

Crystal Structures of Some Niobium and Tantalum Oxides. VIII. The $5\text{Rb}_2\text{O} \cdot 14.6\text{Ta}_2\text{O}_5$ Phase—A Tunnel Structure

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$\text{Rb}_{10}\text{Ta}_{29.20}\text{O}_{78}$ crystallizes in the hexagonal system with unit-cell dimensions (from single-crystal data) $a = 7.503(4) \text{ \AA}$, $c = 36.348(4) \text{ \AA}$, and space group $P6_3/mmc$, $z = 1$. The structure was solved using three-dimensional Patterson and Fourier techniques. Of the 666 unique reflections measured by counter techniques, 515 with $I \geq 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.057 ($R_w = 0.039$). The structure of $\text{Rb}_{10}\text{Ta}_{29.20}\text{O}_{78}$ consists of layers of corner-sharing groups of six edge-shared octahedra separated by layers of single octahedra and double hexagonal tungsten bronze-like layers, these layers being perpendicular to the hexagonal c -axis. Nine-coordinate tricapped trigonal prismatic sites between the hexagonal tungsten bronze-like layers are partially occupied by Ta(V) ions.

Introduction

During a general study of compounds formed between alkali metal oxides and niobium and tantalum pentoxides, in a search for materials with ionic conductivity, a number of crystalline phases was reported (1). Using specimens prepared during the above study single-crystal structure determinations have been carried out on the following compounds: $\text{Rb}_{12.20}\text{Nb}_{33.56}\text{O}_{90}$ (the $4\text{Rb}_2\text{O} \cdot 11\text{Nb}_2\text{O}_5$ phase) (2), $\text{K}_6\text{Ta}_{10.8}\text{O}_{30}$ (3), $\text{KTa}_5\text{O}_{13}$ (4), and $\text{K}_{5.5}\text{Ta}_{15.7}\text{O}_{42}$ (5).

Three compounds, designated the 9-, 11-, and 16-layer hexagonal bronzes, were shown to exist in the $\text{K}_2\text{O} \cdot \text{Ta}_2\text{O}_5$ system (1); the 4:11 ($\text{Rb}_2\text{O} \cdot \text{Nb}_2\text{O}_5$) phase corresponds with the 11-layer material, and all three have been the objects of a parallel, independent high-resolution electron microscopy study (6).

Crystals of composition corresponding to the nine-layer compound, but in the $\text{Rb}_2\text{O} \cdot \text{Ta}_2\text{O}_5$ system were prepared by

Minor *et al.* (7) using MoO_3 as a flux and were kindly supplied by Dr. R. S. Roth, National Bureau of Standards, Washington D. C. We report here the results of a single-crystal structure determination on this material. A brief description of this structure was published earlier (2). A model for the structure, based on X-ray powder work, was deduced during a parallel independent study of these systems (B. Raveau, private communication (8)).

Experimental Details

A colorless prismatic crystal with developed faces 100 , 010 , $1\bar{1}0$, 001 and of dimensions $0.01 \times 0.03 \times 0.02 \times 0.03 \text{ mm}$ was chosen for this study. The data following were determined using a Philips PW 1100 four-circle automatic diffractometer. Least-squares refinement of 2θ values obtained for 20 centered high-angle reflections gave the hexagonal cell parameter $a = 7.503(4) \text{ \AA}$, $c = 36.348(4) \text{ \AA}$.

Crystal Data

$\text{Rb}_{10}\text{Ta}_{29.20}\text{O}_{78}$, $M = 7386.44$, hexagonal, $a = 7.503(4) \text{ \AA}$, $c = 36.348(4) \text{ \AA}$, $U = 1772.07$; $D_c = 6.92$ ($Z = 1$) $\text{g}\cdot\text{cm}^{-3}$; $F(000) = 3125.6$, $\mu = 497.90 \text{ cm}^{-1}$ for $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). Systematic absences observed were $hh\bar{2}hl$, $l = 2n + 1$, and Laue symmetry of $6/mmm$ was observed. This information is consistent with the space groups $P6_3/mmc$, $P\bar{6}2c$, $P6_3mc$. Successful refinement was accomplished in the space group $P6_3/mmc$.

Intensity Measurements

Intensities were collected with graphite monochromated $\text{MoK}\alpha$ radiation. A θ - 2θ scan, $3^\circ < \theta < 25^\circ$, was used with a variable scan width given by $\Delta\theta = (0.9 + 0.3 \tan \theta)$ at a scan rate of $0.02^\circ \text{ sec}^{-1}$. A total of 6307 reflections were collected. These were averaged to yield 666 unique reflections, 515 of which, having $I \geq 3\sigma(I)$, were considered to be observed. Three standard reflections monitored every 2 hr showed no significant variation over the data collection period.

Intensity data were processed with a modified program of Hornstra and Stubbe (9). Background corrected intensities were assigned standard deviations according to $\sigma(I) = [CT + (t_c/t_b)^2(B_1 + B_2) + (\rho I)^2]^{1/2}$, 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 introduced a 4% uncertainty to account for machine errors. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects; the data were also corrected for absorption. The atomic scattering factors for neutral atoms, and the corrections for anomalous dispersion, were taken from Ref. (10). All calculations were performed on the Monash University Burroughs 6700 computer; the major program used was that due to Sheldrick (11).

Structure Solution and Refinement

The structure was solved for the main structural tantalum atom positions based upon the knowledge of the structure of the $4\text{Rb}_2\text{O}:11\text{Nb}_2\text{O}_5$ phase (2), noting that the 0, 0, 12 reflection was strong, thus indicating 12 layers of metal atoms, and a consideration of space group symmetry. Based on these considerations, the following tantalum atom positions were deduced: Ta(1), 0, 0, 0.12; Ta(2), $\frac{1}{6}$, $\frac{1}{3}$, 0.04; Ta(3), $-\frac{1}{6}$, $-\frac{1}{3}$, 0.20. These tantalum positions were assigned full occupancy and a thermal parameter (U) of 0.01 \AA^2 , and structure factors were calculated resulting in a conventional R of 0.391, [$R = \sum ||F_o| - |F_c|| / \sum |F_o|$]. A difference Fourier synthesis, calculated at this stage, revealed the oxygen atom positions and four other atomic positions. Three of these positions were assigned to rubidium, Rb(1) and Rb(3) being given full occupancy, the position designated Rb(2) (Table 1) being given an occupancy one-third of the 12k site it occupies because of its close proximity to a 4f site. The fourth position (Ta(4), Table 1) was assigned to tantalum, because the bond lengths are too short for Rb (Table I) with an occupancy of 0.6 to maintain overall charge balance. Full-matrix least-squares refinement of positional and isotropic thermal parameters gave an R of 0.097.

Refinement with anisotropic thermal parameters for all metal atoms and isotropic thermal parameters for the oxygen atoms gave an R of 0.057. At this stage the occupation factors for Ta(4), Rb(1), Rb(2), and Rb(3) were allowed to refine together with all other variables. The resulting occupation factor figures from this refinement were Ta(4), 0.61(2), Rb(1), 0.99(4), Rb(2), 0.32(1), and Rb(3), 1.04(4); this resulted in an R of 0.056. To maintain charge balance the occupation factors of these four sites were fixed at those values given in Table I and the resulting R factors after three cycles

TABLE I
FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES^a

Atom	x/a	y/b	z/c	Position	U_{11}^b	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	0	0	0.1178(1)	4e	0.0046(7)	0.0046(7)	0.0021(12)	0.0023(3)	0	0
Ta(2)	0.1670(2)	0.3340(3)	0.0343(1)	12k	0.0033(6)	0.0025(8)	0.0046(7)	0.0013(4)	-0.0005(4)	-0.0009(8)
Ta(3)	0.8278(2)	0.6556(3)	0.1965(1)	12k	0.0072(6)	0.0111(10)	0.0107(8)	0.0055(5)	0.0029(4)	0.0058(8)
Ta(4)	0	0	$\frac{1}{4}$	2b(0.6)	0.0056(18)	0.0056(18)	0.0013(32)	0.0028(9)	0	0
Rb(1)	$\frac{2}{3}$	$\frac{1}{3}$	0.0816(4)	4f	0.0608(45)	0.0608(45)	0.1073(102)	0.0304(22)	0	0
Rb(2)	0.3038(10)	0.6075(20)	0.1389(5)	12k(0.33)	0.0521(94)	0.0203(101)	0.0553(87)	0.0102(51)	0.0096(38)	0.0193(75)
Rb(3)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	2c	0.0354(43)	0.0354(43)	0.0272(66)	0.0177(22)	0	0
O(1)	0.1263(17)	0.2525(35)	0.0816(8)	12k	0.0063(57)					
O(2)	0.8757(20)	0.7513(39)	0.1446(8)	12k	0.0137(71)					
O(3)	0.4483(18)	0.8966(35)	0.0360(7)	12k	0.0011(52)					
O(4)	0.8581(19)	0.7161(38)	0.0215(6)	12k	0.0049(64)					
O(5)	0.8078(30)	0.6156(60)	$\frac{1}{4}$	6h	0.0183(98)					
O(6)	0.5404(19)	0.0809(38)	0.1861(8)	12k	0.0116(66)					
O(7)	0.1193(20)	0.2385(39)	0.2919(8)	12k	0.0105(67)					

^a Dependent parameter relationships in this refinement were: sites 2b, 2c, 4e, 4f, $U_{11} = U_{22} = 2U_{12}$; 6h, $y = 2x$; 12k, $y = 2x$, $U_{22} = 2U_{12}$, $U_{23} = 2U_{13}$.

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

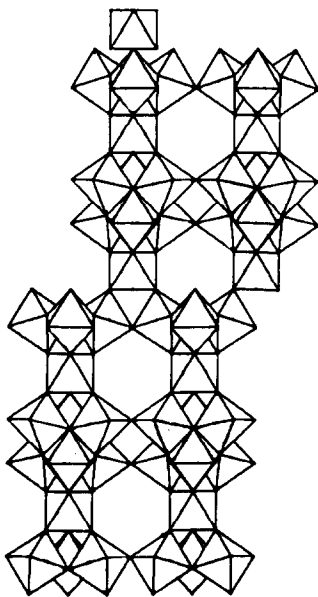


FIG. 1. The structure of $\text{Rb}_{12.20}\text{Nb}_{33.56}\text{O}_{90}$ illustrating the means by which the columns of octahedra are joined to one another.

layers, thus forming double HTB layers (Fig. 2). The columns in both structures are joined by corner sharing of octahedra (as shown in Fig. 1 for the 11-layer compound) to produce three-dimensional structures containing intersecting tunnels, parallel to the xy plane, in which the alkali metal ions are located. For a fuller appreciation of the structure the reader is referred to the diagrams given in Ref. (8).

The structure appears to be stabilized, and to attain electrical neutrality, by the presence of tantalum (Ta(4)) in the nine-coordinate tricapped trigonal prismatic (ttp) sites formed between the double HTB layers. Occupation of sites of this type was observed for compounds of niobium and tantalum adopting the HTB and the tetragonal tungsten bronze (TTB) structures earlier (3, 12), and is strongly supported by the high-resolution electron microscopy study recently reported (6).

This description differs from that of Michel *et al.* (8), in that from Fourier and difference

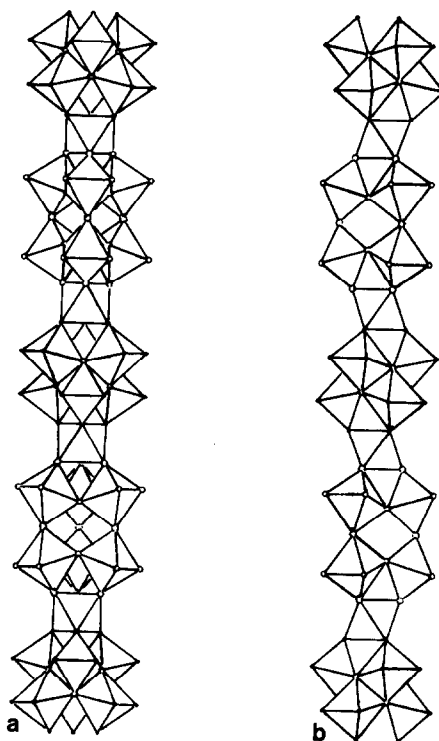


FIG. 2. The structure of $\text{Rb}_{10}\text{Ta}_{29.20}\text{O}_{78}$ viewed (a) perpendicular to the yz plane and (b) viewed down the x axis.

Fourier maps no evidence was obtained for Ta(4) in the $2b$ site to be shifted from that site, nor was there evidence for any electron density in the $4f$ site of Michel *et al.*

Interatomic distances are within the range usually observed for niobium and tantalum compounds. The shortest Ta-Ta distance occurs between the nine-coordinate Ta(4) and Ta(3), 2.965(2) Å. In the TTB analog in the $\text{K}_2\text{O}-\text{Ta}_2\text{O}_5$ system, $\text{K}_6\text{Ta}_{10.8}\text{O}_{30}$ (3), the distances from Ta(3) in the ttp site to neighboring octahedral tantalum atoms are Ta(1)-Ta(3), 2.911(3) Å, and Ta(2)-Ta(3), 2.995(3) Å, values that span the distance observed here.

Within the highly condensed unit of six octahedra the edge-shared distance Ta(2)-Ta(2) is 3.304(2) Å, comparing very favorably with the Nb(3)-Nb(3) distance of 3.308(1) Å in the "11-layer" material.

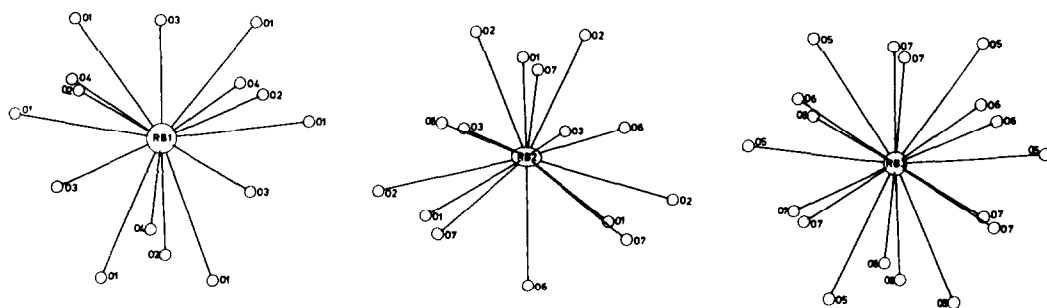


FIG. 3. The coordination polyhedra of Rb(1), Rb(2), and Rb(3) in $\text{Rb}_{10}\text{Ta}_{29.20}\text{O}_{78}$.

The rubidium ions occupy three sites within the tunnels formed in the rigid tantalum octahedra framework; Rb(1) and Rb(3) fully occupy $4f$ and $2c$ sites, respectively, and Rb(2) partially occupies a $12k$ site. The Rb–O distances range from 3.05(3) to 3.97(3) Å, taking the coordination distance out to 4.00 Å. Rb(1) and Rb(2) are considered to be 15-coordinate, whereas Rb(3) has 18 distances to oxygen less than 4.00 Å. The coordination of each rubidium atom is shown in Fig. 3. Also the thermal parameters for Rb are comparatively high which is consistent with the measured ionic exchange properties of this material (7).

In view of the long c -axis dimension (65.12 Å) of the so-called "16-layer" (24 metal atom layers) material and the fact that its structure has been deduced from the electron microscopy study (6) the single-crystal X-ray diffraction work on this compound (2) has been discontinued.

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