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Crystal Structures of Some Niobium and Tantalum Oxides. II. The $4Rb_2O:11Nb_2O_5$ Phase—A Tunnel Structure

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$Rb_{12.20}Nb_{33.56}O_{90}$ crystallizes in the trigonal system with unit-cell dimensions (from single-crystal data) $a = 7.527(6)$, $c = 43.17(2)$ Å and space group $R\bar{3}m$, $z = 1$. The structure was solved using three-dimensional Patterson and Fourier techniques. Of the 843 unique reflections measured by counter techniques, 675 with $I \geqslant 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.072 ($wR = 0.055$). The structure of $Rb_{12.20}Nb_{33.56}O_{90}$ consists of layers of corner-sharing groups of six edge-shared octahedra separated by pyrochlore-like layers of octahedra. The structure can be considered to be derived from that of pyrochlore by the ordered omission of layers of single octahedra.

Introduction

During a general study of compounds formed between alkali metal oxides and niobium and tantalum pentoxides, the so-called 9-, 11-, and 16-layer hexagonal bronzes were reported for the K_2O–Ta_2O_5 system (*1*). Crystals of composition corresponding to the 11-layer compound but in the Rb_2O–Nb_2O_5 system were kindly supplied by Dr. R. S. Roth, National Bureau of Standards, Washington, D.C., and we report here the results of a single-crystal structure determination on this material.

Experimental Details

A colorless hexagonal-shaped crystal was selected from the small sample supplied and crushed; a fragment, approximately spherical in shape and 0.1 mm in diameter was chosen for this study and mounted on a quartz capillary using "araldite." The data following were determined using a Philips P.W. 1100 computer-controlled diffractometer. Unit-cell parameters were determined with a standard diffractometer computer program that investigates rows in the reciprocal lattice through the origin and scans the highest weighted reflections and their antireflections (weighted by intensity and sin θ). The centers of gravity of the eight profiles so determined are then used in a least-squares refinement of the d-spacing for that row.

Crystal Data

$Rb_{12.20}Nb_{33.56}O_{90}$, $M = 5600.59$, Trigonal, $a = 7.527(6)$, $c = 43.17(2)$ Å, $U = 2118.15$ Å^3. $Dc = 4.39$ g cm^{-3} ($z = 1$). $Dm = 4.40(5)$ (Ref. (*7*)). $F(000) = 2547$, $\mu = 117.1$ cm^{-1} for Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å). Systematic absences observed were hkl, $-h + k + l = 3n$ and Laue symmetry of $\bar{3}m$. This information is consistent with the trigonal space groups $R\bar{3}m$, $R3m$, or $R32$. Successful refinement confirmed the space group as $R\bar{3}m$.

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* Following the preparation of this manuscript a paper by Madeleine Gasperin (Acta Crystallogr., *B* **33**, 398 (1977)) appeared, in which the structure is reported for the composition $A^{+}_{12}B^{5+}_{33}O_{88.5}$. The structure has the same octahedral framework as that reported here but we do not observe the oxygen deficiency and the Tl^+ positions in the tunnels differ slightly from those of Rb^+ found in this work.

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Intensity Measurements

Intensity measurements were made using the Philips P.W. 1100 computer-controlled diffractometer with graphite monochromated Mo$K\alpha$ radiation ($\lambda = 0.7107$ Å) up to $\theta = 30°$ operating in a θ–2θ scan mode with a symmetric scan range of $\pm 1.40°$ in 2θ from the calculated Bragg scattering angle at a scan rate of $0.03°\ \mathrm{sec}^{-1}$. A total of 4173 reflections were collected. These were averaged to yield 843 unique reflections, 675 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 of Hornstra and Stubbe (*2*). 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 irregular shape of the fragment of crystal used of necessity for the data collection, no absorption correction was applied. The atomic scattering factors for neutral atoms were taken from Ref. (*3*) and were corrected for anomalous dispersion using values from Ref. (*4*). All calculations were performed on the Monash University CDC 3200 and B 6700 computers. The major program used was that due to Sheldrick (*5*).

Structure Solution and Refinement

The structure was solved for the niobium atom positions by a judicious combination of the Patterson synthesis and intuitive model building based upon knowledge of the structure of $K_6Ta_{15.6}O_{42}$ and that of the hexagonal tungsten bronze (HTB)-like compound, $KTa_{3.4}O_9$ (*6*). The $a(b)$ unit-cell dimension indicated the relationship to the HTB structure, and corner sharing of octahedra along the c-axis direction gives approximately 11 layers of metal atoms as discussed by Roth *et al.* (*1*). However, the trigonal nature of the space group required the layering to be a multiple of 3, i.e., 12 or 15. Examination of the reflection data showed that the 0 0 12 reflection was weak, whereas 0 0 15 was strong, thus suggesting 15 layers of metal atoms, which results in an average octahedral repeat distance of ~2.9 Å. It was evident that the structure would consist of at least a partially condensed octahedral model as in $K_6Ta_{15.6}O_{42}$ (*6*), and in retrospect the strongest reflection (0 0 21) indicated the total number of oxygen-alone and oxygen–metal layers.

Based on the above considerations and $R\bar{3}m$ symmetry, the following niobium positions were deduced: Nb(1) $\frac{1}{2}$, 0, 0; Nb(2) 0, 0, 0.4, and Nb(3) $\frac{1}{6}$, $-\frac{1}{6}$, 0.14. The niobium atoms were assigned the correct occupancy factors, a thermal parameter (U) of 0.02 Å^2, and structure factors were calculated resulting in a conventional R of 0.395 [$R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$]. A difference Fourier synthesis, calculated at this stage, revealed the oxygen atom positions and one Rb atom position. Refinement, using the full-matrix least-squares technique, of positional and isotropic thermal parameters gave an R of 0.163. At this stage of the analysis the formula was "$Rb_6Nb_{33}O_{90}$" with the Rb position fully occupied; the charge imbalance being nine positive charges. Subsequent analysis and refinement revealed further Rb sites at Rb(2) and Rb(3), the relative occupancy being determined by refinement), these two apparently being alternative sites over which six rubidium atoms are distributed, resulting in the composition $Rb_{12}Nb_{33}O_{90}$. Further electron density located in the tunnels in this structure in a number of sites, but not sufficiently well defined to justify or enable refinement of the small amount of density located there (two to three electrons in each case) is thought to be due to the remaining

TABLE I

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x/a	y/b	z/c	Mult.	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	0.5	0.0	0.0	0.25	0.0361(9)	0.0181(10)	0.0150(8)	0.0090(5)	0.0038(4)	0.0077(8)
Nb(2)	0.0	0.0	0.40014(4)	0.1667	0.0112(6)	0.0112(6)	0.0020(8)	0.0056(3)	0.0	0.0
Nb(3)	0.1657(1)	−0.1657(1)	0.13788(2)	0.5	0.0057(3)	0.0057(3)	0.0053(4)	0.0030(4)	0.0002(2)	−0.0002(2)
Rb(1)	0.0	0.0	0.2313(1)	0.1667	0.0541(15)	0.0541(15)	0.0868(33)	0.0270(8)	0.0	0.0
Rb(2)	0.0488(10)	−0.0488(10)	−0.0473(4)	0.11	0.0598(44)	0.0598(44)	0.0394(65)	0.0267(65)	0.0147(40)	−0.0147(40)
Rb(3)	0.0	0.0	0.0452(8)	0.0567	0.0545(92)	0.0545(92)	0.0910(190)	0.0272(46)	0.0	0.0
O(1)	0.2080(6)	−0.2080(6)	−0.0084(2)	0.5	0.0098(17)					
O(2)	0.4567(6)	−0.4567(6)	0.0440(2)	0.5	0.0092(17)					
O(3)	0.2103(7)	−0.2103(7)	0.0975(2)	0.5	0.0109(18)					
O(4)	0.4753(6)	−0.4753(6)	0.1473(2)	0.5	0.0083(17)					
O(5)	−0.1165(7)	0.1165(7)	0.1359(2)	0.5	0.0104(17)					

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

TABLE II

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

Metal–Metal		Metal–Oxygen	
(i) Corner-shared octahedra		Nb(1)–O(2)^{bI}	1.982(8)
Nb(1)–Nb(2)^{II}	3.610(1)	–O(1)	1.993(4)
Nb(3)–Nb(3)^{I}	3.742(1)	Nb(2)–O(2)^{III}	1.885(7)
Nb(1)–Nb(1)^{aI}	3.763(0)	–O(3)^{III}	2.082(7)
Nb(2)–Nb(3)^{III}	3.769(2)	Nb(3)–O(3)	1.838(8)
Nb(3)–Nb(3)^{bI}	3.785(1)	–O(5)^{I}	1.924(5)
		–O(4)^{bI}	2.079(4)
(ii) Edge-shared octahedra		–O(4)^{b}	2.105(9)
Nb(3)–Nb(3)^{IV}	3.308(1)	Rb(1)–O(4)^{bV}	3.169(7)
		–O(5)^{cV}	3.183(7)
(iii) Across the six-octahedra unit		–O(2)^{bV}	3.71(1)
		Rb(2)–O(1)^{VI}	2.98(1)
Nb(3)–Nb(3)^{II}	4.995(1)	–O(3)	3.02(2)
		–O(1)	3.18(2)
		–O(2)^{bI}	3.23(1)
		–O(1)^{VII}	3.75(1)
		–O(3)^{I}	3.79(2)
		Rb(3)–O(1)^{VI}	3.14(2)
		–O(3)	3.55(2)
		–O(1)	3.57(2)

a: +, 0, 0; b: 0, –, 0; c: –, 0, 0.
I $\bar{y}, x-y, z$; II $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$;
III $\frac{2}{3}-x-y, \frac{1}{3}-x, \frac{1}{3}+z$;
IV $\frac{2}{3}+y, \frac{1}{3}-x+y, \frac{1}{3}-z$;
V $\frac{2}{3}-x, \frac{1}{3}-y, \frac{1}{3}-z$;
VI $y, y-x, -z$; VII $-x, -y, -z$.

[d] Nb(1) forms the hexagonal tungsten bronzelike layer; Nb(2) forms the layer of single octahedra; Nb(3) forms the double layer of units of six octahedra.

Rb and Nb corresponding to the formula for the 4:11 phase (*7*, *8*) based on 90 oxygen atoms, $Rb_{12.20}Nb_{33.56}O_{90}$. No evidence was found for partial occupancy by niobium or oxygen in the framework of the structure and the partial occupancy of rubidium ions in this compound is felt to be consistent with its ability to act as a cation exchange material (*9*).

The final weighted R, $R_\omega = [\Sigma\omega^{1/2}(|F_0| - |F_c|(/\Sigma\omega^{1/2}|F_0|]$ was 0.055, $\omega = 1/\sigma^2$, $R = 0.072$, and resulted from the use of anisotropic thermal parameters for all metal atoms and isotropic thermal parameters for the oxygen atoms in full-matrix least-squares refinement. Final atomic parameters and their estimated standard deviations are given in Table I,[1] and selected interatomic distances in Table II.

Discussion

The first indication that a solution might be obtained for this relatively complex structure occurred when the structure of $K_6Ta_{15.6}O_{42}$ was solved (*6*). At that time it was mistakenly thought that the basic unit (Fig. 1) of six edge- and corner-shared octahedra had been observed for the first time, the structure reported is, in fact, the same as the octahedral framework reported by Evans and Katz (*10*) for the section from $z = 0.45$ to $z = 0.60$ in $Ba_{6+x}Nb_{14}Si_4O_{47}$), and is identical to that reported several weeks later (*11*) for the family of niobium oxides $A_3M_8O_{21}$. It is interesting to note that the compound $K_3Nb_8O_{21}$ ($K_6Nb_{16}O_{42}$) contains Nb(IV) as evidenced by its black color, whereas in the tantalum analog reduction to Ta(IV) is strongly resisted resulting in partial occupancy. Groult *et al.* (*11*) report the composition $K_3Nb_7TiO_{21}$ ($K_6Nb_{14}Ti_2O_{42}$) white in color, with full occupancy by the transition elements in an unreduced state.

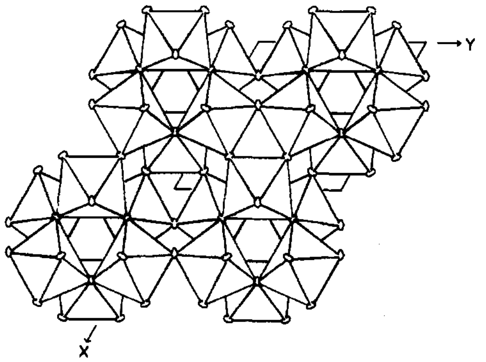

FIG. 1

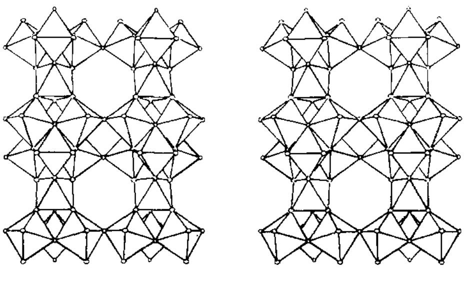

FIG. 2

Whereas, in the structures discussed above, the groups of six octahedra are separated by single octahedra in forming a sheet, in the compound reported here, the six-octahedra groups share corners resulting in a highly condensed layer (Fig. 1). These layers can be considered to be separated from one another in the *c*-axis direction in two ways (Fig. 2), either in terms of a layer of single octahedra followed by an HTB layer and then a second single octahedra layer (this description relates to the structure of the $A_2M_7O_{18}$ compounds (*12*)), or in terms of a layer of pyrochlore-type structure three octahedra deep. The latter description is probably the more informative of the two.

As a result of the stacking of these layers tunnels, of the pyrochlore type, are present within the framework of octahedra perpendicular to the *c*-axis and running in the 1 0 0, 0 1 0, and 1 1 0 directions. The tunnels do not pass through the double layers, but are interconnected through the HTB layers. The rubidium ions are located in the tunnels and can be replaced by cation exchange with other alkali metal ions (*9*).

Unbeknownst to us Michel *et al.* (*12*) had, in a study of cation exchange materials, deduced the identical structure for the composition $Rb_{12}Nb_{30}W_3O_{90}$, deriving the model from the structure of $A_2M_7O_{18}$ and pyrochlore $A_2B_2O_6(A_2M_4O_{10})$ layers, as described in the preceding paper. The atomic parameters listed in Table I were supplied to Michel *et al.* to

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[1] A table of observed and calculated structure factors has been deposited as Document NAPS-03074 with the ASIS National Auxiliary Publications Service c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. A copy may be secured by citing the document number and by remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make check or money order payable to "Microfiche Publications."

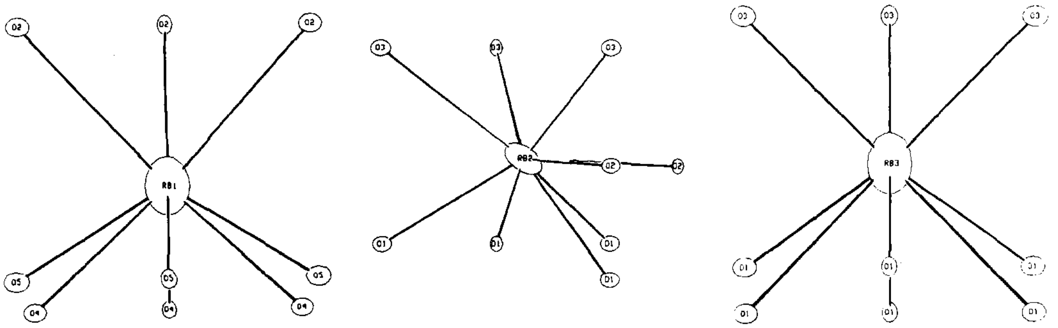

FIG. 3

enable calculation of intensities for the X-ray powder data listed in their paper. The presence of W(VI) enabled these authors to avoid the problems reported here with Rb^+ ions randomly distributed in the tunnels. There is no possibility that M(VI) ions are present in the material used in this study as the crystals were prepared by the Czochralski method (*9*).

Interatomic distances are within the range usually observed for niobium and tantalum compounds. The shortest Nb–Nb distance (3.308(1)) occurs in the unit of six octahedra in which, of necessity, the octahedra are considerably distorted. The Nb–O distances range from 1.838–2.105 Å and no unusual distances are found. The rubidium ions are present as irregular nine-coordinate polyhedra (Fig. 3) in the tunnels in the structure, with the Rb–O distances as set out in Table II.

This composition, referred to as the "11-layer" bronze in several publications (*1*, *6*), should be designated the 15-layer compound as it contains 15-metal-atom layers.

The so-called "9-layer" composition (*1*) should be known as the 12-layer compound as it contains 12-metal-atom layers. Its structure (*13*) consists of the sequence double layer–single octahedra layer–HTB layer–HTB layer–single octahedra layer–double layer and appears to be stabilized to some extent by the presence of a 9-coordinate Ta(V) ion between the two HTB layers as has been reported for other compositions in the alkali-metal oxide–niobium (or tantalum) pentoxide systems (*6*, *14*). We are also currently examining the so-called "16-layer bronze" phase.

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