ACADEMIC
PRESS

A reinvestigation of quaternary layered bismuth oxyhalides of the Sillén X1 type

D.O. Charkin,[a] P.S. Berdonosov,[b] V.A. Dolgikh,[b] and P. Lightfoot[c],*

[a] *Department of Materials Sciences, Moscow State University, 119992 Moscow GSP-2, Russia*
[b] *Department of Chemistry, Moscow State University, 119992 Moscow GSP-2, Russia*
[c] *School of Chemistry, St. Andrews University, Purdie Building, North Haugh, Fife KY16 9ST, UK*

Abstract

A family of layered bismuth oxyhalides, $L_{0.5}^I Bi_{1.5}O_2X$ and $L^{II}BiO_2X$ has been reinvestigated. Formation of X1-type Sillén compounds has been established for L^I = Li, Na, L^{II} = Ca, Sr, Ba, and X = Cl, Br, I, but the details of their crystal structures are different. While all $L_{0.5}^I Bi_{1.5}O_2X$, $CaBiO_2Br$, and $CaBiO_2I$ adopt the disordered tetragonal Nd_2O_2Te structure, all compounds of L^{II} = Sr and Ba are orthorhombic and isostructural to $PbSbO_2Cl$, due to L/Bi cation ordering. Crystal structures have been determined for $CaBiO_2I$, $SrBiO_2Br$, $SrBiO_2I$, and $BaBiO_2I$. We discuss the factors which determine the occurrence and type of cation ordering in the quaternary bismuth and antimony X1-type oxyhalides. We also predict that more isostructural compounds can be prepared with antimony.
© 2003 Elsevier Inc. All rights reserved.

Keywords: Bismuth oxyhalides; Crystal structures; Cation ordering; Sillén phases

1. Introduction

The first members of the Sillén layered family of bismuth oxyhalides were reported as early as 1939 [1,2]; the family now comprises oxyhalides of Bi with Li, Na, Ca, Sr, Ba, Pb, and Cd [3]. Their crystal structures can be regarded as ordered alternation of fluorite-derived $[M_2O_2]$ slices (where M = Bi and its substituents listed above) and single or double halide ion sheets. These layer sequences give rise to ideal tetragonal structures with $a \sim 3.9$ Å (i.e., $\sqrt{2}/2a$(fluorite)) and c varying from 6 to 50 Å dependent on structural complexity. Despite numerous investigations in this area (dedicated both to their crystal chemistry [3–10] and catalytic activity in oxidative coupling of methane [11]) many structural details are as yet unclear. The compounds with the simplest "X1" structure, which corresponds to alternation of $[M_2O_2]^+$ slices and $[X]^-$ halide ion sheets, were initially described as tetragonal, i.e., adopting the ideal structure (which is an anti-type to $ThCr_2Si_2$ [12]). However, as yet only $Na_{0.5}Bi_{1.5}O_2Cl$ has been reported

recently as truly tetragonal (Fig. 1a) [13]. This structure was also reported for Bi_2O_2Se [14] and Nd_2O_2Te [15]. The structures of the oxychlorides with divalent elements, $L^{II}BiO_2Cl$ (L^{II} = Cd, Ca, Sr, Ba) demonstrate two different versions of complete ordering of the L^{II} and Bi^{III} cations contributing to the fluorite layers. The smallest Ca^{2+} [9] and Cd^{2+} [10] give a monoclinic structure (Fig. 1b) while the larger Sr^{2+} [9] and Ba^{2+} [8] result in an orthorhombic superstructure (Fig. 1c) found earlier for the related $BaSbO_2Cl$ [16], $PbSbO_2Cl$ [7,17,18], and $PbBiO_2Cl$ [4]. The lead compounds are peculiar. $PbBiO_2Cl$ crystallizes in the orthorhombic structure as the natural mineral perite [4]; however, synthetic perite is always tetragonal [6]. $PbSbO_2Cl$ may be converted from orthorhombic to tetragonal form by treatment with boiling water [17]; more recent investigation has shown that stoichiometric $PbSbO_2Cl$ and $PbSbO_2Br$ are orthorhombic but a shift of composition to $PbSbO_{2.125}X_{0.75}$ makes the compounds tetragonal [7]. Stoichiometric $PbSbO_2I$ is also tetragonal, akin to $PbBiO_2Br$ and $PbBiO_2I$ [7]. Though both stoichiometry and size of the contributing ions are likely to affect the structural details of these X1-type Bi and Sb oxyhalides, neither the oxybromides nor oxyiodides of bismuth and

*Corresponding author. Fax: +44-1334-463808.
E-mail address: pl@st-and.ac.uk (P. Lightfoot).
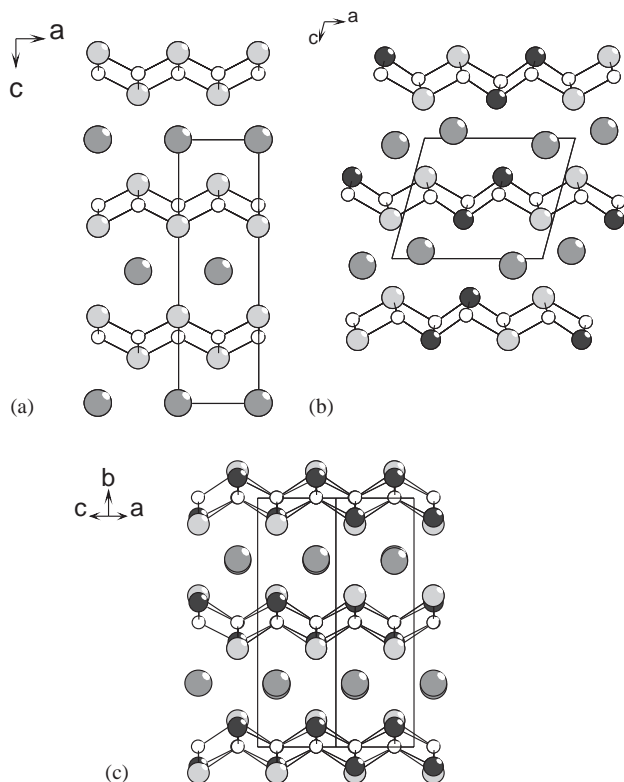
Fig. 1. Crystal structures of the three variants of the Sillen X1 structure type. (a) Tetragonal form (Nd_2O_2Te-type), (b) monoclinic form ($CaBiO_2Cl$-type), (c) orthorhombic form ($PbSbO_2Cl$-type). Note the differing cation ordering schemes for (b) and (c).

alkali and alkaline earth metals, to the best of our knowledge, have been studied in detail since 1941. Moreover, we could not find any reference to existence of $CaBiO_2X$ ($X =$ Br and I[1]) and $SrBiO_2I$; $BaBiO_2I$ was mentioned briefly in Ref. [19], but no data were presented for this compound.

Upon preparation of $BaBiO_2Br$ as a precursor for more complex bismuth oxyhalides [20], we have noticed that it is orthorhombic, similar to $BaBiO_2Cl$ [7] and not tetragonal as reported originally by Sillén [2]. A question arose whether other X1 compounds described originally as tetragonal may actually have lower symmetry. Representatives of this family might also exist among oxyhalides of bismuth and some other L cations. Hence, the whole series of $L^I_{0.5}Bi_{1.5}O_2X$ and $L^{II}BiO_2X$ oxyhalides ($X =$ Br, I) has been reinvestigated, excluding $L^{II}BiO_2Cl$ and Pb compounds (which have been studied recently [6–10]). Preliminary results of our investigation have been reported in Ref. [21]. Besides the known $L =$ Li, Na, Ca, Cd, Sr, and Ba, we also considered $L =$ Sn^{II}, K, Cu^I, and Ag.

---

[1] There is a misprint in Ref. [3]: the cell parameters attributed to $CaBiO_2I$ actually belong to $CdBiO_2I$ [2].

2. Experimental

$CaBiO_2X$ and $SrBiO_2X$ ($X =$ Br, I) were prepared directly from LO and $BiOX$ in alumina crucibles sealed into evacuated silica ampoules by annealing the corresponding 1:1 mixtures at 750°C (Ca) or 800°C (Sr) for 5 days. CaO and SrO were obtained by calcining the carbonates at 1100°C for 2 days. The barium compounds were prepared in a two-step process. First, a 1:1 mixture of $BaCO_3$ and Bi_2O_3 was annealed in dynamic vacuum at ~ 800°C for 8 h. The resulting dark red precursor was mixed with anhydrous BaX_2 (prepared from $BaX_2 \cdot 2H_2O$ at 250°C in dynamic vacuum) and annealed under the same conditions as for $SrBiO_2X$.

In the search for $SnBiO_2X$ ($X =$ Cl, Br, I), SnO and $BiOX$ (1:1) were annealed in evacuated silica tubes at 700°C for 7 days. The precursors were prepared according to [22]. For synthesis of $CdBiO_2X$ ($X =$ Br, I), CdO and $BiOX$ were annealed at the same conditions as given for $CdBiO_2Cl$ [10].

$Na_{0.5}Bi_{1.5}O_2X$ were obtained directly from 1:1:1 mixtures of NaX ($NaI \cdot 2H_2O$ was dehydrated under the same conditions as BaX_2), $BiOX$ and Bi_2O_3 in evacuated silica tubes at 650°C for 10 days. The potassium, copper and silver-containing samples were treated the same way, but for the d-metals, the annealing temperature was lower (400–450°C). The lithium compounds were synthesized from $LiBiO_2$ and $BiOX$ in alumina crucibles sealed into silica ampoules and annealed at 650°C. $LiBiO_2$ in its turn was prepared by melting Li_2CO_3 and Bi_2O_3 in an alumina crucible under dynamic vacuum for 30 min.

The phase purity of all samples was monitored by X-ray powder diffraction using a Guinier camera (FR-552, Enraf-Nonius, Cu$K\alpha_1$ radiation). The reflection positions on the Guinier films were determined with an accuracy of 0.005 mm, converted into interplanar spacings, and cell parameters of the obtained compounds were refined using the whole pattern by least-squares fits using a home-made program.

3. Results

The X-ray diffraction data indicated formation of X1-type compounds only for $L^I =$ Li and Na and $L^{II} =$ Ca, Sr, and Ba with all three halogens. The compounds of Li, Na were found to be tetragonal, in fair agreement with Sillén's original reports [1,2]; $CaBiO_2Br$ and $CaBiO_2I$ are also tetragonal. On the contrary, all compounds of Sr and Ba appeared to be orthorhombic ($PbSbO_2Cl$ type). No new example of the monoclinic $CaBiO_2Cl$ structure type [9] has been found. The cell parameters of the compounds which were obtained single phase are listed in Table 1. A small amount of BiOI was found in the $Li_{0.5}Bi_{1.5}O_2I$ sample;

Table 1
Lattice parameters for the X1 bismuth oxyhalides

(a) Structure type Nd_2O_2Te—SG $I4/mmm$, $Z = 2$

Compound	a (Å)	c (Å)	Compound	a (Å)	c (Å)
$Li_{0.5}Bi_{1.5}O_2Cl$	3.8457(5)	12.060(3)	$Na_{0.5}Bi_{1.5}O_2Br$	3.9205(3)	12.542(2)
$Li_{0.5}Bi_{1.5}O_2Br$	3.8789(5)	12.486(2)	$Na_{0.5}Bi_{1.5}O_2I$	3.9987(5)	13.322(3)
$Li_{0.5}Bi_{1.5}O_2I$[a]	3.935(2)	13.236(4)	$CaBiO_2Br$	3.9617(5)	12.584(3)
$Na_{0.5}Bi_{1.5}O_2Cl$	3.880(1)	12.136(4)	$CaBiO_2I$	4.0222(2)	13.239(1)

(b) Structure type $PbSbO_2Cl$—SG $Cmcm$, $Z = 4$

Compound	a (Å)	b (Å)	c (Å)
$SrBiO_2Br$	5.768(2)	12.806(4)	5.645(2)
$SrBiO_2I$	5.776(3)	13.509(8)	5.863(2)
$BaBiO_2Br$	5.968(2)	13.162(6)	5.748(2)
$BaBiO_2I$	6.052(2)	14.031(6)	5.825(3)

[a] $BiOI$ is present as an impurity phase.

the composition of the target phase was therefore attributed by analogy with the isostructural compounds.

Despite numerous efforts, $CdBiO_2Br$ and $CdBiO_2I$ could not be prepared single-phase; admixtures of X3-type phases (which seem to be more thermally stable compared to X1) were always present. However, powder patterns of X1-richest samples indicated truly tetragonal symmetry akin to the corresponding calcium compounds (no superstructure reflections or splitting of the strongest peaks characteristic for ordered structures have been detected).

The samples aimed at $SnBiO_2X$ appeared black, and X-ray diffraction data indicated presence of SnO_2, $Bi_2Sn_2O_7$ and Bi which means a redox reaction had actually proceeded. The search for $K_{0.5}Bi_{1.5}O_2X$ yielded mixtures of KX and solid solutions based on $Bi_{24}O_{31}X_{10}$ (X = Cl, Br) or $Bi_7O_9I_3$. Diffraction patterns of samples with Cu and Ag yielded mixtures of unknown phases with X = Cl and I. For X = Br, the patterns appeared similar to each other and could be, with moderate success, indexed on the basis of I-centered tetragonal cells with $a \sim 3.9$ Å and $c \sim 22$ Å indicating the existence of a novel, possibly layered bismuth oxyhalide family. Our attempts to prepare tetragonal $L^{II}BiO_{2.125}X_{0.75}$ with L^{II} = Sr and Ba by analogy with $PbSbO_{2.125}X_{0.75}$ also proved unsuccessful, resulting in mixtures of orthorhombic $L^{II}BiO_2X$ and unknown phases.

4. Crystal structures

Structural details have been determined for tetragonal $CaBiO_2I$ and orthorhombic $SrBiO_2Br$, $SrBiO_2I$, and $BaBiO_2I$. The experimental conditions are gathered in Table 2. The powder data sets were collected on a Stoe STADI/P diffractometer using monochromatized $CuK\alpha_1$ radiation. Some samples were attached to the holder with vaseline oil; in such cases, two small 2ϑ regions containing the strongest oil reflections have been

excluded from the refinement. Atomic coordinates of tetragonal $PbBiO_2I$ [6] and orthorhombic $BaBiO_2Cl$ [8] served as initial parameters. The GSAS package software [23] was used for all calculations. Two typical Rietveld refinement plots, one for tetragonal $CaBiO_2I$ and the other for orthorhombic $SrBiO_2I$, are presented in Figs. 2a and b. The atomic coordinates and selected bond distances are given in Tables 3 and 4, respectively.

There are just minor differences in bond distances between isotypic $CaBiO_2I$ and $PbBiO_2I$ [6]. The (L,Bi)–O bond is 0.08 Å shorter but (L,Bi)–I distance 0.02 Å longer in $CaBiO_2I$ compared to $PbBiO_2I$. It is curious to note that in the orthorhombic $SrBiO_2Cl$–$SrBiO_2Br$–$SrBiO_2I$ series, the Sr–X, Bi–X, and Bi–O distances elongate as expected but not Sr–O which shortens slightly when passing from X = Cl to Br and I. This shortening is even more pronounced comparing the structures of $BaBiO_2Cl$ and $BaBiO_2I$ (0.11 Å). When passing from $SrBiO_2I$ to $BaBiO_2I$, both Bi–O and Bi–I distances elongate (by ~ 0.04 and ~ 0.15 Å, respectively). The latter value, together with the Bi–I distances themselves indicates very little or no bonding between Bi and I, at least, in $BaBiO_2I$.

5. Discussion

Our investigations have added several new representatives to the X1 bismuth oxyhalide family. Besides L = Pb, these structures form only with L = Li, Na, Ca, Cd, Sr and Ba, in fair agreement with Sillén's results [2,24]. These cations readily adopt the same coordination environment as Bi^{3+}, and difference between their radii and that of Bi^{3+} does not exceed 0.25 Å [25]. If the difference in ionic radii is larger or the coordination preferences are different, the X1 structure is unlikely to occur, which is the case for L = K, Cu, or Ag. Sn^{2+} meets both these requirements but is perhaps a too

Table 2
Experimental conditions for the powder diffraction experiments

Compound	CaBiO$_2$I	SrBiO$_2$Br	SrBiO$_2$I	BaBiO$_2$I
Formula weight	408.0	408.5	455.5	505.1
Crystal system	Tetragonal		Orthorhombic	
Space group	I4/mmm (# 139)		Cmcm (# 63)	
Cell parameters:				
a (Å)	4.01943(4)	5.7676(1)	5.8723(1)	6.0492(1)
b (Å)	4.01943(4)	12.8246(4)	13.5344(2)	14.0224(2)
c (Å)	13.2144(1)	5.6460(1)	5.7363(1)	5.8212(1)
V (Å^3)	213.490(4)	417.62(2)	455.91(2)	493.78(1)
Z	2		4	
Calculated density	6.346	6.497	6.636	6.796
Diffractometer		STOE STADI/P		
Radiation	CuKα_1 ($\lambda = 1.54059$ Å)			
2ϑ range (deg)	5–100	12–120	5–100	10–100
Number of reflections	48	198	151	199
Number of data points	9499	5338[a]	9499	9919
Number of free parameters	18	27	23	25
Analyzing package		GSAS		
R(F^2)	0.0952	0.0748	0.0858	0.0930
R$_p$	0.1011	0.0880	0.0994	0.0545
R$_{wp}$	0.1376	0.1200	0.1349	0.0770
χ^2	2.29	2.61	2.26	6.75

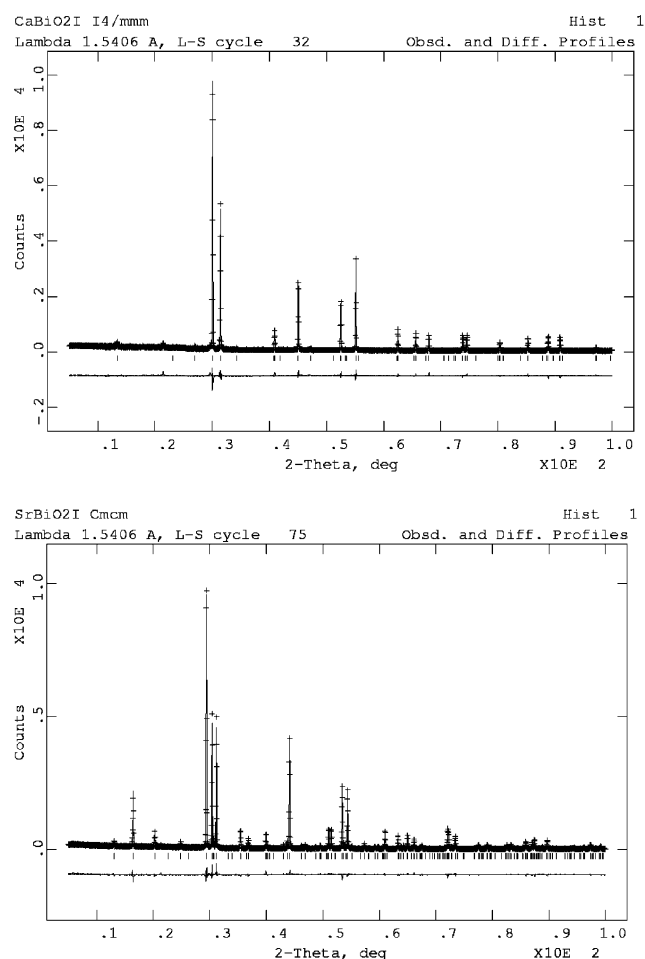[a] The 2ϑ step size is 0.02°, for others 0.01°.

Fig. 2. Final Rietveld plots for (a) CaBiO$_2$I, (b) SrBiO$_2$I.

strong reducing agent to neighbor Bi^{3+} in the same structure.

The occurrence and type of cation ordering in the X1-type bismuth (and perhaps antimony) oxyhalides depends on at least three parameters: the overall stoichiometry of the fluorite layers, the relative size of the ions contributing to the structure, and their electronic structure. The ordering occurs only in the case of a L:Bi (or L:Sb) ratio of 1:1. As soon as the interlayer charge balance requires non-integer stoichiometry of the fluorite layers (0.5:1.5 in case of L^I), only the ideal Nd$_2$O$_2$Te structure is realized. This is consistent with structural data for bismuth oxyhalides with related structures, where Bi^{3+} in the [Bi$_{2-x}$L$_x$O$_2$] layers is substituted by lower-valent L cations so that x is non-integer: the overwhelming majority of these compounds crystallize in the highest-symmetrical tetragonal structures [20,25–27].

The [LMO$_2$]X stoichiometry of the X1 compounds (L = Ca, Cd, Sr, Pb, Ba; M = Sb, Bi) may actually lead to all three structures shown in Fig. 1. The ordered PbSbO$_2$Cl structure seems to be realized when the L^{2+} cations are noticeably larger than M^{3+}, and the X^- anion is, on the contrary not much larger than both L^{2+} and M^{3+}, i.e., chloride. If $1/2(R(L^{2+}) + R(M^{3+})) \ll R(X^-)$, the disordered Nd$_2O_2$Te structure becomes more favorable, which is best demonstrated by the PbSbO$_2$X and CaBiO$_2$X series, where both oxyiodides and CaBiO$_2$Br adopt the Nd$_2$O$_2$Te structure.

The other, as yet very rare, version of cation-ordered X1 structure, adopted hitherto only by CaBiO$_2$Cl and CdBiO$_2$Cl, was assumed to occur due to the small size

Table 3
Atomic coordinates for the new bismuth oxyhalides

(a) Nd_2O_2Te type ($CaBiO_2I$)

Atom	Site	z	$U \times 100$
$Ca_{0.5}Bi_{0.5}$	$4e$ $(0,0,z)$	0.3290(2)	2.0(1)
O	$4d$ $(0,1/2,1/4)$	—	2.6(4)
I	$2a$ $(0,0,0)$	—	3.0(1)

(b) $PbSbO_2Cl$ type

Compound		$SrBiO_2Br$		$SrBiO_2I$		$BaBiO_2I$	
Atom	Site	$x(y)$	$U \times 100$	$x(y)$	$U \times 100$	$x(y)$	$U \times 100$
L	$4c$ $(0,y,1/4)$	0.3943(4)	0.9(1)	0.4050(3)	1.8(1)	0.3971(2)	1.8(1)
Bi	$4c$ $(0,y,1/4)$	0.0796(2)	1.8(1)	0.0739(2)	2.3(1)	0.0689(2)	1.6(1)
O	$8e$ $(x,0,0)$	0.247(2)	2.0(6)	0.247(1)	2.6(4)	0.251(2)	3.2(4)
X	$4c$ $(0,y,1/4)$	0.7456(4)	2.3(2)	0.7445(2)	3.1(1)	0.7480(2)	2.6(1)

Table 4
Selected bond distances for the new bismuth oxyhalides

Compound	$CaBiO_2I$	$SrBiO_2Br$	$SrBiO_2I$	$BaBiO_2I$
L–O	2.265(1) × 4	2.442(9) × 4	2.432(5) × 4	2.543(6) × 4
L–X	3.631(2) × 4	3.345(4) × 2	3.511(3) × 2	3.552(3) × 2
		3.458(4) × 2	3.652(3) × 2	3.677(2) × 2
Bi–O	2.265(1) × 4	2.249(9) × 4	2.272(5) × 4	2.315(6) × 4
Bi–X	3.631(2) × 4	3.605(3) × 2	3.735(2) × 2	3.881(2) × 2
		3.584(3) × 2	3.776(2) × 2	3.931(3) × 2

of Ca^{2+}, which is only seven-coordinated, contrary to eight-fold coordination in both other X1 structures [9], coupled with the smaller size of Cl, leading to only six-coordination of the anion. In contrast, Ca^{2+} is eight-coordinated both in $CaBiO_2Br$ and in $CaBiO_2I$ involving larger halide ions.[2]

The influence of electronic structure of the L cation is an overall factor governing existence of the compound itself and its stoichiometry hence the overall possibility of cation ordering. It is thus more interesting to compare structures of compounds where L^{II} ions have similar radii but different electronic structures. The ionic radii of Ca^{2+} and Cd^{2+} being almost equal [25] and neither of these cations having a lone pair, it is not surprising that compounds of these metals are isostructural. Lead compounds behave differently from their strontium analogs, though the difference in radii of Pb^{2+} and Sr^{2+} is rather small. In the $PbBiO_2X$ series, only the oxychloride may exist in the ordered form, the

others are disordered; this most likely occurs due to the same configuration of Pb^{2+} and Bi^{3+} ($6s^2$). It would be interesting to compare the $PbSbO_2X$ with their strontium analogs, as yet unknown. A systematic study of related antimony (and possible arsenic) oxyhalides could give a deeper insight into crystal chemistry of X1 type oxyhalides. Some of these investigations are now in progress.

Acknowledgments

References

[1] L.G. Sillén, Z. Anorg. Allgem. Chem. 242 (1939) 41.
[2] L.G. Sillén, Naturwissenschaften 22 (1942) 318.
[3] V.A. Dolgikh, L.N. Kholodkovskaya, Russ. J. Inorg. Chem. 37 (1992) 488.
[4] M. Gillberg, Ark. Kemi Mineral. Geol. B2 (44) (1960) 565.
[5] S.S. Lopatin, Russ. J. Inorg. Chem. 32 (1987) 1006.
[6] J. Ketterer, V. Krämer, Mater. Res. Bull. 20 (1985) 1031.
[7] A. Deschanvres, J. Gallay, J.-M. Hunout, M.-Th. Thiault, C. Victor, C. R. Acad. Sci. Paris 270 (1970) 696.
[8] M.A. Kennard, J. Darriet, J. Grannec, A. Tressaud, J. Solid State Chem. 117 (1995) 201.
[9] S.M. Fray, C.J. Milne, P. Lightfoot, J. Solid State Chem. 128 (1997) 115.
[10] S.D. Kirik, E.A. Yakovleva, A.F. Shimanski, Y.G. Kovalev, Acta Crystallogr. Ser. C 57 (2001) 1367.
[11] J.M. Thomas, W. Ueda, J. Williams, K.D.M. Harris, Faraday Discuss. Chem. Soc. 87 (1989) 33.
[12] Z. Ban, M. Sikirica, Acta Crystallogr. 18 (1965) 94.
[13] K.D.M. Harris, Ph.D. Thesis, University of Cambridge, Cambridge, 1989.
[14] H. Boller, Monatsh. Chemie. 104 (1973) 916.
[15] P.M. Raccah, J.M. Longo, H.A. Eick, Inorg. Chem. 6 (1967) 1471.

---

[2] Our investigations in the area of isostructural antimony compounds have shown that a new compound $CaSbO_2Cl$ crystallizes in the $PbSbO_2Cl$ structure with cell parameters $a = 5.658(2)$ Å, $b = 12.114(4)$ Å, and $c = 5.442(1)$ Å. In this case, Ca^{2+} is also probably eight-coordinated, but the cation ordering agrees with that expected based on the Ca^{2+}/Sb^{3+} size contrast, and chloride is expected to be only four-coordinated.

[16] F. Thuillier-Chevin, P. Maraine, G. Perez, Rev. Chim. Miner. 17 (1980) 102.

[17] L.G. Sillén, L. Melander, Z. Krystallogr. 103 (1941) 420.

[18] Y. Porter, P.S. Halasyamani, Z. Naturforsch. 57b (2002) 360.

[19] B. Aurivillius, Chem. Scr. 27 (1987) 397.

[20] D.O. Charkin, P.S. Berdonosov, A.M. Moisejev, R.R. Shagiakhmetov, V.A. Dolgikh, P. Lightfoot, J. Solid State Chem. 147 (1999) 527.

[21] T.Yu. Chaikovski, D.O. Charkin, V.A. Dolgikh, P. Lightfoot, Cation ordering in bismuth—alkaline earth oxyhalides, Proceedings of the Second National Conference on Crystal Chemistry, Chernogolovka, Russia, May 22–26, 2000, Abstracts, p. 114.

[22] G.Brauer, Herg., Handbuch der Präparativen Anorganische Chemie, Ferdinand Enke Verlag, Stuttgart (1975) (Russ.Transl.).

[23] A.C. Larson, R.B. Von Dreele, Los Alamos National Laboratory Report No. LA-UR-86-748, 1987.

[24] L.G. Sillén, Inaugural dissertation, Stockholm, 1940.

[25] R.D. Shannon, Acta Crystallogr. Ser. A 32 (1976) 761.

[26] D.O. Charkin, Ph.D. Thesis, Moscow State University, 2001.

[27] W.J. Zhu, Y.Z. Huang, J.K. Liang, Z.X. Zhao, Mater. Res. Bull. 27 (1991) 885.