

A Mixed Alkali Metal Titanate with the Lepidocrocite-like Layered Structure. Preparation, Crystal Structure, Protonic Form, and Acid–Base Intercalation Properties

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A mixed alkali metal titanate of composition $A_xTi_{2-x/3}Li_{x/3}O_4$ ($A = K, Rb, Cs$) has been prepared and its ion-exchange/intercalation properties have been explored. Solid-state calcination of appropriate mixtures of TiO_2 and alkali metal carbonates produced the titanate at a stoichiometry of $x = 0.80$ for $A = K$, 0.75 for Rb , and 0.70 for Cs . Rietveld refinement on neutron diffraction data confirmed that the orthorhombic structure is comprised of lepidocrocite-related host layers of $Ti_{2-x/3}Li_{x/3}O_4$ and charge-balancing A ions in the interlayer domain. Complete extraction of both alkali metal ions was achieved by acid-leaching, producing a new protonic titanate of $H_{4x/3}Ti_{2-x/3}O_4 \cdot H_2O$. This phase is distinguished from isomorphous related compounds in terms of high proton content as a consequence of exchangeable Li ions located in the host framework. The material took up alkali metal ions and organoammonium ions from aqueous media. These ion-exchange and intercalation reactions brought about expansion/contraction of the gallery height and lateral displacement of the layers. The resulting various types of layer sequence can be understood in terms of the nature of the interlayer species.

Introduction

Increasing attention has been paid to lamellar metal oxide semiconductors owing to their high photocatalytic activities^{1,2} as well as interesting ion-exchange/intercalation properties.³ One of such typical compounds is a layered alkali metal titanate of composition $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ (\square , vacancy).⁴ This is one example in a family of lepidocrocite (γ -FeOOH)-related titanates of general formula $A_xTi_{2-y}M_yO_4$, where $A = K, Rb, Cs$ and $M = Mg, Co, Ni, Cu, Zn, Mn(III), Fe(III)$.⁵ Its ortho-

rhombic layered structure is composed of corrugated host layers of edge-shared octahedra and interlayer alkali metal ions compensating for the minus charge which arises from substitution of lower valence metal ions or vacancies for Ti .

These alkali metal ions are exchangeable with a variety of inorganic and organic cations, providing an opportunity to modify chemical and physical properties.⁶ We have prepared a protonic oxide, $H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$, via acid exchange of $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$ and examined its acid–base intercalation reactions.⁷ In the course of this study, we recently found an interesting phenomenon: the action of quarternary alkylamines induced delamination of this compound into its elementary host layers.⁸ The resulting nanosheet crystallites

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of quasi-TiO₂ exhibit distinct optical properties compared with bulk TiO₂.⁹ Furthermore, the colloidal suspension of the exfoliated nanosheets is useful as a source for further material syntheses. For example, self-standing flaky particulates of TiO₂ and thin films of the original cesium titanate have been fabricated.^{10,11}

These attractive points would be further emphasized by preparation of another protonic oxide with the lepidocrocite-like layered structure. If such a compound bearing a different amount of vacancies can be prepared and can be exfoliated, a deeper understanding of the photophysics of this unusual two-dimensional semiconductor of TiO₂ would be achieved. Its synthesis is also desirable from a viewpoint of industrialization of the thin flaky TiO₂, which is promising for application as pigments, cosmetics, photocatalysts, etc.¹⁰ A proposed processing involving H_{0.7}Ti_{1.825}□_{0.175}O₄·H₂O from the cesium titanate is costly and disadvantageous. Unfortunately a comparable potassium titanate, desirable from economic reasons, cannot be formed. Although there are several isomorphous potassium titanates in which di- or trivalent metals substitutes for Ti, these cannot be converted into titanate acids from which TiO₂ is derived, because the di- and trivalent cations are immobile upon acid leaching.^{6,12}

To overcome these problems, we devote our attention to a Li-containing titanate. It is known that Li ion often occurs in tetrahedral or octahedral sites in a host framework rather than in interstices such as tunnels and interlayer space. Furthermore, it has been reported that Li ions in octahedral sites of various compounds sometimes participate in so-called host-guest reactions. If these observations are true for the lepidocrocite-type titanate, such a material would meet the requirements above and also provide much information on its chemistry and physics. Actually Groult et al.^{5b} have reported the formation of a mixed alkali metal titanate of lepidocrocite type, K_{0.80}Ti_{1.733}Li_{0.267}O₄. However, they did not present detailed data except for lattice constants. Thus we report here preparation of the mixed alkali titanate, its crystal structure, and ion-exchange/intercalation behavior. Its intercalation properties are considerably different from those for the lepidocrocite-type titanate reported so far in which only interlayer cations are involved in ion-exchange reactions.

Experimental Section

Materials. Titanium dioxide (rutile form) and alkali metal carbonates were of 99.9% purity or better and were used as received from Rare Metallic, Co. All other reagents were of analytical grade (Wako Jyunyaku, Co.). Mill-Q filtered water (Millipore Co., >15 MΩ cm⁻¹) was used throughout the experiments.

Preparation of the Mixed Alkali Metal Titanate. Chemicals of A₂CO₃ (A = K, Rb, Cs), Li₂CO₃, and TiO₂ were mixed intimately in a molar ratio of 3x:x:(12 - 2x) to produce the titanate of composition A_xTi_{2-x/3}Li_{x/3}O₄. The range of x explored was 0.60–1.0. The mixture was placed in a Pt crucible and heated at 1073 K for 30 min to be decarbon-

ated. After cooling, the powder was ground and then calcined at temperatures of 1073–1373 K for 20 h.

Protonation of the Titanate. The mixed alkali metal titanate was stirred in a 1 mol dm⁻³ HCl solution at ambient temperature. A solution-to-solid ratio was 100 cm³ g⁻¹. The acid solution was replaced daily with a fresh one by decantation. The product was collected by filtration and washed with copious quantities of water. Then the roughly dried sample was stored over a saturated NaCl solution (relative humidity, 70%) to a constant weight. A degree of removal of alkali metal ions was studied by chemical analysis: a weighed amount (~0.1 g) of sample was decomposed with a mixed acid solution (H₂SO₄ + HF) at 433 K. After removing HF by evaporating the solution to dryness, its residue was dissolved with 100 cm³ of a 1/100 H₂SO₄ solution, which was analyzed for alkali metals by atomic absorption spectroscopy and for Ti by gravimetry from precipitation with Cupferron. The water content was determined by weight loss data at 1273 K.

Equilibration Procedure. Ion-exchange experiments with alkali metal ions were carried out by treating 1 g of the protonic titanate with 100 cm³ of a 1 mol dm⁻³ hydroxide solution of the cations at 298 K. After shaking for 7 days, the sample was filtered, washed, and air-dried. Cation uptakes were determined by chemical analysis of the products, which was conducted in a procedure similar to the one described above.

Complexes with *n*-alkylammonium ions were prepared by equilibrating 1 g of the sample with 100 cm³ of their solution at 298 K. Its concentration was adjusted to 0.1 mol dm⁻³. A 1/1 mixture of ethanol and water was used as a solvent. The organoammonium ion content in the complexes was estimated as follows. Carbon was determined by IR spectroscopy after conversion into CO₂ upon inductive heating of the sample with metal powders (Fe + W + Sn) as susceptor (Leco CS-444LS). Nitrogen was converted into gaseous NH₃ by fusing the sample with NaOH around 600 K, followed by titration with a standard HCl solution. Molar C/N ratio thus obtained agreed with *n* in C_{*n*}H_{2*n*+1}NH₂ within experimental error, confirming the validity of the analysis. Hydrated water content was deduced as a balance between a total weight loss at 1273 K and the value expected for the organic content.

Characterization. Powder X-ray diffraction (XRD) data were acquired on a Rigaku Rint-2000 diffractometer equipped with graphite-monochromatized Cu Kα radiation (λ = 0.15405 nm). Lattice constants were refined by a least-squares procedure.¹³ IR spectra for samples as KBr pellets were recorded with a Digilab S-45 FT-IR spectrometer at a resolution 2 cm⁻¹.

Neutron Diffraction. Neutron diffraction data for K_{0.80}Ti_{1.733}Li_{0.267}O₄ was collected over a 2θ range of 11.00–131.50° using a step width of 0.05° on the HB-4 powder diffractometer (λ = 0.10913 nm) at Oak Ridge National Laboratory. A thin-walled can of vanadium (0.9 cm i.d. × 5 cm high) was used to hold 4.3 g of the sample. The Rietveld refinement was carried out on this intensity data with the program RIETAN-94.¹⁴ Thirty variables including 13 structural parameters were refined on 2400 data points with 284 reflections.

Results and Discussion

Synthesis of the Mixed Alkali Metal Titanates. The titanates of composition A_xTi_{2-x/3}Li_{x/3}O₄ (A = K, Rb, Cs) were obtained by calcination above 1073 K. The powder XRD patterns are shown in Figure 1. Although the nonstoichiometric nature is expected according to the chemical formula, the compositional range for homogeneity was narrow. The single phase was obtained at x = 0.80 for K/Li system, 0.75 for Rb/Li, and

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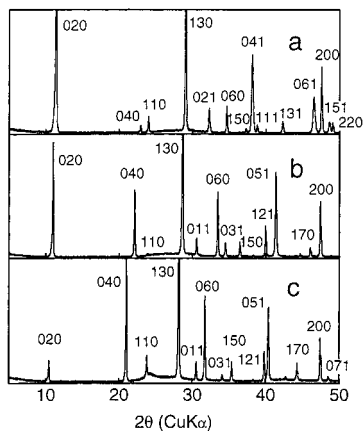


Figure 1. Powder XRD patterns for the mixed alkali metal titanates. (a) $\text{K}_{0.80}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$, (b) $\text{Rb}_{0.75}\text{Ti}_{1.75}\text{Li}_{0.25}\text{O}_4$, and (c) $\text{Cs}_{0.70}\text{Ti}_{1.77}\text{Li}_{0.23}\text{O}_4$.

Table 1. Lattice Parameters for the Mixed Alkali Metal Titanates

compd	x^a	lattice type	a (nm)	b (nm)	c (nm)
K	0.80	<i>C</i>	0.38237(2)	1.5532(1)	0.29727(3)
Rb	0.75	<i>I</i>	0.38311(2)	1.6067(1)	0.29720(2)
Cs	0.70	<i>I</i>	0.38326(2)	1.69245(8)	0.29731(1)

^a x in $\text{A}_x\text{Ti}_{2-x/3}\text{Li}_{x/3}\text{O}_4$, where A denotes alkali metal ions.

0.70 for Cs/Li. For example, hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) and dititanate ($\text{K}_2\text{Ti}_2\text{O}_5$) as well as spinel ($\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$) were present as a minor phase at $x = 0.75$ and 0.85 , respectively.

The orthorhombic lattice constants (see Table 1) are very similar to those reported for other isomorphous varieties such as $\text{K}_x\text{Ti}_{2-x/2}\text{Mg}_{x/2}\text{O}_4$.⁴ The cation, A, governs not only the dimension along the stacking direction or b -axis but also the symmetry of the unit cell: *C* base-centered ($h + k = 2n$ only) for K/Li titanate while body centered ($h + k + l = 2n$) for Rb/Li and Cs/Li phases. Various lattice types depending on the interlayer cations have been reported for the other lepidocrocite-type titanates⁵ and can be accounted for in terms of differences in the layer stacking sequence to provide favorable coordination environments.

Crystal Structure Refinement. The crystal structure of K/Li titanate was refined by the Rietveld procedure on neutron diffraction data. Initial positional parameters for the constituent atoms were deduced from an ideal drawing of the lepidocrocite-type layers stacked in a *C* base-centered symmetry. Four space groups, $C222_1$, $C2cm$, $Cmc2_1$, and $Cmcm$, are possible based on the observed systematic absence of reflections with $00l$ ($l = 2n + 1$) as well as hkl ($h + k = 2n + 1$). The highest symmetry, $Cmcm$, was assumed, which led to satisfactory convergence with residual indices of $R_{wp} = 0.073$, $R_p = 0.062$, $R_1 = 0.072$, $R_F = 0.050$, and $S = 1.2$.¹⁵ (See the final fitted pattern shown in Figure 2.) Figure 3 illustrates the schematic representation of the refined structure for $\text{K}_{0.80}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$. Its structural parameters and selected interatomic distances are listed in Tables 2 and 3, respectively.

(15) $R_{wp} = (\sum w(y_o - y_c)^2 / \sum [w(y_o^2)])^{1/2}$, $R_p = (\sum |y_o - y_c| / \sum y_c)$, $R_1 = \sum |I_o - I_c| / \sum I_o$, $R_F = \sum |I_o^{1/2} - I_c^{1/2}| / \sum I_o^{1/2}$, $S = (\sum w(y_o - y_c)^2 / N - P)^{1/2}$, where N and P are the number of data points and refined parameters, respectively.

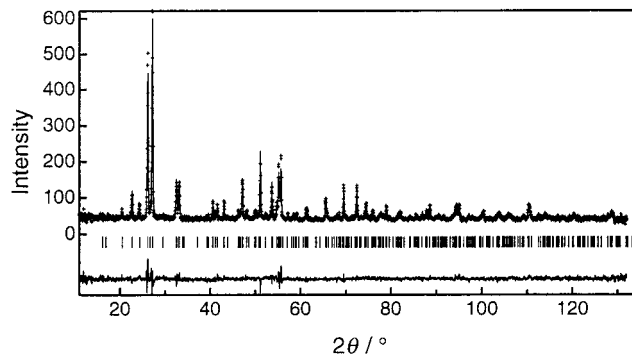


Figure 2. Final results of the Rietveld fitting of neutron diffraction data for $\text{K}_{0.80}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$. Observed and calculated profiles are denoted by dotted and solid lines, respectively. The difference between them and locations of reflections are indicated at the bottom.

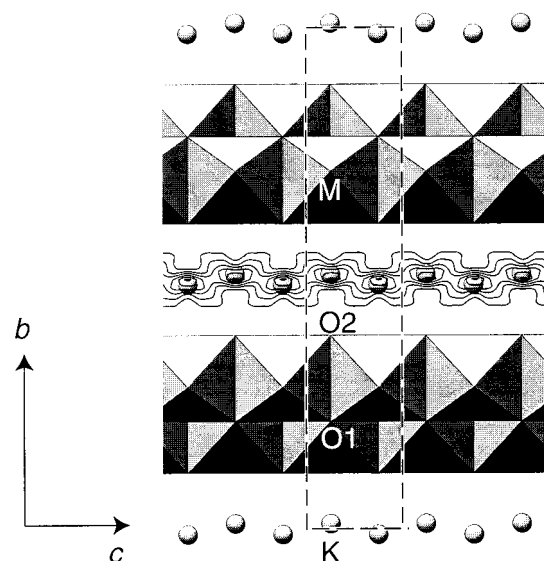


Figure 3. Polyhedral representation of the crystal structure for $\text{K}_{0.80}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ viewed down along the a -axis. Broken lines encircle the *C* base-centered unit cell.

Table 2. Atomic Positional Parameters for K/Li Phase

atom	position	occupancy	x	y	z	B (nm ²) × 10 ²
K	4c	0.4	0.0	0.0105(16)	0.25	10(3) ^b
M ^a	4c	1.0	0.0	0.6844(3)	0.25	0.67(7)
O1	4c	1.0	0.0	0.2156(1)	0.25	0.67(5)
O2	4c	1.0	0.0	0.3887(2)	0.25	1.32(5)

^a Virtual species of $(0.867\text{Ti}^{4+} + 0.133\text{Li}^+)$. ^b Equivalent isotropic thermal factor.

Table 3. Interatomic Distances (nm) in Octahedron

atoms	distance (nm)	atoms	distance (nm)
M^a-O1	(×2) 0.2149(3)	$O1-O1^b$	(×4) 0.2648(2)
M^a-O1^b	(×2) 0.1973(1)	$O1-O2$	(×2) 0.2689(4)
M^a-O2	(×2) 0.1872(3)	$O1-O2^b$	(×4) 0.2915(2)
mean	0.1998	$O1-O1^c$	(×2) 0.29727(3)
		mean	0.2798

^a $x, 1 - y, 3/4$. ^b $x + 1/2, 1/2 - y, 3/4$. ^c $x, y, 1 + z$.

The neighboring host layers produce trigonal prismatic sites (4c position) in which K ions are accommodated. The actual distribution was significantly disordered, particularly parallel to the c -axis, as visualized by a Fourier map superimposed onto the structure. Anisotropic thermal parameters or a splitting atom

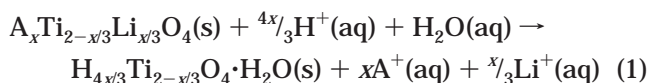
Table 4. Chemical Analysis Data before and after Acid Exchange

no. of acid treatment	TiO ₂	K ₂ O	Li ₂ O	ig loss	total
0	76.8	21.0	2.2	0.2	100.2
(calcd for K _{0.80} Ti _{1.73} Li _{0.27} O ₄)	(76.9)	(20.9)	(2.2)	(0.0)	(100.0)
1	82.3	1.7	0.0	16.1	100.1
2	82.8	0.6	0.0	16.9	100.3
3	82.9	0.2	0.0	17.1	100.1
5	83.1	<0.1	0.0	17.2	100.3
(calcd for H _{1.07} Ti _{1.73} O ₄ ·H ₂ O)	(83.3)	(0.0)	(0.0)	(16.7)	(100.0)

model was necessary to attain a good fit. Simultaneous occupation of two adjacent sites is impossible because they are only 0.152 nm apart. The low content of K ions to the total sites (occupancy = 0.40) suggests some complicated and disordered configuration of cations and vacancies in the gallery, which may account for the broad distribution.

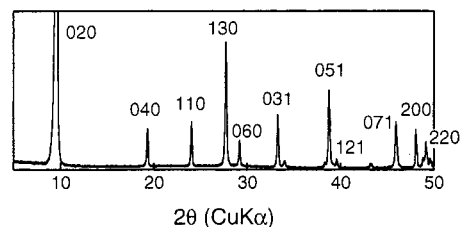
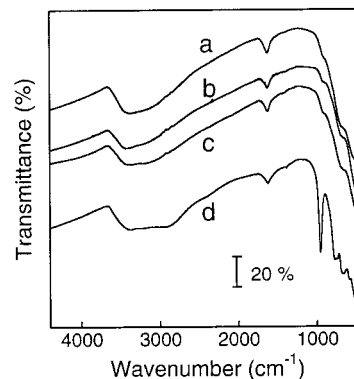
The refined structure is based on the model in which Li ions occupy the octahedral sites in the host layers. Substitution for Ti⁴⁺ ions in the nominal MO₂ framework gives a negative charge that is balanced by interlayer K ions. The isomorphous compounds, e.g., K_xTi_{2-x/2}Mg_{x/2}O₄, have a similar charge-compensation scheme. Accommodation of Li ions in octahedral environments has been widely found in a variety of materials such as spinels Li_{1.33}Ti_{1.67}O₄ and clay minerals (hectorite). We examined another possibility for Li location: Li ions in the interlayer space/vacancies at Ti sites and intermediates between this configuration and the structure described above. These models gave an unstable positional parameter and an unreasonable temperature factor for Li ions. Thus we conclude from this fact as well as from a viewpoint of crystal chemistry that Li ions are situated in the host framework.

Conversion into Protonic Oxide. Alkali metal ions in the titanate, i.e., Li ions in the host framework as well as the interlayer cations, can be extracted by leaching the titanate powder in an acid solution, as exemplified by the chemical analysis data for K/Li titanate (Table 4). Substantially complete removal was achieved by acid exchange repeated three times. The protonation process can be written as



where $x = 0.80$ for A = K, 0.75 for Rb, and 0.70 for Cs. The water content was found to be independent of x , approximately one per formula unit, from the weight loss data at 1273 K.

Powder XRD pattern (see Figure 4) and the lattice parameters (Table 5) of the products reveal that the layer structure was preserved during the acid-exchange reaction, aside from expansion of the interlayer distance. The crystal structure of the protonic oxide can be obtained from the illustration in Figure 3 by gliding the neighboring host layers along the c -axis by $c/2$ with respect to one another. This stacking mode makes surface oxygen atoms in the adjacent layers face each other to produce pseudocubic cavities in the interlayer gallery. The chemical formula above indicates that each cavity accommodates one water molecule.

**Figure 4.** Powder XRD data for the protonic titanate obtained via acid exchange of K_{0.80}Ti_{1.73}Li_{0.27}O₄.**Figure 5.** FT-IR spectra for the acid-exchanged products of K_{0.80}Ti_{1.73}Li_{0.27}O₄, (b) Rb_{0.75}Ti_{1.75}Li_{0.25}O₄, and (c) Cs_{0.70}Ti_{1.77}Li_{0.23}O₄. The data for H₂Ti₄O₉·1.2H₂O is shown in spectrum d for a comparison purpose.**Table 5. Unit Cell Dimensions for the Protonic Titanates**

original form	a (nm)	b (nm)	c (nm)
K/Li	0.37857(2)	1.8402(2)	0.29962(3)
Rb/Li	0.37853(2)	1.8499(2)	0.29934(2)
Cs/Li	0.37841(3)	1.8590(3)	0.29904(3)

This structure is virtually identical to that for H_{0.7}Ti_{1.825}□_{0.175}O₄·H₂O, in which introduced protons are attached to interlayer H₂O molecules; 70% of the interlayer sites are occupied by H₃O⁺ and remaining by H₂O.^{7b} The proton content in the present material is larger by ~50% as a result of the replacement of exchangeable Li ions in the host framework in addition to interlayer guest cations. It is important to know how these protons are accommodated in the structure. The location of protons derived by exchange of Li ions is of particular interest. Are they bonded to an oxygen atom of the octahedra in which the Li ion was originally located, or are they attached to interlayer H₂O? In other words, are they hydroxyl groups or oxonium ions? Such information may be deduced from the IR spectrum shown in Figure 5, which is mainly comprised of a broad band around 3300 cm⁻¹ and an absorption at 1630 cm⁻¹. These features are very similar to those for H_{0.7}Ti_{1.825}□_{0.175}O₄·H₂O and are diagnostic of stretching and bending vibrations of H₂O and/or H₃O⁺.¹⁶ It has been reported that layered protonic titanates such as H₂Ti₃O₇, H₂Ti₄O₉·1.2H₂O, and H₂Ti₅O₁₁·3H₂O include hydroxyl groups¹⁷⁻¹⁹ and exhibit a characteristic ab-

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Table 6. Comparison of Protonic Titanates with the Lepidocrocite-Type Layered Structure

	ion-exchange capacity ^a (mequiv g ⁻¹)	interlayer spacing (nm)	charge density (nm ⁻²)	ref
H _{1.07} Ti _{1.73} O ₄ ·H ₂ O	6.45	0.92	4.72	this study
H _{1.00} Ti _{1.75} O ₄ ·H ₂ O	5.99	0.92	4.41	this study
H _{0.93} Ti _{1.77} O ₄ ·H ₂ O	5.55	0.93	4.11	this study
H _{0.7} Ti _{1.825} □ _{0.175} O ₄ ·H ₂ O	4.12	0.94	3.11	7b
H _{0.7} Ti _{1.65} Mg _{0.35} O ₄ ·H ₂ O	4.11	0.88	3.10	6
H _{0.8} Ti _{1.6} Ni _{0.4} O ₄ ·H ₂ O	4.37	0.88	3.52	12
H _{0.8} Ti _{1.2} Fe _{0.8} O ₄ ·H ₂ O	4.33	0.91	3.52	23

^a Calculated on the basis of the chemical formulas.

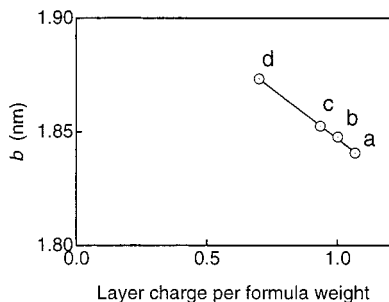


Figure 6. The *b*-parameter of the protonic titanates as a function of the layer charge. Original compounds for points a–d are K_{0.80}Ti_{1.73}Li_{0.27}O₄, Rb_{0.75}Ti_{1.75}Li_{0.25}O₄, Cs_{0.70}Ti_{1.77}Li_{0.23}O₄, and Cs_{0.70}Ti_{1.825}□_{0.175}O₄, respectively

sorption band at 950–1000 cm⁻¹ (see the data for H₂-Ti₄O₉·1.2H₂O in Figure 5d), which is attributable to the bending mode of hydroxyls.¹⁶ The absence of such a band as well as the features above may suggest that the protonic titanate in this study does not have a hydroxyl group but accommodates protons in a form of H₃O⁺.²⁰

Structural and compositional aspects for the layered protonic titanates in this study are compared with those for other titanates in Table 6. The titanates in this study are characterized by their high ion-exchange capacity and charge density. This is due to the fact that Li ions in the host framework are exchangeable. The interlayer spacing for the protonic titanates became larger as the original form goes from K/Li to Rb/Li and to Cs/Li (see Figure 6). The layer charge of each phase, 1.07 for K/Li, 1.00 for Rb/Li, and 0.93 for Cs/Li, may be responsible for this tendency. Interestingly, extrapolation of the linear relationship hit the data for H_{0.7}-Ti_{1.825}□_{0.175}O₄·H₂O, implying close similarities in this series of oxides.

Acid–Base Intercalation Behavior. The protonic titanate obtained showed Brønsted acidity. Ion-exchange and intercalation behaviors were examined for H_{1.07}Ti_{1.73}O₄·H₂O, the acid-exchanged form of K/Li phase. Figure 7 depicts XRD patterns for Li, Na, and K ion-exchanged phases prepared by treating it with the corresponding hydroxide solutions in large excess (~16 times). Their unit cell dimensions as well as

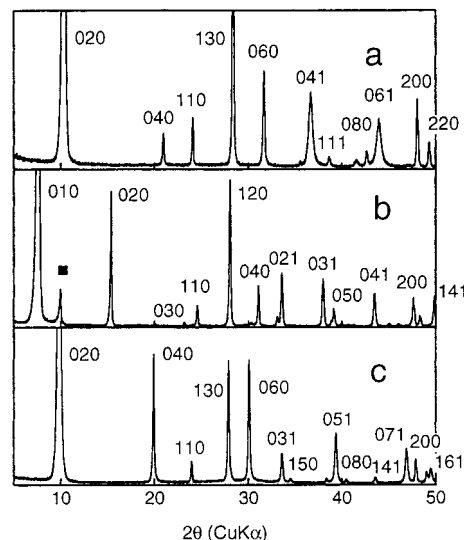


Figure 7. Powder XRD patterns: (a) for Li, (b) Na, and (c) K ion loaded phases. A square in panel b denotes the monolayer hydrate of 0.89 nm coexisted as a minor phase.

Table 7. Chemical Compositions and Unit Cell Dimensions for Alkali Metal Ion Exchanged Phases

composition	lattice type	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)
Li _{0.93} H _{0.14} Ti _{1.73} O ₄ ·H ₂ O	<i>C</i>	0.37859(5)	1.6952(2)	0.30041(8)
Na _{0.78} H _{0.29} Ti _{1.73} O ₄ ·2.0H ₂ O ^a	<i>P</i>	0.38158(5)	1.1507(1)	0.30117(4)
K _{0.51} H _{0.56} Ti _{1.73} O ₄ ·0.7H ₂ O	<i>I</i>	0.37976(4)	1.7818(2)	0.29844(3)

^a Accompanied by a trace amount of a 0.89 nm phase.

chemical compositions are listed in Table 7. Uptakes, hydration state, and interlayer expansion were dependent on the cations incorporated. The K ion-exchanged phase had a body-centered cell, providing pseudocubic cavities with an 8-fold coordination environment in the interlayer space. The stoichiometry indicates half of the sites are occupied by K ions and the remaining half by H₂O. The interlayer spacing of 0.89 nm is compatible with this monolayer arrangement of guests. A higher uptake was achieved for Li and Na ions. The Na ion-loaded sample was composed of two components, a predominant phase of 1.15 nm and a minor one of 0.89 nm. The former may be accounted for by a bilayer hydrate and the latter by a monolayer one. Incorporation of Li ions produced a 0.85 nm phase in a *C* base-centered symmetry. This layer sequence produces two trigonal prismatic sites per formula weight, being similar to the case for the starting K/Li titanate. The chemical composition indicates that these two sites are simultaneously occupied by Li ions and H₂O molecules, most likely in an alternating way. The small size of the Li ion may facilitate stabilization of this monolayer hydrate structure. Cations larger than Na ion cannot be accommodated in a similar configuration.

We have reported alkali metal ion exchange processes in H_{0.7}Ti_{1.825}□_{0.175}O₄·H₂O,^{7b} which also demonstrated formation of mono- and bilayer hydrates, depending on the cations and their uptake amount. Similar monolayer hydrate was obtained for a K ion-exchanged product as a consequence of half occupancy of the interlayer sites. On the other hand, there are several

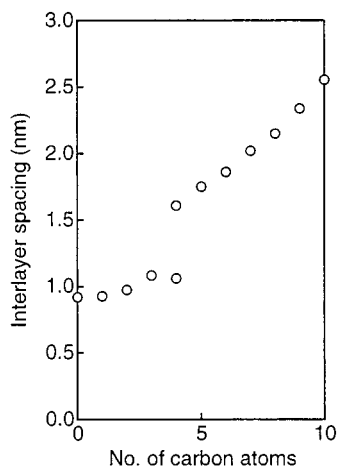
(19) Sasaki, T.; Komatsu, Y.; Fujiki, Y. *Chem. Mater.* **1992**, *4*, 894.

(20) Based on this discussion, the chemical formula of H_{4x/3}-Ti_{2-x/3}O₄·H₂O may be expressed as [4^{x/3}H₃O]⁺Ti_{2-x/3}O₄, where parentheses enclose the interlayer species. This formulation appears to be improper for the protonic oxide derived from K/Li titanate because its proton content of 1.07 (=4^{x/3} × 0.80) exceeds the molar amount of water. However, the actual water content was usually around 1.1, as seen from Table 4, which may allow the introduced protons as H₃O⁺.

Table 8. Stoichiometry and Lattice Parameters for *n*-Alkylammonium Ion Complexes

<i>n</i> -alkyl-ammonium	x^a	$m_{\text{H}_2\text{O}}^a$	lattice type	<i>a</i> (nm)	<i>b</i> (nm)	<i>c</i> (nm)
methyl	0.40	0.5	<i>I</i>	0.37934(6)	1.8528(6)	0.29913(4)
ethyl	0.34	0.5	<i>I</i>	0.37861(8)	1.9497(3)	0.29934(4)
propyl	0.34	0.6	<i>C</i>	0.3797(1)	2.1612(7)	0.29961(7)
butyl ^b	0.39	0.9				
pentyl	0.48	1.3	<i>P</i>	0.3798(3)	1.750(1)	0.2980(2)
hexyl	0.50	1.3	<i>P</i>	0.37945(9)	1.8600(5)	0.29848(7)
heptyl	0.51	1.3	<i>P</i>	0.3793(1)	2.0189(9)	0.29813(9)
octyl	0.52	1.4	turbo ^c	0.3794	2.148(2)	0.2980
nonyl	0.52	1.6	turbo ^c	0.3792	2.339(2)	0.2983
decyl	0.54	1.6	turbo ^c	0.3795	2.557(5)	0.2980

^a x and $m_{\text{H}_2\text{O}}$ in $(\text{C}_n\text{H}_{2n+1}\text{NH}_2)_x\text{H}_{1.07}\text{Ti}_{1.75}\text{O}_4 \cdot m\text{H}_2\text{O}$. ^b A mixture of 1.06 and 1.605 nm phases (approximately 1:1) prevented indexing of the whole pattern. ^c Turbostratic or absence of layer stacking regularity.

**Figure 8.** Interlayer spacing of *n*-alkylammonium ion complexes as a function of alkyl chain length.

differences in Li and Na ion cases. A saturated Na ion uptake by $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4 \cdot \text{H}_2\text{O}$ was 0.56 mol per formula weight, which is much smaller than that (=0.78) for the present material. This reflects the relative abundance of the monolayer and bilayer hydrates. The monolayer hydrate was the principal component, in contrast to the case of the present titanate. A more striking contrast was observed in the Li ion-exchanged material. The protonic oxide $\text{H}_{0.7}\text{Ti}_{1.825}\square_{0.175}\text{O}_4 \cdot \text{H}_2\text{O}$ produced a bilayer hydrate phase of 1.13 nm. These differences may be correlated with layer charge since the layer architecture itself is very similar, as described above.

Table 8 lists compositional and structural data for *n*-alkylammonium ion complexes. A plot of their interlayer distance against alkyl chain length (see Figure 8) clearly indicates two modes of accommodation. The

basal spacing was negligibly dependent on the chain length up to the carbon number of three, strongly suggesting a nearly parallel arrangement of the organoammonium ions in the gallery (named as type I). On the other hand, the interlayer distance for a carbon number of five or more expanded linearly with an increase in the chain length (type II). The successive swelling of 0.13–0.14 nm per additional carbon atom suggests that *n*-alkylammonium ions are packed in intermeshed single layers which are perpendicular to the titanate sheets. The organic content of the type II complexes was almost equal to each other, ~0.5 mol per chemical formula. This indicates that each molecular chain covers the titanate sheet surface by 0.228 nm² (=0.38 nm × 0.30 nm × 2), which is close to the cross sectional area of the alkyl chain (0.182 nm²).²¹ This structural circumstance should be favorable for chain–chain interaction.

Two similar types of orientations depending on the chain length have been reported for a number of layered hosts²² and may be understood in terms of the cohesive energy of the system. The complexes of type I may be stabilized mainly through host–guest electrostatic interaction, which is surpassed by guest–guest hydrophobic interaction for alkylammonium ions with a longer chain. The carbon chain length of four is in the transition region where two types of complexes coexisted. This reflects structural features of the complexes in terms of layer-to-layer registry. The complexes of organoammonium ions with a short chain gave well-defined XRD patterns, indicating a regular layer sequence to produce interlayer cavities having favorable coordination. On the other hand, *hkl* reflections showing three-dimensional periodicities became more diffuse with elongation of the molecular chain. This implies that the system is stabilized predominantly by interaction between the organic species rather than by that between the guests and the inorganic layers.

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Supporting Information Available: Powder XRD data for *n*-alkylammonium ion complexes (2 pages). Ordering information is given on any current masthead page.

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