

A New Alkali Metal Titanotantalate, $\text{KTi}_2\text{Ta}_5\text{O}_{17}$ —A Compound That Exhibits the "Chemically Twinned" Rutile Structure

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$\text{KTi}_2\text{Ta}_5\text{O}_{17}$ crystallizes in the orthorhombic system with unit-cell dimensions (from single-crystal data) $a = 6.672(4) \text{ \AA}$, $b = 8.948(5) \text{ \AA}$, $c = 21.403(9) \text{ \AA}$ and space group $Cmcm$, $Z = 4$. The structure was solved using three-dimensional Patterson and Fourier techniques. Of the 1034 reflections measured by counter techniques, 704 with $I \geq 3 \sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.041 ($\omega R = 0.043$). The structure consists of edge- and corner-shared tantalum octahedra joined such that tunnels are formed in which the potassium ions are located. Slabs of octahedra are of the rutile (TiO_2) type related to one another by mirror planes (in which the potassium ions are located), producing a structure that may be considered as a "chemical twin" of the rutile structure.

Introduction

As part of a systematic structural study of compounds formed between alkali metal oxides and niobium and tantalum pentoxides the crystal structure of $\text{KTa}_5\text{O}_{13}$ (the 1:5 $\text{K}_2\text{O}:\text{Ta}_2\text{O}_5$ phase) was recently determined (1) and shown to be an example of the chemically twinned (2) $\alpha\text{-PbO}_2$ structure. Following this work attempts were made to expand the width of the slabs of the $\alpha\text{-PbO}_2$ structure by reacting $\text{KTa}_5\text{O}_{13}$ with TiO_2 at elevated temperatures. Reaction products consisted of $\text{KTa}_5\text{O}_{13}$ and a compound shown to have the composition $\text{KTi}_2\text{Ta}_5\text{O}_{17}$. We report here the result of the single-crystal structure determination of this compound.

Experimental

An accurately weighed mixture of $\text{K}_2\text{O}:\text{TiO}_2:\text{Ta}_2\text{O}_5$ in the mole ratio 1:8:5 was

thoroughly mixed with approximately 15% by weight of MoO_3 (as a flux) and heated in a gold crucible at 1000°C for 48 hr. From the reaction products a number of light tan-colored, approximately tetragonal, prisms were selected for examination. The composition was determined using a scanning electron microscope equipped with an energy dispersive X-ray analyzer, with $\text{KTa}_5\text{O}_{13}$ and TiO_2 as standards. The compound proved to be $\text{KTi}_2\text{Ta}_5\text{O}_{17}$ and not $\text{KTi}_4\text{Ta}_5\text{O}_{21}$ as anticipated. No molybdenum was detected during the analysis.

A crystal with dimensions $0.016 \times 0.016 \times 0.018 \text{ mm}$ was selected for intensity measurements and checked for cracks or twinning using a polarizing microscope before being mounted on a silica capillary using "Resiweld" epoxy cement. The following data were determined using a Philips PW 1100 computer-controlled diffractometer. Unit-cell parameters were determined

with a standard diffractometer computer program that determines the centers of a reflection chosen with a θ of approximately 10 to 15°. The values obtained are then used in a least-squares refinement of the d -spacings.

Crystal data. $\text{KTi}_2\text{Ta}_5\text{O}_{17}$, $M = 1311.62$, $a = 6.672(4)$ Å, $b = 8.948(5)$ Å, $c = 21.403(9)$ Å, $U = 1277.78$ Å³, $D_c = 6.82$ g cm⁻³ for $Z = 4$. Insufficient material was available for a density measurement. $F(000) = 2255$, $\mu = 423.76$ cm⁻¹ for MoK α radiation ($\lambda = 0.7107$ Å). Systematic absences observed were $h0l$, $l = 2n + 1$, hkl , $h + k = 2n + 1$, indicating space groups $Cmcm$ (D_{2n}^{17}), $Cmc2_1$ (C_{2v}^{12}), or A_{ma2} (C_{2v}^{16}). Space group $Cmcm$ was confirmed by successful refinement.

Intensity measurements. Intensity measurements were made with the crystal described above using the diffractometer and MoK α radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out $2\theta(\text{MoK}\alpha) = 60^\circ$ using the ω -scan technique with a symmetric scan range of $\pm 0.5^\circ$ in 2θ from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of 0.02° sec.⁻¹ No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 1034 independent reflections measured 704 were considered to be significantly above background [$I \geq 3\sigma(I)$] and only these were used in subsequent calculations. Three standard reflections measured at 2-hr intervals showed no significant variations in intensity.

The data were processed using a program (3) described previously (4). An absorption correction, based upon the indexed faces of the crystal, was applied using the program SHELX-76 (5). The atomic scattering factors used were for neutral atoms, K, Ti, Ta, and O from Ref. (6), and were corrected for anomalous dispersion (7). All calculations were performed on the Monash University B6700 computer, the major program used being of Sheldrick (5).

Structure Solution and Refinement

The structure was solved for the heavy atom positions by conventional Patterson techniques. Refinement of these positions followed by calculation of a difference Fourier synthesis enabled location of the potassium and oxygen atoms together with what were believed to be the titanium atoms. The conventional R factor ($R = \Sigma \|F_o| - |F_c| \| / \Sigma |F_o|$) at this stage was 0.098. With a total of 20 Ta(V) and 8 Ti(IV) ions to be distributed in the unit cell, the initial assumption that Ti(IV) would occupy an eightfold site was abandoned following several unsuccessful attempts at refinement. It was also clear at this stage that the metal atoms (Ta + Ti) were not uniformly distributed over all metals sites. The site occupancies were manually adjusted to minimize the peak heights in the difference Fourier syntheses and to retain a uniform set of thermal parameters consistent with minimization of the R factor. Refinement of the site occupancies was not profitable owing

TABLE I
FINAL ATOMIC PARAMETERS WITH ESTIMATED
STANDARD DEVIATIONS (ESDs) IN PARENTHESES
(METAL ATOMS $\times 10^4$, OXYGEN $\times 10^3$)^a

Atom	x/a	y/b	z/c	Occupancy	
				Ta	Ti
K	0	-237(9)	2500		
$B(1)^b$	0	1112(2)	557(1)	0.2050	0.2950
$B(2)$	0	3440(1)	3383(1)	0.4575	0.0425
$B(3)$	0	7349(1)	3895(1)	0.4675	0.0325
$B(4)$	0	5000	5000	0.1200	0.1300
O(1)	0	553(2)	339(1)		
O(2)	0	315(3)	250		
O(3)	0	336(2)	438(1)		
O(4)	0	895(2)	458(1)		
O(5)	0	119(2)	360(1)		
O(6)	208(2)	177(1)	655(1)		
O(7)	306(2)	115(1)	450(1)		

^a Site occupation factors are given for the (Ti + Ta) hybrid species.

^b "B" denotes a site occupied by a hybrid species (Ta + Ti).

TABLE II
THERMAL PARAMETERS WITH ESDs ($\times 10^4$)^a

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	489(56)	132(38)	103(34)	0	0	0
B(1)	43(7)	63(7)	56(7)	7(6)	0	0
B(2)	40(4)	71(4)	72(5)	3(4)	0	0
B(3)	41(4)	79(5)	84(5)	13(3)	0	0
B(4)	31(9)	66(9)	35(9)	1(7)	0	0
O(1)	55(26)					
O(2)	71(44)					
O(3)	103(31)					
O(4)	36(28)					
O(5)	99(34)					
O(6)	75(20)					
O(7)	87(21)					

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

to their high correlation with the thermal parameters. Finally, five cycles of full-matrix least-squares refinement using anisotropic thermal parameters for all metal atoms, isotropic for oxygen, with the data weighted according to ($\omega = 1/\sigma^2(F)$), resulted in a final R of 0.041 and ωR of 0.043 [$\omega R = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F^2]^{1/2}$].

Final atomic parameters with their estimated standard deviations in parentheses are given in Table I. A table of observed and calculated structure factors has been deposited with the ASIS National Auxiliary Publications Service.¹ Selected interatomic distances and angles are listed in Table II, and the numbering scheme is shown in Fig. 1.

Description of the Structure and Discussion

The structure of $\text{KTi}_2\text{Ta}_5\text{O}_{17}$ consists of strings of edge-shared octahedra that are

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corner shared to octahedra in adjacent strings forming blocks of the rutile structure. These blocks are related to adjacent blocks by mirror planes and joined to them by corner sharing of some octahedra (Fig. 1). The potassium ions are located in the mirror planes in pseudo-hexagonal tunnels generated by the reflection operation.

Refinement of this structure has shown that the four heavy metal sites are occupied by tantalum and titanium in varying ratios in the manner not infrequently observed for

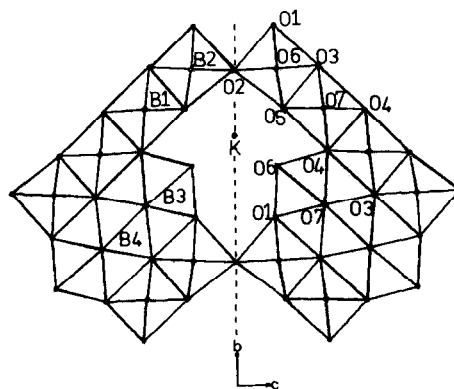


FIG. 1. A single layer of edge- and corner-shared octahedra in $\text{KTi}_2\text{Ta}_5\text{O}_{17}$ showing the numbering scheme used. The mirror planes are indicated by broken lines.

complex minerals. In a study of two alkali titanoniobates, KTiNbO_5 and KTi_3NbO_9 , Wadsley (8) reported that the metal sites (excluding K^+) were occupied by approximately equal weighted atomic species. In KTiNbO_5 the sites were treated as being occupied by hybrid species of the type $\frac{1}{2}(\text{Ti} + \text{Nb})$, whereas in KTi_3NbO_9 the hybrid species was considered to be $\frac{1}{4}(3\text{Ti} + \text{Nb})$. It is interesting to note that KTi_3NbO_9 (related to BaTi_4O_9 (8)) has been discussed in terms of chemical twinning (2). In a new family of titanoniobates and tantalates, $\text{A}_2\text{M}_6\text{TiO}_{18}$ ($\text{A} = \text{Rb}, \text{Cs}; \text{M} = \text{Ta}, \text{Nb}$), reported recently (9), the titanium and either niobium or tantalum were considered

to be statistically distributed over the heavy metal sites.

The four metal atom sites in $\text{KTi}_2\text{Ta}_5\text{O}_{17}$ may be grouped into two pairs, $B(2)$ and $B(3)$ containing 91.50 and 93.50% Ta(V), and $B(1)$ and $B(4)$ containing 41.00 and 48.00% Ta(V), respectively. During refinement of the structure attempts were made to rationalize the site occupancies of Ti and Ta; however, these resulted in such widely divergent values for the thermal parameters as to be unacceptable. It is noted that sites $B(2)$ and $B(3)$ are the octahedra that face into the tunnels whereas $B(1)$ and $B(4)$, within the slab of rutile structure, are surrounded by octahedra.

TABLE III
SELECTED BOND LENGTHS WITH ESDs (Å)

Metal-metal		Metal-oxygen		Oxygen-oxygen	
$B(1)-B(1)$	3.105(3)	$B(1)-O(3)$	2.01(2)	$O(4)-O(4)$	2.61(3)
$B(2)$	3.080(2)	$O(4)$	1.96(2)	$O(4)-O(5)$	2.91(2)
$B(3)$	3.566(2)	$O(4)$	1.94(2)	$O(5)-O(3)$	2.57(2)
$B(3) (\times 2)$	3.706(1)	$O(5)$	1.82(2)	$O(3)-O(4)$	3.04(2)
$B(3)$	3.814(2)	$O(7) (\times 2)$	2.04(1)	$O(3)-O(7) (\times 2)$	2.85(2)
$B(4)$	3.677(2)			$O(7)-O(4) (\times 2)$	2.84(2)
$B(4) (\times 2)$	3.680(1)			$O(7)-O(4) (\times 2)$	2.84(1)
				$O(7)-O(5) (\times 2)$	2.81(2)
$B(2)-B(2)$	3.779(2)	$B(2)-O(1)$	1.87(2)	$O(1)-O(2)$	2.86(2)
$B(3) (\times 2)$	3.645(1)	$O(2)$	1.91(3)	$O(2)-O(5)$	2.93(2)
$B(3)$	3.666(2)	$O(3)$	2.14(2)	$O(5)-O(3)$	2.57(2)
$B(4)$	3.732(1)	$O(5)$	2.07(2)	$O(3)-O(1)$	2.87(2)
		$O(6) (\times 2)$	1.97(1)	$O(1)-O(6) (\times 2)$	2.79(2)
				$O(2)-O(6) (\times 2)$	2.82(1)
				$O(3)-O(6) (\times 2)$	2.79(2)
				$O(5)-O(6) (\times 2)$	2.69(2)
$B(3)-B(4)$	3.164(1)	$B(3)-O(1)$	1.95(2)	$O(6)-O(6)$	2.77(2)
		$O(4)$	2.05(1)	$O(6)-O(7) (\times 2)$	2.92(1)
		$O(6) (\times 2)$	1.85(1)	$O(7)-O(7)$	2.59(2)
		$O(7) (\times 2)$	2.12(1)	$O(1)-O(6) (\times 2)$	2.79(2)
				$O(1)-O(7) (\times 2)$	2.76(2)
				$O(4)-O(6) (\times 2)$	2.86(2)
				$O(4)-O(7) (\times 2)$	2.82(2)
$B(4)$		$B(4)-O(3) (\times 2)$	1.98(2)	$O(7)-O(7) (\times 4)$	2.59(2)
		$O(7) (\times 4)$	1.97(1)	$O(3)-O(7) (\times 8)$	2.76(2)
Potassium		$K-B(2) (\times 2)$	3.793(7)	$K-O(2)$	3.03(2)
		$B(3) (\times 2)$	3.686(5)	$O(5) (\times 2)$	2.67(2)
				$O(6) (\times 4)$	2.82(1)

TABLE IV
REACTION CONDITIONS AND CELL DIMENSIONS OF THE PHASES THAT FORM THE CHEMICALLY TWINNED RUTILE STRUCTURE

Phase	Temperature (°C)	Firing time (hr) (pt. crucible)	Cell dimensions (Å)		
			<i>a</i>	<i>b</i>	<i>c</i>
KTi ₂ Ta ₅ O ₁₇	920	48	6.672(4)	8.948(5)	21.403(9)
NaTi ₂ Ta ₅ O ₁₇	1000	120	6.668(3)	8.966(4)	21.392(7)
KTi ₂ Nb ₅ O ₁₇	1000	200	6.660(4)	8.981(5)	21.474(8)

The metal to oxygen (*B*-O) distances vary from 1.82(2) to 2.14(2) Å (average 1.98 Å), a narrower range than that observed for KTa₅O₁₃ (1.86(2) to 2.17(2) Å; average 2.00 Å), probably as a result of the presence of Ti(IV) in the site (Table III).

The potassium ions are situated in the pseudo-hexagonal tunnels (Fig. 2) and are seven-coordinate with K-O distances that range from 2.67(2) to 3.03(2) Å (average 2.81 Å) compared with the K-O distances (2.69(2) to 3.03(3) Å; average 2.83 Å) in KTa₅O₁₃. The tunnels are parallel to [1 1 0] and are 5.58 Å across (5.65 Å for KTa₅O₁₃), highlighting the similarity between these two structures in the vicinity of the tunnels. Indeed, the octahedra immediately surrounding the tunnels are identically dis-

posed relative to one another, as might be expected since rutile and α-PbO₂ have been shown to be related by a crystallographic shear operation (10) that leaves these particular octahedra unchanged.

Following the determination of the structure of KTi₂Ta₅O₁₇ a series of experiments was carried out to determine which similar elements could be combined to form this chemically twinned rutile structure. The elements used were: *M*⁺ = Na, K, Rb, Ag, *M*^{IV} = Ti, Zr, Sn, and *M*^V = Nb, Ta. Only two combinations of these elements formed crystalline products, under the experimental conditions used, KTi₂Nb₅O₁₇ and NaTi₂Ta₅O₁₇. The reaction conditions and cell dimensions are given in Table IV. While none of the other possible combinations of elements yielded a crystalline product a radical change of reaction conditions may result in the formation of additional phases that exhibit this structure. This possibility is currently being investigated in our laboratory.

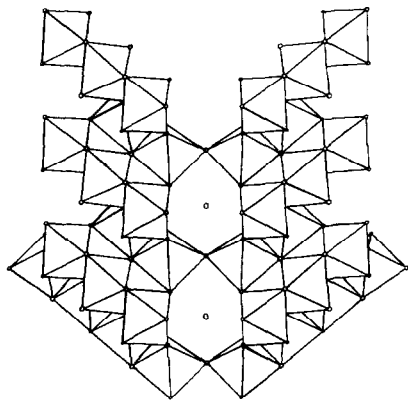


FIG. 2. The structure of KTi₂Ta₅O₁₇ viewed approximately along [1 1 0] in order to illustrate the pseudo-hexagonal tunnels. Part of four layers of octahedra have been included. Potassium ions are shown as small open circles.

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References

1. A. A. AWADALLA AND B. M. GATEHOUSE, *J. Solid State Chem.* **24**, 183 (1978).

2. S. ANDERSSON AND B. G. HYDE, *J. Solid State Chem.* **9**, 93 (1974).
3. J. HORNSTRA AND B. STUBBE, "PW 1100 Data Processing Program," Philips Research Laboratories, Eindhoven, The Netherlands (1972).
4. B. M. GATEHOUSE, T. NEGAS, AND R. S. ROTH, *J. Solid State Chem.* **18**, 1 (1976).
5. G. M. SHELDRIK, "SHELX-76: A Program for Crystal Structure Determination," Cambridge (1976).
6. D. T. CROMER AND J. B. MANN, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
7. D. T. CROMER AND D. LIBERMAN, *J. Chem. Phys.* **53**, 1891 (1970).
8. A. D. WADSLEY, *Acta Crystallogr.* **17**, 623 (1964).
9. G. DESGARDIN, C. ROBERT, D. GROULT, AND B. RAVEAU, *J. Solid State Chem.* **22**, 101 (1977).
10. L. A. BURSILL AND B. G. HYDE, *Progr. Solid State Chem.* **7**, 177 (1972).