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# Intergrowth in Tunnel Structures: The Titanates $(A_2Ti_6O_{13})_n \cdot A'Ti_4O_9$

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A new structural family, $(A_2M_6O_{13})_n \cdot A'M_4O_9$, was isolated and studied by means of X-ray diffraction, electron diffraction, and electron microscopy. The structure consists of an ordered intergrowth of two types of structural units: $A_2Ti_6O_{13}$ and hypothetical $A'M_4O_9$, both characterized by zigzag ribbons of, respectively, 2 × 3 and 2 × 2 edge-sharing octahedra, joined by corner sharing to form a series of open tunnels containing $A$ and $A'$ cations. The monoclinic unit-cell parameters can be deduced, for an "$n$" term, from those of $A_2Ti_6O_{13}$.

The number of oxides with structures characterized by tunnels with a rectangular section is very limited. The best-known example is that of the titanates $A_2Ti_6O_{13}$ (1–3), the tunnels of which can be considered as built up from three edge-sharing perovskite tunnels (3P). To our knowledge, no structure with tunnels resulting from the association of two perovskite (2P) tunnels has been observed. We describe here a new family of titanates, $(A_2Ti_6O_{13})_n \cdot A'Ti_4O_9$, with $A$ = Na, K, Rb and $A'$ = Ba, Sr, Pb characterized by the presence of 3P and 2P tunnels and with a structure related to that of the compounds $A_2Ti_6O_{13}$.

## Structural Relationships

### *The Structure of $A_2Ti_6O_{13}$ ($A$ = NA, K, Rb)*

The structure of $Na_2Ti_6O_{13}$ was determined for the first time by Andersson and Wadsley (*11*); more recently, a similar framework was found for $K_2Ti_6O_{13}$ (*2*) and $Ba_2Ti_6O_{13}$ (*3*). These titanates are monoclinic with $a \simeq 15.5$, Å, $b \simeq 3.8$, Å and $c \simeq 9.13$ Å (space group $C2/m$, $Z = 2$). The host lattice of these compounds can be constructed from structural units of 2 × 3 edge-sharing octahedra (Fig. 1a). The stacking along **b** of these units forms sheets of edge-sharing octahedra, extending indefinitely in this direction, with a width of three octahedra (Fig. 1b). In the (100) and (200) planes, these units share the corners of their octahedra (Fig. 1c); this framework bounds tunnels with an approximately rectangular section, running along the **b** axis. Each tunnel contains three pseudocubic sites per cell analogous to those observed in the perovskites, and will be referred to as 3P; two of the perovskite sites are occupied by the $A$ ions.

### *The Structural Unit of 2×2 Edge-Sharing Octahedra*

Similar units built up from four edge-sharing octahedra (Fig. 2a) have been observed in different oxides (4–6). But none of these compounds show tunnels with a rectangular section. A hypothetical structure derived from the $A_2Ti_6O_{13}$ structure can thus be proposed. The octahedral framework of such

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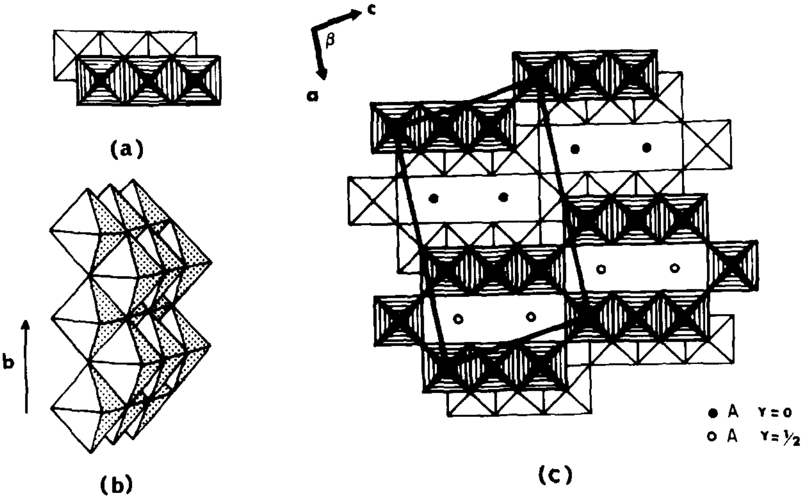

FIG. 1. (a) 2 × 3 edge-sharing octahedra: $Ti_6O_{13}$ unit. (b) Sheet formation by edge-sharing octahedra of the $Ti_6O_{13}^{2-}$ unit. (c) Idealized structure of $A_2Ti_6O_{13}$ in projection onto (010): 3P tunnel formation by the joining of adjacent sheet's corners.

a structure would be built up from infinite sheets of edge-sharing octahedra, with a width of two octahedra (Fig. 2b). These sheets would be linked together by the corners of their octahedra, bounding tunnels which can be considered as the association of two perovskite tunnels (Fig. 2c) and will be referred to as 2P. Regarding the structure of $A_2Ti_6O_{13}$, for which only two perovskite sites of three in the tunnels are occupied, it can be assumed only one pseudocubic site per tunnel is occupied by the $A$ ions. Hence this structure should be obtained for compounds with the general formula

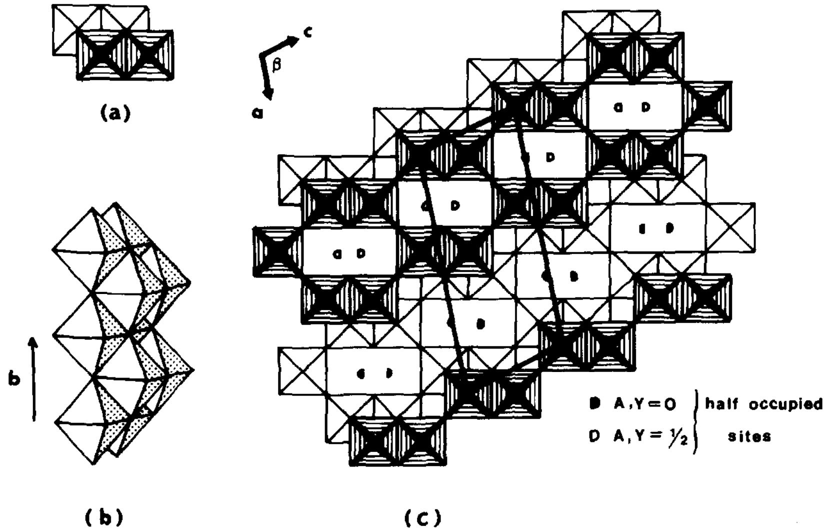

FIG. 2. (a) 2 × 2 edge-sharing octahedra: $M_4O_9$ unit. (b) Sheet formation by edge-sharing octahedra. (c) Idealized drawing of the hypothetical $A'M_4O_9$ with 2P tunnel.

$A'M_4O_9$. However, for this type of ribbon another arrangement is possible, leading to the formation of pentagonal tunnels (Fig. 3). The only known oxides, $BaTi_4O_9$ (*5*) and $KTi_3NbO_9$ (*4*), unfortunately, have this structure, which can be considered as a chemical twin of the hypothetic structure proposed here. Nevertheless, this chemical twin should not be obtained in structures showing simultaneously 2P and 3P tunnels.

### *Structual Hypothesis of a New Series $(A_2Ti_6O_{13})_n \cdot A'Ti_4O_9$*

Mixed structures containing both 2P and 3P tunnels can be predicted by intergrowth of the $A_2Ti_6O_{13}$ structure and the hypothetical $A'M_4O_9$. The host lattice of such an intergrowth is built up of zigzag ribbons of octahedra, sharing corners and edges. Every ribbon is made up of two sorts of structural units, blocks of 2×2 and blocks of 2×3 edge-sharing octahedra; these blocks are connected by the corners of their octahedra.

The idealized structures of these compounds are given in Fig. 4 for the first three terms of the series, which can be formulated as $(A_2Ti_6O_{13})_n \cdot A'M_4O_9$. The comparison of these models with the idealized structure of $A_2Ti_6O_{13}$ (Fig. 1) shows that the octahedra are connected in an identical manner in the **a** and **b** directions, independently of the $n$ value, leading to $a_n$ and $b_n$ parameters close to those of $A_2Ti_6O_{13}$. In turn the arrangement along **c** varies with $n$. We can thus propose, for these different terms, a monoclinic cell for which the parameters can be predicted as a function of those of $A_2Ti_6O_{13}$ by the relationships:

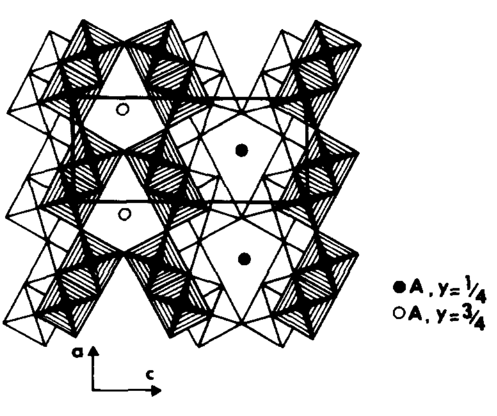

FIG. 3. $AM_4O_9$ in projection showing the union of sheets leading to the pentagonal tunnel formation.

$$a_n \simeq a_{A_2Ti_6O_{13}}, \tag{1}$$

$$b_n \simeq b_{A_2Ti_6O_{13}}, \tag{2}$$

$$c_n \simeq nc_{A_2Ti_6O_{13}} + c_0, \tag{3}$$

$$\beta_n \simeq \beta_{A_2Ti_6O_{13}} + \omega_n, \tag{4}$$

where $c_0$ is a constant close to 6.4 Å corresponding to the structural unit of two octahedra in the hypothetical structure $A'M_4O_9$, and $\omega_n$ is given by the relationship $\tan \omega_n = 1/3(3n+2)$.

## The First Three Terms of the Series $(A_2Ti_6O_{13})_n \cdot ATi_4O_9$

The systems $A_2Ti_6O_{13} \cdot A'Ti_4O_9$ have been studied for $A$ = Na, K, Rb and $A'$ = Ba, Pb, Sr.

### *Synthesis of the compounds $(A_2Ti_6O_{13})_n \cdot A'Ti_4O_9$*

The compounds $(A_2Ti_6O_{13})_n \cdot A'Ti_4O_9$ were prepared from alkali metal carbonates $A_2CO_3$, bivalent metal carbonates $ACO_3$, and titanium dioxide, in the appropriate molar ratios. The mixtures were first heated at temperatures ranging from 900 to 1100°C in order to remove $CO_2$. The samples were then ground, fired for several hours at 1250°C in platinum crucibles, in air, and finally quenched to room temperature. In these conditions, three groups of compounds i.e., 15 compounds, were isolated: $A_2A'Ti_{10}O_{22}$, $A_4A'Ti_{16}O_{35}$, $A_6A'Ti_{22}O_{48}$. They correspond, respectively, to the terms $n = 1$, 2, and 3 of the predicted series.

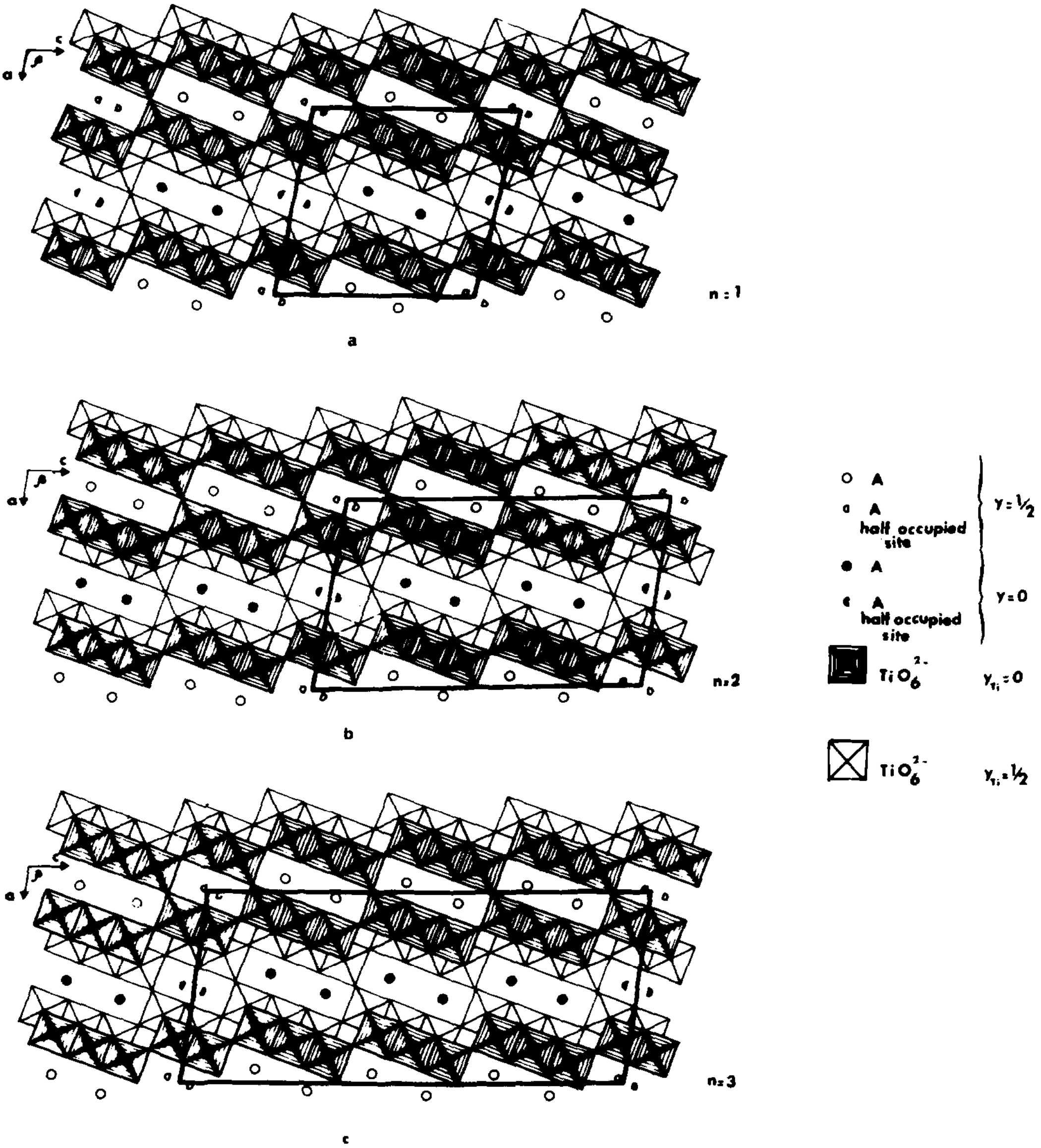

FIG. 4. Idealized drawing of $(A_2Ti_6O_{13})_n \cdot A'M_4O_9$: (a) $A_2A'Ti_{10}O_{22}$, $n = 1$; (b) $A_4A'Ti_{16}O_{35}$, $n = 2$; (c) $A_6A'Ti_{22}O_{48}$, $n = 3$.

### *X-Ray Diffraction and Electron Microscopy Studies*

The X-ray powder diffraction data of these products were obtained with a Philips goniometer using Cu$K_\alpha$ radiation. The specimens for electron microscopy were ground and dispersed on carbon grids in alcohol. For every composition, about 60 microcrystals were observed. with an EM 200 Philips electron microscope. The best resolutions were obtained for the $(Na_2Ti_6O_{13})_n \cdot BaTi_4O_9$ compounds.

In every case, we observed a monoclinic cell for which the $a_n$ and $b_n$ parameters were very close to those of $A_2Ti_6O_{13}$. The systematic absent reflections *hkl* with $h+k=2n$, observed for every term of the series. led to the possible space groups $C_2$, $C2/m$, and $Cm$ already found for $A_2Ti_6O_{13}$. The measurements of the density showed that there were two units of $(A_2Ti_6O_{13})_n \cdot A'Ti_4O_9$ per cell.

### *The Compounds $A_2A'Ti_{10}O_{22}$ ($n = 1$)*

The X-ray powder spectra of the $A_2A'Ti_{10}O_{22}$ compounds are quite different from those of $A_2Ti_6O_{13}$ (Table I). Electron diffraction patterns allowed the determination of the parameters: $a_1$ and $b_1$ are

TABLE I

$(Na_2Ti_6O_{13})_n \cdot BaTi_4O_9$ SERIES: X-RAY POWDER DIFFRACTION DATA

| $n = 1$ ($Na_2BaTi_{10}O_{22}$) | | | $n = 2$ ($Na_4BaTi_{16}O_{35}$) | | | $n = 3$ ($Na_6BaTi_{22}O_{48}$) | | |
|---|---|---|---|---|---|---|---|---|
| $d_{obs}$ | $h\ k\ l$ | $d_{calc}$ | $d_{obs}$ | $h\ k\ l$ | $d_{calc}$ | $d_{obs}$ | $h\ k\ l$ | $d_{calc}$ |
| 7.557 | $0\ 0\ 2$ | 7.5548 | 7.548 | $2\ 0\ \bar{1}$ | 7.5445 | 7.585 | $2\ 0\ \bar{1}$ | 7.5849 |
| 7.439 | $2\ 0\ 0$ | 7.4352 | 7.4555 | $2\ 0\ 0$ | 7.4551 | 7.456 | $2\ 0\ 0$ | 7.4550 |
| 7.326 | $2\ 0\ \bar{1}$ | 7.3268 | 6.9800 | $2\ 0\ \bar{2}$ | 6.9734 | | $2\ 0\ \bar{2}$ | 7.4265 |
| 5.980 | $2\ 0\ 2$ | 5.9838 | 6.0676 | $2\ 0\ \bar{3}$ | 6.0878 | 6.378 | $2\ 0\ 2$ | 6.3890 |
| 5.0365 | $0\ 0\ 3$ | 5.0365 | | $0\ 0\ 4$ | 6.0452 | 6.146 | $2\ 0\ \bar{4}$ | 6.1366 |
| 3.8083 | $4\ 0\ \bar{1}$ | 3.8054 | 4.8407 | $0\ 0\ 5$ | 4.8361 | 4.7500 | $0\ 0\ 7$ | 4.7948 |
| | $2\ 0\ 3$ | 3.8059 | 3.7350 | $2\ 0\ 5$ | 3.7419 | 3.7292 | $4\ 0\ 0$ | 3.7325 |
| 3.6626 | $1\ 1\ 0$ | 3.6644 | 3.7280 | $4\ 0\ 0$ | 3.7275 | 3.6925 | $0\ 0\ 9$ | 3.6935 |
| | $4\ 0\ \bar{2}$ | 3.6634 | 3.6580 | $4\ 0\ \bar{3}$ | 3.6622 | 3.6555 | $4\ 0\ \bar{4}$ | 3.6632 |
| 3.3564 | $4\ 0\ \bar{3}$ | 3.3571 | | $1\ 1\ 0$ | 3.6550 | | $1\ 1\ 0$ | 3.6504 |
| 3.2314 | $1\ 1\ 2$ | 3.2303 | 3.2780 | $4\ 0\ 5$ | 3.2724 | 3.3497 | $4\ 0\ 3$ | 3.3474 |
| 3.0364 | $2\ 0\ \bar{5}$ | 3.0374 | | $2\ 0\ 6$ | 3.2831 | 3.2615 | $2\ 0\ \overline{10}$ | 3.2631 |
| 3.0253 | $\bar{3}\ 1\ 1$ | 3.0252 | 3.0060 | $3\ 1\ 0$ | 3.0036 | | $1\ 1\ \bar{5}$ | 3.2632 |
| 3.0056 | $3\ 1\ 0$ | 3.0062 | | $2\ 0\ \bar{8}$ | 3.0099 | 3.0036 | $3\ 1\ 0$ | 3.0036 |
| 2.9916 | $4\ 0\ \bar{4}$ | 2.9919 | 2.9295 | $4\ 0\ 4$ | 2.9309 | | $2\ 0\ \overline{11}$ | 2.9974 |
| 2.9276 | $3\ 1\ \bar{2}$ | 2.9279 | | $3\ 1\ \bar{3}$ | 2.9283 | 2.9579 | $1\ 1\ \bar{7}$ | 2.9596 |
| 2.8894 | $1\ 1\ 3$ | 2.8909 | 2.8498 | $1\ 1\ 5$ | 2.8518 | 2.9325 | $3\ 1\ \bar{4}$ | 2.9295 |
| 2.8760 | $3\ 1\ 1$ | 2.8773 | 2.7104 | $3\ 1\ 3$ | 2.7132 | 2.8363 | $1\ 1\ 7$ | 2.8348 |
| 2.7427 | $3\ 1\ \bar{3}$ | 2.7442 | | $4\ 0\ 5$ | 2.7109 | 2.7068 | $4\ 0\ 7$ | 2.7051 |
| 2.7242 | $4\ 0\ 3$ | 2.7234 | 2.6266 | $2\ 0\ 8$ | 2.6000 | 2.6853 | $1\ 1\ 8$ | 2.6847 |
| 2.7010 | $1\ 1\ \bar{4}$ | 2.7030 | 2.5171 | $6\ 0\ \bar{3}$ | 2.5149 | 2.5154 | $6\ 0\ \bar{4}$ | 2.5128 |
| 2.6761 | $3\ 1\ 2$ | 2.6755 | | $6\ 0\ \bar{1}$ | 2.5202 | | $1\ 1\ \overline{10}$ | 2.5149 |
| 2.6093 | $2\ 0\ 5$ | 2.5100 | 2.4840 | $6\ 0\ 0$ | 2.4850 | 2.4895 | $6\ 0\ 0$ | 2.4885 |
| 2.5216 | $6\ 0\ \bar{2}$ | 2.5215 | 2.4780 | $6\ 0\ \bar{4}$ | 2.4768 | 2.4832 | $6\ 0\ \bar{5}$ | 2.4836 |
| 3.0056 | $0\ 0\ 6$ | 2.5183 | 2.3449 | $6\ 0\ 2$ | 2.3460 | 2.3425 | $5\ 1\ 4$ | 2.3413 |
| 2.4792 | $6\ 0\ 0$ | 2.4783 | | $5\ 1\ \bar{3}$ | 2.3426 | | $2\ 0\ 13$ | 2.2944 |
| 2.3952 | $1\ 1\ 5$ | 2.3947 | 2.2778 | $1\ 1\ 8$ | 2.2771 | 2.2800 | $5\ 1\ \bar{6}$ | 2.2751 |
| 2.3659 | $6\ 0\ 1$ | 2.3655 | 2.0764 | $4\ 0\ \overline{11}$ | 2.0763 | | $2\ 0\ \overline{15}$ | 2.2386 |
| 2.3487 | $5\ 1\ \bar{2}$ | 2.3484 | | $5\ 1\ 4$ | 2.0783 | 2.2330 | $5\ 1\ 7$ | 2.2289 |
| 2.2544 | $5\ 1\ 1$ | 2.2524 | 2.0555 | $6\ 0\ 5$ | 2.0554 | 2.0796 | $4\ 0\ \overline{15}$ | 2.0789 |
| 2.0696 | $3\ 1\ \bar{6}$ | 2.0683 | 2.0128 | $3\ 1\ 8$ | 2.0166 | | $0\ 0\ 16$ | 2.0776 |
| | $4\ 0\ \bar{7}$ | 2.0651 | | $2\ 0\ 11$ | 2.0066 | 2.0556 | $5\ 1\ 10$ | 2.0566 |
| 2.0553 | $6\ 0\ 3$ | 2.0550 | 1.8981 | $8\ 0\ \bar{3}$ | 1.8963 | | $6\ 0\ 7$ | 2.0556 |
| 2.0221 | $5\ 1\ 5$ | 2.0224 | | $8\ 0\ \bar{2}$ | 1.8964 | 2.0230 | $3\ 1\ 11$ | 2.0222 |
| 2.0044 | $3\ 1\ 5$ | 2.0042 | | $3\ 1\ 9$ | 1.8960 | | $2\ 0\ 15$ | 2.0262 |
| 1.8906 | $0\ 2\ 0$ | 1.8905 | | $5\ 1\ 6$ | 1.9022 | 1.8836 | $3\ 2\ 0$ | 1.8825 |
| | | | 1.8853 | $0\ 2\ 0$ | 1.8850 | | | |

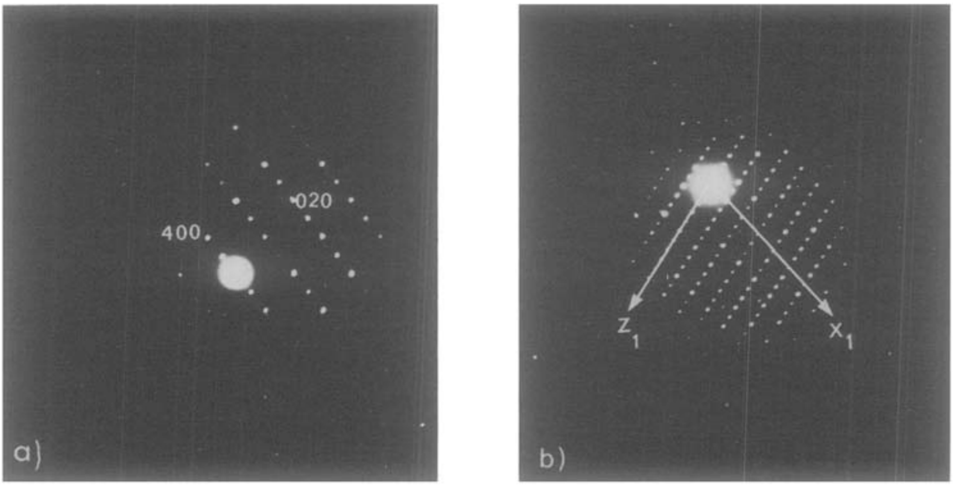

FIG. 5. $Na_2BaTi_{10}O_{22}$ electron diffraction patterns. (a) $hk0$ plane; (b) $h0l$ plane.

close to the $a$ and $b$ parameters of $A_2Ti_6O_{13}$, and $\beta_1$ is slightly greater than $\beta$, while $c_1$ is close to 15.5 Å in agreement with the calculated values from relationships (1–4). Two of the electron diffraction patterns are given as examples in Fig. 5, showing the conditions limiting possible reflections $hk0$, $h + k = 2n$, and $h0l$, $h = 2n$, for $Na_2BaTi_{10}O_{22}$. Seven titanates of this type were isolated, for which crystallographic data are given in Table II. The volume of the cell increases with the mean size of the ions in the tunnels; it must equally be noted that the $a_1$ parameter which corresponds to the width of the rectangular tunnel is more influenced by the size of these ions.

In order to confirm our model, the structure was studied with X-ray powder diffraction data for $Na_2BaTi_{10}O_{22}$ and $Na_2PbTi_{10}O_{22}$. The atoms were set in the $4i$ positions of the most symmetric space group $C2/m$, Na and Ba or Pb being randomly distributed on their sites. The limited number of reflections, about 90, with regard to the great number of variable parameters, 36 without $B$ factors, did not allow an accurate determination. Nevertheless, fixing the $B$ factor to 1 Å$^2$ for every atom, first

TABLE II

$A_2A'Ti_{10}O_{22}$ OXIDES: CRYSTALLOGRAPHIC DATA

| Composition | Monoclinic cell<br>$a_1$ (Å) | $b_1$ (Å) | $c_1$ (Å) | $\beta_1$ (°) | $d_{obs}$ | $d_{calc}$ |
|---|---|---|---|---|---|---|
| $Na_2SrTi_{10}O_{22}$ | $15.09_9$ | $3.75_2$ | $15.48_2$ | $102^{\circ}15_9$ | 3.75 | 3.74 |
| $Na_2PbTi_{10}O_{22}$ | $15.17_2$ | $3.75_9$ | $15.50_7$ | $102^{\circ}28_3$ | 4.27 | 4.17 |
| $Na_2BaTi_{10}O_{22}$ | $15.22_9$ | $3.78_1$ | $15.47_4$ | $102^{\circ}46_0$ | 3.86 | 3.87 |
| $K_2SrTi_{10}O_{22}$ | $15.33_4$ | $3.79_2$ | $15.45_3$ | $102^{\circ}65_0$ | 3.82 | 3.78 |
| $K_2PbTi_{10}O_{22}$ | $15.34_1$ | $3.78_8$ | $15.49_4$ | $102^{\circ}64_0$ | 4.35 | 4.22 |
| $K_2BaTi_{10}O_{22}$ | $15.45_2$ | $3.80_8$ | $15.43_3$ | $102^{\circ}93_0$ | 3.95 | 3.93 |
| $Rb_2BaTi_{10}O_{22}$ | $15.49_0$ | $3.81_5$ | $15.42_0$ | $103^{\circ}13_5$ | 4.38 | 4.27 |

refining the titanium coordinates and second the oxygen coordinates, led to the reliability factor $R_I$, calculated from the intensities close to 0.10. The predicted framework can thus be recognized but, of course without any great accuracy.

### *The Compounds $A_4A'Ti_{16}O_{35}$ ($n = 2$)*

Five titanates corresponding to $n = 2$ were isolated. the compound $Na_4PbTi_{16}O_{35}$ was obtained but was not pure. The $a_2$ and $b_2$ parameters of these compounds are close to those of the term $n = 1$ as shown by the electron diffraction patterns corresponding to ($hk0$) (Fig. 6a); however, the $c_2$ parameter and $\beta_2$ angle are different (Figs. 6b and c). The direct resolution of the ($1\bar{1}0$) plane (Fig. 7) shows that the $c_2$ value is equal to 24.6 Å which corresponds to the calculated value from relationship (3).

These observations allowed an accurate indexing of the X-ray powder patterns of these compounds (Table I). The evolution of the parameters of the monoclinic cell (Table III) is quite similar to that observed for the term $n = 1$ of the series.

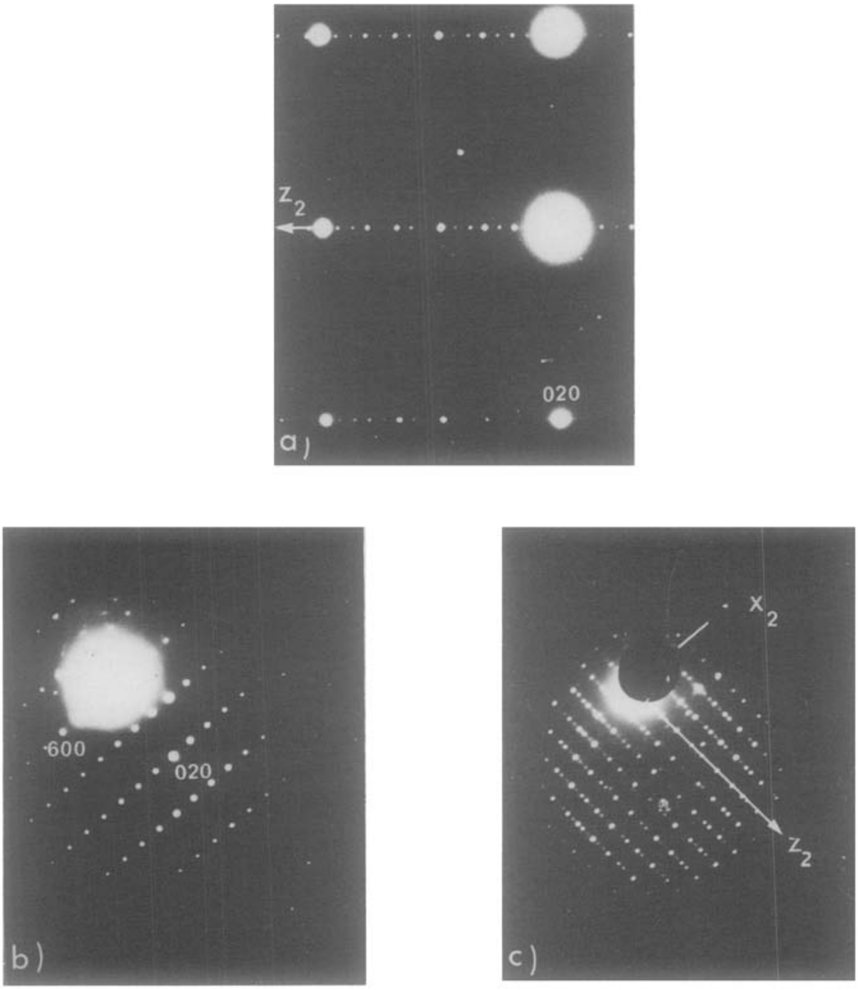

FIG. 6. $Na_4BaTi_{16}O_{35}$ electron diffraction pattern of ($hk$O), (O$kl$), and ($h$O$l$) planes.

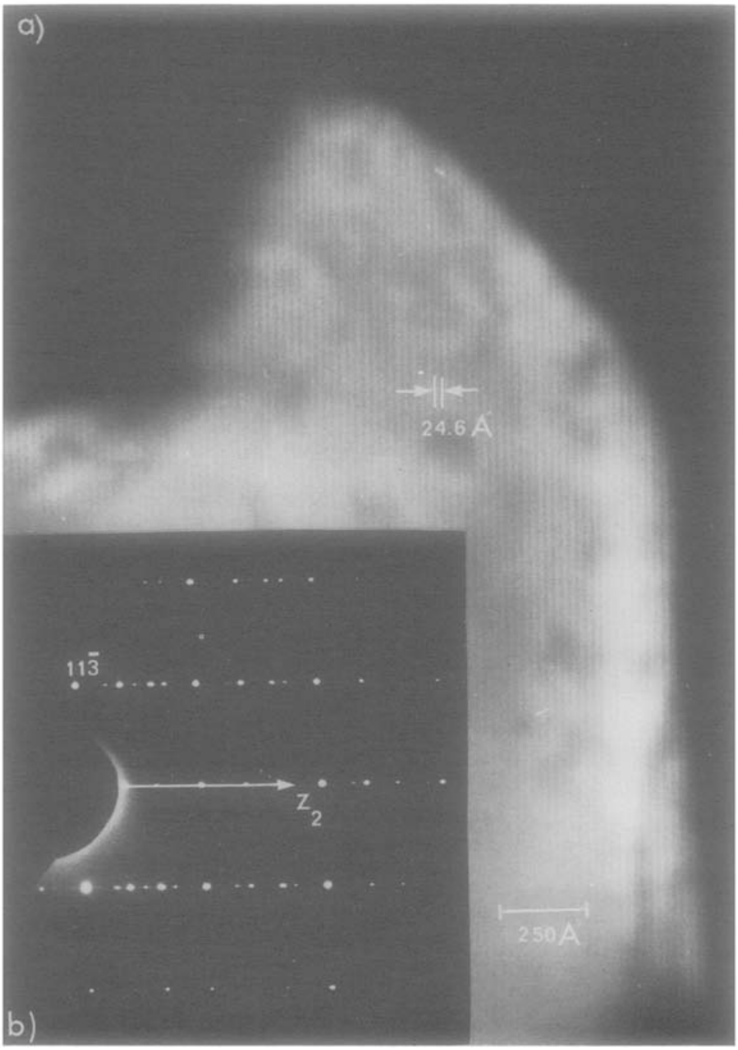

FIG. 7. $Na_4BaTi_{16}O_{35}$, term $n = 2$: direct resolution of the $(1\bar{1}0)$ plane (a), and electron diffraction-related pattern (b).

### *The Compounds $A_7A'Ti_{22}O_{48}$ ($n = 3$)*

Only three titanates were isolated for $n = 3$. Extended annealing times were necessary for obtaining regular crystals. The electron diffraction study (Fig. 8a) and the direct resolution of the $(h0l)$ plane, giving a $c_3$ parameter of 33.8 Å for $Na_6BaTi_{22}O_{48}$ (Fig. 8b), confirm our model. The X-ray diffractograms (Table I) have been precisely indexed; the crystallographic data are given in Table III.

## **Conclusion**

A new structural family, $(A_2M_6O_{13})_n \cdot A'M_4O_9$, has been synthesized as a result of the intergrowth of two types of structural units characterized, respectively, by $2 \times 3$ and $2 \times 2$ edge-sharing octahedra. It has not been possible to synthesize the tetratitanates, $A'M_4O_9$, with 2P tunnels; this kind of phenomenon may be compared with results previously reported by Wadsley and Mumme (*7*), who observed an ordered

TABLE III

$A_4A'Ti_{16}O_{35}$ AND $A_6A'Ti_{22}O_{48}$ OXIDES: CRYSTALLOGRAPHIC DATA

| | Monoclinic cell | | | | | |
|---|---|---|---|---|---|---|
| Composition | $a_2$ (Å) | $b_2$ (Å) | $c_2$ (Å) | $\beta_2$ (°) | $d_{calc}$ | $d_{obs}$ |
| $Na_4SrTi_{16}O_{35}$ | $15.11_1$ | $3.75_5$ | $24.56_1$ | $100°94_3$ | 3.66 | 3.72 |
| $Na_4BaTi_{16}O_{35}$ | $15.19_4$ | $3.77_0$ | $24.64_1$ | $101°09_3$ | 3.73 | 3.80 |
| $K_4SrTi_{16}O_{35}$ | $15.47_4$ | $3.79_7$ | $24.56_4$ | $101°77_0$ | 3.70 | 3.80 |
| $K_4BaTi_{16}O_{35}$ | $15.48_7$ | $3.80_5$ | $24.56_9$ | $101°70_2$ | 3.80 | 3.80 |
| $K_4PbTi_{16}O_{35}$ | $15.44_5$ | $3.79_2$ | $24.60_1$ | $101°64_9$ | 3.99 | 4.10 |
| $Na_6BaTi_{22}O_{48}$ | $15.18_4$ | $3.76_7$ | $33.80_7$ | $100°48_9$ | 3.67 | 3.74 |
| $Na_6SrTi_{22}O_{48}$ | $15.12_4$ | $3.75_2$ | $33.77_4$ | $100°50_5$ | 3.61 | 3.67 |
| $Na_6PbTi_{22}O_{48}$ | $15.14_2$ | $3.75_0$ | $33.79_8$ | $100°50_5$ | 3.82 | 3.90 |

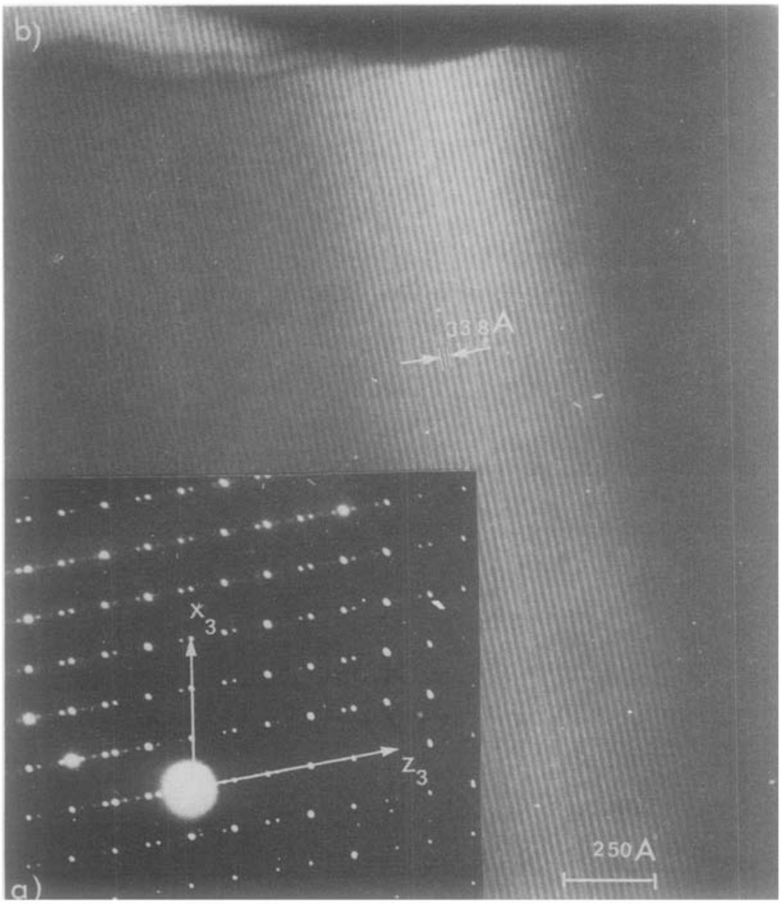

FIG. 8. $Na_6BaTi_{22}O_{48}$, term $n = 3$: (a) ($h0l$) plane; (b) direct resolution showing the $c_2$ value equal to 33.8 Å ($n = 2$ cells appeared as localized defects).

intergrowth of 2×3 and 2×4 edge-sharing octahedra in the same manner, i.e., of sodium hexatitanate $Na_2Ti_6O_{13}$ and of a hypothetical $Na_2Ti_8O_{17}$. The terms with greater $n$ values seem more difficult to obtain and will be the purpose of a further study. The possibility of the existence of multiple intergrowths corresponding to nonintegral $n$ values will be equally studied. Nonstoichiometry concerning the $A$ and $A'$ ions might also be possible.

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