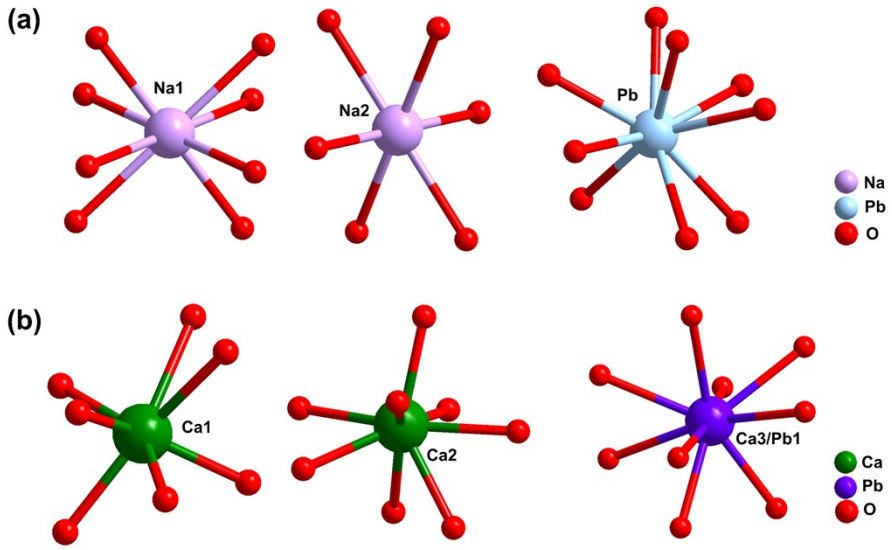

Figure S2. (a and d) The coordination environments of Na, Pb, Ca, and O atoms of **I** and **II**.

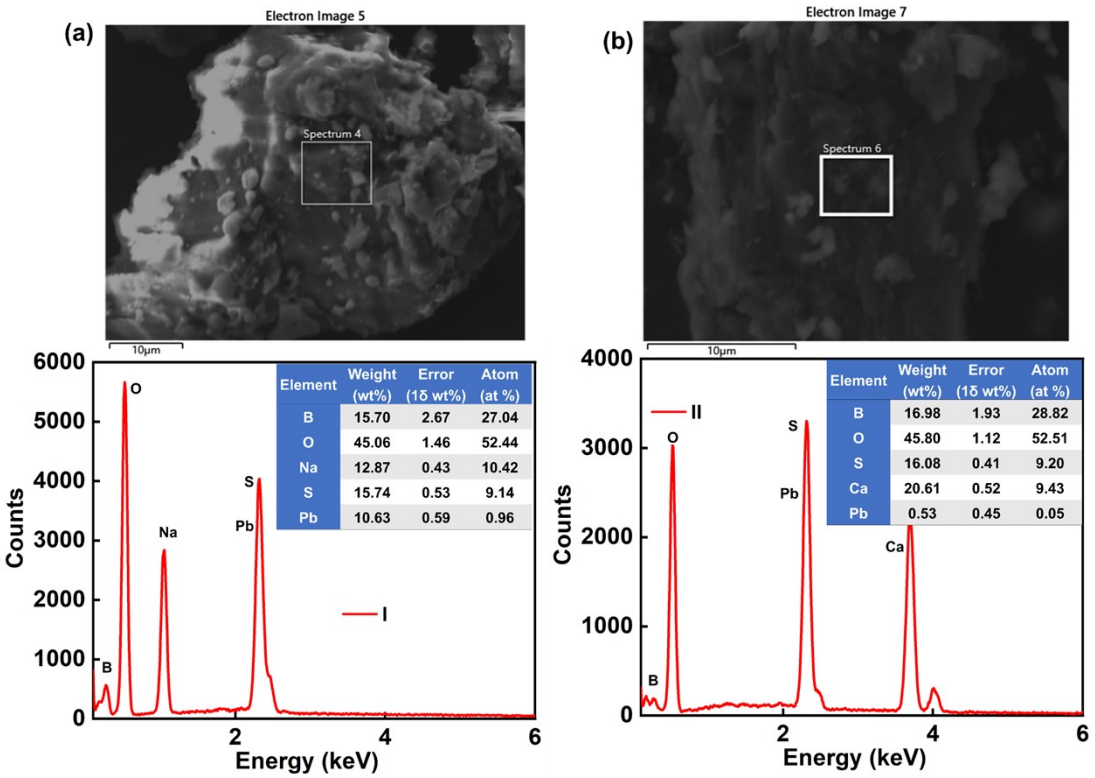

Figure S3. (a) SEM image, the energy-dispersive X-ray spectroscopy of **I**. (b) SEM image and energy-dispersive X-ray spectroscopy of **II**.

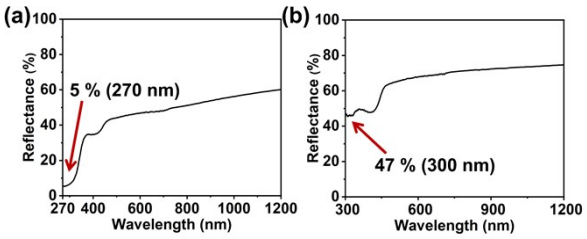

Figure S4. **I**, and **II**: (a, b) UV-vis-NIR diffuse reflectance spectra.

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