

Crystal Structures of Some Niobium and Tantalum Oxides.

VII. $K_{4+5x}Ta_{16-x}O_{42}$ ($x \approx 0.3$)

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$K_{4+5x}Ta_{16-x}O_{42}$ crystallizes in the hexagonal system with unit-cell dimensions (from single-crystal data) $a = 9.085(6)$, $c = 12.254(8)$ Å and space group $P6_3/mcm$, $Z = 1$. The structure was solved by Patterson and Fourier techniques and refinement by full-matrix least-squares methods using 271 reflections, measured by counter techniques, with $I \geq 3.5\sigma(I)$, resulted in an R of 0.060 ($R_w = 0.051$). The structure consists of units of six octahedra, edge- and corner-shared to one another, that are linked by corner sharing through a single octahedron. This structure provided the "key" to other structures in the $K_2O:Ta_2O_5$ and $Rb_2O:Nb_2O_5$ systems. Its significance in this respect is discussed.

Introduction

As part of a systematic study of alkali metal niobium and tantalum oxide systems two phases that are probably only metastable were observed in the $K_2O:Ta_2O_5$ system (1). The structures of a number of alkali metal niobium and tantalum oxides, namely, $M-LiTa_3O_8$ (2), the $4Rb_2O:11Nb_2O_5$ phase (3), $K_6Ta_{10.8}O_{30}$ (4), KTa_5O_{13} (5), and $H-LiTa_3O_8$ (6), were studied recently, and the structure of the $\sim 1:3$ ($K_2O:Ta_2O_5$) low-temperature metastable phase is reported here. A brief preliminary report was made elsewhere (7).

Experimental

An approximately spherical fragment, less than 0.03 mm in diameter, was selected from a crushed hexagonal prism obtained from a small sample kindly supplied by Dr. R. S. Roth of the National Bureau of Standards, Washington, D.C. (1). The following data

were determined using a Philips PW 1100 computer-controlled diffractometer. Unit-cell parameters were determined as previously described (3).

Crystal data. $K_{5.5}Ta_{15.7}O_{42}$, $M = 3727.9$, hexagonal, $a = 9.085(6)$, $c = 12.254(8)$ Å, $U = 875.9$ Å³. $D_c = 7.07$ g cm⁻³ ($Z = 1$). Insufficient material was available to enable the density to be determined. $F(000) = 1586.2$, $\mu = 474.9$ cm⁻¹ for $MoK\alpha$ radiation ($\lambda = 0.7107$ Å). Systematic absences were observed for $h\bar{h}0l$, $l = 2n + 1$, and the Laue symmetry was determined to be $6/mmm$. This information is consistent with the space groups $P6_3/mcm$, $P\bar{6}c2$, and $P6_3cm$. Successful refinement confirmed the space group as $P6_3/mcm$.

Intensity measurements. Intensity measurements were made using the Philips PW 1100 diffractometer with graphite monochromated $MoK\alpha$ radiation ($\lambda = 0.7107$ Å). A total of 2806 reflections was counter-measured out to θ ($MoK\alpha$) = 30.0°, operating in an ω -scan mode with a symmetric scan range of $\pm 0.45^\circ$ in θ (with an

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allowance for dispersion) from the calculated Bragg scattering angle at a scan rate of $0.05^\circ \text{ sec.}^{-1}$. The data were averaged assuming the centric space group $P6_3/mcm$, and yielded 492 unique reflections, 271 of which, having $I \geq 3.5\sigma(I)$, were considered to be observed. Three axial standard reflections monitored every 2 hr showed no significant variation over the data-collection period.

The data were processed with a modified program supplied with the diffractometer (8). The background-corrected intensities were assigned standard deviations according to $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (\rho I)^2]^{1/2}$, 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 $I = CT - (t_c/t_b)(B_1 + B_2)$; ρ 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 irregular shape of the fragment of crystal, used of necessity for the data collection, no absorption correction was applied. Insufficient material was available for a piezoelectric or second harmonic generation test.

Atomic scattering factors for neutral atoms were used (9) and were corrected for anomalous dispersion (10). Initial calculations were performed on a CDC 3200 computer; final calculations on a B 6700. Both computers are at Monash University. The major program used was that of Sheldrick (11).

Structure Solution and Refinement

Due to initial programming restrictions, the structure solution was commenced in the orthorhombic space group $Cmcm$ (the orthorhombic equivalent of the hexagonal space group $P6_3/mcm$). Solution of the Patterson synthesis gave three Ta positions and subsequent difference Fourier syntheses revealed the K and O positions. The coordinates for all atoms were then transformed

into their hexagonal equivalents and least-squares refinement was commenced. After several cycles using isotropic thermal parameters R was 0.110 [$R = \sum ||F_0| - |F_c|| / \sum |F_0|$]. Full occupancy of all sites resulted in the formula $K_6Ta_{16}O_{42}$ that is cation rich. An electron microprobe analysis was obtained, and assuming that tantalum was not reduced and that the oxygen framework was intact the formula was calculated as $K_{5.5}Ta_{15.7}O_{42}$. Refinement using this formula and allowing the Ta occupancies to vary showed that the Ta(2) site was fully occupied and that the Ta(1) site occupancy refined to a value that agreed with the analysis; the R value dropped from 0.11 to 0.099. Introduction of anisotropic thermal parameters for the cations followed by further refinement resulted in convergence of the structure analysis with R 0.060 and R_w 0.051, $w = 3.1/\sigma^2$. [$R_w = \sum w^{1/2}(|F_0| - |F_c|) / \sum w^{1/2}|F_0|$]. The 002 reflection was considered to be extinction affected and was omitted from the final refinement cycles. Final atomic parameters and their estimated standard deviations are given in Table I,¹ and selected interatomic distances in Table II.

Discussion

The structure is shown in Fig. 1 and consists of units of six octahedra linked by edge- and corner-sharing in a highly condensed manner. Three of these units of six share two oxygens each with a single octahedron that thereby links the units into a sheet. The sheets are joined to one another by corner-sharing through 0(1) to form an

¹ A table of observed and calculated structure factors has been deposited as Document NAPS No. 03339. A copy may be obtained by citing the document number and by remitting \$05.00 for photocopies or \$03.00 for microfiche. Make check or money order payable to "Microfiche Publications," and send to ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017.

TABLE I

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Mult	<i>U</i> ₁₁ ^b	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ta(1)	2461(2)	0	965(2)	0.4875	123(7)	15(8)	45(7)	8(4)	-2(9)	0
Ta(2)	$\frac{1}{3}$	$\frac{2}{3}$	0	0.1667	49(9)	49(9)	79(15)	24(4)	0	0
K	5892(17)	0	$\frac{1}{4}$	0.2292	61(58)	158(89)	244(97)	79(44)	0	0
O(1)	2090(48)	0	$\frac{1}{4}$	0.25	86(107)					
O(2)	7992(35)	0	681(25)	0.5	85(79)					
O(3)	1687(29)	4820(29)	967(21)	1.0	143(51)					

^a Standard deviations ($\times 10^4$) are given in parentheses.

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

infinite three-dimensional structure. The potassium ions are situated within these sheets in ten-coordinate sites at the intersections of pairs of mirror planes. There are no tunnels, as such, in this structure.

The partially occupied Ta(1) octahedron that forms the units of six octahedra is considerably distorted, having bond lengths from 1.91(1) to 2.09(1) Å, whereas the fully occupied Ta(2) octahedron is regular in shape with six Ta-O distances of 1.99(2) Å.

It was thought initially that the unit of six octahedra had been observed for the first time (7). However, it was realised that the

structure is, in fact, basically the same as the octahedral framework observed by Evans and Katz (12) for the section from $z = 0.45$ to $z = 0.60$ in $Ba_{6+x}Nb_{14}Si_4O_{47}$. Shortly after the preliminary report (7) of the structure described here was received, a series of compounds of general formula $A_3M_8O_{21}$ was reported (13) (where $A = K, Ba$; $M = Nb, Ti, Cr, Fe, Ni, Mg$ and Zn); the structure had been determined using X-ray powder data and is very similar to that reported here. The composition of the niobium analog of the compound reported here was given as $K_6Nb_{16}O_{42}$ ($K_3Nb_8O_{21}$) and clearly, as the compound was black, some of the Nb^V had been reduced to Nb^{IV} . The known resistance of tantalum to reduction (1) has resulted in partial occupancy of the sites occupied by Ta(1) and K. The deficiency of tantalum is made up by potassium ions and electrical neutrality is maintained. The formula, expressed as $K_{4+5x}Ta_{16-x}O_{42}$ ($x \approx 0.3$), indicates the nonstoichiometric nature of this compound ($K_{5.5}Ta_{15.7}O_{42}$), and is slightly removed from the 1:3 composition that would be $K_{5.25}Ta_{15.75}O_{42}$.

A further series of compounds isostructural with the compound reported here has been described recently (14).

Finally, it is of interest to note that solution of this structure with its units of six octahedra provided the "key" to the solution of three considerably more complex materials. These

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) WITH THEIR ESTIMATED STANDARD DEVIATIONS^{a,b}

Metal-metal		Metal-oxygen	
(i) Corner-shared octahedra		Ta(1)-O(1)	1.91(1)
		-O(3) ^I	1.91(2)
Ta(1)-Ta(1) ^I	3.872(4)	-O(2) ^{III}	2.06(3)
Ta(1)-Ta(2) ^I	3.687(2)	-O(2) ^{IV}	2.09(1)
(ii) Edge-shared octahedra		Ta(2)-O(3)	1.99(2)
Ta(1)-Ta(1) ^{II}		K-O(3) ^I	2.88(3)
3.254(3)		-O(2)	2.93(3)
		-O(3) ^V	3.19(3)
		-O(1) ^V	3.23(1)
		-O(1)	3.45(5)

^a Standard deviations are given in parentheses.

^b I: $y-x, -x, z$; II: $y, y-x, -z$; III: $1-x, -y, -z$; IV: $1+y-x, 1-x, z$; V: $1-y, x-y, z$.

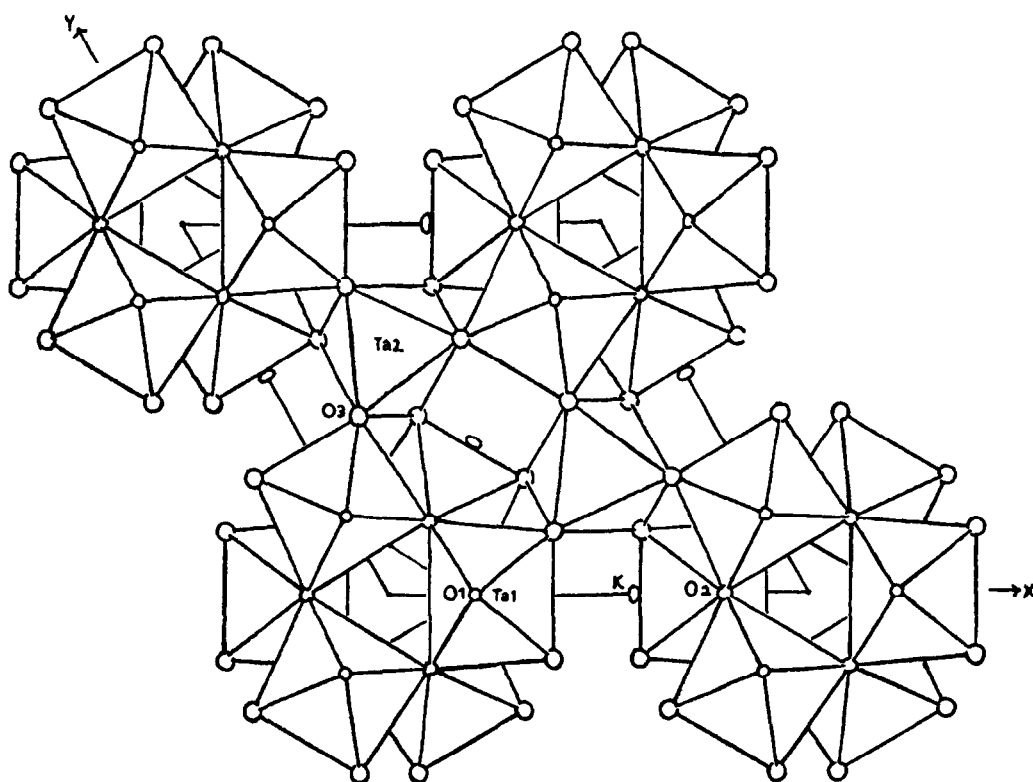


FIG. 1. The structure of $K_{5.5}Ta_{15.7}O_{42}$.

were the $4Rb_2O:11Nb_2O_5$ phase (3), the $\sim 26.2:73.8$ $K_2O:Ta_2O_5$ phase (15), and the $\sim 26.5:73.5$ $K_2O:Ta_2O_5$ phase (15); these compounds were all prepared during a comprehensive study of alkali oxide-metal oxide (Nb_2O_5 and Ta_2O_5) systems (1).

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