

Exploration of Antimony(III) Oxyhalides via Single-site Substitution in Quest of Large Birefringence

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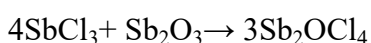
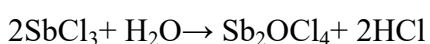
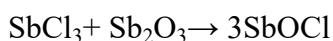
These authors contributed equally to this work.

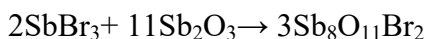
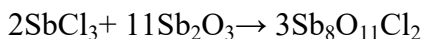
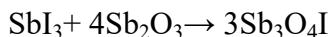
Experimental Section

Single-crystal preparation and the polycrystalline samples of the compounds.

Single crystals of SbOCl and Sb₂OCl₄ were obtained via different methods. The compound SbOCl was found from experiments using autoclaves equipped with 23 mL Teflon liners heated to 220 °C at a rate of 10 °C h⁻¹. The chemical reagents were dissolved in the deionized water (2 mL) with the following stoichiometry: SbCl₃:H₃BO₃=1:3 for SbOCl. The chemical reagents SbCl₃ were dissolved in the deionized water (50 mL), these solutions were heated to 66 °C for Sb₂OCl₄ and kept for evaporation to dryness at room temperature. Transparent single crystals with high quality could be manually separated from reaction products to further determine microscopic single-crystal structures. The quality of data for the Cl analog was superior to that of the Br-containing compound.

The solid-state reaction method was employed to synthesize the polycrystalline samples of SbOCl, Sb₂OCl₄, Sb₃O₄I, Sb₈O₁₁Cl₂, and Sb₈O₁₁Br₂. A mixture of Sb₂O₃ and SbCl₃/SbBr₃/SbI₃ with the stoichiometric ratio was mixed and sealed under 10⁻³ Pa in the quartz tubes, which were further put into furnaces. For example, the results of the implementation are as follows: SbCl₃ (0.878 g) and Sb₂O₃ (1.122 g) for SbOCl, SbCl₃ (1.516 g) and Sb₂O₃ (0.484 g) for Sb₂OCl₄, and SbCl₃ (0.249 g) and Sb₂O₃ (1.751 g) for Sb₈O₁₁Cl₂. Then, the mixtures were heated to 170 °C for SbOCl, 150 °C for Sb₂OCl₄, 306 °C for Sb₃O₄I, 420 °C for Sb₈O₁₁Cl₂, and 500 °C for Sb₈O₁₁Br₂ and finally held for 72 h with several intermittent grindings. Finally, we obtained target product yields of 98.2% for SbOCl(1.964 g), 97.6% for Sb₂OCl₄(1.952 g), and 96.7% for Sb₈O₁₁Cl₂(1.933 g), respectively. Since it is a solid-phase reaction in which all atoms are involved, the yield is close to 100% theoretically. However, it is also related to the purity of the sample, losses during vacuuming, and sampling in practice. Their chemical reaction equations were as follows:





Characterization

Single crystals with good crystalline quality and suitable sizes of SbOCl , and Sb_2OCl_4 , were selected for structure determination. The data were collected on a Bruker D8 Venture with $\text{Mo K}\alpha$ radiation at room temperature. Absorption correction was performed with the Numerical Mu Calculated program. Integration and absorption corrections of the data were completed in SAINT and SCALE programs,¹ respectively. The structures were solved by direct methods and then refined by full-matrix least squares on F^2 with the SHELXTL-14 program,² and all atoms were refined anisotropically. PLATON was used to confirm whether higher.³

Powder X-ray diffraction (PXRD) data were collected by putting the powder sample onto the flat sample holders utilizing a Bruker D2 PHASER X-ray diffractometer equipped with $\text{Mo K}\alpha$ radiation, and the diffraction patterns were taken in the 2θ range from 5 or 10 to 70° .

The infrared (IR) absorption spectra were recorded on a SHIMADZU IRAffinity-1 Fourier transform infrared spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$. The spectral resolution is about 2 cm^{-1} . The samples were pressed into discs (10 mg of the sample and 1000 mg of KBr). The UV-vis-NIR diffuse-reflectance spectra were recorded using a Solid Spec-3700DUV spectrophotometer. The measurements were performed in the spectral range from 200 to 2600 nm with a scan step width of 1 nm at room temperature and in a nitrogen atmosphere.

Thermal Stability Measurement. About 10 mg of SbOCl , Sb_2OCl_4 , $\text{Sb}_3\text{O}_4\text{I}$, $\text{Sb}_8\text{O}_{11}\text{Cl}_2$, and $\text{Sb}_8\text{O}_{11}\text{Br}_2$ were used for the differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis. These measurements are carried out by the NETZSCH STA-2500 thermal analyzer. The measured temperature range is from room temperature to $500\text{ }^\circ\text{C}$ with a rate of $20\text{ }^\circ\text{C}/\text{min}$.

Energy dispersive X-ray spectroscopy. Elemental analysis of Sb_2OCl_4 was carried

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

The refractive index difference of the compound was measured through a polarizing microscope (ZEISS Axio Scope. 5 pol) equipped with a Berek compensator under the light source with an average wavelength of 546 nm. The interference color in the measurement was rated as first, second, and higher-order to ensure the accuracy of measurement as their boundary lines were relatively clear compared to subsequent interference color. The crystals with high optical quality were selected to scan under the polarizing microscope. The theory on which the measurement is based can be expressed as the following formula:

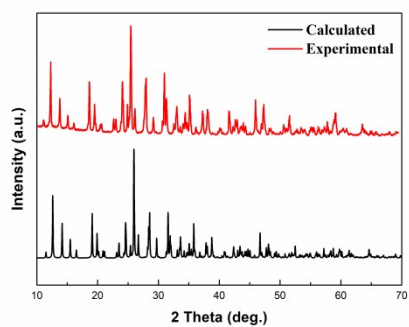
$$R = |N_g - N_p| \times T = \Delta n \times T \quad (1)$$

R , N_g , N_p , T , and Δn refer to optical path difference, refractive index of fast light, refractive index of slow light, thickness of crystal, and birefringence, respectively.

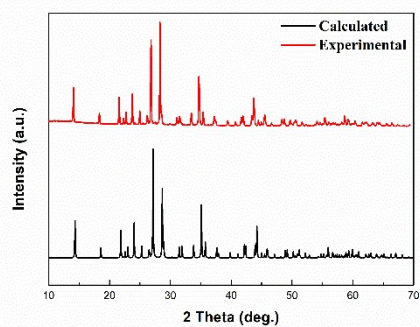
Theoretical calculations

The first-principles calculations were performed to explore the relationship between electronic structure and optical properties for the experimental compounds via using the plane-wave pseudopotential methods based on density functional theory (DFT) implemented in the CASTEP code.^{4,5} The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional was adopted to describe the exchange–correlation energy. To achieve the convergence of calculation results, the plane-wave energy cutoff was set as 750 eV under norm-conserving pseudopotential (NCP), and the Monkhorst-Pack scheme was given by $3 \times 2 \times 3$, $3 \times 2 \times 4$, $4 \times 5 \times 1$, $3 \times 9 \times 2$, $2 \times 3 \times 2$, $3 \times 2 \times 2$, and $3 \times 2 \times 2$ for SbOCl , Sb_2OCl_4 , $\text{Sb}_3\text{O}_4\text{F}$, $\text{Sb}_3\text{O}_4\text{I}$, $\text{Sb}_3\text{O}_4\text{Cl}$, $\text{Sb}_8\text{O}_{11}\text{Cl}_2$, and $\text{Sb}_8\text{O}_{11}\text{Br}_2$, respectively in the irreducible Brillouin zone. Other calculation parameters and convergent criteria were set by the default values of the CASTEP code. The linear optical properties are obtained based on the dielectric function: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, respectively. The imaginary part of the dielectric function ε_2 can be calculated

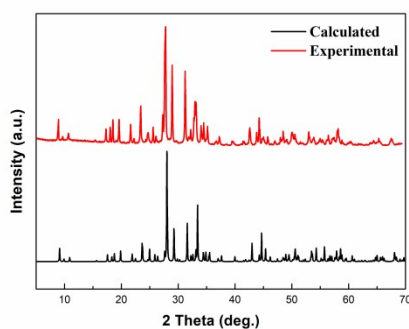
based on the electronic structures and the real part is obtained by the Kramers-Kronig transformation, accordingly, the refractive indices and the birefringence (Δn) can be calculated. The crystal orbital Hamilton Population (COHP) was calculated by the LOBSTER code.⁶



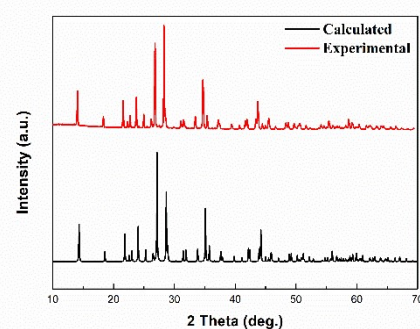
(a)



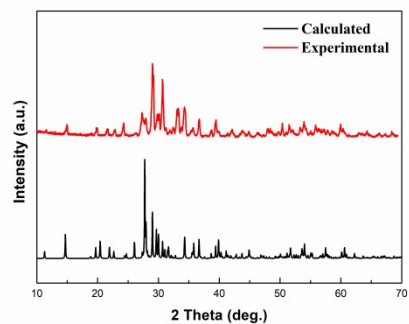
(b)



(c)

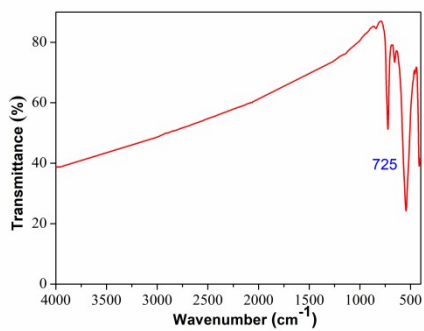


(d)

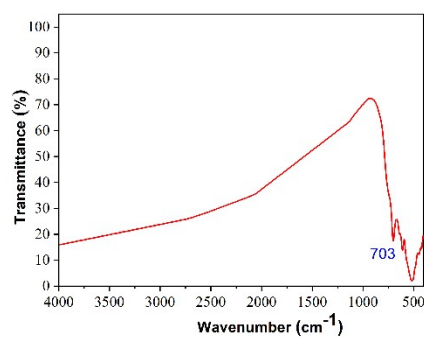


(e)

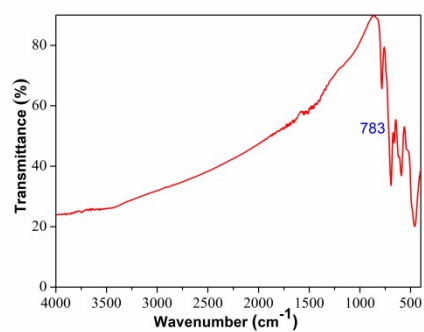
Figure S1. Experimental and calculated XRD patterns of (a) SbOCl , (b) Sb_2OCl_4 , (c) $\text{Sb}_8\text{O}_{11}\text{Cl}_2$, (d) $\text{Sb}_8\text{O}_{11}\text{Br}_2$, and (e) $\text{Sb}_3\text{O}_4\text{I}$.



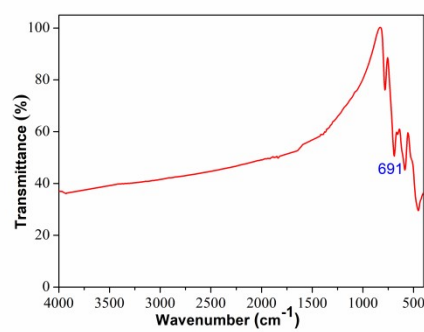
(a)



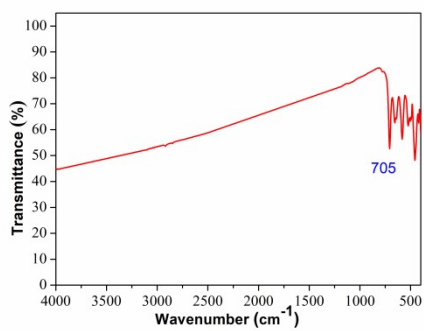
(b)



(c)



(d)



(e)

Figure S2. IR spectra of (a) SbOCl, (b) Sb₂OCl₄, (c) Sb₈O₁₁Cl₂, (d) Sb₈O₁₁Br₂, and (e) Sb₃O₄I.

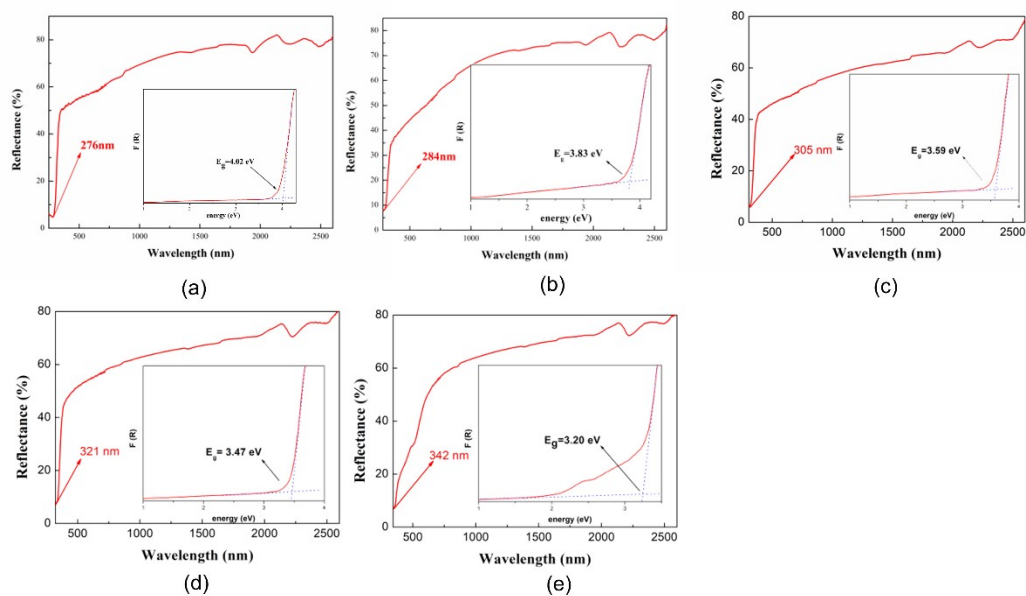


Figure S3. UV-vis-NIR diffuses reflectance spectra and experimental band gap of (a) SbOCl, (b) Sb₂OCl₄, (c) Sb₈O₁₁Cl₂, (d) Sb₈O₁₁Br₂, and (e) Sb₃O₄I.

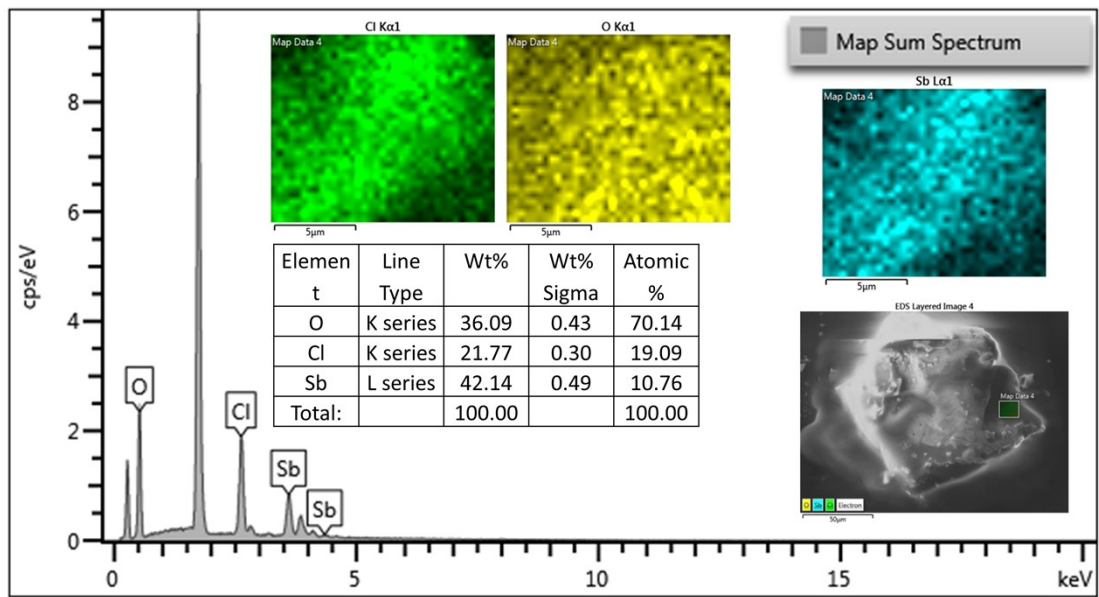


Figure S4. EDS analysis of Sb_2OCl_4 .

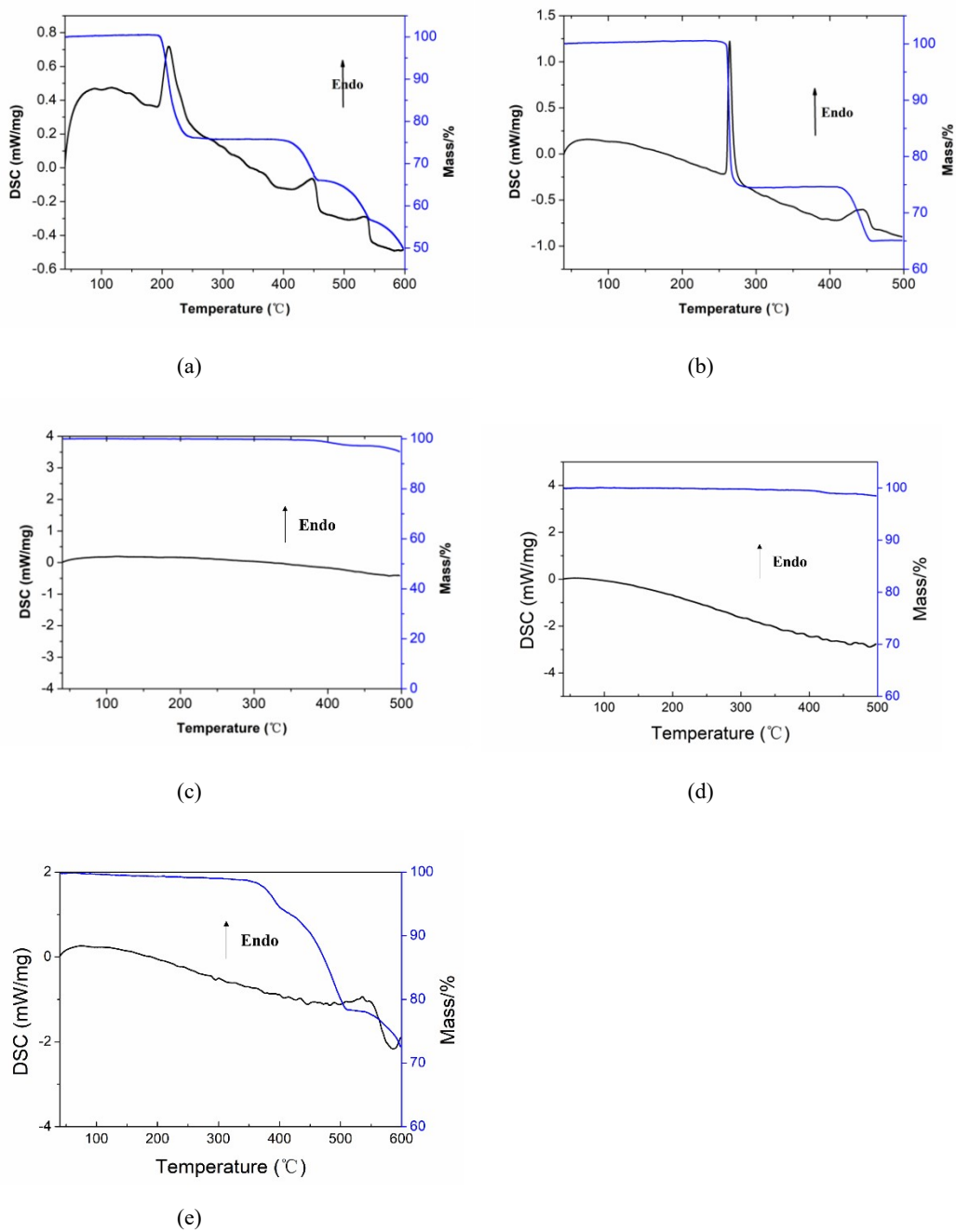


Figure S5. TG and DSC curves for (a) SbOCl , (b) Sb_2OCl_4 , (c) $\text{Sb}_8\text{O}_{11}\text{Cl}_2$, (d) $\text{Sb}_8\text{O}_{11}\text{Br}_2$ and (e) $\text{Sb}_3\text{O}_4\text{I}$.

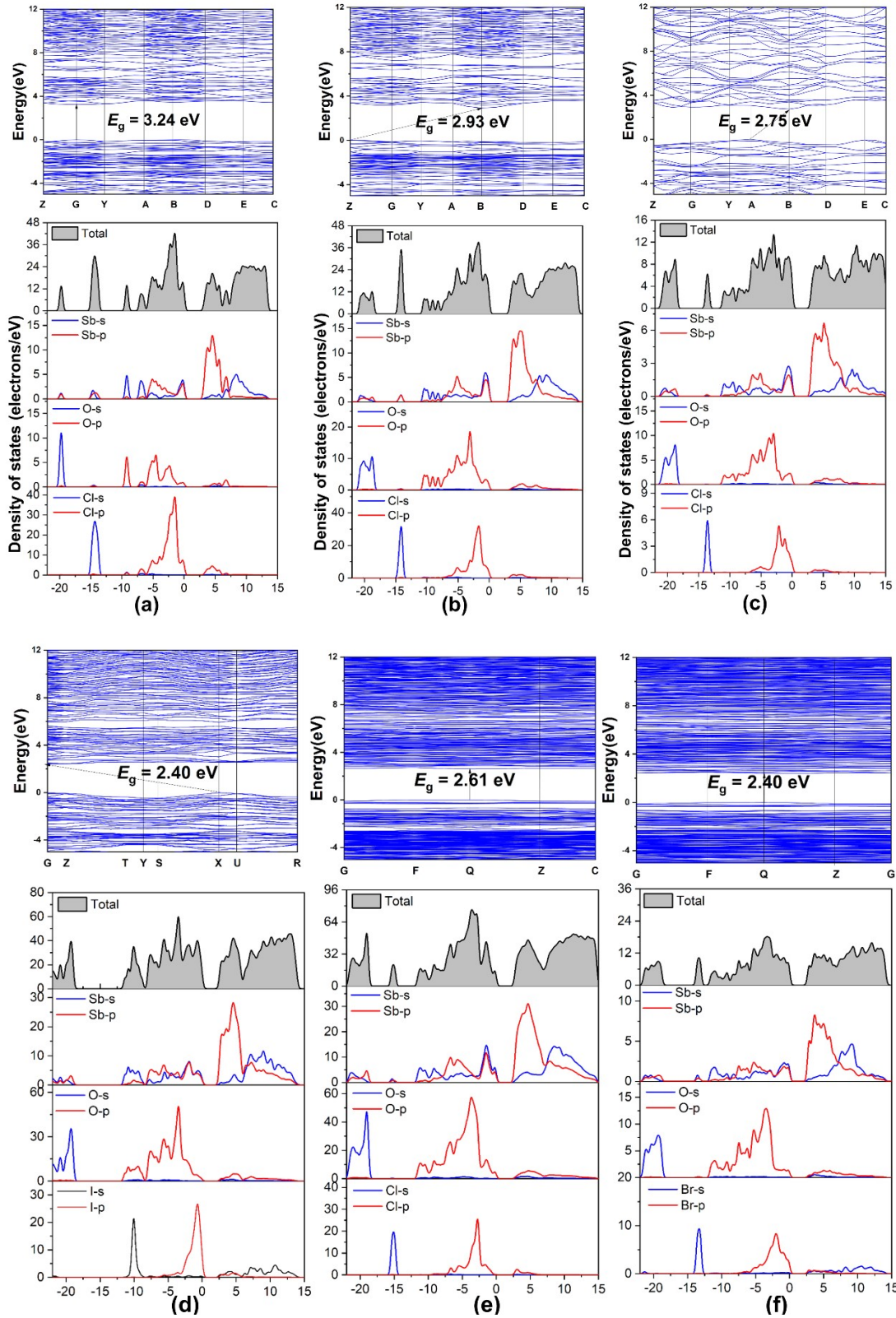


Figure S6. Electronic structures and partial density of states of (a) SbOCl, (b) Sb₂OCl₄, (c) Sb₃O₄Cl, (d) Sb₃O₄I, (e) Sb₈O₁₁Cl₂, and (f) Sb₈O₁₁Br₂.

Table S1. Crystal data and structure refinements for SbOCl, and Sb₂OCl₄.

Empirical formula	SbOCl	Sb ₂ OCl ₄
Temperature	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
Formula weight	173.20	401.30
<i>a</i> (Å)	7.908(9)	10.028(3)
<i>b</i> (Å)	10.732(14)	10.203(3)
<i>c</i> (Å)	9.527(10)	7.593(2)
α (°)	90	90
β (°)	103.65(3)	110.267(11)
γ (°)	90	90
Z, Volume (Å ³)	12, 785.8(16)	4, 728.8(4)
ρ_{Calcd} (mg/m ³)	4.392	3.657
μ (mm)	11.195	8.773
<i>F</i> (000)	912.0	712.0
<i>R</i> (int)	0.0927	0.1375
Goodness-of-fit on <i>F</i> ²	1.012	0.978
Final <i>R</i> indices	<i>R</i> ₁ = 0.0423,	<i>R</i> ₁ = 0.0497,
[<i>F</i> _o ² > 2σ(<i>F</i> _o ²)] ^a	<i>wR</i> ₂ = 0.1041	<i>wR</i> ₂ = 0.0946
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0541,	<i>R</i> ₁ = 0.1113,
	<i>wR</i> ₂ = 0.1114	<i>wR</i> ₂ = 0.1133
Largest diff. peak and hole (e·Å ⁻³)	2.633/-2.104	1.540/-1.073

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

Table S2a. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) forSbOCl. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Sb(1)	2184(1)	5230(1)	5750(1)	20(1)	2.93
Sb(2)	4169(1)	7569(1)	4098(1)	22(1)	2.92
Sb(3)	-190(1)	8282(1)	2693(1)	23(1)	2.80
Cl(1)	6053(3)	6083(2)	6552(2)	28(1)	0.95
Cl(2)	3863(4)	9024(2)	5890(3)	40(1)	0.93
Cl(3)	-910(3)	6432(2)	1311(3)	35(1)	/
O(1)	2204(7)	6616(5)	4434(6)	21(1)	2.14
O(2)	2306(7)	8419(5)	2599(6)	20(1)	2.28
O(3)	-281(7)	9315(5)	936(6)	20(1)	2.34

Table S2b. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for

Sb_2OCl_4 . U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)	BVS
Sb(1)	5046(1)	5681(1)	2963(1)	34(1)	2.83
Sb(2)	1573(1)	5652(1)	3466(1)	38(1)	2.83
Cl(1)	5770(3)	7748(2)	4398(4)	40(1)	0.95
Cl(2)	2662(3)	6734(3)	780(4)	52(1)	0.74
Cl(3)	1067(4)	3681(3)	1767(5)	58(1)	1.00
Cl(4)	1731(3)	4639(3)	6463(4)	50(1)	0.75
O(1)	3717(7)	5288(6)	4405(9)	35(2)	2.21

Table S3a. The selected bond lengths for SbOCl.

Atom	Length/Å
Sb(1)-O(1)	1.947(6)
Sb(1)-O(2)#1	2.265(6)
Sb(1)-O(3)#1	2.058(6)
Sb(1)-O(3)#2	2.161(6)
Sb(2)-O(1)	1.949(6)
Sb(2)-O(2)	2.013(6)
Sb(2)-Cl(2)	2.368(3)
Sb(3)-O(2)	2.002(6)
Sb(3)-O(3)	1.994(6)
Sb(3)-Cl(3)	2.377(3)

Symmetry transformations used to generate equivalent atoms:

#1 $x, -y+3/2, z+1/2$ #2 $-x, y-1/2, -z+1/2$ #3 $x, -y+3/2, z-1/2$
#4 $-x, y+1/2, -z+1/2$

Table S3b. The selected bond lengths for Sb₂OCl₄.

Atom	Length/Å
Sb(1)-Cl(1)	2.369(3)
Sb(1)-Cl(2)	2.621(3)
Sb(1)-O(1)	2.036(6)
Sb(1)-O(1)#1	2.189(7)
Sb(2)-Cl(2)	2.849(3)
Sb(2)-Cl(3)	2.348(3)
Sb(2)-Cl(4)	2.454(3)
Sb(2)-O(1)	2.051(7)

Symmetry transformations used to generate equivalent atoms:

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

Table S4a. The selected bond angles for SbOCl.

Atom	Angle/°
O(3)#1-Sb(1)-O(2)#1	69.4(2)
O(3)#2-Sb(1)-O(2)#1	139.8(2)
O(3)#1-Sb(1)-O(3)#2	70.4(3)
O(1)-Sb(1)-O(2)#1	90.4(2)
O(1)-Sb(1)-O(3)#2	88.8(2)
O(1)-Sb(1)-O(3)#1	91.5(2)
O(2)-Sb(2)-Cl(2)	91.7(2)
O(1)-Sb(2)-Cl(2)	90.4(2)
O(1)-Sb(2)-O(2)	82.9(2)
O(2)-Sb(3)-Cl(3)	98.43(18)
O(3)-Sb(3)-Cl(3)	92.47(19)
O(3)-Sb(3)-O(2)	76.2(2)

Symmetry transformations used to generate equivalent atoms:

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

#4 $-x, y+1/2, -z+1/2$

Table S4b. The selected bond angles for Sb₂OCl₄.

Atom	Angle/°
Cl(1)-Sb(1)-Cl(2)	89.63(10)
O(1)-Sb(1)-Cl(1)	94.70(19)
O(1)#1-Sb(1)-Cl(1)	89.75(18)
O(1)-Sb(1)-Cl(2)	78.3(2)
O(1)#1-Sb(1)-Cl(2)	150.10(18)
O(1)-Sb(1)-O(1)#1	71.9(3)
Cl(3)-Sb(2)-Cl(2)	90.12(11)
Cl(3)-Sb(2)-Cl(4)	94.63(11)
Cl(4)-Sb(2)-Cl(2)	155.43(10)
O(1)-Sb(2)-Cl(2)	72.75(19)
O(1)-Sb(2)-Cl(3)	92.1(2)
O(1)-Sb(2)-Cl(4)	82.98(18)

Symmetry transformations used to generate equivalent atoms:

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

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