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# A New Class of Compound $M_x^+A_x^{3+}Ti_{2-x}O_4$ (0·60 < $x$ < 0·80) Typified by $Rb_xMn_xTi_{2-x}O_4$

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$Rb_xMn_xTi_{2-x}O_4$ is a non-stoichiometric compound with orthorhombic symmetry, space group *Imm*2, and at the composition $x$ = 0·75 has the unit-cell dimensions $a$ = 3·934, $b$ = 15·918, $c$ = 2·933 Å. Its structure contains (Ti, Mn)-oxygen octahedra sharing edges in puckered sheets normal to (010) similar to those in lepidocrocite, FeO(OH), except that the correspondence between sheets has been altered to give $Rb^+$ an irregular eightfold coordination. A number of isomorphous compounds have been prepared and the field of occurrence so far examined, while restricted to the alkali metals $Rb^+$ and $Cs^+$, includes a wide range of trivalent and divalent metals substituting for $Ti^{4+}$ in the octahedral positions. The isomorphism of the member $Cs_xMg_{x/2}Ti_{2-x/2}O_4$ is confirmed by a least-squares refinement of powder diffractometer data.

## Introduction

Oxycompounds containing alkali, trivalent and quadrivalent metals offer a useful means of studying stereochemical relations in solid state chemistry. We recently showed that a number of compounds $NaA^{3+}B^{4+}O_4$ isomorphous with calcium ferrite could be synthesized, but only when $A$ and $B$ were metal ions of spherical symmetry averaged over two virtually identical, but crystallographically different octahedral positions (Reid, Wadsley & Sienko, 1967). Other classes of structure with different stoichiometries were generated when the trivalent ions $A^{3+}$ ordered into positions of special symmetry. For example $NaTi_2Al_5O_{12}$ (Mumme & Wadsley, 1967) and $Na_4Mn_4Ti_5O_{18}$ (Mumme, 1968) formed instead of '$NaAlTiO_4$' and '$NaMnTiO_4$', where Al was present in tetrahedral as well as octahedral sites in the one, and $Mn^{3+}$ octahedral and square pyramidal in the other. One other factor limiting the formation of calcium ferrite structures was the size of the alkali metal ion, the available positions being too large for $Li^+$ and too small for $K^+$, $Rb^+$ or $Cs^+$.

When a stable compound of a new kind emerges from such experimental studies, the composition is often established more rapidly by determining its crystal structure than by isolating enough of it for chemical analysis; thereafter its confirmation by synthesis as a single phase is usually straightforward. However the possibility of a lattice compound being non-stoichiometric is a variable to be considered in a structure analysis, which provides *ab initio* an ideal composition based on point symmetry.

In the present study two classes of oxide phases of variable composition containing $Rb^+$ or $Cs^+$, $Ti^{4+}$, and a number of tri- or divalent metals were recognized. The composition limits of both types were determined experimentally by treating each multicomponent system as a quasi-binary. Fig. 1 shows the Rb–Ti–$Mn^{3+}$–O system reduced to the join $RbMnO_2$–$TiO_2$. One phase had the hollandite structure (Byström & Byström, 1950; Bayer & Hoffman, 1966) with the ideal composition $RbMnTi_3O_8$ (*i.e.* $RbMnO_2.3TiO_2$) but a range of homogeneity $Rb_xMn_xTi_{4-x}O_8$ ($xRbMnO_2.(4-x)TiO_2$) with $x$ approximately bounded by $0{\cdot}6<x<0{\cdot}9$. The other, ideally $RbMnTiO_4$ ($RbMnO_2.TiO_2$) was likewise variable in composition, $Rb_xMn_xTi_{2-x}O_4$, corresponding to $xRbMnO_2.(2-x)TiO_2$ with $x$ limited to $0{\cdot}72<x<0{\cdot}76$. This latter phase, its structure and field of occurrence in related chemical systems, forms the subject of this paper.

## Experimental

Starting materials for the alkali-metal titanates included $RbMnO_4$ and $CsMnO_4$, prepared as dark brown free-flowing crystals by precipitation from hot solutions of $KMnO_4$ and RbCl or CsCl and purified by aqueous extraction. The Rb–Mn–Ti and Cs–Mn–Ti mixed oxides were made by intimately mixing these anhydrous permanganates with an appropriate amount of $TiO_2$ (anatase), heating slowly from 250 to 800°C to convert $Mn^{7+}$ to $Mn^{3+}$ and finally to 1000°C for 20 hours after regrinding. Final weight changes corresponded exactly to the oxygen evolution required for the formation of $Mn^{3+}$. All other compounds were made by reacting recrystallized, finely ground anhydrous $RbNO_3$ or $CsNO_3$ with $TiO_2$ and high purity $Sc_2O_3$, $Fe_2O_3$, $Al_2O_3$ or MgO with a similar heating schedule.

The $RbMnO_2$–$TiO_2$ phase diagram was examined in some detail (Fig. 1). The preparation of the phase with the hollandite structure presented no problems, but the other appeared to have a layer structure, and it was therefore a difficult matter to achieve intimate admixtures of the components after preliminary reaction. Composition boundaries were obtained from lattice parameter-composition graphs.

$Rb_xMn_xTi_{2-x}O_4$ melted congruently, the crystals formed on cooling being brown platelets elongated along [100]. Approximate unit-cell dimensions were obtained from single crystal films, and more accurate values of $\sin^2\theta$ from diffractometer measurements (Table 1). Comparison of observed and calculated intensities ensured that the sub-solidus powder phase had the same structure as the crystals prepared from the melt. The lattice constants for this phase, (Table 2), and its isomorphs, (Table 6), were refined by a least-squares treatment.

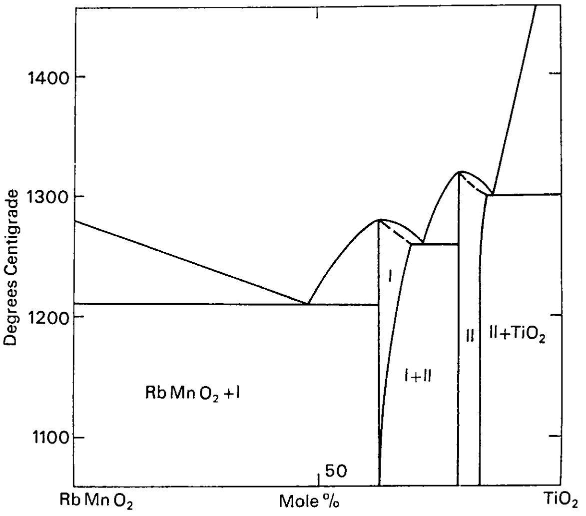


Fig. 1. Phase equilibrium diagram $RbMnO_2$–$TiO_2$. I is $Rb_xMn_xTi_{2-x}O_4$ and II $Rb_xMn_xTi_{4-x}O_8$ (hollandite).

Table 1. *Powder diffraction data for* $Rb_xMn_xTi_{2-x}O_4$ ($x=0{\cdot}75$)

Cu $K\alpha_1$, KCl internal standard

| $h$ | $k$ | $l$ | $\sin^2\theta_{obs}$ | $\sin^2\theta_{calc}$ | $I_{obs}$* | $I_{calc}$ |
|---|---|---|---|---|---|---|
| 0 | 2 | 0 | 0·00935 | 0·00937 | 125 | 118 |
| 0 | 4 | 0 | 0·03744 | 0·03746 | 48 | 19 |
| 1 | 3 | 0 | 0·05937 | 0·05940 | 231 | 226 |
| 0 | 1 | 1 | 0·07130 | 0·07130 | 10 | 24 |
| 0 | 6 | 0 | 0·08432 | 0·08429 | 77 | 32 |
| 0 | 3 | 1 | 0·08997 | 0·09003 | 14 | 32 |
| 1 | 5 | 0 | 0·09688 | 0·09686 | 9 | 4 |
| 1 | 2 | 1 | 0·11661 | 0·11665 | 22 | 55 |
| 0 | 5 | 1 | 0·12751 | 0·12750 | 94 | 102 |
| 1 | 7 | 0 | 0·15330 | 0·15306 | 53 | 7 |
| 2 | 0 | 0 |  | 0·15330 |  | 50 |
| 0 | 7 | 1 | 0·18372 | 0·18369 | 5 | 4 |
| 0 | 2 | 4 | 0·19155 | 0·19076 | 9 | 6 |
| 1 | 6 | 1 |  | 0·19158 |  | 17 |
| 1 | 9 | 0 | 0·22812 | 0·22799 | 14 | 14 |
| 0 | 10 | 0 | 0·23400 | 0·23415 | 14 | 12 |
| 2 | 6 | 0 | 0·23756 | 0·23760 | 14 | 13 |
| 1 | 8 | 1 | 0·25721 | 0·25714 | 38 | 42 |
| 2 | 5 | 1 | 0·28081 | 0·28080 | 34 | 39 |
| 1 | 13 | 0 | 0·43396 | 0·43404 | 14 | 10 |

* $I_{obs}$ exhibits some preferred orientation.

Table 2. *Crystallographic data for* $Rb_xMn_xTi_{2-x}O_4$ ($x=0{\cdot}75$)

| | |
|---|---|
| Symmetry | Orthorhombic |
| Unit-cell dimensions | $a$ 3·934 ± 0·003 Å |
| | $b$ 15·918 ± 0·010 |
| | $c$ 2·933 ± 0·003 |
| Systematically absent reflexions | $hkl$ with $h+k+l\neq 2n$ |
| Possible space groups | *Immm* (No. 71), *Imm*2 (No. 44),<br>$I2_12_12_1$ (no. 24), *I*222 (No. 23). |

$D_x=4{\cdot}14$ g.cm$^{-3}$
$Z=2$
$\mu=586$ cm$^{-1}$

Table 3. *Observed and calculated structure factors* (× 100)

| h | k | l | $F_o$ | $\lvert F_c\rvert$ |
|---|---|---|---|---|
| 0 | 2 | 0 | 1523 | 1660 |
| 0 | 4 | 0 | 1408 | 1366 |
| 0 | 6 | 0 | 2783 | 2753 |
| 0 | 10 | 0 | 3241 | 3024 |
| 0 | 16 | 0 | 1793 | 1658 |
| 0 | 1 | 1 | 1205 | 1586 |
| 0 | 3 | 1 | 1731 | 1999 |
| 0 | 5 | 1 | 4581 | 4451 |
| 0 | 7 | 1 | 945 | 1088 |
| 0 | 11 | 1 | 1689 | 1797 |
| 0 | 0 | 2 | 2403 | 2565 |
| 0 | 2 | 2 | 1837 | 1733 |
| 0 | 6 | 2 | 987 | 787 |
| 0 | 8 | 2 | 1271 | 1208 |
| 0 | 10 | 2 | 1289 | 1188 |
| 0 | 14 | 2 | 640 | 676 |
| 0 | 3 | 3 | 987 | 1011 |
| 0 | 5 | 3 | 1166 | 926 |
| 1 | 3 | 0 | 4153 | 4258 |
| 1 | 5 | 0 | 773 | 713 |
| 1 | 7 | 0 | 1329 | 1239 |
| 1 | 9 | 0 | 2343 | 2334 |
| 1 | 11 | 0 | 905 | 915 |
| 1 | 13 | 0 | 3107 | 2740 |
| 1 | 2 | 1 | 2017 | 2206 |
| 1 | 4 | 1 | 557 | 900 |
| 1 | 6 | 1 | 1624 | 1566 |
| 1 | 8 | 1 | 3345 | 3068 |
| 1 | 1 | 2 | 905 | 883 |
| 1 | 3 | 2 | 1317 | 1515 |
| 1 | 5 | 2 | 775 | 836 |
| 1 | 0 | 3 | 531 | 504 |
| 2 | 2 | 0 | 609 | 716 |
| 2 | 4 | 0 | 1209 | 1331 |
| 2 | 6 | 0 | 2248 | 2252 |
| 2 | 10 | 0 | 2151 | 2293 |
| 2 | 16 | 0 | 1265 | 1379 |
| 2 | 1 | 1 | 1517 | 1386 |
| 2 | 3 | 1 | 1713 | 1416 |
| 2 | 5 | 1 | 3393 | 3096 |
| 2 | 7 | 1 | 798 | 837 |
| 2 | 11 | 1 | 1415 | 1480 |
| 2 | 15 | 1 | 734 | 879 |
| 2 | 0 | 2 | 1969 | 1975 |
| 2 | 2 | 2 | 1485 | 1363 |
| 2 | 6 | 2 | 699 | 629 |
| 2 | 8 | 2 | 973 | 979 |
| 2 | 10 | 2 | 917 | 1001 |
| 2 | 14 | 2 | 551 | 534 |
| 2 | 3 | 3 | 757 | 853 |

Intensities from a crystal of $Rb_xMn_xTi_{2-x}O_4$ at the composition $x = 0{\cdot}75$ were collected for the levels *hkl*, $h = 0, 1, 2$ by the integrating Weissenberg technique using filtered copper radiation, the crystal measuring $0{\cdot}40 \times 0{\cdot}02 \times 0{\cdot}02$ mm. Corrections for absorption were found to be unnecessary. Measurements were made visually with a standardized intensity scale, and the reduction to structure amplitudes, and all subsequent computing, was performed on the Division's Elliott 803 computer using the programming system of Daly, Stephens & Wheatley (1963). Interlayer scaling was adjusted after each least-squares refinement cycle, and the scaled observed data and calculated structure factors are listed in Table 3. Scattering curves for $Na^+$, $Mn^{3+}$ and $Ti^{4+}$ were taken from Cromer & Waber (1965), corrected for $\Delta f'$ and $\Delta f''$ (Cromer, 1965), and $O^{2-}$ from Suzuki (1960). For the least-squares refinement the weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was adopted and the matrix inversion involved the block diagonal approximation.

## Structure determination

Within the permissible space group alternative of highest symmetry, *Immm*, it was logical to assume that Rb was fractionally present in a twofold site, with Mn and Ti jointly occupying a fourfold position and two independent oxygen atoms likewise in fourfold positions. With Rb at the origin of the body-centred orthorhombic unit cell, the Patterson projection $P(vw)$ readily gave the approximate parameters of the composite metal (Mn+Ti), appearing to locate it in 4(*g*) of *Immm*. This simple model, completed by placing one oxygen in 4(*g*) and the other in 4(*h*), failed to refine by electron density projections below an *R* value of 40%. The reduction of symmetry group to *Imm*2 allowed displacements of atoms from one set of reflexion planes, with the consequent formation of distorted octahedra more typical of lattice compounds. Although the 2(*a*) position of *Imm*2 has a finite *z* parameter, the Rb assigned to it was 'anchored' at the origin while the (Mn, Ti) atom was moved from the formerly assumed reflexion plane perpendicular to the *c* axis. This revised proposal rapidly refined with several least-squares cycles including individual isotropic temperature factors, giving a final *R* value of 10·1%, non-observed reflexions omitted. Refinement was stopped when the shift of each variable was less than one-quarter of its

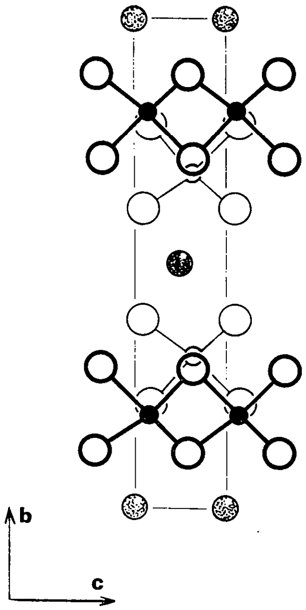


Fig. 2. Structure of $Rb_xMn_xTi_{2-x}O_4$ in projection on to (100). The largest circles are oxygen atoms, the small circles (Mn, Ti) and the stippled ones Rb. The darker and lighter outlines correspond to two planes parallel to the page, and separated by $\frac{1}{2}a$.

Table 4. *Fractional atomic parameters for* $Rb_xMn_xTi_{2-x}O_4$ $(x = 0{\cdot}75)$

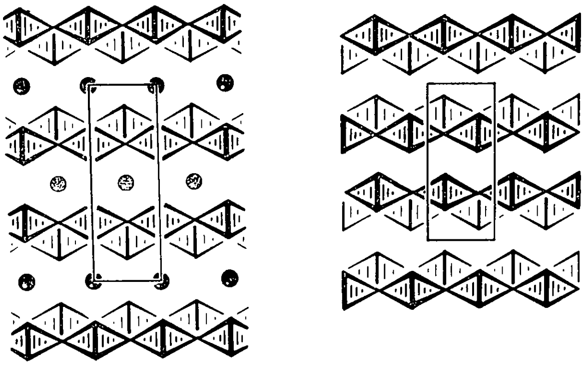
Space group *Imm*2 $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2})+$

|  | Point position | *x* | *y* | *z* | *B* |
|---|---|---|---|---|---|
| *x*Rb | 2(*a*) | 0 | 0 | 0·000 (9) | 2·8 (5) Å$^2$ |
| (Mn, Ti) | 4(*d*) | 0 | 0·3126 (12) | 0·625 (8) | 2·0 (3) |
| O(1) | 4(*d*) | 0 | 0·386 (3) | 0·098 (27) | 0·0 (1·3) |
| O(2) | 4(*d*) | 0 | 0·222 (4) | 0·164 (30) | 0·8 (1·3) |

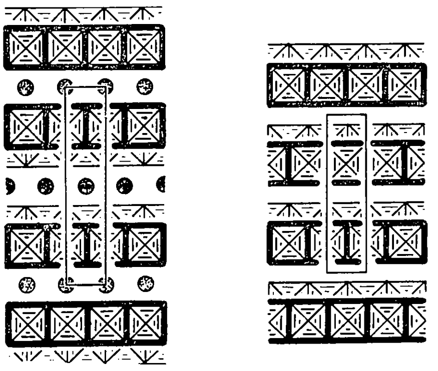
estimated standard deviation. The further reduction of symmetry to $I2_12_12_1$ or $I222$ was not attempted, nor was the occupancy of Rb varied from 0·75, the composition of the phase having been fixed by its synthesis. Fractional parameters and temperature factors are given in Table 4, and the bond lengths in Table 5. The standard deviations of the latter are high, but this is inevitable when the number of observed reflections is small.

## Description

The structure is illustrated by Fig. 2. Each (Mn,Ti) hybrid atom is octahedrally coordinated to six oxygen atoms, with bond lengths ranging from 1·81 to 2·14 Å and averaging 1·99 Å. Randomization of $Mn^{3+}$ and $Ti^{4+}$ in the available sites precludes direct observation of the Jahn–Teller distortion commonly found in compounds containing $Mn^{3+}$.



(*a*) Fig. 3 (*b*)



(*a*) Fig. 4 (*b*)

Figs. 3 and 4. The structures of $Rb_xMn_xTi_{2-x}O_4$ [Figs. 3(*a*) and 4(*a*)] and lepidocrocite FeO(OH) [3(*b*) and 4(*b*)] drawn in projection as idealized octahedra and with the unit cells outlined. The individual layers are the same for both cases, but their packing is determined by the relative sizes of Rb (stippled circles) and the hydrogen atoms (not shown, but presumably at the origin and at the centre of one face of the unit cell). Figs. 3(*a*) and 3(*b*) are projections down the octahedral edges and Figs. 4(*a*) and 4(*b*) are projections down the diagonals.

Table 5. *Interatomic distances*

| | |
|---|---|
| Rb—O(1) | 3·20 (4) Å |
| –O(1′) | 2·93 (4) |
| –O(2) | 3·56 (2) |
| O(1)–O(1′) | 2·93 (4) |
| –O(1″) | 3·63 (4) |
| –O(1) | 3·93 (4) |
| (Mn, Ti)–O(1) | 1·81 (1) |
| –O(1′) | 1·94 (1) |
| –O(2) | 1·98 (1) |
| –O(2′) | 2·14 (1) |
| –O(2″) | 2·04 (2) |
| O(1)——O(1′) | 2·93 (1) |
| –O(2) | 2·62 (2) |
| –O(2″) | 3·09 (2) |
| O(1′)——O(2″) | 2·90 (2) |
| O(2)——O(2′) | 2·93 (1) |
| –O(2″) | 2·61 (2) |
| O(2′)——O(2″) | 2·62 (2) |

e.s.d.'s of Rb–O distances ±0·06; (Mn–Ti)–O, ±0·06; Rb–O, ±0·08 Å.

The metal–oxygen octahedra, joined by edges, form puckered sheets centred around planes perpendicular to the *b* axis. These layers of octahedra are bonded together by the Rb ions, each of which is located off-centre within a rectangular prism of oxygen atoms, four from one layer and four from the next. Rb–O distances are 2·93 (4) and 3·20 (4) Å, and there are two additional oxygen atoms further away at 3·56 Å which are probably unbonded. Considering the limits of error, the structure is virtually centrosymmetrical except for the alkali metals.

The partial occupancy by Rb of the available positions must in some way be associated with overcrowding. Each Rb fits into a plane with periodicities matching those of the (Mn,Ti) octahedra. With four neighbouring equivalent sites, two at a distance of 2·93 Å and two more at 3·93 Å, a greater reduction in occupancy appears to be necessary than for the hollandite phase, ideally $RbMnTi_3O_8$. This is tetragonal with $a = 10{\cdot}206$ and $c = 2{\cdot}957$ Å, and the Rb atoms present in a linear succession of tunnel sites are separated by distances equal to the length of the fourfold axis; the upper limit of composition represents 90% occupancy.

The closest relatives of this remarkably simple new structure are the isomorphous phases lepidocrocite FeO(OH) (Ewing, 1935), boehmite AlO(OH) (Reichertz & Yost, 1946) and ScO(OH) (Milligan & McAtee, 1956). In these cases the metal–oxygen octahedra join to form puckered sheets of the same kind as in $Rb_xMn_xTi_{2-x}O_4$ (Figs. 3 and 4). The difference between the two types reflects the way the sheets are packed relative to each other; in lepidocrocite the protons are effective in bringing them closer together than is possible with the much larger Rb ions. The two phases are polytypes, and the replacement of $H^+$ for $Rb^+$ in the one, or of $Rb^+$ for $H^+$ in the other could result in the formation of a considerable number of compounds of intermediate composition having structures which are intergrowths or hybrids of the two end members. We are examining this possibility.

$Rb_xMn_xTi_{2-x}O_4$ is the structural end member of a series of alkali titanates $Na_2Ti_6O_{13}$ (Andersson & Wadsley, 1962) and $Na_2Ti_7O_{15}$ (Wadsley & Mumme, 1968) related to it by crystallographic shear. This term is defined as the regular disruption of a parent structure by sets of parallel planes, which correspond to changes in the packing of the coordination polyhedra (Wadsley, 1964). For $Na_2Ti_6O_{13}$ the planes disrupt the puckered sheets into blocks of three (Fig. 5) and for $Na_2Ti_7O_{15}$ into alternating blocks of three and four (Fig. 6). The layer character of the end member is lost in these two compounds and the positions available to the alkali metals are reduced in number and also in size.

## Isomorphs of $Rb_xMn_xTi_{2-x}O_4$

We have prepared a number of compounds isomorphous with $Rb_xMn_xTi_{2-x}O_4$ (Table 6). While the list is not intended to be exhaustive, it nevertheless shows that the new structure is common to a potentially large family of compounds and offers considerable scope for studies of host lattices, their formation and their associated properties. Each compound in Table 6 is non-stoichiometric and preliminary experiments have shown that solid solutions are formed between any two members. The field of occurrence could undoubtedly be extended by more exhaustive studies including the possible formation of isomorphous phases containing quadrivalent elements other than $Ti^{4+}$. No potassium compound with this exact structure, however, could be synthesised.

Table 6. *Lattice parameters for isotypes of* $Rb_xMn_xTi_{2-x}O_4$

Space group *Imm*2

| Phase | $x$ | $a_0$ ± 0·003 Å | $b_0$ ± 0·006 Å | $c_0$ ± 0·002 Å |
|---|---|---|---|---|
| $Rb_xMn_xTi_{2-x}O_4$ | 0·75 | 3·934 | 15·918 | 2·933 |
| $Rb_xSc_xTi_{2-x}O_4$ | 0·67 | 3·870 | 16·350 | 3·039 |
| $Cs_xMg_{x/2}Ti_{2-x/2}O_4$* | 0·70 | 3·821 | 17·040 | 2·981 |
| $Cs_xAl_xTi_{2-x}O_4$ | 0·7† | 3·814 | 17·234 | 2·964 |
| $Cs_xSc_xTi_{2-x}O_4$ | 0·67 | 3·857 | 17·254 | 3·035 |
| $Cs_xMn_xTi_{2-x}O_4$ | 0·70 | 3·924 | 16·847 | 2·933 |
| $Cs_xFe_xTi_{2-x}O_4$ | 0·67 | 3·805 | 17·102 | 2·972 |

* Since this was written the compounds $Cs_xM_{x/2}{}^{2+}Ti_{2-x/2}O_4$, M = Fe, Co, Ni, Cu, and Zn have been made, and their properties examined.

† Approximate composition, as a second phase was present.

Table 7. *Fractional atomic parameters* for* $Cs_xMg_{x/2}Ti_{2-x/2}O_4$ ($x$ = 0·70)

Space group *Imm*2, (0,0,0; ½,½,½)+

| | Point position | $x$ | $y$ | $z$ |
|---|---|---|---|---|
| $x$ Cs | 2(*a*) | 0 | 0 | 0·00 (2) |
| (Mg, Ti) | 4(*d*) | 0 | 0·312 (4) | 0·64 (3) |
| O(1) | 4(*d*) | 0 | 0·373 (9) | 0·10 (11) |
| O(2) | 4(*d*) | 0 | 0·216 (10) | 0·11 (12) |

* Refined from powder diffractometer intensities.

$Cs_xMg_{1/2x}Ti_{2-1/2x}O_4$ was particularly easy to prepare as a powder below the solidus, and an attempt was made to refine the atomic positions by a least-squares analysis of powder diffractometer data. The metal positions were well-defined, but the oxygens were not obtained with any great precision (Table 7). *R* could not be reduced below 15·7% and preferred orientation evidently had not been entirely eliminated. Within the rather wide limits of error, this compound is nevertheless exactly isomorphous with $Rb_xMn_xTi_{2-x}O_4$.

The variety of trivalent ions (and Mg) accommodated in this layer structure contrasts with the results of parallel studies we have made or are making of isomorphous substitution in closely related systems. The present structure will accommodate metal ions tolerating or requiring some distortion in their bonding to

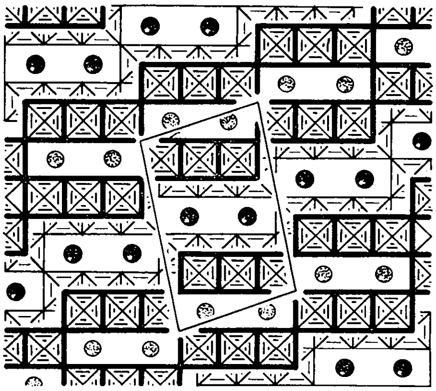


Fig. 5

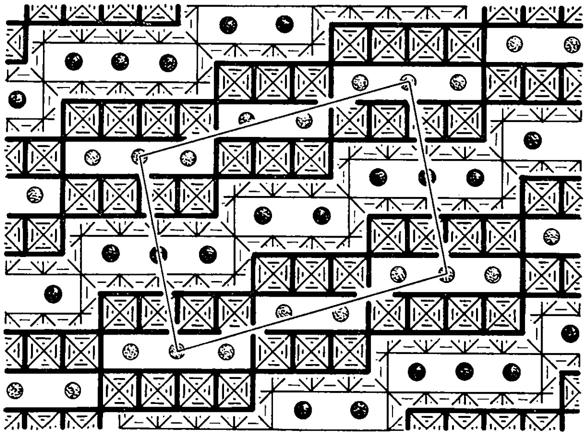


Fig. 6

Figs. 5 and 6. $Na_2Ti_6O_{13}$ (Fig. 5) and $Na_2Ti_7O_{15}$ (Fig. 6) showing the relationship to $Rb_xMn_xTi_{2-x}O_4$ in the orientation of Fig. 4(*a*). The eight Na atoms in the unit cell of $Na_2Ti_7O_{15}$ are distributed over ten positions.

oxygen, including $Al^{3+}$, $Mn^{3+}$ or $Mg^{2+}$, but none of these in association with $Ti^{4+}$ formed a calcium ferrite isomorph of the type $NaScTiO_4$ (Reid, Wadsley & Sienko, 1967). $Cr^{3+}$ cannot form either structure, but prefers instead a hollandite $M^+Cr^{3+}Ti_3O_8$, where M is any one of the alkali metals Na, K, Rb or Cs. Although in each of these three structures $Ti^{4+}$ and either a tri- or divalent metal are randomized in the available octahedral positions, more than a superficial stereochemical consideration is required to decide in advance whether any one of them is likely to form.

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# Refinement of the Crystal Structure of Groutite, α-MnOOH

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The structure of α-MnOOH (groutite) has been refined from three-dimensional data. Large variations in Mn–O bond lengths can be attributed to the Jahn–Teller effect. Some other factors affecting metal–oxygen bond lengths are discussed.

## Introduction

Groutite (α-MnOOH) was first studied by Gruner (1947) who determined its orthorhombic unit-cell dimensions (Table 1) and noted that it was isostructural with goethite (α-FeOOH) and diaspore (α-AlOOH). Collin & Lipscomb (1949) determined its space group (*Pbnm*) and general structure, but did not attempt any further refinement. In particular, they were not able to say whether there was any significant variation in the Mn–O bond lengths. The present study aimed to refine the structure and investigate this possibility.

Table 1. *Unit-cell determinations of groutite* (Å)

| Reference | *a* | *b* | *c* |
|---|---|---|---|
| Gruner | 4·56 | 10·70 | 2·85 |
| Collin & Lipscomb | 4·58 | 10·76 | 2·89 |
| Present investigation | 4·560 | 10·700 | 2·870 |

## Experimental

Crystals were selected from a sample of groutite from the Cuyuna Range, Minnesota, kindly supplied by Dr Roy Phillips of the Geology Department, Durham University. Rotation and Weissenberg photographs, taken using Cu *Kα* and Co *Kα* radiation, confirmed that they were pure groutite and two of these crystals were selected for intensity measurements. The first (GX1) was a large jet-black wedge-shaped crystal, about 750 microns long and set about the *a* axis. The second (GX2) was a small, near-spherical crystal, about 200 microns in diameter, and was set about the *c* axis. The intensity measurements were made using a Hilger and Watts automatic linear diffractometer with Mo *Kα* radiation and the data were processed on an Elliott 803B computer, mainly using programs kindly made available by Daly, Stephens & Wheatley (1963). After correction for Lorentz-polarization factors, the intensities were converted to structure amplitudes and placed