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

II. $Pb_2Nb_3O_7F_5$: A Structure Composed of Slabs of "ReO_3"-Type Separated by $Pb_2F_2^{2+}$-Layers

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The structure of $Pb_2Nb_3O_7F_5$ has been determined from single crystal X-ray data. The symmetry is tetragonal, space group $I4/mmm$, with $a = 3.8938(4)$ Å and $c = 32.128(5)$ Å. The structure is built of slabs of ReO_3 structure type with net composition $Nb_3O_7F_3^{2-}$, separated by $Pb_2F_2^{2+}$ layers, and is closely related to the structure of $Bi_4Ti_3O_{12}$. The cubo-octahedral positions in the ReO_3-type matrix, occupied by Bi^{3+} ions in $Bi_4Ti_3O_{12}$, are empty in the present compound. © 1985 Academic Press, Inc.

Introduction

The family of compounds $A_2O_2B_{n-1}M_nO_{3n+1}$ was first studied by Aurivillius (*1*). A large number of compounds belonging to this family have been reported (*2*), with $A = Bi^{3+}$, B = Bi, Pb, Na, K, Sr, Ca, Ba, and several rare earth atoms, with M = Ti, Nb, Ta, W, and Fe and with n values from 1 to 5. The compounds are often ferroelectric at room temperature, with orthorhombic or monoclinic symmetry, but transform to a para-electric state with tetragonal symmetry at higher temperature (*2*). Figure 1 shows a projection of the idealized structure (space group $I4/mmm$) of such a compound with $n = 3$. The structure is built of slabs of perovskite structure, n octahedra thick, separated by a bismuth oxide sheet of net composition BiO^+. The M atoms are octahedrally coordinated by oxygen, and the B atoms fill the 12-coordinated holes formed by the corner-sharing octahedra.

In the course of phase analysis of the system Pb(II)–Nb(V)–O–F, a compound $Pb_2Nb_3O_7F_5$ was discovered (*3*) with a unit cell similar to that of the high-temperature form of the Aurivillius phase $Bi_4Ti_3O_{12}$ (*1*). A comparison of the compositions of $Pb_2Nb_3O_7F_5$ and $Bi_4Ti_3O_{12}$ suggests that the former has the structure shown in Fig. 1, with Pb in the A sites and the B sites empty. The possibility that Pb^{2+} can substitute for Bi^{3+} in the A sites has been suggested by Armstrong *et al.* (*4*), but it has not previously been experimentally confirmed. For this reason a single crystal X-ray investigation of the structure of $Pb_2Nb_3O_7F_5$ has been undertaken.

Experimental

The starting materials were PbF_2 (Ventron, ultrapure), NbO_2F (prepared as in Ref. (*5*)) and Nb_2O_5 (Merck, optipure, purified from oxide fluorides by several hours

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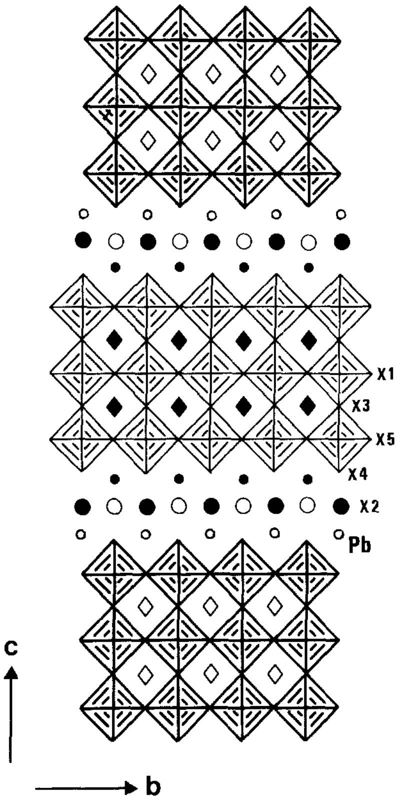

FIG. 1. The idealized structure of the tetragonal high-temperature form of an Aurivillius phase A_2X_2 $B_{n-1}M_nX_{3n+1}$ with $n = 3$ projected along [100]. Octahedra in fine and bold lines have their centres at $x = 0$ and $x = \frac{1}{2}$ respectively. ○ ●, A site at $x = 0$ and $x = \frac{1}{2}$; ◇ ◆, B site at $x = 0$ and $x = \frac{1}{2}$; ○ ●, interlayer X (= O,F) at $x = 0$ and $x = \frac{1}{2}$.

of heating in air at 1275 K). Appropriate amounts of these substances were carefully mixed in an agate mortar and subsequently heat-treated at 895 K in a sealed Pt ampoule for 3 weeks. The product consisted of colorless square plates. The X-ray powder pattern was recorded in a Guinier–Hägg focusing camera, with KCl ($a = 6.2930$ Å at 298 K) (*6*) added as an internal standard. It could be fully indexed with a body-centered tetragonal cell with $a = 3.8938$ Å and $c = 32.128$ Å, as described previously (*3*). The density of the crystals is given in Table I.

A crystal measuring 0.040 × 0.050 × 0.008 mm^3 was selected for diffraction data collection. Weissenberg photographs indicated that the crystal was of good quality. The crystal was mounted on a PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator and a MoKα radiation source. Six hundred fifty-seven reflections with $h \geq k \geq 0$ and $l \geq 0$, and with $\theta \leq 45°$, were collected using the θ–2θ scan technique. The peaks were scanned with a constant speed of 0.01° sec^{-1} over an interval of ±0.50°. Three test reflections were measured with an interval of 120 min. Their intensity did not vary more than $\pm 2\sigma$. The integrated intensities were corrected for Lorentz, polarization, and absorption effects ($\mu = 368$ cm^{-1}). Atomic scattering factors and anomalous scattering parameters were taken from Ref. (*7*).

Structure Determination

The Weissenberg photographs showed the Laue symmetry to be $4/mmm$, and the only condition limiting possible reflections was $h + k + l = 2n$. This limits the possible space groups to $I422$ (No. 97), $I4mm$ (No. 107), $I\bar{4}m2$ (No. 119), $I\bar{4}2m$ (No. 121), and $I4/mmm$ (No. 139), of which only the last is centrosymmetric. As the E values indicated a centrosymmetric structure, the space group was assumed to be $I4/mmm$—the same as that of high-temperature $Bi_4Ti_3O_{12}$. A comparison of observed and calculated

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Pb_2Nb_3O_7F_5$

Unit cell	$a = 3.8938(4)$ Å $c = 32.128(5)$ Å
Space group	$I4/mmm$ (No. 139)
Unit cell content	$Z = 2$
Density	
calc	6.14 g cm^{-3}
obs	6.15 g cm^{-3}

density showed that the unit cell contains two formula units of $Pb_2Nb_3O_7F_5$ (cf. Table I).

Positions for the Pb and Nb atoms were derived from a three-dimensional Patterson map. These metal atom positions were used to calculate a difference Fourier map that yielded reasonable anion positions. Least-squares refinement of the structure thus derived using isotropic thermal parameters for all atoms and unit weights, gave an R value of 9.6%. A difference Fourier map calculated at this stage indicated that the thermal motion of the metal atoms, in particular that of the Nb atoms, was anisotropic. Further refinement with anisotropic thermal parameters for all metal atoms gave $R = 6.9\%$. An inspection of observed and calculated structure factors indicated that the two strongest reflections, 200 and 110, suffered from extinction effects. They were therefore excluded in the following refinements.

In order to distinguish between the F and O atoms, a comparison of the lead anion distances (cf. Table III and Fig. 1) with Pb–O and Pb–F distances in compounds with lead in a similar coordination was carried out. It indicated that the $X(2)$ and $X(4)$ positions are occupied by fluorine (the details of this discussion are given below). This would account for eight of the ten F atoms in the unit cell. There are no twofold anion positions in the structure, which means that the remaining fluorines can at best occupy one of the remaining positions to 50%. With no clear indication from the bond length, and bearing in mind the close similarity in scattering power between oxygen and fluorine, it seemed pointless to try to localize the two remaining fluorines. The $X(1)$, $X(3)$, and $X(5)$ positions were therefore treated as oxygens. A refinement based on this hypothesis gave $R = 6.7\%$. The only other effect on the structure parameters was that the thermal parameters of $X(2)$ and $X(4)$ increased to the same magnitude as those of $X(3)$ and $X(5)$. A final difference map calculated at this stage showed no remaining peaks corresponding to more than 50% of an oxygen atom. To further check that the B sites were empty, a refinement was made with a small initial amount of lead (10% of full occupancy) in the B position. The R value increased dramatically and did not drop back until the occupancy factor had refined to zero. As the R value obtained is quite high for absorption corrected diffractometer data, the possibility that the structure was noncentrosymmetric was considered. It was therefore refined in the four remaining space groups. All structural parameters from these refinements were, however, well within three standard deviations of the centrosymmetric values, and the R value did not improve. Thus the

TABLE II

THE FINAL POSITIONAL AND THERMAL PARAMETERS IN $Pb_2Nb_3O_7F_5$

Atom	Position	x	y	z	U or U_{11}[a]	U_{33}
Pb	4(*e*)	0	0	0.20210(5)	172(6)	158(1)
Nb(1)	2(*b*)	0	0	$\frac{1}{2}$	271(22)	95(3)
Nb(2)	4(*e*)	0	0	0.38198(10)	210(15)	39(1)
$X(1)$	4(*c*)	0	$\frac{1}{2}$	0	397(80)	
$X(=F)(2)$	4(*d*)	0	$\frac{1}{2}$	$\frac{1}{4}$	68(42)	
$X(3)$	4(*e*)	0	0	0.4392(8)	166(85)	
$X(=F)(4)$	4(*e*)	0	0	0.3158(7)	87(55)	
$X(5)$	8(*g*)	0	$\frac{1}{2}$	0.1288(5)	156(45)	

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

TABLE III

INTERATOMIC DISTANCES IN $Pb_2Nb_3O_7F_5$

Pb–F(2)	4 × 2.482(1) Å
Pb–F(4)	4 × 2.813(5) Å
Nb(1)–O(1)	4 × 1.947(1) Å
Nb(1)–O(3)	2 × 1.95(3) Å
Nb(2)–O(3)	1.84(3) Å
Nb(2)–O(5)	4 × 1.977(3) Å
Nb(2)–F(4)	2.13(3) Å

centrosymmetric refinement was considered correct, and the final positional and thermal parameters of this refinement are given in Table II.

Description and Discussion

The structure of $Pb_2Nb_3O_7F_5$ is similar to that shown in Fig. 1, with Pb in the *A* sites, Nb in the *M* sites, and the *B* sites empty. Relevant interatomic distances are summarized in Table III.

The Nb(1) atom is situated at the center of a very regular octahedron with the Nb–*X* distance 1.95 Å, the same value as in NbO_2F (*5*). The Nb(2) atom, on the other hand, is shifted 0.14 Å toward the oxygen shared with Nb(1), giving four equatorial oxygens at 1.98 Å and two different apical oxygens at 1.84 and 2.13 Å, respectively. The Nb atom in the shear plane of Nb_3O_7F (*8*) shows a similar distribution of Nb–*X* distances: 2 × 1.96, 2 × 1.99, 1.86, and 2.20 Å.

The lead atom is situated at the apex of a tetragonal pyramid with four F(2) atoms at a distance of 2.482 Å. This pyramid shares all its basal edges with other pyramids, but these have their apices pointing in the opposite direction. The arrangement is similar to that in tetragonal PbO (*9*). The Pb atom also has four F(4) atoms at a distance of 2.813 Å, which together with the four F(2) atoms form a distorted Archimedean antiprism. A similar coordination around lead is found in PbFCl (*10*) and Pb_2OFCl (*11*). The choice of fluorine for the *X*(2) and *X*(4) positions is, as previously mentioned, supported by the Pb–*X* bond distances. In tetragonal PbO and in Pb_2OFCl the Pb–O bonds are 2.30 and 2.311 Å, respectively, while the Pb–F bonds in PbFCl and Pb_2OFCl are 2.52 and 2.514 Å, to be compared with 2.482 Å in $Pb_2Nb_3O_7F_5$. The average of the eight Pb–F(2) and Pb–F(4) bonds is 2.647 Å, in good agreement with 2.66 Å for the nine Pb–F bonds in the low-temperature form of PbF_2 ($PbCl_2$ type) (*12*) and 2.57 Å for the eight bonds in the high-temperature form (CaF_2 type) (*13*).

Newnham *et al.* (*2*) discuss the occurrence of ferroelectricity in the Aurivillius phases. They point out that a distortion of the bismuth coordination, resulting in the formation of a fifth short Bi–O distance, is one of the main features accompanying the ferroelectric phase transition in these compounds. The compound $Bi_2W_2O_9$ (*14*), which is of the Aurivillius type but with the *B* sites empty as in the present compound, shows the same type of distortion and is probably antiferroelectric at room temperature. $Pb_2Nb_3O_7F_5$ does not show this type of distortion, and DSC measurements in the temperature range 150–500 K show no sign of a phase transition.

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References

1. B. AURIVILLIUS, *Ark. Kemi* **1**, 463 (1949).
2. R E. NEWNHAM, R. W. WOLFE AND J. F. DORRIAN, *Mater. Res. Bull.* **6**, 1029 (1971).
3. Ö. SÄVBORG AND M. LUNDBERG, *Mater. Res. Bull.* **15**, 1433 (1980).

4. R. A. Armstrong and R. E. Newnham, *Mater. Res. Bull.* **7,** 1025 (1972).

5. L. K. Frevel and H. W. Rinn, *Acta Crystallogr.* **9,** 626 (1956).

6. P. G. Hambling, *Acta Crystallogr.* **6,** 98 (1953).

7. *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham (1974).

8. S. Andersson, *Acta Chem. Scand.* **18,** 2339 (1964).

9. W. J. Moore and L. Pauling, *J. Amer. Chem. Soc.* **63,** 1392 (1941).

10. W. Nieuwenkamp and J. M. Bijvoet, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **81,** 469 (1932).

11. B. Aurivillius, *Chem. Scr.* **11,** 208 (1977).

12. P. Boldrini and B. O. Loopstra, *Acta Crystallogr.* **22,** 744 (1967).

13. A. Byström, *Ark. Kemi Mineral. Geol.* **24A,** No. 33 (1947).

14. Y. Bando, A. Watanabe, Y. Sekikawa, M. Goto, and S. Horiuchi, *Acta Crystallogr. A* **35,** 142 (1979).