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Crystal Structure of Some Niobium and Tantalum Oxides. IV.* The Structure of KTa_5O_{13} and Its Relationship to the α-PbO_2 Structure

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KTa_5O_{13} crystallizes in the orthorhombic system with unit-cell dimensions $a = 5.653(3)$, $b = 10.708(5)$, and $c = 16.799(7)$ Å with space group *Pbcm*, $z = 4$. The structure was solved by conventional methods; of 1445 unique reflections measured by counter methods, 982 that obeyed the condition $I \geqslant 3\sigma(I)$ were used in the refinement of the model to a conventional R of 0.053 ($R_w = 0.052$). The structure consists of edge- and corner-shared tantalum–oxygen octahedra joined such that tunnels are formed in which the potassium ions are located. Slabs of octahedra are of the α-PbO_2 type and are related to one another by a mirror plane (in which the potassium ions are located) producing a structure that may be considered as a "chemical twin" of the α-PbO_2 structure.

Introduction

As part of a systematic structural study of compounds formed between alkali metal oxides and niobium and tantalum pentoxides the crystal structure of the 1:5 ($K_2O:Ta_2O_5$) phase has been determined.

Following an earlier report of the phase equilibrium diagram for the K_2O–Ta_2O_5 systems (*1*) in which two compounds between Ta_2O_5 and $KTaO_3$ were found, Roth *et al.* (*2*) published a preliminary diagram indicating nine compounds, together with two metastable phases, in this system. Of these, structures have been reported for the ~1:2 phase ($K_6Ta_{10.8}O_{30}$) (*3*), the 4:11 phase in the Rb_2O–Nb_2O_5 system ($Rb_{12.2}Nb_{33.56}O_{90}$) (*4*), the ~2:7 phase ($KTa_{3.4}O_9$) (*5*), the ~1:3 metastable (low-temperature) phase ($K_6Ta_{15.6}O_{42}$) (*7*, *8*).

Crystals of composition corresponding to the 1:5 compound ($K_2O:Ta_2O_5$) were kindly supplied by Dr. R. S. Roth, National Bureau of Standards, Washington, D.C., and the results of a single crystal structure determination are reported here. A preliminary account of this structure was published elsewhere (*8*).

Experimental

A pale tan, approximately cubic crystal was selected (approx. 0.02 × 0.02 × 0.02 mm) using a polarizing microscope and mounted on a silica capillary using "Araldite." Preliminary oscillation and Weissenberg photography indicated that the crystal was orthorhombic and that no unusual effects were present. Accurate unit-cell parameters were obtained using a Philips PW 1100 single crystal diffractometer (*4*).

Crystal data. KTa_5O_{13}, $M = 1151.83$, $a = 5.653(3)$, $b = 10.708(5)$, $c = 16.799(7)$ Å, $U = 1016.88$ Å^3, $D_c = 7.52$ g cm^{-3}, $z = 4$. Insufficient material was available to enable a

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* The paper by B. M. Gatehouse, T. Negas, and R. S. Roth, *J. Solid State Chem.* 18, 1 (1976) is considered as Part I of this series.

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density to be measured. $F(000) = 1952$, $\mu = 569.3\ \mathrm{cm}^{-1}$ for Mo$K\alpha$ radiation ($\lambda = 0.7107$ A). Systematic absences observed were $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; space groups $Pbcm$ (D_{2h}^{11}) or $Pca2_1$ (C_{2v}^{5}), successful refinement confirmed the former as the most likely correct space group.

Intensity measurements. Intensity measurements were made using the Philips PW1100 computer-controlled diffractometer with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) out to $\theta = 30°$ operating in a θ–2θ scan mode with a symmetric scan range of $\pm 1.00°$ in 2θ from the calculated Bragg scattering angle at a scan rate of $0.0168°\ \mathrm{sec}^{-1}$. A total of 1657 reflections were collected and were reduced to yield 1445 unique reflections, 982 of which, having $I \geqslant 3\sigma(I)$, were considered to be observed. Three nearly orthogonal standard reflections monitored every hour showed no significant variation over the data collection period.

Intensity data were processed with a modified program written by Hornstra and Stubbe (*9*). Background corrected intensities were assigned standard deviations according to:

$$\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (PI)^2]^{1/2},$$

where CT is the total integrated peak count obtained in scan time t_c, B_1, and B_2 are background counts each obtained in time $\frac{1}{2}t_b$ and $I = CT - (t_c/t_b)(B_1 + B_2)$; P was selected as 0.04 and introduces a 4% uncertainty to account for machine errors. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. Due to the small size and irregular shape of the crystal no absorption correction was applied ($\mu R = 0.57$). The atomic scattering factors for neutral atoms were taken from Ref. (*10*), and were corrected for anomalous dispersion (*11*).

All calculations were carried out on the Monash University CDC 3200 and B6700 computers using programs that have been referred to previously (*4*).

Structure solution and refinement. The structure was solved by conventional Patterson methods for the tantalum atom positions, and the potassium atom was located in the subsequent Fourier difference synthesis. The conventional R value at this stage was 0.21 and $R_w = 0.23 \cdot [R = \sum \|F_o| - |F_c\|/\sum |F_o|$ and

$$R_w = \sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o||.$$

Refinement of an overall scale factor followed by a Fourier difference synthesis enabled the

TABLE I

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	x/a	y/b	z/c	U_{11}[b]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta(1)	1615(2)	622(1)	765(1)	75(4)	17(4)	22(4)	−2(4)	2(4)	0(4)
Ta(2)	3431(2)	3659(1)	1370(1)	83(4)	18(4)	23(4)	0(3)	5(4)	12(4)
Ta(3)	3349(3)	7500	0	74(6)	14(6)	26(5)	−6(4)	0	0
K(1)	2056(20)	6744(10)	2500	358(59)	258(49)	70(36)	−113(125)	0	0
O(1)	90(3)	484(2)	138(1)	7(4)					
O(2)	127(3)	218(2)	126(1)	7(3)					
O(3)	124(3)	604(2)	−4(1)	1(3)					
O(4)	369(4)	346(2)	250	6(5)					
O(5)	366(3)	373(2)	12(1)	9(4)					
O(6)	408(3)	−4(2)	136(1)	9(4)					
O(7)	394(3)	749(2)	111(1)	4(3)					

[a] Metal parameters are × 10^4, oxygen × 10^3.

[b] The anisotropic temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$.

positions of the seven oxygen atoms to be determined. Refinement was continued by the block-diagonal least-squares technique and anisotropic thermal parameters were introduced for the tantalum and potassium atoms. Finally, after five cycles of full-matrix least-squares refinement the calculations converged with $R = 0.053$ and $R_w = 0.052$, using the weighting scheme $w = 1/\sigma^2(F)$. Final atomic parameters and their estimated standard deviations are given in Table I[1], and selected interatomic distances in Table II.

Discussion

The structure of KTa_5O_{13} consists of edge- and corner-shared TaO_6 octahedra joined in such a way as to produce slabs of α-PbO_2 type

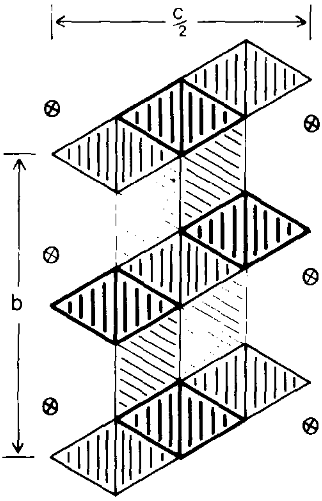

FIG. 1. The idealized structure of KTa_5O_{13} drawn to emphasize the α-PbO_2 nature of the slabs of octahedra. Potassium sites marked ⊗.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

		Oxygen–Oxygen (<3.0 Å)	
Ta(1)–O(6)	1.86(2)		
O(2)	1.87(2)	O(1)–O(3)	2.72(2)
O(1)^{1a}	1.95(2)	O(3)^{4c}	2.73(2)
O(5)^{b}	2.01(2)	O(2)^{a}	2.80(2)
O(3)^{1a}	2.15(2)	O(6)^{a}	2.82(2)
O(3)^{b}	2.17(2)	O(6)^{3a}	2.84(2)
---O(7)^{2a}	3.26(2)	O(4)	2.86(3)
		O(2)	2.86(2)
Ta(2)–O(1)	1.91(2)	O(5)	2.89(2)
O(4)	1.92(0)		
O(6)^{3a}	1.98(2)	O(2)–O(7)^{2a}	2.74(2)
O(7)^{2a}	1.99(2)	O(4)	2.85(2)
O(2)	2.01(2)	O(5)^{b}	2.85(2)
O(5)	2.10(2)	O(6)	2.87(2)
---O(3)^{4c}	3.48(2)	O(3)^{1a}	2.87(2)
		O(5)	2.87(2)
Ta(3)–O(7)	1.90(2)	O(7)^{1a}	2.98(2)
O(7)^{4b}	1.90(2)		
O(3)	1.97(2)	O(3)–O(3)^{4c}	2.64(2)
O(3)^{4b}	1.97(2)	O(5)^{4c}	2.79(2)
O(5)^{5c}	2.15(2)	O(5)	2.84(2)
O(5)^{3a}	2.15(2)	O(7)^{4b}	2.84(2)
---O(2)^{4c}	3.37(2)	O(5)^{5c}	2.89(2)
---O(2)^{a}	3.37(2)	O(7)	2.91(2)
		O(6)^{b}	2.95(2)
K(1)–O(7)	2.69(2)		
O(7)^{d}	2.69(2)	O(4)–O(6)^{3a}	2.80(3)
O(1)	2.85(2)	O(6)^{3e}	2.80(3)
O(1)^{d}	2.85(2)	O(7)^{2a}	2.88(2)
O(2)^{a}	2.85(2)	O(7)^{2e}	2.88(2)
O(2)^{e}	2.85(2)		
O(4)^{3a}	3.03(3)	O(5)–O(7)^{2a}	2.53(2)
---O(6)^{3a}	3.47(2)	O(5)^{b}	2.67(2)
---O(6)^{3e}	3.47(2)	O(6)^{3a}	2.78(2)
		O(5)–O(7)^{5c}	2.80(2)
		O(6)^{b}	2.87(2)
		O(6)–O(7)^{1}	2.68(2)
		O(7)^{2a}	2.96(3)

[a] Numbers indicate unit-cell relationship and letters indicate equivalent position transformation. (1) 0, −, 0; (2) +, −, 0; (3) +, 0, 0; (4) 0, +, 0; (5) +, +, 0. (a) $\bar{x}, \frac{1}{2} + y, z$; (b) $x, \frac{1}{2} - y, \bar{z}$; (c) $\bar{x}, \bar{y}, \bar{z}$; (d) $x, y, \frac{1}{2} - z$; (e) $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.

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[1] A table of observed and calculated structure factors has been deposited as Document No. NAPS-03182 with the ASIS National Auxiliary Publications Service, C/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York, 10017, U.S.A. A copy may be obtained by citing the document number and by remitting \$5.00 for photocopies or \$3.00 for microfiche. Advanced payment is required. Make check or money order payable to "Microfiche Publications."

structure.[2] Figure 1 is drawn to emphasize the α-PbO_2 nature of the slabs, and Fig. 2 shows the manner in which these slabs are joined by corner-sharing of octahedra along the crystallographic mirror plane leaving tunnels in which the potassium ions are situated. The tunnels extend through the structure in the ab plane at $c = 0$ and $\frac{1}{2}$, and are not interconnected in the c direction. Interatomic distances are within the range usually observed for niobium and tantalum compounds (see Table II and Ref. (*3*)). For the tantalum octahedra the Ta–O distances range from 1.86–2.17 (mean 2.00) Å, and for the seven coordinate potassium ions the K–O distances range from 2.69–3.03 (mean 2.83) Å. The next nearest-neighbor oxygen atoms at 3.47 Å are considered to be outside the coordination sphere of potassium. The numbering scheme used is shown in Fig. 3. The shortest oxygen–oxygen distance, O(5) to O(7) is 2.53(2) Å and is the shared edge of the Ta(2) and Ta(3) octahedra.

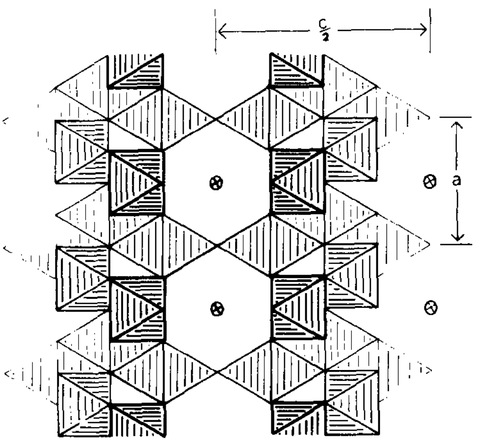

FIG. 2. The idealized KTa_5O_{13} structure showing the potassium ions ⊗ situated in the tunnels. The tunnels are bisected by a mirror plane that is considered to be the twin plane in this "chemically twinned" α-PbO_2 type structure.

The structure of *M*–$LiTa_3O_8$ reported earlier (*12*) has an octahedral arrangement based on that of α-PbO_2, but in this case the lithium ions are sufficiently small to occupy octahedral sites. In KTa_5O_{13} the potassium ions

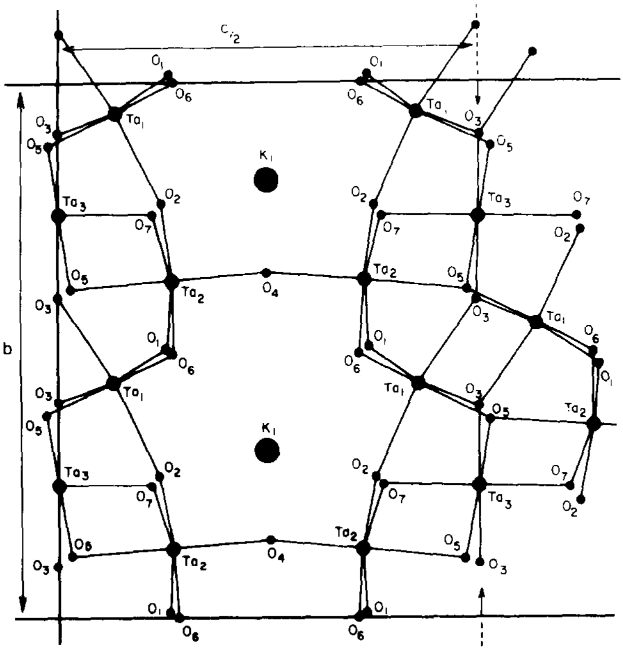

FIG. 3. The numbering scheme used for KTa_5O_{13}.

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[2] Our attention was drawn to this relationship by Dr. S. Andersson, University of Lund, Sweden.

require a higher coordination and occur between slabs (mirror related) of α-PbO_2-type structure. This results in a structure that in Andersson and Hyde's (*13*) terms may be described as a 'chemically twinned' structure, with the potassium ions occupying sites created at the twin boundary, in the manner described for KTi_3NbO_9 (*13*). It is possible that by varying the width of the slabs of octahedra and the nature of the M^+ ion that compounds with useful conductivity properties may result.

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