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A novel family of layered bismuth compounds II: the crystal structures of $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Z_2$, Z = Cl, Br, and I

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Abstract

Using various synthetic approaches, we have prepared over 50 new multinary bismuth oxyhalides which crystallize in four layered structure types. Most of the compounds belong to the three previously reported structure types involving fluorite- and CsCl-like metal–oxygen vs. metal–halogen layers as well as single or double halide ion sheets. The majority of $Bi_{2-x}A_xQ_{0.6}O_2Z_2$ (A = Li, Na, K, Ca, Sr, Ba, Pb; Q = Rb, Cs; Z = Cl, Br, I) compounds crystallize in the tetragonal structure of $Pb_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$ (Y2) while both $Bi_{1.4}Ba_{0.6}Q_{0.6}O_2I_2$ (Q = Rb, Cs) oxyiodides adopt its orthorhombically distorted, partially ordered version. Due to the lower degree of substitution, the fluorite-like layers in the Y2 structure accommodate more A cations than previously known for related Bi compounds. However, very large Tl^+ or Rb^+ give compounds with another, as yet unknown, structure. We discuss the influence of size and charge of A cations and stoichiometry of $[Bi_{2-x}A_xO_2]$ fluorite layers on structure and stability of layered oxyhalides of bismuth. Also, we predict formation of isostructural compounds with smaller Q cations like Tl^+ and K^+.

Keywords: Bismuth oxyhalides; Layered compounds; Crystal structures; Cation ordering

1. Introduction

Compounds with layered (2D) structures constitute a huge class of inorganic and hybrid organic–inorganic materials famous for the amazing versatility of both their crystal chemistry and applied properties. A vast subset of the class consists of compounds with structures comprising layers derived from fluorite or anti-fluorite. Its representatives are known as bi-dimensional ionic conductors (both cationic [1] and anionic [2]), ferroelectrics [3,4], superconductors [5,6], catalysts for oxidative coupling of methane [7], ion exchangers [8,9], etc. Their crystal chemistry exhibits many phenomena less often met among 1D or 3D structures like stabilization of unusual oxidation states, coordination polyhedra, and even unknown polymorphs (in the form of 2D fragments).

Recently [10], we briefly surveyed the set of structure types involving fluorite- and anti-fluorite-derived layers and proposed their classification based on 3D structure prototypes for all kinds of layers forming the structure. Our survey also led us to a conclusion that this set is incomplete and far from being exhausted. A novel structure type representing a "CaF_2–CsCl" layer sequence has been predicted and successfully realized among multinary bismuth oxyhalides. The compounds have an overall composition $[Bi_{1.4}M_{0.6}O_2][Q_{0.6}Z_2]$[1] ($M$ = $Bi_{0.5}Na_{0.5}$, Pb, Ba; Q = Rb, Cs; Z = Cl, Br) and crystallize in space group $I4/mmm$. Compositional, structural, and environmental parameters of fluorite-related layers in these compounds appeared to be very similar to those in the so-called Sillén phases, another abundant family of multinary bismuth oxyhalides [11]. Indeed, intergrowth structures between the two families are easy to form.

Fig. 1 represents two most common structure types of Sillén phases, $PbBiO_2Cl$ (X1) and BiOCl (X2) together

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[1] As in [10], we use the symbol Z for halogens instead of conventional X, to avoid confusion with the Xn used for notation of Sillén phases.

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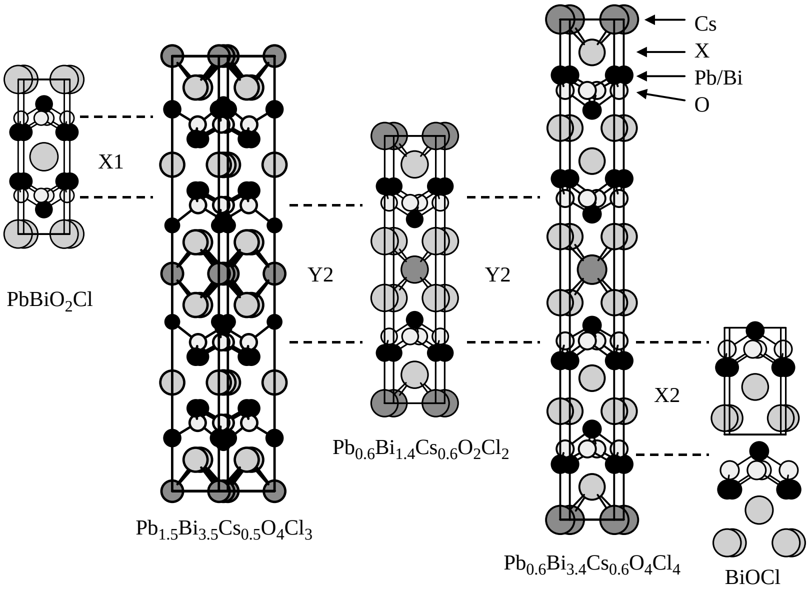

Fig. 1. Crystal structures of bismuth oxyhalides (left to right): $PbBiO_2Cl$ (X1), $Ca_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$ (X1Y2), $Pb_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$ (Y2), $Pb_{0.6}Bi_{3.4}Cs_{0.6}O_4Cl_4$ (X2Y2) and BiOCl (X2). The dashed lines illustrate formation of intergrowth structures.

with $Pb_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$ (denoted by analogy as Y2), and their intergrowths, $Pb_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$ (X1Y2) and $Pb_{0.6}Bi_{3.4}Cs_{0.6}O_4Cl_4$ (X2Y2). In X1Y2-type compounds, the metal ions in the metal–oxygen layers and vacancies in the metal–halogen sheets are to some extent ordered yielding a weak $\sqrt{2}a_0 \times \sqrt{2}a_0 \times 2c_0$ superstructure which was not observed in Y2 and X2Y2-type compounds. The compositions of vacancy-ordered and disordered metal–halide layers also differ slightly.

In Sillén phases, the fluorite-related $[Bi_{2-x}A_xO_2]$ layers accommodate a variety of A cations [11] of which only several were tested in our previous search for Y2 compounds and their intergrowths [10]. Evidently, most (or perhaps all) of these cations should also substitute for Bi^{3+} in the Y2-type compounds. Moreover, since the degree of substitution in Y2 phases is less than in X1 Sillén phases (30% vs. 50% for A^{2+} and 15% vs. 25% for A^{+}), one can expect formation of Y2 compounds with some A cations which are not tolerated in X1 structures, e.g. due to high mismatch in size of Bi^{3+} and A^{n+}. The search for intergrowth compounds like X1Y2 or X2Y2 should likely be restricted to divalent A substituents since no mixed-layered structure has been obtained for any univalent substituent despite known efforts [12,13].

In the current paper, we report results of our extensive search for new Y2 compounds $[Bi_{2-x}A_xO_2][Q_{0.6}Z_2]$ with Q = Rb and Cs, Z = Cl, Br, and I, ($x = 0.3$ if A is univalent and 0.6 if A is divalent) and their intergrowths. The range of A substituents included all alkali and alkaline earth cations (d^0s^0), their $d^{10}s^2$ (Tl^+, Pb^{2+}), and $d^{10}s^0$ (Cu^+, Ag^+, Cd^{2+} and Hg^{2+}) analogs. Various synthetic approaches were attempted to ensure that appropriate synthesis conditions for a given compound were not overlooked.

2. Experimental

The starting compounds were high-purity ($\geqslant$99.5%) lithium and alkaline earth carbonates, alkali (except Li), copper (I), silver (I), and thallium (I) halides, and oxides of bismuth, lead, cadmium and mercury, as well as bismuth oxyhalides, BiOZ (Z = Cl, Br, I). For synthesis of the target compounds containing lithium or alkaline earth ions, X1-type precursors MBiO_2Z ($M = Li_{0.5}Bi_{0.5}$, Ca, Sr, Ba) were prepared first. A preliminary report on their crystal structures was presented in [14], and details will be described elsewhere. Alkali halides were dehydrated at 150°C/2 h prior to reactions. All operations with AgZ were conducted under red light, to prevent photodecomposition.

Stoichiometric mixtures of the corresponding oxides, halides, and oxyhalides, were ground, placed in fused silica tubes, sealed, and annealed in vacuo at various conditions with several intermediate grindings. For samples containing copper, silver, and thallium, the upper temperature limit was fixed at 450°C, and for those with mercury, at 350°C. Whenever a sample was found to attack ampoule walls, the experiment was repeated with the sample either pelletized or placed in alumina crucible sealed into the capsule. As the optimized conditions appeared to differ essentially for various series, they are discussed below in detail. The annealed samples were characterized by XPD in a

Guinier camera using Cu$K\alpha_1$ radiation, and their unit cell parameters were generated by least-squares fits.

The stoichiometry of starting samples was fixed as $(Bi,A)_2Q_{0.6}O_2Z_2$, $(Bi,A)_4Q_{0.5}O_4Z_3$, and $(Bi,A)_4Q_{0.6}O_4Z_4$ for Y2, X1Y2, and X2Y2-type compounds, since our earlier investigations revealed fairly narrow homogeneity areas for selected representatives [10]. In addition, chemical analysis had been performed for another representative, $Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$, which is rather difficult to prepare single-phase [17], so the question of actual stoichiometry is sound. The microprobe analysis carried out on the CAMEBAX analyzer yielded the following atomic percentage (±0.5%, oxygen not accounted): Ba, 14; Bi, 32; Rb, 13; Cl, 41 which is very close to the values calculated for $Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$: Ba, 13; Bi, 30; Rb, 13; Cl, 43.

3. Results and discussion

3.1. New compounds and optimized synthetic conditions

3.1.1. The Y2 series

Table 1 summarizes cell parameters of the novel Y2 compounds. The typical M_{20} values upon indexing their XDPs are 30±3. The heavier A and Z, the less strong lines are observed since all heavy atoms form a distorted and ordered α-Fe arrangement. As expected, almost all A cations involved in formation of X1 Sillén phases also contribute to formation of their Y2 analogs. In addition, four compounds with $A=K^+$ have been synthesized, in agreement with our earlier predictions [10]. For $d^{10}s^0$ cations, the diffraction patterns could not be interpreted in favor of any known or expected compound. The only possible exception is the "$Bi_{1.7}Ag_{0.3}Cs_{0.6}O_2Cl_2$" sample whose X-ray pattern, after removing rather weak reflexions of BiOCl, could be indexed by analogy with known Y2 compounds. No Y2 was either found for $A=$Tl and Rb. Meanwhile, "$Tl_{0.3}Bi_{1.7}Cs_{0.6}O_2Cl_2$", on the one hand, and "$A_{0.3}Bi_{1.7}Cs_{0.6}O_2Br_2$" ($A=$Tl, Rb), on the other hand, form two series of the same stoichiometry but quite different structure compared to each other and Y2. Except for a few weak lines, XDPs of the bromides could be indexed on the basis of I-centered tetragonal cells with $a\sim3.95$ Å and $c\sim39.9$ Å (Table 2). The patterns are similar to those of X2Y2-type compounds, but generated cell parameters are significantly larger (cf. Table 4). Maximal yields were obtained after two cycles of 650°C/10-day annealing. A similar phase was detected also in a sample of nominal composition $Cs_{0.9}Bi_{1.7}O_2Br_2$, but its formation is very slow. These compounds have not yet been studied in detail.

Table 1
Lattice parameters for the new Y2-type oxyhalides (tetragonal, s.g. $I4/mmm$[a])

Compound	a (Å)	b (Å)	c (Å)
$Ag_{0.3}Bi_{1.7}Cs_{0.6}O_2Cl_2$[b]	3.843(1)		20.51(1)
$Ba_{0.6}Bi_{1.4}Cs_{0.6}O_2I_2$	5.844(2)	5.788(2)	23.37(1)
$Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$	5.853(2)	5.782(2)	22.43(1)
$Ca_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$	3.865(1)		20.67(1)
$Ca_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$	3.857(1)		19.91(1)
$Ca_{0.6}Bi_{1.4}Cs_{0.6}O_2Br_2$	3.923(1)		21.71(1)
$Ca_{0.6}Bi_{1.4}Rb_{0.6}O_2Br_2$	3.912(1)		20.78(1)
$K_{0.3}Bi_{1.7}Cs_{0.6}O_2Cl_2$	3.895(1)		20.86(1)
$K_{0.3}Bi_{1.7}Rb_{0.6}O_2Cl_2$[b]	3.889(1)		20.20(1)
$K_{0.3}Bi_{1.7}Cs_{0.6}O_2Br_2$	3.964(1)		21.58(1)
$K_{0.3}Bi_{1.7}Rb_{0.6}O_2Br_2$[b,c]	3.936(1)		20.88(1)
$Li_{0.3}Bi_{1.7}Cs_{0.6}O_2Cl_2$	3.851(1)		20.55(1)
$Li_{0.3}Bi_{1.7}Rb_{0.6}O_2Cl_2$	3.845(1)		19.87(1)
$Li_{0.3}Bi_{1.7}Cs_{0.6}O_2Br_2$	3.899(1)		21.80(2)
$Li_{0.3}Bi_{1.7}Rb_{0.6}O_2Br_2$	3.896(1)		20.75(1)
$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$[b]	4.010(1)		22.32(2)
$Sr_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$	3.912(1)		20.64(1)
$Sr_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$	3.900(1)		19.92(1)
$Sr_{0.6}Bi_{1.4}Cs_{0.6}O_2Br_2$	3.957(1)		21.64(1)
$Sr_{0.6}Bi_{1.4}Rb_{0.6}O_2Br_2$	3.951(1)		20.83(1)
$Sr_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$	4.059(1)		22.38(1)

[a] Except for $Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$ and $Ba_{0.6}Bi_{1.4}Cs_{0.6}O_2I_2$.
[b] Composition assigned by analogy.
[c] Low-temperature phase.

Most of the target oxychlorides and oxybromides have been prepared single-phase at 600°C. After 10-day annealing, the samples were ground, re-sealed, and fired again under the same conditions. In pelletized samples, the Y2 compounds usually form more rapidly and at lower temperatures (e.g. formation of $Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2Br_2$ at 450°C completes within a week), but their degree of crystallinity is much poorer since XDPs contain very broad lines. Above 650°C, the oxyhalides decompose into unknown products.

The compounds $K_{0.3}Bi_{1.7}Rb_{0.6}O_2Z_2$ ($Z=$Cl, Br) could not be prepared at 600°C. At higher temperatures, the chloride sample gives an XDP of BiOCl while the bromide converts to a new compound isostructural to $Tl_{0.3}Bi_{1.7}Rb_{0.6}O_2Br_2$ (Table 2). Both Y2 phases were prepared between 400°C and 450°C with only a moderate yield. We were unable as yet to synthesize $K_{0.3}Bi_{1.7}Q_{0.6}O_2I_2$, but attempts to prepare some other

Table 2
Lattice parameters for the new bismuth oxyhalides of novel non-identified structure types (I-centered tetragonal)[a]

Compound	a (Å)	c (Å)
$Tl_{0.3}Bi_{1.7}Cs_{0.6}O_2Cl_2$	4.019(1)	39.80(1)
$K_{0.3}Bi_{1.7}Rb_{0.6}O_2Br_2$[b]	3.943(1)	39.61(2)
$Tl_{0.3}Bi_{1.7}Rb_{0.6}O_2Br_2$	3.945(1)	39.31(2)
$Rb_{0.9}Bi_{1.7}O_2Br_2$	3.941(1)	39.48(1)
$Tl_{0.3}Bi_{1.7}Cs_{0.6}O_2Br_2$	3.946(1)	40.23(2)
$Rb_{0.3}Bi_{1.7}Cs_{0.6}O_2Br_2$	3.941(1)	39.62(2)

[a] Actual composition may slightly deviate from the given formula.
[b] High temperature phase.

oxyiodides were successful (Table 1). Single-phase iodide samples with $A = \mathrm{Sr}$ and Ba were obtained by annealing pellets at 450°C for 10 days twice with an intermediate grinding. $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$ could not be obtained as single-phase; some $PbBiO_2I$ and RbI were always present, and pelletizing gives even poorer yields. Difficulties in obtaining the ending members of isostructural series are not surprising, particularly when low synthesis temperatures are employed [17]. Among oxyiodides with barium, we meet the first examples of orthorhombic distortion of the Y2 structure, as well as the first oxyiodide with $Q = \mathrm{Cs}$. The cell parameters of the compounds lie between those of $BaBiO_2I$ ($a = 6.052$ Å, $b = 5.825$ Å) and BiOI ($a\sqrt{2} = 5.629$ Å [11]).

Our attempts to prepare oxychlorides and oxybromides with $A = \mathrm{Cd}$ have not been successful as yet. As some auxiliary experiments have shown, even more simple oxyhalides like $CdBiO_2Z$ are rather difficult to prepare, and X3 admixtures were always present. Since crystal structures (hence XRD patterns) of X3 and Y2 type compounds are very similar, it was not possible to distinguish our reaction products between Y2 and X3.

The compounds with $A = \mathrm{Pb}$, Na, K, and possibly Li are stable in air over long periods of time. In the meantime, samples with $A = \mathrm{Ba}$, Sr, and especially Ca decompose sufficiently within weeks' exposure to moist air. While no changes were detected in the X-ray pattern of air-exposed $Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$, the XDPs of $Ca_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$ show increasing intensities of crystalline decomposition products. The percentage of decay after 1 month was estimated to be about 15%. Microprobe analysis of air-exposed $Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$ has shown that amorphous admixtures not containing bismuth were present, but the composition of the main phase remains unchanged.

3.1.2. The intergrowth $XnY2$ ($n = 1, 2$) series

The tested A cations were Li^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} (in the case of oxyiodides). As expected, the compounds could not be obtained with univalent A substituents where annealing always returned mixtures of unreacted $Xn + Y2$. Surprisingly, the same result was found in the search of mixed-layered oxyiodides, and attempts to raise the annealing temperature led to liberation of $BiOZ$ together with other Sillén phases. All the other proposed compounds were found to exist. Their cell parameters are given in Tables 3 and 4. As usual, X1Y2 compounds exhibit a weak superstructure while their X2Y2 analogs do not.

Table 3
Lattice parameters for the new X1Y2-type oxyhalides (tetragonal, s.g. $I4/mmm$)

Compound	a (Å)	c (Å)
$Ca_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$[a]	5.477(1)	32.36(1)
$Ca_{1.5}Bi_{2.5}Rb_{0.5}O_4Cl_3$	5.485(1)	32.22(1)
$Ca_{1.5}Bi_{2.5}Cs_{0.5}O_4Br_3$	5.519(2)	33.99(2)
$Ca_{1.5}Bi_{2.5}Rb_{0.5}O_4Br_3$	5.517(1)	33.07(1)
$Sr_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$	5.563(1)	32.84(1)
$Sr_{1.5}Bi_{2.5}Rb_{0.5}O_4Cl_3$	5.581(1)	32.35(1)
$Sr_{1.5}Bi_{2.5}Cs_{0.5}O_4Br_3$	5.648(1)	34.31(1)
$Sr_{1.5}Bi_{2.5}Rb_{0.5}O_4Br_3$	5.640(2)	33.22(2)
$Ba_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$	5.696(3)	33.36(2)
$Ba_{1.5}Bi_{2.5}Rb_{0.5}O_4Cl_3$	5.686(1)	32.87(1)
$Ba_{1.5}Bi_{2.5}Cs_{0.5}O_4Br_3$	5.777(4)	34.67(3)
$Ba_{1.5}Bi_{2.5}Rb_{0.5}O_4Br_3$	5.762(3)	34.05(3)

[a] Ref. [15].

Table 4
Lattice parameters for the new X2Y2-type oxyhalides

Compound	a (Å)	c (Å)
$Ca_{0.6}Bi_{3.4}Cs_{0.6}O_4Cl_4$	3.875(1)	35.39(2)
$Ca_{0.6}Bi_{3.4}Rb_{0.6}O_4Cl_4$	3.874(1)	34.84(1)
$Ca_{0.6}Bi_{3.4}Cs_{0.6}O_4Br_4$	3.917(1)	38.26(2)
$Ca_{0.6}Bi_{3.4}Rb_{0.6}O_4Br_4$	3.917(1)	37.34(2)
$Sr_{0.6}Bi_{3.4}Cs_{0.6}O_4Cl_4$	3.898(1)	35.38(1)
$Sr_{0.6}Bi_{3.4}Rb_{0.6}O_4Cl_4$	3.899(1)	34.75(1)
$Sr_{0.6}Bi_{3.4}Cs_{0.6}O_4Br_4$	3.942(1)	37.74(2)
$Sr_{0.6}Bi_{3.4}Rb_{0.6}O_4Br_4$	3.939(1)	37.00(1)
$Ba_{0.6}Bi_{3.4}Cs_{0.6}O_4Cl_4$	3.913(1)	35.99(2)
$Ba_{0.6}Bi_{3.4}Rb_{0.6}O_4Cl_4$	3.899(1)	35.47(2)
$Ba_{0.6}Bi_{3.4}Cs_{0.6}O_4Br_4$	3.960(1)	37.94(1)
$Ba_{0.6}Bi_{3.4}Rb_{0.6}O_4Br_4$	3.952(1)	37.13(1)

Preparation of X1Y2-type compounds requires more delicate approaches as compared to both Y2 and X2Y2 series. The "traditional" scheme of firing pellets at 600°C twice with one intermediate grinding is appropriate only for $A = \mathrm{Sr}$ and Ca, except $Ca_{1.5}Bi_{2.5}Rb_{0.5}O_4Cl_3$. In the latter case, this approach yields a product with quite typical XDP, but generated cell parameters ($a = 5.509(1)$Å, $c = 34.45(1)$Å) are sufficiently larger than even those of the cesium compound. Hence, the product has a related but different crystal structure upon the same stoichiometry. The desired compound with a true X1Y2 structure ($d_{0\,0\,2} = 16$ Å) could be obtained only by annealing a mixture of $CaBiO_2Cl$, BiOCl, and RbCl at 600°C in an open alumina crucible for 10 days with everyday grinding. This method, with annealing temperatures of 650–700°C, is also the only way for preparation of X1Y2-type oxychlorides with $A = \mathrm{Ba}$. Indeed, it is also valid for synthesis of $Ca_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$, $Sr_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$, and $Sr_{1.5}Bi_{2.5}Cs_{0.5}O_4Cl_3$, but the cell parameters of samples annealed in vacuo and in air differ by $\sim 1\%$, possibly due to minor evaporation of $BiCl_3$ upon firing in air. With $Ba_{1.5}Bi_{2.5}Q_{0.5}O_4Br_3$, the procedure had to be conducted in crucibles sealed into ampoules. The discrepancies between observed and calculated interplanar spacings are minor in the case of $A = \mathrm{Ca}$ and Sr but increase twofold with $A = \mathrm{Ba}$, mostly for ($hk0$) and, slightly less, for ($00l$) series. This might be indicative of some structural disorder in barium compounds, which may arise due to incomplete ordering of Ba^{2+} and Bi^{3+} (along [100]), or X1- and Y2-type slabs (along [001]).

Contrary to X1Y2, X2Y2-type compounds are very stable, and higher temperatures may be employed to facilitate their rapid formation. The optimal synthesis conditions are 600–700°C/10 days in pellets, or 20 days without pelletizing. All attempts to prepare X3Y2 compounds starting from the composition $Ca_{1.85}Bi_{2.9}Q_{0.6}O_4Z_5$ ($\equiv Ca_{1.25}Bi_{1.5}O_2Z_3 \cdot Ca_{0.6}Bi_{1.4}Q_{0.6}O_2Z_2$) were unsuccessful.

3.2. Structures of $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Z_2$, Z=Cl, Br, I

To compare structural features of various Y2 oxyhalides, we determined positional parameters for the $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$ and $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$ compounds (together with the structure of the oxybromide [17], this gives the complete data set for the $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Z_2$ series). For the chloride, we were able to grow single crystals of acceptable quality at 700 ± 50°C. As mentioned above, the oxyiodide could not be prepared single-phase, therefore, the data were collected using a multiphase powder sample. An essential amount of $PbBiO_2I$ (12(1)%) and traces of RbI and metallic bismuth (<1%) were found upon phase analysis and accounted during the refinement. The stoichiometry was therefore fixed at $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$ by analogy with other Y2 compounds, $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Z_2$ (Z = Cl, Br) and $A_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$ (A = Sr, Ba). Rather high thermal parameters of Rb might be indicative of its slight displacement from (0,0,0); however, attempts to model it did not improve the fit. This picture looks somewhat similar to structures of LaOAgS-type compounds where fluorite layers, $[L_2O_2]$ (L = Bi, Ln, An), are separated by anti-isostructural $[T_2X_2]$ (T = transition metal, X = chalcogen or pnicogen): despite exact $LOTX$ stoichiometry, transition metal atoms sometimes exhibit high thermal parameters [17,19–21].

The structure of $Ba_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$ was also studied starting from the partially ordered, $BaBiO_2Cl$-related model. As yet, only an approximate model could be obtained which however shows a Y2-derived structure. Experimental conditions, atomic parameters, and selected bond distances for the tetragonal lead compounds are gathered in Tables 5–8. The starting model in all cases was the structure of $Pb_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$ [10]. Final Rietveld refinement plot for $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$ is given in Fig. 2.

In all three structures of $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Z_2$, the OM_4 tetrahedra are somewhat flattened, while the RbZ_8 cubes are stretched along the tetragonal axis. The distortions in the OM_4 units increase in parallel with the size of halide ion, and angular changes are more pronounced than radial. Comparison of M–O and M–Cl bond lengths and MOM angles in the two isostructural oxychlorides, $Pb_{0.6}Bi_{1.4}Cs_{0.6}O_2Cl_2$ and $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$ [10], reveals their equality within

Table 5
Experimental conditions for the powder diffraction experiment

Chemical formula	$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$
Formula weight	755.05
Crystal system	Tetragonal
Space group	$I4/mmm$ (#139)
Cell parameters:	
a (Å)	4.0386(1)
c (Å)	22.3213(4)
Z	2
Calculated density	6.894
Diffractometer	STOE
Radiation and wavelength	$CuK\alpha_1$ ($\lambda = 1.5406$ Å)
Analyzing package	GSAS [16]
2ϑ range	10–130
Number of reflections[a]	127/301
Number of data points	5806
Number of variables[b]	49
R_p[c]	0.0681/0.0695
R_{wp}[c]	0.0889/0.0949
R_{F^2}	0.0600
R_B[d]	0.0445
χ^2	3.30

[a] Left: target phase; right: total.
[b] Total number of variables.
[c] Left: background not subtracted; right: background subtracted.
[d] Magnitude for the target phase.

Table 6
Experimental conditions for the single crystal experiment

Molecular weight	1142.16
Chemical formula	$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$
Color	Colorless
Crystal habit	Irregular-shaped platelet
Symmetry	Tetragonal
Space group	$I4/mmm$ (#139)
Cell parameters	
a (Å)	3.900(2)
c (Å)	20.078(3)
V (Å^3)	305.5(2)
Z	2
Calculated density	6.21
Diffractometer	Rigaku AFC7S
Radiation and wavelength	$MoK\alpha$ ($\lambda = 0.7107$ Å)
h, k, l range	0–6, 0–6, 0–25
Total number of reflections	289
Number of reflections with $I > 3\sigma(I)$	163
Number of free variables	11
Analyzing package	TEXSAN [18]
Absorption correction	DIFABS
R	0.043
R_w	0.056
Weighting scheme	$W = 1/\sigma^2(F_0)$
S	1.8

Table 7
Atomic parameters for the $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Z_2$ oxyhalides

Compound	$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$		$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Br_2$ [17]		$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$	
Atom	z	B	z	B	z	B
$Pb_{0.6}Bi_{1.4}$ (00z)	0.1881(1)	2.4(1)	0.1916(1)	2.2(1)	0.1962(1)	2.3(1)
$Rb_{0.6}$ (000)		5.7(2)		2.2(9)		5.5(5)
Z ($\frac{1}{2}\frac{1}{2}z$)	0.1063(5)	3.1(1)	0.1054(1)	2.8(1)	0.1074(2)	2.9(1)
O ($\frac{1}{2}0\frac{1}{4}$)		1.6(3)		2.2(2)		2.3(6)

Table 8
Bond distances in the tetragonal $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Z_2$ oxyhalides

Bond	$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Cl_2$	$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2Br_2$ [17]	$Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$
M–4O	2.312(1)	2.324(1)	2.349(1)
M–4Z	3.230(5)	3.328(1)	3.477(2)
Rb–8Z	3.488(6)	3.561(1)	3.728(2)

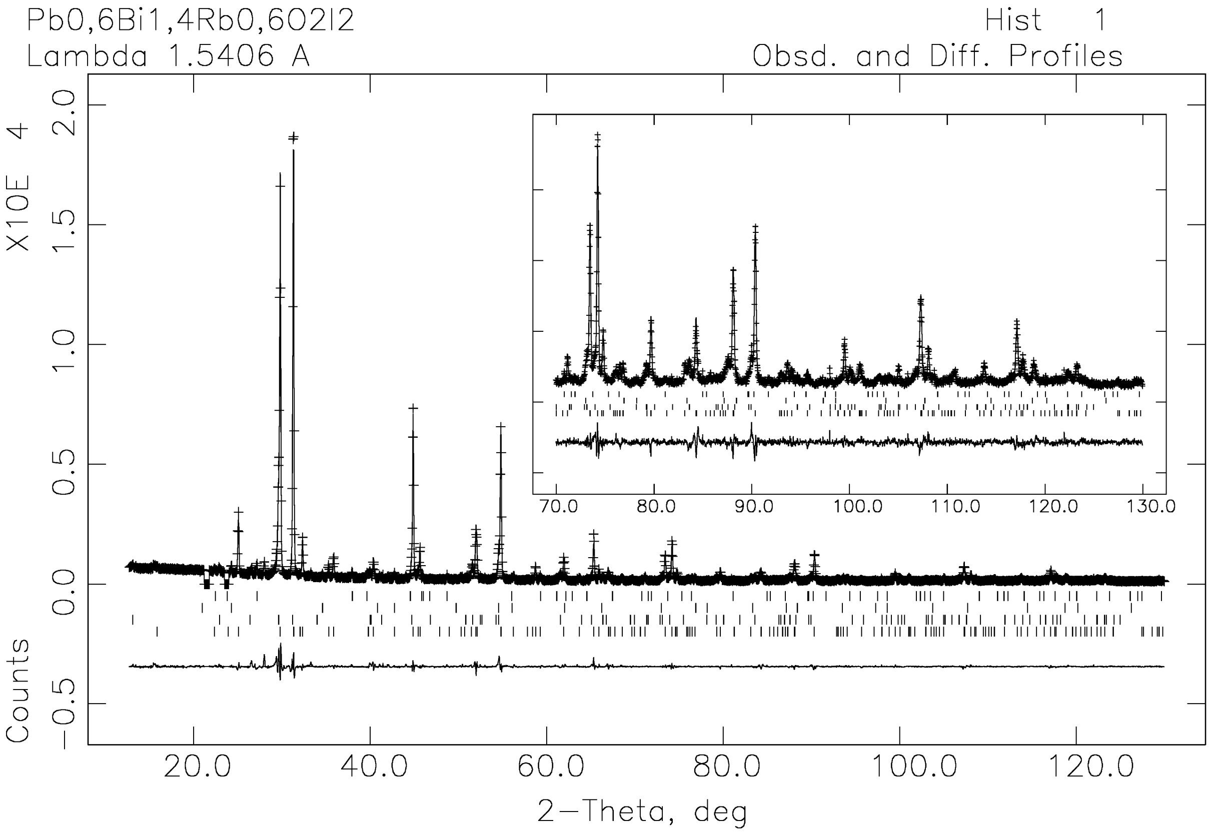

Fig. 2. Final Rietveld refinement plot for $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$. Two regions (at $2\vartheta\sim22^\circ$ and 25°) containing reflections from vaseline oil used in the sample holder are excluded from the refinement. The ticks mark reflections, for top to bottom, of impurity phases Bi, RbI and $PbBiO_2I$, and the target phase $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$.

experimental errors. This explains our earlier observation of a cell parameters of various Y_2 and X_nY_2 oxyhalides being almost insensitive to the nature of the Q^+ ion. The compounds listed in Tables 1, 3 and 4 also follow this trend. Considering the whole structure as a result of mutual adjustment of the CaF_2- and CsCl-derived layers, one may be tempted to suppose that the a parameter (which reflects the adjustment) is governed predominantly by the $[Bi_{2-x}A_xO_2]$ metal–oxygen layer. However, the nature of the halide ion also has a strong effect on a, and it is a matter of taste whether to attribute this effect only to halogen–halogen repulsion or to consider these ions as a part of coordination polyhedron of Bi^{3+} (and A^{n+}). The minor effect of the Q^{+} ion comes from the predominantly ionic character of the Q–Z bond since the contribution of angular distortions of ionic polyhedra to the deformation energy is usually small compared to contribution from radial distortions. This should be no longer the case if the Q–Z bond becomes more covalent; however, no large univalent cation is known to form eight substantially covalent bonds to halogens, so direct comparison within one structure type is not feasible.

3.3. The "crystal chemical boundaries" and further prospectives of Y2 and intergrowth structure types

Our results have added a vast new group to a family of layered bismuth oxyhalides, which is almost as large as the previously known set of Sillén phases. Evidently, further studies will further expand it by adding new representatives to both known and novel structure types.

As we have noticed above, crystal chemical features of the $[Bi_{2-x}A_xO_2]$ layers are generally similar throughout the whole set of oxyhalides of bismuth. Comparison of the novel group with the Sillén group reveals several differences and overall trends. We begin with the already noted relationship between mismatch in size and/or coordination preferences between A^{n+} and Bi^{3+}, the degree of substitution (x), and existence of a given compound: the larger the mismatch, the smaller x values are permitted and the less stable is the compound, if it exists. Consider the alkali metal ions as an example. For $A = Li^{+}$ ($r(A)$–$r(Bi^{3+}) = -0.25$ Å [22]), and Na^{+} ($r(A)$–$r(Bi^{3+}) \approx 0$), both X1 ($x = 0.25$) and Y2 ($x = 0.15$) compounds do exist. For K^{+} ($r(A)$–$r(Bi^{3+}) = 0.34$ Å), the Y2 structure remains while X1 already does not. With Rb^{+} ($r(A)$–$r(Bi^{3+}) = 0.44$ Å), neither structure survives. (As usual, it is easier to accommodate A cations smaller than larger compared to the "matrix" Bi^{3+}.) However, if in some new family a value of $x \ll 0.15$ were required, Rb^{+} could be welcome into the $[Bi_{2-x}A_xO_2]$ layers together with the smaller A cations (but possibly not Cs^{+}). If the oxybromides listed in Table 2 belong to the layered family we are discussing (as their metrics would suggest), they may provide an illustration.

Obviously, the change of structure type upon (approximately) the same stoichiometry indicates that the tolerance limit of the Y2 structure is exhausted, likely due to lattice strain caused by mismatching ions occupying the same crystallographic site. An alternative way to relieve the strain is to split the "ill" site and to distribute the mismatching cations among the new sites formed. However, perfect cation ordering can be (not always) found only in X1-type Sillén compounds with $x = 1$ [14,23–27]. In other cases, ordering seems to be hampered by low and non-integer x values. In X1Y2-type compounds with the largest x value (0.75), the cations tend to order, but the ordering is far from ideal [15] due to non-integer stoichiometry. When the substituting ion is equal in size or smaller than Bi^{3+}, the lattice strain is small, so the resulting compounds are stable and easily formed. For compounds with the largest divalent substituent, Ba^{2+} ($r(A)$–$r(Bi^{3+}) = 0.25$ Å), the strain becomes sufficient to turn their preparation into a challenging synthetic problem. (For X2Y2 compounds with the smallest x of 0.30, the induced strain is minimal which correlates with their maximal chemical stability.) Proceeding from chlorides to bromides and iodides, the lattice expands so the BiO_4 pyramids become more and more distorted. This may account for the low thermal stability of oxyiodides and, for cation ordering which is likely to occur in Y2-type barium compounds despite unfavorable stoichiometry.[2] The low thermal stability is also likely to preclude or severely hamper formation of XnY2 oxyiodide intergrowths since preparation of mixed-layered compounds often requires high temperatures [12].

Another reason for the low thermal stability of oxyiodides lies in the metal–halogen layers. The distortion of QI_8 cubes has already been mentioned. In addition, cubic coordination of Rb^{+} with I^{-} is not very favorable (under ambient conditions, RbI prefers NaCl but not CsCl arrangement). Actually, Rb^{+} may even shift from the cube center which is a probable reason for the large thermal parameter of Rb observed upon structure refinement of $Pb_{0.6}Bi_{1.4}Rb_{0.6}O_2I_2$. Actually, all Y2 compounds and their intergrowths with $Q = Rb$ illustrate stabilization of unfavorable 3D polymorphs as 2D fragments. Evidently, the more unfavorable the polymorph, the more difficult is for a layered structure to stabilize it. Considering possible new representatives of the structure types under discussion, oxybromides with K^{+} at the Q site seem to be the only reliable candidates with alkali ions. According to our preliminary results, $Li_{0.3}Bi_{1.7}K_{0.6}O_2Br_2$ adopts the Y2 structure, but the chloride and iodide analogs are unlikely to exist. On the contrary, Tl^{+} favors cubic coordination with all three heavier halogens so developing the thallium-based family (where several Y2 and X2Y2 representatives have also been found [17]) will evidently result in many more Y2 and XnY2 compounds. Investigations are currently underway to find out possible new representatives, novel structure types, thus to further explore the crystal chemical possibilities of this fascinating layered family.

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[2] Discrepancies upon indexing powder patterns of $Ba_{1.5}Bi_{2.5}Q_{0.5}O_4Z_3$ may also come from very subtle distortions of the tetragonal superlattice.

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