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The Structure of Thorikosite, a Naturally Occurring Member of the Bismuth Oxyhalide Group*

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Thorikosite, $(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$, is a naturally occurring member of the bismuth oxyhalide group isostructural with $LiBi_3O_4Cl_2$. The space group is $I4/mmm$ with a = 3.919(1) Å, c = 12.854(5) Å, and Z = 1. A crystal structure analysis showed complete solid solution of Pb^{2+}, Sb^{3+}, and As^{3+} on the single cation site and large atomic temperature factors indicative of pervasive structural disorder. The latter is due to the structural adjustments necessary to accommodate cations of very different sizes in the same site. Thorikosite is closely related to synthetic tetragonal $PbSbO_2Cl$ through the coupled substitution $Sb^{3+}O^{2-} \rightleftharpoons Pb^{2+}(OH)^-$.

Introduction

The bismuth oxyhalides are a large group of layered compounds consisting of cation–oxygen layers having the tetragonal PbO (litharge) structure alternating with single or multiple thickness sheets of halide ions. The halide layers may also contain additional cations in their interstices. Large cations such as Pb^{2+} and Ca^{2+} often occur in place of Bi^{3+} and play the same structural role as that ion. Numerous compounds of this group were synthesized by Sillén and his co-workers (*1, 2*), and many more are theoretically possible by varying the compositions and stacking sequences of the basic halide and PbO-like units. A few of the simpler compositions are represented in nature as the minerals nadorite ($PbSbO_2Cl$), perite ($PbBiO_2Cl$), blixite ($Pb_2(O,OH)_{<2}Cl$), bismutite ($Bi_2O_2CO_3$), beyerite ($CaBi_2O_2(CO_3)_2$), kettnerite ($CaBiOFCO_3$), and possibly ecdemite and heliophyllite (both ca. $Pb_3AsO_{<4}Cl_{<2}$) (*3*). In addition to the bismuth oxyhalides, certain of the lead fluorohalides also adopt these structures (*4*).

Sillén was able to determine crystal structures for many of his synthetic products and a few of their naturally occurring congeners. The determinations were, how-

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ever, only semiquantitative, the oxygen positions being deduced from crystal chemical considerations. We now report a quantitative structure for a new, naturally occurring member of the bismuth oxyhalide family, this being the mineral thorikosite ($(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$). A description of the physical and chemical properties of this phase and those of the closely related mineral freedite ($Pb_{15}(Cu,Fe)_3As_4O_{19}Cl_{10}$) will appear in a separate publication (*5*).

Structure Determination

Weissenberg, precession, and powder X-ray diffraction studies (*5*) indicated that thorikosite was tetragonal, *I*422, $I\bar{4}2m$, *I*4*mm*, or *I*4/*mmm*, with a = 3.919(1) and c = 12.854(5) Å. The available crystals were of poor quality, being composed of one major and one or more minor individuals. The best of these, a lath-shaped euhedral crystal of dimensions 0.31 × 0.14 × 0.04 mm, was selected for data collection. The intensities of 92 reflections having $\sin\theta \leq 0.460$ and constituting one asymmetric unit were measured with a Supper–Pace diffractometer system, employing Weissenberg equi-inclination geometry, graphite crystal monochromatized Mo$K\alpha$ radiation, a scintillation counter, and a scanning rate of 2°/min.

Because of the multiple nature of the crystal, it was necessary to examine the profile of each reflection for evidence of overlap between peaks of the major and minor individual. (The intensities of reflections from the latter did not exceed ca. 50% of those from the former.) This was accomplished by recording the profiles on strip chart paper, drawing a "corrected profile" on the overlapped side of each affected peak by reflecting the profile from the non-overlapped side, and measuring the peak areas with a planimeter. Desite its relative crudeness, this procedure yielded satisfactory results as judged from the outcome of the structure refinement. The intensities were then converted to structure factor amplitudes by correction for Lorentz, polarization, and absorption (μ_l = 683 cm^{-1}) effects. The only unobserved reflection, 1 · 0 · 15, was omitted from the final data set.

The symmetry, unit cell dimensions, and stoichiometry of thorikosite are similar to those of one of the simpler bismuth oxyhalides, $LiBi_3O_4Cl_2$ (*5*). The structure of the latter compound was determined in space group *I*4/*mmm* by Sillén (*6*), who found complete solid solution between lithium and bismuth on equipoint 4*e*, a rather improbable situation considering the large difference in size between Li^+ and Bi^{3+}. The four oxygen atoms could not be located experimentally and were placed in 4*d* on crystal chemical grounds.

Assuming that it was isostructural with $LiBi_3O_4Cl_2$, a least-squares refinement of the thorikosite structure was carried out in *I*4/*mmm* using the program RFINE2 (*7*), neutral atom scattering factors (*8*), anomalous dispersion factors (*9*), and unit weights for all reflections. An electron microprobe analysis of thorikosite yielded 3.0 Pb, 0.6 Sb, and 0.4 As per cell (*5*). In the structure refinement this was simplified to 3 Pb + 1 Sb disordered on the 4*e* (cation) site. The atomic coordinates given by Sillén for $LiBi_3O_4Cl_2$ were used as the initial coordinates in thorikosite.

When the refinement with isotropic temperature factors had reached a conventional residual of 0.097, anisotropic temperature factors were introduced, leading to a final residual of 0.069. At this point, site occupancy factors were refined yielding 0.74(1) Pb + 0.26 Sb for the cation site, 0.96(7) for the chlorine site, and 0.98(10) for the oxygen site. For uncertain reasons three intense reflections, 004, 006, and 213, showed very poor agreement between $|F|_{obs}$ and $|F|_{cal}$ and were therefore excluded from the refinement in its last stages. The value of the residual, omitting these three reflections, is 0.054.

A difference electron density synthesis showed no additional atoms, but there remained an ambiguity in the space group symmetry. Of the possible space groups other than $I4/mmm$, $I422$ and $I\bar{4}2m$ could be eliminated because their two- and fourfold equipoints are identical to those of $I4/mmm$. An attempt was also made to refine the structure in the remaining possibility, $I4mm$, but this failed when it led to impossibly higher parameter errors and correlation coefficients of 1.0. The isostructural relationship between thorikosite and $LiBi_3O_4Cl_2$ is therefore confirmed along with the ability of this structure type to accommodate cations of very different sizes in solid solution on the same site. Final values of the atomic parameters are listed in Table I and the observed and calculated structure factor amplitudes in Table II. Interatomic distances and angles calculated with the program OR FFE (*11*) and thermal ellipsoid parameters are given in Tables III and IV, respectively.

Structure Description

The structure refinement combined with a quantitative chemical analysis (*5*) yielded the formula $(Pb^{2+}_{3.0}Sb^{3+}_{0.6}As^{3+}_{0.4})O_4Cl_2$, for which the ionic valences are out of balance by one excess negative charge. Since the refinement indicated full occupancy of both anion sites, we have assumed the presence of one $(OH)^-$ disordered over the oxygen site, leading to the formula $(Pb_3Sb_{0.6}As_{0.4})(O_3OH)Cl_2$.

TABLE I

Atomic Coordinates and Temperature Factors

		x	y	z	β_{11}	β_{22}	β_{33}	B_{eq}
M	$4e$	0	0	0.1475(2)	0.043(1)	0.043(1)	0.0052(1)	2.9
Cl	$2b$	0	0	$\frac{1}{2}$	0.05(1)	0.05(1)	0.014(3)	5.2
O	$4d$	0	$\frac{1}{2}$	$\frac{1}{4}$	0.09(2)	0.09(2)	0.03(2)	4.4

Note. The B_{eq} are equivalent isotropic temperature factors defined by Hamilton (*10*). Anisotropic temperature factors are of the form $\exp - \left\{ \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j \beta_{ij} \right\}$ for which $\beta_{12} = \beta_{13} = \beta_{23} = 0$ by symmetry in $I4/mmm$.

Standard errors are in parentheses.

Structurally, thorikosite belongs to the simplest class among the bismuth oxyhalides, that designated as the X_1 type by Sillén (*2*). This consists of cation–oxygen layers (MO_2M) like those in tetragonal PbO and layers of halide ions (H) one atom thick stacked along [001] in the sequence $-H-MO_2M-H-MO_2M-$. The resulting general formula is M_2O_2H, where M has an average valence of $+\frac{5}{2}$. The cation site is therefore necessarily a site of mixed occupancy, unless some hydroxyl ions are substituted into the oxygen site.

Alternatively, the thorikosite structure can be described in terms of the articulation of its cation coordination polyhedra, i.e., as being composed of distorted MO_4Cl_4 square Archimedean antiprisms linked together through shared faces and edges. The square antiprism with four oxygens forming one square face and four chlorines the other is very common in Pb(II) oxyhalides and is perhaps the preferred coordination polyhedron for this ion in such compounds. In thorikosite the antiprisms form double layers normal to [001]. Each unit cell (Fig. 1) encompasses one double layer from $z = \frac{1}{4}$ to $\frac{3}{4}$ and parts of the two adjacent double layers. Each double layer is bisected by a mirror plane at $z = 0$ or $\frac{1}{2}$ and is related to adjacent layers by glide planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. Within a given double layer each antiprism is linked in the [001] direction to one other antiprism by sharing a square (4 Cl) face and in lateral directions to four other antiprisms by sharing four of its eight triangular (2 Cl + 1 O) faces. Connections between neighboring double layers are accomplished by having each antiprism share the four edges of a square (4 O) face with four antiprisms in the neighboring layer.

Discussion

Thorikosite is isostructural with $LiBi_3$

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THORIKOSITE

h k l	F_{obsd}	F_{calc}	*h k l*	F_{obsd}	F_{calc}	*h k l*	F_{obsd}	F_{calc}
0 0 4	117.9	149.2	4 0 2	17.8	18.3	4 1 1	40.3	39.7
0 0 6	119.7	137.1	4 0 4	54.7	54.4	4 1 3	69.3	71.8
0 0 8	77.1	83.6	4 0 6	53.3	49.3	4 1 5	9.9	8.9
0 0 10	108.4	114.6	4 0 8	31.9	26.1	4 1 7	52.2	50.9
0 0 12	17.5	19.0	4 0 10	42.4	41.0	4 1 9	26.2	22.5
0 0 14	42.4	47.4	5 0 1	24.7	25.2	2 2 0	157.9	154.7
0 0 16	23.1	20.1	5 0 3	48.2	45.0	2 2 2	33.1	32.8
1 0 1	114.1	121.0	1 1 0	225.0	226.2	2 2 4	91.9	88.0
1 0 3	228.7	231.6	1 1 2	25.6	21.2	2 2 6	80.8	79.8
1 0 5	30.1	29.9	1 1 4	167.4	161.0	2 2 8	46.1	44.1
1 0 7	159.9	142.5	1 1 6	164.8	143.2	2 2 10	69.9	66.2
1 0 9	58.6	61.6	1 1 8	51.2	51.3	2 2 12	10.7	10.0
1 0 11	63.0	66.4	1 1 10	76.4	85.3	2 2 14	30.6	30.9
1 0 13	54.7	53.6	1 1 12	12.2	5.8	3 2 1	53.5	50.8
2 0 0	197.2	216.3	1 1 14	43.2	50.1	3 2 3	89.3	92.2
2 0 2	43.5	46.9	1 1 16	22.0	24.0	3 2 5	14.9	11.5
2 0 4	115.1	113.6	2 1 1	85.1	87.4	3 2 7	63.4	64.3
2 0 6	105.5	103.3	2 1 3	229.6	161.7	3 2 9	25.8	28.4
2 0 8	62.7	59.3	2 1 5	23.2	20.5	3 2 11	35.7	32.1
2 0 10	92.3	86.0	2 1 7	111.3	107.0	4 2 0	72.2	69.4
2 0 12	14.1	13.5	2 1 9	50.5	46.8	4 2 2	12.5	14.2
2 0 14	36.5	38.2	2 1 11	50.5	51.4	4 2 4	39.6	43.4
3 0 1	66.3	65.9	2 1 13	38.6	42.3	4 2 6	38.1	39.3
3 0 3	118.5	120.4	2 1 15	10.3	7.5	4 2 8	24.6	20.5
3 0 5	19.8	15.1	3 1 0	118.8	123.9	3 3 0	78.4	75.2
3 0 7	81.6	82.2	3 1 2	17.0	18.9	3 3 2	11.6	12.9
3 0 9	31.2	36.2	3 1 4	85.3	86.0	3 3 4	55.7	51.6
3 0 11	43.3	40.4	3 1 6	74.2	77.7	3 3 6	47.5	46.7
3 0 13	31.9	33.7	3 1 8	36.4	32.4	3 3 8	22.8	20.7
4 0 0	88.3	89.0	3 1 10	55.4	53.6	4 3 1	26.7	25.2
						4 3 3	45.3	45.0

O$_4$Cl$_2$ and its Na, Cd, Br, and I analogs (*6*); with Pb$_{3.6}$O$_4$Cl$_{1.8}$ (*12*); and with the synthetic tetragonal dimorph of nadorite, PbSbO$_2$Cl (*13*), and its numerous isotypes (*14–17*). (However, BaSbO$_2$Cl has ordered cations (*18*) and is therefore isostructural with nadorite.) The relationship of thorikosite to tetragonal nadorite is particularly close. Both have the X_1 structure, show complete solid solution between lead and antimony, and are related chemically by the coupled ionic substitution Sb^{3+}O^{2-} ⇌ Pb^{2+}(OH)$^-$, as can be seen by comparing their unit cell contents, Pb$^{2+}_2$Sb$^{3+}_2$O$_4$Cl$_2$ and Pb$^{2+}_3$(Sb,As)$^{3+}$(O$_3$OH)Cl$_2$. There is also a more distant relationship to the recently described mineral freedite (Pb$_{15}$(Cu,Fe)$_3$As$_4$O$_{19}$Cl$_{10}$). The latter is monoclinic, *C*2, *Cm*, or *C*2/*m*, but has

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE MO_4Cl_4 SQUARE ANTIPRISM

M–O	2.361(2)	4×	O–M–O	71.87(6)	4×
M–Cl	3.358(2)	4×		112.19(11)	2×
Cl–Cl	3.919(1)	4×	Cl–M–Cl	71.40(4)	4×
O–O	2.771(1)	4×		111.23(8)	2×
Cl–O	3.764(1)	8×	O–M–Cl	80.25(2)	8×
M–M (shortest)	3.793(6)			143.07(1)	8×

Note. Standard errors are in parentheses.

TABLE IV

THERMAL DISPLACEMENTS (Å) AND ANGLES BETWEEN THERMAL ELLIPSOID AND UNIT CELL AXES (°)

	Axis	rms displacement	Angle with *a*	Angle with *b*	Angle with *c*
M	1	0.182(2)	180	90	90
	2	0.182(2)	180	90	90
	3	0.208(2)	90	90	0
Cl	1	0.206(2)	180	90	90
	2	0.206(2)	180	90	90
	3	0.339(4)	90	90	0
O	1	0.152(5)	90	90	0
	2	0.268(4)	180	90	90
	3	0.268(4)	0	90	90

Note. Standard errors are in parentheses.

a body-centered orthogonal pseudocell with parameters $A = 4.02$, $B = 3.59$, and $C = 13.57$ Å, and the approximate cell contents $Pb_3(Cu,Fe,As)O_4Cl_2$. This pseudocell is the analog of the tetragonal cell of thorikosite (*5*).

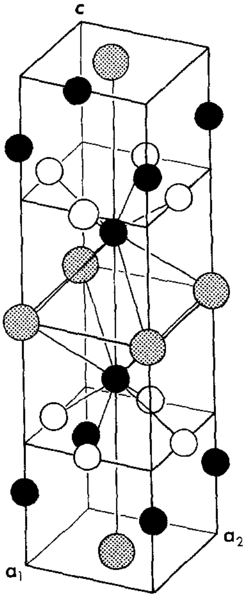

FIG. 1. The unit cell of thorikosite showing the square antiprismatic coordination of the *M* (cation) site. Dark circles represent the cations, open circles oxygen, and shaded circles chlorine.

It is remarkable that the X_1 structure (and others of the bismuth oxyhalide group) are able to tolerate solid solution among cations of such diverse size and charge. For example, while lead(II) commonly occurs in eightfold square antiprismatic coordination, arsenic and antimony are virtually unknown with coordination numbers above 6. One may therefore expect some adjustments in the cation and anion positions in thorikosite depending upon which element, Pb, Sb, or As, occupies the cation position in a given unit cell. That is, the atomic positions in Table I represent only a weighted average of the actual positions and the structure is characterized by a modest, but pervasive, degree of positional disorder. This manifests itself in the unusually large isotropic temperature factors in Table I and in the final difference electron density synthesis, which showed positive residuals of ca. 9 and 6 electrons/Å^3 centered at the cation and chlorine positions, respectively, but streaked out ca. $1\frac{1}{2}$ Å along the *c* axis.

The derivation of thorikosite from tetragonal nadorite by substitution of lead for antimony has already been noted. It is of interest to extend this to the whole compositional series $Pb^{2+}_m Sb^{3+}_n O_4Cl_p$ by allowing m and n to vary from 0 to 4, subject to the restriction that $m + n = 4$, which is the maximum occupancy of the cation site. The variable p is simply the number of chloride ions necessary to maintain charge balance. Table V contains the resulting compositions along with some pertinent structural data. Compositions for which $n = 0$, 1, and 2 exist as well-established phases, all of which are based on the litharge structure. For $n = 3$ the predicted lead antimony oxychloride $PbSb_3O_4Cl_3$ is not known to exist, but its bismuth analog, $PbBi_3O_4Cl_3$, has been synthesized with an X_1X_2-type structure (*19*).

The composition for which $n = 4$ is SbOCl, whose structure is not one of those of the bismuth oxyhalide group. However,

TABLE V

COMPOSITIONS IN THE SERIES $Pb_m^{2+}Sb_n^{3+}O_4Cl_p$

Pb	Sb	Name	Structure type	Composition	Space group	Cell parameters (Å)
4	0	Litharge	X_0	$Pb_4O_4(=PbO)$	*P4/nmm*	$a = 3.973$ $c = 5.019$
3	1	Thorikosite	X_1	$Pb_3Sb(O,OH)_4Cl_2$	*I4/mmm*	$a = 3.919$ $c = 12.854$
2	2	Tetragonal nadorite	X_1	$Pb_2Sb_2O_4Cl_2$	*I4/mmm*	$a = 3.895$ $c = 12.29$
1	3	—	—	$PbSb_3O_4Cl_3$	Unknown as a compound	
		—	X_1X_2	$PbBi_3O_4Cl_3$	*I4/mmm*	$a = 3.91$ $c = 27.05$
0	4	—	—	$Sb_4O_4Cl_4(=SbOCl)$	Different structure	
		—	—	SbOF	*Pbca*	$a = 11.673$ $b = 5.587$ $c = 12.267$

one of its fluorine analogs, *M*–SbOF, has a structure containing PbO-like layers (*20*). In this case the structure contains corrugated layers of distorted $Sb(O,F)_4$ square pyramids rather than the flat layers of ideal PbO_4 square pyramids in litharge. Note also that the cell parameters of *M*–SbOF are $a \approx 2 \times 4\sqrt{2}$, $b \approx 4\sqrt{2}$, and $c \approx 12$ Å; i.e., there is a pseudocell for which $A \approx 4$ and $C \approx 12$ Å. This is the characteristic relationship between the tetragonal X_1 bismuth oxyhalides and their orthorhombic derivatives. The absence of SbOCl in one of the bismuth oxyhalide structure types is curious in view of the fact that the compounds of the group MOCl, where *M* includes Bi^{3+} and the trivalent lanthanides and actinides, have X_2 structures.

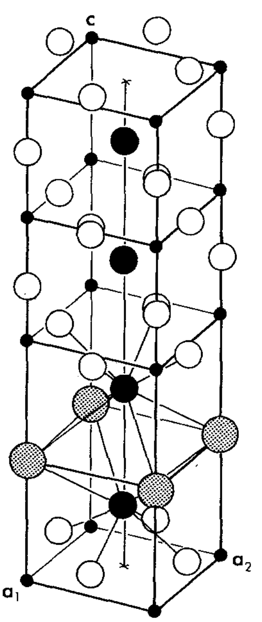

FIG. 2. The unit cell of hematophanite showing the double square antiprismatic and perovskite-like layers. Large and small dark circles represent lead and iron, respectively, open circles oxygen, and shaded circles chlorine.

Lastly, mention should be made of a relationship between the structure of thorikosite and that of the mineral hematophanite (Fig. 2). The latter is also a tetragonal lead oxyhalide layer structure and has the idealized formula $Pb_4Fe_3O_8Cl$ (*21, 22*). Hematophanite can be derived from thorikosite simply by replacing every other double PbO_4Cl_4 antiprismatic layer with a double $PbFeO_3$ perovskite-like layer in such a way that the body-centering is lost and all of the lead atoms are positioned along the line $\frac{1}{2}, \frac{1}{2}, z$.

References

1. *Struct. Rep.* **11,** 305 (1947–1948).
2. L. G. Sillén, *Naturwissenschaften* **30,** 318 (1942).
3. H. Strunz, "Mineralogische Tabellen," 5th ed., Akademische Verlagsgesellschaft, Leipzig (1970).
4. B. Aurivillius, *Chem. Scr.* **15,** 153 (1980).
5. P. J. Dunn and R. C. Rouse, *Amer. Mineral.,* in press.
6. L. G. Sillén, *Z. Anorg. Allg. Chem.* **242,** 41 (1939).
7. L. W. Finger, "RFINE2. A Fortran IV Computer Program for Structure Factor Calculation and Least-Squares Refinement of Crystal Structures," Geophysical Laboratory, Washington, D.C. (1972).
8. P. A. Doyle and P. S. Turner, *Acta Crystallogr. Sect. A* **24,** 390 (1968).
9. D. T. Cromer and D. Liberman, *J. Chem. Phys.* **53,** 1891 (1970).
10. W. C. Hamilton, *Acta Crystallogr.* **12,** 609 (1959).
11. W. R. Busing, K. O. Martin, and H. A. Levy, "OR FFE. A Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn. (1964).
12. M. Gasperin, *Bull. Soc. Fr. Mineral. Cristallogr.* **87,** 278 (1964).
13. L. G. Sillén and L. Melander, *Z. Kristallogr.* **103,** 420 (1941).
14. L. G. Sillén, *Z. Anorg. Allg. Chem.* **246,** 115 (1941).
15. L. G. Sillén, *Z. Anorg. Allg. Chem.* **246,** 331 (1941).
16. L. G. Sillén and A. S. Gjörling-Husberg, *Z. Anorg. Allg. Chem.* **248,** 135 (1941).
17. L. G. Sillén and E. Jörnstad, *Z. Anorg. Allg. Chem.* **250,** 173 (1942).
18. F. Thuillier-Chevin, P. Maraine, and G. Perez, *Rev. Chem. Mineral.* **17,** 102 (1980).
19. A. Deschanvres, J. Gallay, J. M. Hunout, M. T. Thiault, and C. Victor, *C.R. Acad. Sci. Paris C* **270,** 696 (1970).
20. A. Åström, *Acta Chem. Scand.* **26,** 3849 (1972).
21. R. C. Rouse, *Mineral. Mag.* **39,** 49 (1973).
22. J. Pannetier and P. Batail, *J. Solid State Chem.* **39,** 15 (1981).