

## Crystal Structure of Octatitanate $M_2Ti_8O_{17}$ ( $M = K, Rb$ )

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Octatitanate crystals of  $M_2Ti_8O_{17}$  ( $M = K, Rb$ ) have been studied by Rietveld refinement of X-ray diffraction data, electron diffraction and high-resolution electron microscopy. They crystallize in the monoclinic system, space group  $C2/m$  with the unit cell dimensions  $a = 15.678(2)$  Å,  $b = 3.775(1)$  Å,  $c = 11.951(1)$  Å,  $\beta = 95.67(1)^\circ$  for  $K_2Ti_8O_{17}$  and  $a = 15.961(3)$  Å,  $b = 3.786(1)$  Å,  $c = 11.918(2)$  Å,  $\beta = 96.05(2)^\circ$  for  $Rb_2Ti_8O_{17}$ . The host framework of  $[Ti_8O_{17}]_x$  makes a one-dimensional tunnel with a rectangular cross section enclosed by  $4 \times 1$  octahedra. The tunnel accommodates alkali metal ions at a low content for its volume. K ions are statistically distributed over two kinds of pseudocubic sites. In contrast, Rb ions are likely to arrange in an ordered way, which is suggested from superlattice reflections ( $a = 2 \times a_0$ ,  $b = 2 \times b_0$ ,  $c = 2 \times c_0$ ) found in X-ray and electron diffraction patterns.

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### Introduction

Alkali metal octatitanates  $M_2Ti_8O_{17}$  ( $M$ : alkali metal) have been synthesized through unique processes (1-3); tetratitanate layers of composition  $Ti_4O_9^-$  are hydrolyzed to  $Ti_4O_8(OH)^-$  layers, which are thermally condensed in a topotactic manner, resulting in a three-dimensional framework of  $Ti_8O_{17}^{2-}$ .

Marchand *et al.* first reported the synthesis of  $K_2Ti_8O_{17}$  (1). It is supposed that  $K_2Ti_8O_{17}$  is isostructural with a bronze-like material  $K_3Ti_8O_{17}$  reported by Watts (4) because of the similarity in unit cell dimensions. The structure for  $K_3Ti_8O_{17}$  is characterized by a one-dimensional tunnel enclosed by  $4 \times 1$  octahedra (4).

The octatitanates  $M_2Ti_8O_{17}$  are character-

ized by their low alkali metal content compared with the volume of the tunnel. It is expected that the low content of tunnel cation gives rise to distinctive properties; the octatitanates are metastable probably due to imperfections in local charge neutrality.  $K_2Ti_8O_{17}$  exhibits ionic conduction, suggesting diffusion of K ions (5). Patarin *et al.* (5) tried to interpret the phenomenon on the basis of structural features, but a lack of accurate structure information inevitably forced their discussion to be inconclusive.

Recently we prepared crystals of  $K_2Ti_8O_{17}$  and  $Rb_2Ti_8O_{17}$  having a fibrous texture (3). In order to get insight to their properties, we report here the structural features of  $K_2Ti_8O_{17}$  and  $Rb_2Ti_8O_{17}$  derived from Rietveld refinements, electron diffraction, and high-resolution transmission electron microscopic studies.

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## Experimental

Crystals of  $M_2Ti_8O_{17}$  ( $M = K, Rb$ ) having a fibrous texture were prepared from potassium tetratitanate  $K_2Ti_4O_9$ , as described previously (3): Crystals of  $K_2Ti_4O_9$ , flux-grown by slow-cooling a 1 : 3 molar mixture of  $K_2O$  and  $TiO_2$  (6), were converted into a protonated form,  $H_2Ti_4O_9 \cdot nH_2O$ . Half of the exchangeable protons were replaced with K or Rb ions by ion-exchange in aqueous media. Dehydration at 500°C gave the octatitanates,  $K_2Ti_8O_{17}$  and  $Rb_2Ti_8O_{17}$ .

The obtained crystals were too thin (average size: 1 mm in length  $\times$  0.01 mm in thickness) to be analyzed by single crystal X-ray techniques. They were ground manually for powder X-ray diffraction measurements. The profile data were collected in a step-scan mode with a Rigaku Denki RAD-2B diffractometer using monochromatized  $CuK\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ). Rietveld refinement was carried out with the RIETAN system (7) on a FACOM M-360 computer.

Electron diffraction and transmission electron microscope studies were performed with a JEOL JEM-2000EX high-resolution microscope operated at an accelerating voltage of 200 kV. The microscope is equipped with a double tilting ( $\pm 25^\circ$ ) sample holder. Fibrous crystals were crushed in a mortar and then supported on a holey carbon copper grid. Specimens for lattice imaging along the direction of crystal elongation were prepared by slicing the crystals with a LKB-2088 Microtome.

## Results and Discussion

### Rietveld Refinement of the Crystal Structure for $K_2Ti_8O_{17}$

Table I summarizes the details of the X-ray data acquisition and structure refinement. The initial positional parameters for Ti and O atoms were derived from an

TABLE I

DETAILS OF RIETVELD REFINEMENTS FOR  $K_2Ti_8O_{17}$ 

Lattice constants	
$a(\text{\AA})$	15.678(2)
$b(\text{\AA})$	3.775(1)
$c(\text{\AA})$	11.951(1)
$\beta(^{\circ})$	95.67(1)
Volume( $\text{\AA}^3$ )	703.9(1)
No. of molecules in unit cell (Z)	2
Density ( $\text{g cm}^{-3}$ ) (calc)	3.45
Space group	$C2/m$
$2\theta$ range	20–110° ( $CuK\alpha$ )
Step scan increment ( $2\theta$ )	0.03°
No. of reflections	569
No. of structural parameters refined	32
No. of profile parameters	6

ideal drawing of the structural model [space group  $C2/m$ (No. 12)] proposed by Marchand *et al.* (1) The locations of K ions were examined separately as described below.

Figure 1 shows the final results of the refinement; the observed, calculated, and difference patterns. The reliability factors converged to the values  $R_{wp} = 0.0816$ ,  $R_p = 0.0622$ ,  $R_I = 0.0196$ ,  $R_F = 0.0126$ ,  $R_E = 0.0295$ . Structural parameters and selected interatomic distances are presented in Tables II and III, respectively.

The refinement demonstrated that the host framework is identical with that in the bronze-like  $K_3Ti_8O_{17}$  (4). The framework (Fig. 2) is built up from corrugated ribbons of  $TiO_6$  octahedra edge-shared four in a row, which are then corner-shared so as to make a one-dimensional tunnel. The interatomic distances for the  $TiO_6$  octahedra show similar spread of values as in other alkali metal titanates (4, 8–11).

Only two K ions are accommodated in a unit tunnel, which can crystallographically hold four cations. Several modes of cation distribution were tested in the refinement procedure by referring to two members of alkali metal titanates with a tunnel of the

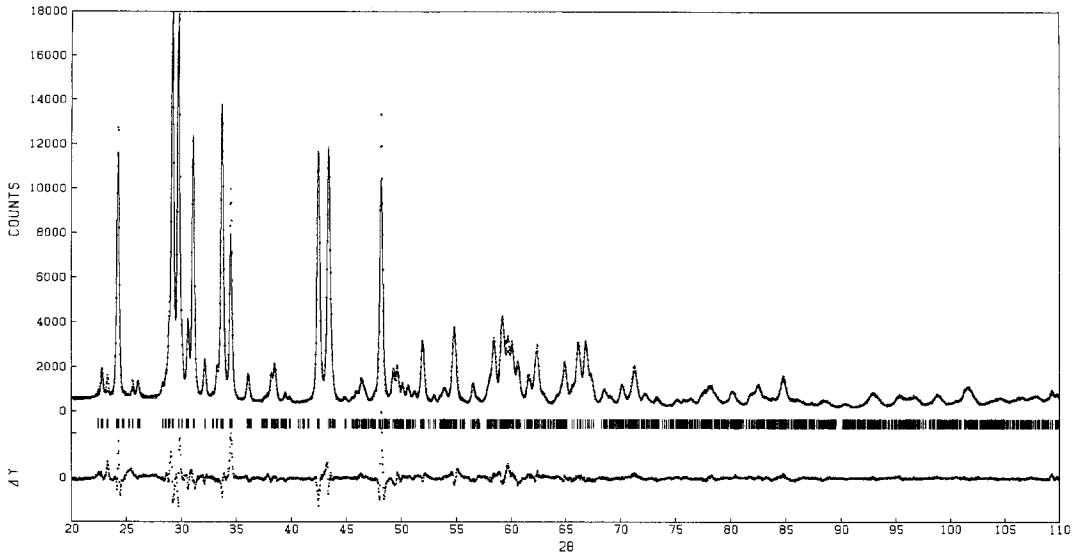


FIG. 1. The final patterns of Rietveld refinement for  $K_2Ti_8O_{17}$  structure. Top: solid line, calculated; dotted line, observed. Bottom: difference.

same geometry as that of octatitanates. One is the sodium heptatitanate  $Na_2Ti_7O_{15}$  (11) and the other is the bronze-like  $K_3Ti_8O_{17}$  (4). In the former phase, Na ions occupy two kinds of sites,  $M0$  and  $M1$  in Fig. 3; a twofold position ( $M0$ ) is fully occupied while a fourfold position ( $M1$ ) is  $\frac{3}{4}$  occupied. In the

bronze-like  $K_3Ti_8O_{17}$ , K ions are situated in two kinds of pseudocubic sites,  $M1$  and  $M2$  in Fig. 3, with full and half occupation, respectively.

The occupation of  $M0$  site by a K ion in  $K_2Ti_8O_{17}$  is unlikely because it is larger than the Na ion. Actually this possibility was ex-

TABLE II  
STRUCTURAL PARAMETERS FOR  $K_2Ti_8O_{17}$

Atom	Position	Occupancy	$x$	$y$	$z$	$B_{eq}(\text{\AA}^2)$
K1	4( <i>i</i> )	0.68(1)	0.4442(7)	0.0	0.1935(9)	1.4(2)
K2	4( <i>i</i> )	0.32(1)	0.482(2)	0.0	0.364(2)	1.4
Ti1	4( <i>i</i> )	1.0	0.1084(4)	0.0	0.0716(5)	0.70(6)
Ti2	4( <i>i</i> )	1.0	0.1519(5)	0.0	0.3250(7)	0.70
Ti3	4( <i>i</i> )	1.0	0.1947(6)	0.0	0.5768(7)	0.70
Ti4	4( <i>i</i> )	1.0	0.2409(4)	0.0	0.8334(6)	0.70
O1	2( <i>a</i> )	1.0	0.0	0.0	0.0	0.6(1)
O2	4( <i>i</i> )	1.0	0.063(1)	0.0	0.221(2)	0.6
O3	4( <i>i</i> )	1.0	0.108(2)	0.0	0.459(2)	0.6
O4	4( <i>i</i> )	1.0	0.155(1)	0.0	0.705(2)	0.6
O5	4( <i>i</i> )	1.0	0.173(1)	0.0	0.938(2)	0.6
O6	4( <i>i</i> )	1.0	0.226(1)	0.0	0.178(2)	0.6
O7	4( <i>i</i> )	1.0	0.275(1)	0.0	0.428(2)	0.6
O8	4( <i>i</i> )	1.0	0.318(2)	0.0	0.683(2)	0.6
O9	4( <i>i</i> )	1.0	0.364(1)	0.0	0.913(2)	0.6

TABLE III  
INTERATOMIC DISTANCES (Å) IN  
TITANIUM-OXYGEN OCTAHEDRA

Ti1-O1	1.836(7)	O-O	in Ti1 octahedron
O2	1.97(2)	Max	2.95
O5'	1.98(2)	Min	2.56
O6	2.15(2)	Av	2.77
O9'	1.938(5) × 2		
Av	1.97		
Ti2-O2	1.70(2)	O-O	in Ti2 octahedron
O3	1.76(2)	Max	3.15
O6	2.19(2)	Min	2.63
O7	2.19(2)	Av	2.81
O8'	1.934(6) × 2		
Av	1.95		
Ti3-O3	1.87(3)	O-O	in Ti3 octahedron
O4	1.69(2)	Max	2.96
O7	2.33(2)	Min	2.62
O8	2.31(2)	Av	2.73
O7'	1.953(6) × 2		
Av	2.02		
Ti4-O4	1.94(2)	O-O	in Ti4 octahedron
O5	1.74(2)	Max	3.08
O8	2.27(2)	Min	2.56
O9	2.09(2)	Av	2.78
O6'	1.964(6) × 2		
Av	1.99		

cluded by larger reliability factors as well as by there being no detectable peak in a difference Fourier map. Thus a statistical distribution over  $M1$  and  $M2$  sites was examined in the refinement. Site occupancies were refined under a constraint that the sum is unity. Refined occupancies were approximately  $\frac{2}{3}$  for  $M1$  site and  $\frac{1}{3}$  for  $M2$  site. The  $M1$  site is favored probably due to a better coordination environment.

Both kinds of K ions are eight-coordinated: K1 has two bonds each of 2.97, 2.77, 2.71, and 3.20 Å while K2 has two each of 2.85, 2.96, 2.96, and 2.94 Å. K1 is constrained in an off-centered position of a coordinated cube of oxygen atoms. Similar

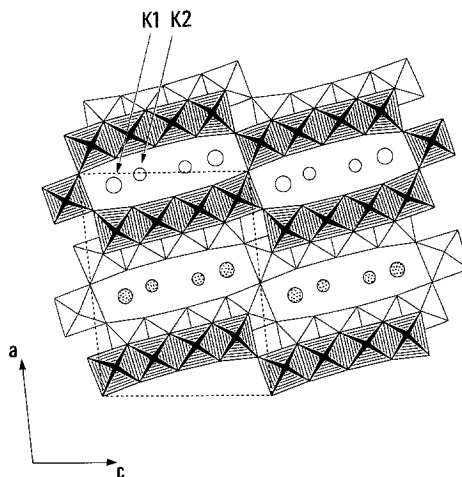


FIG. 2. Refined crystal structure for  $K_2Ti_8O_{17}$ . Projection along the  $b$  axis. Hatched octahedra and dotted circles are on the plane of  $y = 0$ .

features have been found for tunnel cations in titanates having identical geometry of surrounding oxygen atoms, e.g., hexatitanates,  $M_2Ti_6O_{13}$  ( $M = Na, Rb$ ) (10), as well as the bronze-like material,  $K_3Ti_8O_{17}$  (4). One of the most noticeable differences between  $K_2Ti_8O_{17}$  and  $K_3Ti_8O_{17}$  is the environment of the K2 ion: K2 in  $K_2Ti_8O_{17}$  is situated near the center of a coordinated cube of eight oxygen atoms while the corresponding cation in  $K_3Ti_8O_{17}$  is displaced to a position

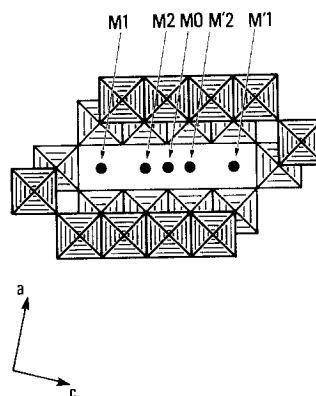


FIG. 3. Possible cation location in the unit tunnel.

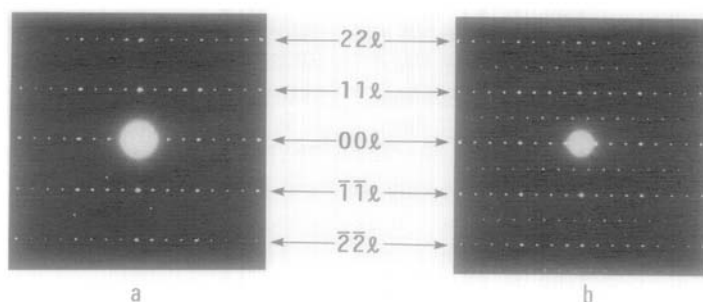


FIG. 4. Electron diffraction patterns of  $hhl^*$  for  $K_2Ti_8O_{17}$  and  $Rb_2Ti_8O_{17}$ . (a)  $K_2Ti_8O_{17}$ , (b)  $Rb_2Ti_8O_{17}$ .

with a quasi-square planer coordination of four oxygen atoms. This may be related to the site occupancy as follows: In the bronze-like  $K_3Ti_8O_{17}$ , corresponding  $M1$  and  $M2$  sites have full and half occupancy, respectively. This means that either the  $M2$  or the  $M2'$  site in the unit tunnel is occupied. This induces the displacement of the K ion in the  $M2$  (or  $M2'$ ) site toward the vacant  $M2'$  (or  $M2$ ) to relax electrostatic repulsion between it and the K ion in the neighboring  $M1$  site. In contrast, the K ion in  $K_2Ti_8O_{17}$  occupies either the  $M1$  or the  $M2$  site with the re-

maining site being vacant. It is most likely that the K ion in the  $M2$  site has vacancies on both sides and therefore has no need to be displaced.

The ionic conduction measured by Patarin *et al.* (5) suggests diffusion of K ions. A diffusion along the  $a$  axis is unlikely due to the large barrier of the  $[Ti_8O_{17}^{2-}]_{\infty}$  framework. Along the  $b$  and  $c$  axes, in contrast, adjacent sites for K ions are connected through square windows. The windows have free openings, subtracting the size of the O atom, as given below:

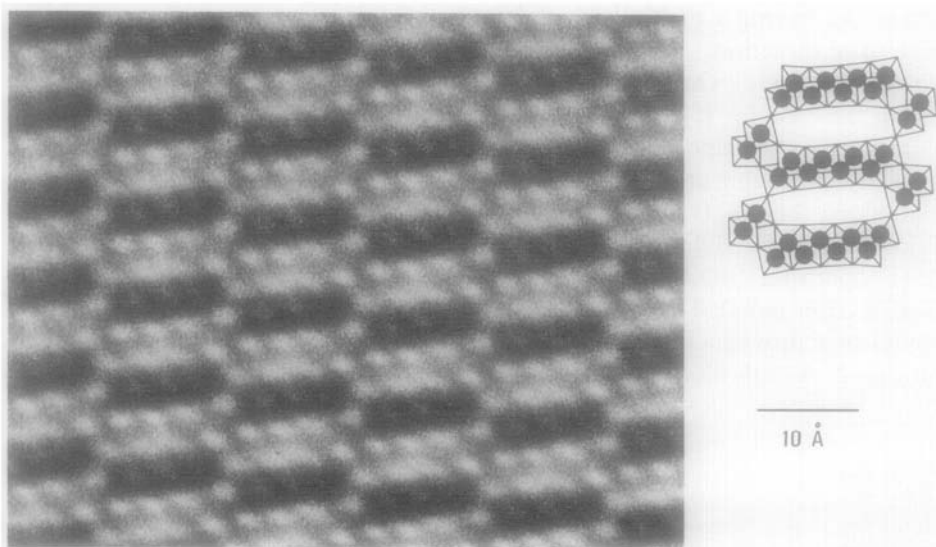


FIG. 5. High-resolution lattice image for  $Rb_2Ti_8O_{17}$  along the  $b$  axis.

- 1.2 Å × 1.8 Å for  $M1-M1'$  along the  $b$ ,  
 1.8 Å × 2.2 Å for  $M2-M2'$  along the  $b$ ,  
 2.5 Å × 2.5 Å for  $M1-M2$  along the  $c$ ,  
 2.6 Å × 2.6 Å for  $M2-M2'$  along the  $c$ .

These values imply that K ions (radius for eight coordination: 1.51 Å (12)) are likely to hop to adjacent vacancies along the  $c$  axis with a low activation energy. The ionic conduction observed (5) may be ascribed to this hopping motion.

### High-Resolution Electron Microscopy and Electron Diffraction

The lattice parameters for  $Rb_2Ti_8O_{17}$  [ $a = 15.961(3)$  Å,  $b = 3.786(1)$  Å,  $c = 11.918(2)$  Å,  $\beta = 96.05(2)^\circ$ ] are very close to those for  $K_2Ti_8O_{17}$  (see Table I), suggesting an isomorphous relationship. The Rietveld refinement for  $Rb_2Ti_8O_{17}$  did not converge to a satisfactory fitting. This is mainly due to extra reflections which cannot be indexed by the ordinary unit cell above but by a cell with doubled dimensions for each axis.

This can be understood more clearly by comparing  $hhl^*$  electron diffraction patterns for the K and Rb compounds in Fig. 4. Superlattice spots, commensurate with the sublattice and having a multiplicity of 2 in all three axial directions, are distinctly observed for  $Rb_2Ti_8O_{17}$ . On the other hand, this is not the case for  $K_2Ti_8O_{17}$ .

Figure 5 shows the high-resolution lattice image from a sliced thin crystal of  $Rb_2Ti_8O_{17}$  oriented along the  $b$  axis. The observation conditions were as follows: underfocus,  $\sim 380$  Å; aperture,  $\sim 0.8$  Å $^{-1}$  (enclosing  $\sim 190$  diffraction spots). The image displays the tunnel structure which is comparable to that in Fig. 2. A dark block corresponds to

eight Ti atoms in the edge-shared octahedra forming corrugated ribbons. Rb ions are discernible as a dark contrast in the tunnel. It is evident that the host framework for  $Rb_2Ti_8O_{17}$  is identical to that for  $K_2Ti_8O_{17}$  and that Rb ions are accommodated in the sites comparable to  $M1$  and  $M2$  sites in  $K_2Ti_8O_{17}$ . Based on the observations above, the superstructure may be interpreted in terms of an ordered occupation of Rb ions over the sites in the tunnel: Rb ions and vacancies are arranged in such a way as to evolve a supercell of  $(2 \times a_0, 2 \times b_0, 2 \times c_0)$ .

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