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The Structures of $Na_2Ti_6O_{13}$ and $Rb_2Ti_6O_{13}$ and the Alkali Metal Titanates

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The crystal structures of the isomorphous hexatitanates of sodium and rubidium have been determined by electron-density projections. Each forms a lattice of titanium–oxygen octahedra in an open framework, in which the interstitial tunnels are occupied by the alkali-metal atoms. Relationships with $Na_2Ti_3O_7$ and Ti_3O_5 are pointed out, and there is evidence that they constitute a structural sequence $B_nTi_6O_{10+n}(0 \leq n \leq 4)$, B being the number of interstitial positions and not necessarily the number of alkali-metal atoms occupying them. The alkali-metal tetratitanates are discussed in terms of ordered units of both tri- and hexatitanate structures occurring in a region of variable composition.

Introduction

Several compounds which are formed by the alkali metals with titanium dioxide can be represented as a composition series $A_2O.nTiO_2$ $(1 \leq n \leq 6)$. We have examined some of these with the object of clarifying the relations within the system between crystal structure and chemical composition, and descriptions of $K_2Ti_2O_5$ and $Na_2Ti_3O_7$ have already been published (Andersson & Wadsley, 1961*a*, 1961*b*). In the present study we attempted to conclude the 'series' by the structure analysis of the remaining members, so that the crystal chemistry of the whole system could be studied. $Rb_2Ti_4O_9$ (i.e. $n=4$) was reported to have a congruent melting point and therefore was possibly the easiest of the tetratitanates to prepare (Schmitz-Dumont & Reckhard, 1959). Good crystals of $Na_2Ti_6O_{13}$ $(n=6)$ were readily made, and the relationship between this and $K_2Ti_6O_{13}$, a new inorganic fibre of potential economic importance (Berry, Aftandilian, Gilbert, Meibohm & Young, 1960), was of some additional interest. The member $n=5$ has never been expressly identified.

Experimental

$Na_2Ti_6O_{13}$ can be made by heating Na_2CO_3 and TiO_2 (anatase) in the molar ratio 1:6, firstly at 1000 °C. to drive off CO_2 and then at 1300 °C. Better crystals, in the form of colorless needles well suited to structure analysis, were obtained by heating crystalline $Na_2Ti_3O_7$ at 950 °C. in air for several days, and were evidently formed by the loss of some of the alkali metal and oxygen.

The preparation of the tetra- and hexa-titanates was discussed in some considerable detail in the paper by Berry *et al.* (1960) which appeared when this work was in progress. They reported many difficulties in the isolation of potassium tetratitanate except from fluoride-containing molten salts, and then only as a phase of doubtful chemical identity and with poor diffraction characteristics. Our attempts to prepare $Rb_2Ti_4O_9$ by direct fusion in a closed crucible of Rb_2CO_3 and TiO_2 in the molar ratio 1:4 gave a fibrous material of indeterminate composition, a crystal of which was found to be isomorphous with sodium hexatitanate.

Both substances were examined, particular emphasis being given to $Na_2Ti_6O_{13}$. The crystallographic data, together with those for $K_2Ti_6O_{13}$ reported in brief by Berry *et al.* (1960) are given in Table 1, and the Guinier diffraction pattern of $Na_2Ti_6O_{13}$ in Table 2. The $h0l$ and $h1l$ intensities for both compounds were obtained on multiple films by the integrated Weissen-

Table 1. *Crystallographic data for the alkali metal hexatitanates*

Symmetry: monoclinic

		$Na_2Ti_6O_{13}$	$K_2Ti_6O_{13}$*	$Rb_2Ti_6O_{13}$
Unit cell dimensions	a	$15 \cdot 131 \pm 0 \cdot 002$ Å	15·60 Å	15·89 Å
	b	$3 \cdot 745 \pm 0 \cdot 002$	3·80	3·82
	c	$9 \cdot 159 \pm 0 \cdot 002$	9·13	9·11
	β	$99 \cdot 30 \pm 0 \cdot 05°$	99·6°	100·4°
Systematic absent reflexions		hkl with $h+k \neq 2n$		
Possible space groups		$C2/m$, $C2$, or Cm		
D_o (g.cm.$^{-3}$)		$3 \cdot 48 \pm 0 \cdot 05$	3·58	—
D_c (g.cm.$^{-3}$), $Z=2$		3·51	3·58	4·07

* From Berry, Aftandilian, Gilbert, Meibohm & Young (1960).

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Table 2. $Na_2Ti_6O_{13}$ *Guinier powder pattern, Cu* $K\alpha_1$ *radiation*

Internally calibrated with KCl

Intensity	$\sin^2 \theta$ (obs.)	*hkl*	$\sin^2 \theta$ (calc.)
s	0·01064	200	0·01064
ms	0·01507	$20\bar{1}$	0·01506
vw	0·04272	400	0·04256
s	0·04495	110	0·04495
vw	0·05361	111	0·05363
ms	0·06625	310	0·06623
ms	0·06747	$20\bar{3}$	0·06746
ms	0·06927	$31\bar{1}$	0·06923
mw	0·07673	112	0·07683
w	0·07773	311	0·07775
m	0·08280	402	0·08296
mw	0·09483	$60\bar{1}$	0·09450
vw	0·10604	$11\bar{3}$	0·10603
ms	0·13621	$40\bar{4}$	0·13600
ms	0·14162	602	0·14184
s	0·16913	020	0·16916

berg method using filtered copper radiation, and measured by means of a calibrated film strip. The *h*2*l* and *h*3*l* data were also recorded. Very small crystals were used, and no absorption corrections were considered necessary. The calculations for the structure factors, modified eventually by an isotropic temperature factor $B = 0{\cdot}6$ Å^{-2} obtained experimentally for each substance independently, incorporated the ionized scattering curves used in a previous determination of the structure of $Na_2Ti_3O_7$ (Andersson & Wadsley, 1961*b*), and that of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for Rb^+.

Structure determination of $Na_2Ti_6O_{13}$

The equality of the intensity distribution of the *h*0*l* and *h*2*l* reflexions of similar index, and also of the *h*1*l* and *h*3*l* terms, favoured the centrosymmetrical space group *C*2/*m*, one of the three alternatives given by the systematically absent reflexions (Table 1).

The *h*0*l* terms included several strong spots whose indices could be referred to a pseudocubic sub-cell. This is related to the real unit cell by the transform

$$\text{cubic} \rightarrow \text{monoclinic} = 30\bar{2}/010/102.$$

We have previously shown (Andersson & Wadsley, 1961*b*) that sub-cell geometry can be very useful in helping to solve problems of the present kind. Whilst there may be little or no actual resemblance to any simple cubic substance, the atoms in projection form a more or less square network, as Harrison (1957) pointed out in the analogous case of $BaTi_2O_5$. The matrix is determined by the orientation of this grid.

The Patterson projection $P(u, w)$ bore a striking resemblance to that which could be expected of a perovskite structure, ABO_3. If $Na_2Ti_6O_{13}$ itself is regarded as a 'defective perovskite' $Na_{0{\cdot}33}TiO_{2{\cdot}17}$, with ordered defects of some kind, the solution of the function *ab initio* is a matter of considerable difficulty. The selection of trial models of the structure, however, can be reduced to the problem of finding the correct numbers of atoms within the unit cell, as the matrix determines their average direction relative to one another. The numbers of oxygen atoms may be made variable by considering whether adjacent octahedra (in this instance) have corners, edges or even faces in common, and with squared paper a great many models can be rapidly devised and tested with the aid of the Patterson function. The only model fulfilling these various conditions refined by successive Fourier and difference syntheses on to (010) until the final reliability factor for the *h*0*l* terms was 11·9%, non-observed reflexions omitted.

Many oxide structures, and in particular those having an axis of symmetry which corresponds in length to an octahedral diagonal, give a space-group ambiguity which it is difficult to resolve. The limited number of *hk*0 reflexions, and the length of the *c* axis (9·16 Å), resulting in extensive overlap of the atoms, preclude the use of additional electron-density projections to distinguish between the space group assumed on reasonable ground to be *C*2/*m*, and the remaining non-centrosymmetrical alternative *C*2, statistical methods proving to be not sufficiently definite. The positional parameters *x* and *z* were combined with $y = 0$ for all atoms, in accord with the space group *C*2/*m* already inferred, in a set of *h*1*l* structure factors. These gave a reliability factor of 15·9% and further refinement of the *y* coordinates was not considered.

Table 3. *Fractional atomic parameters*

Space group *C*2/*m*. $(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0)+$

		$Na_2Ti_6O_{13}$		$Rb_2Ti_6O_{13}$	
Atom	Point position	*x*	*z*	*x*	*z*
Ti_1	4(*i*)	0·1137 ± 0·0005	0·0895 ± 0·0009	0·114	0·093
Ti_2	4(*i*)	0·1705 ± 0·0004	0·4332 ± 0·0010	0·174	0·435
Ti_3	4(*i*)	0·2287 ± 0·0006	0·7726 ± 0·0010	0·236	0·778
Na or Rb	4(*i*)	0·4540 ± 0·0008	0·2508 ± 0·0014	0·456	0·250
O_1	2(*a*)	0	0	0	0
O_2	4(*i*)	0·228 ± 0·002	0·247 ± 0·004	0·233	0·237
O_3	4(*i*)	0·071 ± 0·001	0·291 ± 0·002	0·084	0·305
O_4	4(*i*)	0·282 ± 0·002	0·574 ± 0·004	0·273	0·577
O_5	4(*i*)	0·124 ± 0·001	0·617 ± 0·002	0·134	0·612
O_6	4(*i*)	0·358 ± 0·002	0·884 ± 0·004	0·351	0·908
O_7	4(*i*)	0·167 ± 0·001	0·927 ± 0·002	0·165	0·919

Table 4. $Na_2Ti_6O_{13}$.

Comparison between F_o and F_c

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
001	< 9	13	$\bar{7}$	102	111	$\bar{4}$	< 32	0	1	21	$\overline{25}$
2	23	$\overline{34}$	$\bar{8}$	< 32	17	$\bar{5}$	< 30	20	0	< 20	9
3	38	$\overline{35}$	$\bar{9}$	< 31	$\bar{4}$	$\bar{6}$	< 29	15	$\bar{1}$	< 20	$\overline{11}$
4	< 19	18	$\overline{10}$	27	$\overline{29}$	$\bar{7}$	< 29	11	2	< 21	$\bar{3}$
5	< 24	2	809	< 21	14	$\bar{8}$	52	49	$\bar{3}$	52	$\overline{62}$
6	154	$\overline{171}$	8	47	41	$\bar{9}$	< 18	$\bar{5}$	$\bar{4}$	148	162
7	< 29	5	7	53	$\overline{53}$	16,0,4	< 19	$\overline{21}$	$\bar{5}$	< 29	35
8	< 32	18	6	< 32	$\overline{20}$	3	65	63	$\bar{6}$	< 32	0
9	69	71	5	31	$\overline{25}$	2	< 25	4	$\bar{7}$	< 34	$\bar{5}$
10	< 27	6	4	51	34	1	< 30	$\bar{4}$	$\bar{8}$	< 35	20
2,0,10	< 25	$\bar{7}$	3	< 27	0	0	< 28	$\bar{8}$	$\bar{9}$	34	48
9	< 30	1	2	< 25	22	$\bar{1}$	29	23	$\overline{10}$	69	$\overline{80}$
8	32	34	1	68	70	$\bar{2}$	< 29	23	719	< 25	$\overline{22}$
7	30	31	0	46	37	$\bar{3}$	41	$\overline{49}$	8	44	40
6	152	149	$\bar{1}$	79	77	$\bar{4}$	< 28	$\overline{12}$	7	< 35	12
5	85	$\overline{77}$	$\bar{2}$	40	$\overline{33}$	$\bar{5}$	< 26	$\overline{15}$	6	< 36	$\overline{20}$
4	< 21	$\bar{9}$	$\bar{3}$	< 24	$\overline{26}$	$\bar{6}$	42	43	5	35	$\overline{44}$
3	45	$\overline{51}$	$\bar{4}$	94	$\overline{115}$	$\bar{7}$	< 21	0	4	32	47
2	< 15	$\overline{21}$	$\bar{5}$	< 28	$\bar{4}$	1,1,10	< 28	35	3	47	57
1	< 12	0	$\bar{6}$	< 29	11	9	58	40	2	180	180
0	100	$\overline{115}$	$\bar{7}$	30	$\overline{30}$	8	36	$\overline{36}$	1	48	$\overline{65}$
$\bar{1}$	83	104	$\bar{8}$	32	39	7	< 34	$\bar{1}$	0	< 25	0
$\bar{2}$	35	46	$\bar{9}$	< 30	23	6	32	44	$\bar{1}$	< 25	14
$\bar{3}$	173	179	$\overline{10}$	72	69	5	39	$\overline{31}$	$\bar{2}$	< 25	$\bar{5}$
$\bar{4}$	35	$\overline{26}$	10,0,8	< 22	6	4	51	$\overline{49}$	$\bar{3}$	37	$\overline{26}$
$\bar{5}$	24	$\overline{41}$	7	< 27	8	3	41	$\overline{29}$	$\bar{4}$	149	$\overline{150}$
$\bar{6}$	27	$\overline{35}$	6	< 30	29	2	93	77	$\bar{5}$	44	64
$\bar{7}$	< 27	2	5	32	21	1	43	28	$\bar{6}$	< 33	11
$\bar{8}$	< 32	5	4	89	$\overline{94}$	0	118	113	$\bar{7}$	61	40
$\bar{9}$	94	$\overline{83}$	3	30	$\overline{36}$	$\bar{1}$	< 12	$\bar{7}$	$\bar{8}$	< 35	2
$\overline{10}$	49	39	2	41	$\overline{32}$	$\bar{2}$	31	30	$\bar{9}$	< 33	9
4,0,10	< 23	$\overline{12}$	1	74	$\overline{64}$	$\bar{3}$	58	61	$\overline{10}$	34	40
9	< 28	7	0	38	$\overline{25}$	$\bar{4}$	< 24	$\overline{29}$	918	51	65
8	44	44	$\bar{1}$	27	$\overline{19}$	$\bar{5}$	< 27	0	7	59	$\overline{59}$
7	< 32	$\overline{14}$	$\bar{2}$	121	120	$\bar{6}$	115	$\overline{104}$	6	< 35	$\overline{22}$
6	< 29	$\overline{14}$	$\bar{3}$	62	56	$\bar{7}$	< 34	8	5	< 36	$\overline{17}$
5	109	120	$\bar{4}$	43	39	$\bar{8}$	< 35	4	4	< 35	15
4	66	62	$\bar{5}$	60	$\overline{59}$	$\bar{9}$	< 34	0	3	< 33	$\bar{4}$
3	69	47	$\bar{6}$	< 31	$\bar{6}$	$\overline{10}$	< 30	26	2	59	$\overline{88}$
2	186	$\overline{199}$	$\bar{7}$	< 31	$\overline{19}$	3,1,10	< 26	$\bar{7}$	1	86	110
1	23	$\overline{23}$	$\bar{8}$	< 30	$\overline{15}$	9	< 32	$\overline{13}$	0	51	63
0	36	$\overline{37}$	$\bar{9}$	< 28	$\bar{6}$	8	57	58	$\bar{1}$	82	68
$\bar{1}$	15	$\overline{39}$	$\overline{10}$	< 22	$\bar{5}$	7	35	49	$\bar{2}$	80	$\overline{82}$
$\bar{2}$	40	$\overline{32}$	12,0,7	47	40	6	93	93	$\bar{3}$	< 30	$\overline{22}$
$\bar{3}$	37	$\overline{43}$	6	< 25	$\bar{5}$	5	42	$\overline{67}$	$\bar{4}$	32	41
$\bar{4}$	221	250	5	< 29	$\bar{5}$	4	< 26	$\overline{11}$	$\bar{5}$	< 33	$\overline{17}$
$\bar{5}$	41	50	4	< 31	23	3	43	51	$\bar{6}$	35	$\overline{28}$
$\bar{6}$	60	55	3	< 32	4	2	39	$\overline{46}$	$\bar{7}$	71	$\overline{71}$
$\bar{7}$	38	$\overline{18}$	2	< 32	5	1	69	$\overline{71}$	$\bar{8}$	73	85
$\bar{8}$	< 32	$\bar{9}$	1	62	$\overline{69}$	0	146	$\overline{146}$	$\bar{9}$	< 31	29
$\bar{9}$	< 31	$\bar{3}$	0	< 30	$\bar{7}$	$\bar{1}$	142	138	$\overline{10}$	< 25	11
$\overline{10}$	48	$\overline{54}$	$\bar{1}$	< 30	8	$\bar{2}$	47	50	11,1,7	62	69
6,0,10	< 18	1	$\bar{2}$	53	66	$\bar{3}$	< 21	$\bar{1}$	6	< 30	$\bar{8}$
9	< 25	4	$\bar{3}$	< 30	2	$\bar{4}$	< 24	4	5	< 33	0
8	95	$\overline{87}$	$\bar{4}$	< 31	0	$\bar{5}$	55	48	4	79	$\overline{67}$
7	< 32	$\bar{3}$	$\bar{5}$	45	53	$\bar{6}$	69	89	3	< 36	$\bar{8}$
6	< 31	2	$\bar{6}$	< 32	29	$\bar{7}$	34	$\overline{35}$	2	35	$\overline{25}$
5	41	42	$\bar{7}$	< 32	6	$\bar{8}$	< 35	$\overline{27}$	1	< 34	22
4	< 26	$\overline{11}$	$\bar{8}$	84	$\overline{83}$	$\bar{9}$	59	$\overline{44}$	0	< 33	18
3	< 24	$\overline{18}$	$\bar{9}$	< 24	$\bar{2}$	$\overline{10}$	< 30	34	$\bar{1}$	< 33	$\overline{15}$
2	211	233	14,0,5	< 23	10	5,1,10	< 21	8	$\bar{2}$	145	148
1	28	34	4	38	37	9	< 29	$\bar{9}$	$\bar{3}$	< 33	20
0	< 19	$\bar{9}$	3	< 29	$\bar{2}$	8	34	$\overline{33}$	$\bar{4}$	34	29
$\bar{1}$	113	$\overline{95}$	2	31	23	7	< 35	13	$\bar{5}$	61	$\overline{35}$
$\bar{2}$	< 20	0	1	< 31	11	6	< 35	1	$\bar{6}$	< 36	$\bar{8}$
$\bar{3}$	24	26	0	< 32	$\overline{25}$	5	106	95	$\bar{7}$	< 34	25
$\bar{4}$	58	$\overline{79}$	$\bar{1}$	< 32	$\overline{11}$	4	< 29	$\bar{1}$	$\bar{8}$	64	$\overline{72}$
$\bar{5}$	< 25	$\bar{6}$	$\bar{2}$	78	82	3	< 26	29	$\bar{9}$	< 28	$\bar{4}$
$\bar{6}$	< 28	14	$\bar{3}$	32	28	2	29	$\overline{39}$			

Table 4 (*cont.*)

hkl	F_o	F_c	*hkl*	F_o	F_c
13,1,6	< 23	6	2	< 31	24
5	< 29	24	1	51	41
4	110	112	0	58	$\overline{57}$
3	34	$\overline{41}$	$\bar{1}$	34	$\overline{36}$
2	< 35	$\overline{31}$	$\bar{2}$	48	$\overline{26}$
1	66	$\overline{33}$	$\bar{3}$	< 33	7
0	50	27	$\bar{4}$	< 33	$\bar{1}$
$\bar{1}$	< 36	$\bar{3}$	$\bar{5}$	44	$\overline{40}$
$\bar{2}$	75	$\overline{88}$	$\bar{6}$	57	65
$\bar{3}$	36	54	$\bar{7}$	40	40
$\bar{4}$	35	39	17,1,2	< 21	1
$\bar{5}$	81	60	1	< 24	9
$\bar{6}$	< 33	$\overline{26}$	0	79	76
$\bar{7}$	< 31	$\bar{6}$	$\bar{1}$	< 27	3
$\bar{8}$	< 27	5	$\bar{2}$	< 28	9
$\bar{9}$	< 21	11	$\bar{3}$	60	$\overline{39}$
15,1,4	< 24	$\bar{9}$	$\bar{4}$	< 26	$\bar{4}$
3	40	49	$\bar{5}$	< 23	$\bar{2}$

Table 5. *Interatomic distances*

$Na_2Ti_6O_{13}$

	No.	Length		No.	Length
Ti_1–O_1	1	1·81 Å	O_2–$O_4{}^1$	2	2·51 Å
Ti_1–O_2	1	2·02	O_3–$O_4{}^1$	2	3·02
Ti_1–O_3	1	1·97	O_4–$O_4{}^1$	2	2·43
Ti_1–O_7	1	1·88	O_5–$O_4{}^1$	2	3·06
Ti_1–$O_6{}^1$	2	1·93	Ti_3–O_4	1	2·11
O_1–O_7	1	2·71	Ti_3–O_5	1	1·95
O_7–O_2	1	2·93	Ti_3–O_6	1	2·05
O_2–O_3	1	2·42	Ti_3–O_7	1	1·82
O_1–O_3	1	2·70	Ti_3–$O_2{}^1$	2	2·00
O_1–$O_6{}^1$	2	2·92	O_4–O_5	1	2·48
O_7–$O_6{}^1$	2	2·62	O_4–O_6	1	2·89
O_2–$O_6{}^1$	2	2·47	O_6–O_7	1	2·98
O_3–$O_6{}^1$	2	2·79	O_5–O_7	1	2·80
Ti_2–O_2	1	2·04	O_4–$O_2{}^1$	2	2·51
Ti_2–O_3	1	1·83	O_6–$O_2{}^1$	2	2·47
Ti_2–O_4	1	1·95	O_7–$O_2{}^1$	2	3·07
Ti_2–O_5	1	1·93	O_5–$O_2{}^1$	2	3·03
Ti_2–$O_4{}^1$	2	2·01	Na–O_3	2	2·56
O_2–O_3	1	2·42	Na–O_5	2	2·59
O_2–O_4	1	2·97	Na–O_7	2	2·92
O_4–O_5	1	2·48	Na–O_1	2	3·13
O_3–O_5	1	2·97			

$Rb_2Ti_6O_{13}$

	No.	Length		No.	Length
Ti_1–O_1	1	1·86 Å	O_2–$O_4{}^1$	2	2·57
Ti_1–O_2	1	2·10	O_3–$O_4{}^1$	2	3·01
Ti_1–O_3	1	2·07	O_4–$O_4{}^1$	2	2·40
Ti_1–O_7	1	1·90	O_5–$O_4{}^1$	2	3·12
Ti_1–$O_6{}^1$	2	2·10	Ti_3–O_4	1	2·02
O_1–O_7	1	2·85	Ti_3–O_5	1	2·00
O_7–O_2	1	2·90	Ti_3–O_6	1	1·99
O_2–O_3	1	2·55	Ti_3–O_7	1	1·85
O_1–O_3	1	2·86	Ti_3–$O_2{}^1$	2	1·98
O_1–$O_6{}^1$	2	3·04	O_4–O_5	1	2·29
O_7–$O_6{}^1$	2	2·46	O_4–O_6	1	3·05
O_2–$O_6{}^1$	2	2·56	O_6–O_7	1	2·97
O_3–$O_6{}^1$	2	3·03	O_5–O_7	1	2·75
Ti_2–O_2	1	2·18	O_4–$O_2{}^1$	2	2·57
Ti_2–O_3	1	1·69	O_6–$O_2{}^1$	2	2·56
Ti_2–O_4	1	1·84	O_7–$O_2{}^1$	2	3·00
Ti_2–O_5	1	1·84	O_5–$O_2{}^1$	2	2·99
Ti_2–$O_4{}^1$	2	2·10	Rb–O_3	2	2·77
O_2–O_3	1	2·55	Rb–O_5	2	2·82
O_2–O_4	1	3·05	Rb–O_7	2	2·94
O_4–O_5	1	2·29	Rb–O_1	2	3·14
O_3–O_5	1	2·77			

For our purposes, the structure can nevertheless be described in terms of $C2/m$. Some of the lighter atoms could perhaps be shifted slightly from the mirror planes in which they are assumed to lie; the effects of these displacements will be to alter the interatomic distances by small amounts, but will not concern the structure as a whole.

The standard deviations were estimated by the method outlined by equation *308·4* in Lipson & Cochran (1953, p. 308). The central curvature for each atom was obtained from the Gaussian ellipsoid approximation (Dawson, 1961) on the peaks of the final F_o synthesis, and the r.m.s. values of slopes parallel to a and c in the final $h0l$ difference synthesis were estimated in the regions of the map in which atoms do not occur. Lipson & Cochran point out that this may result in a slight underestimate.

The atomic parameters and their standard deviations are given in Table 3, the observed and calculated structure factors in Table 4, and the interatomic distances in Table 5. The standard deviations, averaged for contacts of the same kind, are ±0·030 Å for Ti–O, ±0·045 Å for Na–O, and ±0·055 Å for O–O.

The structure of the rubidium compound

Whilst we had intended to prepare the tetratitanate $Rb_2Ti_4O_9$, the relationship with $Na_2Ti_6O_{13}$ which appeared when the space-group data were assembled suggested that both compounds might be isomorphous and with the same exact chemical composition. On the other hand, the Debye-Scherrer evidence presented by Schmitz-Dumont & Reckhard (1959) from their phase equilibria studies made it appear likely that one or more of the titania-rich phases in the systems with the alkali metals could perhaps have an extended homogeneity range. This possibility was examined.

A trial structure very similar to that of $Na_2Ti_6O_{13}$ but with the composition $Rb_2Ti_4O_9$ can be constructed very plausibly and simply. The reduction of symmetry to the space group $C2$ permits additional metal atoms to be introduced into the 2(b) positions $(0, y, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}+y, \frac{1}{2})$ with y approximately equal to $\frac{1}{2}$, as well as an additional oxygen statistically distributed over another pair of the same sites for which the y parameter is approximately zero. In this way reasonable interatomic distances can be obtained in a unit cell of the same size as the hexatitanate, but containing $Rb_6Ti_{12}O_{27}$ (i.e. $3 \times Rb_2Ti_4O_9$). Because of the fibrous nature of the crystals, reliable density measurements, which would have been of considerable help at this stage, could not be made, and a chemical analysis was indecisive. The interpretation of the Patterson function $P(u, w)$ was weighted with this model in mind, but attempted refinement proved it to be wrong.

The alkali titanates have a tendency to lose both alkali metal and oxygen when they are heated, and the attempted preparation of $Rb_2Ti_4O_9$ at 1350° may have resulted in the partial formation of $Rb_2Ti_6O_{13}$

instead. On this assumption the refinement of the $h0l$ data by Fourier and difference syntheses, based upon a model isomorphous with $Na_2Ti_6O_{13}$ and with the same unit-cell contents, proceeded slowly until a reliability factor of 14·9% was reached. Considerable anisotropic spread of several of the atoms was seen, but since this could have been due to stacking disorders, which are discussed below, as well as to thermal motions, it was not considered expedient to proceed further with this analysis. The atomic coordinates and the interatomic distances, without estimations of errors, are given in Tables 3 and 5, again assuming the space group to be $C2/m$. The table comparing F_o with F_c is omitted.

Description of $Na_2Ti_6O_{13}$

The structure of the alkali–metal hexatitanate is a framework of titanium and oxygen atoms which enclosed the alkali–metal ions (Figs. 1 and 4(*b*)). Each titanium has six oxygen neighbours at the corners of a distorted octahedron. The Ti–O distances vary from 1·82 Å to 2·11 Å, and unlike $Na_2Ti_3O_7$ (Andersson & Wadsley, 1961*b*) there appears to be no tendency towards five coordination which occurs unambiguously in $K_2Ti_2O_5$ (Andersson & Wadsley, 1961*a*). There is some variation in the O–O distances, with the shortest, ranging from 2·42 Å to 2·51 Å, corresponding to pairs which are common to two adjacent titanium atoms, a familiar feature of oxide structures.

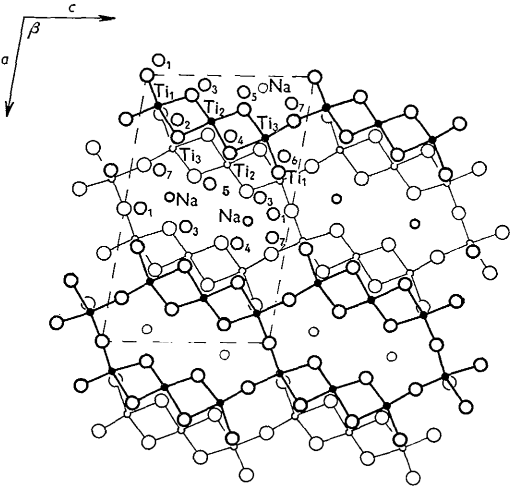

Fig. 1. Structure of $Na_2Ti_6O_{13}$ projected on to (010). Small circles are titanium, medium are sodium, and the largest, oxygen. The atoms in heavier outline are at $y=0$ and the lighter at $y=\frac{1}{2}$.

The octahedra share edges at one level in linear groups of three. Each is joined above and below to similar groups by further edge sharing, and form a zig-zag ribbon extending in the y direction (Fig. 3). The hexatitanate structure consists of these ribbons sharing all the terminal corners with identical ribbons (Fig. 4(*b*)), resulting in an open octahedral framework enclosing tunnels, or continuous rows of interstitial positions, in which the sodium ions are situated.

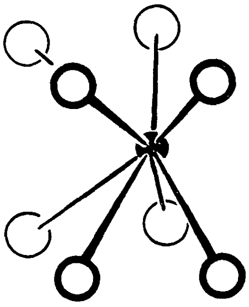

Fig. 2. Perspective drawing of the immediate oxygen environment of a sodium ion (black).

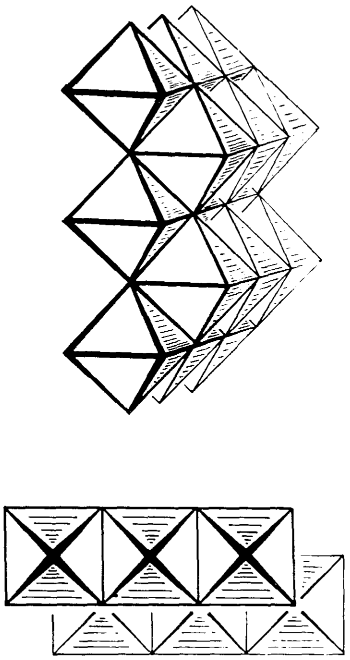

Fig. 3. Clinographic projection of a treble octahedral ribbon (upper) and as viewed down the axis of elongation (lower).

There are three approximately cubic positions within a unit tunnel, and if these are designated by the letter B, the structure can be given a 'formula' $B_3Ti_6O_{13}$, the significance of which is discussed below. The sodium ions occupy only two B positions, and are displaced towards the central unoccupied site, forming four short bonds to oxygen of 2·58 Å, and four longer ones averaging 3·02 Å (Fig. 2). The displacement of titanium atoms of the host lattice from the octahedral centres is in the general direction of the tunnels, and this could possibly influence the positions adopted by sodium.

The a and b axes of the alkali metal hexatitanates increase in the order Na → K → Rb as would be expected, but the *c* axial lengths show a corresponding decrease (Table 1). For purposes of general description the structures of the sodium and rubidium compounds are identical, and the small parameter differences and the variations of interatomic distance noted in Tables 3 and 5 simply reflect the readjustment of the host framework to accommodate the larger rubidium ions. We can imagine this elongation along the *a* axis to result from a compressive force or squeeze applied parallel to the *c* axis. Whilst this has little significant effect upon the Ti–O and O–O distances averaged over the whole of each compound, some individual contacts are considerably changed by the need to enlarge the tunnels. O_5 is the atom most affected, and the distance O_4–O_5 is reduced from 2·48 Å in $Na_2Ti_6O_{13}$ to 2·29 Å in $Rb_2Ti_6O_{13}$.

Structural relationship of the alkali titanates

For purposes of this discussion the somewhat idealized interlayer or interstitial positions which may be called 'cubic' *B* sites are considered equivalent to one another.

The similarities between $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$ are quite striking. The tri-titanate (Fig. 4(*a*)) is constructed of layers of the composition $(Ti_3O_7)^{2-}$ held together by sodium ions occupying all of the 'cubic' sites, and it has the formula $B_4Ti_6O_{14}$ (Andersson & Wadsley, 1961*b*). Each layer consists of zig-zag ribbons of the kind shown in Fig. 3 joined by corners. If one layer is translated relative to another along the *c* direction by a distance roughly equal to an octahedral edge, and also moved upwards (out of the plane of the paper) by *b*/2, half an octahedral diagonal, the corners indicated by arrows will coincide. This, then, is the framework of the hexatitanate (Fig. 4(*b*)). The number of 'cubic' interstitial positions is reduced from four to three, and only two of these are occupied. In view of these similarities, it is not altogether surprising that prolonged heating of a crystal of

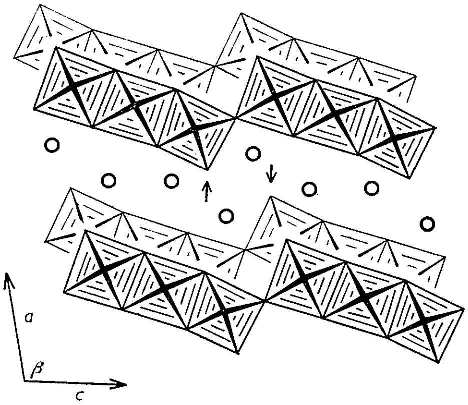

Fig. 4(*a*). $Na_2Ti_3O_7$ consists of ribbons of octahedra (as in Fig. 3) joined by corners to form isolated sheets held together by the alkali metal ion (circles) occupying all the pseudocubic interstitial positions. The arrows indicate the corners which are shared in the hexatitanate.

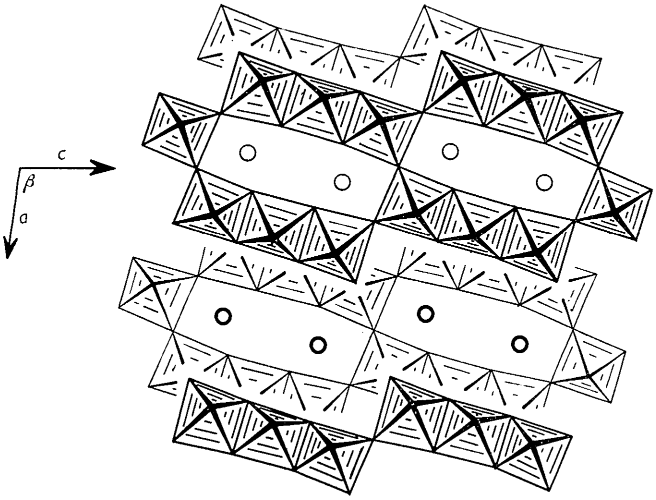

Fig. 4(*b*). $Na_2Ti_6O_{13}$ in projection. The corners join adjacent sheets to form a framework enclosing tunnels. Two sodium ions (circles) are present in a unit tunnel which contains three pseudocubic positions.

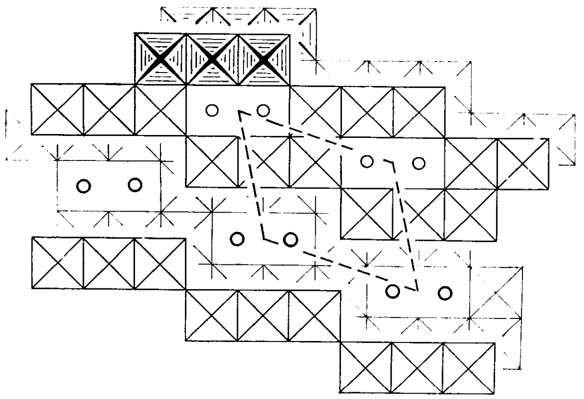

Fig. 4(*c*). Additional condensation of trititanate sheets give a hypothetical substance $B_2Ti_6O_{12}$ (idealized). One of the octahedral ribbons is hatched. Half the unit cell is drawn in broken lines, and the interstitial positions *B* are drawn as circles.

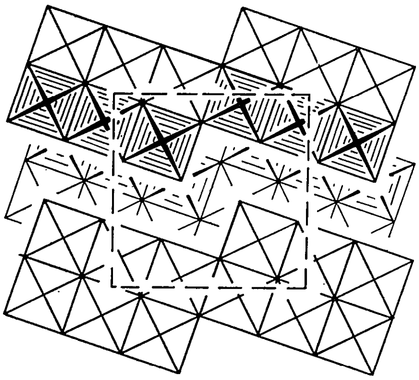

Fig. 4(*d*). The low temperature form of Ti_3O_5 (idealized). Two ribbons are hatched, and there are no interstitial positions. The unit cell is shown.

Table 6. *Crystallographic constants*

Symmetry: monoclinic

		$Na_2Ti_3O_7$	$Na_2Ti_6O_{13}$	Ti_3O_5	$K_2Ti_4O_{9-x}F_{2x}$	
					Crystal 1	Crystal 2
Unit cell Dimensions	a	8·571 Å	15·131 Å	9·752 Å	12·74 Å	12·1 Å
	b	3·804	3·745	3·802	3·80	3·80
	c	9·135	9·159	9·442	8·94	8·82
		101·57°	99·30°	91·55°	104°	99°

$Na_2Ti_3O_7$, with the inevitable loss of some sodium and oxygen, will result in the transformation to a crystal of $Na_2Ti_6O_{13}$.

It might be supposed that the sheets occurring in these two substances could be present in other titanates as well. An additional translation along c of one sheet with respect to another gives the structure shown in Fig. 4(c). Some edges are now shared by the adjacent sheets and the 'cubic' sites reduced to two. This hypothetical compound of formula $B_2Ti_6O_{12}$ (B again being the number of interstitial positions) would have a unit cell

$$a=14{\cdot}1,\ b=3{\cdot}8,\ c=8{\cdot}7\ \text{Å};\ \beta=119{\cdot}8^\circ,$$

space group $C2/m$, the lengths calculated upon the assumption of an average O–O distance of 2·75 Å. It might occur either as an alkali-free form of TiO_2 of new structure, or else as a substance in which the net valency of the titanium was less than four. This could be a bronze. Attempts to prepare it by the reduction at 950 °C. in hydrogen of $Na_2Ti_3O_7$ did, in fact, give a new bronze, but of a different kind (Wadsley & Andersson, 1961); perhaps it could be prepared under different conditions.

Two additional translations of one $(Ti_3O_7)^{2-}$ sheet with respect to another are still possible. The first, having two edges of each octahedral ribbon in common with two from the next sheet, gives $B_1Ti_6O_{11}$ with one 'cubic' position; the second, with all three edges shared, is Ti_6O_{10} with none (Fig. 4(d)). This is the structure of the low-temperature form of Ti_3O_5 (Åsbrink & Magnéli, 1959), shown here in idealized form.

In the introduction to this paper the alkali titanates were written conveniently as a composition series, $A_2O.nTiO_2$. If the structures, real and imaginary, which are discussed here are to be represented as a sequence, a general formula should be based upon geometrical features common to them all. This will be $B_nTi_6O_{10+n}$ or $B_{4-n}Ti_6O_{14-n}$ ($0 \leq n \leq 4$) where B, as above, is the number of sites and not the alkali metal actually present in them. Since titanium is five-coordinated in the dititanate $K_2Ti_2O_5$, it does not conform.

The alkali metal tetratitanates

Table 6, which summarizes the lattice dimensions of the three known members of the structural series, includes measurements made by Berry *et al.* (1960) on two forms of imperfectly crystallized potassium tetratitanate, $K_2Ti_4O_{9-x}F_{2x}$, prepared from fluoride melts. The c dimension corresponds to the repeat distance of the $(Ti_3O_7)^{2-}$ sheets, which evidently form the basic unit of the tetratitanate as well. From melts of different composition, it was shown by these authors that the tetratitanate structure developed at the expense of the hexatitanate through a region of crystalline disorder. This is in agreement with the data of Schmitz-Dumont & Reckhard (1959).

Since both tri- and hexatitanates contain the same sheets having virtually identical interatomic distances, it might be expected that overgrowth of one structure upon the other could occur on a unit-cell scale, substances of intermediate composition containing the elements of both. Insertion in the hexatitanate structure of discrete $(Ti_3O_7)^{2-}$ sheets, bonded through

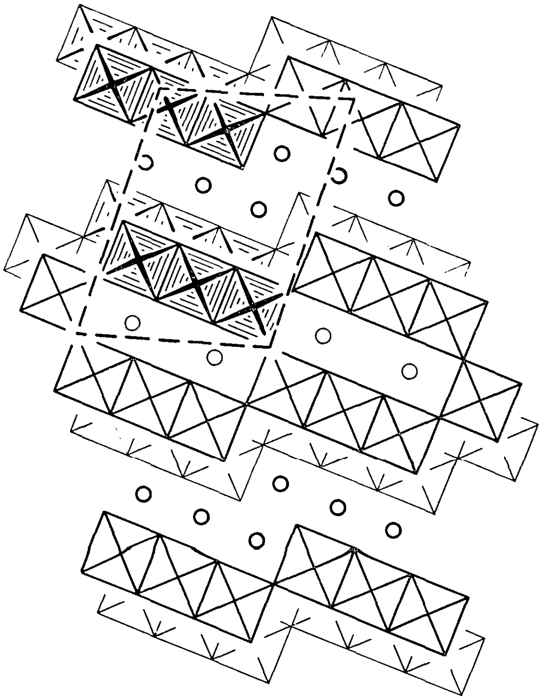

Fig. 5. The hypothetical substance $Na_{10}Ti_{18}O_{41}$ which resembles the alkali tetratitanate in many respects. It consists of single $(Ti_3O_7)^{2-}$ sheets alternating with $(Ti_6O_{13})^{2-}$ sheets, bonded by means of sodium ions (circles). The asymmetric unit is outlined. This demonstrates a possible mechanism by means of which a transition from the hexa- to the trititanate could take place.

sodium ions and having none of the terminal oxygen atoms in common, will give a simple alternative method by which both the sodium and the oxygen content can be made variable, and if they are present at random will undoubtedly provide evidence of disorder. Ordering will most likely occur at intermediate points where the ratio of the two kinds of unit are simple whole numbers.

Such a one (Fig. 5) comprises single units of the sodium tri- and hexatitanates alternating with one another. In one orientation the dimensions of the unit cell are

$$a=46\cdot8,\ b=3\cdot8,\ c=8\cdot7\ \text{Å};\ \beta=105\cdot1^\circ,$$

space group $C2/m$ (the average O–O distance again assumed to be 2·75 Å), and with the formula of the asymmetric unit $Na_{10}Ti_{18}O_{41}$, reducing to $Na_{2.2}Ti_4O_{9.1}$. The agreement with the figures in Table 6 for one form of poorly crystallized potassium tetratitanate is quite striking, except for a which is four times greater; a large axis and the likelihood of disorder, however, create difficult problems of identification in single-crystal diffraction films. The formula would approach that of a tetratitanate more closely if some $(Ti_3O_7)^{2-}$ layers were missing, and this would be accompanied by increased disorder and dimensional changes.

Berry *et al.* (1960) provided convincing evidence that potassium hexatitanate is fibrous, and whilst it is undoubtedly isomorphous with the corresponding sodium and rubidium compounds, the crystal structures of these two give no clear explanation of why this should be so except in terms of the closely coordinated octahedral tunnels. The fibrous property of these compounds may perhaps be related to their composition. Any additional $(Ti_3O_7)^{2-}$ sheets present would be expected to improve cleavages, in one direction at least.

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$Na_xTi_4O_8$, an Alkali Metal Titanium Dioxide Bronze

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A chemically inert ternary oxide $Na_xTi_4O_8$ (x approximately 0·8), prepared by the reduction in hydrogen of $Na_2Ti_3O_7$ at 950 °C., is monoclinic, space group $C2/m$, with unit-cell dimensions

$$a=12\cdot146,\ b=3\cdot862,\ c=6\cdot451\ \text{Å};\ \beta=106\cdot85^\circ.$$

It has a new kind of AX_2 host lattice with very distorted cubic interstitial positions partly occupied by sodium ions, and is a bronze, a non-stoichiometric oxide with some of the properties of a metal. The host structure is the end member of an homologous series $Me_{2n}O_{5n-2}$, n being here equal to two.

Introduction

In a recent discussion of the crystal chemistry of the alkali metal titanates (Andersson & Wadsley, 1962) we noted the existence of a sequence of structures with the general formula $B_nTi_6O_{10+n}$ $(0 \leq n \leq 4)$, B representing an interstitial position which could hold an alkali-metal ion. The three known members, the low temperature form of Ti_3O_5 $(n=0)$, $Na_2Ti_6O_{13}$ $(n=3)$ and $Na_2Ti_3O_7$ $(n=4)$, all contained common structural features, and the likely existence of addi-

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