Electronic Supplementary Information

Tuning birefringence in alkaline-earth metal oxyhalides through diverse mixed-cation coordination architectures

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Experimental Section

Reagents

Lead (II) oxide (PbO, 99.0 %), lead (II) bromide ($PbBr_2$, 99.0 %), cadmium (II) oxide (CdO, 99.0 %), selenium (IV) dioxide (SeO_2, 99.5 %), barium (II) carbonate ($BaCO_3$, 99.5 %), barium (II) chloride dihydrate ($BaCl_2 \cdot 2H_2O$, 98.0 %), cadmium (II) bromide ($CdBr_2$, 99.9%) were obtained from Aladdin Chemical Industry Co., Ltd. All materials were used as received.

Single crystal synthesis and polycrystalline sample preparation

1. $Ba_5Pb_4O_4Br_{10}$

$Ba_5Pb_4O_4Br_{10}$ single crystals were grown in a closed system high-temperature solution. The synthesis processes are as follows: the raw materials $BaCO_3$, PbO and $PbBr_2$ were weighed according to the molar ratio of 1: 1: 1. After grinding and mixing in an agate mortar, the mixture was fully ground and placed in a 17 mm (inner diameter) tubular corundum crucibles, and then the cover at the opening of the corundum crucible was sealed with a high-temperature resistant binder. The sealed crucible is placed in a programmable constant temperature furnace, gradually heated to 700 °C, holding for 24 hours to ensure that the raw material is fully melted and evenly mixed. Then, it was cooled to 400 °C at a rate of 1 °C/h, then to 250 °C at a rate of 2 °C/h, and finally to room temperature within 2 days. After reactions, better crystals were manually picked under an optical microscope for structural determination.

The synthesis process of the $Ba_5Pb_4O_4Br_{10}$ polycrystalline sample is as follows: $BaBr_2$ (3.15 mmol, 0.937 g), PbO (2.5 mmol, 0.563 g) with a molar ratio of 5: 4 was fully ground and mixed in an agate mortar and transferred into a quartz tube, and the quartz tube was sealed with a hydrogen-oxygen flame in a vacuum environment (10^{-4} Pa). The sealed tube was then placed in a single crystal furnace for slow heating to 615 ˚C and kept at this temperature for 12 hours, then rapidly cooling to room temperature. The purity of the samples was examined by powder XRD diffraction.

2. $Ba_2CdSe_2O_6Cl_2$

Herein, the single crystal of $Ba_2CdSe_2O_6Cl_2$ was obtained also by using the high-temperature solution method. The reactants with a molar ratio of $BaCl_2 \cdot 2H_2O$: CdO: SeO_2 = 1: 1: 1 was fully ground and mixed in the agate mortar and transferred into a quartz tube, and the quartz tube was sealed with a hydrogen-oxygen flame in a vacuum environment (10^{-4} Pa). The sealed quartz tube was placed in a programmable constant temperature furnace, gradually heated to 798 ˚C, and kept at this temperature for 24 hours to ensure the uniformity of the solution. Then Perform a gradient cooling operation. The temperature is reduced to 600 °C at a rate of 1 °C/h, and then slowly reduced to 50 °C at a rate of 2 °C/h, and then the furnace was closed. The best crystals are manually picked under a light microscope for structural determination.

The powder sample of $Ba_2CdSe_2O_6Cl_2$ can be fully ground by a mixture of $BaCl_2 \cdot 2H_2O$ (1 mmol, 0.244 g), CdO (1 mmol, 0.128 g), SeO_2 (2 mmol, 0.344g) and $BaCO_3$ (1 mmol, 0.197 g) in agate mortar and moved into a quartz tube, and the quartz tube was sealed with a hydrogen-oxygen flame in a vacuum environment (10^{-4} Pa). Then placed in a single crystal furnace for slow heating to 590 ˚C and maintained at this temperature for 15 hours, followed by rapidly cooling to room temperature. The purity of the sample was examined by powder XRD diffraction.

3. $BaCdSeO_3Br_2$

Single crystals of the title compound were grown from a high-temperature solution. A reaction mixture with 0.197 g (1 mmol) of $BaCO_3$, 0.172 g (1 mmol) of SeO_2, 0.128 g (1 mmol) of CdO and 0.272 g (1 mmol) of $CdBr_2$ was placed in a quartz tube, and sealed in a vacuum environment (10^{-4} Pa) under a hydrogen-oxygen flame. The mixture was melted at 700 °C, held at this temperature for 24 h. Then the temperature was decreased to 500 °C at a rate of 1 °C/h. After that the sample was cooled to 50 °C at a rate of 2 °C/h. Finally, it was naturally cooled to room temperature and the colorless block crystals were obtained. Transparent crystals were selected for structure determination.

The powder sample of $BaCdSeO_3Br_2$ was prepared by standard solid-state reaction methods. A stoichiometric mixture of $BaCO_3$, SeO_2, CdO and $CdBr_2$ was ground thoroughly and loaded into a quartz tube, and the quartz tube was sealed with a hydrogen-oxygen flame in a vacuum environment (10^{-4} Pa). Then placed in a single crystal furnace for slow heating to 600 ˚C and maintained at this temperature for 15 hours, followed by rapidly cooling to room temperature. The purity of the samples was confirmed by powder X-ray diffraction (XRD) analyses.

Single crystal X-ray diffraction

A high-quality transparent single crystal was used for the data collection. The crystal structure were determined at room temperature on a Bruker D8 Venture single-crystal X-ray diffractometer using the Mo-Kα radiation (λ = 0.71073 Å). Numerical absorption corrections were carried out using the SCALE program for the area detector and integrated with the SAINT program.[2] Then, the crystal structure was solved by direct methods and refined using the SHELXTL crystallographic software package.[3-4] All atoms were refined with anisotropic displacement parameters. The program PLATON was used for verifying the possible missing symmetry elements,[5] but no higher symmetries were found. Finally, the crystal structure of compounds were confirmed. Table S1 presents the crystal data and structure refinements of the compound. The atomic coordinates, bond valence sum (BVS) calculations, bond distances and angles, and isotropic displacement parameters are presented in Tables S2-7.

Powder X-ray diffraction

The purity of the synthesized above compounds polycrystalline samples was verified by powder X-ray diffraction (PXRD), using a Bruker D2 Phaser diffractometer equipped with a diffracted beam monochromator set for Cu-Kα radiation (λ = 1.5418 Å). The PXRD pattern was recorded from 5° to 70° (2θ) with a scan step width of 0.01° and a fixed counting time of 1s per step.

Thermal analysis

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured on a simultaneous NETZSCH STA 449F3 thermal analyzer instrument at a temperature range of 40-800 °C with a heating rate of 5 °C /min in an atmosphere of flowing N_2.

Infrared (IR) spectroscopy

The Infrared spectrum was recorded with a NICOLET iS50 FT-IR Fourier transform infrared spectrometer in the range of 400-4000 cm^{-1}. A small amount (0.1-1 mg) of powder polycrystalline samples was weighed, and the powder sample was ground to a micron level (particle size < 10 μm) to reduce scattering interference. Wipe the ATR clean with an ethanol cotton ball Crystal surface and probe, and then take a small amount of ground samples placed on the surface of the crystal, gently compacted with a pressure bar. Ensure that the sample is in close contact with the crystal, set the parameters, scan and deduct the background (air or blank crystal), and click the "sample scanning" button in the software, the spectrometer begins to scan the sample and collect the infrared absorption spectrum of the sample. During the scanning process, it is necessary to maintain the stability of the sample and the instrument to avoid external vibration or interference.

UV-Vis-NIR diffuse reflectance spectroscopy

The diffuse reflectance spectrum of the $Ba_5Pb_4O_4Br_{10}$, $Ba_2CdSe_2O_6Cl_2$ and $BaCdSeO_3Br_2$ powder sample in the 200-2600 nm was measured using a Shimadzu Solid Spec-3700 DUV spectrophotometer at room temperature.

Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy. Elemental analysis was carried out on clean single crystal surfaces with the aid of a field emission scanning electron microscope (SEM, SUPRA 55VP) equipped with an energy dispersive X-ray spectroscope (EDS, BRUKER x-flash-sdd-5010).

Calculation details

The target compound's electronic structures and optical properties were performed based on the density functional theory (DFT) method implemented in the CASTEP package.[6-7] The exchange-correlation potential was treated by the Perdew-Burke-Ernzerh (PBE) of method in the generalized gradient approximation (GGA) and the interactions between the ionic cores and electrons were described by norm-conserving pseudopotential (NCP), the following orbital electrons were treated as valence electrons: Ba $5s^2$ $5p^6$ $6s^2$, Pb $6s^2$ $6p^2$, Cd $4d^{10}$ $5s^2$, Se $3d^{10}$ $4s^2$ $4p^4$, O $2s^2$ $2p^4$, Cl $3s^2$ $3p^5$, and Br $3d^{10}$ $4s^2$ $4p^5$ in the calculations. The kinetic energy cutoffs of 750 eV and 1 × 1 × 2 were chosen, and Monkhorst-Pack k-point meshes spanning 0.05/Å in the Brillouin zone.[8]

Fig. S1. The corresponding EDS spectra for (a) $Ba_5Pb_4O_4Br_{10}$, (b) $Ba_2CdSe_2O_6Cl_2$, and (c)$BaCdSeO_3Br_2$.

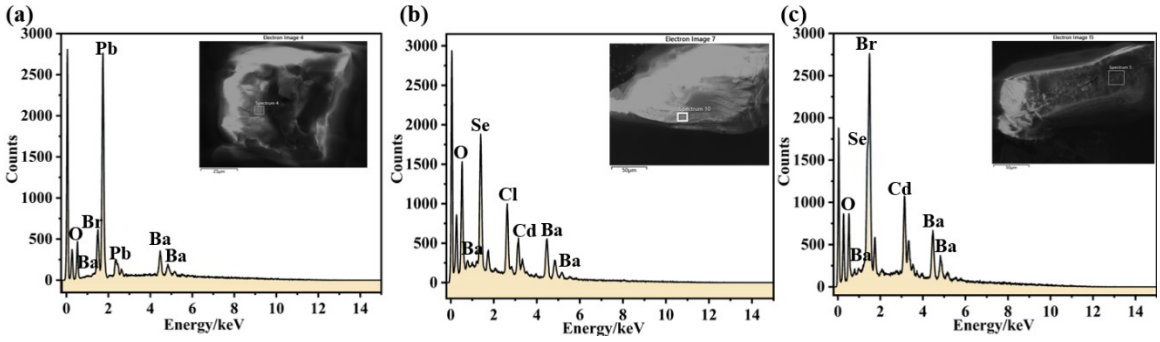


Fig S2. Structure symmetry comparison of (a) $Ba_5Pb_4O_4Br_{10}$ and (b) $Ba_{27}Pb_8O_8Cl_{54}$.

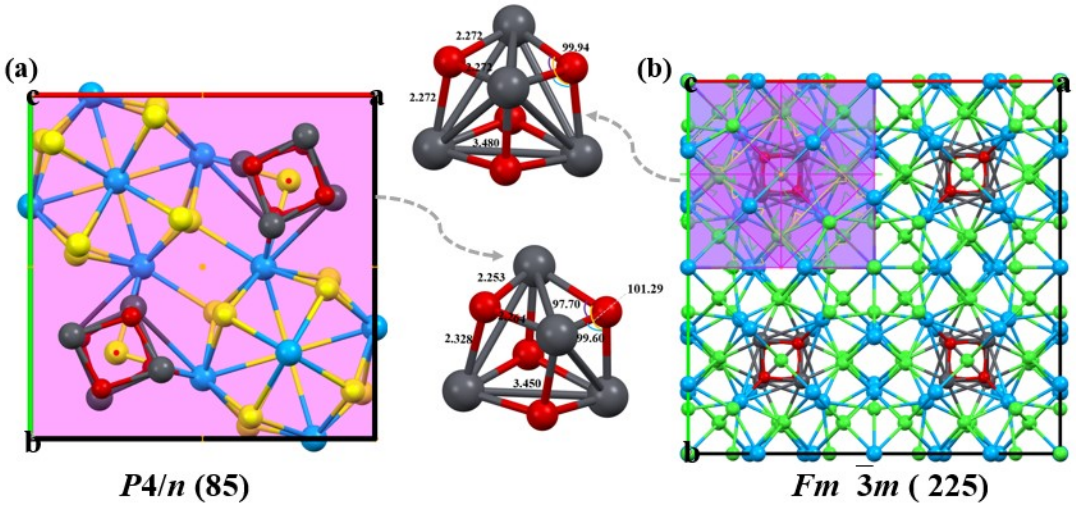


Table S1. Crystal data and structure refinement for $Ba_5Pb_4O_4Br_{10}$, $Ba_2CdSe_2O_6Cl_2$ and $BaCdSeO_3Br_2$.

Empirical formula	$Ba_5Pb_4O_4Br_{10}$	$Ba_2CdSe_2O_6Cl_2$	$BaCdSeO_3Br_2$
Formula weight	2378.56	711.9	536.52
Temperature(K)	298	298	298
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Tetragonal	orthorhombic	orthorhombic
space group	*P*4/*n* (No.85)	*Pnma* (No.62)	*Pnma* (No.62)
a (Å)	12.8099(16)	6.7782(8)	9.2162(15)
b (Å)	12.8099(16)	13.1189(15)	5.5496(10)
c (Å)	8.3153(15)	5.5337(7)	13.422(3)
α /°	90	90	90
β /°	90	90	90
γ /°	90	90	90
Volume(Å^3)	1364.5(4)	492.07(10)	686.5(2)
Z, Density calculated (Mg.m^{-3})	2, 5.789	2, 4.805	4, 5.191
Absorption coefficient (mm^{-1})	46.315	17.986	25.661
F (000)	1980	620	928
Theta range for data collection (°)	2.248 to 27.517	3.106 to 27.541	2.681 to 27.563
Limiting indices	-16 ≤ h ≤ 13, -16 ≤ k ≤ 16, -10 ≤ l ≤ 10	-8 ≤ h ≤ 8, -17 ≤ k ≤ 16, -7 ≤ l ≤ 7	-11 ≤ h ≤ 10, -7 ≤ k ≤ 7, -17 ≤ l ≤ 17
Reflections collected/unique	9629/1571 [*R*int= 0.0535]	9291/628 [*Rint* = 0.0573]	13663/865 [*Rint* = 0.0527]
Completeness (%)	99.9	99.8	99.4
Data/restraints/parameters	1571/0/55	628/0/39	865/0/47
Goodness-of-fit on F^2	1.258	1.088	1.158
Final *R* indexes [$F_o^2>2\sigma(F_o^2)$][a]	$R_1 = 0.0235$, $wR_2 = 0.0513$	$R_1 = 0.0220$, $wR_2 = 0.0595$	$R_1 = 0.0165$, $wR_2 = 0.0363$
R indexes [all data][a]	$R_1 = 0.0250$, $wR_2 = 0.0527$	$R_1 = 0.0221$, $wR_2 = 0.0596$	$R_1 = 0.0175$, $wR_2 = 0.0367$
Largest diff. peak and hole e·Å^{-3}	1.36 and-1.42	1.12 and -1.68	0.96 and -0.71

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

Table S2. Selected bond lengths (Å) and angles (°) for $Ba_5Pb_4O_4Br_{10}$.

Pb(1)-O(1)#3	2.328(4)	Br(2)-Ba(1)-Br(2)#5	72.07(2)
Pb(1)-O(1)	2.264(4)	Br(2)#5-Ba(1)-Br(3)	108.474(19)
Pb(1)-O(1)#1	2.253(4)	O(1)#1-Ba(1)-Br(4)	67.94(10)
Ba(1)-Br(1)	3.3508(6)	O(1)#1-Ba(1)-Br(4)#7	90.27(10)
Ba(1)-Br(2)#5	3.3458(8)	Br(2)#5-Ba(2)-Br(1)#5	60.467(18)
Ba(1)-Br(2)	3.3025(9)	Br(2)-Ba(2)-Br(1)#5	60.467(18)
Ba(1)-Br(2)#6	3.3507(9)	Br(2)#9-Ba(2)-Br(1)#5	60.467(18)
Ba(1)-Br(3)	3.6466(5)	Br(2)#10-Ba(2)-Br(1)#5	60.467(18)
Ba(1)-Br(4)#7	3.2487(9)	Br(2)-Ba(2)-Br(2)#9	120.93(4)
Ba(1)-Br(4)	3.3921(9)	Br(2)#9-Ba(2)-Br(2)#10	75.938(16)
Ba(1)-O(1)#1	2.536(4)	Br(2)-Ba(2)-Br(2)#8	75.938(16)
Ba(2)-Br(1)#5	3.6114(18)	Br(2)#9-Ba(2)-Br(2)#8	75.938(16)
Ba(2)-Br(2)	3.5675(9)	Br(2)-Ba(2)-Br(2)#10	75.938(16)
Ba(2)-Br(2)#8	3.5675(9)	Br(2)#10-Ba(2)-Br(2)#8	120.93(4)
Ba(2)-Br(2)#9	3.5675(9)	Br(4)#11-Ba(2)-Br(1)#5	125.659(18)
Ba(2)-Br(2)#10	3.5675(9)	Br(4)#12-Ba(2)-Br(1)#5	125.659(18)
Ba(2)-Br(4)#11	3.4143(9)	Br(4)#13-Ba(2)-Br(1)#5	125.659(18)
Ba(2)-Br(4)#12	3.4143(9)	Br(4)#1-Ba(2)-Br(1)#5	125.659(18)
Ba(2)-Br(4)#13	3.4143(9)	Br(4)#11-Ba(2)-Br(2)#10	65.22(2)
Ba(2)-Br(4)#1	3.4143(10)	Br(4)#12-Ba(2)-Br(2)	108.202(17)
		Br(4)#13-Ba(2)-Br(2)#10	105.209(17)
O(1)-Pb(1)-O(1)#3	78.29(17)	Br(4)#1-Ba(2)-Br(2)#10	108.202(17)
O(1)#1-Pb(1)-O(1)#3	79.47(17)	Br(4)#11-Ba(2)-Br(2)#8	173.64(3)
O(1)#1-Ba(1)-O(1)	80.84(18)	Br(4)#11-Ba(2)-Br(2)	105.210(17)
Br(1)-Ba(1)-Br(3)	135.98(2)	Br(4)#1-Ba(2)-Br(2)#8	105.209(17)
Br(1)-Ba(1)-Br(4)	70.27(2)	Br(4)#13-Ba(2)-Br(2)#9	65.22(2)
Br(2)-Ba(1)-Br(1)	134.91(2)	Br(4)#12-Ba(2)-Br(2)#8	65.22(2)
Br(2)#6-Ba(1)-Br(1)	65.29(2)	Br(4)#12-Ba(2)-Br(2)#10	173.64(3)
Br(2)#5-Ba(1)-Br(1)	65.34(2)	Br(4)#12-Ba(2)-Br(2)#9	105.209(17)
Br(2)-Ba(1)-Br(2)#6	123.12(2)	Br(4)#1-Ba(2)-Br(2)	65.22(2)
Br(2)#5-Ba(1)-Br(2)#6	81.92(3)	Br(4)#1-Ba(2)-Br(2)#9	173.64(3)
Br(2)-Ba(1)-Br(3)	71.214(15)	Br(4)#11-Ba(2)-Br(2)#9	108.202(17)
Br(2)#6-Ba(1)-Br(4)	85.56(2)	Br(4)#13-Ba(2)-Br(2)	173.64(3)
Br(2)#5-Ba(1)-Br(4)	135.14(2)	Br(4)#13-Ba(2)-Br(2)#8	108.202(17)
Br(2)-Ba(1)-Br(4)	146.20(2)	Br(4)#13-Ba(2)-Br(4)#11	70.132(18)
Br(4)#7-Ba(1)-Br(1)	72.01(2)	Br(4)#1-Ba(2)-Br(4)#13	108.68(4)
Br(4)#7-Ba(1)-Br(2)#6	136.50(2)	Br(4)#1-Ba(2)-Br(4)#12	70.132(18)
Br(4)#7-Ba(1)-Br(2)	92.86(2)	Br(4)#12-Ba(2)-Br(4)#11	108.68(4)
Br(4)#7-Ba(1)-Br(2)#5	87.95(2)	Br(4)#12-Ba(2)-Br(4)#13	70.132(18)
Br(4)#7-Ba(1)-Br(3)	151.281(17)	Br(4)#1-Ba(2)-Br(4)#11	70.133(18)
Br(4)-Ba(1)-Br(3)	107.506(16)	Pb(1)#2-O(1)-Pb(1)	99.60(17)
O(1)#1-Ba(1)-Br(1)	137.85(10)	Pb(1)#2-O(1)-Pb(1)#3	97.71(17)
O(1)#1-Ba(1)-Br(2)	82.29(10)	Pb(1)-O(1)-Pb(1)#3	101.29(17)
O(1)#1-Ba(1)-Br(2)#6	115.91(10)	Pb(1)#2-O(1)-Ba(1)#2	122.66(19)

O(1)#1-Ba(1)-Br(2)#5	154.17(10)	Pb(1)-O(1)-Ba(1)#2	121.96(18)
O(1)#1-Ba(1)-Br(3)	64.57(10)	Pb(1)#3-O(1)-Ba(1)#2	109.28(17)

Symmetry transformations used to generate equivalent atoms:
#1 1-Y,-1/2+X,2-Z; #2 1/2+Y,1-X,2-Z; #3 3/2-X,1/2-Y,+Z; #4 1/2-Y,-1+X,+Z; #5 2-X,-Y,3-Z; #6 1/2+Y,1-X,3-Z; #7 1+Y,1/2-X,+Z; #8 3/2-Y,-1+X,+Z; #9 5/2-X,1/2-Y,+Z; #10 1+Y,3/2-X,+Z; #11 1/2+X,1/2+Y,2-Z; #12 2-X,-Y,2-Z; #13 3/2+Y,1-X,2-Z; #14 3/2-X,-1/2-Y,+Z; #15 1-Y,-1/2+X,3-Z.

Table S3. The basic imformation of oxocentered [OPb_nA_{4-n}] tetrahedra in the crystal structure of lead heterometallic oxyhalides.

Compounds	Space group	Type of oxocentered units	Oxide substructures	Ref.
$RbPb_8O_4Cl_9$	*P*4/*n*	$[OPb_4]$	$[O_4Pb_8]^{8+}$ tetramer	1
$Cs_2Pb_{24}O_{21}I_8$	*P*4$_2$/n	$[OPb_3]$, $[OPb_4]$	rod-like $[Pb_8O_7]^{2+}$ chains	2
Pb_6LaO_7Cl	*C*2/*m*	$[OPb_2La_2]$, $[OPb_3La]$, $[OPb_4]$	$[O_8Pb_{10}La_3]^{13+}$ cluster	3
Pb_6LaO_7Br	*Cmcm*	$[OPb_2La_2]$, $[OPb_3La]$, $[OPb_4]$	$[O_8Pb_{10}La_3]^{13+}$ cluster	4
$PbSbO_2Cl$	*Cmcm*	$[OPb_2Sb_2]$	$^2_\infty[O_2PbSb]^+$ layers	5
$PbBiO_2Cl$	*Cmcm*	$[OPb_2Bi_2]$	$^2_\infty[O_2PbBi]^+$ layers	6
$PbSbO_2Br$	*I*4/*mmm*	$[OPb_2Sb_2]$	$^2_\infty[O_2PbSb]^+$ layers	7
$PbSbO_2I$	*I*4/*mmm*	$[OPb_2Sb_2]$	$^2_\infty[O_2PbSb]^+$ layers	8
$PbBiO_2Br$	*I*4/*mmm*	$[OPb_2Bi_2]$	$^2_\infty[O_2PbBi]^+$ layers	9
$PbBiO_2I$	*I*4/*mmm*	$[OPb_2Bi_2]$	$^2_\infty[O_2PbBi]^+$ layers	10
$CdPbOCl_2$	*P*2$_1$/*c*	$[OPb_2Cd_2]$	$^2_\infty[OPbCd]^{2+}$ layers	11
$CdPb_2O_2Cl_2$	*C*2/*m*	$[OPb_3Cd]$	$^2_\infty[O_2Pb_2Cd]^{2+}$ layers	12
$CdPb_2O_2Br_2$	*C*2/*m*	$[OPb_3Cd]$	$^2_\infty[O_2Pb_2Cd]^{2+}$ layers	13
$HgPb_2O_2Cl_2$	*C*2/m	$[OPb_3Hg]$	$^2_\infty[O_2Pb_2Hg]^{2+}$ layers	14
$HgPb_2O_2Br_2$	*C*2/m	$[OPb_3Hg]$	$^2_\infty[O_2Pb_2Hg]^{2+}$ layers	15
$AgPb_4O_4Cl$	*P*4/*n*	$[OPb_3Ag]$	$^2_\infty[O_4Pb_4Ag]^+$ layers	16
$Ag_2Pb_8O_7Cl_4$	*P*2$_1$/*c*	$[OPb_4]$	$^2_\infty[O_7Pb_8]^{2+}$ layers	17
AgPbOBr	*P*4/*nmm*	$[OPb_4]$	$^2_\infty[OPb]^+$ layers	18
$Ba_{27}Pb_8O_8Cl_{54}$	*Fm* $\bar{3}$*m*	$[OPb_3Ba]$	$[O_4Pb_4Ba_4]^{8+}$ species	19
*$Ba_5Pb_4O_4Br_{10}$	*P*4/*n*	$[OPb_3Ba]$	$[O_4Pb_4Ba_4]^{8+}$ species	This work
$Ba_8SrPb_{24}O_{24}Cl_{18}$	*I*4/m	$[OPb_3Ba]$, $[OPb_2Ba_2]$	$^2_\infty[O_3BaPb_3]^{2+}$ layers	20

Table S4. Fractional atomic coordinates (×10^4), equivalent isotropic displacement parameters(Å^2×10^3), and bond valence sum (BVS) for $Ba_5Pb_4O_4Br_{10}$, $Ba_2CdSe_2O_6Cl_2$ and $BaCdSeO_3Br_2$. U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.

Atoms	Wyckoff	*x*	*Y*	*z*	U(eq)	BVS[a)]
			$Ba_5Pb_4O_4Br_{10}$			
Pb(1)	8g	7992.2(2)	1204.2(2)	8577.1(3)	13.72(9)	2.32
Ba(1)	8g	8231.2(3)	-8.8(3)	13260.6(5)	15.12(11)	2.42
Ba(2)	2c	12500	2500	11904.9(11)	22.08(19)	1.71
O(1)	8g	6454(3)	2068(3)	8742(5)	11.8(8)	2.41
Br(1)	2c	7500	-2500	13752.0(17)	18.1(3)	1.26
Br(2)	8g	10374.7(5)	1336.2(5)	14019.7(9)	22.56(16)	1.04
Br(3)	2b	7500	2500	15000	25.9(3)	0.98
Br(4)	8g	6393.3(5)	-638.6(5)	10488.7(9)	20.84(16)	1.08
			$Ba_2CdSe_2O_6Cl_2$			
Ba(1)	4g	1901.0(4)	2693.6(2)	0	11.60(18)	2.05
Cd(1)	2d	10000	5000	5000	10.63(19)	2.09
Se(1)	4g	7296.2(7)	4161.6(3)	0	9.79(19)	4.08
O(1)	8h	8821(4)	3825.3(17)	2333(4)	15.2(5)	2.12
O(2)	4g	5717(6)	3185(3)	0	20.0(7)	2.05
Cl(1)	4g	6717.5(17)	6064.3(10)	5000	20.2(3)	0.88
			$BaCdSeO_3Br_2$			
Ba(1)	4c	5828.4(3)	7500	2011.2(2)	15.13(9)	1.94
Cd(1)	4c	3938.0(3)	2500	3819.4(2)	13.42(10)	2.07
Se(1)	4c	2735.6(4)	2500	1604.7(3)	10.53(11)	4.13
O(1)	8d	3326(2)	4825(4)	2314.8(16)	17.2(5)	2.06
O(2)	4c	985(3)	2500	1980(3)	27.0(8)	2.10
Br(1)	4c	1319.7(5)	2500	4601.3(4)	20.54(12)	0.88
Br(2)	4c	4387.8(6)	-2500	4315.6(3)	21.78(13)	1.04

a) The bond valence sum is calculated by bond-valence theory ($Sij = \exp[(R_0-R)/B$, where R is an empirical constant, R_0 is the length of bond I (in angstroms), and $B = 0.37$).

Table S5. The statistics of Pb/A-O-Pb/A angles (°) and O-Pb/A bond distances(Å) in the crystal structure of lead heterometallic oxyhalide compounds.

Compounds	Basic units	The O-Pb/A bond distances (Å)	The average value (Å)	The Pb/A-O-Pb/A angles (°)	The average value (°)
Pb_6LaO_7Cl	$[OPb_2La_2]$, $[OPb_3La]$, $[OPb_4]$	d(O1-Pb) = 2.2608 d(O1-Pb) = 2.0910 d(O1-La) = 2.5436 d(O1-La) = 2.5436	2.35975	∠(Pb-O1-Pb) = 120.847 ∠(Pb-O1-Pb) = 106.850 ∠(Pb-O1-Ba) = 107.982 ∠(La-O1-La) = 105.333	110.253
		d(O2-Pb) = 2.1654 d(O2-Pb) = 2.3216 d(O2-Pb) = 2.3911 d(O2-La) = 2.5988	2.369225	∠(Pb-O2-Pb) = 125.266 ∠(Pb-O2-Pb) = 121.088 ∠(Pb-O2-La) = 98.256 ∠(Pb-O2-La) = 103.386	111.999
		d(O3-Pb) = 2.2043 d(O3-Pb) = 2.2008 d(O3-La) = 2.5227 d(O3-La) = 2.5227	2.362625	∠(Pb-O3-Pb) = 121.687 ∠(Pb-O3-La) = 108.020 ∠(Pb-O3-La) = 105.824 ∠(La-O3-La) = 106.591	110.530 5
		d(O4-Pb) = 2.4401 d(O4-Pb) = 2.3157 d(O4-Pb) = 2.1711 d(O4-La) = 2.5698	2.374175	∠(Pb-O4-Pb) = 126.116 ∠(Pb-O4-Pb) = 118.510 ∠(Pb-O4-La) = 97.183 ∠(Pb-O4-La) = 104.164	111.493 25
		d(O5-Pb) = 2.2085 d(O5-Pb) = 2.6915 d(O5-Pb) = 2.2085 d(O5-Pb) = 2.4506	2.389775	∠(Pb-O5-Pb) = 97.975 ∠(Pb-O5-Pb) = 94.544 ∠(Pb-O5-Ba) = 94.544 ∠(Pb-O5-Ba) = 97.975	96.2595
Pb_6LaO_7Br	$[OPb_2La_2]$, $[OPb_3La]$, $[OPb_4]$	d(O1-Pb) = 2.2644 d(O1-Pb) = 2.2050 d(O1-La) = 2.5413 d(O1-La) = 2.5413	2.388	∠(Pb-O1-La) = 120.227 ∠(Pb-O1-La) = 107.399 ∠(Pb-O1-La) = 106.272 ∠(La-O1-La) = 108.912	110.702 5
		d(O2-Pb) = 2.4562 d(O2-Pb) = 2.2169 d(O2-Pb) = 2.3277 d(O2-La) = 2.6279	2.407175	∠(Pb-O2-Pb) = 122.750 ∠(Pb-O2-Pb) = 126.131 ∠(Pb-O2-La) = 103.198 ∠(Pb-O2-La) = 96.770	112.212 25
		d(O3-Pb) = 2.3277 d(O3-Pb) = 2.2169 d(O3-Pb) = 2.4562 d(O3-La) = 2.6279	2.407175	∠(Pb-O3-Pb) = 122.750 ∠(Pb-O3-Pb) = 99.813 ∠(Pb-O3-La) = 103.198 ∠(Pb-O3-La) =102.766	107.131 75
		d(O4-Pb) = 2.2050 d(O4-Pb) = 2.2644 d(O4-La) = 2.5413 d(O4-La) = 2.5413	2.388	∠(Pb-O4-Pb) = 120.227 ∠(Pb-O4-La) = 106.272 ∠(Pb-O4-La) = 107.399 ∠(Pb-O4-La) =108.912	110.702 5
		d(O5-Pb) = 2.4562 d(O5-Pb) = 2.2169 d(O5-Pb) = 2.3277 d(O5-La) = 2.6279	2.407175	∠(Pb-O5-La) = 122.750 ∠(Pb-O5-La) = 126.131 ∠(Pb-O5-La) = 103.198 ∠(Pb-O5-La) = 96.770	112.212 25
		d(O6-Pb) = 2.2615 d(O6-Pb) = 2.2615	2.404	∠(Pb-O6-Pb) = 96.002 ∠(Pb-O6-Pb) = 96.002	96.002

		d(O6-Pb) = 2.5465 d(O6-Pb) = 2.5465		∠(Pb-O6-Pb) = 96.002 ∠(Pb-O6-Pb) = 96.002	
		d(O7-Pb) = 2.4562 d(O7-Pb) = 2.2169 d(O7-Pb) = 2.3277 d(O7-La) = 2.6279	2.407175	∠(Pb-O7-Pb) = 122.750 ∠(Pb-O7-Pb) = 126.131 ∠(Pb-O7-La) = 103.198 ∠(Pb-O7-La) = 96.770	112.21225
		d(O8-Pb) = 2.2050 d(O8-Pb) = 2.2644 d(O8-La) = 2.5413 d(O8-La) = 2.5413	2.388	∠(Pb-O8-Pb) = 120.227 ∠(Pb-O8-La) = 106.272 ∠(Pb-O8-La) = 107.399 ∠(La-O8-La) =108.912	110.7025
		d(O9-Pb) = 2.2050 d(O9-Pb) = 2.2644 d(O9-La) = 2.5413 d(O9-La) = 2.5413	2.388	∠(Pb-O9-Pb) = 120.227 ∠(Pb-O9-La) = 106.272 ∠(Pb-O9-La) = 107.399 ∠(La-O9-La) =108.912	110.7025
		d(O10-Pb) = 2.4562 d(O10-Pb) = 2.2169 d(O10-Pb) = 2.3277 d(O10-La) = 2.6279	2.407175	∠(Pb-O10-Pb) = 99.813 ∠(Pb-O10-Pb) = 122.750 ∠(Pb-O10-La) = 102.766 ∠(Pb-O10-La) = 103.198	103.13175
		d(O11-Pb) = 2.4562 d(O11-Pb) = 2.2169 d(O11-Pb) = 2.3277 d(O11-La) = 2.6279	2.407175	∠(Pb-O11-Pb) = 99.813 ∠(Pb-O11-Pb) = 122.750 ∠(Pb-O11-La) = 102.766 ∠(Pb-O11-La) = 103.198	107.13175
		d(O12-Pb) = 2.4562 d(O12-Pb) = 2.2169 d(O12-Pb) = 2.3277 d(O12-La) = 2.6279	2.407175	∠(Pb-O12-Pb) = 99.813 ∠(Pb-O12-Pb) = 122.750 ∠(Pb-O12-La) = 102.766 ∠(Pb-O12-La) = 103.198	107.13175
		d(O13-Pb) = 2.4562 d(O13-Pb) = 2.2169 d(O13-Pb) = 2.3277 d(O13-La) = 2.6279	2.407175	∠(Pb-O13-Pb) = 99.813 ∠(Pb-O13-Pb) = 122.750 ∠(Pb-O13-La) = 102.766 ∠(Pb-O13-La) = 103.198	107.13175
		d(O14-Pb) = 2.2615 d(O14-Pb) = 2.2615 d(O14-Pb) = 2.5465 d(O14-Pb) = 2.5465	2.404	∠(Pb-O6-Pb) = 96.002 ∠(Pb-O6-Pb) = 96.002 ∠(Pb-O6-Pb) = 96.002 ∠(Pb-O6-Pb) = 96.002	96.002
		d(O15-Pb) = 2.4562 d(O15-Pb) = 2.2169 d(O15-Pb) = 2.3277 d(O15-La) = 2.6279	2.407175	∠(Pb-O15-Pb) = 122.750 ∠(Pb-O15-Pb) = 126.131 ∠(Pb-O15-La) = 103.198 ∠(Pb-O15-La) = 96.770	112.21225
		d(O16-Pb) = 2.2050 d(O16-Pb) = 2.2644 d(O16-La) = 2.5413 d(O16-La) = 2.5413	2.388	∠(Pb-O16-Pb) = 120.227 ∠(Pb-O16-La) = 106.272 ∠(Pb-O16-La) = 107.399 ∠(Pb-O16-La) =108.912	110.7025
		d(O17-Pb) = 2.4562 d(O17-Pb) = 2.2169 d(O17-Pb) = 2.3277 d(O17-La) = 2.6279	2.407175	∠(Pb-O17-Pb) = 122.750 ∠(Pb-O17-Pb) = 126.131 ∠(Pb-O17-La) = 103.198 ∠(Pb-O17-La) = 96.770	112.21225
		d(O18-Pb) = 2.4562 d(O18-Pb) = 2.2169	2.407175	∠(Pb-O18-La) = 122.750	107.13175

		d(O18-Pb) = 2.3277 d(O18-La) = 2.6279		∠(Pb-O18-La) = 99.813 ∠(Pb-O18-La) = 103.198 ∠(Pb-O18-La) = 102.766	
		d(O19-Pb) = 2.2050 d(O19-Pb) = 2.2644 d(O19-La) = 2.5413 d(O19-La) = 2.5413	2.388	∠(Pb-O19-Pb) = 120.227 ∠(Pb-O19-La) = 106.272 ∠(Pb-O19-La) = 107.399 ∠(La-O19-La) =108.912	110.7025
		d(O20-Pb) = 2.4562 d(O20-Pb) = 2.2169 d(O20-Pb) = 2.3277 d(O20-La) = 2.6279	2.407175	∠(Pb-O20-Pb) = 122.750 ∠(Pb-O20-Pb) = 126.131 ∠(Pb-O20-La) = 103.198 ∠(Pb-O20-La) = 96.770	112.21225
		d(O21-Pb) = 2.2615 d(O21-Pb) = 2.2615 d(O21-Pb) = 2.5465 d(O21-Pb) = 2.5465	2.404	∠(Pb-O21-Pb) = 96.002 ∠(Pb-O21-Pb) = 96.002 ∠(Pb-O21-Pb) = 96.002 ∠(Pb-O21-Pb) =96.002	96.002
		d(O22-Pb) = 2.4562 d(O22-Pb) = 2.2169 d(O22-Pb) = 2.3277 d(O22-La) = 2.6279	2.407175	∠(Pb-O22-Pb) = 122.750 ∠(Pb-O22-Pb) = 126.131 ∠(Pb-O22-La) = 103.198 ∠(Pb-O22-La) = 96.770	112.21225
		d(O23-Pb) = 2.2050 d(O23-Pb) = 2.2644 d(O23-La) = 2.5413 d(O23-La) = 2.5413	2.388	∠(Pb-O23-La) = 120.227 ∠(Pb-O23-La) = 107.399 ∠(Pb-O23-La) = 106.272 ∠(Pb-O23-La) = 108.912	110.7025
		d(O24-Pb) = 2.2050 d(O24-Pb) = 2.2644 d(O24-La) = 2.5413 d(O24-La) = 2.5413	2.388	∠(Pb-O24-Pb) = 120.227 ∠(Pb-O24-La) = 106.272 ∠(Pb-O24-La) = 107.399 ∠(La-O24-La) = 108.912	110.7025
		d(O25-Pb) = 2.4562 d(O25-Pb) = 2.2169 d(O25-Pb) = 2.3277 d(O25-La) = 2.6279	2.407175	∠(Pb-O25-Pb) = 122.750 ∠(Pb-O25-Pb) = 99.813 ∠(Pb-O25-La) = 103.198 ∠(Pb-O25-La) = 102.766	107.13175
		d(O26-Pb) = 2.4562 d(O26-Pb) = 2.2169 d(O26-Pb) = 2.3277 d(O26-La) = 2.6279	2.407175	∠(Pb-O26-Pb) = 122.750 ∠(Pb-O26-Pb) = 99.813 ∠(Pb-O26-La) = 103.198 ∠(Pb-O26-La) = 102.766	107.13175
		d(O27-Pb) = 2.4562 d(O27-Pb) = 2.2169 d(O27-Pb) = 2.3277 d(O27-La) = 2.6279	2.407175	∠(Pb-O27-Pb) = 122.750 ∠(Pb-O27-Pb) = 99.813 ∠(Pb-O27-La) = 103.198 ∠(Pb-O27-La) = 102.766	107.13175
		d(O28-Pb) = 2.2615 d(O28-Pb) = 2.2615 d(O28-Pb) = 2.5465 d(O28-Pb) = 2.5465	2.404	∠(Pb-O28-Pb) = 96.002 ∠(Pb-O28-Pb) = 96.002 ∠(Pb-O28-Pb) = 96.002 ∠(Pb-O28-Pb) =96.002	96.002
		d(O29-Pb) = 2.4562 d(O29-Pb) = 2.2169 d(O29-Pb) = 2.3277 d(O29-La) = 2.6279	2.407175	∠(Pb-O29-Pb) = 122.750 ∠(Pb-O29-Pb) = 126.131 ∠(Pb-O29-La) = 103.198 ∠(Pb-O29-La) = 96.770	112.21225

$PbSbO_2Cl$	$[OPb_2Sb_2]$	d(O-Pb) = 2.5421 d(O-Pb) = 2.5421 d(O-Sb) = 2.0733 d(O-Sb) = 2.0733	2.3077	∠(Pb-O-Sb) = 116.715 ∠(Pb-O-Sb) = 116.715 ∠(Pb-O-Pb) = 103.239 ∠(Sb-O-Sb) = 107.695	111.091
$PbBiO_2Cl$	$[OPb_2Bi_2]$	d(O-Pb) = 2.4420 d(O-Pb) = 2.4420 d(O-Bi) = 2.2742 d(O-Bi) = 2.2742	2.3581	∠(Pb-O-Pb) = 109.650 ∠(Pb-O-Bi) = 114.734 ∠(Pb-O-Bi) = 114.734 ∠(Bi-O-Bi) = 103.576	110.6735
$PbSbO_2Br$	$[OPb_2Sb_2]$	d(O-Pb) = 2.3998 d(O-Pb) = 2.3998 d(O-Pb) = 2.3998 d(O-Pb) = 2.3998 d(O-Sb) = 2.2374 d(O-Sb) = 2.2374 d(O-Sb) = 2.2374 d(O-Sb) = 2.2374	2.3186	∠(Pb-O-Sb) = 105.556 ∠(Pb-O-Sb) = 105.556 ∠(Pb-O-Sb) = 105.556 ∠(Pb-O-Sb) = 105.556 ∠(Pb-O-Sb) = 105.556 ∠(Pb-O-Sb) = 105.556 ∠(Pb-O-Sb) = 105.556 ∠(Pb-O-Sb) = 105.556	105.556
$PbSbO_2I$	$[OPb_2Sb_2]$	d(O-Pb) = 2.4285 d(O-Pb) = 2.4285 d(O-Pb) = 2.4285 d(O-Pb) = 2.4285 d(O-Sb) = 2.2401 d(O-Sb) = 2.2401 d(O-Sb) = 2.2401 d(O-Sb) = 2.2401	2.3343	∠(Pb-O-Sb) = 104.634 ∠(Pb-O-Sb) = 104.634 ∠(Pb-O-Sb) = 104.634 ∠(Pb-O-Sb) = 104.634 ∠(Pb-O-Sb) = 104.634 ∠(Pb-O-Sb) = 104.634 ∠(Pb-O-Sb) = 104.634 ∠(Pb-O-Sb) = 104.634	104.634
$PbBiO_2Br$	$[OPb_2Bi_2]$	d(Pb|Bi-O) = 2.3279 d(Pb|Bi-O) = 2.3279 d(Pb|Bi-O) = 2.3279 d(Pb|Bi-O) = 2.3279	2.3279	∠(Pb|Bi-O-Pb|Bi) = 105.579 ∠(Pb|Bi-O-Pb|Bi) = 105.579 ∠(Pb|Bi-O-Pb|Bi) = 105.579 ∠(Pb|Bi-O-Pb|Bi) = 105.579	105.579
$PbBiO_2I$	$[OPb_2Bi_2]$	d(Pb|Bi-O) = 2.3473 d(Pb|Bi-O) = 2.3473 d(Pb|Bi-O) = 2.3473 d(Pb|Bi-O) = 2.3473	2.3473	∠(Pb|Bi-O-Pb|Bi) = 104.748 ∠(Pb|Bi-O-Pb|Bi) = 104.748 ∠(Pb|Bi-O-Pb|Bi) = 104.748 ∠(Pb|Bi-O-Pb|Bi) = 104.748	104.748
$CdPbOCl_2$	$[OPb_2Cd_2]$	d(O-Pb) = 2.2203 d(O-Pb) = 2.2948 d(O-Cd) = 2.2082 d(O-Cd) = 2.2386	2.240475	∠(Pb-0-Cd) = 98.597 ∠(Pb-O-Cd) = 95.554 ∠(Pb-O-Pb) = 120.168 ∠(Cd-O-Cd) = 116.889	107.802
$CdPb_2O_2Cl_2$	$[OPb_3Cd]$	d(O-Pb) = 2.3414 d(O-Pb) = 2.2928 d(O-Pb) = 2.3414 d(O-Cd) = 2.1586	2.28355	∠(Pb-O-Cd) = 103.516 ∠(Pb-O-Cd) = 103.516 ∠(Pb-O-Cd) = 115.370 ∠(Pb-O-Cd) = 115.370	109.443
$CdPb_2O_2Br_2$	$[OPb_3Cd]$	d(O-Pb) = 2.302	2.290125	∠(Pb-O-Pb) = 102.538	109.5722

		d(O-Pb) = 2.3456 d(O-Pb) = 2.3456 d(O-Cd) = 2.1673		∠(Pb-O-Pb) = 111.494 ∠(Pb-O-Cd) = 114.569 ∠(Pb-O-Cd) = 109.688	5
$HgPb_2O_2Cl_2$	$[OPb_3Hg]$	d(O-Pb) = 2.3885 d(O-Pb) = 2.3407 d(O-Pb) = 2.3885 d(O-Hg) = 2.0478	2.291375	∠(Pb-O-Pb) = 105.993 ∠(Pb-O-Pb) = 105.993 ∠(Pb-O-Hg) = 113.105 ∠(Pb-O-Hg) = 113.105	109.549
$HgPb_2O_2Br_2$	$[OPb_3Hg]$	d(O-Pb) = 2.4087 d(O-Pb) = 2.3400 d(O-Pb) = 2.4087 d(O-Hg) = 2.0676	2.30625	∠(Pb-O-Pb) = 105.016 ∠(Pb-O-Cd) = 105.016 ∠(Pb-O-Pb) = 112.751 ∠(Pb-O-Cd) = 112.751	108.8835
$AgPb_4O_4Cl$	$[OPb_3Ag]$	d(O-Pb) = 2.2461 d(O-Pb) = 2.2242 d(O-Pb) = 2.2361 d(O-Ag) = 2.4684	2.2937	∠(Pb-O-Pb) = 128.058 ∠(Pb-O-Pb) = 104.253 ∠(Pb-O-Ag) = 94.750 ∠(Pb-O-Ag) = 94.451	105.378
$Ag_2Pb_8O_7Cl_4$	$[OPb_4]$	d(O1-Pb) = 2.2435 d(O1-Pb) = 2.4609 d(O1-Pb) = 2.4014 d(O1-Pb) = 2.3016	2.35185	∠(Pb-O1-Pb) = 119.819 ∠(Pb-O1-Pb) = 102.547 ∠(Pb-O1-Pb) = 99.276 ∠(Pb-O1-Pb) = 101.72	105.8405
		d(O2-Pb) = 2.3587 d(O2-Pb) = 2.3174 d(O2-Pb) = 2.2275 d(O2-Pb) = 2.2700	2.2934	∠(Pb-O2-Pb) = 106.331 ∠(Pb-O2-Pb) = 101.844 ∠(Pb-O2-Pb) = 106.208 ∠(Pb-O2-Pb) = 110.131	106.1285
		d(O3-Pb) = 2.4815 d(O3-Pb) = 2.4562 d(O3-Cd) = 2.2855 d(O3-Cd) = 2.1991	2.355575	∠(Pb-O3-Pb) = 101.983 ∠(Pb-O3-Pb) = 96.617 ∠(Pb-O3-Pb) = 101.636 ∠(Pb-O3-Pb) = 123.652	105.972
		d(O4-Pb) = 2.4469 d(O4-Pb) = 2.2947 d(O4-Pb) = 2.1889 d(O4-Pb) = 2.3926	2.330775	∠(Pb-O4-Pb) = 98.755 ∠(Pb-O4-Pb) = 101.654 ∠(Pb-O4-Pb) = 109.972 ∠(Pb-O4-Pb) = 106.482	104.21575
		d(O5-Pb) = 2.3096 d(O5-Pb) = 2.5768 d(O5-Pb) = 2.2130 d(O5-Pb) = 2.3277	2.356775	∠(Pb-O5-Pb) = 97.637 ∠(Pb-O5-Pb) = 97.307 ∠(Pb-O5-Pb) = 98.271 ∠(Pb-O5-Pb) = 117.682	102.72425
		d(O6-Pb) = 2.1424 d(O6-Pb) = 2.5795 d(O6-Pb) = 2.4492 d(O6-Pb) = 2.2843	2.36385	∠(Pb-O6-Pb) = 123.257 ∠(Pb-O6-Pb) = 100.267 ∠(Pb-O6-Pb) = 93.821 ∠(Pb-O6-Pb) = 94.697	103.0105
		d(O7-Pb) = 2.3224 d(O7-Pb) = 2.4430 d(O7-Pb) = 2.071 d(O7-Pb) = 2.4759	2.328075	∠(Pb-O7-Pb) = 98.934 ∠(Pb-O7-Pb) = 93.895 ∠(Pb-O7-Pb) = 100.962 ∠(Pb-O7-Pb) = 106.081	99.968
AgPbOBr	$[OPb_4]$	d(O-Pb) = 2.2881 d(O-Pb) = 2.2881 d(O-Pb) = 2.2881 d(O-Pb) = 2.2881	2.2881	∠(Pb-O-Pb) = 106.085 ∠(Pb-O-Pb) = 106.085 ∠(Pb-O-Pb) = 106.085 ∠(Pb-O-Pb) = 106.085	106.085

$RbPb_8O_4Cl_9$	$[OPb_4]$	d(O-Pb) = 2.2347 d(O-Pb) = 2.2738 d(O-Pb) = 2.3730 d(O-Pb) = 2.3247	2.30155	∠(Pb-O-Pb) = 116.278 ∠(Pb-O-Pb) = 125.342 ∠(Pb-O-Pb) = 99.462 ∠(Pb-O-Pb) = 103.247	111.08225
$Cs_2Pb_{24}O_{21}I_8$	$[OPb_4]$, $[OPb_3]$	d(O1-Pb) = 2.2772 d(O1-Pb) = 2.3049 d(O1-Pb) = 2.3246 d(O1-Pb) = 2.3862	2.323225	∠(Pb-O1-Pb) = 101.672 ∠(Pb-O1-Pb) = 119.728 ∠(Pb-O1-Pb) = 94.645 ∠(Pb-O1-Pb) = 98.847	103.723
		d(O2-Pb) = 2.2040 d(O2-Pb) = 2.1671 d(O2-Pb) = 2.2606	2.21057	∠(Pb-O2-Pb) = 106.538 ∠(Pb-O2-Pb) = 120.218 ∠(Pb-O2-Pb) = 107.562	111.4393
		d(O3-Pb) = 2.2630 d(O3-Pb) = 2.3145 d(O3-Pb) = 2.4494 d(O3-Pb) = 2.3197	2.33665	∠(Pb-O3-Pb) = 122.060 ∠(Pb-O3-Pb) = 120.896 ∠(Pb-O3-Pb) = 121.523 ∠(Pb-O3-Pb) = 96.986	115.36625
		d(O4-Pb) = 2.2511 d(O4-Pb) = 2.2599 d(O4-Pb) = 2.4610 d(O4-Pb) = 2.4747	2.361675	∠(Pb-O4-Pb) = 96.040 ∠(Pb-O4-Pb) = 121.955 ∠(Pb-O4-Pb) = 96.649 ∠(Pb-O4-Pb) = 92.078	101.6805
		d(O5-Pb) = 2.3744 d(O5-Pb) = 2.3744 d(O5-Pb) = 2.3744 d(O5-Pb) = 2.3744	2.3744	∠(Pb-O5-Pb) = 96.859 ∠(Pb-O5-Pb) = 96.859 ∠(Pb-O5-Pb) = 96.859 ∠(Pb-O5-Pb) = 96.859	96.859
		d(O6-Pb) = 2.2664 d(O6-Pb) = 2.3454 d(O6-Pb) = 2.2516 d(O6-Pb) = 2.3226	2.2965	∠(Pb-O6-Pb) = 100.510 ∠(Pb-O6-Pb) = 103.275 ∠(Pb-O6-Pb) = 103.470 ∠(Pb-O6-Pb) = 100.463	101.93225
$Ba_{27}Pb_8O_8Cl_{54}$	$[OPb_3Ba]$	d(O-Pb) = 2.2725 d(O-Pb) = 2.2725 d(O-Pb) = 2.2725 d(O-Ba) = 2.5450	2.340625	∠(Pb-0-Pb) = 99.940 ∠(Pb-O-Pb) = 99.940 ∠(Pb-O-Ba) = 117.851 ∠(Pb-O-Ba) = 117.851	108.8955
*$Ba_5Pb_4O_4Br_{10}$	$[OPb_3Ba]$	d(O-Pb) = 2.3282 d(O-Pb) = 2.2534 d(O-Pb) = 2.2640 d(O-Ba) = 2.536	2.3454	∠(Pb-0-Pb) = 97.704 ∠(Pb-O-Pb) = 99.601 ∠(Pb-O-Ba) = 121.968 ∠(Pb-O-Ba) = 109.277	107.1375
$Ba_8SrPb_{24}O_{24}Cl_{18}$	$[OPb_3Ba]$, $[OPb_2Ba_2]$	d(O1-Pb) = 2.2577 d(O1-Pb) = 2.2806 d(O1-Pb) = 2.2853 d(O1-Ba) = 2.4687	2.323075	∠(Pb-O1-Pb) = 102.166 ∠(Pb-O1-Pb) = 127.705 ∠(Pb-O1-Ba) = 103.891 ∠(Pb-O1-Ba) = 99.844	108.4015
		d(O2-Pb) = 2.2834 d(O2-Pb) = 2.1449 d(O2-Ba) = 2.4364 d(O2-Ba) = 2.4854	2.337525	∠(Pb-O2-Pb) = 121.080 ∠(Pb-O2-Ba) = 102.916 ∠(Pb-O2-Ba) = 100.726 ∠(Ba-O2-Ba) = 101.507	106.55725
		d(O3-Pb) = 2.1832 d(O3-Pb) = 2.2914 d(O3-Pb) = 2.3035 d(O3-Ba) = 2.5283	2.3266	∠(Pb-O3-Pb) = 128.980 ∠(Pb-O3-Pb) = 100.435 ∠(Pb-O3-Ba) = 101.526 ∠(Pb-O3-Ba) = 100.450	107.84775

Table S6. Selected bond lengths (Å) and angles (°) for $Ba_2CdSe_2O_6Cl_2$.

Ba(1)-Cl(1)#3	3.2533(12)	O(1)#6-Ba(1)-O(2)#2	109.02(8)
Ba(1)-Cl(1)#4	3.3448(8)	O(2)-Ba(1)-Cl(1)#5	67.08(4)
Ba(1)-Cl(1)#5	3.3448(8)	O(2)#8-Ba(1)-Cl(1)#3	63.96(6)
Ba(1)-O(1)#6	2.869(2)	O(2)-Ba(1)-Cl(1)#4	67.08(4)
Ba(1)-O(1)#7	2.800(2)	O(2)#8-Ba(1)-Cl(1)#4	61.04(7)
Ba(1)-O(1)#1	2.869(2)	O(2)#2-Ba(1)-Cl(1)#5	61.04(7)
Ba(1)-O(1)#2	2.800(2)	O(2)#2-Ba(1)-Cl(1)#3	63.96(6)
Ba(1)-O(2)#2	3.1029(18)	O(2)#2-Ba(1)-Cl(1)#4	172.31(7)
Ba(1)-O(2)#8	3.1029(18)	O(2)-Ba(1)-Cl(1)#3	152.93(9)
Ba(1)-O(2)	2.666(4)	O(2)#8-Ba(1)-Cl(1)#5	172.31(7)
Cd(1)-Cl(1)	2.6268(12)	O(2)-Ba(1)-O(1)#2	73.81(9)
Cd(1)-Cl(1)#9	2.6268(11)	O(2)-Ba(1)-O(1)#1	125.52(8)
Cd(1)-O(1)#10	2.279(2)	O(2)-Ba(1)-O(1)#7	125.52(8)
Cd(1)-O(1)#9	2.279(2)	O(2)-Ba(1)-O(1)#6	73.81(9)
Cd(1)-O(1)#11	2.279(2)	O(2)-Ba(1)-O(2)#8	109.93(8)
Cd(1)-O(1)	2.279(2)	O(2)#2-Ba(1)-O(2)#8	126.17(13)
Se(1)-O(1)#12	1.712(2)	O(2)-Ba(1)-O(2)#2	109.93(8)
Se(1)-O(1)	1.712(2)	Cl(1)-Cd(1)-Cl(1)#11	180
Se(1)-O(2)	1.670(4)	O(1)#12-Cd(1)-Cl(1)#11	86.42(6)
		O(1)-Cd(1)-Cl(1)#11	86.42(6)
Cl(1)#4-Ba(1)-Cl(1)#5	111.63(4)	O(1)#13-Cd(1)-Cl(1)#11	93.58(6)
Cl(1)#3-Ba(1)-Cl(1)#5	122.08(2)	O(1)#11-Cd(1)-Cl(1)#11	93.58(6)
Cl(1)#3-Ba(1)-Cl(1)#4	122.08(2)	O(1)#11-Cd(1)-Cl(1)	86.42(6)
O(1)#2-Ba(1)-Cl(1)#5	77.32(5)	O(1)#13-Cd(1)-Cl(1)	86.42(6)
O(1)#2-Ba(1)-Cl(1)#3	83.28(5)	O(1)-Cd(1)-Cl(1)	93.58(6)
O(1)#1-Ba(1)-Cl(1)#3	77.96(5)	O(1)#12-Cd(1)-Cl(1)	93.58(6)
O(1)#2-Ba(1)-Cl(1)#4	130.73(5)	O(1)#11-Cd(1)-O(1)#12	99.26(11)
O(1)#7-Ba(1)-Cl(1)#3	77.96(5)	O(1)-Cd(1)-O(1)#12	80.74(11)
O(1)#1-Ba(1)-Cl(1)#4	65.12(5)	O(1)#11-Cd(1)-O(1)#13	80.74(11)
O(1)#1-Ba(1)-Cl(1)#5	108.90(5)	O(1)-Cd(1)-O(1)#11	180
O(1)#6-Ba(1)-Cl(1)#5	130.73(5)	O(1)#12-Cd(1)-O(1)#13	180.00(8)
O(1)#6-Ba(1)-Cl(1)#3	83.28(5)	O(1)-Cd(1)-O(1)#13	99.26(11)
O(1)#7-Ba(1)-Cl(1)#4	108.90(5)	O(1)-Se(1)-O(1)#16	97.92(16)
O(1)#7-Ba(1)-Cl(1)#5	65.12(5)	O(2)-Se(1)-O(1)	100.92(12)
O(1)#6-Ba(1)-Cl(1)#4	77.32(5)	O(2)-Se(1)-O(1)#16	100.92(12)
O(1)#2-Ba(1)-O(1)#7	117.99(4)	Ba(1)#10-O(1)-Ba(1)#14	101.95(7)
O(1)#6-Ba(1)-O(1)#1	117.99(4)	Cd(1)-O(1)-Ba(1)#14	112.72(10)
O(1)#2-Ba(1)-O(1)#6	63.61(9)	Cd(1)-O(1)-Ba(1)#10	107.63(8)
O(1)#6-Ba(1)-O(1)#7	160.67(8)	Se(1)-O(1)-Ba(1)#14	103.50(9)
O(1)#2-Ba(1)-O(1)#1	160.67(8)	Se(1)-O(1)-Ba(1)#10	107.48(11)
O(1)#7-Ba(1)-O(1)#1	53.49(8)	Se(1)-O(1)-Cd(1)	121.74(12)
O(1)#7-Ba(1)-O(2)#8	113.91(8)	Ba(1)-O(2)-Ba(1)#10	99.27(8)
O(1)#1-Ba(1)-O(2)#2	113.91(8)	Ba(1)-O(2)-Ba(1)#15	99.27(8)

O(1)#7-Ba(1)-O(2)#2	66.59(8)	Ba(1)#15-O(2)-Ba(1)#10	126.18(13)
O(1)#6-Ba(1)-O(2)#8	52.12(8)	Se(1)-O(2)-Ba(1)#10	96.84(9)
O(1)#2-Ba(1)-O(2)#2	52.12(8)	Se(1)-O(2)-Ba(1)#15	96.84(9)
O(1)#2-Ba(1)-O(2)#8	109.02(8)	Se(1)-O(2)-Ba(1)	143.9(2)
O(1)#1-Ba(1)-O(2)#8	66.59(8)		

Symmetry transformations used to generate equivalent atoms:
#1 -1+X,+Y,+Z; #2 -1/2+X,1/2-Y,-1/2+Z; #3 1/2-X,-1/2+Y,1/2-Z; #4 1-X,1-Y,1-Z; #5 1-X,1-Y,-Z; #6 -1/2+X,1/2-Y,1/2-Z; #7 -1+X,+Y,-Z; #8 -1/2+X,1/2-Y,1/2+Z; #9 3/2-X,1/2+Y,1/2-Z; #10 1/2+X,1/2-Y,1/2+Z; #11 2-X,1-Y,1-Z; #12 +X,+Y,1-Z; #13 2-X,1-Y,+Z; #14 1+X,+Y,+Z; #15 1/2+X,1/2-Y,-1/2+Z; #16 +X,+Y,-Z; #17 1/2-X,1/2+Y,1/2-Z.

Table S7. Selected bond lengths (Å) and angles (°) for $BaCdSeO_3Br_2$.

Ba(1)-Br(1)#2	3.5480(6)	O(1)#4-Ba(1)-O(2)#1	59.58(7)
Ba(1)-Br(1)#1	3.5480(6)	O(1)#5-Ba(1)-O(2)#1	50.47(7)
Ba(1)-Br(2)#1	3.7326(8)	O(1)-Ba(1)-O(2)#1	117.07(7)
Ba(1)-Br(2)#3	3.3659(8)	O(1)#5-Ba(1)-O(2)#2	106.71(7)
Ba(1)-O(1)	2.773(2)	O(1)-Ba(1)-O(2)#2	59.58(7)
Ba(1)-O(1)#2	2.885(2)	O(1)#2-Ba(1)-O(2)#2	50.47(7)
Ba(1)-O(1)#4	2.773(2)	O(2)#2-Ba(2)-Br(1)#2	63.84(6)
Ba(1)-O(1)#5	2.885(2)	O(2)#1-Ba(2)-Br(1)#1	63.84(6)
Ba(1)-O(2)#2	3.0907(16)	O(2)#2-Ba(2)-Br(1)#1	164.44(6)
Ba(1)-O(2)#1	3.0907(16)	O(2)#1-Ba(2)-Br(1)#2	164.44(6)
Cd(1)-Br(1)	2.6314(6)	O(2)#2-Ba(2)-Br(2)#3	67.41(6)
Cd(1)-Br(2)#3	2.8836(5)	O(2)#1-Ba(2)-Br(2)#3	67.41(6)
Cd(1)-Br(2)	2.8835(5)	O(2)#1-Ba(2)-Br(2)#1	99.67(6)
Cd(1)-Br(2)#6	2.9403(7)	O(2)#2-Ba(2)-Br(2)#1	99.67(6)
Cd(1)-O(1)#7	2.462(2)	O(1)#1-Ba(2)-O(2)#2	127.74(12)
Cd(1)-O(1)	2.462(2)	Br(1)-Cd(1)-Br(2)#9	98.15(2)
Cd(1)-O(2)#1	2.170(3)	Br(1)-Cd(1)-Br(2)	92.277(13)
Se(1)-O(1)	1.694(2)	Br(1)-Cd(1)-Br(2)#3	92.277(13)
Se(1)-O(1)#7	1.694(2)	Br(2)-Cd(1)-Br(2)#9	74.215(11)
Se(1)-O(2)	1.691(3)	Br(2)-Cd(1)-Br(2)#3	148.43(2)
		Br(2)#3-Cd(1)-Br(2)#9	74.214(11)
Br(1)#2-Ba(1)-Br(1)#1	102.90(2)	Br(1)#10-Cd(1)-Br(1)	96.73(5)
Br(1)#1-Ba(1)-Br(2)#1	66.223(10)	Br(1)-Cd(1)-Br(1)	96.73(5)
Br(1)#2-Ba(1)-Br(2)#1	66.223(10)	Br(1)#10-Cd(1)-Br(2)	73.62(5)
Br(2)#3-Ba(1)-Br(1)#1	127.651(10)	Br(1)-Cd(1)-Br(2)#9	144.93(5)
Br(2)#3-Ba(1)-Br(1)#2	127.651(10)	Br(1)-Cd(1)-Br(2)	136.61(5)
Br(2)#3-Ba(1)-Br(2)#1	141.728(15)	Br(1)-Cd(1)-Br(2)#3	73.62(5)
O(1)#2-Ba(1)-Br(1)#1	119.47(4)	Br(1)#10-Cd(1)-Br(2)#9	144.93(5)
O(1)-Ba(1)-Br(1)#1	127.92(5)	Br(1)#10-Cd(1)-Br(2)#3	136.61(5)
O(1)#4-Ba(1)-Br(1)#2	127.92(5)	Br(1)-Cd(1)-O(1)#10	63.21(10)
O(1)#5-Ba(1)-Br(1)#2	119.47(4)	O(2)#2-Cd(1)-Br(1)#4	173.86(9)

O(1)#4-Ba(1)-Br(1)#1	77.11(5)	O(2)#2-Cd(1)-Br(2)	89.39(3)
O(1)-Ba(1)-Br(1)#2	77.12(5)	O(2)#2-Cd(1)-Br(2)#3	89.39(3)
O(1)#5-Ba(1)-Br(1)#1	71.76(5)	O(2)#2-Cd(1)-Br(2)#9	87.99(9)
O(1)#2-Ba(1)-Br(1)#2	71.76(5)	O(2)#2-Cd(1)-O(1)	78.07(9)
O(1)#5-Ba(1)-Br(2)#1	56.51(4)	O(2)#2-Cd(1)-O(1)#10	78.07(9)
O(1)-Ba(1)-Br(2)#1	143.23(4)	O(1)#10-Se(1)-O(1)	99.22(15)
O(1)#4-Ba(1)-Br(2)#3	62.41(5)	O(2)-Se(1)-O(1)	97.99(11)
O(1)#5-Ba(1)-Br(2)#3	91.53(4)	O(2)-Se(1)-O(1)#10	98.00(11)
O(1)#4-Ba(1)-Br(2)#1	143.23(4)	Ba(1)-O(1)-Ba(1)#7	115.74(7)
O(1)#2-Ba(1)-Br(2)#1	56.51(4)	Cd(1)-O(1)-Ba(1)#7	101.26(7)
O(1)-Ba(1)-Br(2)#3	62.41(5)	Cd(1)-O(1)-Ba(1)	102.17(7)
O(1)#2-Ba(1)-Br(2)#3	91.53(4)	Se(1)-O(1)-Ba(1)#7	108.17(10)
O(1)-Ba(1)-O(1)#2	110.00(7)	Se(1)-O(1)-Ba(1)	126.33(11)
O(1)-Ba(1)-O(1)#4	64.75(9)	Se(1)-O(1)-Cd(1)	97.81(10)
O(1)#5-Ba(1)-O(1)#2	61.94(9)	Ba(1)#7-O(2)-Ba(1)#8	127.74(12)
O(1)#4-Ba(1)-O(1)#5	110.00(7)	Cd(1)#7-O(2)-Ba(1)#8	100.14(7)
O(1)-Ba(1)-O(1)#5	153.273(18)	Cd(1)#7-O(2)-Ba(1)#7	100.14(7)
O(1)#4-Ba(1)-O(1)#2	153.274(18)	Se(1)-O(2)-Ba(1)#8	100.08(7)
O(1)#2-Ba(1)-O(2)#1	106.71(7)	Se(1)-O(2)-Ba(1)#7	100.08(7)
O(1)#4-Ba(1)-O(2)#2	117.07(7)	Se(1)-O(2)-Cd(1)#7	133.01(19)

Symmetry transformations used to generate equivalent atoms:
#1 1/2+X,1+Y,1/2-Z; #2 1/2+X,+Y,1/2-Z; #3 +X,1+Y,+Z; #4 +X,3/2-Y,+Z; #5 1/2+X,3/2-Y,1/2-Z; #6 +X,-1+Y,+Z; #7 -1/2+X,+Y,1/2-Z; #8 -1/2+X,-1+Y,1/2-Z; #9 1-X,-Y,1-Z; #10 +X,1/2-Y,+Z; #11 1/2-X,1-Y,1/2+Z.

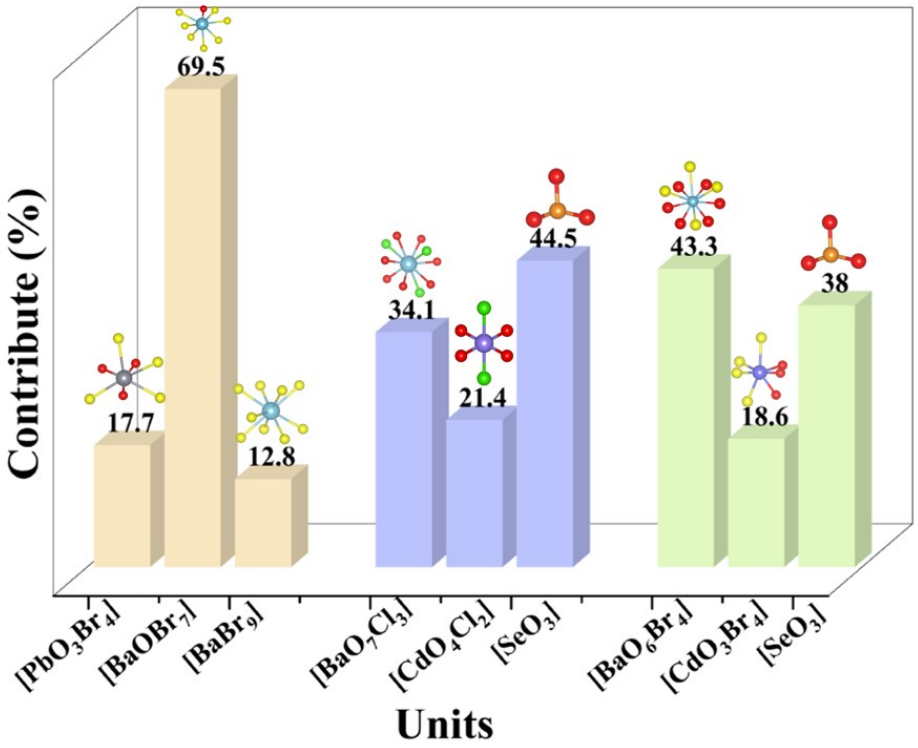
Table S8. Some mixed-metal oxyhalide compounds with optical properties have been reported.

Compounds	Space group	Band gap(ex)	Birefringence	Ref.
$RbPb_8O_4Cl_9$	*P*4/n	3.66	0.012@1064 nm	
$Cs_2Pb_{24}O_{21}I_8$	$P4_2/n$	2.73	0.03@550 nm	
$PbBi_3O_4Cl_3$	*I*4/*mmm*	2.70	-	
$PbBi_3O_4Br_3$	*I*4/*mmm*	2.44	-	
$PbBiO_2Br$	*I*4/*mmm*	2.47	-	
$Pb_3(TeO_3)Cl_4$	$Pna2_1$	3.79	-	
$Pb_3(TeO_3)Br_4$	$Pna2_1$	3.32	0.066@1064 nm	
$Pb_3(SeO_3)_2Br_2$	*C*2/*c*	3.73	-	
$Pb_3(SeO_3)Br_4$	$P2_12_12_1$	3.35	0.04@1064nm	
$CdPbOCl_2$	$P2_1/c$	3.63	0.0065@1064 nm	
$Cd_2TeO_3Cl_2$	$P\bar{1}$	4.25	0.065@2010 nm	
$Rb_2Sb_2OCl_6$	$P2_1/n$	3.67	0.136@1064 nm	

$Rb_3Sb_2OCl_7$	*Pnnm*	3.49	0.098@1064 nm	
$PbSbO_2Br$	*I*4/*mmm*	2.67	-	
$PbSbO_2I$	*I*4/*mmm*	2.48	-	
$Sr_4(Te_3O_8)Cl_4$	*C*2/*m*	4.0	-	
$Sr_3Se_3O_8Cl_2$	*Pnma*	4.4	-	
$CdBiO_2Cl$	$P2_1/m$	3.05	-	
$CdBiO_2Br$	*I*4/*mmm*	2.76	-	
$CaBiO_2Cl$	$P2_1/m$	3.52	-	
$SrBiO_2Cl$	*Cmcm*	3.53	-	
$BaBiO_2Cl$	*Cmcm*	3.28	-	
$BaBiO_2Br$	*Cmcm*	3.15	-	
$CaBi_4O_6Cl_2$	*Immm*	2.72	-	
$SrBi_4O_6Cl_2$	*Immm*	2.82	-	
$BaBi_4O_6Cl_2$	*I*4/*mmm*	2.98	-	
$Bi_2O(AsO_3)Cl$	*C*2/*c*	3.43	-	
$Ba_{27}Pb_8O_8Cl_{54}$	$Fm\bar{3}m$	3.9	-	
*****$Ba_5Pb_4O_4Br_{10}$	*P4/n*	3.49	0.019@1064 nm	This work
*****$Ba_2CdSe_2O_6Cl_2$	*Pnma*	5.03	0.085@1064 nm	This work
*****$BaCdSeO_3Br_2$	*Pnma*	3.72	0.091@1064 nm	This work
$BaLiTe_2O_5Cl$	$P2_1/n$	4.25	0.139@1064 nm	
$BaLiTe_2O_5Br$	$P2_1/n$	4.13	0.141@1064 nm	
$Rb_3CdV_4O_{12}Br$	*Pba*2	3.23	0.085@1064 nm	
$Rb_4CdV_5O_{15}Br$	*P*4	2.32	0.021@1064 nm	
$Ba_8SrPb_{24}O_{24}Cl_{18}$	*I*4/*m*	3.09	0.014@1064 nm	
$CdPb_2Te_3O_8Cl_2$	*Aba*2	3.89	-	
$Cd_{13}Pb_8Te_{14}O_{42}Cl_{14}$	$P\bar{1}$	3.78	-	
$CdPb_8(SeO_3)_4Br_{10}$	*C*2/*c*	3.32	0.014@1064 nm	
$Pb_2Cd(SeO_3)_2Cl_2$	$P2_12_12_1$	4.10	-	
$Pb_2Cd(SeO_3)_2Br_2$	$P2_12_12_1$	3.91	-	
$PbBi(SeO_3)_2F$	$Pca2_1$	3.75	0.103@1064 nm	
$Pb_2Bi(SeO_3)_2Cl_3$	*C*2	3.45	0.186@1064 nm	
$Pb_2Cu(SeO_3)_2Cl_2$	$P2_1/n$	2.90	-	
$Ba_2Cu(SeO_3)_2Cl_2$	*Pnnm*	3.20	-	
$Ba_2Ni(SeO_3)_2Cl_2$	*Pnnm*	4.85	-	
$Ba_2Co(SeO_3)_2Cl_2$	*Pnnm*	4.74	-	
$Ba_2Mn(SeO_3)_2Cl_2$	*Pnnm*	4.56	-	
$Pb_2NbO_2(SeO_3)_2Br$	$P2_1$	3.17	-	
$Pb_2NbO_2(SeO_3)_2Cl$	$P2_1$	3.67	-	
$Pb_2VO_2(SeO_3)_2Cl$	$P2_1$	2.41	-	

Table S9. The bonding electron density difference (Δρ) of all units in $Ba_5Pb_4O_4Br_{10}$, $Ba_2CdSe_2O_6Cl_2$ and $BaCdSeO_3Br_2$ calculated by the response electron distribution anisotropy (REDA) method

Compound	$Ba_5Pb_4O_4Br_{10}$			$Ba_2CdSe_2O_6Cl_2$			$BaCdSeO_3Br_2$		
$\Delta\rho$ ($\times10^{-3}$) / Proportions	$[PbO_3Br_4]$	0.128	17.71%	$[BaO_7Cl_3]$	1.614	34.12%	$[BaO_6Br_4]$	3.930	43.34%
	$[BaOBr_7]$	0.502	69.48%	$[CdO_4Cl_2]$	1.010	21.36%	$[CdO_3Br_4]$	1.690	18.64%
	$[BaBr_9]$	0.093	12.81%	$[SeO_3]$	2.106	44.52%	$[SeO_3]$	3.448	38.02%
		0.723	100%		4.730	100%		9.069	100%



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