Multiple Anion Chemistry for Ionic Layer Thickness Tailoring in Bi \(2^{+2 \ n} \ O \ 2^{+2 \ n} \ Se \ n \ X \ 2\) (\(X = Cl, Br\)) van der Waals Semiconductors with Low Thermal Conductivities

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Multiple Anion Chemistry for Ionic Layer Thickness Tailoring in \( \text{Bi}_{2+2n} \text{O}_{2+2n} \text{Se}_n \text{X}_2 \) (\( \text{X} = \text{Cl}, \text{Br} \)) van der Waals Semiconductors

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Abstract

Layered materials coupling a two-dimensional strong-bonding layered network with much weaker van der Waals (vdW) interaction between the layers are sought after for the development of nanoelectronic and energy conversion devices. It is important to elucidate the layer stacking rules in these vdW materials and control the thickness of the strong-bonding layers for tuning the nanosheet height during exfoliation and therefore tailor physical properties. Here we show that the single Bi$_2$O$_2$Se ionic layer in the three-anion vdW semiconductor Bi$_4$O$_4$SeCl$_2$ showing extremely low thermal conductivity can be expanded to higher-order layers forming a homologous series Bi$_{2+2n}$O$_{2+2n}$Se$_n$X$_2$ ($X = \text{Cl, Br}$) with variable ionic layer thicknesses. Bi$_4$O$_4$SeX$_2$ ($n=1$) and Bi$_6$O$_6$Se$_2$X$_2$ ($n=2$) were isolated as single-phase materials, showing ~50% Se replaced by X anions in the Bi$_2$O$_2$Se slab as a common feature. Materials with larger layer thicknesses such as Bi$_8$O$_8$Se$_3$Cl$_2$ ($n=3$) contain different defect-intergrowth structures at the crystallite scale. The anionic disorder of Se and $X$ within the Bi$_2$O$_2$Se and Bi$_2$O$_2$Cl$_2$ slabs reduces the lattice strain on the sandwiched Bi$_2$O$_2$ interface, introduces charge separation on Bi$_2$O$_2$Se and Bi$_2$O$_2$X$_2$ layers, and allows the combination of different structural motifs. All of the materials show similar optical indirect band gaps of ~1.05 eV, originating from the electronic states in the Bi$_2$O$_2$Se slabs. Pellets prepared from these vdW materials possess low bulk resistivities (100 $\Omega$.cm) and exceptionally low and tunable thermal conductivities (0.66 W/mK and lower) parallel to the pressing axis of the pellets (heavier the halogen is, lower is the thermal conductivity). The results presented here provide new insight into multiple anion chemistry for tailoring the ionic-bonding network into different thicknesses in the vdW layered structures and therefore their physical properties.
I. Introduction

Oxides have attracted extensive interest in solid-state material chemistry, where cationic substitutions are traditionally used to tune the crystal structures and associated physical properties. The anionic substitution, an alternative route to modify the properties and access new mixed-anion compounds, has been largely ignored due to the often-poor stability at ambient atmosphere and the tough synthesis requirements of mixed-anion compounds. 1 Among the known inorganic compounds, numerous inorganic oxides (up to 55781 in the Inorganic Crystal Structure Database, (ICSD, https://icsd.fiz-karlsruhe.de), as of 2nd May 2021) have been reported, whereas only a limited number of mixed-anion compounds (~3365, i.e. 0.6%) are known, particularly in systems containing ≥ 2 distinct anion species. The crystal structures of oxides are usually described with (pseudo) close-packed arrangements of O\(^{2-}\) anions (and similar sized cations with O\(^{2-}\)) and smaller-sized cations filling the resulting voids, for which the typical structures include A\(_3\)O\(_4\) spinel, AO rock-salt, and ABO\(_3\) perovskite based on the common coordination polyhedra as building units (e.g. AO\(_4\) tetrahedron, AO\(_6\) octahedron, and AO\(_{12}\) cuboctahedron). However, for anionic substitution, as most of the anions are larger (and more polarizable, or softer) than O\(^{2-}\) e.g. Cl\(^{-}\), Se\(^{2-}\) and As\(^{3-}\), they tend to aggregate two-dimensionally to minimally mix with smaller sized (and harder) O\(^{2-}\) layers to save space, and destroy the 3-dimensional (3D) close packing of the anions. Distinct 2-dimensional (2D) structures are thus generated and exhibit rich physical properties including the technologically-important high T\(_{\text{c}}\) superconductivity (e.g. LaOFeAs), 2 thermoelectricity (e.g. BiOCuSe and BiOCuTe), 3-5 transparent p-type semiconductivity (e.g. LaOCuS), 6 ionic conductivity (i.e. LaOAgS and LaOCl), 7, 8 and photocatalysis (BiOCl and Bi\(_4\)NbO\(_8\)Cl). 9, 10 Multiple anion compounds have been standing at the frontier of solid-state materials chemistry and physics. 1, 11

Up to now, the exploration of multiple-anionic systems is mainly limited to several binary anionic systems, such as oxyhydrides, oxyhalides, and oxychalcogenides. Among these binary-anionic systems, layered structures containing the common structural motif of fluorite-type A\(_2\)O\(_2\)\(^{2+}\) (A = Ln\(^{3+}\), Bi\(^{3+}\)) layers
with a significant contribution of covalent interactions are attracting more and more attention, e.g. Bi$_2$O$_2$Se, $^{12}$ Bi$_2$O$_2$Cl$_2$, $^{10}$ Bi$_2$O$_2$Cu$_2$Se, $^{13}$ and La$_2$O$_2$Fe$_2$OSe$_2$. $^{14}$ In these layered multiple anionic compounds, the fluorite-type A$_2$O$_2^{2+}$ layers, which are constructed from edge-sharing O$_4$ tetrahedra, alternate with the charge-balancing anionic layers. In the simplest case, the charge-balancing anionic layers are single-layered $Ch^{2-}$ anions (Figure 1a), as shown in Bi$_2$O$_2$Ch ($Ch^{2-} = S^{2-}$, Se$^{2-}$, Te$^{2-}$, or NCN$^{2-}$), $^{12,15-17}$ and double-layered $X^-$ anions (Figure 1b) in the case of Bi$_2$O$_2X_2$ (or BiO$X$ equally, $X = Cl^-$, Br$^-$, or I$^-$). $^{10,18,19}$ Filling of the tetrahedral voids between the double anionic layers in these structures generates antifluorite-type $M_2Pn_2^{-2}$ layers forming quaternary $A_2O_2M_2Pn_2$ materials ($A = La^{3+}$ or Bi$^{3+}$, $M^{2+} = Fe^{2+}$ or Mn$^{2+}$, $Pn^{3-} = As^{3-}$, P$^{3-}$, or Sb$^{3-}$) with ZrCuSiAs-like structures (Figure 1c). $^{2,13,20}$ In the case of A$_2$O$_2M_2$OSe$_2$ materials ($A = La^{3+}$ - Sm$^{3+}$, $M^{2+} = Fe^{2+}$ or Mn$^{2+}$), Se$^{2-}$ anionic double layers embedded by an $M_2O^{2-}$ planar layer of anti-CuO$_2$ type in between are incorporated between the A$_2$O$_2^{2+}$ cationic layers to compensate the positive charge, $^{14,21}$ as shown in Figure 1d.

![Figure 1](image_url)

**Figure 1.** Typical layered structures with two anions: (a) Bi$_2$O$_2$Se, (b) Bi$_2$O$_2$Cl$_2$, (c) Bi$_2$O$_2$Cu$_2$Se, and (d) La$_2$O$_2$Fe$_2$OSe$_2$.

In these above-mentioned layered structures, Bi$_2$O$_2$Se, Bi$_2$O$_2$Cu$_2$Se, and La$_2$O$_2$Fe$_2$OSe$_2$ are ionic layered materials, featuring alternative stacking of cationic and anionic layers, forming two-dimensional covalent-dominant structural units which are connected by ionic bonding interactions in the third dimension. Interestingly, the Bi$_2$O$_2X_2$ ($X = Cl^-$, Br$^-$, or I$^-$) structure is composed of cationic fluorite Bi$_2$O$_2^{2+}$
layers bound on either side to terminal $X^-$ anion layers in the sequence $X$-$\text{Bi}_2\text{O}_2$-$X$-$X$-$\text{Bi}_2\text{O}_2$-$X$, forming a van der Waals gap in the successive halide layers. Thus, this material can be described as layered $X\text{Bi}_2\text{O}_2X$ slabs stacked by $X\cdots X$ van der Waals interactions in the third dimension, and allow easy exfoliation or deposition as atomically thin nanosheets, $^{22, 23}$ which is useful in the fabrication of functional heterostructures and devices, spanning electronic to energy materials. Thus, among these charge-redeeming layers inserted between $\text{A}_2\text{O}_2^{2+}$ layers, the double-layer $X^-$ anions are most spectacular in structural modification and can act as scissors cutting the 3D ionic layered structures into 2D van der Waals slabs, leading to new van der Waals materials with highly anisotropic physical properties, as proposed in the recently reported multiple anion material $\text{La}_5\text{O}_4\text{Cu}_4\text{As}_4\text{Cl}_2$ along with a $\text{P}$-containing analogue. $^{24, 25}$

Given the common fluorite-type $\text{A}_2\text{O}_2^{2+}$ structural building units in these binary anionic layered structures, it would be expected that more complex structures may be generated through intergrowth of these structure types, thus allowing tailoring the physical properties when three or more anions are included in a single structure. However, these compounds are rarely explored, and there is very limited research on such multiple-anionic compounds. Some of them are isoelectronic and isostructural to materials with two-anion compounds, e.g. $(\text{SrF})_2\text{Fe}_2\text{OSe}_2$ $^{26}$ is isostructural with $(\text{LaO})_2\text{Fe}_2\text{OSe}_2$. $^{14}$

The direct combination of $\text{Bi}_2\text{O}_2\text{Se}$ and $\text{Bi}_2\text{O}_2\text{Cu}_2\text{Se}_2$ slabs remained unsuccessful but was recently circumvented by the addition of a third halide anion, leading to a series of multiple anionic $\text{Bi}_{2+2n}\text{O}_{2+2n}\text{Cu}_{2-n}\text{Se}_{2+n-n-n}\delta$ ($X = \text{Cl and Br}$, $n = 1$ and 2) defective-layer materials. $^{27, 28}$

The partial substitution of the $X^-$ anions for $\text{Se}^{2-}$ in the $\text{Bi}_2\text{O}_2\text{Se}$ slab and the resulting charge-compensating Cu vacancies in the $\text{Bi}_2\text{O}_2\text{Cu}_2\text{Se}_2$ layers are of vital importance in the stabilization of the $\text{Bi}_{2+2n}\text{O}_{2+2n}\text{Cu}_{2-n}\text{Se}_{2+n-n-n}\delta$ series. These intergrowth materials showed exceptionally low thermal conductivity (0.4 W/mK and lower) and narrow bandgaps (< 0.5 eV), compared with both parent compounds, $^{4, 29-31}$ making them potential thermoelectric materials. $^{27, 28}$ Later, another novel layered structure $\text{Bi}_4\text{O}_4\text{SeCl}_2$ was stabilized as a 1:1 superlattice of the structural units present in the van der Waals insulator $\text{Bi}_2\text{O}_2\text{Cl}_2$ and the ionic layered semiconductor $\text{Bi}_2\text{O}_2\text{Se}$. This compound can be noted as ($m = 1$,
alternative stacking between Bi$_2$O$_2$Cl$_2$ and Bi$_2$O$_2$Se units (Figure 2a), respectively, featuring partial anionic disorder of Se and Cl between the Bi$_2$O$_2^{2+}$ cationic layers. The van der Waals semiconductor Bi$_4$O$_4$SeCl$_2$ retains the high and anisotropic electronic mobility of Bi$_2$O$_2$Se $^{12, 32}$ while reducing the dimensionality of the ionic bonding network of Bi$_2$O$_2$Se to allow facile exfoliation of Bi$_4$O$_4$SeCl$_2$ to 1.4 nm height. $^{33}$ Due to the anisotropic bond contrast in vdW Bi$_2$O$_2$Cl$_2$ slab and the interface mismatch (between the Bi$_2$O$_2^{2+}$ and Se$^{2-}$ layers) in the Bi$_2$O$_2$Se slab, the contribution of the longitudinal and transverse phonons to heat transport are significantly suppressed in the layered materials Bi$_4$O$_4$SeCl$_2$, leading to an extremely low thermal conductivity of 0.1W/mK at room temperature along the c-axis direction, which is about only four times the thermal conductivity of air. $^{34}$

Figure 2. Comparison of the crystal structures of (a) Bi$_4$O$_4$SeCl$_2$, (b) Bi$_6$O$_6$Se$_2$Cl$_2$, and (c) Bi$_8$O$_8$Se$_3$Cl$_2$ illustrating different intergrowths between the Bi$_2$O$_2$Se−type and Bi$_2$O$_2$X− type layers in Bi$_{2+2n}$O$_{2+2n}$Se$_n$X$_2$. The Bi, Se, Cl, and O atoms are displayed in purple, green, brown, and red, respectively.
In Bi₄O₄SeCl₂, the stacking arrangement of Bi₂O₂Se and Bi₂O₂X₂-type units is not well understood and questions remain regarding the possible control of the thicknesses of the ionic-bonding layers for tuning the exfoliated nanosheet heights for structure fabrication and associated physical properties. Here, based on the dimensionality tailoring effect of double-layer halogen anions in the Bi₂O₂Se network into van der Waals slabs, we expand the Bi₂O₂X₂-Bi₂O₂Se intergrowth of van der Waals compounds from the reported compound Bi₄O₄SeCl₂ to the homologous series Bi₂₊₂nO₂₊₂nSe₂ₓ₂ (X = Cl and Br) via stoichiometry tuning, building a series of van der Waals materials with different thicknesses of ionic-bonding layers, as illustrated in Figures 2a-c, which demonstrates new insight into multiple anion chemistry for tailoring the ionic-bonding network into different thicknesses in the layered structures.

II. Experimental Procedure

Synthesis. The polycrystalline samples of Bi₆O₆SeCl₄, Bi₄O₄SeX₂ (X = Cl and Br), Bi₆O₆Se₂X₂ (X = Cl and Br), and Bi₈O₈Se₃Cl₂ were prepared by solid-state reaction method. The starting materials of Bi (99.99%, Aladdin), Bi₂O₃ (99.9%, Aladdin), Se (99.9%, Aladdin), and lab-made reagents BiOX (X = Cl and Br, see details below) were weighed according to the correct stoichiometric ratios and thoroughly mixed in an agate mortar with a pestle. The mixtures were pressed into pellets of ~6 mm in diameter and ~2 mm in thickness under a uniaxial pressure of ~150 MPa and transferred to alumina crucibles, and then sealed into an evacuated quartz tube, which was fired at 700 °C for 48 hours with one intermediate pressing and grinding, and finally slowly cooled down to room temperature at 5 °C/min. The experimental densities of the ceramic pellets were calculated using the measured geometric sizes (diameters and thicknesses) and the masses of the pellets, while the theoretical densities were calculated based on the chemical compositions and refined lattice parameters by Rietveld methods. The obtained dark pellets of Bi₄O₄SeX₂ and Bi₆O₆Se₂X₂ (X = Cl and Br) reached ~80% of the X-ray theoretical densities.

The BiOX (X = Cl and Br) precursors were synthesized using an hydrothermal reaction from the
starting materials of Bi(NO$_3$)$_3$·5H$_2$O (99.9%, Aladdin), NaCl (99.5%, Xilong Scientific), and KBr (99.5%, Aladdin) and their phase purities were confirmed by powder X-ray diffraction (XRD). All the materials used and obtained here are air-stable and safe to be handled in ambient conditions.

**Characterization.** Phase formations were examined by powder XRD at ambient conditions, which was conducted on a PANalytical X'Pert Pro diffractometer in Bragg-Brentano geometry using Cu K$_\alpha$ radiation. The samples were dispersed on a zero-background Si substrate using a drop of ethanol to reduce preferred orientation because of its layered structural feature. High-quality laboratory XRD data for Rietveld refinements were collected over the 2\(\theta\) range of 10-120°, using sample spinning mode. Time-of-flight (TOF) neutron powder diffraction (NPD) data were collected on the General-Purpose Powder Diffractometer (GPPD) at China Spallation Neutron Source (CSNS). *Ab initio* structure solutions for Bi$_6$O$_6$Se$_2$X$_2$ were carried out in EXPO2014, using the direct space method.\textsuperscript{35,36} Rietveld refinements were performed against XRD and NPD data utilizing the Topas Academic 6 program.\textsuperscript{37} Bond valence sums (BVSs) were calculated by Brown and Altermatt’s method.\textsuperscript{38}

Selected-area electron diffraction (SAED) and convergent-beam electron diffraction (CBED) patterns were recorded on a JEOL JEM-2100F transmission electron microscope (TEM) with an accelerating voltage of 200 kV. High-resolution scanning transmission electron microscopy (STEM) - high-angle annular dark-field (HAADF) / annular bright-field (ABF) imaging was performed on a JEOL ACCELARM 200 cold FEG TEM operating at 200 kV, equipped with double spherical aberration (Cs) correctors. The STEM-HAADF/ABF images were acquired with an inner-outer collection angle of 90-370mrad / 16-32mrad respectively and a 0.1 nm probe size. The sample was first crushed and dispersed in ethanol, and one drop of the solution with the small crystallites in suspension was deposited onto a carbon-coated copper grid. Before the observations, the grid was cleaned for 1 minute with a plasma to prevent carbon contamination. Scanning electron microscopy (SEM) was performed with a GeminiSEM 300 (ZEISS, Germany) on the polished surface of the ceramic sample, which was deposited on a carbon
tape attached to an aluminum stub and coated with a thin film of gold before performing imaging.

The optical diffuse reflectance data were collected in the 280-2500 nm range using a Lambda 750 PerkinElmer spectrometer equipped with an integrating sphere. AC impedance spectroscopy measurements were performed on a Solartron 1260 frequency response analyzer over a frequency range of $10^{-1}$-$10^7$ Hz within 7-300 K. The silver paste was coated on the opposite faces of the pellets, which were then clamped with the copper pads in the Physike SHI-4-2 cryostat. An oil-free Edwards T-station 85 molecular pump was used to produce a vacuum below $10^{-4}$ mbar in the cryostat. Then, a Sumitomo HC-4E compressor was employed to cool the system to the desired temperatures through a Physike C22 temperature controller. The impedance data analysis was carried out through the equivalent circuit fitting using ZView software. 39

High precision thermal conductivity of pellets was measured perpendicular to the pellet plane in the 70-300 K temperature range by a two-probe method under high vacuum conditions on the homemade Cryogenic Property Measurement System (CPMS-77). The thermal conductivity data have ~ 4% standard deviation based on the calibration against the stainless-steel standard sample. 40

**Theoretical calculations.** Geometry optimization and electronic structure calculations were performed by using the Vienna *Ab initio* Simulation Package (VASP) based on density functional theory (DFT). 41, 42 The projector-augmented-wave potential and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional were employed. 43 The cutoff energy of 520 eV was specified for the plane-wave basis set, and the smallest allowed spacing of the reciprocal space between $k$ points was set by the KSPACING parameter with a value of 0.2 Å$^{-1}$. The conjugate gradient algorithm was used to perform the structural energy minimization, and the convergence criteria were set to $10^{-6}$ eV and 0.01 eV/Å for total energy and atomic force, respectively. The DFT-D2 method of Grimme was adopted to describe the van der Waals interactions of the layered materials. 44 According to the experimental data of the studied materials, the ideal structure models without atomic mixed-occupancy were built and further
optimizations were carried out to relax the atomic positions and lattice constants. As shown in Table S1, the theoretically optimized lattice constants are consistent with our experimental determined values, demonstrating the validity of the calculation parameters.

### III. Results

**Crystal Structures of Bi$_4$O$_4$SeX$_2$ (X = Br and Cl).** The crystal structure of Bi$_4$O$_4$SeCl$_2$ was previously reported based on single-crystal X-ray diffraction by Gibson et al.\textsuperscript{33} However, because the X-ray scattering length is proportional to the atomic number ($Z$) of the elements, the XRD intensity of the Bi$_4$O$_4$SeCl$_2$ data is dominated by the bismuth atoms contribution. The lighter elements Se ($Z$ = 34), Cl ($Z$ = 17) and O ($Z$ = 8) each contribute to only $\sim$7.5% of the total electron density per formula and thus XRD intensity, resulting in low-intensity statistics insufficient for accurate determination of the occupancies and positions on these anionic. The information for these light elements can be improved using neutron diffraction since the neutron coherent scattering lengths for Cl, Se and Bi are of same order (9.577, 7.970, and 8.532 fm respectively) and even the lightest O has a decent neutron scattering length (5.083 fm).\textsuperscript{45}

In this study, Rietveld refinements of Bi$_4$O$_4$SeCl$_2$ were carried out against both NPD and XRD data simultaneously (as shown in Figures 3a and 3b), starting from the previously reported X-ray structure. To retain the nominal stoichiometry and charge neutrality during the refinement, the Cl occupancy on the two-fold Se1 site in the Bi$_2$O$_2$Se layers was set as twice the amount of Se substitution rate on the four-fold Cl2 site in the Bi$_2$O$_2$Cl$_2$ layers, subject to the overall occupancies of either anionic site being unity. Good fits were obtained with an overall weighted profile $R_{wp}$ factor of 5.78 % and goodness of fit $\chi^2$ of 1.17.
Figure 3. Rietveld plots of (a) XRD and (b) NPD data for Bi$_4$O$_4$SeCl$_2$. The inset in (a) enlarges the fit to the strongest XRD reflection around 2\(\theta = 32.6^\circ\).

The final refined structural parameters and selected interatomic distances in Bi$_4$O$_4$SeCl$_2$ are close to those previously reported based on single X-ray data only. Lattice parameters and Bi-O bond distances are listed in Table 1. Only the Se (Cl) occupancies at Se1 and Cl1 site show a significant discrepancy. Compared with the reported values 0.48(2) and 0.242(13) by Gibson et al., the Cl substitution rate in the Bi$_2$O$_2$Se layers 0.55(1) and the Se substitution rate in the Bi$_2$O$_2$Cl$_2$ layers 0.278(5) are more reliable given the smaller standard deviations. The greater extent of Se and Cl mixing in the Bi$_2$O$_2$Se and Bi$_2$O$_2$Cl$_2$ layers lead to a larger configurational entropy, which plays an important role stabilizing in the formation of phase.

Table 1. Final refined crystallographic parameters and selected bond lengths for Bi$_4$O$_4$SeCl$_2$*.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>(B_{iso}) (Å$^2$)</th>
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<tr>
<td>Bi1</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0.56852(3)</td>
<td>1</td>
<td>0.03(2)</td>
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<tr>
<td>Bi2</td>
<td>4e</td>
<td>0.5</td>
<td>0.5</td>
<td>0.66137(3)</td>
<td>1</td>
<td>0.03(2)</td>
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<tr>
<td>O1</td>
<td>8g</td>
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<td>0</td>
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<td>1</td>
<td>0.03(5)</td>
</tr>
<tr>
<td>Se1/Cl1</td>
<td>2a</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.45(1)/0.55(1)</td>
<td>0.45(6)</td>
</tr>
</tbody>
</table>

*
<table>
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<tr>
<th>Cl2/Se2</th>
<th>4e</th>
<th>0</th>
<th>0</th>
<th>0.70856(6)</th>
<th>0.722(5)</th>
<th>0.278(5)</th>
<th>0.03(5)</th>
</tr>
</thead>
</table>

Bond lengths (Å)

Bi1-O1 (× 4) 2.278(1) Bi2-O1 (× 4) 2.360(1)

Bi1-Se1 (Cl1) (× 4) 3.321(1) Bi2-Cl2 (Se2) (× 4) 3.037(1)

* space group I 4/mmm, a = 3.89873(3) Å, c = 27.0290(4) Å, V = 410.84(1) Å³, ρ = 8.4862(2) g/cm³, 
  
  \[ R_{wp} = 5.78\%, \chi^2 = 1.12. \]

Synthesis of the Br-substituted analogue was also attempted at similar synthetic conditions and a pure phase sample of composition Bi₄O₄SeBr₂ was identified with a similar XRD pattern (Figure 4a) as that of Bi₄O₄SeCl₂. The crystal structure of Bi₄O₄SeBr₂ was refined simultaneously against the XRD and NPD data (Figures 4a and 4b), using the Bi₄O₄SeCl₂ structure as the starting model (Figure 2a). Here neutron diffraction is essential to discern the Se and Br atoms Bi₄O₄SeBr₂ as they are indistinguishable in the X-ray data. The coherent scattering lengths for Se and Br are 7.97 and 6.795 fm, respectively, leading to a small but existing contrast between these two atoms in the NPD data refinement. The site occupancies of Se and Br atoms were refined under the similar constraints used for the Cl-compound case, which leads to a Br substitution rate on the Se1 site ~ 0.41(4) and a Se substitution rate on the Br2 site ~ 0.21(2). Good Rietveld refinements are obtained with an overall \( R_{wp} \) of 6.32% and \( \chi^2 \) of 1.74. The final refined structural parameters and selected interatomic distances in Bi₄O₄SeBr₂ are given in Table 2. Bi₄O₄SeBr₂ is isostructural with Bi₄O₄SeCl₂ (Figure 2a), built with alternating Bi₂O₂Se and Bi₂O₂Br₂ type layers.
Figure 4. Rietveld plots of (a) XRD and (b) NPD data for Bi$_4$O$_4$SeBr$_2$. The inset in (a) enlarges the fit to the main XRD peaks around $2\theta = 31.8^\circ$.

Table 2. Final refined crystallographic parameters for Bi$_4$O$_4$SeBr$_2$*.

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<th>atoms</th>
<th>site</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>occupancy</th>
<th>$B_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$4e$</td>
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<td>0.5</td>
<td>0.65656(3)</td>
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</tr>
<tr>
<td>O1</td>
<td>$8g$</td>
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<td>0</td>
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<td>1</td>
<td>0.06(9)</td>
</tr>
<tr>
<td>Se1/Br1</td>
<td>$2a$</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.59(4)/0.41(4)</td>
<td>0.02(5)</td>
</tr>
<tr>
<td>Br2/Se2</td>
<td>$4e$</td>
<td>0</td>
<td>0</td>
<td>0.70662(5)</td>
<td>0.79(2)/0.21(2)</td>
<td>0.02(3)</td>
</tr>
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</table>

Bond lengths (Å)

- Bi1-O1 ($\times 4$) 2.276(2)
- Bi2-O1 ($\times 4$) 2.379(2)
- Bi1-Se1(Se1) ($\times 4$) 3.378(1)
- Bi2-Br2(Se2) ($\times 4$) 3.116(1)

* space group $I 4/mmm$, $a = 3.93007(5)$ Å, $c = 28.1763(6)$ Å, $V = 435.196(9)$ Å$^3$, $\rho = 8.6899(2)$ g/cm$^3$, $R_{wp} = 6.32\%$, $\chi^2 = 1.74$.

Compared with its Cl analogue, the Bi$_4$O$_4$SeBr$_2$ has a similar lattice parameter $a$ but significantly longer $c$ lattice parameter (by 1.147 Å) and thus larger volume. This variation is related to the larger ionic size of Br$^-$ (1.96 Å) than Cl$^-$ (1.81 Å)$^{46}$ and the layered structural anisotropy. However, the difference between
the \( c \)-lattice parameter of \( \text{Bi}_4\text{O}_4\text{SeX}_2 \) (\( X = \text{Br} \) and \( \text{Cl} \)), as deduced from the sum of one \( c \)-lattice parameter of \( \text{Bi}_2\text{O}_2\text{Se} \) and two \( c \)-lattice parameters of \( \text{Bi}_2\text{O}_2\text{X}_2 \), should be even larger \(~1.50 \, \text{Å}\), supposing no \( \text{Se}/X \) disorder occurred in \( \text{Bi}_4\text{O}_4\text{SeX}_2 \) and its \( \text{Bi}_2\text{O}_2\text{Se} \) and \( \text{Bi}_2\text{O}_2\text{X}_2 \) slabs were identical with those in the end members. Thus, the reduced \( c \)-periodicity difference between the \( \text{Cl} \) and \( \text{Br} \) analogue keeps with \( \text{Se}/X \) anionic disorder in the relaxed \( \text{Bi}_2\text{O}_2\text{Se} \) and \( \text{Bi}_2\text{O}_2\text{X}_2 \) slab, which leads to a more compacted layer stacking and helps to stabilize the layered structures of \( \text{Bi}_4\text{O}_4\text{SeX}_2 \). Furthermore, compared with the ionic layered compounds \( \text{Bi}_4\text{O}_4\text{Cu}_{1.7}\text{Se}_{2.7}X_{0.3} \) having 30\% Se atoms replaced by halide in the \( \text{Bi}_2\text{O}_2\text{Se} \) layer, \(^{27, 28}\) the \( X \) substitution rates on the Se site in the \( \text{Bi}_2\text{O}_2\text{Se} \) layer reach \(~50\%\) in the van der Waals materials \( \text{Bi}_4\text{O}_4\text{SeX}_2 \), i.e. 0.55(1) and 0.41(4) for the \( X = \text{Cl}^- \) and \( \text{Br}^- \) compounds. This results in a high content of substituted Se defects by \( X \) anions, close to the Se vacancies level \(~50\%\) in the well-relaxed surface layers of \( \text{Bi}_2\text{O}_2\text{Se} \) crystal. \(^{32}\) This observation indicates that the weak interlayer vdW interactions in the \( \text{Bi}_2\text{O}_2\text{Cl}_2 \) slab allow nearly free relaxation of \( \text{Bi}_2\text{O}_2\text{Se} \) layers in the \( ab \) plane in the vdW materials \( \text{Bi}_4\text{O}_4\text{SeX}_2 \), while the strong bond interaction in the \( \text{Bi}_2\text{O}_2\text{Cu}_2\text{Se}_2 \) slab limits the relaxation of \( \text{Bi}_2\text{O}_2\text{Se} \) layers in the \( \text{Bi}_4\text{O}_4\text{Cu}_{1.7}\text{Se}_{2.7}X_{0.3} \) materials.

**Synthesis of Higher-Order Homologues.** In order to expand the search to higher-order homologues, synthesis attempts were carried out for \( (m = 1, n = 2) \), \( (m = 1, n = 3) \), and \( (m = 2, n = 1) \) stackings, corresponding to the Cl-based compositions \( \text{Bi}_6\text{O}_6\text{Se}_2\text{Cl}_2 \), \( \text{Bi}_8\text{O}_8\text{Se}_3\text{Cl}_2 \), and \( \text{Bi}_6\text{O}_6\text{SeCl}_4 \), respectively. No evidence of the \( (m = 2, n = 1) \) phase was found in the synthesis attempts of \( \text{Bi}_6\text{O}_6\text{SeCl}_4 \), which produce a mixed \( (m = 1, n = 1) \) phase \( \text{Bi}_4\text{O}_4\text{SeCl}_2 \) and \( \text{Bi}_2\text{O}_2\text{Cl}_2 \) as the final product, as evidenced by the Rietveld XRD plot (Figure S1). In contrast, the synthesis endeavors for \( (m = 1, n = 2) \) phase at the composition of \( \text{Bi}_6\text{O}_6\text{Se}_2\text{Cl}_2 \) produced a single-phase compound, and its structural analysis is provided in the following sections. The synthesis of \( (m = 1, n = 3) \) phase at the composition of \( \text{Bi}_8\text{O}_8\text{Se}_3\text{Cl}_2 \) produced several mixed phases, as revealed by the XRD patterns. Most of XRD reflections can be indexed with a unit cell of \( a = \)
3.904(1) Å and \( c = 54.1580(1) \) Å with space group \( I4/mmm \) as indicated by the Pawley fit (Figure S2a), suggesting the existence of an \((m = 1, n = 3)\) type structure. The dominant impurity peaks, marked with arrows, are ascribed to the \((m = 1, n = 2)\) secondary phase, which is confirmed by significantly improved refinement \( (R_{wp} = 4.41\%) \) of the XRD data after including the Bi\(_6\)O\(_6\)Se\(_2\)Cl\(_2\) phase in Rietveld mode (Figure S2b). Furthermore, according to the stoichiometry, a second impurity phase with composition Bi\(_2\)O\(_2\)Se can be present, which was also confirmed by further fit improvement \( (R_{wp} = 4.08\%) \) of the XRD data after considering Bi\(_2\)O\(_2\)Se in the Rietveld refinement (Figure S2c). Further evidence of the phase composition of the Bi\(_8\)O\(_8\)Se\(_3\)Cl\(_2\) sample is provided in the following STEM-HAADF/ABF imaging section. Synthesis of the phase-pure sample of \((m = 1, n = 3)\)-type Bi\(_8\)O\(_8\)Se\(_3\)Cl\(_2\) was not successful although multiple reactions were attempted through changing the firing temperature and time as well as the stoichiometries.

**Crystal Structure of Bi\(_6\)O\(_6\)Se\(_2\)Cl\(_2\).** An *ab initio* method coupling was employed to determine the crystal structure of Bi\(_6\)O\(_6\)Se\(_2\)Cl\(_2\) from powder diffraction data. First the XRD pattern of Bi\(_6\)O\(_6\)Se\(_2\)Cl\(_2\) could be indexed with a tetragonal cell using the \( a = 3.8996 \) (1) Å and \( c = 19.6496(4) \) Å cell parameters. Systematic absences of reflections on XRD data correspond to \( h00, h = 2n+1 \) and \( hk0, h + k = 2n+1 \). These conditions suggest two probable space groups, \( P4/n \) or \( P4/nmm \). Electron diffraction was then performed to confirm the symmetry and lattice parameters and gain more information about the Laue class. Selected-area electron diffraction (SAED) patterns recorded along the [100] and [001] zone axes (Figures 5b and 5c) can be indexed with the tetragonal lattice parameters previously proposed by XRD. Then, the convergent beam electron diffraction (CBED) pattern recorded along the [001] zone axis contains a 4-fold axis and two sets of mirror planes (Figure 5a), which suggest \( P4/nmm \) as the proper space group.
Figure 5. (a) CBED pattern along [001] direction, and SAED patterns along (b) [100] and (c) [001] projections for the Bi₆O₆Se₂Cl₂ sample. The arrows in (a) mark the mirror planes.

The *ab initio* structure solution for Bi₆O₆Se₂Cl₂ based on the XRD data was then performed in the space group P4/nmm by the direct method using EXPO 2014,³⁵,³⁶ in which the initial positions of heavier bismuth and selenium atoms can be directly determined. Subsequently, the positions of the lighter oxygen and chlorine atoms were obtained by difference Fourier analysis. Rietveld refinements of lattice parameters, atomic positions, and isotropic displacement parameters (Biso) were carried out simultaneously against XRD and NPD data. Similarly to the Bi₄O₄SeX₂ case, neither oxygen vacancy nor anionic disorder was observed on the O1 and O2 sites in the Bi₂O₂²⁺ layers, while the anionic mixing of Se and Cl on the Se1 and Cl2 sites were identified. Therefore, the Cl occupancy on the Se1 site was set identical with the Se occupancy on the Cl2 site as the Se1 and Cl2 sites have the same multiplicity (Table 3), and the overall occupancies of both Se1 and Cl2 sites are subject to unity in the following refinements. The final refinement converged to $R_{wp}$ of 7.16% and $\chi^2$ of 2.6, and the Rietveld plots of XRD and NPD data are shown in Figure 6. The final refined atomic coordinates and selected bond distances are given in Table 3.
Figure 6. The Rietveld plots of (a) XRD and (b) NPD data for Bi₆O₆Se₂Cl₂ sample. The inset in (a) enlarges the fit to the main XRD peaks around 2θ = 32.4°.

Table 3. Final refined crystallographic parameters of Bi₆O₆Se₂Cl₂*.

<table>
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<tr>
<th>atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>occupancy</th>
<th>Biso (Å²)</th>
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<td>1</td>
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<td>0.1503(2)</td>
<td>0.57(1)/0.43(1)</td>
<td>0.4(1)</td>
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<td>2c</td>
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<td>0.75</td>
<td>0.5561(2)</td>
<td>0.57(1)/0.43(1)</td>
<td>0.03(13)</td>
</tr>
</tbody>
</table>

Bond lengths (Å)

| Bi1-O2 (× 4) | 2.376(3) | Bi2-Se1/Cl1 (× 4) | 3.371(2) |
| Bi1-Cl2/Se2 (× 4) | 3.040(2) | Bi3-O1 (× 4) | 2.320(1) |
| Bi2-O2 (× 4) | 2.267(3) | Bi3-Se1/Cl1 (× 4) | 3.228(2) |

* space group P4/nmm, a = 3.8927 (1) Å, c = 19.621(1) Å, V = 297.32(2) Å³, ρ = 8.8173(2) g/cm³, Rwp = 7.16%, χ² = 2.6.
The structure of Bi$_6$O$_6$Se$_2$Cl$_2$ can be considered as a 2:1 intergrowth between Bi$_2$O$_2$Se and Bi$_2$O$_2$Cl$_2$ slabs (corresponding to the same composition parent compounds), resulting in a -Bi$_2$O$_2$-Se-Bi$_2$O$_2$-Se-Bi$_2$O$_2$-Cl-Cl- layer sequence (Figure 2b), in contrast to the ($m = 1$, $n = 1$) phase Bi$_4$O$_4$SeCl$_2$ showing a stacking sequence of -Bi$_2$O$_2$-Se-Bi$_2$O$_2$-Cl-Cl- (Figure 2a). The successive Cl$^-$ layers introduce the van der Waals gap and prevent further extension of ionic bonding interactions along the $c$ axis in Bi$_6$O$_6$Se$_2$Cl$_2$. Therefore, the Bi$_6$O$_6$Se$_2$Cl$_2$ structure can be represented as ideally charge-neutral Bi$_6$O$_6$Se$_2$Cl$_2$ slabs of 1.96 nm thickness, stacked by van der Waals forces along the $c$ direction.

The Bi$_6$O$_6$Se$_2$Cl$_2$ slab (Figure 7a) can be seen as a Bi$_4$O$_4$SeCl$_2$ slab intergrown with a Bi$_2$O$_2$Se monolayer alternatively, which contains a central symmetric Bi$_2$O$_2$$^{2+}$ layer with bridging Se$^{2-}$ layers on both sides, and two asymmetric Bi$_2$O$_2$$^{2+}$ layers adjacent to the terminal Cl$^-$ layers. The central oxygen layer of the latter shifts backward against the terminal Cl layer. Similar observations can also be made in the Bi$_4$O$_4$SeCl$_2$ slab. Three distinct square antiprismatic Bi environments are present in the Bi$_6$O$_6$Se$_2$Cl$_2$ slab, all of which are coordinated to four oxide and four non-oxide anions. Due to the different nature of the Se layer and Cl layers, the bond lengths at the three Bi sites are different (Figure 7b). The Bi1 atom adjacent to the terminal Cl layer exhibits the shortest Bi-Cl/Se bonds of 3.040(2) Å, compensated with the largest Bi-O bonds of 2.376(3) Å. The Bi2 and Bi3 atoms adjacent to the bridging Se layer have longer Bi-Se/Cl bonds of 3.371(2) Å and 3.228(2) Å, and reduced Bi-O bonds of 2.267(3) Å and 2.320(1) Å, respectively.
Role of anionic disorder on layer stacking. The significant anion mixing across the Se1 and Cl2 sites are also present in the Bi$_6$O$_6$Se$_2$Cl$_2$, similar to that in Bi$_4$O$_4$SeX$_2$ (X = Cl and Br). The bridging Se layers of Bi$_6$O$_6$Se$_2$Cl$_2$ have composition of 57(1)% Se + 43(1)% Cl, similar with that of 45(1)% Se + 0.55(1)% Cl in Bi$_4$O$_4$SeCl$_2$. The terminal Cl layers of Bi$_6$O$_6$Se$_2$Cl$_2$ have a composition of 57(1)% Cl + 43(1)% Se, in contrast with that of 72.2(5)% Cl + 27.8(5)% Se in Bi$_4$O$_4$SeCl$_2$. Anionic disorder occurs in the Bi$_4$O$_4$SeX$_2$ and Bi$_6$O$_6$Se$_2$Cl$_2$ compounds, indicating its importance in stabilizing layer van der Waals materials, although anionic disorder does not change the charge-neutrality of Bi$_4$O$_4$SeCl$_2$ (and Bi$_6$O$_6$SeCl$_2$) slabs and the van der Waals interaction that stacks these slabs into three-dimensional crystals. Anionic disorder significantly decreases the internal energy of the Bi$_4$O$_4$SeCl$_2$ (and Bi$_6$O$_6$SeCl$_2$) vdW slabs in the following three aspects.

First, the Slater atomic radius ratio $f = (R_A)/(R_X + 0.2R_M)$ of Bi$_2$O$_2$Se, which was defined for the AM$_2$X$_2$
structure (here $A = \text{Se}$, $M = \text{Bi}$, and $X = \text{O}$), is 1.25, which places $\text{Bi}_2\text{O}_2\text{Se}$ on the phase boundary between the trigonal 6-coordinated anti-$\text{CaAl}_2\text{Si}_2$ structure (Figure S3a) and tetragonal 8-coordinated anti-$\text{ThCr}_2\text{Si}_2$ structure (Figure S3b). This suggests that Se is undersized in its eight-coordinate environment (with a long 3.4 Å Bi–Se bond) through mismatch to the $\text{Bi}_2\text{O}_2$ layer dimensions. The internal lattice strain from this bonding frustration at the bridging $\text{Bi}_2\text{O}_2$-Se interface positions the tetragonal structure adjacent to a distorted phase that is achieved through in-plane static displacements in orthorhombic ultrathin, freestanding $\text{Bi}_2\text{O}_2\text{Se}$ nanosheets. This phase stability of the tetragonal $\text{Bi}_2\text{O}_2\text{Se}$ slab versus the distorted orthorhombic $\text{Bi}_2\text{O}_2\text{Se}$ slab can be enhanced by the introduction of Se deficiency via chemical substitution of Cl$^-$ on the Se site.

Second, the parent compounds $\text{Bi}_2\text{O}_2\text{Se}$ and $\text{Bi}_2\text{O}_2\text{Cl}_2$ have slightly different $\text{Bi}_2\text{O}_2^{2+}$ layers due to the coordination requirement of Se$^{2-}$ and Cl$^-$ in the charge-balancing layers, as reflected by their tetragonal lattice parameter $a = 3.897(2)$ Å and 3.8870(5) Å respectively. Thus, in the hypothetical perfectly ordered $\text{Bi}_4\text{O}_4\text{SeCl}_2$ (and $\text{Bi}_6\text{O}_6\text{Se}_2\text{Cl}_2$) structure, the sandwiched $\text{Bi}_2\text{O}_2^{2+}$ layers between the $\text{Bi}_2\text{O}_2\text{Se}$ and $\text{Bi}_2\text{O}_2X_2$ intergrowth layers are thus strained due to the different requirement of Se and Cl ions on either side. This internal lattice strain from the different bonding requirements of Se and Cl ions at the bridging $\text{Bi}_2\text{O}_2$-Se interface and terminal $\text{Bi}_2\text{O}_2$-Cl interface can be partially released by the mutual anionic substitution of Se and Cl on both sides.

Third, the anion disorder will break the charge neutrality of bridging $\text{Bi}_2\text{O}_2\text{Se}$ layers, and introduce the charge fluctuation in the terminal $\text{Bi}_2\text{O}_2X_2$ layers. Opposite charges for these two intergrowth layers and thus electrostatic interactions between the two slabs to further decrease the total energy.

Based on the observations on the anionic site disorder and its importance on the stacking stability of $\text{Bi}_2\text{O}_2\text{Se}$ and $\text{Bi}_2\text{O}_2X_2$ layers elucidated above, we can reasonably suppose that the bridging Se layers in these intergrowth series has an ideal composition of 50% Se +50% Cl, which has the same Se defects content as that in the surface layer of $\text{Bi}_2\text{O}_2\text{Se}$ if the single-phase $\text{Bi}_{2+2n}\text{O}_{2+2n}\text{Se}_n\text{Cl}_2$ compound can be
stabilized. Then, terminal Cl layer of Bi$_{2+2n}$O$_{2+2n}$Se$_n$Cl$_2$ should have a Se: Cl ratio of n: 4-n based on the stoichiometry. Therefore, the terminal Cl layer in hypothetical stable single-phase Bi$_8$O$_8$Se$_3$Cl$_2$ ($n = 3$) and Bi$_{10}$O$_{10}$Se$_4$Cl$_2$ ($n = 4$) has a composition of 75% Se + 25% Cl and 100% Se, respectively. These Se-rich chemical compositions are very unlikely to be stable as a terminal layer due to the dominant presence of the Se elements, which prefers a 6-8 coordination with Bi forming a bridging Bi$_2$O$_2$Se-type interface rather than a 4-coordination in the terminal Bi$_2$O$_2$Cl$_2$-type layer. The instability of the Bi$_8$O$_8$Se$_3$Cl$_2$ phase has been evidenced by the XRD and the following STEM-HAADF/ABF images, showing coexistence of different intergrowth structures or multiple phases, which include Bi$_8$O$_8$Se$_3$Cl$_2$ type structure, Bi$_6$O$_6$Se$_2$Cl$_2$ type structure, and Bi$_2$O$_2$Se phases as the dominated phases.

The hypothetical ($m = 2$, $n = 1$) Bi$_6$O$_6$SeCl$_4$ phase is expected to contain two successive vdW layered Bi$_2$O$_2$Cl$_2$ slabs alternating with Bi$_2$O$_2$Se ionic layers, as shown in Figure S4, i.e. 2:1 superlattice of Bi$_2$O$_2$Cl$_2$ and Bi$_2$O$_2$Se structural units. The unstable ($m = 2$, $n = 1$) structure may be also explained from the anionic disorder point of view. As indicated by the anionic mixing in the vdW layers of Bi$_4$O$_4$SeCl$_2$ and Bi$_6$O$_6$Se$_2$Cl$_2$ containing ~ 30-40% Se, the Se content in the ($m = 2$, $n = 1$) structure could be not sufficient to maintain such an amount of anionic mixing in the high-order Bi$_2$O$_2$Cl$_2$ slabs, which essentially destabilizes the supposed Bi$_6$O$_6$SeCl$_4$ phase and transforms it into a mixed phase of Bi$_4$O$_4$SeCl$_2$ and Bi$_2$O$_2$Cl$_2$. The inaccessible high-order Bi$_2$O$_2$Cl$_2$ slabs in the 2:1 superstructure are therefore in great contrast with the ionic high-order Bi$_2$O$_2$Se slabs showing variable thickness.

**STEM-HAADF/ABF imaging of Bi$_8$O$_8$Se$_3$Cl$_2**. As stated above, an ($m = 1$, $n = 3$) type structure has been identified in the Bi$_8$O$_8$Se$_3$Cl$_2$ sample. However, the Rietveld fit of the related XRD data using the ($m = 1$, $n = 3$) type structure is rather poor with several unfitted peaks (Figure S3).

**Figure 8a and b** show a SAED pattern and a HRTEM image of the Bi$_8$O$_8$Se$_3$Cl$_2$ sample along the [100] zone axis, which indicates a layered structure nature. The periodical strong main reflection spots observed
on the corresponding FFT image (Figure 8c) can be indexed with the lattice parameters of Bi$_2$O$_2$Se ($a = 3.88(4)$ Å, $c = 12.16(3)$ Å, $I4/mmm$), while the presence of sporadic weaker spots rather than streaks between the main reflections indicate that the stacking periodicity does not vary continuously but show discrete values. The highest $d$-spacing observed along the $c$ axis is around 50 Å, which could correspond to the 002 reflection of the $(m = 1, n = 7)$ member as revealed by the following STEM-HAADF image (Figure 8d). However it could also correspond to the 001 reflection of the Bi$_8$O$_8$Se$_3$Cl$_2$ structure, which should be extincted according to space group $I4/mmm$ but may be present due to double diffraction effects.

In order to examine the layer stacking in the structure of the Bi$_8$O$_8$Se$_3$Cl$_2$ sample, STEM-HAADF/ABF imaging was performed on different zones of the Bi$_8$O$_8$Se$_3$Cl$_2$ sample oriented along the [100]* direction. Along this direction, each atomic column is composed of only one type of crystallographic sites with the same density. The lower magnification STEM-HAADF image presented Figures 8d consists of bright dot arrays separated by dark columns with different thickness and contrast. These are detailed as atomic arrays with weaker intensity on the higher magnification views (Figure 8e and 8g left). Since, the contrast in the STEM-HAADF images is related to the average atomic number of the elements ($Z$) and the thickness of the sample ($e$). At the atomic resolution, the thickness is estimated constant for an observed area (∼ 5nm * 5nm) and the image intensity $I$ can be approximated by $I \propto Z^n$ ($n = 1.6$-2). Therefore, the intensity profiles can be used to analyze the elemental atomic distribution by ranking the atomic columns from the brightest to the darkest spots in relation to the heaviest to the lightest atoms: Bi ($Z = 83$) layers $>$ Se ($Z = 34$) layers $>$ Cl ($Z = 17$) layers $>$ O ($Z = 8$) layers. However, only three different intensities are observed on the high-resolution STEM-HAADF image (Figure 8e and 8g left), and the brightest, intermediate and weakest columns correspond to the Bi, Se (yellow dashed lines on Figure 8e), and Cl (green dashed lines on Figure 8e) layers, while the lightest oxygen is absent due to its extremely weak intensity.

As STEM-ABF image intensity $I$ is proportional to $Z^{1/3}$, the ABF image contrast is more sensitive to
light elements than the STEM-HAADF image. Thus, STEM-ABF images were collected on the same zone to localise oxygen layers. In contrast with bright spheres on the STEM-HAADF image, the atoms on the STEM-ABF image appear as black dots. The large black dots correspond to the Bi arrays, and the intermediate ones correspond to Se and Cl arrays, as shown in Figure 8g right. The small black dots pointed by red arrows correspond to the oxygen layers. It should be noted that even on the ABF image the signal from oxygen atoms is still very weak due to its localization at short distances from much heavier Bi cations. By coupling both HAADF and ABF imaging modes, the entire atomic position information in the structure can be accessible (Figure 8g middle): The bold dark column on the low-magnification STEM-HAADF image (Figure 8d) is confirmed as the double Cl layers, whilst the thin dark column corresponds to the single Se layers.

As shown in Figure 8d, for most cases, the bold dark columns (double Cl layers) are well separated from each other at a distance > 2.0 nm by a thin dark column (Se layer), revealing the succession of multiple different stacking members, Bi$_6$O$_6$Se$_2$Cl$_2$, Bi$_8$O$_8$Se$_3$Cl$_2$ and other ($m = 1, n > 3$) structures in one crystalline piece. Given that single-layer Bi$_2$O$_2$Cl$_2$ and Bi$_2$O$_2$Se slabs have constant separations of ~ 0.8 nm and ~0.6 nm respectively, the layer thickness $d$ of ($m = 1, n$) type intergrowth structure is related to the number of single-layer Bi$_2$O$_2$Se slabs $n$ according to the relation $d = 0.6n + 0.8$ (nm). Therefore, based on the measured thickness $d$ from the neighboring dark thick columns (double Cl layers), the number of Bi$_2$O$_2$Se slabs $n$ in the ($m = 1, n$) type intergrowth structure can be derived, changing from bottom to top according to the sequence of $3 - 3 - 7 - 2 - 0 - 2 - 4 - 6 - 3 - 5 - 3$ in zone 1. The most-populated intergrowth structure is the ($m = 1, n = 3$) type Bi$_8$O$_8$Se$_3$Cl$_2$ and the second one is the ($m = 1, n = 2$) type Bi$_6$O$_6$Se$_2$Cl$_2$ on zone 1 as shown in Figure 8d. In zone 2, as shown in Figure 8f, much larger interlayer distances (~ 5.0 nm – 14.0 nm – 8nm) are observed, which correspond to the ($m = 1, n$) type intergrowth structure with $n$ values varying according to $6 - 21 - 11$. This intergrowth structure has such a long c axis that the Bi$_2$O$_2$Cl$_2$ layer appears almost as a planar defect in the Bi$_2$O$_2$Se lattice. The corresponding SAED pattern (Figure 8a) has principal bright spots, which can be also indexed with the lattice parameters of
$\text{Bi}_2\text{O}_2\text{Se}$, and many less intense spots between the main reflections, indicating the formation of complex superstructures due to the insertion of $\text{Bi}_2\text{O}_2\text{Cl}_2$ layers. The materials are sensitive to electron beam (Figure 8d) and will transform to a trigonal or hexagonal phase, which is probably the 6-coordinated anti-$\text{CaAl}_2\text{Si}_2$ structure (Figure S3a) under long-time electron radiation.
Figure 8. On all the images the sample is oriented along the [100]* direction. (a) Typical SAED pattern for the Bi$_8$O$_8$Se$_3$Cl$_2$ samples oriented along the [100]* direction. (b) HRTEM image of one grain and (c) its corresponding FFT pattern. (d) STEM-HAADF image and (e) the enlarged image on the rectangular area of figure (d). (f) STEM-HAADF image in another location. (f) Atomic resolution STEM - HAADF (left) and ABF (right) images with the corresponding structure model (central). Figures (b)-(e) and (g) are collected on the same zone, while the other figures, (a) and (f), are on another zone.

UV-Vis Reflectivity Spectra and Band Structure. UV-vis diffuse reflectivity data were collected and transformed into optical absorbance coefficient $F(R)$ using the Kubelka-Munk equation. All the samples, namely Bi$_4$O$_4$SeCl$_2$, Bi$_4$O$_4$SeBr$_2$, and Bi$_6$O$_6$Se$_2$Cl$_2$, have nearly identical absorption curves below 1000 nm (Figure 9a). The absorption tail at ~ 1250 nm for Bi$_4$O$_4$SeBr$_2$ and Bi$_4$O$_4$SeCl$_2$ can be attributed to the extrinsic defect states. Given that the Bi$_2$O$_2$Se and Bi$_2$O$_2$Cl$_2$ (Bi$_2$O$_2$Br$_2$) end-member materials have indirect bandgaps of ~0.8 eV and 3.46 eV (2.92 eV) respectively, the intergrowth materials composed of Bi$_4$O$_4$SeX$_2$ and Bi$_6$O$_6$Se$_2$X$_2$ blocks most probably have indirect bandgaps, which could be obtained on the Tauc plot as the intercept on the dashed baseline from the linear fits to the $[F(R)E]^{1/2}$ at the intrinsic absorption edge of 860-1000 nm. From the corresponding Tauc plots (Figure 9b), the indirect bandgaps of Bi$_4$O$_4$SeBr$_2$, Bi$_4$O$_4$SeCl$_2$, and Bi$_6$O$_6$Se$_2$Cl$_2$ were estimated to be 1.07(5), 1.05(5), and 1.04(5) eV respectively, the value for Bi$_4$O$_4$SeCl$_2$ matching well with the previously reported value of 1.15(5) eV. An extrinsic defect-related sub-bandgap was estimated to be 0.73(5) and 0.75(5) eV for Bi$_4$O$_4$SeBr$_2$ and Bi$_4$O$_4$SeCl$_2$ respectively (Figure 9b).
As shown in Figures 10 and S6, the band structures of Bi$_4$O$_4$Se$_2$X$_2$ and Bi$_6$O$_6$Se$_2$X$_2$ (X = Cl and Br) calculated by DFT show similar dispersion characteristics. The valence band maximum (VBM) and conduction band minimum (CBM) are located at different high-symmetric points, confirming the nature of indirect bandgap semiconductors. The theoretically calculated band gap values are 0.697, 0.601, 0.575 and 0.523 eV for Bi$_4$O$_4$SeCl$_2$, Bi$_4$O$_4$SeBr$_2$, Bi$_6$O$_6$Se$_2$Cl$_2$ and Bi$_6$O$_6$Se$_2$Br$_2$, respectively. Although they are lower than the experimentally measured values, the differences between the experimental results and calculated values are understandable because conventional DFT calculations often underestimate the band gaps, which can be improved by the HSE06 hybrid functional. Furthermore, such distinction would not influence our qualitative analysis of the electronic properties of Bi$_{2+2n}$O$_{2+2n}$Se$_n$X$_2$. The CBM is mainly derived from the Bi site bound to the bridging Se anion (Bi 6$p$ states), whereas the VBM is dominated by the Se 4$p$ states, which are originated from the Bi$_2$O$_2$Se slabs as seen from the corresponding charge densities in Figure 11. By contrast, the Cl 3$p$ and Br 4$p$ states (blue curves) lie in the lower energy regions below those of the Se 4$p$ state in the valence band. Therefore, the terminal BiOCl layers do not contribute to the CBM and VBM. In addition, the interlayer dispersions are very weak due to the layered structure characteristics and the vdw gaps between the slabs, which results in that the energies of the top (bottom)
of the valence band (conduction band) at R and X (Γ and Z) points are close to each other. As a result, the VBM (CBM) has changed from R (Γ) to X (Z) along with Bi₄O₄SeX₂ transforming to Bi₆O₆Se₂X₂. The variations of the band structure around the Fermi level imply that the Bi₂O₂Se slabs can be used to modulate the bandgap and the resultant optical properties of the Bi₂₊₂nO₂₊₂nSeₙX₂.

**Figure 10.** Band structures of (a) Bi₆O₆Se₂Cl₂ and (b) Bi₄O₄SeBr₂ by DFT calculations. The orbital projections onto the Bi 6p, Se 4p, Cl 3p (Br 4p), and O 2p states are depicted with red, orange, blue and gray circles, whose contributions are proportional to the size of the circles.

**Figure 11.** Charge densities of the VBM and CBM of (a) Bi₄O₄SeCl₂, (b) Bi₄O₄SeBr₂, (c) Bi₆O₆Se₂Cl₂,
and (d) Bi$_6$O$_6$Se$_2$Br$_2$. The CBM is mainly derived from the Bi 6$p$ orbitals (in light blue), and the VBM is consisting of Se 4$p$ orbitals (in orange), which are originated from the bridging Bi$_2$O$_2$Se layers.

**Transport properties and Morphology.** In order to examine the electrical transport properties, AC impedance data of Bi$_4$O$_4$Se$X_2$ and Bi$_6$O$_6$Se$_2$X$_2$ ($X =$ Cl and Br) pellets were collected. Figure 12a shows typical complex impedance plots for Bi$_4$O$_4$SeBr$_2$ at 7 K, consisting of one semicircular arc with capacitances varying within $10^{-10} - 10^{-11}$ F/cm, which could be ascribed to grain boundary response. The arc has two positive intercepts on the $Z'$-axis, the low and high-frequency intercepts correspond to the bulk and total resistances, respectively. The arc becomes smaller and eventually disappears as temperature increases, as shown in Figure 12a inset at 240 K. A similar temperature-dependent behavior is also observed on the Bi$_6$O$_6$Se$_2$Cl$_2$ samples, while the inductance dominates all the impedance data for the other two pellets of Bi$_4$O$_4$SeCl$_2$ and Bi$_6$O$_6$Se$_2$Br$_2$.

The bulk resistivity of both Bi$_4$O$_4$SeBr$_2$ and Bi$_6$O$_6$Se$_2$Cl$_2$ pellet slightly increases with temperature, as shown in Figure 12b, and indicates typical degenerate semiconductors which are dominated by mobility rather than carrier concentration, similar to that of Bi$_4$O$_4$SeCl$_2$ single crystal in the $ab$ plane. The bulk resistivity of a randomly oriented ceramic corresponds to the average value of a corresponding single crystal sample measured along different directions. However, uniaxial pressure tends to stack the flaky crystals of Bi$_4$O$_4$Se$X_2$ and Bi$_6$O$_6$Se$_2$X$_2$ with 2D layer structure on the basal $ab$ plane predominately, forming highly (001) texture pellets, as confirmed by SEM imaging and powder XRD patterns shown in Figures 13 and S7-S9. Thus, the bulk resistivity of Bi$_4$O$_4$SeBr$_2$ and Bi$_6$O$_6$Se$_2$Cl$_2$ pellets are dominated by the resistivity perpendicular to the $ab$ plane. The resistivity of the Bi$_4$O$_4$SeBr$_2$ and Bi$_6$O$_6$Se$_2$Cl$_2$ single crystals along the $c$ axis can be estimated to be about $10^2$ $\Omega$ cm, while the in-plane resistivity can be estimated to be $\sim 10^2$ $\Omega$ cm as referenced from previous Bi$_4$O$_4$SeCl$_2$ single crystal measurements. The high anisotropic resistivity showing about 4 orders of magnitude difference along and perpendicular to
the ab plane is in line with the layered crystal structure nature. Similar anisotropic conductivity is also observed in other 2D vdW material systems, such as graphite. The total resistivity of these four samples (Figure 12b) shows clear decreasing trends with temperature, indicating the overall nondegenerate semiconductors which carrier concentration dominates the resistivity over mobility in the grain boundary.

**Figure 12.** (a) Typical complex impedance plots for Bi$_4$O$_4$SeBr$_2$ composition at 7 K and 240 K (inset). (b) The total and bulk resistivity of the Bi$_{2+n}$O$_{2+n}$SeX$_n$ (X = Cl and Br) ceramic samples.

![Complex Impedance Plots](image1)

![Total and Bulk Resistivity](image2)

**Figure 13.** Imaging and orientation of the Bi$_4$O$_4$SeBr$_2$ pellet. (a) SEM image, (b) experimental XRD patterns collected along the pellet surface (solid black line) compared with calculated isotropic XRD patterns.
pattern (dashed red line), showing a strong increase in the intensity of (00l) peaks and a reduction of (hk0) peaks (highlighted in the inset), indicating a strong preferred orientation of the [001] direction.

Thermal conductivity measurements performed parallel to the pressing axis of the pellet on all compounds showed very low thermal conductivities at room temperature, with values of 0.66(3), 0.58(2), 0.33(1), and 0.13(1) W/mK for Bi₆O₆Se₂Cl₂, Bi₆O₆Se₂Br₂, Bi₄O₄SeCl₂, Bi₄O₄SeBr₂, respectively (Figure 14). The value of our Bi₄O₄SeCl₂ pellet is larger than the reported value of 0.10(2) W/mK measured on a (001) textured Bi₄O₄SeCl₂ pellet obtained using spark plasma sintering (SPS). We stipulate that this difference is related to the fact that our pellet sample is less (001) textured and therefore shows more contribution from the in-plane thermal conductivity of 1.0 W/mK. Nevertheless, all compounds exhibit exceptionally low thermal conductivities for crystalline compounds, as well as an unusual temperature dependence. Because the pellets have similar density and extent of (001) texture (Figures 14 and S7-S9), their thermal conductivity can be compared. The thermal conductivity and total electronic conductivity of the four samples above 100 K have similar trends and decrease from Bi₄O₄SeBr₂, Bi₄O₄SeCl₂, Bi₆O₆Se₂Br₂ to Bi₆O₆Se₂Cl₂. This observation indicates that the heat transport of Bi₂+nO₂+nSeXₐ materials is probably mediated not only by photons scattering but also by electron scattering as observed in metals and alloys given their high carrier concentration. Compared with the Bi₄O₄SeX₂ (X = Br and Cl) materials, the Bi₆O₆Se₂X₂ (X = Br and Cl) pellets exhibit higher thermal conductivities, which can be linked to the higher proportion of the Bi₂O₂Se slab. The Bi₂O₂Se slab allows much larger thermal conductivity along the c axis than the Bi₂O₂X₂ slab with strong bond contrast, as revealed by the Bi₂O₂Se and Bi₂O₂Cl₂ pellets demonstrating a thermal conductivity of ~ 1.25 and 0.25 W/mK respectively. ³³

Furthermore, for Bi₄O₄SeX₂ and Bi₆O₆Se₂X₂ structures, the Br-containing materials show lower thermal conductivity than their Cl analogues. A similar observation has been reported for the Bi₄O₄Cu₁.₇Se₂.₇X₀.₃ and Bi₆O₆Cu₁.₆Se₃.₆X₀.₄ layered materials. ²⁷,²⁸ The phenomenon can be related to the
fact that Cl possesses stronger electron affinity and lighter atomic weight than Br. Therefore, compared with the Br analogues, the Cl-containing materials have larger internal energy $E$, as evidenced by higher Debye temperature of BiOCl than BiOBr, and lower density $\rho$ (Table 1-3), which leads to a larger photon velocity $v$ according to the $v = (E/\rho)^{0.5}$ and an increased photon-mediated thermal conductivity.

**Figure 14.** Thermal conductivity versus temperature plots for Bi$_4$O$_4$Se$_2$X$_2$ and Bi$_6$O$_6$Se$_2$X$_2$ ($X = \text{Cl and Br}$).

**Conclusion**

A series of multiple-anionic vdW materials Bi$_{2+2n}$O$_{2+2n}$Se$_n$X$_2$ ($n = 1$-$3$, $X = \text{Cl, Br}$) were synthesized using solid-state reactions, leading to high-order layers with variable ionic Bi$_2$O$_2$Se layer thicknesses through the Bi$_2$O$_2$Cl$_2$ cutting effect. Bi$_4$O$_4$SeX$_2$ and Bi$_6$O$_6$Se$_2$X$_2$ were isolated as single-phase materials, showing $\sim$50% Se replaced by $X$ anions in the Bi$_2$O$_2$Se slab as a common feature, while the other stackings appear to be mixed phase. The Bi$_8$O$_8$Se$_2$Cl$_2$ composition leads to an interesting mixed phase containing different and complex intergrowth structures in crystal single crystallite. The Se/X anionic disorder in the Bi$_2$O$_2$Se and Bi$_2$O$_2$Cl$_2$ slabs plays an important role in the stabilization of the Bi$_4$O$_4$SeX$_2$ and Bi$_6$O$_6$Se$_2$X$_2$ polymorphs, which reduces the lattice strain on the sandwiched Bi$_2$O$_2$ interface and introduces charge separation on Bi$_2$O$_2$Se and Bi$_2$O$_2$X$_2$ layers, allowing for the combination of different structural motifs. All
of the materials show a similar optical band indirect gap of \( \sim 1.05 \) eV, which is related to the CBM and VBM originated by the electronic state in the Bi\(_2\)O\(_2\)Se slabs. The vdW materials possess low bulk resistivity (100 \( \Omega \) cm) and exceptionally low thermal conductivity (0.66 W/mK and lower) parallel to the axis of pressing of the pellets, showing the heavier halogen, the lower thermal conductivity. The new multiple anion chemistry of layer stacking in the vdW materials complemented here will be helpful in the design of new vdW materials and their physical property tailoring.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Comparison of the theoretical calculated and experimental measured lattice constants; The XRD data taken on the synthesis attempt of \((m = 2, n = 1)\) phase Bi\(_6\)O\(_6\)SeCl\(_4\); Fits to the XRD plot for a synthesis attempt at the composition Bi\(_8\)O\(_8\)Se\(_3\)Cl\(_2\); The schematic presentation of two classic AM\(_2\)X\(_2\) structure types including (a) the trigonal CaAl\(_2\)Si\(_2\) structure, and (b) the tetragonal ThCr\(_2\)Si\(_2\) structure; The crystal structure of the hypothetical Bi\(_6\)O\(_6\)SeCl\(_4\) phase and its decomposition into the Bi\(_4\)O\(_4\)SeCl\(_2\) and Bi\(_2\)O\(_2\)Cl\(_2\) phase; The Rietveld plot of XRD data for the composition Bi\(_8\)O\(_8\)Se\(_3\)Cl\(_2\); Band structures of (a) Bi\(_6\)O\(_6\)Se\(_2\)Br\(_2\) and (b) Bi\(_4\)O\(_4\)SeCl\(_2\) from DFT calculations; Imaging and orientation of the Bi\(_4\)O\(_4\)SeCl\(_2\), Bi\(_6\)O\(_6\)Se\(_2\)Cl\(_2\), and Bi\(_6\)O\(_6\)Se\(_2\)Br\(_2\) pellet.
Notes

The authors declare no competing financial interests.

CSD 2127176, 2126165, 2127172, and 2127058 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data-request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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