Crystal Structures of Some Niobium and Tantalum Oxides. III* $K_6Ta_{10.8}O_{30}$—A Partially "Filled" Tetragonal Tungsten Bronze-Like Structure

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$K_6Ta_{10.8}O_{30}$ crystallizes in the tetragonal system with unit-cell dimensions $a = 12.579(6)$, $c = 3.978(2)$ Å, and space group $P4/mbm$, $z = 1$. The calculated and measured densities are 7.04 and 7.00(2) g cm^{-3}, respectively. The structure was solved using conventional methods; of 539 unique reflections measured by countermethods, 435 that obeyed the condition $I \geqslant 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.038 ($wR = 0.036$). Basically, the structure is of the tetragonal tungsten bronze-type ($K_6Ta_{10.8}O_{30} = 10 \times K_{0.6}Ta_{1.08}O_3$) with the additional tantalum in nine-coordinate (tricapped trigonal prismatic) sites. The presence of the additional tantalum (Ta^{5+}) enables this framework, frequently met for M^{6+} compounds, to attain electrical neutrality.

Introduction

Considerable attention has been given to phase equilibria studies in the K_2O–Ta_2O_5 system. Reisman *et al.* (*1*) identified four intermediate phases in this system, but no attempts were made to determine the unit-cell dimensions or index with X-ray powder patterns. Sawaguchi and Kikuchi (*2*), using powder diffraction methods, reported the tetragonal bronze-type structure for $K_2O:2Ta_2O_5$ with a range of composition. No structural study was made by these authors, however, owing to a space group ambiguity and a lack of a sufficiently large single crystal. The tetragonal bronze structure was also reported by Whiston and Smith (*3*) for the 1:2 composition, but with the *a*-axis tripled.

As a result of these inconsistencies Roth *et al.* (*4*) reinvestigated the KTaO₃–Ta₂O₅ system and produced crystals suitable for a single-crystal structure determination. This work describes the detailed structure of the compound known as the 1:2 phase in the $K_2O:Ta_2O_5$ system. A preliminary report of this structure was made elsewhere (*5*).

Experimental

The crystals used in this study were kindly supplied by Dr. R. S. Roth, National Bureau of Standards, Washington, D.C., and were grown by vapor evaporation at 1400°C (*4*). A small colorless tetragonal needle-like crystal (0.025 × 0.025 × 0.038 mm) was selected using a polarizing microscope and mounted on a silica capillary using "Araldite." Preliminary oscillation and Weissenberg photography indicated that the crystal was tetragonal and that no unusual effects, such as doubling of axes, were present. Accurate unit-cell parameters were obtained using a Philips

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* The paper by B. M. Gatehouse, T. Negas, and R. S. Roth, *J. Solid State Chem.* 18, 1–7 (1976) is considered as Part I in this series.

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PW 1100 single-crystal diffractometer (MoK$_\alpha$ radiation), which, using a standard program, investigates rows in the reciprocal lattice through the origin and scans the four highest weighted reflections and their antireflections (weighted by intensity and sin θ). The centres of gravity of these eight profiles are then used in a least-squares refinement of the d-spacing for that row.

The crystal used for the data collection was analyzed by dispersive X-ray analysis with a scanning electron microscope and by electron probe microanalysis. The standards used were orthoclase (KAlSi$_3$O$_8$, 13.65% K) and Spec pure Tantalum (Ta 99.99%). Spot counts and scans over the crystal confirmed that the relative amounts of K$_2$O and Ta$_2$O$_5$ were 10.6% and 89.4% by weight, respectively, corresponding to the formula, K$_6$Ta$_{10.8}$O$_{30}$. No examination has been made of the possible variation of symmetry with temperature in these laboratories. The amount of material available was insufficient to enable examination for second harmonic generation (eight very small crystals).

Crystal Data

K$_6$Ta$_{10.8}$O$_{30}$, $M = 2668.8$, tetragonal, $a = 12.569(6)$, $c = 3.978(2)$ Å, $U = 629.4$ Å^3, $Dc = 7.04$ g cm^{-3}, $Dm = 7.00(2)$ g cm^{-3} (Ref. (6)), $z = 1$, $\mu = 458.1$ cm^{-1} for MoK$_\alpha$ radiation ($\lambda = 0.7107$ Å). Systematic absences observed were $0kl$ for $k = 2n + 1$, indicating space groups $P4/mbm$ (D_{4h}^5), $P4bm$ (C_{4v}^2), or $P\bar{4}b2$ (D_{2d}^7); $P4/mbm$ was selected from final refinement.

Intensity Measurement

Intensity measurements were made with the crystal and diffractometer described above using graphite monochromated Mo–K$_\alpha$ radiation. A unique data set was collected out to 2θ(MoK$_\alpha$) $= 60°$ using the θ–2θ scan technique with a symmetric scan range of $\pm 0.5°$ in 2θ from the calculated scattering angle at a scan rate of $0.0168°$ sec^{-1}. No reflection was sufficiently intense to warrant the insertion of

an attenuation filter. Of 856 reflections measured by this technique, data reduction produced for $P4/mbm$ and $P4bm$ 539, and for $P\bar{4}b2$ 856 unique reflections; of these, 435 for the first two space groups, and 666 for the third one, were considered to be significantly above the background [$I \geqslant 3\sigma(I)$] and only these were used in the refinement. Three standard reflections monitored at 2-hour intervals showed no significant variation in intensity.

The data were processed using a program written specifically for the Philips diffractometer (7). The 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 a scan time t_c; B_1 and B_2 are background counts each obtained in $\frac{1}{2}t_b$, and $I = CT - (t_c/t_b)(B_1 + B_2)$, p was given the value 0.04 and is a term included to allow for "machine errors." Values of I and $\sigma(I)$ were then corrected for Lorentz and polarization effects. Since the plane of reflection of the graphite monochromator is perpendicular to that of the specimen crystal, the Lorentz-polarization correction was:

$$(Lp)^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/$$
$$(\cos^2 2\theta + \cos^2 2\theta_m)$$

where m is the Bragg angle of the monochromator.

An absorption correction was applied to the data for each space group ($\mu R = 0.72$) following the calculation of direction cosines for the reflection data. No extinction correction was applied although in the later stages of refinement it became apparent that the 0 0 1 and 0 0 2 reflections were severely affected by extinction. These reflections were omitted in the final refinement stages. The scattering factors for neutral atoms were taken from Ref. (8) and corrected for anomalous dispersion (9). All calculations were performed on the Monash University CDC 3200 and

B6700 computers; the major program used was that due to Sheldrick (10) and direction cosines were calculated using a program written by Taylor (11) for the PW 1100 diffractometer.

Structure Solution and Refinement

The unit-cell dimensions and systematic absences indicated that the structure of this compound was very similar to that of the tetragonal potassium tungsten bronze reported by Magnéli (12), with the tungsten(VI) replaced by tantalum(V). Inspection of the Patterson synthesis confirmed this similarity and refinement was commenced using tantalum atom positions derived from the tungsten bronze model. Several cycles of full-matrix least-squares refinement, in which the function $\Sigma\omega(|F_o| - |F_c|)^2$ was minimized (F_o and F_c are the observed and calculated structure amplitudes, respectively, and ω is the weight of each individual reflection and is equal to $1/\sigma^2(F)$) followed by difference Fourier synthesis led to the location of potassium and oxygen atoms. An additional peak in the difference Fourier synthesis, observed following the first tantalum only calculation, was assigned as tantalum and given an isotropic temperature factor similar to that of the other tantalum atoms. The occupany of this site was then varied.

Refinement was carried out initially in space group $P4/mbm$ and converged smoothly, using anisotropic thermal parameters for the metal atoms, isotropic thermal parameters for oxygen atoms (32 parameters varied, including one scale factor), to $R = 0.038$ and $R_\omega = 0.036$.

$$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$$

and

$$R_\omega = [\Sigma\omega^{1/2}(||F_o| - |F_c||)/\Sigma\omega^{1/2}|F_c|].$$

Refinement was attempted in $P\bar{4}b2$ and $P4bm$ (40 parameters and 45 parameters varied, respectively) but problems were encountered

with nonpositive definite thermal parameters for some of the tantalum and potassium atoms. The structure is reported here in space group $P4/mbm$. The final parameters with their estimated standard deviations in parentheses are given in Table I.[1]

Description of the Structure

The tetragonal tungsten bronze structure, first reported by Magnéli (12), consists of an assemblage of corner-shared MO_6 octahedra (M is commonly Ti, Nb, Ta, or W) arranged in a manner that results in the presence of three types of interstitial sites in which a variety of cations can be accommodated. The composition and resulting properties of a number of these compounds were summarized by Jamieson *et al.* (13) and the occupancy of
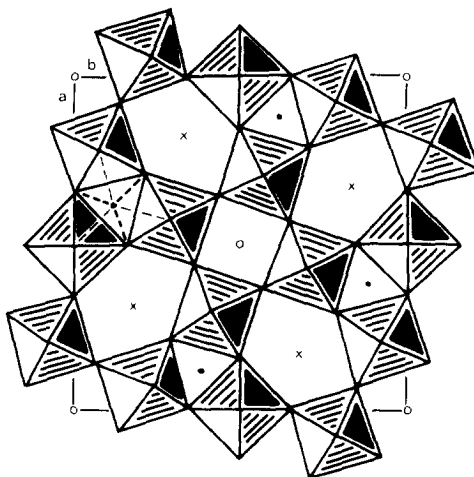

FIG. 1. The structure of $K_6Ta_{10.8}O_{30}$ viewed down the c-axis. Open circles indicate K(1) in the $A1$ sites, crosses indicate K(2) in the A2 sites, and solid circles Ta(3) O(2)

[1] A table of observed and calculated structure factors has been deposited as Document No. NAPS–03103 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 remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make check or money order payable to "Microfiche Publications."

TABLE I

FINAL ATOMIC PARAMETERS ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS[a] IN PARENTHESES

Atom	x/a	y/b	z/c	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	0	5000	5000	127(4)	127(4)	121(8)	−75(5)	0	0
Ta(2)	761(1)	2079(1)	5000	65(3)	64(3)	168(4)	7(2)	0	0
Ta(3)[c]	1195(3)	3805(3)	0	95(13)	95(13)	51(21)	8(16)	0	0
K(1)	0	0	0	117(19)	117(19)	35(31)	0	0	0
K(2)	3270(3)	1730(3)	0	291(20)	291(20)	82(26)	−144(25)	0	0
O(1)	0	5000	0	11(5)					
O(2)	764(11)	2096(11)	0	17(3)					
O(3)	2101(9)	2899(9)	5000	12(3)					
O(4)	−4(14)	3449(12)	5000	30(4)					
O(5)	1418(9)	672(9)	5000	8(2)					

[a] These refer here, and in subsequent tables, to the least significant digits.

[b] The anisotropic temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

[c] Multiplier for Ta(3) was 0.050(1) giving 0.2 Ta per site, 0.8 total in cell.

the various sites discussed. In terms of the description used by the authors cited above (13), in the structure reported here K(1) occupies the A1 site, K(2) the A2 site, Ta(1) the B1 site, and Ta(2) the B2 site. Ta(3) fractionally occupies the C site, and in so doing provides
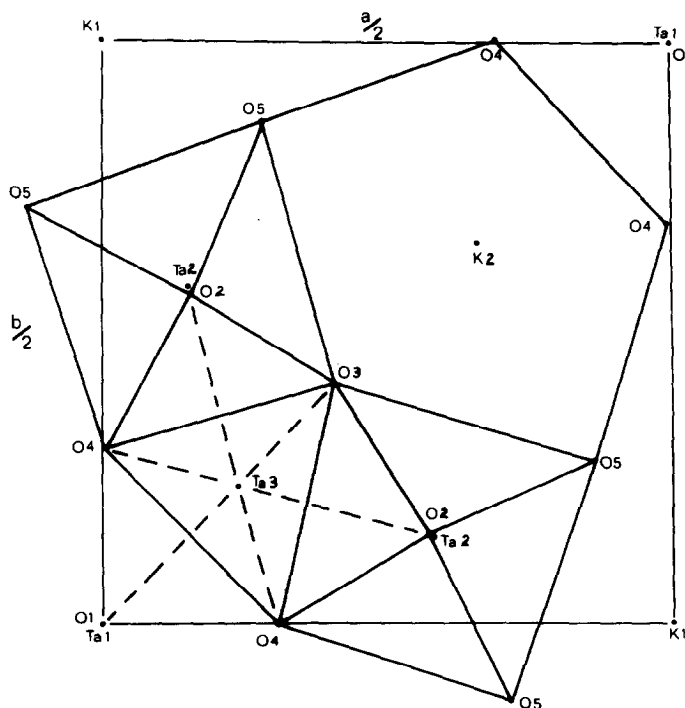

FIG. 2. The numbering scheme used in the determination of the $K_6Ta_{10.8}O_{30}$ structure given for one-quarter of the unit-cell projected down the c-axis.

TABLE II

SELECTED INTERATOMIC DISTANCES AND ANGLES WITH ESTIMATED STANDARD
DEVIATIONS IN PARENTHESES (Å)

Ta(1)	Ta(3)	2.911(3)		K(1)	O(5)	2.802(8)	[8]
	Ta(2)	3.797(1)			O(2)	2.81(1)	[4]
	K(2)[a]	3.664(3)					
Ta(2)	Ta(3)	2.995(3)		K(2)	O(3)	2.878(9)	[2]
	Ta(2)[b]	3.843(1)			O(4)[d]	2.95(1)	[4]
	Ta(2)[a]	3.938(2)			O(1)[c]	3.078(4)	
	K(1)	3.422(1)			O(2)	3.19(1)	[2]
	K(2)	3.756(3)					
Ta(3)	K(2)	3.691(5)		K(2)	O(5)	3.34(1)	[4]
	K(2)[a]	3.740(5)			O(2)[d]	3.47(1)	[2]
Ta(1)	O(1)	1.989(0)	[2][e]				
	O(4)	1.95(2)	[4]				
Ta(2)	O(5)	1.95(1)					
	O(4)	1.97(2)					
	O(3)	1.98(1)					
	O(2)	1.989(0)	[2]				
	O(5)[a]	1.99(1)					
Ta(3)	O(1)	2.126(4)					
	O(2)	2.22(1)	[2]				
	O(4)	2.54(1)	[4]				
	O(3)[c]	2.560(8)	[2]				

[a] $-y, x, z.$
[b] $\frac{1}{2} - y, \frac{1}{2} - x, z.$
[c] $x, y, -1 + z.$
[d] $y, -x, z.$
[e] [ ] indicates the number of contacts of this distance and type.

the additional positive charge necessary for this M^{5+} structure. The structure is illustrated in Fig. 1 and the numbering scheme used in Fig. 2.

K(1) fully occupies the cube-octahedral $A1$ site with K–O bond lengths of 2.802 and 2.81 Å. Interatomic distances are set out in Table II. K(2) fully occupies the $A2$ site that may be described as a tricapped trigonal prism with additional longer contacts. The bonded K–O distances range from 2.878 to 3.19 Å (mean 3.03 Å) with nonbonded distances of 3.34 and 3.47 Å. These distances may be compared with those for $Ba_{0.27}Sr_{0.75}$-$Nb_2O_{5.78}$ (13) in which Ba/Sr bonded distances range from 2.707–2.87 Å (mean 2.826 Å) with nonbonded distances of 3.21 and 3.48 Å,

and with those of other compounds (Table III).

Ta(1) and Ta(2) fully occupy octahedral sites, the mean Ta–O distance in the two octahedra is 1.97 Å compared with 1.967 Å for Nb(1) and 1.981 Å for Nb(2) in $Ba_{0.27}Sr_{0.75}$-$Nb_{5.78}$ (13). The O–Ta–O octahedral axes are parallel, within the errors, to the c-axis.

Ta(3) partially occupies the so-called C site with distorted tricapped trigonal prismatic coordination. The mean Ta–O distance is 2.43 Å with a range over the nine contacts from 2.126–2.560 Å. The M^V–O distances in a number of niobium and tantalum compounds are listed in Table III together with the M^I–O distances. The longest octahedral distance is 2.47 Å in N–Nb_2O_5, and the longest trigonal prismatic distance of 2.62 Å is

TABLE III

INTERATOMIC DISTANCES IN SOME NIOBIUM AND TANTALUM MIXED OXIDES

Compound	M^V–O (Å)		M^1–O (Å)		
	Range	Mean	Range	Mean	Ref.*
H–Nb_2O_5	1.73–2.31	2.00			a
$NaNb_6O_{15}F$	1.75–2.13(oct)†	1.98	2.62—2.80	2.72	b
	1.96–2.13(pbp)	2.03			
$NaNb_{13}O_{33}$	1.71–2.39	2.00	2.59	2.59	c
$GaNbO_4$	1.797–2.333	2.031	—	—	d
N–Nb_2O_5	1.73–2.47	2.01	—	—	e
L–$LiNb_3O_8$	1.818–2.320	2.005	2.076–2.343	2.188	f
L–$LiNb_3O_8$	1.825–2.327	2.053	2.056–2.350	2.187	g
$Bi_3Nb_{17}O_{47}$	1.48–2.46(oct)	1.98	—	—	h
	1.65–2.29(pbp)	2.05			
$Rb_{12.2}Nb_{33.56}O_{30}$	1.982–2.105	1.988	2.98–3.79	3.367	i
M–$LiTa_3O_8$	1.85–2.25	1.99	2.02–2.41	2.18	j
$KTa_{3.4}O_9$	1.88–2.04(oct)	1.96	2.96–3.74	3.38	k
	1.90–2.62(tbp)	2.32			
H–$LiTa_3O_8$	1.89–2.08(oct)	1.96	—	—	l
	1.92–2.15(pbp)				
KTa_5O_{13}	1.86–2.18	1.99	2.85–3.02	2.83	m

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i G. D. Fallon and B. M. Gatehouse, *J. Solid State Chem.*, in press.

j B. M. Gatehouse, T. Negas, and R. S. Roth, *J. Solid State Chem.* 18 (1976).

k, l, m See Ref. (5).

† oct = octahedron, pbp = pentagonal bipyramid, tbp = trigonal bipyramid.

found in $KTa_{3.4}O_9$ (5), the hexagonal tungsten bronze analog of the compound reported here. An earlier observation of this coordination for Nb^{5+} was made (14) for $RbNb_{3.4}O_9$.

It is suggested that occupancy of the C-tricapped trigonal prismatic sites in the tetragonal and hexagonal tungsten bronze structures, when formed by Nb or Ta oxides and alkali metal oxides, and in which the $A1$ and $A2$ sites are fully occupied by M^+, is the means by which these compounds achieve electrical neutrality.

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