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

V. $Pb_xM(O,F)_{3+x/2}$ ($x \sim 0.25$, M = Nb, Ta): A Disordered Superstructure of the Hexagonal Tungsten Bronze Type

ÖRJAN SÄVBORG

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

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The crystal structures of the compounds $Pb_xM(O,F)_{3+x/2}$ (M = Nb, Ta; $x \sim 0.25$) have been determined from single crystal X-ray data. The apparent symmetry is hexagonal (space group *P6/mmm*) and the unit cell dimensions are $a_{Nb} = 7.567(1)$ Å and $c_{Nb} = 3.928(1)$ Å. The structures are related to the hexagonal tungsten bronze type, but differ from that type in that the lead atoms are located in the tunnels at approximately the same level as the metal atoms in the MX_3 framework. Some anions also reside in the hexagonal tunnels. A disordered superstructure has been observed by electron diffraction methods; it may be explained by a model implying lateral shifts of the lead atoms and the formation of Pb–X–Pb groups. © 1985 Academic Press, Inc.

Introduction

In the course of studies of niobium and tantalum oxide fluorides containing divalent lead, a phase was discovered which had unit cell dimensions very similar to those of hexagonal tungsten bronze (HTB) (*1, 2*). The phase analysis indicated that the composition was $Pb_xM(O,F)_{3+x/2}$ with $x \sim 0.25$ for both M = Nb and Ta. I attempted a single crystal X-ray structure analysis in order to investigate how Pb(II), with its tendency toward one-sided coordination due to the lone pair, is accommodated in the hexagonal tunnels of the HTB structure and, if possible, to find the reason for the deviation from normal HTB stoichiometry, A_xMO_3.

Experimental

A crystal of the niobium compound in the form of a hexagonal plate was selected from a single phase sample with the gross composition $Pb_{0.21}Nb_{0.79}O_{1.87}F_{0.63}$ prepared as in Ref. (*1*). Under the same conditions the corresponding tantalum compound was obtained from the gross composition $Pb_{0.21}Ta_{0.79}O_{1.87}F_{0.63}$. This was a two-phase sample, however, and contained a tetragonal phase, $Pb_3Ta_4O_{12}F_2$ (*3*) as well. This indicates that the hexagonal compound has a somewhat lower lead content than the Nb phase. The samples from which the crystals were chosen were all colourless. Crystallographic data are given in Table I.

Single crystals of both compounds were mounted on a Weissenberg camera with the *c* axis parallel to the rotation axis. Oscillation and *hk*0–*hk*3 layer photographs were registered for both phases. In addition, the niobium crystal was remounted with *a* parallel to the rotation axis, and oscillation and zero level photographs were taken. The

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TABLE I

CRYSTALLOGRAPHIC DATA FOR $Pb_xM(O,F)_{3+x/2}$ (M = Nb, Ta)

	Nb ($x = 0.26$)	Ta ($x = 0.24$)
Unit cell (Å)		
a	7.567(1)	7.548(2)
c	3.928(1)	3.941(1)
Space group	$P6/mmm$	
Density (g cm^{-3})		
obs	5.11	—
calc	5.09	7.24
Crystal size (mm^3)	0.094 × 0.074 × 0.022	0.078 × 0.074 × 0.038
Absorption coefficient μ (cm^{-1})	193	559
Scan type	θ–2θ	θ–2θ
Scan speed (deg sec^{-1})	0.02	0.02
Scan width (deg)	1.20	1.20
2θ range (deg)	4–60	4–60
Number of registered reflections	211	236
Number of reflections with $I > 2.5\ \sigma(I)$ used in least-squares refinement	112	164

crystals were then mounted on a PW 1100 automatic diffractometer. Details of the data collection are summarized in Table I.

Structure Analysis

The Weissenberg photographs showed the Laue symmetry to be $6/mmm$ for both crystals. They also confirmed that the unit cells, as derived from Guinier powder photographs, were correct. No indication of either superstructure reflections or diffuse streaks could be detected.

The structure analysis was started using data collected from the niobium compound. Scattering factors and anomalous scattering parameters were taken from (*4*). The calculated Patterson function was fully consistent with the distribution of Pb in the point position 1a (0,0,0) and Nb in 3f ($\frac{1}{2}$,0,0) in space group $P6/mmm$; i.e., all the metal atoms are situated in one plane. Fourier and difference Fourier maps calculated with these metal coordinates showed peaks corresponding to X atoms arranged as in the HTB structure type. A small peak was found at (0,0,$\frac{1}{2}$), however, which could be interpreted as 50% X occupation, in agreement with the assumed composition. Least-squares refinement of this structure model with isotropic thermal parameters for all atoms (the temperature factor of the X atoms were fixed at $U = 0.012$ Å^2) converged to $R = 0.19$. The temperature factor of Nb was, however, very large ($U = 0.025$ Å^2) and strongly correlated to that of Pb. Anisotropic thermal parameters for Nb and Pb were introduced at this stage, but did not alleviate the problem. Several attempts were made to lower the symmetry, and the space group $P6mm$ was found to give the most satisfactory results. The R value dropped to 0.11 with the isotropic temperature factor fixed at $U = 0.006$ Å^2 for Nb.

Due to the high correlation of the Pb and Nb thermal parameters, attention was switched to the tantalum phase. The structure model based on the space group $P6/mmm$ with Pb in position 1a and Ta in 3f proved unsatisfactory in this case also. The correlation of the Pb and Ta temperature factors was, however, not as strong as that of Pb and Nb.

It was found that a model with the lead

TABLE II

Positional and Thermal Parameters for $Pb_{0.24}Ta(O,F)_{3.12}$ (Space Group $P6/mmm$)

Atom	Point position	x	y	z	Occupancy factor	U_{11}[a]	U_{33}	U_{12}
Ta	$3f$	$\frac{1}{2}$	0	0	1	0.0086(5)	0.0141(6)	0.0034(8)
Pb	$12o$	0.0193(9)	0.0387(18)	0.0734(21)	0.059(2)	0.0263(39)		
$X1$	$6l$	0.2108(17)	0.4217(34)	0	1	0.0198(37)		
$X2$	$3g$	$\frac{1}{2}$	0	$\frac{1}{2}$	1	0.0157(43)		
$X3$	$1b$	0	0	$\frac{1}{2}$	0.36(2)	0.010		

Note. Standard deviations are given in parentheses.

[a] Anisotropic temperature factors are given in the form $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2hlb^*c^*U_{23})\}$.

atom split across the mirror plane perpendicular to (001), i.e., Pb in position $2e$ with $z = 0.06$, converged to $R = 0.07$. A difference Fourier map calculated from this model showed that it still did not give a good description of the lead position, since a ring of remaining electron density was found to surround it in the xy plane, while negative values appeared on each side along z. The anomaly was removed by introducing an anisotropic temperature factor for Pb, which became very large in the xy plane ($U_{11} = U_{22} = 0.047$ Å^2) or by displacing the Pb atom not only out of the plane of the hexagonal ring but also to one side of it. No distinct peaks were observed in the difference map; however, a small maximum with the coordinates 0.02, 0.04, 0.06 appeared, and a refinement with lead randomly distributed over the 12-fold position $12o$ gave $R = 0.068$. The small peak remained at $(0,0,\frac{1}{2})$, corresponding in size to half occupancy of an anion site. The final refinements included an anion with 50% occupancy situated at this site, but the R value did not improve significantly.

The composition derived from this refinement is $Pb_{0.24}TaX_{3.12}$, which, as expected, is somewhat lower than the gross composition of the sample. The positional and thermal parameters are given in Table II, and the relevant interatomic distances are summarized in Table III.

As the refined structure model comprises a lead atom displaced from the center of the tunnel in the HTB matrix and randomly distributed over a 12-fold position, it was considered reasonable to investigate, by electron diffraction methods, whether this disorder is complete or whether there is any evidence of short range order. All available evidence indicated that the niobium and the tantalum compounds are identical, apart from a possible difference in the content; and since diffuse scattering due to disorder of the Pb atom would be relatively stronger

TABLE III

Some Interatomic Distances in Å in $Pb_{0.24}Ta(O,F)_{3,12}$

		Mean value
Ta–X(1)	4 × 1.95(1)	1.96
–X(2)	2 × 1.97(1)	
a. Distances obtained with Pb as a "split" atom (point position $12o$)		
Pb–X(1)	2.55(2)	2.72
–X(1′)	2 × 2.68(2)	
–X(1″)	2 × 2.93(2)	
–X(1‴)	3.05(2)	
–X(3)	2.27(1)	
b. Distances obtained with Pb situated at the origin ($1a$)		
Pb–X(1)	6 × 2.78(1)	2.66
–X(3)	1.97(1)	

Note. Standard deviations are given in parentheses.

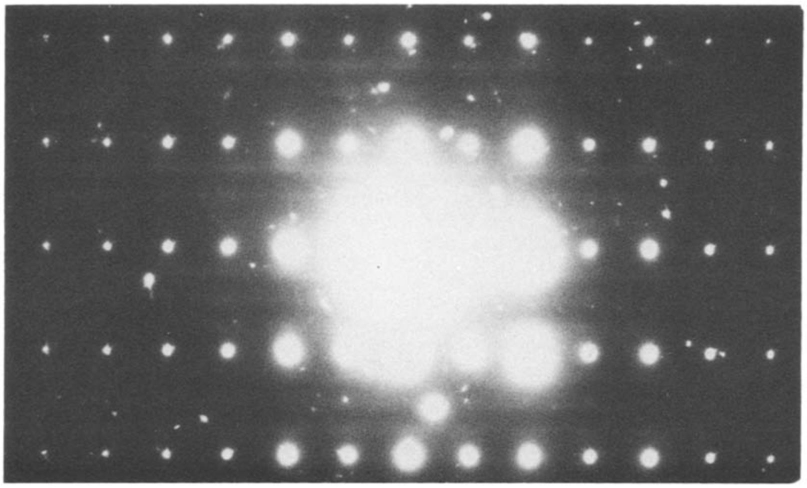

FIG. 1. Electron diffractogram (*h*0*l* zone) recorded from a crystal of the $Pb_{0.26}Nb(O,F)_{3.13}$ phase. Note the faint superstructure streaks.

in the Nb compound, the latter was studied by this technique.

The *hk*0 and *h*0*l* zones were registrated in a Jeol 200CX microscope. No evidence of diffuse scattering or a superstructure was found in the *hk*0 zone, but in the *h*0*l* zone continuous streaks corresponding to a fourfold multiplicity of the *c* axis were observed (cf. Fig. 1). These very weak streaks indicate a disordered superstructure.

Discussion

Although the general type of the present structure (cf. Fig. 2) is HTB (5), there are several differences. First, the lead atoms are not located in the cages of anions *between* the layers of transition metal atoms as the alkali atoms in normal HTB but rather, *in* these layers, are surrounded by a ring of six anions. Second, there are additional anions in the tunnels at sites normally containing alkali atoms. Third, the tantalum atoms are located at the position ($\frac{1}{2}$,0,0) and are not displaced along x as in the alkali bronzes (where this gives rise to a doubling of the c axis).

The streaks observed in the electron diffraction pattern of the $Pb_{0.26}NbX_{3.13}$ phase could be interpreted as a shift of the Nb atoms out of their ideal positions, as a displacement of the Pb atom out of the (0,0,0) position, or possibly both. The composition, the unit cell dimensions and the appearance of the X-ray diffraction patterns all indicate that the niobium and tantalum compounds are isomorphous. In both cases problems were encountered in refining the lead atom in position 1*a*, since areas of large positive and negative values were invariably found in the Fourier difference

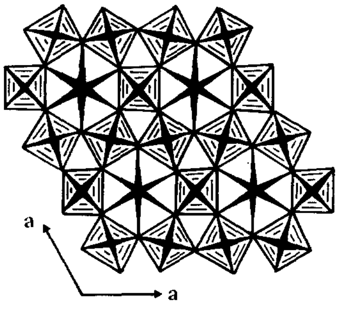

FIG. 2. The structure of $Pb_xM(O,F)_{3+x/2}$ viewed along [001]. The Pb atoms are located in the hexagonal tunnels at approximately the same level as the M atoms.

maps. This may be taken as an indication that the disordered superstructure is mainly caused by a displacement of the Pb atom, although a simultaneous minor shift of the Nb atoms cannot be definitely excluded. It follows from the value of the Pb–$X(3)$ distance that the Pb atoms must be displaced in both compounds. If the Pb atoms are placed at (0,0,0), the Pb–$X(3)$ distance will be 1.97 Å (cf. Table IV) which is 0.15 Å shorter than the shortest Pb–O distance reported. This short distance can be increased by an ordered displacement of the Pb atoms so as to form pairwise longer and shorter Pb–Pb distances along the hexagonal tunnels. The $X(3)$ atom is thus bridging the longer of these distances, forming Pb–$X(3)$–Pb groups.

The short Pb–Pb distance is approximately 3.4 Å, but insertion of an X atom would lead to a Pb–X distance of 1.7 Å, which is clearly much too short. On the other hand, the longer Pb–Pb distance along the tunnels is 4.5 Å, and insertion of an X atom would yield a Pb–X distance of 2.3 Å, which seems reasonable in comparison with, for example, PbO (2.30 Å in the tetragonal form (*6*) and 2.21 Å in the orthorhombic modification (*7*)).

If the strength of the Pb–$X(3)$ bond is calculated from the formula $s = (R/R_0)^{-N}$, with the parameters $R_0 = 2.044$ and $N = 5.5$ for Pb–O bonds (*8*), the proposed model gives $\Sigma s = 1.1$ for the $X(3)$ position, suggesting that it is occupied by fluorine. If, on the other hand, $X(3)$ is assumed to be oxygen, the Pb–$X(3)$ distance required to give $\Sigma s = 2.0$ is 2.04 Å, which is shorter than any distance previously reported for Pb–O bonds.

Figure 3 shows a model of the ordering of Pb and X atoms along the hexagonal tunnel taking the observed Pb displacement into account. This model breaks the hexagonal symmetry of the crystal so as to leave maximum room for the lone pairs on the Pb atoms (cf. Fig. 3). It is, however, likely that all the six orientations of the Pb–X arrangement are present in the crystal and that this disorder is responsible for the streaking of the superstructure reflections.

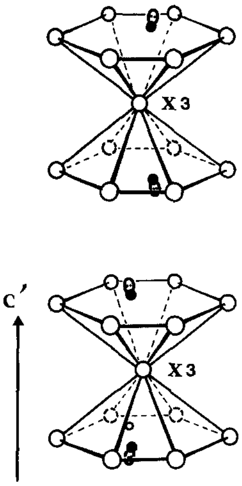

FIG. 3. A view of the suggested arrangement of Pb–X–Pb groups in the hexagonal tunnels.

Table III summarizes the relevant interatomic distances for this structure model. The lead atom is surrounded by one $X(3)$ anion at a distance of 2.27 Å and six X atoms at distances between 2.55 and 3.05 Å. This type of PbX_7 hexagonal pyramid has also been observed in lead niobates of pyrochlore type (*9*) with a quite similar distribution of Pb–X distances. The Ta atom is at the center of a quite regular octahedron with an average Ta–X distance of 1.96 Å, in excellent agreement with 1.95 Å in TaO_2F (*10*).

A general discussion of the crystal and coordination chemistry of lead in the present type of compounds is presented elsewhere (*11*).

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