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Layer Structure: The Oxides $A_3Ti_5MO_{14}$

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Five new oxides, $K_3Ti_5MO_{14}$, $Rb_3Ti_5MO_{14}$ (M = Ta, Nb), and $Tl_3Ti_5NbO_{14}$, have been synthesized. The structure of these oxides consists of octahedral layers similar to those observed for $Na_2Ti_3O_7$ and held together by monovalent ions; the sheets consist of blocks of 2 × 3 edge-sharing octahedra, which are then joined to each other by the corners of the octahedra. The relative disposition of the layers is similar to that observed for $Tl_2Ti_4O_9$. These oxides can be considered as the member $n = 3$ of a series of closely related structures with formula $A_nB_{2n}O_{4n+2}$, where n indicates the number of octahedra which determines the width of the blocks of 2 × n octahedra.

Introduction

Among the titanates with a layer structure (*1–5*) the titanate $Na_2Ti_3O_7$ behaves differently.

The structure of this oxide, which was established by Andersson and Wadsley (*1*), consists of Ti_3O_7 layers built up from blocks of six edge-sharing octahedra (Fig. 1a), and held together by sodium ions. These authors showed that this structure differed from that of the other titanates, in that each alternate sheet Ti_3O_7 was displaced by a distance $b/2$. They proposed the existence of a dimorph, the hypothetical structure of which (Fig. 1b) was obtained by such a translation of the layers.

Several attempts were made to prepare this dimorph, but they remained unsuccessful for reasons which were not obvious. This failure cannot be due only to the nature of the monovalent ion A, since no titanate $A_2Ti_3O_7$ with such a structure has, to our knowledge, been synthesized. An explanation for the destabilization of the structure could be the very short A–A distances resulting from the large number of A ions at the same level between the octahedral sheets (Fig. 1b).

We have thus considered the possibility of the existence of oxides $A_{2-x}M_3O_7$. The present paper deals with titanoniobates and titanotantalates $A_3Ti_5MO_{14}$.

Experimental Procedure

The titanoniobates and titanotantalates $A_3Ti_5MO_{14}$ (M = Ta, Nb) were synthesized from the mixtures of carbonates A_2CO_3 (A = K, Rb, Tl) and Nb_2O_5 or Ta_2O_5 and TiO_2 oxides.

The alkali metal oxides were heated at temperatures of 800, 900, 1000, and 1100°C for about 12 hr at each temperature. It should be noted that these compounds can be obtained similarly at lower temperatures but the heating time is correspondingly longer (greater than 1 week).

For the thallium I oxides, three temperatures were used: 600°C, 5 hr; 750°C, 4 hr; 850°C, 1 hr.

For each oxide the change in weight was

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determined and the product remixed and examined by X-ray diffraction after each heating at each temperature.

The resulting compounds were studied by X-ray powder diffractometry using the Cu$K\alpha$ radiation, and their density was measured by picnometry in CCl_4. This study was completed by electron diffraction observation using a EM 200 Philips microscope.

Results

Using the experimental method previously described, five new oxides were synthesized: $K_3Ti_5NbO_{14}$, $K_3Ti_5TaO_{14}$, $Rb_3Ti_5NbO_{14}$, $Rb_3Ti_5TaO_{14}$, and $Tl_3Ti_5NbO_{14}$.

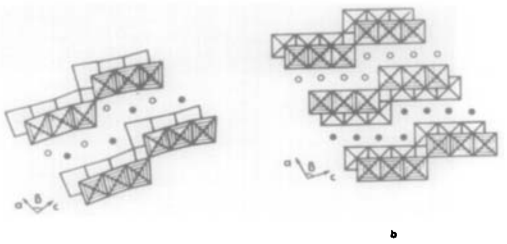

FIG. 1. (a) $Na_2Ti_3O_7$: projection of the structure on to the (0 1 0) plane. (b) Hypothetical possible structure proposed by S. Andersson and A. D. Wadsley.

The X-ray patterns of these compounds showed some similarity to those of $Na_2Ti_3O_7$ (*1*) and $Tl_2Ti_4O_9$ (*2*). They were indexed (Table I) in a monoclinic cell corresponding to that of the hypothetical structure (Fig. 1b) and whose parameters were related to those of $Na_2Ti_3O_7$ and $Tl_2Ti_4O_9$ in the following way:

$$a > 2a_{Na_2Ti_3O_7}; \quad b \simeq b_{Na_2Ti_3O_7}; \quad c \simeq c_{Na_2Ti_3O_7}; \quad \beta \simeq \beta_{Na_2Ti_3O_7};$$

$$a \simeq a_{Tl_2Ti_4O_9}; \quad b \simeq b_{Tl_2Ti_4O_9}; \quad c \neq c_{Tl_2Ti_4O_9}; \quad \beta \simeq \beta_{Tl_2Ti_4O_9}.$$

An electron diffraction study (Fig. 2) was used to confirm the systematically absent reflections: h, k, l with $h + k \neq 2n$, giving three possible space groups: $C2$, Cm, and $C2/m$.

The observed densities (Table I) agree with 2 units $A_3Ti_5MO_{14}$ per cell.

In order to confirm the proposed model, a structure determination was carried out, from X-ray powder patterns for three compounds: $K_3Ti_5MO_{14}$ (M = Ta, Nb) and $Rb_3Ti_5NbO_{14}$. The thallium oxide could not be studied due to orientation phenomena.

The calculations were made in the most symmetric group $C2/m$, for the first 60 measured reflexions, i.e., 150 $h\ k\ l$.

The atoms were initially placed in positions close to those of the hypothetical structure: K^+ or Rb^+ on 2(*a*) and 4(*i*), respectively; titanium and niobium or tantalum atoms, statistically distributed on three sorts of 4(*i*) sites; and oxygen atoms

TABLE I

$A_3(Ti_5M)O_{14}$: (M = Ta, Nb) CRYSTALLOGRAPHIC DATA

Compounds	*a* (Å)	*b* (Å)	*c* (Å)	β	d_{obs}	d_{cal} ($Z = 2$)
$K_3(Ti_5Nb)O_{14}$	18.371 (*6*)	3.794 (*1*)	9.199 (*3*)	101°21 (*4*)	3.54	3.55
$K_3(Ti_5Ta)O_{14}$	18.363 (*2*)	3.791 (*1*)	9.174 (*1*)	101°28 (*1*)	3.95	4.03
$Rb_3(Ti_5Nb)O_{14}$	19.073 (*7*)	3.814 (*1*)	9.223 (*4*)	100°93 (*4*)	4.07	4.10
$Rb_3(Ti_5Ta)O_{14}$	19.11 (*1*)	3.810 (*2*)	9.232 (*4*)	101°04 (*4*)	4.53	4.54
$Tl_3(Ti_5Nb)O_{14}$	19.074 (*7*)	3.797 (*1*)	9.214 (*4*)	102°00 (*4*)	6.07	5.95

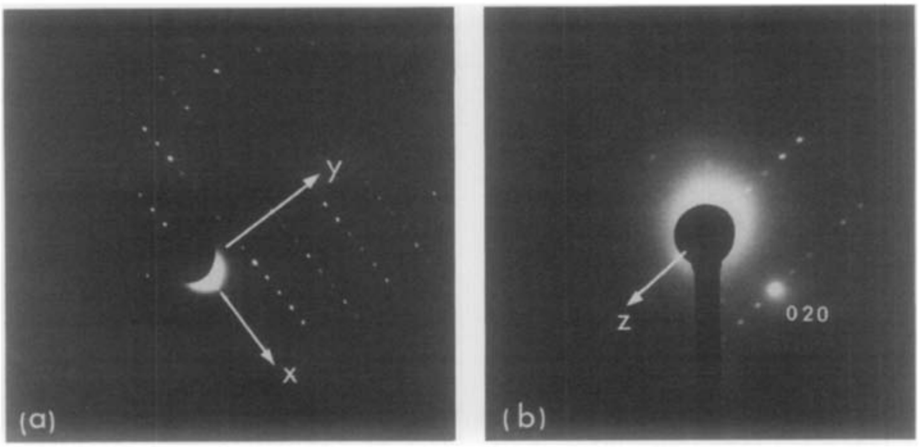

FIG. 2. $K_3(Ti_5Nb)O_{14}$: electron diffraction patterns of (a) (*h k* 0), (b) (0 *k l*) planes showing systematical reflections.

on 7 × 4(*i*). The discrepancy factors obtained after successive refinements of the free parameters ($R_I > 0.14$) as well as the *B* factors of the titanium and niobium (or tantalum) atoms remained relatively high. An ordered distribution of the transition elements over the three types of 4(*i*) sites, similar to that observed for KM_2O_5 compounds (*7*) was then considered. A value of 0.07 for the discrepancy factor R_I was reached for both potassium compounds. However, the value of R_I remained relatively high for the rubidium oxide (0.14). Moreover the thermal parameter of Rb^+ fixed at a rather high value ($B = 8.6$ Å^2) and the K–O distances for the potassium located in 2(*a*) appeared too small (2.60 Å). A statiscal distribution of K^+ or Rb^+ over 4(*i*) sites resulting from the splitting of the 2(*a*) sites thus seemed more probable. This distribution did not change the discrepancy factor for the potassium compounds due to the small scattering factor of K^+, but in the case of the rubidium oxide R_I decreased drastically, to the value 0.06, as did the B_{Rb} value, which fixed at 1.7 Å^2. For the three compounds the K–O and Rb–O distances obtained after refinement were more reasonable. Calculations in other space groups were not carried out due to the larger number of free parameters which would have had to be introduced, bearing in mind the limited number of observed reflections.

The final atomic parameters are listed in Table II. From Table III it can be seen that no discrepancy could be observed between the calculated and measured intensities.

Discussion

From the projection of the structure onto the (010) plane (Fig. 3) it can be seen that the geometry of the ribbons built up from 2 × 3 edge-sharing octahedra is very similar to that of $Na_2Ti_3O_7$. The important distortions of the octahedra with O–O distances ranging from 2.48 to 3.27 Å (Fig. 4) are close to those observed for $Na_2Ti_3O_7$ (*1*).

The interatomic distances (Table IV) show an appreciable displacement of the transition metal inside its octahedron, towards the oxygen atoms which are located on the outer wall of the ribbon, decreasing the electrostatic repulsion between metal atoms. It results in metal–oxygen distances close to 1.75 Å, somewhat smaller than the sum of the ionic radii (*6*). This phenomenon agrees with the results obtained for the other layer titanates and titanoniobates or tantalates (*1*, *2*, *7*) which are characterized

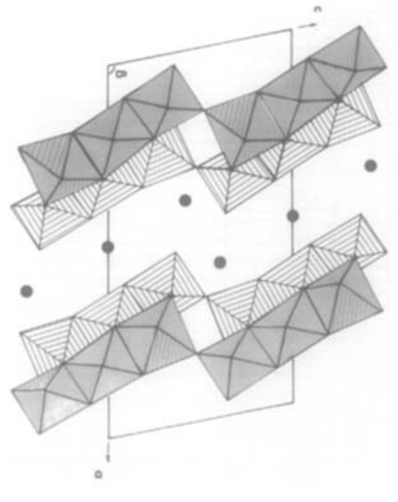

FIG. 3. $K_3(Ti_5Nb)O_{14}$: projection of the structure onto the (0 1 0) plane.

by similar ribbons built up from blocks of $n \times 2$ edge-sharing octahedra (n = 2, 3, 4).

Almost all the niobium or tantalum atoms are located in the type I octahedra (Fig. 4) which share one corner between two blocks. This phenomenon, similar to that observed for $A_{1-x}M_2O_5$ (7), can be explained in the same way: the three edge-sharing octahedra of type I cause a less electrostatic repulsion between metallic atoms than the type II and type III octahedra (Fig. 4) which share six and five edges, respectively.

Two different types of coordination are found for the potassium and rubidium ions. One potassium, $K_{(2)}$ (or rubidium $Rb_{(2)}$), is located in nearly cubic positions, as are the thallium ions in $Tl_2Ti_4O_9$. A coordination of 10 is obtained for $K_{(1)}$ or $Rb_{(1)}$, with four

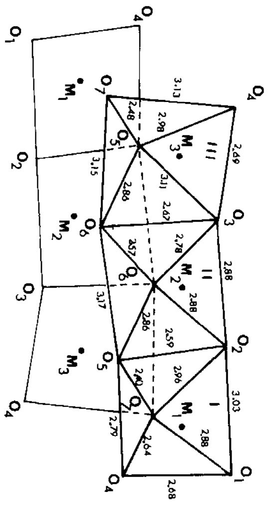

FIG. 4. $K_3(Ti_5Nb)O_{14}$: the distorded octahedra types I, II, III, and interatomic distances O–O.

TABLE II

ATOMIC POSITION PARAMETERS, ISOTROPIC THERMAL PARAMETERS, AND OCCUPANCY FACTORS FOR $K_3Ti_5MO_{14}$ (M = Nb,Ta)[a]

Atoms		K_1/Rb_4	K_2/Rb_2	Ti_1/M	Ti_2/M	Ti_3/M	O_1	O_2	O_3	O_4	O_5	O_6	O_7
$K_3(Ti_5Nb)O_{14}$	x	−0.012 (*2*)	0.0800 (*5*)	0.6268 (*3*)	0.6795 (*6*)	0.7294 (*6*)	0.540 (*2*)	0.598 (*1*)	0.653 (*1*)	0.678 (*1*)	0.726 (*1*)	0.793 (*1*)	0.848 (*1*)
R_1 = 0.07	z	0.070 (*4*)	0.602 (*2*)	0.330 (*1*)	0.016 (*2*)	0.712 (*1*)	0.373 (*4*)	0.086 (*3*)	0.813 (*3*)	0.534 (*4*)	0.265 (*2*)	0.972 (*4*)	0.669 (*4*)
	B (Å²)	1	2.1	1.2	0.61	0.50	1	1	1	1	1	1	1
	α^b	0.5	1	0.575 0.425	0.925 0.075	1 0	1	1	1	1	1	1	1
$K_3(Ti_5ta)O_{14}$	x	−0.010 (*2*)	0.0806 (*6*)	0.6253 (*3*)	0.6784 (*6*)	0.7310 (*6*)	0.528 (*2*)	0.600 (*1*)	0.651 (*1*)	0.683 (*1*)	0.741 (*1*)	0.794 (*1*)	0.848 (*1*)
R_1 = 0.07	z	0.054 (*4*)	0.623 (*2*)	0.321 (*1*)	0.020 (*2*)	0.716 (*1*)	0.387 (*4*)	0.104 (*3*)	0.801 (*4*)	0.524 (*4*)	0.250 (*3*)	0.981 (*4*)	0.661 (*4*)
	B (Å²)	1	0.99	0.40	0.98	1.2	1	1	1	1	1	1	1
	α^b	0.5	1	0.6 0.4	0.95 0.05	0.95 0.05	1	1	1	1	1	1	1
$Rb_3(Ti_5Nb)O_{14}$	x	−0.012 (*1*)	0.0730 (*4*)	0.6317 (*4*)	0.6856 (*7*)	0.7328 (*8*)	0.5354 (*2*)	0.610 (*1*)	0.660 (*1*)	0.683 (2)	0.741 (*1*)	0.788 (2)	0.850 (2)
R_1 = 0.06	z	0.049 (2)	0.627 (*1*)	0.333 (*1*)	0.014 (2)	0.708 (2)	0.361 (*5*)	0.106 (*3*)	0.815 (*4*)	0.538 (*4*)	0.268 (*3*)	0.946 (*4*)	0.657 (*4*)
	B (Å²)	1.7	1.7	0.5	1.05	0.8	1	1	1	1	1	1	1
	α^b	0.5	1	0.45 0.55	0.95 0.05	1 0	1	1	1	1	1	1	1

[a] Space group $C2/m$ (0, 0, 0; ½, ½, 0). All atoms on 4(i).

[b] The occupancy factors for Ti, Nb, Ta, were determined by a trial-and-error method.

TABLE III

OBSERVED AND CALCULATED INTENSITIES FOR $K_3(Ti_5Ta)O_{14}$[a]

$h\ k\ l$	I_o	I_c	$h\ k\ l$	I_o	I_c	$h\ k\ l$	I_o	I_c
2 0 0 0 0 1	100	98.2	8 0 1 2 0 4 3 1 3 7 1 $\bar{2}$	45	46.8	10 0 2 8 0 $\bar{5}$ 6 2 $\bar{2}$ 4 2 $\bar{3}$ 9 1 2	32	29.5
2 0 $\bar{1}$	11.2	14.1	1 1 $\bar{4}$	5	3.5	6 2 1 2 2 3	11	10.2
2 0 1	52	50.8	7 1 1 8 0 $\bar{3}$ 6 0 $\bar{4}$	3.5	3.3	12 0 $\bar{1}$ 11 1 $\bar{1}$ 9 1 $\bar{4}$ 12 0 $\bar{2}$	9.4	9.6
4 0 0 0 0 2	16.5	16	0 2 0 1 1 4 7 1 $\bar{3}$	41	44.2	4 0 $\bar{6}$ 11 1 $\bar{2}$ 3 1 5 11 1 0 0 0 6 7 1 $\bar{5}$	21.8	18.2
2 0 $\bar{2}$ 4 0 $\bar{1}$	7	7.3	8 0 2 4 0 4	6.8	6.2	6 2 3	1.0	1.1
4 0 1 2 0 2 1 1 0	37.5	38.2	2 2 0 0 2 1 5 1 3	4.5	5.2	6 0 $\bar{6}$ 2 2 $\bar{4}$	7	6.1
4 0 $\bar{2}$	4	5.4	5 1 $\bar{4}$ 10 0 $\bar{1}$ 2 0 $\bar{5}$ 2 2 $\bar{1}$	12.5	10.2	8 0 4 11 1 $\bar{3}$ 8 2 0	6.2	5.8
1 1 $\bar{1}$	1	1.1	7 1 2	2	2.3	7 1 4 2 0 6 8 2 $\bar{2}$ 4 2 $\bar{4}$	13.4	13.1
1 1 1	2	3.4	2 2 1 4 0 $\bar{5}$ 9 1 $\bar{1}$	8	9.7	9 1 3 10 0 $\bar{5}$ 3 1 $\bar{6}$ 1 1 $\bar{6}$	10	9.5
3 1 0	67	67.3	8 0 $\bar{4}$ 9 1 0	2.5	2.5	8 2 1 2 2 4	15	15.9
3 1 $\bar{1}$	27	22.8	3 1 4 9 1 $\bar{2}$ 4 2 0 0 2 2	37.4	35.8	5 1 5 9 1 $\bar{5}$	7	7.8
6 0 $\bar{1}$ 2 0 $\bar{3}$ 6 0 0 0 0 3	64.6	65.1	2 0 5 6 0 $\bar{5}$ 2 2 2 7 1 $\bar{4}$ 9 1 1	14.8	17.1	8 2 $\bar{3}$ 6 2 $\bar{4}$	1	1.7
3 1 1 1 1 $\bar{2}$ 4 0 2	66	66.2	4 2 $\bar{2}$	0.8	0.8	11 1 $\bar{4}$	2	1.5
6 0 $\bar{2}$ 4 0 $\bar{3}$ 3 1 $\bar{2}$	69	70.5	8 0 3 6 0 4 1 1 $\bar{5}$ 3 1 $\bar{5}$	13.5	13.4	6 2 3 11 1 2	7	6.8
6 0 1 2 0 3	29	28.3	6 2 $\bar{1}$	0.5	0.5	8 2 2 4 2 4 7 1 $\bar{6}$	6.5	5.6
5 1 0 5 1 $\bar{1}$	5	7	0 2 3 5 1 4 1 1 5 5 1 $\bar{5}$	28	24.8	10 2 $\bar{1}$	2.8	1.9
3 1 2	13.6	15.8	7 1 3	0.8	0.6			
5 1 1 5 1 $\bar{2}$	3.9	2.3						
1 1 $\bar{3}$ 6 0 $\bar{3}$	7	10.4						
3 1 $\bar{3}$	3.5	3.7						
8 0 $\bar{1}$ 2 0 $\bar{4}$	1	1						
1 1 3	1	1.1						
8 0 0 0 0 4	2.5	2.4						
8 0 $\bar{2}$ 4 0 $\bar{4}$	36.5	32.8						
7 1 $\bar{1}$	7.0	10.2						
5 1 $\bar{3}$ 7 1 0 5 1 2	3.0	1.2						

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[a] Space group $C2/m$; $K_{(1)}$ on 2 (a).

TABLE IV

INTERATOMIC DISTANCES (Å) METAL–OXYGEN FOR $A_3(Ti_5Nb)O_{14}$[a] (A = K, Rb) AND $K_3(Ti_5Ta)O_{14}$[a]

Distances	$K_3(Ti_5Nb)O_{14}$	$K_3(Ti_5Ta)O_{14}$	$Rb_3(Ti_5Nb)O_{14}$
$A'_{(1)}$–$O_{(2)}$ (×4)	2.70 (*3*)	2.74 (*3*)	2.85 (*2*)
$A'_{(1)}$–$O_{(2')}$ (×2)	2.76 (*3*)	2.74 (*3*)	2.98 (*2*)
$A'_{(1)}$–$O_{(3)}$ (×2)	3.54 (*4*)	3.65 (*5*)	3.81 (*3*)
$A'_{(1)}$–$O_{(6)}$	3.52 (*4*)	3.53 (*4*)	3.75 (*4*)
$A'_{(1)}$–$O_{(7)}$	3.46 (*4*)	3.56 (*4*)	3.70 (*3*)
$A'_{(1)}$–$O_{(1)}$ (×2)	3.35 (*4*)	3.54 (*4*)	3.43 (*4*)
$A_{(2)}$–$O_{(1)}$ (×2)	2.83 (*3*)	2.90 (*3*)	3.08 (*4*)
$A_{(2)}$–$O_{(1')}$ (×2)	2.95 (*7*)	2.74 (*3*)	2.83 (*3*)
$A_{(2)}$–$O_{(3)}$ (×2)	2.86 (*4*)	2.67 (*3*)	2.88 (*2*)
$A_{(2)}$–$O_{(4)}$ (×2)	2.77 (*6*)	2.93 (*2*)	3.06 (*2*)
$Ti_{(1)}$–$O_{(1)}$	1.72 (*4*)	2.00 (*4*)	1.90 (*4*)
$Ti_{(1)}$–$O_{(2)}$	2.20 (*3*)	1.96 (*3*)	2.06 (*4*)
$Ti_{(1)}$–$O_{(4)}$	1.93 (*3*)	1.96 (*3*)	1.96 (*3*)
$Ti_{(1)}$–$O_{(5)}$	2.02 (*2*)	2.34 (*2*)	2.27 (*2*)
$Ti_{(1)}$–$O_{(7)}$ (×2)	1.95 (*1*)	1.96 (*1*)	1.94 (*1*)
$Ti_{(2)}$–$O_{(2)}$	1.74 (*3*)	1.76 (*3*)	1.81 (*3*)
$Ti_{(2)}$–$O_{(3)}$	1.83 (*3*)	1.98 (*5*)	1.81 (*4*)
$Ti_{(2)}$–$O_{(5)}$	2.28 (*2*)	2.20 (*3*)	2.38 (*3*)
$Ti_{(2)}$–$O_{(6)}$	2.19 (*3*)	2.22 (*3*)	2.16 (*4*)
$Ti_{(2)}$–$O_{(6')}$ (×2)	1.96 (*1*)	1.96 (*1*)	1.99 (*1*)
$Ti_{(3)}$–$O_{(3)}$	1.83 (*3*)	1.79 (*6*)	1.85 (*3*)
$Ti_{(3)}$–$O_{(4)}$	1.73 (*3*)	1.81 (*4*)	1.67 (*3*)
$Ti_{(3)}$–$O_{(5)}$ (×2)	2.06 (*1*)	1.97 (*1*)	1.97 (*1*)
$Ti_{(3)}$–$O_{(6)}$	2.45 (*3*)	2.47 (*4*)	2.24 (*4*)
$Ti_{(3)}$–$O_{(7)}$	2.29 (*3*)	2.30 (*4*)	2.37 (*2*)

[a] Space group $C2/m$.

short M–O distances (K_1–O ≃ 2.74 Å; Rb_1–O ≃ 2.92 Å) and six much larger distances (3.30–3.60 Å for $K_{(1)}$–O and 3.40–3.80 Å for $Rb_{(1)}$–O). This geometry can likewise be compared to that of $Tl_2Ti_4O_9$, for which one Tl^+ ion is displaced towards one face of the distorted cube where it is located, giving four short Tl–O distances (2.70–2.91 Å) and four long distances (3.08–3.42 Å). However, for $A_3Ti_5MO_{14}$, the distortion of the octahedra involves for the $K_{(1)}^+$ and $Rb_{(1)}^+$ two additional oxygen neighbors on the same level as alcalin.

The similarity of the structures $A_3Ti_5MO_{14}$ and $Tl_2Ti_4O_9$ should be emphasized: they both consist of octahedral sheets which are themselves built up of blocks of edge-sharing octahedra, characterized by a width of n octahedra. What is noteworthy is the relative disposition of the sheets which determines the number of A cations between the layers. These octahedra, surrounding one layer of A cations, are all located at the same level, contrary to $Na_2Ti_3O_7$. In this respect, these structures are related to the oxides $A_x(M_xTi_{2-x})O_4$ (*4, 5*) which are formed of parallel layers of edge-sharing octahedra (M_2O_4), the width of the octahedral block corresponding in this case to $n = \infty$. It can be seen that a single shear of these octahedral layers along the ⟨101⟩ direction (indicated by the arrows on Fig. 5) leads to the $Rb_x(M_xTi_{2-x})O_4$ structure (*4*). It can be considered that these oxides belong to a large family of closely related structures with the formula $A_nB_{2n}O_{4n+2}$, where n indicates the number of octahedra, which determine the width of the unit blocks of 2 × n octahedra. $A_3Ti_5MO_{14}$ and $Tl_2Ti_4O_9$ are thus the numbers n = 3 and n = 4 of the series, respectively, while $Rb_x(Ti_{2-x}M_x)O_4$ corresponds to $n = \infty$. Greater values of n have not yet been investigated. The term n = 2 does not exist: it corresponds to the oxides $ATiMO_5$ (*8*), which are likewise characterized by similar layers built up from 2 × 2 edge-sharing octahedra, but in which the alternate sheets are oriented in a different manner. This particular behavior of the 2 × 2 edge-sharing octahedra has already been observed in titanoniobates and titanates with a tunnel structure, $A_2Ti_6O_{13}$ (*9*), and the intergrowths $(A_2M_6O_{13})_n \cdot AM_4O_9$ (*10, 11*) show analogous ribbons of 2 × 3 and 2 × 2 edge-sharing octahedra, with the

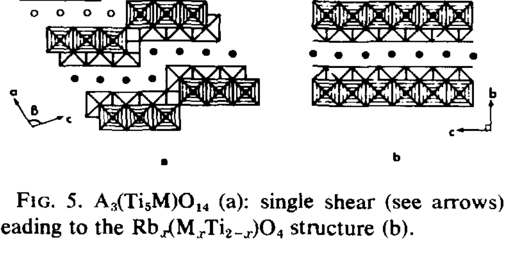

FIG. 5. $A_3(Ti_5M)O_{14}$ (a): single shear (see arrows) leading to the $Rb_x(M_xTi_{2-x})O_4$ structure (b).

same disposition as that described there. The only difference is that the "sheets" so formed are connected by the corners of their octahedra. However, the limiting compound AM_4O_9, does not have the hypothetical structure which could be foreseen from this series but can in fact be considered as a chemical twin of the hypothetical structure (*7–11*). The possibility of intergrowths in these layer structures, corresponding to noninteger values of *n*, will likewise be considered.

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