

the structure determination by YAST. As was expected, a very large peak density, which was as large as those of the O atoms, was observed at the Li(1) position. Fig. 3 shows a comparison of the structure amplitudes with $h1l$ for the two crystals. The linearity found in Fig. 3 indicates that the value of ε may be taken to a first approximation as constant for all diffuse $h1l$ reflections. Such a linearity was also found for reflections with hkl ($k = 3, 5, 7, \dots$) though slightly steeper slopes were found as k increased.

On the basis of the above result, YAST (1979) obtained several sets of F_o 's by multiplying the original F_o 's (k odd) by a constant value of $1/\varepsilon$ for $\varepsilon > 0.8$ and carried out least-squares calculations for each set of F_o 's. A plausible value of $\varepsilon = 0.92$ was then obtained on the assumption that the temperature factor for Li(1) is approximately equal to that for Li(2). An approximate value of ε for the 110 reflection from the crystal used in this study can then be estimated from the slope

of 0.67 of Fig. 3 to be $\varepsilon = 0.92 \times 0.67 = 0.62$. Substituting this value and $\alpha = 0.045$ ($x = -0.91$) into equation (5) gave $\Delta\eta = 0.01$. Using this value we have an approximate value of $\alpha \approx 0.008$ for the crystal used for structure determination.

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Structure of the Potassium Tantalum Fluoride Oxide $K_3Ta_4F_7O_8$

BY A. BOUKHARI, J. P. CHAMINADE, M. POUCHARD AND M. VLASSE

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence CEDEX, France

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Abstract

$K_3Ta_4F_7O_8$ crystallizes in space group $Pmn2_1$ with $a = 3.918$ (3), $b = 18.072$ (7), $c = 19.057$ (7) Å, $Z = 4$. The structure was refined to $R = 0.083$. The main structure is formed by TaX_6 ($X = O, F$) distorted octahedra sharing common corners. It can be described as an assembly of two-dimensional $[Ta_4X_{15}]_n$ infinite blocks parallel to the (001) plane held together by the K atoms.

Introduction

Compounds with layer or tunnel structures may be particularly suitable for fast-ion transport, so far as they offer to the inserted ion a certain degree of freedom. This property is conditioned by the nature of the structural pathways and of the transporting ion (Pouchard & Hagenmuller, 1978).

Many structures derived from or related to the tungsten-bronze types are made up of a triangular motif of three BX_6 octahedra sharing common corners (B_3X_{15}). These basic blocks can be joined together by

common corners, in one plane, giving rise to complex structures having infinite tunnels normal to such sheets. The tunnels can be hosts to monovalent or divalent cations.

Many phases have been isolated in the study of the system A^I-B^V-O,F ($A = Li, Na, K, Ag$; $B = Nb, Ta$) (Vlasse, Chaminade & Pouchard, 1973, 1976; Chaminade, Vlasse, Pouchard & Hagenmuller, 1974; Vlasse, Chaminade, Massies & Pouchard, 1975; Vlasse, Chaminade, Saux & Pouchard, 1977). In particular, the study of the subsystem K-Ta-O-F has produced four new phases. The structures of $K_6Ta_{6.5}F_{9.5}O_{14.5}$, $K_2Ta_4F_4O_9$ and $K_{12}Ta_{15.5}F_{18.5}O_{35.5}$ have been reported (Vlasse, Boukhari, Chaminade & Pouchard, 1979; Boukhari, Chaminade, Vlasse & Pouchard, 1979; Boukhari, Chaminade, Pouchard & Vlasse, 1979). The present report deals with the analysis of $K_3Ta_4F_7O_8$.

Experimental

Single crystals were obtained by reacting appropriate quantities of K_2TaF_7 , $KTaO_3$ and Ta_2O_5 in a sealed

gold tube heated between 973 and 1173 K. The product was then cooled slowly, yielding small plate-like crystals.

Single-crystal photographs indicate orthorhombic symmetry with possible space groups $Pmnm$ or $Pmn2_1$ ($h0l: h + l = 2n$). The cell parameters refined from Guinier data are $a = 3.918$ (3), $b = 18.072$ (7), $c = 19.057$ (7) Å (Cu $K\alpha_1$, $\lambda = 1.5405$ Å); $d_x = 5.35$ (8) and $d_c = 5.42$ Mg m^{-3} for $Z = 4$.

A single crystal in the form of a rectangular plate ($0.16 \times 0.09 \times 0.02$ mm) was used for intensity measurements which were made on a three-circle automatic diffractometer (Enraf-Nonius CAD-3) with Mo $K\alpha_1$ graphite-monochromated radiation ($\lambda = 0.70929$ Å) and a multiple $\theta/2\theta$ scanning technique up to $\theta_{max} = 35^\circ$. Three standard reflexions were measured for every batch of 50 reflexions with no significant fluctuation in their intensities. 1423 symmetry-independent reflexions were measured [$I \geq 3\sigma(I)$] and corrected for Lorentz and polarization factors but not for absorption [$\mu(\text{Mo } K\alpha) = 36.7 \text{ mm}^{-1}$].

Structural determination

Attempts to solve the structure by the heavy-atom method were not successful, probably due to the large number of Ta atoms in the unit cell. Since the a parameter (3.918 Å) represents the diagonal of a TaX_6 octahedron ($X = O, F$), we can safely assume no superposition of the Ta atoms in this direction. The structure was then solved by direct methods (Sheldrick, 1976) from the $Ok\bar{l}$ reflexions. The resulting E map indicated

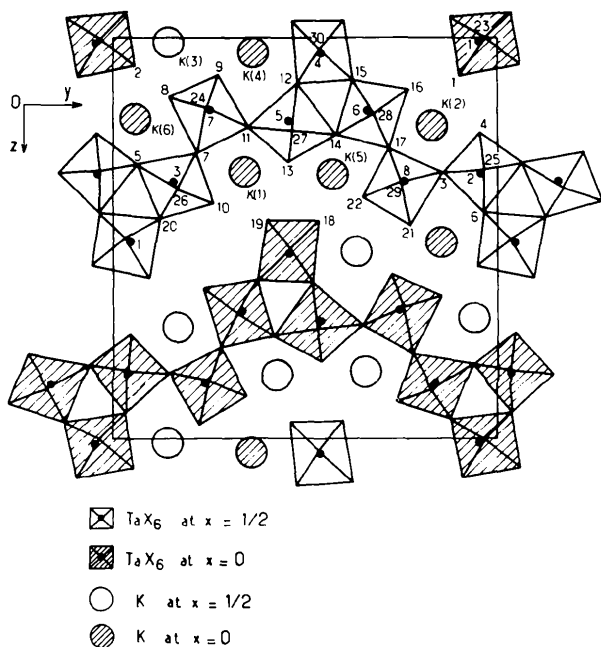


Fig. 1. Projection of the structure of $K_3Ta_4F_7O_8$ on the (100) plane.

Table 1. Atomic coordinates and isotropic thermal parameters B (B_{eq} for Ta atoms) (\AA^2) for $K_3Ta_4F_7O_8$

	x	y	z	B_{eq}/B
Ta(1)	0	0.9587 (3)*	0.0100	1.53
Ta(2)	$\frac{1}{2}$	0.9613 (2)	0.3330 (2)	1.52
Ta(3)	$\frac{1}{2}$	0.1654 (2)	0.3593 (3)	1.34
Ta(4)	$\frac{1}{2}$	0.5395 (2)	0.0334 (3)	0.82
Ta(5)	$\frac{1}{2}$	0.4617 (2)	0.2050 (2)	1.19
Ta(6)	$\frac{1}{2}$	0.6629 (2)	0.1812 (3)	1.09
Ta(7)	$\frac{1}{2}$	0.2513 (2)	0.1806 (3)	0.83
Ta(8)	$\frac{1}{2}$	0.7527 (2)	0.3572 (4)	1.87
K(1)	0	0.344 (2)	0.331 (2)	1.29 (3)
K(2)	0	0.832 (1)	0.221 (2)	1.06 (5)
K(3)	$\frac{1}{2}$	0.147 (1)	0.011 (2)	1.29 (7)
K(4)	0	0.365 (1)	0.036 (2)	1.15 (8)
K(5)	0	0.571 (2)	0.340 (3)	1.51 (9)
K(6)	0	0.060 (2)	0.201 (2)	1.26 (7)
X(1)	0	0.904 (9)	0.099 (9)	1.59 (9)
X(2)	0	0.054 (5)	0.070 (6)	1.52 (7)
X(3)	$\frac{1}{2}$	0.855 (8)	0.337 (6)	1.27 (5)
X(4)	$\frac{1}{2}$	0.952 (6)	0.236 (5)	1.52 (7)
X(5)	$\frac{1}{2}$	0.065 (6)	0.312 (7)	1.52 (7)
X(6)	$\frac{1}{2}$	0.966 (5)	0.436 (5)	0.90 (5)
X(7)	$\frac{1}{2}$	0.221 (9)	0.288 (8)	1.52 (7)
X(8)	$\frac{1}{2}$	0.145 (6)	0.146 (7)	1.52 (7)
X(9)	$\frac{1}{2}$	0.271 (7)	0.091 (6)	2.08 (10)
X(10)	$\frac{1}{2}$	0.264 (7)	0.411 (6)	1.52 (7)
X(11)	$\frac{1}{2}$	0.350 (9)	0.220 (7)	1.52 (7)
X(12)	$\frac{1}{2}$	0.480 (5)	0.113 (5)	1.09 (6)
X(13)	$\frac{1}{2}$	0.458 (7)	0.310 (5)	1.52 (7)
X(14)	$\frac{1}{2}$	0.580 (5)	0.238 (6)	1.52 (7)
X(15)	$\frac{1}{2}$	0.622 (5)	0.101 (6)	1.53 (8)
X(16)	$\frac{1}{2}$	0.763 (9)	0.128 (9)	1.25 (6)
X(17)	$\frac{1}{2}$	0.718 (9)	0.277 (9)	2.09 (10)
X(18)	0	0.538 (6)	0.475 (6)	1.81 (8)
X(19)	0	0.401 (9)	0.458 (9)	1.52 (7)
X(20)	$\frac{1}{2}$	0.124 (6)	0.450 (6)	1.52 (7)
X(21)	$\frac{1}{2}$	0.775 (6)	0.463 (6)	1.52 (7)
X(22)	$\frac{1}{2}$	0.649 (6)	0.398 (7)	1.52 (7)
X(23)	$\frac{1}{2}$	0.967 (6)	-0.001 (5)	1.52 (7)
X(24)	0	0.243 (6)	0.172 (6)	1.52 (7)
X(25)	0	0.963 (9)	0.325 (9)	1.52 (7)
X(26)	0	0.169 (5)	0.378 (5)	1.52 (7)
X(27)	0	0.469 (9)	0.230 (9)	1.52 (7)
X(28)	0	0.677 (5)	0.187 (5)	1.52 (7)
X(29)	0	0.748 (6)	0.358 (7)	1.52 (7)
X(30)	0	0.537 (5)	0.027 (4)	0.76 (8)

* Numbers in parentheses are the e.s.d.'s.

the positions of the Ta and some of the K atoms. Subsequent Fourier and difference syntheses revealed the positions of the remaining K and X ($X = O, F$) atoms. The structure was refined by isotropic and anisotropic full-matrix least squares (Busing, Martin & Levy, 1962) to a final $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.083$. The space group $Pmn2_1$ was adopted for the refinement since the structure contains no mirror plane normal to c . A final difference synthesis showed no significant residual electron density.*

* Lists of structure factors and anisotropic thermal parameters for the Ta atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34828 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å), with e.s.d.'s in parentheses, for K₃Ta₄F₇O₈*

Ta(1)–X(1)	1.963 (11)	K(1)–X(7)	3.074 (11) [2]	K(6)–X(1)	3.424 (8)	X(11)–X(12)	3.111 (12)
X(2)	2.067 (7)	X(10)	2.873 (8) [2]	X(2)	2.500 (7)	X(13)	2.592 (12)
X(6 ^b)	1.960 (6)	X(11)	2.885 (8) [2]	X(4)	2.845 (8) [2]	X(24)	2.901 (12) [2]
X(20 ^b)	1.882 (8)	X(13)	2.871 (8) [2]	X(5)	2.885 (9) [2]	X(27)	2.849 (15) [2]
X(23)	1.976 (7) [2]*	X(19)	2.630 (11)	X(7)	3.890 (11) [2]		
⟨Ta(1)–X⟩	1.971 (8)	X(24)	3.537 (8)†	X(8)	2.701 (9) [2]	X(12)–X(14)	2.990 (9)
		X(26)	3.287 (7)	X(24)	3.353 (8)	X(15)	2.576 (9)
Ta(2)–X(3)	1.923 (9)	X(27)	2.900 (11)	X(25)	3.097 (12)	X(18 ^b)	2.650 (10)
X(4)	1.856 (7)	⟨K(1)–X⟩	2.894 (9)	X(26)	3.906 (7)	X(27)	2.982 (13) [2]
X(5)	1.916 (8)			⟨K(6)–X⟩	2.807 (8)	X(30)	2.754 (8) [2]
X(6)	1.965 (7)	K(2)–X(1)	2.664 (11)				
X(25)	1.960 (11) [2]	X(3)	2.983 (9) [2]	X(1)–X(2)	2.767 (13)	X(13)–X(14)	2.597 (10)
⟨Ta(2)–X⟩	1.930 (9)	X(4)	2.936 (7) [2]	X(20 ^b)	2.884 (13)	X(27)	2.485 (14) [2]
		X(16)	2.921 (11) [2]	X(23)	2.961 (9) [2]		
Ta(3)–X(5)	2.026 (8)	X(17)	3.037 (11) [2]			X(14)–X(15)	2.719 (10)
X(7)	1.690 (10)	X(25)	3.213 (11)	X(2)–X(6 ^b)	2.579 (9)	X(17)	2.602 (13)
X(10)	2.036 (8)	X(28)	2.875 (7)	X(8)	2.939 (11) [2]	X(27)	2.873 (13) [2]
X(20)	1.885 (7)	X(29)	3.020 (8)	X(23)	2.853 (10) [2]	X(28)	2.803 (9) [2]
X(26)	1.992 (6) [2]	⟨K(2)–X⟩	2.938 (9)				
⟨Ta(3)–X⟩	1.937 (8)			X(3)–X(4)	2.603 (11)	X(15)–X(16)	2.600 (13)
		K(3)–X(2)	2.815 (7)	X(6)	2.754 (11)	X(19 ^b)	2.757 (13)
Ta(4)–X(12)	1.859 (7)	X(3)	3.851 (9) [2]	X(17)	2.727 (14)	X(28)	2.741 (9) [2]
X(15)	1.970 (7)	X(6 ^b)	3.170 (6) [2]	X(21)	2.803 (12)	X(30)	2.861 (9) [2]
X(18 ^b)	1.789 (8)	X(8)	2.573 (8)	X(25)	2.766 (14) [2]		
X(19 ^b)	1.795 (11)	X(9)	2.710 (8)	X(29)	2.782 (12) [2]	X(16)–X(17)	2.954 (16)
X(30)	1.963 (6) [2]	X(21 ^b)	2.581 (8) [2]			X(28)	2.742 (13) [2]
⟨Ta(4)–X⟩	1.890 (8)	X(23)	3.216 (7)	X(4)–X(5)	2.504 (11)		
		X(25 ^b)	3.900 (11)	X(25)	2.727 (13) [2]	X(17)–X(22)	2.622 (14)
Ta(5)–X(11)	2.039 (10)	X(29 ^b)	3.479 (8)	X(5)–X(6)	2.964 (10)	X(29)	2.552 (14) [2]
X(12)	1.784 (6)	⟨K(3)–X⟩	2.800 (6)	X(7)	2.856 (13)		
X(13)	2.002 (7)			X(20)	2.838 (11)	X(18)–X(19)	2.500 (14)
X(14)	2.229 (7)	K(4)–X(9)	2.799 (8) [2]	X(25)	2.725 (14) [2]	X(22)	3.165 (11) [2]
X(27)	2.016 (11) [2]	X(12)	3.211 (6) [2]	X(26)	2.992 (10) [2]	X(30 ^b)	2.580 (10) [2]
⟨Ta(5)–X⟩	2.014 (9)	X(18 ^b)	2.874 (8) [2]				
		X(21 ^b)	2.887 (8)				
Ta(6)–X(14)	1.848 (7)	X(22 ^b)	2.642 (8)	X(6)–X(20)	2.868 (10)	X(19)–X(30)	2.612 (15) [2]
X(15)	1.698 (7)	X(24)	3.403 (8)	X(23 ^b)	2.597 (10) [2]		
X(16)	2.074 (11)	X(30)	3.113 (6)	X(25)	2.747 (13) [2]	X(20)–X(23 ^b)	2.723 (10) [2]
X(17)	2.080 (11)	⟨K(4)–X⟩	2.885 (8)			X(26)	2.526 (10) [2]
X(28)	1.979 (6) [2]			X(7)–X(8)	3.045 (13)		
⟨Ta(6)–X⟩	1.943 (8)	K(5)–X(13)	2.887 (8) [2]	X(10)	2.470 (15)	X(21)–X(22)	2.592 (11)
		X(14)	2.764 (8) [2]	X(11)	2.667 (14)	X(29)	2.843 (11) [2]
Ta(7)–X(7)	2.119 (11)	X(17)	3.512 (12) [2]	X(24)	2.980 (13) [2]		
X(8)	2.034 (8)	X(18)	2.641 (8)	X(26)	2.768 (12) [2]	X(22)–X(29)	2.760 (11) [2]
X(9)	1.744 (8)	X(19)	3.807 (12)			⟨X–X⟩	2.701 (11)
X(11)	1.935 (10)	X(22)	2.655 (9) [2]	X(8)–X(9)	2.507 (13)		
X(24)	1.972 (8) [2]	X(27)	2.852 (12)	X(24)	2.687 (11) [2]	⟨Ta–X⟩	1.962
⟨Ta(7)–X⟩	1.963 (9)	X(28)	3.489 (7)			⟨Ta–Ta⟩	3.702
		X(29)	3.217 (9)	X(9)–X(11)	2.843 (13)	⟨Ta–K⟩	3.813
Ta(8)–X(3)	1.888 (9)	⟨K(5)–X⟩	2.763 (9)	X(24)	2.545 (11) [2]	⟨K–X⟩	2.848
X(17)	1.652 (11)						
X(21)	2.056 (8)			X(10)–X(20)	2.637 (11)	Symmetry code	
X(22)	2.029 (8)			X(26)	2.680 (16) [2]	(i) $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$	
X(29)	1.961 (8) [2]						
⟨Ta(8)–X⟩	1.925 (9)						

* Numbers in square brackets indicate the number of equal distances.

† K–X distances >3.20 Å are not included in the mean.

Scattering factors were those of McMaster, Kerr del Grande, Mallet & Hubbel (1969), and anomalous-dispersion corrections those of Dauben & Templeton (1962).

Tables 1 and 2 give the final positional and thermal parameters, and the interatomic distances.

Description and discussion of the structure

Fig. 1 represents the projection of the structure on the (100) plane.

The structure of K₃Ta₄F₇O₈ is an assembly of moderately distorted TaX₆ octahedra sharing partially

common corners. In this assembly the basic triangular blocks $[Ta_3X_{15}]$ made up of three TaX_6 octahedra (found equally in the three previously reported structures: $K_6Ta_{6.5}F_{9.5}O_{14.5}$, $K_2Ta_4F_4O_9$ and $K_{12}Ta_{15.5}F_{18.5}O_{35.5}$) are linked together by another TaX_6 octahedron sharing two of its *cis* corners to give an infinite $[Ta_4X_{19}]_n$ zigzag chain running along *b*. These infinite chains are then stacked one upon the other along *a*, by sharing their axial vertices, to give an infinite $[Ta_4X_{15}]_n$ sheet parallel to the (001) plane. Two such infinite sheets displaced with respect to one another by *c*/2 are held together by the K atoms found in the wide channels located between these sheets (Fig. 1).

By comparison with the three sister structures found in the K-Ta-O-F system, which all have three-dimensional octahedral frameworks, the present phase has, on the contrary, only a two-dimensional sheet structure. However, the basic building block in all four structures is the triangular ring group $[Ta_3X_{15}]$.

The spreads of individual Ta-X distances (1.652 to 2.229 Å) and of the average $\langle Ta-X \rangle$ distances (1.890 to 2.014 Å) in this structure are much greater than that found in the other three [$K_6Ta_{6.5}F_{9.5}O_{14.5}$: 1.944 to 1.947 Å (av.); $K_2Ta_4F_4O_9$: 1.957 to 1.965 Å (av.); $K_{12}Ta_{15.5}F_{18.5}O_{35.5}$: 1.915 to 1.976 Å (av.)]. This indicates the greater distortion and at the same time the greater degree of freedom of the TaX_6 octahedron in the present case. This spread in Ta-X distances could also indicate ordering between O and F atoms.

The coordination for K is rather variable and again indicates the distorted nature of the structure. K(1) and K(2) have ten- and eleven-fold environments respectively, K(3) and K(4) are seven-fold coordinated, while K(5) and K(6) have an eight-fold coordination. The average distances range from 2.763 to 2.938 Å. These values compare well with average distances found in the three previous phases. Only values < 3.20 Å were considered in the averages.

In conclusion the present structure differs from the other three in some important ways. It is first of all a two-dimensional sheet structure rather than a three-dimensional framework. Secondly, some of the K atoms here act as binding agents rather than being simply inserted ions.

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Structure du Vanadate d'Indium: $InVO_4$

PAR MARCEL TOUBOUL ET PAUL TOLÉDANO

Laboratoire de Chimie Structurale des Matériaux, Université P. et M. Curie, 4 place Jussieu, Bâtiment F, 75230 Paris CEDEX 05, France

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Abstract

$InVO_4$ ($M_r = 229.8$) crystallizes in the orthorhombic space group *Cmcm* with $a = 5.765$ (4), $b = 8.542$ (5), c

$= 6.592$ (4) Å, $Z = 4$, $d_m = 4.65$, $d_x = 4.70$ Mg m⁻³, $V = 324.6$ Å³. 1158 reflexions were used in the solution and refinement of the structure to $R = 0.029$ ($R_w = 0.037$), after absorption and extinction corrections.

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