JOURNAL OF SOLID STATE CHEMISTRY 39, 1–6 (1981)

Preparation and Structure Refinement of KTi_3TaO_9 and $K_3TiTa_7O_{21}$

B. M. GATEHOUSE* AND M. C. NESBIT

Department of Chemistry, Monash University,
Clayton, Victoria 3168, Australia

Received August 13, 1980; in final form October 27, 1980

KTi_3TaO_9 crystallizes in the orthorhombic system with unit-cell dimensions $a = 6.392(2)$, $b = 3.793(1)$, $c = 14.877(4)$ Å, $z = 2$ and space group *Pnmm*. $K_3TiTa_7O_{21}$ crystallizes in the hexagonal system with unit-cell dimensions $a = 9.095(3)$, $c = 12.063(4)$ Å, $z = 2$ and space group $P6_3/mcm$. The structures were solved by conventional Patterson and Fourier techniques, the former, using 283 unique reflections ($I \geq 3\sigma(I)$), was refined by full-matrix least-squares techniques to an R of 0.0551 (R_w = 0.0496), the latter, using 343 unique reflections ($I \geq 3\sigma(I)$), was refined using the same technique to an R of 0.0354 (R_w = 0.0279). Intensity data were measured using counter methods and the "ω" scan technique. KTi_3TaO_9 is isostructural with KTi_3NbO_9, whose structure was previously derived from powder data; and $K_3TiTa_7O_{21}$ adopts the same structure as found for the nonstoichiometric phase $K_{5.5}Ta_{15.7}O_{42}$ in this laboratory. Both materials were obtained as single crystals by the use of a flux in their preparation. The distribution of titanium and tantalum over the octahedral sites is discussed relative to previously determined structures.

Introduction

Early interest in the system $K_2O:TiO_2:M_2O_5$ (M = Nb, Ta) resulted in the preparation and characterization of two phases, $KTiNbO_5$ and KTi_3NbO_9 (*1*). A third phase in this system, $KTi_2Nb_5O_{17}$, was prepared in this laboratory, and the structure of the analogous titanotantalate determined (*2*). During the study of the related $M^I_2O:M^V_2O_5$ system (*3*) (M^I = K, Rb; M^V = Nb, Ta) the structure of the nonstoichiometric phase $K_{5.5}Ta_{15.7}O_{42}$ was determined (*4*) and its relationships to the structure of $K_3TiTa_7O_{21}$, proposed from powder diffraction studies, was noted (*5*). The preparation and structural refinements of a family of compounds that exhibit the structure observed for $KTiNbO_5$ have been reported (*6*).

A growing interest in the preparation, from fluxes, of single-crystal materials within this system and in the variable distribution of titanium and tantalum in the octahedral sites of these structures prompted further investigation. As part of the systematic study of $K_2O:TiO_2:Ta_2O_5$ system high-quality single crystals of KTi_3TaO_9 and $K_3TiTa_7O_{21}$ were prepared in the presence of a flux. We report here the preparation, structure determination, and refinement of KTi_3TaO_9 and $K_3TiTa_7O_{21}$.

Experimental

Heating a 1 : 1 : 1 mole ratio of $K_2O:TiO_2:Ta_2O_5$ to 1000°C for 48 hr in an open platinum crucible using V_2O_5 (~20%) as a flux produced two crystalline products; $KTi_2Ta_5O_{17}$, the subject of an earlier report (*2*), and hexagonal prisms of $K_3TiTa_7O_{21}$.

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* To whom correspondence should be addressed.

0022-4596/81/100001-06$02.00/0

No crystalline or microcrystalline material that could be the $K_2O:TiO_2:Ta_2O_5$ phase was observed.

KTi_3TaO_9 was prepared by firing at 1000°C for 48 hr in a platinum crucible an intimately mixed 1-g charge of $K_2O:TiO_2:Ta_2O_5$ in the mole ratio 1:2:3 with MoO_3 (~20%) present as a flux. Two crystalline materials were observed from this preparation, $KTi_2Ta_5O_{17}$ and clear, thin plate-like crystals of KTi_3TaO_9. No material corresponding to $K_2O:2TiO_2:3Ta_2O_5$ was observed.

A scanning electron microscope fitted with an energy-dispersive analyzer was used to qualitatively test all crystalline products for the presence of the flux elements, molybdenum in KTi_3TaO_9, and vanadium in $K_3TiTa_7O_{21}$. No trace of flux material was observed.

Single crystals of each phase were selected, a plate (0.04 × 0.04 × 0.02 mm) of KTi_3TaO_9 and a prism (0.01 × 0.01 × 0.02 mm) of $K_3TiTa_7O_{21}$, checked for cracking and twinning using a polarizing microscope, and mounted on quartz capillaries using Resiweld. Accurate cell dimensions and all data were obtained using a Philips PW1100 automatic four-circle diffractometer.

TABLE I

CRYSTAL DATA

	KTi_3TaO_9	$K_3TiTa_7O_{21}$
MW	507.74	1767.80
Crystal System	orthorhombic	hexagonal
a (Å)	6.392(2)	9.095(3)
b (Å)	3.793(1)	
c (Å)	14.877(4)	12.063(4)
Space group	$Pnmm^a$	$P6_3/mcm$
V (Å^3)	360.69	864.15
z	2	2
D_c (g/cm^3)	4.67	6.79
μ (cm^{-1})	180.98	434.74
$F(000)$	459.85	1515.24
λ (Å)	Mo$K\alpha$ (0.7107)	Mo$K\alpha$ (0.7107)
Systematic, absences	$0kl, k + l = 2n + 1$ $0k0, k = 2n + 1$ $00l, l = 2n + 1$	$h\bar{h}0l, l = 2n + 1$
Possible space groups	$Pnmm^{a,b}$ $Pn2_1m$	$P6_3/mcm^b$ $P\bar{6}c2$ $P6_3cm$

[a] Space group in nonstandard setting as adopted by Wadsley.

[b] Space group as selected from final refinement.

TABLE II

DATA COLLECTION PARAMETERS

	KTi_3TaO_9	$K_3TiTa_7O_{21}$
θ limits (°)	$3 \leq \theta \leq 30$	$3 \leq \theta \leq 30$
Scan type	ω	ω
Scan width (°)	1.40, 0.30	1.10, 0.30
Scan Speed (°/sec)	0.05	0.05
No. reflections	618	486
$I \geq 3\sigma(I)$	283	343
R^a	0.0551	0.0354
$R_\omega{}^b$	0.0496	0.0279

[a] $R = \Sigma \,||F_o| - |F_c|| / \Sigma |F_o|$.

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

All crystal data are given in Table I.

Intensity Measurements

All intensity measurements were made with the diffractometer and crystals described above using graphite monochromated Mo$K\alpha$ radiation. Data collection parameters are in Table II.

In each data collection three standard reflections were monitored at 90-min intervals and showed no systematic variation in intensity.

All data were processed using a program written specifically for the Philips diffractometer (*7*). Lorentz and polarization corrections were applied in a manner described previously (*4*) and the data satisfying the condition $I \geq 3\sigma(I)$ were used in subsequent structure solutions and refinements. Corrections for absorption effects were applied to each set of reflection data. The scattering factors for neutral atoms were taken from Ref. (*8*) and corrected for anomalous dispersion (*9*). All calculations were carried out on the Monash University B6700 computer, the major program was that due to Sheldrick (*10*).

Structure Solutions

KTi_3TaO_9

The structure was solved by conventional Patterson and Fourier techniques. The metal atom sites were initially assumed to be occupied by the $\frac{1}{4}(3Ti + Ta)$ hybrids as suggested by Wadsley (*1*). Refinement of the complete model with isotropic thermal parameters produced an R value of 0.184. It was evident that the two metal atom sites contained different distributions of titanium and tantalum in a manner similar to that observed in $KTi_2Ta_5O_{17}$ (*2*). The large atomic-weight difference between titanium and tantalum made impossible least-squares refinement of the site occupation factors. Consequently they were manually adjusted to minimize the peak height in the difference Fourier synthesis and to retain a uniform set of thermal parameters consistent with a minimization of R factor. The number of oxygen and potassium atoms observed in the difference Fourier synthesis defined the number of positive charges within the structure to be distributed between titanium and tantalum atoms. The empirical formula, which contains four metal atoms with total positive charge of 17, was unambiguously determined as KTi_3TaO_9.

$K_3TiTa_7O_{21}$

The structure solution of $K_3TiTa_7O_{21}$ was obtained by essentially the same method. Refinement of the model obtained from the Patterson and difference Fourier syntheses resulted in $R = 0.109$. Site occupation factors and the titanium and tantalum distributions were derived in the same manner as for KTi_3TaO_9. Final refinement of positional and thermal parameters, anisotropic for all metal atoms and isotropic for oxygen, using data corrected for absorption and weighted by a factor $w(w = (1/\sigma)^2)$ yielded final R and R_w values of 0.0334 and 0.0279, respectively. Final atomic parameters are given in Table V[1] with selected interatomic bond lengths in Table VI.

TABLE III

POSITION AND THERMAL PARAMETERS FOR KTi_3TaO_9 ($\times 10^4$, OXYGEN ATOM PARAMETERS $\times 10^3$)

Atom	x/a	y/b	z/c	Occupancy	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	2718(18)	2500(0)	7500(0)	2500	282(53)	192(43)	192(51)	0(0)	0(0)	0(0)
*B*1	2595(4)	2500(0)	1301(2)	2100(0) 2900(0)[b]	36(8)	38(7)	106(10)	0(0)	5(11)	0(0)
*B*2	8074(5)	2500(0)	412(2)	400(0) 4600(0)[b]	54(17)	34(17)	23(23)	0(0)	13(13)	0(0)
O1	263(3)	750(0)	951(1)	500(0)	6(3)					
O2	145(3)	250(0)	−9(1)	500(0)	7(4)					
O3	−39(3)	250(0)	148(1)	500(0)	11(4)					
O4	323(4)	250(0)	250(0)	250(0)	20(7)					
O5	556(3)	250(0)	93(2)	500(0)	14(4)					

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

[b] Tantalum multiplicity given first; general position is eightfold.

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[1] See NAPS document No. 03769 for 4 pages (KTi_3TaO_9) and No. 03769 for 4 pages ($K_3TiTa_7O_{21}$) of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P. O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only for each NAPS Accession Number. Institutions may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside of the U.S. and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

TABLE IV

SELECTED BOND LENGTHS FOR KTi_3TaO_9 (Å)

Metal–Oxygen		Metal–Metal		Oxygen–Oxygen	
		*B*1 Octahedron			
*B*1–O1 (×2)	1.97(1)	*B*1–*B*1	3.567(5)	O1–O2 (×2)	2.56(2)
*B*1–O2	2.19(2)	*B*1–*B*1 (×2)	3.793(1)	O1–O3 (×2)	2.82(2)
*B*1–O3	1.93(2)	*B*1–*B*2	3.178(4)	O1–O4 (×2)	3.01(1)
*B*1–O4	1.83(1)	*B*1–*B*2 (×2)	3.206(4)	O1–O5 (×2)	2.67(2)
*B*1–O5	1.98(2)	*B*1–*B*2	3.743(4)	O2–O3	2.62(3)
				O2–O5	3.03(3)
				O3–O4	2.76(3)
				O4–O5	2.78(3)
		*B*2 Octahedron			
*B*2–O1	2.08(2)	*B*2–*B*2 (×2)	3.341(5)	O1–O2 (×2)	2.56(2)
*B*2–O2 (×2)	1.98(1)	*B*2–*B*2 (×2)	3.793(1)	O1–O4	2.91(3)
*B*2–O2	2.29(2)			O1–O5	3.02(3)
*B*2–O3	1.87(2)			O2–O2 (×2)	2.67(3)
*B*2–O5	1.78(2)			O2–O3	2.62(3)
				O2–O3 (×2)	2.89(2)
				O2–O5 (×2)	2.97(2)
				O3–O5	2.72(3)
		Potassium			
K–O2 (×2)	3.68(2)				
K–O3 (×4)	2.85(2)				
K–O4 (×2)	3.21(2)				
K–O5 (×4)	3.21(2)				

Descriptions

The structure of KTi_3TaO_9 consists of pairs of edge-shared octahedra joined by further edge sharing to identical pairs above and below forming "double zigzag units." (*1*) The corner sharing of these units produces tunnels in which the potassium ions are located (Fig. 1). The 12-coordinate potassium ion lies on a mirror plane providing another example in this system of the chemical twinning phenomenon observed

TABLE V

POSITION AND THERMAL PARAMETERS FOR $K_3TiTa_7O_{21}$ (× 10^4, OXYGEN PARAMETERS × 10^3)

Atom	*x/a*	*y/b*	*z/c*	Occupancy	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	4076(7)	0(0)	2500(0)	2500(0)	161(22)	245(35)	152(31)	0(0)	0(0)	123(17)
*B*1	2473(1)	0(0)	5959(1)	4167(0) 833(0)[b]	39(3)	39(3)	49(3)	0(0)	−3(3)	19(2)
*B*2	3333(0)	6667(0)	0(0)	1667(0)	46(3)	46(3)	105(6)	0(0)	0(0)	23(2)
O1	686(1)	169(2)	404(1)	1000(0)	8(2)					
O2	0(0)	200(1)	73(1)	500(0)	6(3)					
O3	797(2)	0(0)	250(0)	500(0)	132(4)					

[a] Anisotropic thermal parameter as for KTi_3TaO_9.

[b] Tantalum multiplicity given first, general position is 24 fold.

TABLE VI

SELECTED BOND LENGTHS FOR $K_3TiTa_7O_{21}$ AND $K_{5.5}Ta_{15.7}O_{42}$ (Å)

	Metal–Oxygen		Oxygen–Oxygen	
	$K_3TiTa_7O_{21}$	$K_{5.5}Ta_{15.7}O_{42}$		
	*B*1 Octahedron			
*B*1–O1 (×2)	1.91(1)	1.91(1)	O1–O1	2.66(2)
*B*1–O2	2.08(1)	2.06(3)	O1–O2 (×2)	2.74(2)
*B*1–O2 (×2)	2.09(1)	2.09(1)	O1–O2 (×2)	3.03(2)
*B*1–O3	1.90(1)	1.91(2)	O1–O3 (×2)	2.89(2)
			O2–O2 (×2)	2.52(2)
			O2–O2 (×1)	3.14(2)
			O2–O3 (×2)	2.82(1)
	*B*2 Octahedron			
*B*2–O3 (×6)	1.97(1)	1.99(2)	O1–O1 (×3)	2.67(2)
			O1–O1 (×6)	2.76(2)
			O1–O1 (×3)	2.97(2)
	Potassium Ion			
K–O1 (×4)	2.88(1)			
K–O1 (×4)	3.18(1)			
K–O2 (×2)	2.86(1)			
K–O3 (×2)	3.21(1)			
K–O3 (×1)	3.54(2)			

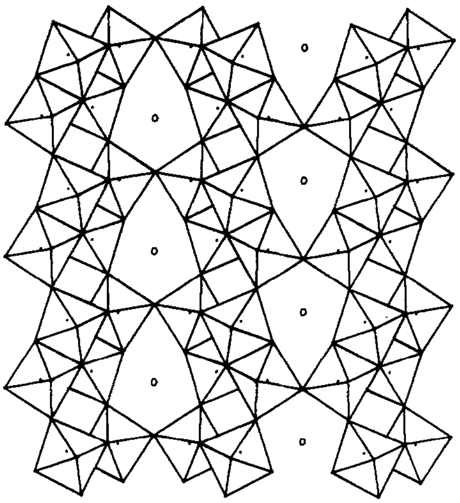

FIG. 1. The structure of KTi_3TaO_9 projected down [010]. Potassium ions are represented as open circles. The positions of the octahedral metal ions are indicated by dots, the *B*1 octahedra are those with one oxygen atom in the mirror plane.

in $KTi_2Ta_5O_{17}$ and discussed previously for KTi_3NbO_9 (*11*).

$K_3TiTa_7O_{21}$ exhibits the structure first observed by Evans and Katz as part of the compound $Ba_{6+n}Nb_{14}Si_4O_{47}$ ($n \approx 0.23$) (*12*) and is isostructural with the compound $K_{5.5}Ta_{15.7}O_{42}$ (Fig. 2). The single-crystal structure solution is in good general agreement with the results reported by Groult *et al.* (*5*) for the powder diffraction study on the family of compounds $A_3(Ta_{8-n}M_n)O_{21}$ (where A = K, M = Ti, Cr, Fe, Mg, Ni, Zn; A = Ba, M = Ti, Cr, Fe) (*5*).

Discussion

For the purposes of structure determination, Wadsley assumed that the metal atom octahedral sites of KTi_3NbO_9 contained ¼(3Ti + Nb) (*1*). The distribution observed here is 42% Ta, 58% Ti in *B*1; and 8% Ta, 92% Ti in *B*2. This disordering phenome-

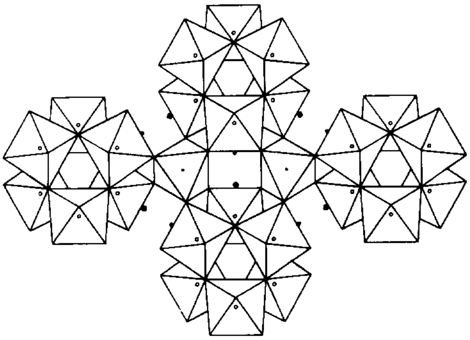

FIG. 2. The structure of $K_3TiTa_7O_{21}$ projected onto the *x–y* plane. The octahedral metal ion positions are represented as open circles. The *B*1 octahedra are those in the edge-shared units of six octahedra. The potassium ions at $z = \frac{1}{4}$ are shown as filled squares, while those at $z = \frac{3}{4}$ are filled circles.

non has been observed in $KTi_2Ta_5O_{17}$, $K_3TiTa_7O_{21}$, and the recent refinement from powder data of $KTiTaO_5$ (*6*) and can be assumed to be an inherent characteristic of this system.

Comparison of the metal–oxygen and oxygen–oxygen bond lengths observed for $K_3TiTa_7O_{21}$ and $K_{5.5}Ta_{15.7}O_{42}$ (Table VI) shows that the octahedron *B*1 is not significantly smaller than Ta1 in $K_{5.5}Ta_{15.7}O_{42}$ even though *B*1 consists of approximately 20% of the smaller element titanium. The octahedron, *B*1, is not significantly different in size from *B*2 which contains no titanium. The partial occupation of *B*1 by titanium is related to the relative number of edge- and corner-shared nearest neighbours. *B*1 shares two edges (metal–metal distance 3.227(1) Å) and one corner (3.717(1) Å) to form a unit of six octahedra while Ta1 shares all six corners with *B*1 (3.676(1) Å). The close approach of metal atoms brought about by edge sharing of octahedra produces large ionic repulsive forces which, in the case of $K_3TiTa_7O_{21}$, are partially relieved by the total incorporation of titanium in place of the larger tantalum atom in the *B*1 site. Such is the case for KTi_3TaO_9 also where *B*1 with 58% Ti has three edges and two corners and B2 with 92% Ti has five edges and one corner shared. The same rationalization of site occupancies can be applied to $KTi_2Ta_5O_{17}$.

The use of fluxes is a well-known technique for the growth of single crystals. Their use in the general examination of a system such as that reported here is perhaps not as widely recognized, in that the phases obtained varied widely from the initial mole ratios used, while changing the mole ratios produced different phases. The more general use of fluxes in studying systems of this type could prove to be rewarding.

Acknowledgments

This work forms part of a project supported by the Australian Research Grants Committee. We acknowledge the award of a Monash Graduate Scholarship (M.C.N.).

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