Supporting Information

$Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$: Structural Insights into An *Ortho*-borate with Uncondensed BO_4 Tetrahedra

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Experimental Procedures

Reagents

Both H_3BO_3 (AR, 99.5%) and $BaCO_3$ (AR, 99.0%) were purchased from Shanghai Aladdin Chemistry Co., Ltd., $PbCl_2$ (AR, 99.5%), $BaCl_2{\cdot}2H_2O$ (99.5%) and PbO (99.0%) were purchased from Tianjin Fu Chen Chemical Co., Ltd., all of the reagents were used as received without further treatment.

Synthesis

Polycrystalline samples of $Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$ were prepared by the standard high-temperature solid-state reaction. The loaded compositions are $BaCO_3$ (0.295 g, 1.5 mmol), H_3BO_3 (0.062 g, 1 mmol), $BaCl_2{\cdot}2H_2O$ (1.098 g, 4.5 mmol) for $Ba_6BO_3Cl_9$ and PbO (0.558 g, 2.5 mmol), H_3BO_3 (0.062 g, 1 mmol), $PbCl_2$ (0.973 g, 3.5 mmol) for $Pb_6BO_4Cl_7$. All the reagents were mixed thoroughly ground in an agate mortar, heated to 300 ℃ for 10 h to decompose CO_2 and H_2O. Then the mixtures were heated to 750 ℃ for $Ba_6BO_3Cl_9$ and 345 ℃ for $Pb_6BO_4Cl_7$, and held at these temperatures for 3 days with three intermittent grindings every day. The phase purity of $Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$ were confirmed by powder X-ray diffraction (XRD) analysis.

Crystal Growth

The single crystals of $Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$ were synthesized by high-temperature solution method. The crystals of $Ba_6BO_3Cl_9$ were obtained with a mixture of $BaCO_3$ (0.295g), H_3BO_3 (0.062 g), and $BaCl_2{\cdot}2H_2O$ (1.098 g) in the stoichiometric ratio of 1.5:1:4.5, while crystals of $Pb_6BO_4Cl_7$ were grown in a chlorine-rich solution of PbO (0.335 g), H_3BO_3 (0.062 g), $PbCl_2$ (1.251 g) with a molar ratio of 1.5:1:4.5. The mixtures were put into a platinum crucible, which was put in a vertical programmable temperature furnace. The samples were heated at 850 ℃ for $Ba_6BO_3Cl_9$ (450 ℃ for $Pb_6BO_4Cl_7$) and kept for 1 h at this temperature to ensure complete melting and homogeneity of the raw materials. Then, the melts were cooled at a rate of 2 ℃/h until the colorless and transparent crystals were observed, followed by cooling to room temperature at a rate of 20 ℃/h.

Single crystal X-ray diffraction

The crystal data of $Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$ were collected with the monochromatic Mo Kα radiation at 293(2) K on a Bruker SMART APEX II CCD di□ractometer and integrated with the SAINT program.[1] All calculations were performed with programs from the SHELXTL

crystallographic software package. The structures were solved by direct methods using SHELXS system.[2] The atomic positions of the structure are refined with anisotropic displacement parameters and secondary extinction correction. PLATON[3] was used to check the structure for missing symmetry elements, and no higher symmetry was found.

Powder X-ray Di□raction

Powder XRD data for the polycrystalline powder of the title compounds were obtained on a SmartLab9KW X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature. The 2θ range was 10°-70° with a step size of 0.02° and a fixed counting time of 2 s/step.

Infrared Spectroscopy

A Nicolet iS50 FT-IR spectrometer was used to record the IR spectra of $Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$ in the range of 400-4000 cm^{-1}. The sample was placed on the test platform for testing.

UV-vis-NIR di□use reflectance spectroscopy

The optical di□use reflectance spectra of title compounds were performed on a Hitachi UV-VIS-NIR spectrophotometer in the range of 190-2500 nm at 25 °C. The absorption (K/S) data are calculated from Kubelka-Munk function $F(R) = (1-R)^2/2R = K/S$, where R represents the reflectance, K the absorption, and S the scattering.[4,5]

Thermal Stability

A NETZSCH STA 4495 thermal analysis instrument was used to the thermal gravity-di□erential scanning calorimetric (TG-DSC) analysis for $Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$. The powder samples were placed in a platinum crucible and heated from 25 °C to 950 °C for $Ba_6BO_3Cl_9$ and from 25 °C to 500 °C for $Pb_6BO_4Cl_7$, and then cooled to room temperature at a rate of 10 °C /min with the help of flowng nitrogen atmosphere.

Table S1. Crystal data and structure refinement for $Ba_6BO_3Cl_9$ and $Pb_6BO_4Cl_7$.

Empirical formula	**$Ba_6BO_3Cl_9$**	**$Pb_6BO_4Cl_7$**
Formula weight	1201.90	1566.00
Temperature	300(2) K	300(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions	a =8.229(2) Å b = 12.2589(17) Å c = 19.080(4) Å β = 90.203(12) °	a =8.001(3) Å b = 8.054(3) Å c = 13.116(5) Å α= 89.522(13) ° β = 89.663(14) ° γ= 69.943(12) °
Volume	1924.7(7) Å^3	793.9(5) Å^3
Z	4	2
Density (g/cm^3)	4.148	6.687
Absorption coefficient (mm^{-1})	13.322	64.567
F(000)	2072	1326
Theta range for data collection	2.692 to 27.519°	2.692 to 28.282°
Limiting indices	-10≤ h ≤10, -13≤ k ≤15, -24 ≤ l ≤22	-10≤ h ≤10, -10≤ k ≤10, -17 ≤ l ≤17
Reflections collected / unique	24716 / 4422 [R(int) = 0.0736]	10851 / 3944 [R(int) = 0.0734]
Completeness to theta	99.9 %	99.8 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4422 / 0 / 173	3944 / 0 / 163
Goodness-of-fit on F^2	1.273	1.005
Final R indices [F_o^2>2σ(F_o^2)][a]	R_1 =0.0339 wR_2 = 0.0683	R_1 = 0.0481 wR_2 = 0.0931
R indices (all data)[a]	R_1 = 0.0521 wR_2 =0.1555	R_1 = 0.0832 wR_2 = 0.1090
Largest diff. peak and hole	1.358 and -1.236 e·Å^{-3}	2.143 and -2.991 e·Å^{-3}

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

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Ba_6BO_3Cl_9$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
Ba(1)	-531(1)	1730(1)	5081(1)	16(1)	2.13
Ba(2)	-517(1)	1748(1)	2422(1)	16(1)	2.17
Ba(3)	4198(1)	3293(1)	4981(1)	18(1)	1.91
Ba(4)	4214(1)	3302(1)	2531(1)	18(1)	1.95
Ba(5)	4562(1)	384(1)	3729(1)	14(1)	2.24
Ba(6)	-486(1)	4569(1)	3767(1)	14(1)	2.46
Cl(1)	-600(2)	-136(1)	6286(1)	21(1)	0.98
Cl(2)	-2055(2)	4251(2)	5210(1)	23(1)	1.07
Cl(3)	-1502(2)	7089(1)	3689(1)	22(1)	1.01
Cl(4)	-2127(2)	4392(2)	2309(1)	24(1)	1.03
Cl(5)	-440(2)	-57(1)	1228(1)	20(1)	1.09
Cl(6)	3074(2)	754(2)	2267(1)	22(1)	1.19
Cl(7)	7311(2)	2235(2)	3737(1)	23(1)	1.04
Cl(8)	7048(2)	-566(2)	4798(1)	25(1)	1.10
Cl(9)	3570(2)	-2046(1)	3820(1)	22(1)	1.08
B(1)	2039(10)	2759(6)	3754(5)	15(2)	2.97
O(1)	1276(6)	2987(4)	4383(3)	15(1)	2.16
O(2)	1282(6)	3022(4)	3131(3)	15(1)	2.15
O(3)	3593(6)	2371(4)	3756(3)	14(1)	2.24

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Pb_6BO_4Cl_7$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U(eq)	BVS
Pb(1)	1080(1)	109(1)	8679(1)	31(1)	1.91
Pb(2)	5458(1)	-178(1)	6766(1)	30(1)	2.02
Pb(3)	4385(1)	2893(1)	9254(1)	33(1)	1.96
Pb(4)	3584(1)	5138(1)	6489(1)	32(1)	1.90
Pb(5)	379(1)	2005(1)	5729(1)	32(1)	1.95
Pb(6)	-945(1)	5475(1)	8075(1)	34(1)	1.79
Cl(1)	166(6)	-1504(6)	6843(3)	34(1)	0.79
Cl(2)	7203(5)	-665(6)	9354(3)	31(1)	0.76
Cl(3)	4488(6)	7011(6)	8165(4)	35(1)	0.76
Cl(4)	6510(6)	1317(6)	4905(3)	32(1)	0.80
Cl(5)	6572(6)	2670(6)	7466(3)	32(1)	1.20
Cl(6)	-1955(7)	5665(6)	5804(4)	38(1)	0.73
Cl(7)	-1367(7)	3583(6)	9848(4)	43(1)	0.72
B(1)	2220(20)	2610(30)	7492(14)	27(4)	2.99
O(1)	404(14)	2549(14)	7494(9)	27(3)	2.23
O(2)	2930(14)	2272(13)	6444(8)	18(2)	1.87
O(3)	2185(15)	4358(14)	7854(8)	24(3)	2.20
O(4)	3354(14)	1217(14)	8192(8)	22(2)	2.22

Table S4. Selected bond distances (Å) and angles (deg) for $Ba_6BO_3Cl_9$.

Ba(1)-O(1)	2.525(4)	Ba(4)-O(2)	2.696(5)
Ba(1)-Cl(7)#1	3.175(2)	Ba(4)-Cl(5)#5	3.263(2)
Ba(1)-Cl(8)#2	3.208(2)	Ba(4)-Cl(1)#10	3.275(2)
Ba(1)-Cl(3)#3	3.220(2)	Ba(4)-Cl(6)	3.299(2)
Ba(1)-Cl(1)	3.2425(19)	Ba(4)-Cl(4)#9	3.323(2)
Ba(1)-Cl(9)#4	3.2922(19)	Ba(4)-Cl(3)#7	3.3477(19)
Ba(1)-Cl(2)	3.344(2)	Ba(4)-Cl(9)#5	3.469(2)
Ba(1)-Cl(1)#4	3.3916(19)	Ba(4)-Cl(6)#5	3.569(2)
Ba(1)-Cl(8)#1	3.490(2)	Ba(5)-O(3)	2.564(5)
Ba(2)-O(2)	2.539(5)	Ba(5)-Cl(6)	3.076(2)
Ba(2)-Cl(7)#1	3.143(2)	Ba(5)-Cl(9)	3.0926(18)
Ba(2)-Cl(5)	3.1772(19)	Ba(5)-Cl(8)	3.111(2)
Ba(2)-Cl(6)	3.211(2)	Ba(5)-Cl(8)#2	3.1186(19)
Ba(2)-Cl(9)#5	3.2246(18)	Ba(5)-Cl(4)#7	3.1442(19)
Ba(2)-Cl(3)#6	3.264(2)	Ba(5)-Cl(7)	3.2046(19)
Ba(2)-Cl(1)#4	3.288(2)	Ba(5)-Cl(1)#4	3.275(2)
Ba(2)-Cl(4)	3.508(2)	Ba(6)-O(2)	2.683(5)
Ba(2)-Cl(4)#6	3.517(2)	Ba(6)-O(1)	2.689(5)
Ba(3)-O(3)	2.643(5)	Ba(6)-Cl(2)	3.0707(19)
Ba(3)-O(1)	2.684(5)	Ba(6)-Cl(4)	3.094(2)
Ba(3)-Cl(5)#8	3.2286(19)	Ba(6)-Cl(6)#5	3.1570(18)
Ba(3)-Cl(5)#5	3.2373(18)	Ba(6)-Cl(2)#3	3.201(2)
Ba(3)-Cl(9)#2	3.303(2)	Ba(6)-Cl(3)	3.2028(18)
Ba(3)-Cl(2)#9	3.327(2)	Ba(6)-Cl(5)#11	3.384(2)
Ba(3)-Cl(3)#3	3.408(2)	Ba(6)-Cl(7)#1	3.3878(19)
Ba(3)-Cl(2)#3	3.509(2)	B(1)-O(3)	1.365(9)
Ba(3)-Cl(8)#2	3.521(2)	B(1)-O(2)	1.379(11)
Ba(4)-O(3)	2.652(5)	B(1)-O(1)	1.384(9)
O(3)-Ba(1)-Cl(6)	75.91(15)	O(3)-B(1)-O(2)	120.8(9)
O(3)-Ba(1)-Cl(8)	146.30(13)	O(1)-B(1)-O(2)	118.7(8)
Cl(6)-Ba(1)-Cl(8)	95.26(7)	O(3)-Ba(2)-O(1)	52.95(18)
O(3)-Ba(1)-Cl(9)	122.91(15)	O(3)-Ba(2)-Cl(5)#5	162.77(13)
Cl(6)-Ba(1)-Cl(9)	155.37(6)	O(1)-Ba(2)-Cl(5)#5	119.21(13)
Cl(8)-Ba(1)-Cl(9)	77.06(7)	O(3)-Ba(2)-Cl(5)#6	72.26(13)
O(3)-Ba(1)-Cl(9)#1	77.19(14)	O(1)-Ba(2)-Cl(5)#6	93.92(13)
Cl(6)-Ba(1)-Cl(9)#1	129.58(7)	Cl(5)#5-Ba(2)-Cl(5)#6	94.50(5)

Cl(8)-Ba(1)-Cl(9)#1	84.51(6)	O(3)-Ba(2)-Cl(8)#1	121.13(13)
Cl(9)-Ba(1)-Cl(9)#1	73.59(7)	O(1)-Ba(2)-Cl(8)#1	136.44(12)
O(3)-Ba(1)-Cl(4)#2	126.24(13)	Cl(5)#5-Ba(2)-Cl(8)#1	75.55(6)
Cl(6)-Ba(1)-Cl(4)#2	75.64(7)	Cl(5)#6-Ba(2)-Cl(8)#1	127.35(6)
Cl(8)-Ba(1)-Cl(4)#2	80.85(6)	O(3)-Ba(2)-Cl(2)#7	116.03(13)
Cl(9)-Ba(1)-Cl(4)#2	80.02(7)	O(1)-Ba(2)-Cl(2)#7	158.96(13)
Cl(9)#1-Ba(1)-Cl(4)#2	152.09(7)	Cl(5)#5-Ba(2)-Cl(2)#7	65.38(6)
O(3)-Ba(1)-Cl(7)	63.00(14)	Cl(5)#6-Ba(2)-Cl(2)#7	65.04(6)
Cl(6)-Ba(1)-Cl(7)	100.18(7)	Cl(8)#1-Ba(2)-Cl(2)#7	63.90(6)
Cl(8)-Ba(1)-Cl(7)	150.21(7)	O(3)-Ba(2)-Cl(3)#8	118.65(13)
Cl(9)-Ba(1)-Cl(7)	78.35(7)	O(1)-Ba(2)-Cl(3)#8	73.41(13)
Cl(9)#1-Ba(1)-Cl(7)	104.35(7)	Cl(5)#5-Ba(2)-Cl(3)#8	66.52(6)
Cl(4)#2-Ba(1)-Cl(7)	78.55(7)	Cl(5)#6-Ba(2)-Cl(3)#8	145.55(6)
O(3)-Ba(1)-Cl(1)#3	77.23(14)	Cl(8)#1-Ba(2)-Cl(3)#8	77.43(6)
Cl(6)-Ba(1)-Cl(1)#3	67.28(6)	Cl(2)#7-Ba(2)-Cl(3)#8	123.75(6)
Cl(8)-Ba(1)-Cl(1)#3	69.45(6)	O(3)-Ba(2)-Cl(2)#8	100.45(13)
Cl(9)-Ba(1)-Cl(1)#3	128.64(6)	O(1)-Ba(2)-Cl(2)#8	68.10(12)
Cl(9)#1-Ba(1)-Cl(1)#3	65.63(7)	Cl(5)#5-Ba(2)-Cl(2)#8	63.07(6)
Cl(4)#2-Ba(1)-Cl(1)#3	129.02(7)	Cl(5)#6-Ba(2)-Cl(2)#8	63.18(6)
Cl(7)-Ba(1)-Cl(1)#3	140.21(6)	Cl(8)#1-Ba(2)-Cl(2)#8	138.42(6)
O(3)-B(1)-O(1)	120.3(10)	Cl(2)#7-Ba(2)-Cl(2)#8	100.10(6)
Cl(3)#8-Ba(2)-Cl(2)#8	82.41(5)	Cl(8)#3-Ba(3)-Cl(2)	63.79(5)
O(3)-Ba(2)-Cl(9)#1	69.23(12)	O(1)-Ba(3)-Cl(1)#3	77.40(14)
O(1)-Ba(2)-Cl(9)#1	69.94(12)	Cl(7)#9-Ba(3)-Cl(1)#3	69.20(6)
Cl(5)#5-Ba(2)-Cl(9)#1	125.05(6)	Cl(9)#1-Ba(3)-Cl(1)#3	63.36(6)
Cl(5)#6-Ba(2)-Cl(9)#1	140.40(6)	Cl(3)#8-Ba(3)-Cl(1)#3	132.62(6)
Cl(8)#1-Ba(2)-Cl(9)#1	68.87(6)	Cl(1)-Ba(3)-Cl(1)#3	98.30(5)
Cl(2)#7-Ba(2)-Cl(9)#1	126.15(6)	Cl(8)#3-Ba(3)-Cl(1)#3	140.06(6)
Cl(3)#8-Ba(2)-Cl(9)#1	65.85(5)	Cl(2)-Ba(3)-Cl(1)#3	133.84(6)
Cl(2)#8-Ba(2)-Cl(9)#1	132.91(5)	O(1)-Ba(3)-Cl(9)#9	138.29(14)
O(1)-Ba(3)-Cl(7)#9	77.40(15)	Cl(7)#9-Ba(3)-Cl(9)#9	73.44(6)
O(1)-Ba(3)-Cl(9)#1	77.49(15)	Cl(9)#1-Ba(3)-Cl(9)#9	99.22(6)
Cl(7)#9-Ba(3)-Cl(9)#1	129.87(7)	Cl(3)#8-Ba(3)-Cl(9)#9	140.38(6)
O(1)-Ba(3)-Cl(3)#8	78.84(15)	Cl(1)-Ba(3)-Cl(9)#9	61.95(6)
Cl(7)#9-Ba(3)-Cl(3)#8	142.01(6)	Cl(8)#3-Ba(3)-Cl(9)#9	75.97(6)
Cl(9)#1-Ba(3)-Cl(3)#8	71.80(7)	Cl(2)-Ba(3)-Cl(9)#9	122.83(6)
O(1)-Ba(3)-Cl(1)	144.77(15)	Cl(1)#3-Ba(3)-Cl(9)#9	64.74(6)
Cl(7)#9-Ba(3)-Cl(1)	134.35(6)	O(2)-Ba(4)-Cl(2)	123.02(13)

Cl(9)#1-Ba(3)-Cl(1)	69.69(6)	O(1)-Ba(4)-Cl(2)	75.16(13)
Cl(3)#8-Ba(3)-Cl(1)	79.10(6)	O(2)-Ba(4)-Cl(4)	77.30(15)
O(1)-Ba(3)-Cl(8)#3	135.64(13)	O(1)-Ba(4)-Cl(4)	125.04(14)
Cl(7)#9-Ba(3)-Cl(8)#3	93.75(7)	Cl(2)-Ba(4)-Cl(4)	127.82(7)
Cl(9)#1-Ba(3)-Cl(8)#3	133.47(6)	O(2)-Ba(4)-Cl(6)#6	72.68(12)
Cl(3)#8-Ba(3)-Cl(8)#3	83.03(6)	O(1)-Ba(4)-Cl(6)#6	105.53(13)
Cl(1)-Ba(3)-Cl(8)#3	67.48(6)	Cl(2)-Ba(4)-Cl(6)#6	152.37(7)
O(1)-Ba(3)-Cl(2)	72.37(14)	Cl(4)-Ba(4)-Cl(6)#6	75.17(7)
Cl(7)#9-Ba(3)-Cl(2)	70.72(6)	O(2)-Ba(4)-Cl(2)#8	103.97(14)
Cl(9)#1-Ba(3)-Cl(2)	137.90(7)	O(1)-Ba(4)-Cl(2)#8	73.17(14)
Cl(3)#8-Ba(3)-Cl(2)	74.05(6)	Cl(2)-Ba(4)-Cl(2)#8	77.67(7)
Cl(1)-Ba(3)-Cl(2)	126.29(6)	Cl(4)-Ba(4)-Cl(2)#8	149.53(6)
O(2)-Ba(4)-Cl(3)	143.45(13)	Cl(7)#9-Ba(5)-Cl(8)#6	141.69(6)
O(1)-Ba(4)-Cl(3)	148.93(14)	Cl(5)-Ba(5)-Cl(8)#6	77.39(6)
Cl(2)-Ba(4)-Cl(3)	93.09(6)	Cl(6)-Ba(5)-Cl(8)#6	69.37(6)
Cl(4)-Ba(4)-Cl(3)	85.00(7)	O(2)-Ba(5)-Cl(3)#11	134.54(14)
Cl(6)#6-Ba(4)-Cl(3)	71.97(6)	Cl(7)#9-Ba(5)-Cl(3)#11	93.75(7)
Cl(2)#8-Ba(4)-Cl(3)	76.27(7)	Cl(5)-Ba(5)-Cl(3)#11	68.90(6)
O(2)-Ba(4)-Cl(5)#10	129.44(14)	Cl(6)-Ba(5)-Cl(3)#11	132.80(6)
O(1)-Ba(4)-Cl(5)#10	128.97(13)	Cl(8)#6-Ba(5)-Cl(3)#11	80.61(6)
Cl(2)-Ba(4)-Cl(5)#10	66.15(6)	O(2)-Ba(5)-Cl(1)#3	79.09(14)
Cl(4)-Ba(4)-Cl(5)#10	65.29(6)	Cl(7)#9-Ba(5)-Cl(1)#3	70.94(6)
Cl(6)#6-Ba(4)-Cl(5)#10	124.24(6)	Cl(5)-Ba(5)-Cl(1)#3	96.43(6)
Cl(2)#8-Ba(4)-Cl(5)#10	125.63(6)	Cl(6)-Ba(5)-Cl(1)#3	65.62(6)
Cl(3)-Ba(4)-Cl(5)#10	67.08(6)	Cl(8)#6-Ba(5)-Cl(1)#3	133.68(6)
O(2)-Ba(4)-Cl(7)#9	71.66(12)	Cl(3)#11-Ba(5)-Cl(1)#3	140.38(6)
O(1)-Ba(4)-Cl(7)#9	71.63(13)	O(2)-Ba(5)-Cl(4)	71.45(14)
Cl(2)-Ba(4)-Cl(7)#9	71.38(6)	Cl(7)#9-Ba(5)-Cl(4)	69.94(6)
Cl(4)-Ba(4)-Cl(7)#9	72.16(7)	Cl(5)-Ba(5)-Cl(4)	127.44(6)
Cl(6)#6-Ba(4)-Cl(7)#9	135.75(6)	Cl(6)-Ba(5)-Cl(4)	133.83(6)
Cl(2)#8-Ba(4)-Cl(7)#9	137.75(6)	Cl(8)#6-Ba(5)-Cl(4)	73.71(5)
Cl(3)-Ba(4)-Cl(7)#9	132.37(6)	Cl(3)#11-Ba(5)-Cl(4)	63.78(6)
Cl(5)#10-Ba(4)-Cl(7)#9	65.45(6)	Cl(1)#3-Ba(5)-Cl(4)	134.91(6)
O(2)-Ba(5)-Cl(7)#9	77.62(14)	O(2)-Ba(5)-Cl(4)#11	138.31(14)
O(2)-Ba(5)-Cl(5)	143.22(14)	Cl(7)#9-Ba(5)-Cl(4)#11	74.00(6)
Cl(7)#9-Ba(5)-Cl(5)	135.81(6)	Cl(5)-Ba(5)-Cl(4)#11	62.88(6)
O(2)-Ba(5)-Cl(6)	75.56(14)	Cl(6)-Ba(5)-Cl(4)#11	102.16(6)
Cl(7)#9-Ba(5)-Cl(6)	132.19(7)	Cl(8)#6-Ba(5)-Cl(4)#11	139.37(6)

Cl(5)-Ba(5)-Cl(6)	69.55(6)	Cl(3)#11-Ba(5)-Cl(4)#11	77.66(6)
O(2)-Ba(5)-Cl(8)#6	79.82(14)	Cl(1)#3-Ba(5)-Cl(4)#11	63.15(6)
Cl(4)-Ba(5)-Cl(4)#11	123.96(2)	Cl(1)#13-Ba(6)-Cl(3)#2	76.81(6)
O(3)-Ba(6)-O(2)	52.86(18)	Cl(6)-Ba(6)-Cl(3)#2	68.45(5)
O(3)-Ba(6)-Cl(5)#6	71.65(13)	Cl(4)#7-Ba(6)-Cl(3)#2	64.98(6)
O(2)-Ba(6)-Cl(5)#6	92.55(13)	O(3)-Ba(6)-Cl(8)#6	118.33(14)
O(3)-Ba(6)-Cl(1)#13	160.77(12)	O(2)-Ba(6)-Cl(8)#6	73.20(14)
O(2)-Ba(6)-Cl(1)#13	116.08(14)	Cl(5)#6-Ba(6)-Cl(8)#6	144.71(6)
Cl(5)#6-Ba(6)-Cl(1)#13	95.02(6)	Cl(1)#13-Ba(6)-Cl(8)#6	65.02(6)
O(3)-Ba(6)-Cl(6)	70.96(13)	Cl(6)-Ba(6)-Cl(8)#6	65.45(6)
O(2)-Ba(6)-Cl(6)	72.13(12)	Cl(4)#7-Ba(6)-Cl(8)#6	123.40(6)
Cl(5)#6-Ba(6)-Cl(6)	141.42(6)	Cl(3)#2-Ba(6)-Cl(8)#6	78.51(6)
Cl(1)#13-Ba(6)-Cl(6)	123.56(6)	O(3)-Ba(6)-Cl(6)#6	99.41(12)
O(3)-Ba(6)-Cl(4)#7	117.54(14)	O(2)-Ba(6)-Cl(6)#6	65.56(12)
O(2)-Ba(6)-Cl(4)#7	156.57(13)	Cl(5)#6-Ba(6)-Cl(6)#6	64.23(6)
Cl(5)#6-Ba(6)-Cl(4)#7	64.30(6)	Cl(1)#13-Ba(6)-Cl(6)#6	61.74(5)
Cl(1)#13-Ba(6)-Cl(4)#7	65.52(6)	Cl(6)-Ba(6)-Cl(6)#6	131.66(3)
Cl(6)-Ba(6)-Cl(4)#7	128.11(6)	Cl(4)#7-Ba(6)-Cl(6)#6	98.87(6)
O(3)-Ba(6)-Cl(3)#2	122.21(12)	Cl(3)#2-Ba(6)-Cl(6)#6	138.35(6)
O(2)-Ba(6)-Cl(3)#2	138.29(13)	Cl(8)#6-Ba(6)-Cl(6)#6	80.52(6)
Cl(5)#6-Ba(6)-Cl(3)#2	127.16(6)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+1,-y,-z+1 #3 -x,-y+1,-z+1

#4 -x,-y,-z+1 #5 -x+1/2,y+1/2,-z+1/2 #6 -x-1/2,y-1/2,-z+1/2

#7 -x+1/2,y-1/2,-z+1/2 #8 x+1/2,-y+1/2,z+1/2

#9 x+1,y,z #10 x+1/2,-y+1/2,z-1/2 #11 -x-1/2,y+1/2,-z+1/2

#12 x-1/2,-y+1/2,z+1/2 #13 x-1/2,-y+1/2,z-1/2

Table S5. Selected bond distances (Å) and angles (deg) for $Pb_6BO_4Cl_7$.

Pb(1)-O(4)	2.360(12)	O(4)-Pb(2)-Cl(5)	75.4(3)
Pb(1)-O(1)	2.402(11)	O(2)-Pb(2)-Cl(4)	78.1(3)
Pb(1)-Cl(1)	2.955(5)	O(4)-Pb(2)-Cl(4)	132.2(3)
Pb(1)-Cl(2)#1	3.036(5)	Cl(5)-Pb(2)-Cl(4)	74.64(14)
Pb(1)-Cl(3)#2	3.074(6)	O(2)-Pb(2)-Cl(4)#3	74.5(3)
Pb(2)-O(2)	2.335(12)	O(4)-Pb(2)-Cl(4)#3	109.7(3)
Pb(2)-O(4)	2.506(12)	Cl(5)-Pb(2)-Cl(4)#3	144.19(13)
Pb(2)-Cl(5)	2.886(5)	Cl(4)-Pb(2)-Cl(4)#3	77.00(14)
Pb(2)-Cl(4)	2.954(5)	O(4)-Pb(3)-O(3)	59.7(4)
Pb(2)-Cl(4)#3	3.031(5)	O(4)-Pb(3)-Cl(5)	78.3(3)
Pb(3)-O(4)	2.303(12)	O(3)-Pb(3)-Cl(5)	75.5(3)
Pb(3)-O(3)	2.538(12)	O(4)-Pb(3)-Cl(2)	76.4(3)
Pb(3)-Cl(5)	2.889(5)	O(3)-Pb(3)-Cl(2)	130.6(3)
Pb(3)-Cl(2)	2.982(5)	Cl(5)-Pb(3)-Cl(2)	74.30(14)
Pb(4)-O(3)	2.298(12)	O(3)-Pb(4)-O(2)	60.2(4)
Pb(4)-O(2)	2.540(11)	O(3)-Pb(4)-Cl(5)	80.3(3)
Pb(4)-Cl(5)	2.836(5)	O(2)-Pb(4)-Cl(5)	76.5(3)
Pb(4)-Cl(3)	2.908(5)	O(3)-Pb(4)-Cl(3)	77.5(3)
Pb(5)-O(2)	2.319(11)	O(2)-Pb(4)-Cl(3)	131.5(3)
Pb(5)-O(1)	2.367(14)	Cl(5)-Pb(4)-Cl(3)	73.83(15)
Pb(5)-Cl(6)	2.898(5)	O(2)-Pb(5)-O(1)	61.3(4)
Pb(5)-Cl(4)#3	3.080(5)	O(2)-Pb(5)-Cl(6)	99.7(3)
Pb(6)-O(1)	2.361(13)	O(1)-Pb(5)-Cl(6)	79.5(3)
Pb(6)-O(3)	2.373(13)	O(2)-Pb(5)-Cl(4)#3	73.7(3)
Pb(6)-Cl(7)	2.852(5)	O(1)-Pb(5)-Cl(4)#3	111.9(3)
Pb(6)-Cl(6)	3.078(5)	Cl(6)-Pb(5)-Cl(4)#3	160.09(15)
B(1)-O(1)	1.471(2)	O(1)-Pb(6)-O(3)	61.3(4)
B(1)-O(3)	1.476(3)	O(1)-Pb(6)-Cl(7)	80.0(3)
B(1)-O(4)	1.481(6)	O(3)-Pb(6)-Cl(7)	101.4(3)
B(1)-O(2)	1.490(2)	O(1)-Pb(6)-Cl(6)	75.8(3)
O(4)-Pb(1)-O(1)	60.8(4)	O(3)-Pb(6)-Cl(6)	97.3(3)
O(4)-Pb(1)-Cl(1)	106.6(3)	Cl(7)-Pb(6)-Cl(6)	137.21(17)
O(1)-Pb(1)-Cl(1)	79.3(3)	O(1)-B(1)-O(3)	110.4(15)
O(4)-Pb(1)-Cl(2)#1	74.1(3)	O(1)-B(1)-O(4)	109.5(14)
O(1)-Pb(1)-Cl(2)#1	114.3(3)	O(3)-B(1)-O(4)	109.6(14)
Cl(1)-Pb(1)-Cl(2)#1	163.06(14)	O(1)-B(1)-O(2)	107.8(14)
O(4)-Pb(1)-Cl(3)#2	70.4(3)	O(3)-B(1)-O(2)	110.5(14)

O(1)-Pb(1)-Cl(3)#2	114.3(3)	O(4)-B(1)-O(2)	109.1(15)
Cl(1)-Pb(1)-Cl(3)#2	75.34(14)		
Cl(2)#1-Pb(1)-Cl(3)#2	89.37(14)		
O(2)-Pb(2)-O(4)	60.0(4)		
O(2)-Pb(2)-Cl(5)	78.6(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+2 #2 x,y-1,z #3 -x+1,-y,-z+1

#4 x,y+1,z

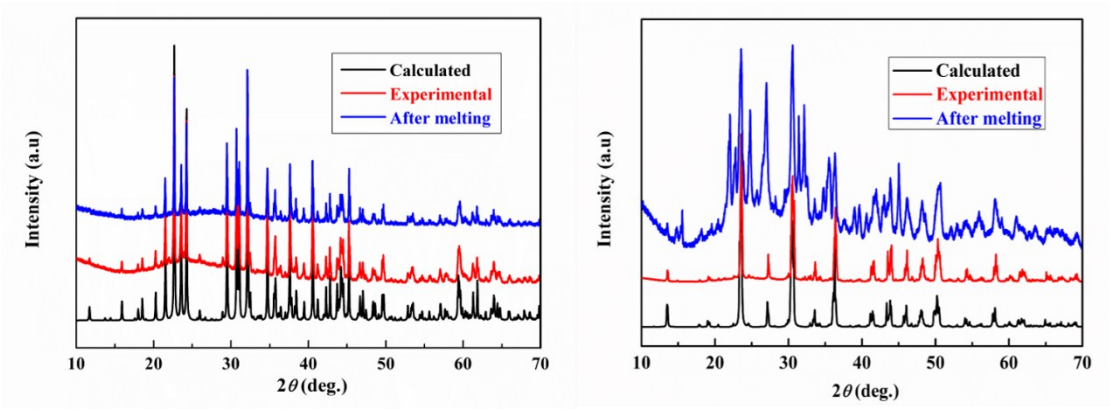
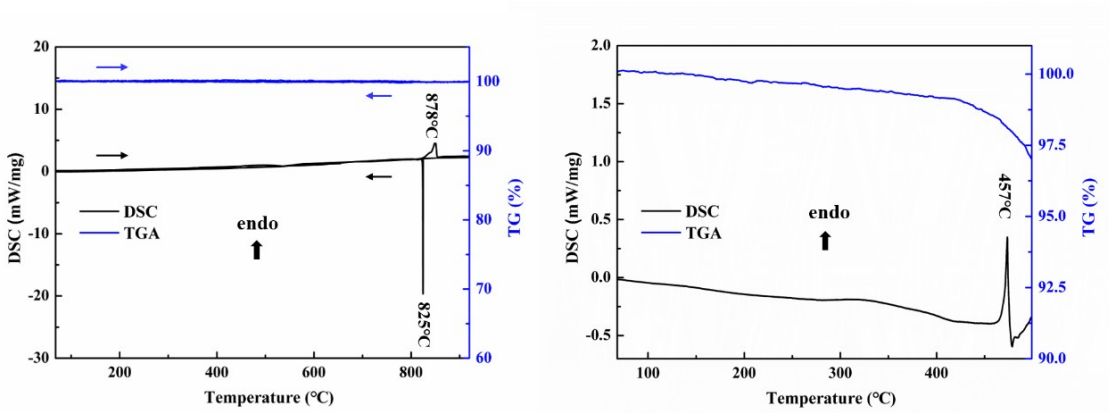
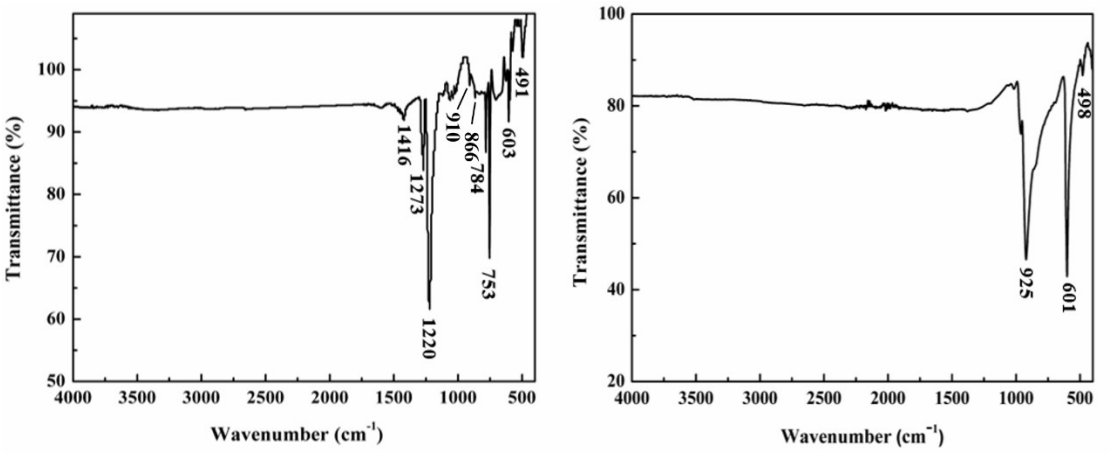


Fig. S1 X-ray powder diffraction patterns of $Ba_6BO_3Cl_9$ (a) and $Pb_6BO_4Cl_7$(b).



(a) **(b)**

Fig. S2 DSC-TG curves of $Ba_6BO_3Cl_9$ (a) and $Pb_6BO_4Cl_7$ (b).



(a) **(b)**

Fig. S3 IR spectra of $Ba_6BO_3Cl_9$ (a) and $Pb_6BO_4Cl_7$ (b).

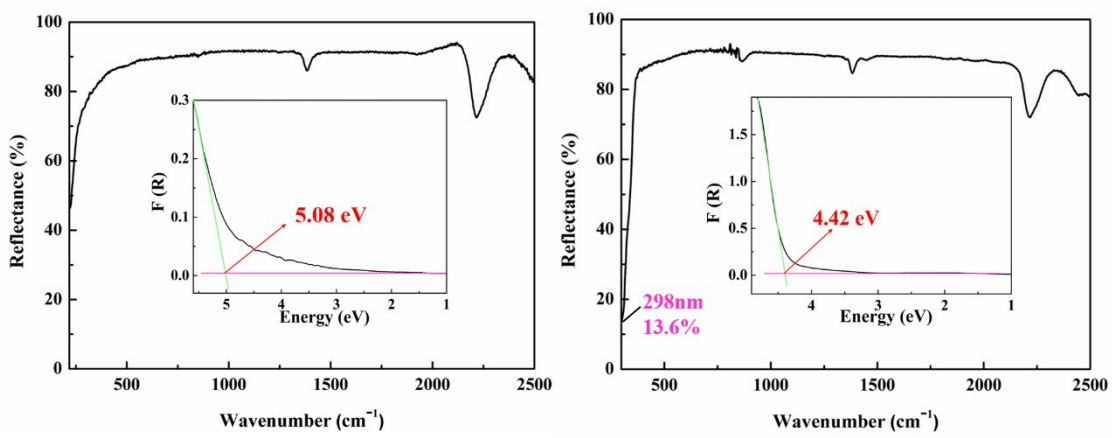
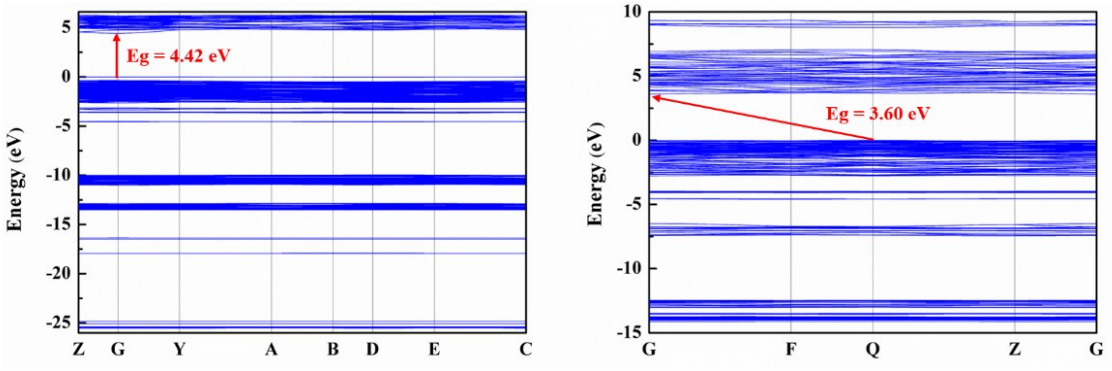


Fig. S4 UV−vis−NIR spectra of $Ba_6BO_3Cl_9$ (a) and $Pb_6BO_4Cl_7$ (b).



(a) **(b)**

Fig. S5 The calculated band gaps of $Ba_6BO_3Cl_9$ (a) and $Pb_6BO_4Cl_7$ (b).

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