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Alkali Titanoniobates: The Crystal Structures of $KTiNbO_5$ and KTi_3NbO_9

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Two orthorhombic alkali titanoniobates $KTiNbO_5$ and KTi_3NbO_9 have been prepared and described. The first, with the space group *Pnma* and the unit-cell dimensions

$$a = 6{\cdot}459,\ b = 3{\cdot}792,\ c = 18{\cdot}472\ \text{Å}$$

is a layer structure, where each sheet consists of double zigzag strings of octahedra sharing corners. These are bonded through potassium ions in distorted cubic environments. A limited examination of KTi_3NbO_9, which is isomorphous with $BaTi_4O_9$ (Lukaszewicz, 1957) gave the space group *Pnmm* for the unit cell

$$a = 6{\cdot}392,\ b = 3{\cdot}785,\ c = 14{\cdot}865\ \text{Å}\ .$$

The crystal chemistry of the two compounds is discussed.

Introduction

The structures of many binary and ternary oxides of Group IV, V, and VI metals contain zigzag ribbons of octahedra. These can be formed by one, two or three octahedra sharing edges in a particular plane and, when joined to identical groups above and below, extend throughout the crystal in one direction, usually an axis of symmetry. We have recently commented upon the similarities of the alkali titanates $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ to the binary oxide Ti_3O_5 (Andersson & Wadsley, 1962*a*) where, as a unifying feature, all three contain zigzag treble units of the same kind, and these are grouped in a characteristic way for each phase by additional corner and edge sharing. A fourth compound Na_xTiO_2, prepared by reducing $Na_2Ti_3O_7$ in hydrogen at an elevated temperature (Andersson & Wadsley, 1962*b*), differed in one important respect. The host structure was built up from *double* zigzag units (Fig. 1).

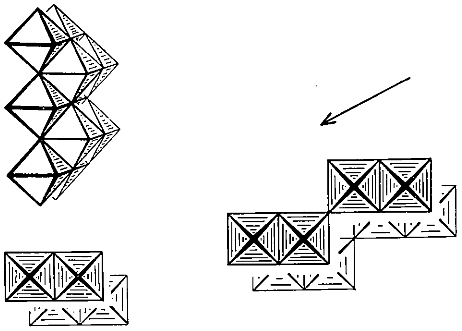


Fig. 1. Left: Double zigzag string of octahedra, in perspective (upper) and in projection (lower). — Right: Strings joined by sharing corners. The arrow gives the direction of the *a* axes in both potassium titanoniobates.

It is possible to 'design' additional structures with these double groups linked into three-dimensional networks around the interstitial atoms in the same way as the treble groups of the alkali titanates. The formulae of these hypothetical substances can be readily established by counting atoms within the unit cells, and the problem is then to make and to identify them. The octahedrally coordinated metals will need to have valencies in between four and five, and in view of the readiness with which Ti^{4+} and Nb^{5+} form pseudobinary oxides of mixed valency (Wadsley, 1961) the compounds could perhaps be sought as ternary titanoniobates. The presence of these two elements as isomorphous substituents will ensure close control of the valency and of the overall composition, if single phases are formed by reaction of the component oxides in the solid state or by fusion.

No comprehensive phase equilibria studies of the ternary systems alkali metal oxide–TiO_2–Nb_2O_5 appear to have been reported. Although efforts to synthesize $Na_3(Ti_3Nb)O_{10}$ and $Na(Ti_3Nb)O_9$, related respectively to $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$, were unsuccessful, the potassium compounds $KTiNbO_5$ and KTi_3NbO_9 were readily made. An X-ray examination has now established that both contain the double zigzag ribbons of octahedra, but these are linked together in ways that were not foreseen.

The structure of $KTiNbO_5$

$KTiNbO_5$ was readily prepared as a white solid by heating intimately mixed K_2CO_3, TiO_2 (anatase) and Nb_2O_5 in the molar ratios 1:2:1 at 1150 °C. It consisted of very small anisotropic crystals of poor quality with cracks and flaws running in the direction of maximum elongation, the crystallographic *b* axes. Tests for ferroelectricity, kindly made by Dr. J. S. Dryden, C.S.I.R.O. Division of Electrotechnology, were negative.

Table 1. *Crystallographic data for* $KTiNbO_5$

Symmetry: orthorhombic.
Unit-cell dimensions:

$a=6{\cdot}459\pm0{\cdot}002,\ b=3{\cdot}792\pm0{\cdot}002,\ c=18{\cdot}472\pm0{\cdot}004$ Å

Systematically absent reflexions:

$0kl$ with $k+l\neq2n$; $hk0$ with $h\neq2n$; $h00$, $0k0$, $00l$ with h, k, and $l\neq2n$

Possible space groups:

Pnma (No. 62) or $Pn2_1a$ (No. 33)	
D_x, calculated for $Z=4$,	$3{\cdot}82$ g.cm^{-3}
D_m	$3{\cdot}80\pm0{\cdot}03$ g.cm^{-3}

A minute crystal of dimensions $0{\cdot}15\times0{\cdot}01\times0{\cdot}02$ mm proved to have orthohombic symmetry with the space group alternatives *Pnma* or $Pn2_1a$. The dimensions of the unit cell, given in Table 1 with the estimated standard deviations, were determined from a Guinier powder pattern internally calibrated with KCl, and the density was measured on a torsion microbalance. Weissenberg photographs gave very few data, the Bragg reflexions being supplemented by numerous diffuse streaks caused by disorder of some kind. These could arise from short range order accompanying the random distribution of Ti and Nb in positions of the same kind, or from non-periodic imperfections within the crystal, due perhaps to the slow interaction with water vapour from the atmosphere, noted during the dielectric measurements.

The *h0l* intensities were obtained on multiple films with copper $K\alpha$ radiation by the integrating Weissenberg method, but only 50 of 158 possible reflexions were recorded. The upper level data were too poor to be useful in deriving the structure, but the *0kl* terms were gathered as an integrated intensity series, albeit of poor quality, by remounting the crystal about the *a* axis. The compound was nevertheless considered worth examining as far as the data would permit, even although no great accuracy could be expected. It evidently had a structure of a new kind which could perhaps serve as a model for other possible $AB'B''O_5$ or AB_2O_5 compounds of greater stability.

Intensity measurements were made by comparison with a calibrated film strip and corrected for Lorentz and polarization effects but not for absorption, the linear absorption coefficient of this particular crystal being very small. Structure factors were computed with the scattering curve for Nb^{5+} derived from the tables of Thomas & Umeda (1957), Ti^{4+} from the self-consistent field curve for Ti^{3+} (Freeman & Watson, 1959) rounded off to a value of 18·0 at $\sin\theta=0$, both corrected for dispersion, and Freeman's (1959) and Suzuki's (1960) values for K^+ and O^{2-} respectively.

With four formula units in the cell, all the atoms evidently occupy fourfold positions, 4(*c*) for space group *Pnma* or 4(*a*) for $Pn2_1a$. In the former they are fixed by symmetry in mirror planes at $y=\pm\frac{1}{4}$, but are present in the latter in more general positions along the twofold screw axis. Since *b* is only 3·8 Å in length the projection on to (010), centrosymmetrical for both cases, would be expected to give a clearly resolved picture of all the atoms except Ti and Nb, both of which — if their coordination is octahedral — will be overlaid by the oxygens present as the terminal atoms of the body diagonals. The Patterson projection $P(u,w)$ was prepared without sharpening or modifying, and from it the positions of two metal atoms of about the same scattering power, as well as a third atom of somewhat reduced electron density, were deduced by trial-and-error image-seeking methods. The five oxygen atoms could then be placed in positions around the two heavier atoms in only one way, giving octahedral coordination to them both and, at the same time, a roughly cubic environment for the third atom which is evidently potassium. Preliminary structure factor calculations soon made it clear that the metals with the octahedral environment, as suggested by the Patterson function, were about the same atomic number.

Table 2. *Comparison of observed and calculated structure factors*

The non-observed reflexions, none of which is at variance with F_c, are omitted

hkl	F_o	F_c	*hkl*	F_o	F_c
002	113	118	403	87	$\overline{72}$
00,10	116	118	404	100	$\overline{89}$
00,12	98	$\overline{88}$	405	72	$\overline{87}$
00,14	110	$\overline{109}$	406	57	$\overline{41}$
00,22	75	$\overline{76}$	40,10	51	63
101	33	$\overline{38}$	40,14	52	$\overline{64}$
102	43	41	502	71	60
103	55	$\overline{54}$	503	87	$\overline{101}$
106	216	$\overline{174}$	504	51	66
107	64	$\overline{71}$	603	65	62
108	158	$\overline{154}$	604	91	104
10,16	75	$\overline{74}$	606	52	68
10,20	104	106	702	74	$\overline{74}$
200	256	$\overline{240}$	704	46	$\overline{54}$
201	33	17	70,10	70	$\overline{70}$
202	49	$\overline{49}$	804	65	$\overline{75}$
203	58	39	011	100	$\overline{75}$
205	32	45	013	203	$\overline{170}$
209	70	86	017	69	55
20,10	95	$\overline{91}$	019	85	119
20,11	78	70	01,11	109	$\overline{138}$
20,12	75	61	01,17	86	74
20,14	115	101	020	322	307
20,22	46	56	022	89	85
301	43	59	02,10	70	90
302	122	$\overline{97}$	02,12	60	$\overline{75}$
303	153	146	02,14	86	$\overline{97}$
304	83	$\overline{80}$	031	58	$\overline{40}$
305	39	46	033	118	$\overline{108}$
306	138	123	039	61	$\overline{82}$
307	42	63	03,11	85	$\overline{96}$
308	97	93	03,17	69	60
30,20	67	$\overline{76}$	040	139	142
400	120	94			

Both positions were assigned one-half atom of each kind, $\frac{1}{2}$(Ti+Nb), corresponding to a random distribution, even although the space group requirements can be satisfied by placing Ti and Nb in separate sites of their own.

The parameters were refined by Fourier and difference syntheses projected on to (010). The oxygens superimposed upon the mixed Ti and Nb atoms were difficult to locate with any certainty by this method, and the data weighted by Rollett's procedure (1961) were refined further by three cycles of least squares. For the final structure factors listed in Table 2 the isotropic temperature factors were averaged for atoms of the same kind, the values of B being 0·3, 0·5 and 0·8 Å^{-2} respectively. This gave a reliability of 12·4% for the $h0l$ terms. The $0kl$ data gave a reliability index of 11·8% on the assumption that the atoms were all in positions 4(c) for *Pnma*, where $y = \pm\frac{1}{4}$. In view of this reasonable agreement it was considered unprofitable to attempt to fit the poor experimental data to the alternative space group, where y parameters for all atoms are additional variables. The positions are listed in Table 3.

Table 3. *Fractional atomic parameters for* KTiNbO$_5$

Space group *Pnma* (No. 62). All atoms in 4(c)

$\pm x, \frac{1}{4}, z;\ \pm\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z$

Atom	x	y	z
K	0·790 ± 0·002	$\frac{1}{4}$	0·8083 ± 0·0005
B(1)*	0·315 ± 0·002	$\frac{1}{4}$	0·0297 ± 0·0003
B(2)*	0·759 ± 0·002	$\frac{1}{4}$	0·1100 ± 0·0003
O(1)	0·086 ± 0·006	$\frac{1}{4}$	0·074 ± 0·002
O(2)	0·664 ± 0·007	$\frac{1}{4}$	0·001 ± 0·003
O(3)	0·453 ± 0·006	$\frac{1}{4}$	0·121 ± 0·002
O(4)	0·828 ± 0·006	$\frac{1}{4}$	0·209 ± 0·002
O(5)	0·234 ± 0·006	$\frac{1}{4}$	0·926 ± 0·003

* B denotes $\frac{1}{2}$(Ti+Nb) as a single scattering unit.

The projection of the structure is shown in Figs. 2 and 4(a). The Ti and Nb atoms are present at random in two sets of positions, the octahedron associated with the 'hybrid' atom B(1) having an average metal to oxygen distance of 1·98 Å and that of B(2) 2·03 Å, the differences being not significant. Two octahedra have an edge in common, and by additional edge sharing to similar pairs above and below extend as double zigzag strings elongated in the direction of the b axis. The metals are displaced from the octahedral centres so that considerable variations of interatomic distance are found (Table 4), a feature usually associated with strings of a related kind in other compounds. The double strings are joined by sharing octahedral corners to form puckered infinite sheets parallel to (100) with the composition $(B_2O_5)_n^{n-}$. Alternate sheets are related by the a-glide plane, whereby the terminal oxygen atoms are brought together as cubic interlayer positions, somewhat distorted. These are occupied by the potassium ions cementing the structure together.

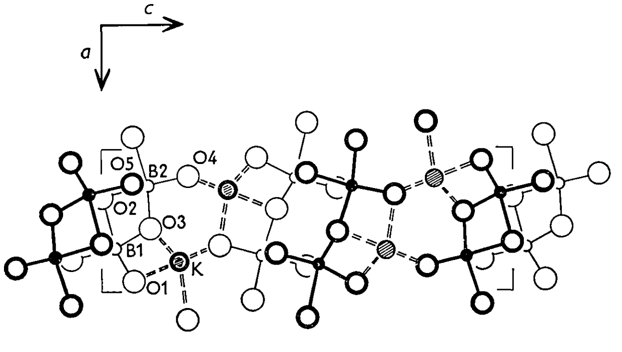


Fig. 2. Positions of the atoms in KTiNbO$_5$. Largest circles oxygen, intermediate ones hatched are potassium and the smallest Ti or Nb. Atoms in heavier outline (black for titanium) are at $y=\frac{3}{4}$, the lighter ones at $y=\frac{1}{4}$. The unit cell corners are indicated.

Table 4. *Interatomic distances in* KTiNbO$_5$

B represents $\frac{1}{2}$(Ti+Nb)

	No.	Length		No.	Length
B(1)–O(1)	1	1·69 Å	B(2)–O(1)	1	2·21 Å
B(1)–O(3)	1	1·91	B(2)–O(2)	1	2·10
B(1)–O(2)	1	2·32	B(2)–O(5′)	2	2·01
B(1)–O(5)	1	1·99	O(2)–O(3)	1	2·60
B(1)–O(2′)	2	1·98	O(3)–O(4)	1	2·92
O(1)–O(3)	1	2·53	O(4)–O(1)	1	3·00
O(3)–O(2)	1	2·60	O(1)–O(2)	1	3·04
O(2)–O(5)	1	3·10	O(3)–O(5′)	2	2·91
O(5)–O(1)	1	2·90	O(4)–O(5′)	2	3·16
O(1)–O(2′)	2	2·85	O(2)–O(5′)	2	2·42
O(2′)–O(3)	2	3·04	O(1)–O(5′)	2	2·80
O(2′)–O(2)	2	2·84	K–O(1)	2	2·99
O(2′)–O(5)	2	2·42	K–O(3)	2	2·79
B(2)–O(3)	1	1·98	K–O(4)	2	2·75
B(2)–O(4)	1	1·88	K–O(4′)	2	3·13

The average estimated standard deviations of interatomic distance are metal–oxygen ± 0·04 Å, oxygen–oxygen ± 0·07 Å.

Both V$_2$O$_5$ (Byström, Wilhelmi & Brotzen, 1950; Bachmann, Ahmed & Barnes, 1961) and K$_2$Ti$_2$O$_5$ (Andersson & Wadsley, 1961) are layer substances with sheets of the same composition if not the same charge, but in these cases V^{5+} and Ti^{4+} are in fivefold coordination, and their structures have few features of any kind in common with that of KTiNbO$_5$. It would not be surprising if the alkali metals were exchangeable for other ions or long-chain aliphatic groups, a feature of a wide variety of layer compounds, from silicate minerals to alkali titanates and vanadates.

The structure of KTi$_3$NbO$_9$

KTi$_3$NbO$_9$ is formed at 1300 °C by the solid state reaction between K$_2$CO$_3$, TiO$_2$ (anatase) and Nb$_2$O$_5$ in the molar ratios 1:6:1. It is a white microcrystalline solid decomposing on fusion into a mixture of phases, and all efforts to isolate a crystal were unsuccessful. The structure was established solely with X-ray power diffraction data. Although it is a difficult matter to examine a multi-parameter problem by these means, the general features of this particular compound can nevertheless be recognized, but without any great accuracy.

Table 5. *Crystallographic data for* KTi$_3$NbO$_9$

Symmetry: orthorhombic

Unit-cell dimensions:

$a = 6{\cdot}392 \pm 0{\cdot}002$, $b = 3{\cdot}785 \pm 0{\cdot}002$, $c = 14{\cdot}865 \pm 0{\cdot}002$ Å

Systematically absent reflexions:

$0kl$ with $k+l \neq 2n$; $0k0$, $00l$ with k and $l \neq 2n$

Possible space groups:

*Pnmm** (No. 59), or *Pn*2$_1$*m* (No. 31)

D_m: $3{\cdot}85 \pm 0{\cdot}05$ g.cm^{-3}
D_x (for $Z = 2$): $3{\cdot}88$ g.cm^{-3}

* The sub-group of the standard setting *Pmmn* is used because of the relation it bears to *Pnma*, the space group of KTiNbO$_5$.

The crystallographic constants in Table 5 were derived by trial and error from a calibrated Guinier film. Intensities were first gathered on the diffractometer by step-scanning the peaks out to $2\theta = 60°$, but these proved subsequently to include orientation effects which were difficult to eliminate. Much more reliable data were obtained with a conventional powder camera of diameter 11·46 cm into which four films were simultaneously loaded, numerical values of intensities then being obtained by comparison with a calibrated strip. To avoid uncertainties arising from the inevitable overlap of two or more reflexions of different classes, the calculated structure factors were squared, corrected for multiplicity and for Lorentz polarization effects, and compared directly with these measurements placed on the same scale.

The unit cell contains the same number of B atoms as KTiNbO$_5$, now assumed to be 'hybrids' $\frac{1}{4}$(3Ti + Nb), but fewer oxygen and potassium atoms. The length of the *a* axis is virtually the same for both compounds, and in the present case it evidently corresponds once more to the repeat distance of the double zigzag strings joined by corners. The change of symmetry group from *Pnma* to *Pnmm* (or the alternative *Pn*2$_1$*m*) requires the substitution of a mirror plane for an *a* glide. The unshared oxygen atoms of the strings may be placed on these planes at the special position 2(*a*), $\pm x, \frac{1}{4}, \frac{1}{4}$ for P*nmm*, where they will then be common to pairs of adjacent strings. This eliminates two oxygen atoms from the unit cell, and the reduction in length of the *c* axis, from 18·5 Å in KTiNbO$_5$ to 14·9 Å in KTi$_3$NbO$_9$, becomes a direct consequence of this regrouping of the zigzag units. The octahedral structure derived in this way now contains a twofold interstitial position bounded by ten oxygens, appearing in projection on to (010) as a pentagon (Figs. 3 and 4*b*). Evidently the potassium is present at the centre of this site which is the special position 2(*b*), $\pm x, \frac{3}{4}, \frac{1}{4}$ for *Pnmm*. The *x* parameters of the atoms of the octahedral host structure will be much the same as in KTiNbO$_5$, while the values of *z* can be readily evaluated. These are given in Table 6.

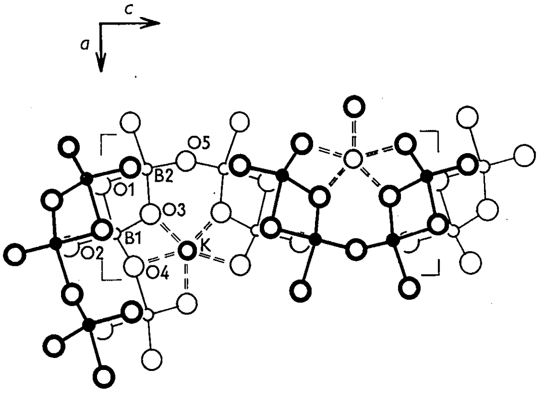
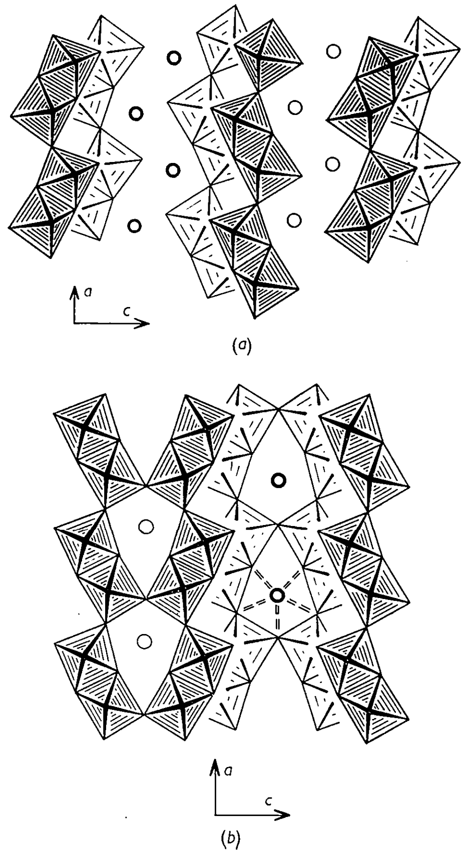


Fig. 3. Positions postulated for atoms in KTi$_3$NbO$_9$. The atoms are drawn so as to be uniform with those in Fig. 2.



(*a*)

(*b*)

Fig. 4. (*a*) Structure of KTiNbO$_5$ drawn as octahedra, with potassium circles. (*b*) KTi$_3$NbO$_9$, showing the union of the sheets in Fig. 4(*a*) through octahedral corners. Potassium drawn as circles.

Intensities calculated with this model showed it to be substantially correct, but attempted improvements

Table 6. *Atomic parameters for* KTi_3NbO_9

Space group *Pnmm* (No. 59), origin at $\bar{1}$.

Comparison with positions in $BaTi_4O_9$ (Lukaszewicz, 1957) transposed from the standard setting (*Pmmn*) and with the origin changed to $\frac{1}{2}$,0,0

KTi_3NbO_9					$BaTi_4O_9$				
Atom	Point position	x	y	z	Atom	Point position	x	y	z
K	2(*b*)	0·222	$\frac{3}{4}$	$\frac{1}{4}$	Ba	2(*b*)	0·209	$\frac{3}{4}$	$\frac{1}{4}$
B(1)*	4(*f*)	0·315	$\frac{1}{4}$	0·033	Ti(1)	4(*f*)	0·307	$\frac{1}{4}$	0·035
B(2)*	4(*f*)	0·759	$\frac{1}{4}$	0·126	Ti(2)	4(*f*)	0·750	$\frac{1}{4}$	0·126
O(1)	4(*f*)	0·66	$\frac{1}{4}$	0·53	O(1)	4(*f*)	0·640	$\frac{1}{4}$	0·510
O(2)	4(*f*)	0·23	$\frac{1}{4}$	0·62	O(2)	4(*f*)	0·233	$\frac{1}{4}$	0·592
O(3)	4(*f*)	0·45	$\frac{1}{4}$	0·17	O(3)	4(*f*)	0·458	$\frac{1}{4}$	0·154
O(4)	4(*f*)	0·09	$\frac{1}{4}$	0·10	O(4)	4(*f*)	0·050	$\frac{1}{4}$	0·100
O(5)	2(*a*)	0·83	$\frac{1}{4}$	$\frac{1}{4}$	O(5)	2(*a*)	0·840	$\frac{1}{4}$	$\frac{1}{4}$

* B denotes $\frac{1}{2}$(Ti + Nb) as a single scattering unit.

Table 7. *Powder diffraction data for* KTi_3NbO_9

Cu $K\alpha$ radiation. $\sin^2\theta$ from Guinier film

hkl	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	*I*(obs.)	*I*(calc.) ($\times 10^7$)
200	0·01073	0·01074	26·1	20·71
001	0·01452	0·01452	2·9	2·58
101	0·01718	0·01721	5·1	4·18
201	0·02526	0·02526	5·1	5·70
301	0·03866	0·03869	2·2	3·45
400	—	0·04296	—	0·48
110	0·04405	0·04411	15·2	13·07
011	—	0·05594	—	0·73
401	—	0·05748	—	0·77
002	0·05807	0·05808	19·6	17·11
111	—	0·05863	—	0·45
102	—	0·06077	—	0·34
310	0·06563	0·06559	17·4	17·24
211	0·06669	0·06668	19·6	22·60
202	0·06889	0·06882	1·5	1·87
311	—	0·08011	—	0
501	0·08160	0·08165	16·3	16·47
302	—	0·08225	—	0·99
600	—	0·09666	—	0·06
411	0·09890	0·09890	2·9	3·58
012	0·09935	0·09950	1·5	1·53
402	—	0·10104	—	0·01
112	—	0·10219	—	0·23
510	—	0·10855	—	0·82
212	—	0·11024	—	0·05
601	0·11126	0·11118	2·9	3·01
511	—	0·12307	—	0
312	0·12371	0·12367	4·4	4·76
502	—	0·12521	—	0·85
003	—	0·13068	—	0·63
103	0·13347	0·13337	1·5	1·86
203	0·14145	0·14142	5·8	5·66
412	—	0·14246	—	1·37
701	0·14615	0·14609	5·8	7·22
611	—	0·15260	—	0·16
602	0·15478	0·15474	2·9	0·24
303		0·15485		3·29
020	0·16567	0·16568	8·7	9·62
512	—	0·16663	—	0·08
800	0·17171	0·17184	3·6	2·46
013		0·17210		1·11
710	—	0·17299	—	0·46
403	—	0·17364	—	0·49
113	—	0·17479	—	0·26
220	0·17646	0·17641	1·5	1·20
021	—	0·18019	—	0·21
213	0·18290	0·18284	2·9	2·66
121		0·18288		0·42
801	—	0·18636	—	0·02
711	—	0·18751	—	1·16
702	0·18990	0·18965	2·2	1·57
221		0·19093		0·68
612	—	0·19616	—	0
313	—	0·19627	—	1·05
503	0·19779	0·19781	3·6	3·45
321	—	0·20436	—	0·54
420	—	0·20863	—	0·08
413	0·21517	0·21506	4·4	5·01
421	—	0·22315	—	0·17
022	0·22360	0·22375	4·4	4·89
122	—	0·22644	—	0·06
603	0·22754	0·22734	6·5	0·37
811		0·22778		7·35
802	—	0·22992	—	1·55
712	—	0·23107	—	0·67
901	—	0·23201	—	0·42
004	—	0·23232	—	1·13
222	—	0·23449	—	0·62
104	—	0·23501	—	0
513	0·23910	0·23923	2·2	2·32
204	—	0·24306	—	0·01
521	0·24686	0·24732	5·8	6·42
322	—	0·23792	—	0·43

by a least-squares refinement were not altogether successful as the number of Debye-Scherrer lines which could be unambiguously indexed severely limited the experimental data. Better agreement was reached with Lucaszewicz's (1957) parameters for $BaTi_4O_9$, included in Table 6, which evidently has the same structure. The isomorphism of the two compounds is not altogether surprising. Both have the same general formula, and potassium and barium are ions with roughly the same radii. A comparison of observed and calculated intensities (Table 7) tends to confirm the structure of KTi_3NbO_9, in principle if not in detail.

Discussion

The mutual substitution of titanium and niobium provides a means of forming stable potassium titanoniobates. These two elements, functioning virtually as a single ionic species of fractional valency between four and five, are associated with the oxygen atoms as double zigzag strings of octahedra forming the structural basis of both compounds. These strings unite with corners in common to form sheets, and in $KTiNbO_5$ are joined only through the potassium ions giving a layer structure. The differences of composition between the two compounds are a reflexion of the condensation of these sheets by additional corner sharing into a tunnel structure for KTi_3NbO_9, where the potassium ions are isolated in continuous linear strings of interstitial positions.

This follows the pattern set by the alkali titanates, where the sheets of treble octahedral groups of $Na_2Ti_3O_7$, although organized rather differently through sodium ions, are nevertheless regrouped into tunnels by corner sharing of octahedra from adjacent sheets to form the structure of $Na_2Ti_6O_{13}$. There are several other ways whereby the treble groups can be expected to join up with each other by edge-sharing as well, but Ti_3O_5 is the only one so far known (Andersson & Wadsley, 1962*a*). It is difficult to foresee additional titanoniobate structures based on this scheme. Edge sharing between one sheet and the next one can arise only by regrouping the double zigzag sheets in more drastic ways.

A further contrast to the alkali titanates is also noted. A tetratitanate with the approximate formula $Na_2Ti_4O_9$ is not an equilibrium phase but is believed to have a chance composition corresponding to the more or less ordered intergrowth of sheet and tunnel units of $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ in equal proportions (Andersson & Wadsley, 1962*a*). This compound, formed hydrothermally or from fluoride melts (Berry, Aftandilian, Gilbert, Meibohm & Young, 1960), owes its existence to the similarities of the parent phases. We might expect the same intergrowth of $KTiNbO_5$ and KTi_3NbO_9, where a composition $K_5Ti_7Nb_5O_{29}$ would represent a regular sequence of the sheet and tunnel elements. Preliminary experiments with this in view have not been successful, and it seems probable that the two phases we have described are the only potassium titanoniobates related to each other in a simple way.

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