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$K_3Ti_8O_{17}$, a New Alkali Titanate Bronze

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A new alkali titanate oxide bronze $K_3Ti_8O_{17}$ has been prepared by fused oxide electrolysis at 1010°C. It is monoclinic, space group C2/m, with unit cell dimensions $a = 15.68$, $b = 3.809$, $c = 12.06$ Å, $\beta = 95.0°$. Its structure is defined by a framework of titanium–oxygen octahedra and at any one level the octahedra edge-share in blocks of four with their diagonals directed along the 3.8 Å c axis. Each block edge-shares to similar blocks above and below it to form zigzag ribbons of closely packed octahedra. The ribbons are corner joined to similar units to form staggered sheets which join still further to form prismatic tunnels which contain potassium atoms side by side in groups of three. The structure is closely related to two known sodium titanates $Na_2Ti_6O_{13}$ and $Na_2Ti_7O_{15}$.

Introduction

Oxide "bronzes" form a special group in the families of oxide compounds. They have a three-dimensional framework of metal–oxygen polyhedra in which all metal sites are occupied, and which encloses crystallographically defined sets of positions that are partly or wholly occupied by other metal ions. These ions are commonly those of the alkali or alkaline earth metals but may include Al^{3+}, In^{3+} or the trivalent rare earths. In all cases variations in the occupancy of the "enclosed" sites is charge compensated in the host framework. For normal insulating oxides this compensation involves alterations in compositional ratios, e.g., in titanates such as $Cs_xMg^{2+}Ti^{4+}_{2-x/2}O_4$ or $Cs_xFe^{3+}Ti^{4+}_{2-x}O_4$, the Mg^{2+}/Ti^{4+} or Fe^{3+}/Ti^{4+} ratios alter with x. In the case of bronzes however, charge compensation is achieved by a reduction in valency of a fraction of the host metal ion, e.g., Na_xTiO_2 (*1*) may be regarded formally as $Na_x(Ti^{3+}_xTi^{4+}_{1-x})O_2$. Bronzes can be prepared in a number of ways notably by electrolysis (*2*) and (*3*), but except for those of vanadium, do not as a rule appear during a normal phase study. A recent review by Banks and Wold (*2*) emphasizes the need for reducing conditions in the preparation of bronzes. Two titanium bronze compounds have been identified among the products obtained by reducing various alkali titanates in hydrogen (*1*); one was Na_xTiO_2 which has a unique structure and the other K_xTiO_2, which with the Rb and Cs analogues is isomorphous with the mineral hollandite (*4*). Subsequently the sodium titanium bronze was synthesized by solid state reaction in the ternary system $Na_2Ti_3O_7$–TiO_2–Ti (*5*).

As reported elsewhere in this journal we have studied the electrolysis of fused oxide systems based upon $K_2Ti_2O_5$ (*6*). We were able to synthesize K_xTiO_2 (hollandite) from pure molten $K_2Ti_2O_5$ and $K_2Ti_2O_5$–TiO_2 systems, but the same melts with 1.5–2.0% Nb_2O_5 added gave a "bronze" with a different structure. The present work establishes that this new bronze has a composition $K_3Ti_8O_{17}$ and a structure very close to that predicted by Wadsley and Mumme (*7*) for the hypothetical titanate "$Na_2Ti_8O_{17}$." The theory is also discussed that the large polyanions which form the basic building blocks of this and similar bronzes probably exist in oxide melts prior to their aggregation in crystalline form.

Experimental

The apparatus used for the preparation of the bronze is described in detail elsewhere in this journal (*6*). The melt composition used in the initial preparation was 30.3 mole% K_2O (as K_2CO_3) 68.2 mole% TiO_2 and 1.5 mole% Nb_2O_5. The melt was electrolysed under argon at 1010°C for 16 hours at a current of 60 mA/cm². The resulting cathode deposit appeared grey in colour, but when viewed under the microscope it contained individual black needle-like crystals up to 0.5 mm in length embedded in the colourless melt. The needles were separated from the melt by dissolution of the latter in warm 1:1 HCl. In a further preparation carried out at a higher mole fraction of Nb_2O_5 (1.90 mole%) at a temperature of 1030°C and at 100 mA/cm^2, the same product was obtained. However, upon lowering the temperature to 990°C at both these compositions, the main phase isolated from the cathode was potassium hollandite (K_xTiO_2) and only very small amounts of the bronze were present.

Electrolysis of a melt containing K_2O and TiO_2 in the mole ratio 1:2 at temperatures of 1020, 1030, and 990°C and at various current densities gave only crystals of K_xTiO_2.

Results

The black needle-like crystals of the bronze were found to have monoclinic symmetry with the crystallographic constants given in Table I. The cell dimensions were determined from single crystal data together with a refinement of the *b* axis with the Guinier powder data given in Table II. Initial chemical analysis was not undertaken because it could be seen that there was a strong resemblance between this phase and the hexa- and heptatitanates (*7*) and (*8*). The potassium content was found subsequently by the procedure detailed in the structural analysis and the final composition limits were determined by the space group point positions. No reliable measurement of the density could be made as it proved difficult to isolate sufficiently large quantities.

Intensity data *h*0*l* to *h*3*l* were recorded on multiple films with CuKα radiation using an integrating Weissenberg goniometer. Intensity measurements were made visually by comparison with a standard scale. The physical dimensions of the crystal were 0.52 × 0.06 × 0.03 mm, and no absorption corrections were considered necessary. Scattering curves for neutral Ti and K were taken from International Tables of X-ray crystallography (*9*). Suzuki's (*10*) value for O^{2-} were used for oxygen. All calculations were made on an Elliott 803 Computer with the aid of programs from Daly, Stephens and Wheatley (*11*).

TABLE I

CRYSTALLOGRAPHIC DATA FOR $K_3Ti_8O_{17}$

Symmetry:	monoclinic
Unit cell dimensions:	$a = 15.68 \pm 0.01$ Å $b = 3.809 \pm 0.003$ Å $c = 12.06 \pm 0.01$ Å $\beta = 95.0°$
Systematically absent reflections:	hkl with $k + k \neq 2n$
Possible space groups:	C2/m (No. 12), Cm (No. 8), C2 (No. 5)
	$Dc = 3.57$ g cm^{-3}
	$Z = 2$
	$\mu_c = 480.5$ cm^{-1}

TABLE II

GUINIER POWDER PATTERN OF $K_3Ti_8O_{17}$

CuKα_1 Radiation

hkl	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	I
110	0.04330	0.04333	VS
310	0.06281	0.06282	MS
31$\bar{1}$	0.06532	0.06525	M
20$\bar{1}$	0.07113	0.07111	MS
113	0.08201	0.08208	VW
403	0.08252	0.08248	S
60$\bar{1}$	0.08830	0.08835	VW
11$\bar{4}$	0.10670	0.10677	VVW
40$\bar{5}$	0.13076	0.13072	W
020	0.16358	0.16355	M

Structure Determination

The Patterson projection *P*(*u*,*w*) consisted of parallel rows of peaks at approximately 15° from the positive direction of the *a* axis, and bore a strong resemblance to the Patterson function of $Na_2Ti_7O_{15}$ (*7*). It was assumed that the *b*-axis length of 3.81 Å corresponded to the octahedral body diagonal and the ideal structure for the new bronze was drawn up to scale along the [010] direction and used as the initial basis for the structure determination. Vector coincidences were found to occur at 3.0–3.2 Å, corresponding to edge shared octahedra at the same level in periods of four and other coincidences corresponded to edge shared octahedra at different levels. This procedure of determining vectors representing complete octahedra and not just atoms, developed by Wadsley and co-workers (*12*) and (*13*), lead to a nearly definite solution of the structure, with the two potassium atoms K(1) and K(2) placed initially in the 2(*d*) and 4(*i*) positions of the space group C2/m.

The ideal parameters for titanium and oxygen together with those for the two potassium atoms were taken from the model for structure factor

TABLE III

h	k	l	F_o	F_c
0	0	3	-68	-82
0	0	4	-70	-57
0	0	8	-199	-219
0	0	12	142	133
2	0	0	-94	-127
2	0	4	-87	-85
2	0	7	-93	-79
2	0	8	214	208
2	0	11	64	42
2	0	-1	92	104
2	0	-2	52	41
* 2	0	-4	203	257
2	0	-8	-58	-51
2	0	-12	-130	-117
2	0	-13	82	63
* 4	0	3	205	263
4	0	4	64	57
4	0	6	78	72
4	0	7	192	189
4	0	11	64	55
4	0	-1	-48	-60
4	0	-2	-50	-56
4	0	-3	-68	-72
4	0	-4	-47	-35
* 4	0	-5	262	351
4	0	-6	74	81
4	0	-8	56	44
4	0	-13	-97	-93
6	0	2	58	57
* 6	0	3	233	347
6	0	6	-53	-47
6	0	7	59	60
6	0	11	-157	-139
6	0	-1	-162	-191
6	0	-4	60	45
6	0	-5	-156	-141
6	0	-9	172	175
8	0	0	41	55
8	0	1	44	42
8	0	2	115	115
8	0	6	63	52
8	0	7	-63	-57
8	0	10	-93	-90
8	0	11	84	69
8	0	-1	70	93
8	0	-5	-133	-127
8	0	-10	92	88
8	0	-13	97	91
10	0	0	-50	-48
10	0	1	-58	-77
10	0	2	97	86
10	0	6	-158	-171
10	0	-1	-53	-51
10	0	-2	189	232
10	0	-3	87	75
10	0	-4	75	84
10	0	-6	-101	-116
10	0	-10	-51	-45
12	0	2	-110	-124
12	0	6	90	71
12	0	10	70	74
12	0	-6	91	100
12	0	-10	-120	-107
14	0	9	66	83
14	0	-10	78	59
16	0	5	105	111
16	0	-3	-104	-114
18	0	1	53	60
18	0	-7	-74	-93
1	1	0	111	90
1	1	3	118	136
1	1	5	-60	-50
1	1	6	-79	-78
1	1	7	-76	-65
1	1	8	79	66
1	1	11	-58	-57
1	1	12	56	55
1	1	-3	76	73
1	1	-4	87	81
1	1	-5	-40	-33
1	1	-8	-135	-118
3	1	0	-155	-192
3	1	1	-91	-99
3	1	2	-87	-84
3	1	3	-56	-51
3	1	4	85	85
3	1	7	-106	-92
3	1	8	119	84
3	1	10	70	68
3	1	11	101	95
3	1	-1	184	206
3	1	-2	68	60
3	1	-3	67	67
3	1	-7	70	74
3	1	-8	133	127
3	1	-11	-68	-70
3	1	-12	-86	-73
5	1	2	-58	-52
5	1	7	127	115
5	1	-4	-90	-92
5	1	-5	156	172
5	1	-12	67	57
5	1	-13	-106	-94
7	1	2	-88	-97
7	1	3	151	178
7	1	4	65	60
7	1	5	70	64
7	1	6	92	93
7	1	7	-65	-57
7	1	8	-71	-76
7	1	-4	-88	-100
7	1	-5	-162	-176
7	1	-6	93	89
7	1	-9	58	44
7	1	-13	77	66
9	1	0	58	64
9	1	1	74	65
9	1	2	125	133
9	1	3	-107	-99
9	1	10	-78	-77
9	1	11	71	60
9	1	-1	84	88
9	1	-2	-102	-106
9	1	-5	64	52
9	1	-8	-62	-69
9	1	-9	-114	-105
9	1	-10	103	94
11	1	6	-64	-56
11	1	10	85	99
11	1	-2	140	158
11	1	-5	52	70
11	1	-10	-103	-108
13	1	5	-68	-78
13	1	6	117	130
13	1	7	51	57
13	1	-2	-133	-144
13	1	-3	81	73
13	1	-5	58	72
13	1	-6	100	87
15	1	1	-87	-84
15	1	2	53	64
15	1	5	67	65
15	1	-6	-73	-66
15	1	-7	101	93
15	1	-9	58	55
15	1	-10	60	65
17	1	1	91	115
17	1	-3	-60	-60
17	1	-7	-65	-75
19	1	1	-51	-45
19	1	-3	79	93
19	1	-4	-53	-59
0	2	3	-68	-52
0	2	4	-74	-54
0	2	8	-177	-172
0	2	12	111	117
2	2	0	-100	-81
2	2	4	-96	-78
2	2	7	-77	-64
2	2	8	181	161
2	2	-1	108	73
2	2	-2	35	26
2	2	-4	190	193
2	2	-12	-101	-102
2	2	-13	56	54
4	2	3	-180	-192
4	2	4	51	44
4	2	6	63	53
4	2	7	160	151
4	2	-1	-60	-45
4	2	-2	-53	-42
4	2	-3	-58	-52
4	2	-5	231	249
4	2	-9	-51	-48
4	2	-13	-73	-82
6	2	3	210	247
6	2	11	-112	-121
6	2	-1	-143	-159
6	2	-5	-111	-100
6	2	-9	146	149
6	2	-13	-28	-46
8	2	2	83	86
8	2	10	-74	-78
8	2	11	59	58
8	2	-1	71	80
8	2	-5	-102	-103
8	2	-10	76	74
8	2	-13	62	81
10	2	2	63	70
10	2	6	-129	-144
10	2	9	41	60
10	2	10	41	39
10	2	-2	146	177
10	2	-6	-107	-101
10	2	-12	-77	-45
12	2	2	-87	-108
12	2	-6	83	87
14	2	-7	45	41
16	2	7	-29	-19
16	2	-3	-93	-102
16	2	-7	33	31
18	2	1	44	54
1	3	0	57	48
1	3	3	94	78
1	3	4	-71	-57
1	3	5	-39	-34
1	3	6	-61	-46
1	3	-3	49	42
1	3	-4	80	70
1	3	-8	-75	-84
3	3	0	-119	-115
3	3	1	-67	-64
3	3	2	-70	-54
3	3	3	-58	-44
3	3	4	68	55
3	3	7	-65	-62
3	3	8	51	58
3	3	-1	128	126
3	3	-2	48	39
3	3	-3	47	33
3	3	-8	75	89
5	3	7	81	87
5	3	-4	-68	-60
5	3	-5	110	106
7	3	2	-64	-61
7	3	3	100	112
7	3	-4	-66	-67
7	3	-5	-96	-118
7	3	-6	49	61
9	3	2	67	95
9	3	3	-52	-66
9	3	-2	-70	-69
9	3	-9	-69	-82
11	3	-2	97	109
13	3	-2	-96	-103
13	3	-6	57	68

* Affected by extinction.

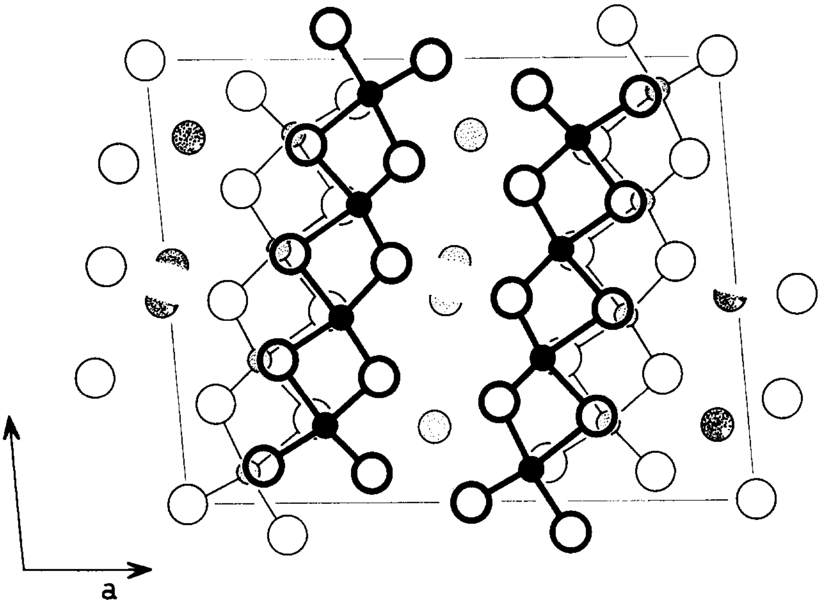

FIG. 1. Structure of $K_3Ti_8O_{17}$. Smallest circles Ti, largest O, intermediate stippled K.

calculations using the *h*0*l* level data. Electron density maps along the [010] direction were used to refine these parameters and final structure factor calculations using all the three-dimensional data gave after refinement a reliability value of 18.0. Closer observation of the electron density projections indicated that the peak due to the potassium atom K(1) was elongated across the centre of the cell. Shifting this atom to the fourfold 4(i) position with a corresponding decrease in the scattering power to $\frac{1}{2}$K, rapidly reduced the R value to 11.8 and also decreased the isotropic temperature factor for K(1) from 5.5 to 1.8 Å^2. Therefore, the compound possesses the limiting formulae $K_3Ti_8O_{17}$ with a formal charge distribution given by $K_3Ti^{3+}Ti_7^{4+}O_{17}$. It is possible that statistically less than three potassium atoms occupy each unit cell with a consequent decrease in the Ti^{3+}/Ti^{4+} ratio. As correctly predicted by Wadsley and Mumme (*7*), the basic framework of the structure is built up from four octahedra sharing edges at one level, which combine with similar units above and below into zigzag ribbons of octahedra.

The ribbons are joined to similar units by corner sharing to form staggered sheets which are further joined to form prismatic tunnels in which the potassium atoms are situated. The potassium atom K(1) is randomly distributed in its 4(i) position and the 4(i) sites containing the K(2) atoms are fully occupied.

A comparison of observed and calculated structure factors are given in Table III. The structure is illustrated in Fig. 1 as a ball and spoke model showing half potassium for K(1). Final atomic parameters are given in Table IV, the standard

TABLE IV

FRACTIONAL ATOMIC PARAMETERS FOR $K_3Ti_8O_{17}$
SPACE GROUP C2/m E.S.D./S IN PARENTHESES

	Point position	*x*	*y*	*z*	*β*(Å^2)
$\frac{1}{2}$K (1)	4 (*i*)	0.4871 (22)	0	0.46102 (6)	1.7 (6)
K (2)	4 (*i*)	0.4429 (9)	0	0.1715 (2)	1.0 (2)
Ti (1)	4 (*i*)	0.1134 (7)	0	0.0736 (8)	0.5 (2)
Ti (2)	4 (*i*)	0.1484 (7)	0	0.3249 (9)	0.5 (2)
Ti (3)	4 (*i*)	0.1984 (8)	0	0.5769 (9)	1.0 (2)
Ti (4)	4 (*i*)	0.2457 (7)	0	0.8311 (9)	0.8 (2)
O (1)	2 (*a*)	0	0	0	1.8 (1.3)
O (2)	4 (*i*)	0.064 (2)	0	0.230 (3)	0.2 (6)
O (3)	4 (*i*)	0.103 (3)	0	0.461 (4)	1.0 (8)
O (4)	4 (*i*)	0.144 (4)	0	0.713 (5)	2.7 (1.2)
O (5)	4 (*i*)	0.172 (3)	0	0.931 (4)	1.3 (9)
O (6)	4 (*i*)	0.233 (3)	0	0.191 (4)	2.3 (1.1)
O (7)	4 (*i*)	0.279 (2)	0	0.433 (3)	0.0 (6)
O (8)	4 (*i*)	0.317 (3)	0	0.678 (4)	2.0 (1.0)
O (9)	4 (*i*)	0.361 (2)	0	0.913 (3)	0.0 (7)

TABLE V

INTERATOMIC DISTANCES FOR Ti OCTAHEDRA IN $K_3Ti_8O_{17}$ E.S.D. FOR Ti–O DISTANCES ±0.10 Å AND O–O DISTANCES ±0.15 Å

Metal	Bonds to oxygen atoms	Distances Å	Average	Average O–O distances Å
Ti (1)	9′ (2); 5′, 6, 2, 1	1.95 (2), 2.04 2.25 2.10 1.92	2.03	2.86
Ti (2)	8′ (2); 7, 6, 3, 2	1.98 (2), 2.33 2.18 1.85 1.67	2.00	2.78
Ti (3)	7′ (2); 8, 7, 4, 3	1.94 (2), 2.14 2.24 1.92 1.95	2.02	2.84
Ti (4)	6′ (2); 9, 8, 5, 4	1.96 (2), 1.99 2.25 1.74 2.05	1.99	2.79

Number followed by (2) and semicolon refers to atoms lying above and below the metal.

temperature factors being averaged out for atoms of the same kind. The Ti–O separations, listed in Table V, show a wider spread of distances than observed in the sodium titanates, $Na_2Ti_6O_{13}$ (*8*) and $Na_2Ti_7O_{15}$ (*7*). The short Ti–O bonds of 1.57–2.00 Å found in $K_2Ti_2O_5$ (*14*) were attributed to the possible repulsion between nearest-neighbour metal atoms. In $K_3Ti_8O_{17}$ the oxygen atoms of the two short Ti–O bonds, 1.67 and 1.78 Å, also form part of the K(1) atom coordination sphere and repulsion between the potassium atoms may well have the effect of decreasing these two Ti–O bond lengths.

The two kinds of potassium atoms differ in their coordination with oxygen. K(1) has four short bonds, two at each of 2.60 and 2.64 Å to form a nearly square planar $K–O_4$ configuration. The next nearest oxygens are at distances of 3.39 Å (*2*) and 3.60 Å (*2*) and are therefore nonbonding. A similar coordination has been observed for one of the sodium atoms in $Na_2Ti_7O_{15}$ (*7*). K(2) on the other hand is essentially eight coordinate. The six shorter bonds, two at each of 2.78, 2.83, and 2.74 Å, have an average length of 2.78 Å, equal to the average eight-coordinate K–O distances found in scheelite-type structures KBO_4, where B is Ru (*15*), Re (*16*) or I (*17*). The two additional bonds K(2)–O(1) are longer because the oxygen atoms are constrained in special positions. This has also been observed in $Na_2Ti_6O_{13}$ (*8*).

Discussion

The original aim of the preparative experiment was the formation of a mixed $Nb^{4+}–Ti^{4+}/Ti^{3+}$ alkali-metal oxide. The oxide phase that formed in all the experiments appeared to contain relatively little niobium, as several crystals prepared from melts with different niobium contents gave exactly the same diffraction data. No immediate reason can be put forward as to why the presence of Nb_2O_5 is necessary for the formation of the bronze. It has been shown however that Nb^{5+} substitutes isomorphously for Ti^{4+} in the compounds $KTiNbO_5$ and KTi_3NbO_9 (*18*) and therefore some Nb^{5+} may be randomly substituted for Ti^{4+} in $K_3Ti_8O_{17}$, with a corresponding increase in the Ti^{3+}/Ti^{4+} ratio, to give a phase of composition $K_3Ti^{3+}_{1+x/2}Ti^{4+}_{7-x}Nb^{5+}_{x/2}O_{17}$ with $x \leqslant 1$. Similar stabilization phenomena has been observed for several other alkali metal titanate systems. For example, sodium heptatitanate (*7*) was formed by solid state reaction in the presence of a high percentage of Al_2O_3, and in the electrolysis of certain $Na_2TiO_3–TiO_2$ melts (*6*), a bronze phase was readily formed with Al_2O_3 in the melt, but not when it was absent. When a different Group V metal, oxide namely V_2O_5, was added to a $K_2Ti_2O_5–TiO_2$ melt electrolysis resulted in the formation of a new phase (*19*) of composition close to $K_{0.8}V_{0.8}Ti_{1.2}O_4$, with a layer structure related to that of rubidium manganese titanate (*20*).

As predicted by Wadsley and Mumme (*7*) the stoichiometric octatitanate $Na_2Ti_8O_{17}$ had the same arrangement of 4 × 1 blocks of $Ti–O_6$ octahedra as presently found in $K_3Ti_8O_{17}$, except that in their model the Na atoms occupied two-thirds of the 4(*i*) positions and two of the twofold positions corresponding 2(*d*) in the space group C2/m. The potassium atom K(1) in $K_3Ti_8O_{17}$ was found to be displaced from the idealized 2(*d*) position and randomly distributed in the tunnels in the 4(*i*) positions, with the other potassium K(2) in the same environment as originally suggested. The relatively large isotropic temperature factors for the potassium atoms can be attributed to their unhindered motion in the tunnel directions and the value of 1.2(6) $Å^2$ for K(1) is not abnormal. B for Na in $Na_2Ti_6O_{13}$ (*8*) was found to be 2.3 $Å^2$.

The relationships between the hexatitanate, heptatitanate and the present octatitanate phase

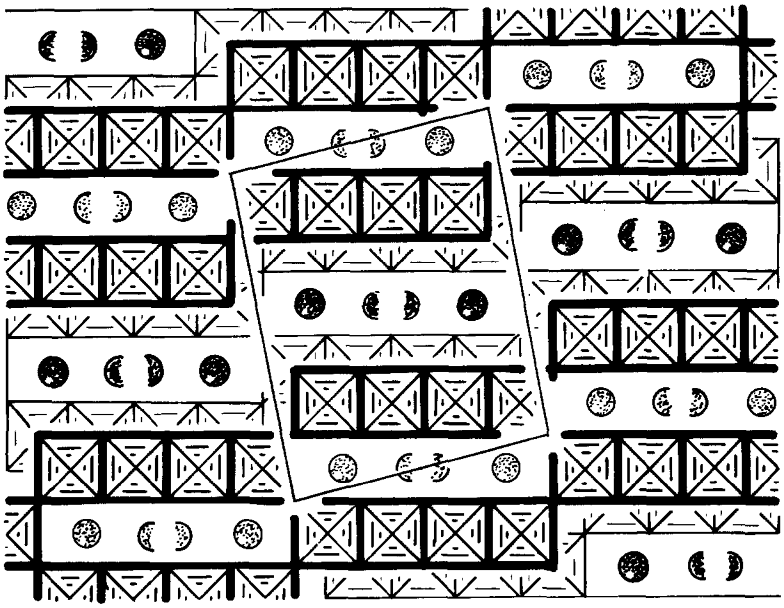

FIG. 2. Idealized structures of $K_3Ti_8O_{17}$ in projection on to (010). The squares are Ti–O octahedra; the heavy and light outlines represent the two levels in the unit cell.

have been discussed by Wadsley and Mumme (*7*). Figure 2 shows the idealized arrangement of Ti–O octahedra for $K_3Ti_8O_{57}$ as postulated by these workers. All three of these phases are built up in the solid state from 3 × 1 or 4 × 1 blocks of edge shared octahedra which join by corner sharing to give a step-like configuration as shown. In the parent compound $Rb_xMnTi_{2-x}O_4$ (*20*) discrete blocks of $Ti–O_6$ octahedra do not form and the structure consists of infinitely extended layers of edge shared octahedra.

The outstanding common structural feature of all these titanates are the polyhedral groups of $Ti–O_6$ octahedra with their diagonals directed along the *b* axis of their unit cells and repeating infinitely in this direction. Some of these polyhedral ribbons or sheets may be regarded as being built up from separate polyanionic groups of a general formulae $(Ti_nO_{2n+1})^{2-}$, $n > 1$, as in the dititanate, $(Ti_2O_5)^{2-}$ $n = 2$, trititanate $(Ti_3O_7)^{2-}$ $n = 3$ and hexatitanate $(Ti_6O_{13})^{2-}$ $n = 6$ (n is not necessarily the same as the block width which, for $Na_2Ti_6O_{13}$ is 3). Such polyanions have been found as structural features of other alkali metal bronzes. For example the two potassium molybdenum bronzes $K_{0.26}MoO_3$ (*21*) and $K_{0.28}MoO_3$ (*22*), prepared from electrolysis of $K_2O–MoO_3$ melts (*3*) were shown to contain large ions of the type $Mo_6O_{22}^{8-}$ and $Mo_{10}O_{36}^{12-}$ as their basic frameworks (*21*) and (*23*). These ions are made up of Mo–O octahedra united by edge and corner sharing to form infinite sheets of polynuclear groups similar to those found in $K_3Ti_8O_{17}$ and related alkali titanates. These polyanions have a strong resemblance to the isopolymolybdate anions, $Mo_8O_{26}^{4-}$ and $Mo_7O_{24}^{6-}$, found in molybdates prepared from solutions (*24*).

The formation of large complex anionic species in various solutions and melts has been the subject of numerous studies. The investigations by Flood and Knapp (*25*) of silicate melts containing Group IVA metal oxides are relevant to the present molten titanate systems. These workers were able to calculate the stability in melts of certain silicate ions such as $(SiO_{2.5})_6^{6-}$ by determining the activity of SiO_2 and applying the concepts of acid–base equilibria. Recently, these concepts have been applied to determine the heats of solution of MoO_3 in molten Na_2MoO_4, in terms of the formation of anions such as $(Mo_nO_{3n+1})^{2-}$ (*26*).

The existence in the solid state of large polymeric groups as the basic building blocks of bronzes and titanates suggests that such groups may also be present in the oxide melts from which the compounds have been prepared. The existence, domain of stability and character of these anions will depend upon the activity of the host metal oxide as well as the acid-base equilibria and O^{2-} ion activity in the melt. For example the formation of the anion $(Ti_2O_5)^{2-}$ may proceed through the formation of the intermediate $[Ti_2O_{10}]^{12-}$ according to the following reaction using Flood and Förland's (*27*) original proposal of acid base equilibrium in molten oxides.

$$\underset{[\text{acid}]}{6O^{2-} + 2TiO_2} \rightleftharpoons [Ti_2O_{10}]^{12-} \rightleftharpoons \underset{[\text{base}]}{[Ti_2O_5]^{2-} + 5O^{2-}}$$

the O^{2-} ion arising from the ionization of K_2O

$$K_2O \rightleftharpoons 2K^+ + O^{2-}.$$

In the present case the formation of the potassium octatitanate bronze by the electrochemical reduction of molten $K_2Ti_2O_5$–TiO_2 may have proceeded through a reaction sequence involving the formation of an additional intermediate anion $(Ti_8O_{17})^{3-}$ perhaps stabilized by the presence of Nb^{5+} ions in the melt.

$$\begin{aligned} \tfrac{3}{2}K_2O &\rightarrow 3K^+ + \tfrac{3}{2}O^{2-} \\ 2TiO_2 + O^{2-} &\rightarrow [Ti_2O_5]^{2-} \\ [Ti_2O_5]^{2-} + [6TiO_2] &\rightarrow [Ti_8O_{17}]^{2-} \\ [Ti_8O_{17}]^{2-} + e &\rightarrow [Ti_8O_{17}]^{3-} \quad \text{cathode} \\ [Ti_8O_{17}]^{3-} + 3K^+ &\rightarrow K_3Ti_8O_{17} \\ \tfrac{1}{2}O^{2-} - e &\rightarrow \tfrac{1}{4}O_2 \quad \text{anode} \end{aligned}$$

The bronze should, therefore, be crystallized near but not necessarily at the cathode, a supposition which is supported by the observation that crystals of $K_3Ti_8O_{17}$ were found throughout the cathode compartment. In melts in which $Ti_8O_{17}^{2-}$ polyanions are the stable species, it may be possible to conceive certain acid-base conditions under which the octatitanate $M_8^{2+}Ti_8^{4+}O_{17}$ might form, but such conditions have not yet been found. Electrolysis of $K_2Ti_2O_5$ melts containing substantial amounts of V_2O_5 produced a new layer titanate $K_xV_xTi_{2-x}O_4$ (*19*). This compound is structurally related to $K_3Ti_8O_{17}$, but it contains infinite sheets of $[M_xO_{2x}]^-$ $(x = \infty)$ polyanions parallel to the 3.8 Å axis with V^{3+} ions randomly distributed with Ti^{4+} in the octahedral sites. This may indicate that substitution of Ti^{4+} by V^{3+} stabilizes fragments of these large sheets in the melt as ions such as $[M_4O_8]^-$ which join in the solid state into infinite two-dimensional layers. To establish the nature of the species which exist in the various molten alkali metal titanate systems would require their isolation or characterization under varying conditions in the melt, at temperatures near 1000°C. High temperature electrochemical, infrared, and Raman spectroscopic methods have allowed considerable advances in the understanding of the processes taking place in silicate and halide melts, and it may be possible by the application of such techniques to determine if titanate polyanions do form in the molten state.

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