

Structures of Niobium and Tantalum Oxide Fluorides Containing Lone Pair-Ions

III. $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$: A Layer Structure Comprising Unidimensionally Infinite PbX ($X = \text{O}$ or F) Elements

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The crystal structure of $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$ has been determined from single crystal X-ray data. The symmetry is orthorhombic (space group *Amam*) with $a = 22.48 \text{ \AA}$, $b = 20.83 \text{ \AA}$, and $c = 3.928 \text{ \AA}$. The structure is built up from slabs of ReO_3 structure type, cut parallel to (110) ReO_3 , and bands of $\text{PbO}(\text{red})$ structure type. © 1985 Academic Press, Inc.

Introduction

During phase analysis studies of the systems $\text{Pb}(\text{II})\text{-Nb}(\text{V})\text{-O-F}$ and $\text{Pb}(\text{II})\text{-Ta}(\text{V})\text{-O-F}$ (1, 2) several new phases have been prepared. In these phases the coordination around $\text{Pb}(\text{II})$ shows considerable variation. For example, in $\text{Pb}_3\text{Nb}_4\text{O}_{12}\text{F}_2$ one of the lead atoms occurs in nearly regular cubic coordination (3); in $\text{Pb}_{0.27}\text{NbO}_{2.367}\text{F}_{0.80}$, structurally related to HTB, lead is situated at the center of a flat six-membered ring of anions (1), and in $\text{Pb}_2\text{Nb}_3\text{O}_7\text{F}_5$ the coordination polyhedron is a distorted Archimedean antiprism (4).

The studies of the tantalum system yielded a new phase. This compound, however, could not be prepared as a single phase sample from the available starting materials PbO , PbF_2 , TaO_2F , and Ta_2O_5 , since its fluorine content was too high. It was tentatively concluded that the phase is stoichiometric, as no shifts in the positions of the lines were observed, even upon very careful inspection of the powder patterns

from samples with different gross compositions. In order to establish the stoichiometry and the coordination around $\text{Pb}(\text{II})$ a single crystal X-ray structure determination was performed, and the results are presented in this article.

Experimental

A needle-shaped crystal was picked from a sample with the gross composition $\text{Pb}_{0.25}\text{Ta}_{0.75}\text{O}_{1.625}\text{F}$, prepared at 600°C . The powder pattern of this sample showed that, apart from the phase studied, it contained another phase with the preliminary composition $\text{PbTa}_3\text{O}_7\text{F}_3$ (2). Oscillation and Weissenberg photographs showed that the crystal was orthorhombic with the unit cell parameters $a = 22.48 \text{ \AA}$, $b = 20.83 \text{ \AA}$, and $c = 3.928 \text{ \AA}$. Systematic absences were observed for hkl with $k + l = 2n + 1$, $0kl$ with $k = 2n + 1$ and $h0l$ with $h = 2n + 1$. The possible space groups thus are *Ama2* (No. 41) and *Amam* (No. 63 in an unconventional setting). Intensity data were col-

TABLE I
CRYSTALLOGRAPHIC DATA FOR $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$

Unit cell	$a = 22.48 \text{ \AA}$ $b = 20.83 \text{ \AA}$ $c = 3.928 \text{ \AA}$
Space group	$Amam$ (No. 63 in an unconventional setting)
Unit cell content	$Z = 4$
Density calculated	6.92 g cm^{-3}

lected with a PW 1100 automatic four-circle diffractometer. Crystallographic data for $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$ and details of the data collection are summarized in Tables I and II, respectively.

The structure was solved in space group $Amam$ by direct methods and refined by least-squares techniques. Atomic scattering factors and anomalous scattering parameters for uncharged atoms were taken from Ref. (5). Throughout the refinement all anions were treated as fluorine. During the refinement it became obvious that some reflections suffered heavily from extinction effects. For this reason an isotropic extinction parameter was included in the final refinement, which reduced the R value from 0.09 to 0.055. At this stage refinement in $Ama2$ was tried, but the R value did not improve, and the atoms shifted less than two standard deviations from their centrosymmetric positions. A difference Fourier map calculated from the final refinement showed no significant remaining peaks. The final positional and thermal parameters are given in Table III and the relevant interatomic distances are summarized in Table IV.

The structure analysis yields the composition $\text{Pb}_3\text{Ta}_5\text{X}_{22}$. It is not possible to determine the O/F ratio from either the refinement or the phase analysis. The crystals are, however, colorless and transparent, indicating that the oxidation states of the metal atoms are strictly Ta(V) and Pb(II). Charge balancing then gives the composition $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$.

Description

The structure of $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$ projected along [001] is shown in Fig. 1. It can be described as being built from slabs of ReO_3 structure type, cut parallel to (110) ReO_3 . Adjacent slabs are shifted along a relative to one another, having their Ta atoms located alternately at $z = 0$ and $z = \frac{1}{2}$. Every fourth row of octahedra, counted along a , is absent, resulting in grooves parallel to [001] which are filled with Pb and X atoms.

The lead atoms are at the apices of square pyramids with four X atoms at an average distance of 2.47 \AA . The Pb(2) pyramids share all their basal edges with Pb(1) pyramids. The latter have two unshared edges and are instead connected to the slabs by corner sharing (cf. Fig. 1b). In this way infinite ribbons are formed, which may be described as being cut out of a layer in the structure of red PbO (6). The lead atoms have four additional anion neighbors at distances ranging from 2.70 to 2.73 \AA , so that distorted Archimedean antiprisms are formed. These long distances form the only connection between the slabs. The averages of the eight Pb-X distances are 2.59 \AA for Pb(1) and 2.60 \AA for Pb(2), in good agreement with 2.57 \AA in $\beta\text{-PbF}_2$ (7).

TABLE II
DETAILS OF DATA COLLECTION

Crystal size	$0.020 \times 0.016 \times 0.274 \text{ mm}^3$
μ	
Used in absorption correction	500 cm^{-1}
Calculated from final composition	548 cm^{-1}
Scan type	$\theta-2\theta$
2θ range	$4-60^\circ$
Radiation	$\text{MoK}\alpha$
Scan speed	$0.02^\circ \text{ sec}^{-1}$
Scan width	1.0°
Number of reg. reflections	1805
Number of reflections with $I > 2.5 (\sigma I)$, used in refinement	1047

TABLE III
THE FINAL POSITIONAL AND THERMAL PARAMETERS FOR $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$ $z = 0$ FOR ALL ATOMS

Atom	Position	x	y	U or U_{11}^a	U_{22}	U_{33}	U_{12}
Pb(1)	8(f)	0.6419(1)	0.2540(1)	136(6)	156(7)	118(7)	-34(6)
Pb(2)	4(c)	$\frac{1}{4}$	0.3713(1)	117(8)	134(9)	108(9)	0
Ta(1)	8(f)	0.1194(1)	-0.0090(1)	36(5)	69(6)	208(8)	11(5)
Ta(2)	8(f)	0.0087(1)	0.1276(1)	40(5)	55(6)	187(7)	5(4)
Ta(3)	4(c)	$\frac{1}{4}$	0.1057(1)	35(7)	52(8)	211(11)	0
X(1)	8(f)	0.073(1)	0.195(1)	185(48)			
X(2)	8(f)	0.066(1)	0.059(1)	184(55)			
X(3)	8(f)	-0.058(1)	0.072(2)	277(73)			
X(4)	8(f)	-0.045(1)	0.199(1)	261(58)			
X(5)	8(f)	0.188(2)	0.048(2)	334(81)			
X(6)	8(f)	0.307(1)	0.177(1)	300(62)			
X(7)	8(f)	-0.179(1)	0.080(1)	299(62)			
X(8)	8(f)	0.016(1)	0.636(2)	219(66)			
X(9)	8(f)	0.128(2)	0.480(3)	505(122)			
X(10)	4(c)	$\frac{1}{4}$	0.608(2)	236(95)			
X(11)	8(f)	0.158(1)	0.307(1)	72(37)			
X(12)	4(c)	$\frac{1}{4}$	0.799(1)	118(58)			

^a Anisotropic temperature factors are given in the form $\exp\{-2\pi^2 \cdot 10^{-4}(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12})\}$.

TABLE IV
SELECTED INTERATOMIC
DISTANCES IN Å IN $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$

Pb(1)-X(11)(F)	$2 \times 2.37(1)$
-X(4) (F)	2.46(2)
-X(12)(F)	2.67(1)
-X(6) (F)	$2 \times 2.70(2)$
-X(1) (F)	$2 \times 2.72(2)$
Pb(2)-X(11)(F)	$2 \times 2.46(2)$
-X(12)(F)	$2 \times 2.47(2)$
-X(7) (F)	$4 \times 2.73(2)$
Ta(1)-X(2) (O)	1.86(3)
-X(3) (O)	1.90(3)
-X(5) (O)	1.94(3)
-X(9)	$2 \times 1.99(1)$
-X(7) (F)	1.99(3)
Ta(2)-X(3) (O)	1.90(3)
-X(2) (O)	1.92(3)
-X(4) (F)	1.92(3)
-X(8)	$2 \times 1.98(1)$
-X(1) (F)	2.01(2)
Ta(3)-X(5) (O)	$2 \times 1.85(3)$
-X(6) (F)	$2 \times 1.96(3)$
-X(10)	$2 \times 1.96(1)$

The 4 + 4 coordination in the form of a distorted Archimedean antiprism around lead is quite common. It has previously been observed in, for example, Pb_2OFCl (8) and $\text{Pb}_2\text{Nb}_3\text{O}_7\text{F}_5$ (4). In the structure analysis of the latter compound it was possible to determine which positions were occupied by fluorine by comparing the bond distances with typical Pb-F and Pb-O bonds, and this choice was supported by successful refinement. In the present case no improvement was found when the structure was refined with different distributions of oxygen and fluorine over the anion sites. However, a comparison of observed Pb-X distances with Pb-O and Pb-F bonds in $\text{PbO}(\text{red})$, Pb_2OF_2 (9), $\alpha\text{-PbF}_2$ (10) and $\beta\text{-PbF}_2$ suggests that the X(1), X(4), X(6), X(7), X(11), and X(12) positions are occupied by fluorine, which would account for 44 of the 52 F atoms in the unit cell.

A systematic way of analyzing bond distances in order to determine the distribution of atoms between different sites in a

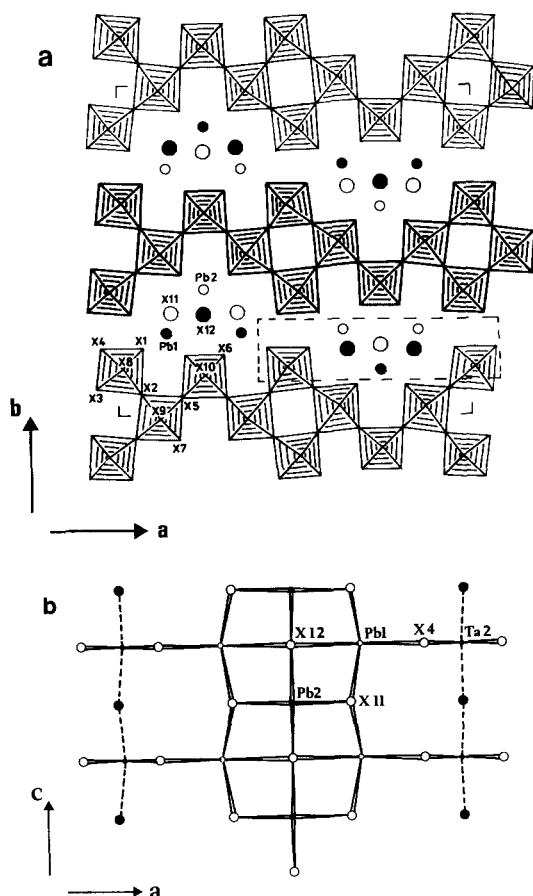


FIG. 1. (a) The structure of $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$ projected along $[0\ 0\ 1]$. Octahedra in fine and bold lines contain Ta at $z = 0$ and $z = \frac{1}{2}$, respectively. \circ \bullet , Lead at $z = 0$ and $z = \frac{1}{2}$; \circ \bullet , X atom at $z = 0$ and $z = \frac{1}{2}$. (b) The dashed line encloses the part of the structure that is shown viewed along $[0\ 1\ 0]$.

structure is provided by the bond strength–bond length relationship of Brown and Shannon (11). Unfortunately, only the parameters for Ta–O and Pb–O bonds are available (12), but as Brown and Shannon demonstrate, it is possible to use universal bond strength–bond length curves for Me –O bonds for each period, and it thus seems reasonable to use curves for Me –O bonds also for Me –F bonds. This was tested by calculating bond strength sums for some niobium and lead oxide fluorides in which

the fluorine positions are known (Table V). From this table it seems clear that the use of the Me –O bond strength parameters of Brown and Kang (12) for both Me –O and Me –F bonds in oxide fluorides will yield an overestimation of the cation valency, but will also quite clearly point out which sites are occupied by fluorine.

The bond strength sums calculated in this way for $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$ are given in Table VI. The anion positions are quite clearly divided into three groups. The $X(1)$, $X(4)$, $X(6)$, $X(7)$, $X(11)$, and $X(12)$ positions form one group with an average bond strength sum of 1.25, and $X(8)$, $X(9)$, and $X(10)$ form another group with an average bond strength sum of 1.65, while the average bond strength sum for $X(2)$, $X(3)$, and $X(5)$ is 2.05. This finding thus supports the previously made choice of sites for fluorine, and it also indicates that the remaining eight F atoms are not localized on one of the remaining anion positions. Table VI also strongly suggests that the $X(2)$, $X(3)$, and $X(5)$ positions are fully occupied by oxygen, which means that eight F atoms are randomly distributed over the $X(8)$, $X(9)$, and $X(10)$ positions. If these sites thus have

TABLE V
AVERAGE BOND STRENGTH SUMS FOR SOME FLUORIDES AND OXIDE FLUORIDES WITH KNOWN FLUORINE POSITIONS, CALCULATED USING PARAMETERS FOR Me –O BONDS FROM REF. (12)

NaNbO_2F_2 (16)	α - PbF_2 (10)
Nb 5.4	Pb 2.2
Na 1.2	F 1.2
O 2.0	β - PbF_2 (7)
F 1.3	
$\text{Pb}_2\text{Nb}_3\text{O}_7\text{F}_5$ (4)	Pb 2.3
	F 1.1
Nb 5.3	
Pb 2.1	
O 1.9	
F 1.3	

one-third F character and two-thirds O character, and if the "bond valencies" 1.25 for F and 2.00 for O are assumed, one arrives at an expected "valency" of 1.75 for these sites, which compares well with the observed average of 1.65. If this assignment is correct the lead atoms are bonded only to fluorine, while the tantalum atoms form their two or three shortest bonds to oxygen atoms concentrated in the middle of the ReO_3 type slabs.

Phases belonging to the homologous series $A_nB_nO_{3n+2}$, occurring for example in the systems Ca-Nb-O, Ca-Nb-Ti-O, and Na-Ca-Nb-O (13) (cf. Fig. 2), are built up of the same type of slab as $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$, although in these compounds the cubo-octahedral interstices are filled with Ca^{2+} or Na^+ to give slabs of the perovskite type. In these phases no octahedra are removed from the slabs, and every second slab is

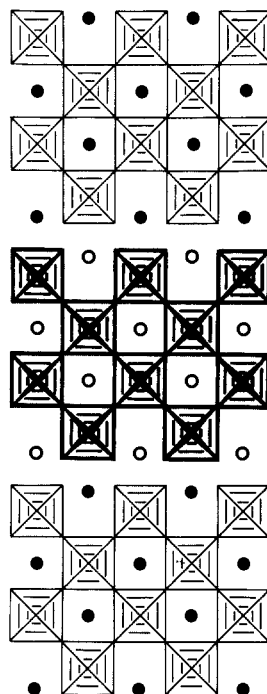


FIG. 2. The idealized structure of $\text{Ca}_2\text{Nb}_2\text{O}_7$ ($A_nB_nO_{3n+2}$, $n = 4$).

TABLE VI
BOND STRENGTH
SUMS FOR $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$
CALCULATED WITH
PARAMETERS FOR
Pb-O AND Ta-O
BONDS FROM REF.
(12)

Atom	ΣS_{calc}
Pb(1)	2.3
Pb(2)	2.2
Ta(1)	5.5
Ta(2)	5.4
Ta(3)	5.8
X(1)	1.2
X(2)	2.1
X(3)	2.0
X(4)	1.3
X(5)	2.1
X(6)	1.3
X(7)	1.2
X(8)	1.7
X(9)	1.6
X(10)	1.7
X(11)	1.2
X(12)	1.2

shifted by approximately 2.8 Å (the width of an octahedral edge) along [100] relative to the arrangement in $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$. In these compounds there are only A^{2+} (e.g., Ca^{2+} , Sr^{2+}) ions between the slabs, while in the present compound there are also anions not belonging to the octahedra, which together with the lead atoms form bands of square pyramids as described above. $\text{Pb}_3\text{Ta}_5\text{O}_9\text{F}_{13}$ is thus related to the $A_nB_nO_{3n+2}$ phases in a manner similar to the relation between the Aurivillius phases and the $A_2A'_{n-1}B_nO_{3n+1}$ compounds (e.g., $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (14) and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ (15)).

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References

1. Ö. SÄVBORG AND M. LUNDBERG, *Mater. Res. Bull.* **15**, 1433 (1980).
2. Ö. SÄVBORG, I. ELGENMARK, AND M. LUNDBERG, to be published.
3. Ö. SÄVBORG AND M. LUNDBERG, *J. Solid State Chem.* **57**, 135 (1985).
4. Ö. SÄVBORG, *J. Solid State Chem.* **57**, 143 (1985).
5. *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch Press, Birmingham (1974).
6. W. J. MOORE AND L. PAULING, *J. Amer. Chem. Soc.* **63**, 1392 (1941).
7. A. BYSTRÖM, *Ark. Kemi Mineral. Geol.* **24A**, 7 (1947).
8. W. NIEUWENKAMP AND J. M. BIJVOET, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **81**, 469 (1932).
9. B. AURIVILLIUS, *Chem. Scripta* **10**, 156 (1976).
10. P. BOLDRINI AND B. O. LOOPSTRA, *Acta Crystallogr.* **22**, 744 (1967).
11. I. D. BROWN AND R. D. SHANNON, *Acta Crystallogr. A* **29**, 266 (1973).
12. I. D. BROWN AND KANG KUN WU, *Acta Crystallogr. B* **32**, 1957 (1976).
13. M. NANOT, F. QUEYROUX, F. C. GILLES, A. CARPY, AND J. GALY, *J. Solid State Chem.* **11**, 272 (1974).
14. B. AURIVILLIUS, *Ark. Kemi* **1**, 499 (1950).
15. R. J. D. TILLEY, *J. Solid State Chem.* **21**, 293 (1977).
16. S. ANDERSSON AND J. GALY, *Acta Crystallogr. B* **25**, 847 (1969).