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Synthesis and Characterization of Fibrous Octatitanate $M_2Ti_8O_{17}$ (M = K, Rb)

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The fibrous octatitanate $M_2Ti_8O_{17}$ (M = K, Rb) was prepared by substitution of cations for half of the exchangeable protons in the protonic-layered tetratitanate fibers $H_2Ti_4O_9 \cdot nH_2O$, followed by dehydration at 500°C. The crystal structure is characterized by a one-dimensional tunnel, the cross section of which is four octahedra wide. Leaving large vacant rooms, a unit tunnel accommodates two alkali metal ions which are distributed between two kinds of nearly cubic sites. The octatitanate was decomposed into a mixed phase of hexatitanate and titanium dioxide at temperature above 760°C for $K_2Ti_8O_{17}$ and above 940°C for $Rb_2Ti_8O_{17}$. The action of K vapor at 260°C gave rise to insertion of additional K into vacant rooms in the tunnel, resulting in a mixed valent compound $K_xM_2Ti_8O_{17}$ ($x \simeq 1$). © 1989 Academic Press, Inc.

Introduction

Alkali metal titanates, a series of ternary compounds of $M_2O \cdot nTiO_2$ (M: alkali metal; $1 \leqq n \leqq 9$), have been studied extensively. Their crystal structures are dependent on the stoichiometry, n, which invites a wide variety of properties from compound to compound. The di-, tri-, and tetratitanates (n = 2, 3, 4), for example, have been characterized by their layer structures, distinctive intercalation abilities, and catalytic activities (*1–11*). Tunnel structures occur for the compounds with lower alkali metal content. The hexatitanate (n = 6) exhibits a high thermal insulating ability and chemical stability (*3, 12, 13*). Fibrous crystals of the material are used as a filler for fiber-reinforced plastics and metals.

In contrast to these compounds, octatitanate (n = 8) has been little studied. Recently Marchand *et al.* have reported the synthesis of potassium octatitanate $K_2Ti_8O_{17}$ by partially hydrolyzing tetratitanate $K_2Ti_4O_9$, followed by a heat treatment at 500°C (*6, 14–16*).

A protonated form of tetratitanate $H_2Ti_4O_9 \cdot mH_2O$ ($m \simeq 1$) contains exchangeable protons between the host macroanions of $[Ti_4O_9^{2-}]_\infty$ sheets (*10*) as illustrated in Fig. 1. We have studied the intercalation behavior of the material in a fibrous form (*10, 17–20*). The half-exchanged phases $MHTi_4O_9 \cdot m'H_2O$ were obtained in ion-exchange processes with alkali metal ions. The dehydration of these phases ought to yield the octatitanate $M_2Ti_8O_{17}$. In the present study potassium and rubidium salts of octatitanate were synthesized by dehydrating the half-cation-substituted phases of the protonic tetratita-

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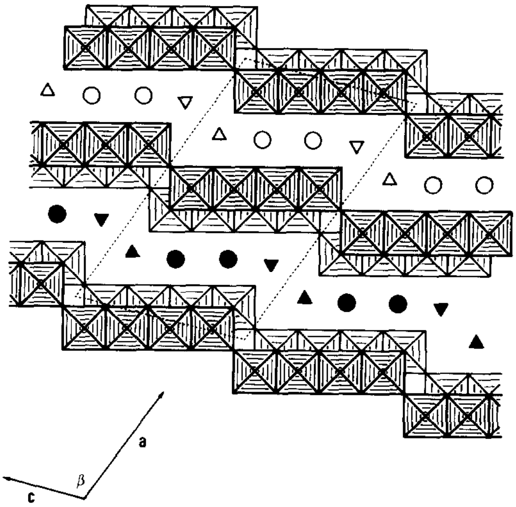

FIG. 1. Idealized structure of $H_2Ti_4O_9 \cdot H_2O$ in projection onto the (010) plane. The open circles and triangles represent the possible positions of oxonium ions and hydroxyls, respectively, at $y = 0$. The solid circles and triangles correspond to the interlayer species at $y = \frac{1}{2}$.

nate, and they were characterized in several ways in order to shed light upon the properties of the material.

Experimental

Reagents. The TiO_2, KCl, and RbCl used were of 99.98% purity. All the other chemicals were reagent grade. The hydroxide solutions of KOH and RbOH were standardized against potassium hydrogen phthalate. Distilled and deionized water was used.

Preparation of the protonic-layered titanate $H_2Ti_4O_9 \cdot nH_2O$ and its titration. A K_2MoO_4 flux melt containing a mixture of K_2O–TiO_2 (1/3 molar ratio) was cooled slowly from 1100°C at a rate of 4°C min^{-1}, inducing growth of fibrous crystals of potassium tetratitanate $K_2Ti_4O_9$ (*21*).

The fibrous potassium tetratitanate was converted into a protonated form by treatment with a HCl aqueous solution (*10, 17*):

$$K_2Ti_4O_9(s) + 2H^+(aq) + nH_2O(aq) \rightarrow H_2Ti_4O_9 \cdot nH_2O(s) + 2K^+(aq). \quad (1)$$

The resulting product, dried over a saturated NaCl solution (relative humidity 72%) at room temperature, had a water content of $n = 1.2$.

The titration of $H_2Ti_4O_9 \cdot nH_2O$ was carried out batchwise by the procedure described previously (*10*): A weighed amount of the material was shaken with a mixed solution of *M*Cl–*M*OH (*M* = K, Rb) at 25°C. The solution to solid ratio was 100 $cm^3\ g^{-1}$ and the ionic strength of the titrant was adjusted to 0.1. After 1 week equilibration, the supernatant solutions were analyzed for their pH values and cation contents. The cation uptake was deduced from differences between initial and residual concentrations. The solids were filtered off, washed with water, and conditioned over a saturated NaCl solution. The water contents of the resulting products were determined from the weight loss at 800°C.

K insertion. The octatitanate $M_2Ti_8O_{17}$ (*M* = K, Rb) and K metal block were put at each end of a sealed glass tube which was evacuated beforehand. The tube was heated at 260°C for several days, allowing the vaporized K metal to interact with the material. After the reaction the products were analyzed chemically to determine how much K had been inserted.

Characterization of the material. The X-ray powder diffraction data were collected with a Rigaku Denki RAD-2B diffractometer with monochromated Cu*Kα* radiation ($\lambda = 1.5405$ Å). The unit cell dimensions were refined by means of the least-squares procedure (*22*).

A Rigaku Denki TAS 100 thermal analyzer was employed to obtain the differential thermal analysis and thermogravimetry data.

The SEM photographs were obtained by using a Akashi ISI-DS130 scanning electron microscope operating at 5 kV.

The chemical composition of the octatitanate and its K-inserted materials were determined by wet analysis as follows: A weighed amount of sample was dissolved at 160°C with a mixed acid solution of 1/1 H_2SO_4, conc. HNO_3, and conc. HF. The resulting solution was analyzed for its titanium and alkali metal contents. The titanium was determined by complexometric titration while alkali metal was determined by atomic absorption spectroscopy.

Results and Discussion

Synthetic Process

In the first step in the preparation of $M_2Ti_8O_{17}$, cations are substituted for half of the exchangeable protons in $H_2Ti_4O_9 \cdot nH_2O$. Figure 2 shows the uptake of K and Rb as a function of the pH value for $H_2Ti_4O_9 \cdot nH_2O$. It has been established that the cations are taken up stepwise, replacing one quarter of the exchangeable protons at a time (*10, 18–20*). This process resulted in $n/4$ loaded phases ($n = 1, 2, 3, 4$) with different degrees of swelling. Under the conditions employed in the titration experiment, the chloride and hydroxide ratio of 72/28 in the titrant was required for the formation of the 1/2 loaded phases, $KHTi_4O_9 \cdot 0.5H_2O$ and $RbHTi_4O_9 \cdot H_2O$.

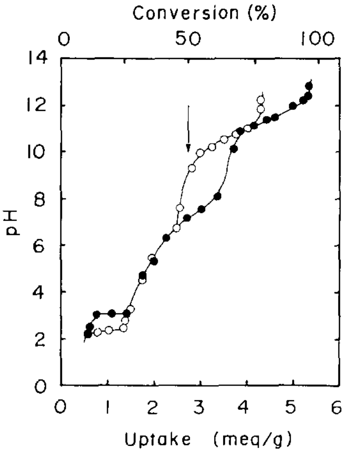

FIG. 2. Cation uptake as a function of pH value for $H_2Ti_4O_9 \cdot nH_2O$. (●) K, (○) Rb. Solid: 0.2 g of $H_2Ti_4O_9 \cdot nH_2O$; titrant: 20 cm^3 of 0.1 mol dm^{-3} (MCl + MOH; M = K, Rb).

As demonstrated in Fig. 3, the 1/2 loaded phases lost water in two steps: Step I took place at 40–140°C and step II at 140–500°C. The weight losses in the steps were approximately 1/1 in ratio for the K 1/2 loaded phase and 2/1 for the Rb 1/2 loaded phase. The completely dehydrated product was identified as the octatitanate $M_2Ti_8O_{17}$ (M = K, Rb) from its X-ray powder diffraction pattern. The dehydration processes may be formulated as follows:

$$\begin{array}{lcc}
 & KHTi_4O_9 \cdot 0.5H_2O & RbHTi_4O_9 \cdot H_2O \\
 & (9.0\ \text{Å}) & (9.3\ \text{Å}) \\
\text{Step I} & \downarrow{\scriptstyle -0.5H_2O} & \downarrow{\scriptstyle -H_2O} \\
 & KHTi_4O_9 & RbHTi_4O_9 \\
 & (8.2\ \text{Å}) & (8.6\ \text{Å}) \\
\text{Step II} & \downarrow{\scriptstyle -0.5H_2O} & \downarrow{\scriptstyle -0.5H_2O} \\
 & 1/2\ K_2Ti_8O_{17} & 1/2\ Rb_2Ti_8O_{17} \\
 & (7.8\ \text{Å}) & (8.0\ \text{Å})
\end{array}$$

The numbers in parentheses give spacings for (200) reflections which correspond to the intersheet distances.

The weight loss in Step I is ascribed to the evaporation of interlayer water. The intermediate phases $MHTi_4O_9$ (M = K, Rb) tended to swell again in the air, suggesting that the layer structure is maintained in Step I. The phases exhibit diffuse X-ray diffraction patterns except for sharp (200) and (020) reflections. The sheet–sheet registry is loose while the host framework of $[Ti_4O_9^{2-}]_\infty$ remains unchanged. The protons in these phases are likely to be attached to the nonshared oxygen atoms in the host framework to make hydroxyls since they are the most electronegative. The structure contains four nonshared oxygen atoms per unit cell. By the subsequent heat treatment, the hydroxyls of adjacent layers are con-

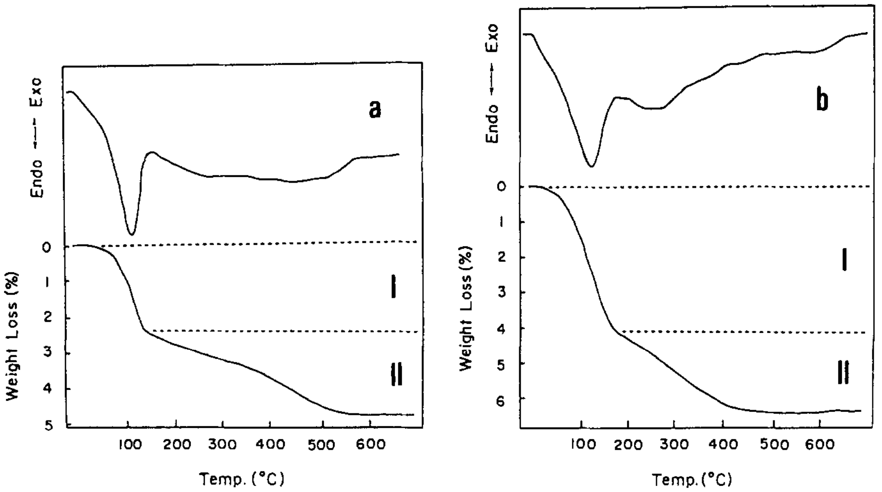

FIG. 3. DTA–TG curves for the half cation-substituted phases of (a) $KHTi_4O_9 \cdot 0.5H_2O$ and (b) $RbHTi_4O_9 \cdot H_2O$. Heating rate: 10°C min^{-1}.

densed to make additional corner sharings, which yield the tunnel structure described below. Alkali metal ions are no longer extracted by treatment with acid solutions.

A fibrous form of the parent-layered titanate $H_2Ti_4O_9 \cdot nH_2O$ was preserved during the synthetic process. The scanning electron micrograph (Fig. 4) demonstrates that fibrous crystals of the obtained octatitanate are composed of an aggregation of tablet-shaped chips. The size of a fiber is 0.5–1.0 mm in length and 0.01–0.03 mm in thickness.

Attempts to prepare other alkali metal salts by similar synthetic route were unsuccessful.

Structural Features and Thermal Stability

The octatitanate $M_2Ti_8O_{17}$ (M = K, Rb) has a monoclinic cell whose refined dimensions are listed in Table I. The crystal structure has been refined using X-ray powder pattern profile fitting techniques (*23*). Details will be published elsewhere. The refinements (Table II) confirmed Marchand's suggestion that $K_2Ti_8O_{17}$ has the same host framework as that of the bronze-like compound $K_3Ti_8O_{17}$ (*24*). Figure 5 shows the idealized polyhedral representation of the structure projected onto the (010) plane. The linkage of TiO_6 octahedra is very similar to that in the parent tetratitanate except for the fact that two additional vertex sharings per unit cell are introduced in the octatitanate. These corner sharings result in a one-dimensional tunnel, extending along the *b*-axis, which has a cross section of one by four octahedra. The tunnel offers four nearly cubic sites for cations per unit period of the *b*-axis, which are classified into two crystallographically equivalent sets of M_1 and M_2 (see Fig. 5). Only two alkali metal

TABLE I

LATTICE PARAMETERS FOR $M_2Ti_8O_{17}$ (M = K, Rb)

	a (Å)	*b* (Å)	*c* (Å)	*β* (°)
$K_2Ti_8O_{17}$	15.678(2)	3.775(1)	11.951(1)	95.67(1)
$Rb_2Ti_8O_{17}$	15.961(3)	3.786(1)	11.918(2)	96.05(2)
$K_2Ti_8O_{17}$[a]	15.62(2)	3.771(2)	11.93(3)	95.8(3)

Note. Estimated standard deviations in the last digit are given in parentheses.

[a] Marchand's data for a comparison use (6).

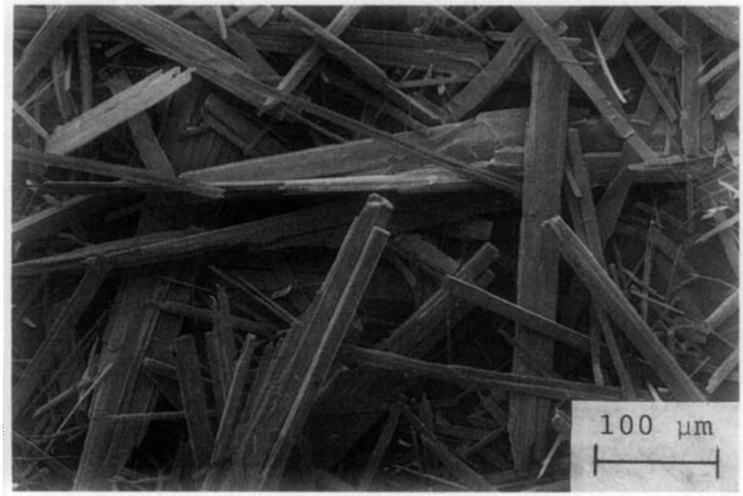

FIG. 4. Scanning electron micrograph of $K_2Ti_8O_{17}$.

ions are accommodated within a unit tunnel, leaving relatively large rooms. The cations in $K_2Ti_8O_{17}$ are distributed statistically between the M_1 and M_2 sites, occupancies of which are approximately $\frac{2}{3}$ and $\frac{1}{3}$, respectively. On the other hand, it is likely that the rubidium ions are ordered in $Rb_2Ti_8O_{17}$. This is suggested from the electron diffraction patterns as well as the X-ray powder diffraction data which require a super lattice of $a = 2a_0$, $b = 2b_0$, and $c = 2c_0$. A study of the rubidium ordering is in progress.

The differential thermal analysis curves are shown in Fig. 6. An endotherm was observed around 600°C, which was followed by a sharp exothermic peak at 760°C for $K_2Ti_8O_{17}$ and at 940°C for $Rb_2Ti_8O_{17}$. On the

TABLE II

POSITIONAL PARAMETERS FOR $K_2Ti_8O_{17}$

Atom	Position	Occupancy	x	y	z
K(1)	4(*i*)	0.68(1)	0.4442(7)	0.0	0.1935(9)
K(2)	4(*i*)	0.32(1)	0.482(2)	0.0	0.364(2)
Ti(1)	4(*i*)	1.0	0.1084(4)	0.0	0.0716(5)
Ti(2)	4(*i*)	1.0	0.1519(5)	0.0	0.3250(7)
Ti(3)	4(*i*)	1.0	0.1947(6)	0.0	0.5768(7)
Ti(4)	4(*i*)	1.0	0.2409(4)	0.0	0.8334(6)
O(1)	2(*a*)	1.0	0.0	0.0	0.0
O(2)	4(*i*)	1.0	0.063(1)	0.0	0.221(2)
O(3)	4(*i*)	1.0	0.108(2)	0.0	0.459(2)
O(4)	4(*i*)	1.0	0.155(1)	0.0	0.705(2)
O(5)	4(*i*)	1.0	0.173(1)	0.0	0.938(2)
O(6)	4(*i*)	1.0	0.226(1)	0.0	0.178(2)
O(7)	4(*i*)	1.0	0.275(1)	0.0	0.428(2)
O(8)	4(*i*)	1.0	0.318(2)	0.0	0.683(2)
O(9)	4(*i*)	1.0	0.364(1)	0.0	0.913(2)

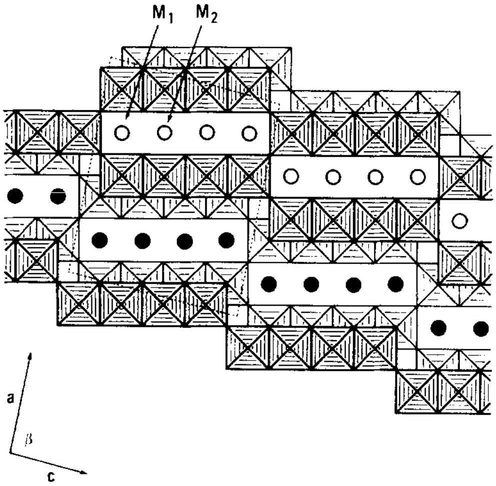

FIG. 5. Crystal structure of $M_2Ti_8O_{17}$ drawn in idealized form. Projection along the b-axis. The open and solid circles represent the cation sites at $y = 0$ and $y = \frac{1}{2}$, respectively. The sum of the occupancies of sites M_1 and M_2 is unity.

basis of the X-ray diffractometry, the octatitanate structure was confirmed to be maintained below the exothermic peak temperature, although relative intensities and linewidth of reflections started to change slightly above 600°C. Heated above exothermic peak temperature, the octatitanate $M_2Ti_8O_{17}$ (M = K, Rb) was disproportionated into hexatitanate $M_2Ti_6O_{13}$ and titanium dioxide (anatase or rutile) as given by

$$M_2Ti_8O_{17} \rightarrow M_2Ti_6O_{13} + 2TiO_2. \quad (2)$$

In the octatitanate half of the cation sites in the tunnel are vacant. According to Pauling's electrostatic valence rule (*25*), such an ionic crystal should be unstable because of the imperfection of local charge neutrality. The octatitanate structure is modified into another structure where oxygen atoms are neutralized more effectively.

K Insertion into the Tunnels

The color of $M_2Ti_8O_{17}$ (M = K, Rb) turned black upon exposure to K vapor. This color is characteristic of trivalent titanium. Chemical analyses summarized in Table III indicate that approximately 1 mol of K per formula weight was incorporated into the titanates. The resulting black materials have the following lattice constants:

$$K_xK_2Ti_8O_{17}: \quad a = 15.54(1)\ \text{Å},$$
$$b = 3.836(3)\ \text{Å},$$
$$c = 12.04(2)\ \text{Å},$$
$$\beta = 94.04(8)^\circ$$
$$K_xRb_2Ti_8O_{17}: \quad a = 15.88(1)\ \text{Å},$$
$$b = 3.832(3)\ \text{Å},$$
$$c = 12.08(1)\ \text{Å},$$
$$\beta = 94.63(9)^\circ,$$

where $x = 1.3$. These data are comparable with the values in Table I, indicating that the octatitanate structure was preserved after the reaction.

TABLE III

CHEMICAL ANALYSES DATA FOR $M_2Ti_8O_{17}$ (M = K, Rb) AND ITS REDUCED PRODUCT

		K (wt%)	Rb (wt%)	Ti (wt%)	Total (%)	Composition
M = K	White	10.6	—	52.0	99.7	$K_{2.00}Ti_8O_{17}$
	Black	16.1	—	47.9	99.4	$K_{3.30}Ti_8O_{17}$
M = Rb	White	—	20.3	46.3	99.5	$Rb_{1.96}Ti_8O_{17}$
	Black	5.9	19.4	43.1	99.1	$K_{1.32}Rb_{2.01}Ti_8O_{17}$

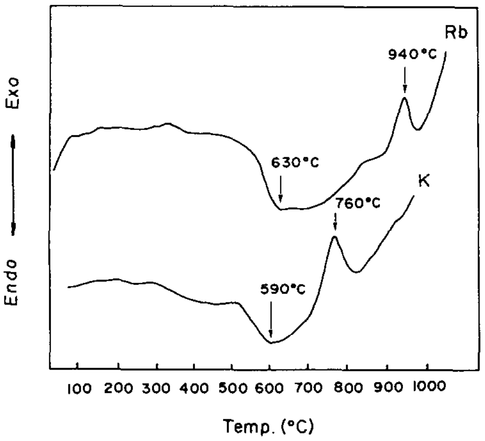

FIG. 6. DTA curves for $M_2Ti_8O_{17}$ (M = K, Rb). Heating rate: 10°C min^{-1}.

All the above results lead to the conclusion that K was reductively inserted into the titanates, yielding a mixed valent compound $K_xM_2Ti_8O_{17}$ as follows:

$$M_2Ti_8^{IV}O_{17}(s) + xK(g) \rightarrow K_xM_2Ti_x^{III}Ti_{8-x}^{IV}O_{17}(s). \quad (3)$$

As described above, the unit tunnel contains four sites, only two of which are occupied by cations. The inserted K is accommodated in the remaining vacant sites, which reduces some part of the tetravalent titanium to trivalent. Watts has prepared black needle-like crystals of $K_3Ti_8O_{17}$ by electrolyzing fused oxides of K_2O–TiO_2–Nb_2O_5 (*24*). This compound should be identical to the obtained $KM_2Ti_8O_{17}$ where M is K.

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