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A Large Tunnel Structure of Triclinic $Na_2Ti_4O_9$

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A new polymorph of sodium titanate $Na_2Ti_4O_9$ crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 10.653(4)$ Å, $b = 11.647(3)$ Å, $c = 2.9392(6)$ Å, $\alpha = 97.25(3)°$, $\beta = 90.00(11)°$, $\gamma = 102.44(2)°$, and $Z = 2$. The structure was determined from a single-crystal X-ray diffraction method and refined to the conventional values $R = 0.053$ and $R_w = 0.065$ for 2706 independent reflections. The framework of this compound is described as a large tunnel structure, built up from single, double and triple rutile-type chains with sharing vertices, and is quite different from that of the monoclinic form, which was previously reported to have a staggered sheet structure. The present compound contains a considerable amount of Na defects. The site occupancies for three types of sodium, determined by the structure analysis, are 0.97 for Na(1), 0.48 for Na(2), and 0.63 for Na(3), and these give the chemical formula $Na_{2.08}Ti_4O_9$. The relationship to the other compounds with rutile-type tunnel structure, e.g., hollandite-type manganese oxides, is discussed.

Introduction

In the system Na_2O–Ti_2O_3–TiO_2, we have recently isolated a mixed valence sodium titanate, $NaTi_2O_4$ (*1*), which has the calcium ferrite-type structure (*2*). The framework of this compound was built up from "double rutile" chains, and two types of Ti sites were randomly occupied by Ti^{3+} and Ti^{4+}. The edge-shared linkage of TiO_6 octahedra along the *c*-axis in $NaTi_2O_4$ is like that of the rutile-type structure (repeat distance about 3.0 Å), and is quite different from those in the compounds of the system Na_2O–TiO_2, for example, $Na_2Ti_3O_7$ (*3*), $Na_2Ti_4O_9$ (*4*), and $Na_2Ti_9O_{19}$ (*5*). The rutile-type linkage of the TiO_6 octahedra was previously observed in alkali-titanates of the formulae $A_xTi_8O_{16}$ (A = K, Rb, Cs) (*6*) with the hollandite-type structure, and $CaTi_2O_4$ (*7*). No alkali titanates with the rutile-type TiO_6 linkage, which contain only Ti^{4+} cations, have been obtained yet.

We examined the system Na_2O–Ti_2O_3–TiO_2 and prepared single crystals of a new polymorph of $Na_2Ti_4O_9$ having the rutile-type TiO_6 chains. The present paper describes the growth, crystal structure, and site occupancy of Na ions in comparison with the other titanates and manganates.

Experimental

Sample Preparation

Synthesized Ti_2O_3 powder and amorphous Na_2O (98%) were placed in a roughly sealed iron vessel, heated in a resistance furnace at 1273 K in a vacuum (5×10^{-5} Torr) for 20 hr, and slowly cooled to room

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temperature. A leakage of sodium vapor from the vessel was observed, and in many cases the samples were almost oxidized on heating runs, as in the case of the synthesis of $NaTi_2O_4$ (*1*).

Some dark, opaque crystals ($0.5 \times 0.5 \times 0.2$ mm^3 in size) were grown together with colorless crystals. The former crystals were identified to have a new type structure, and the latter were determined to be $Na_8Ti_5O_{14}$ (JCPDS 28-1155) from the result of X-ray powder diffraction. The dark crystals were very reactive with air atmosphere and changed to brown or colorless ones after a few days in a desiccator filled with Ar gas, with a deposition of white powder on the surface, and the bulk part became transparent. This fact suggests that an oxidation of the crystals accompanied by a migration of Na ions to the crystal surface progressed and sodium defects were introduced in the crystal.

Electron microprobe analyses showed that the brown crystal was sodium titanate and was free from iron contamination from the vessel. The chemical composition of this crystal derived from the present structure analysis is $Na_{2.08}Ti_4O_9$.

Precession photographs indicate that the crystal belongs to the triclinic system. The lattice parameters, determined by a least-squares refinement using the 2θ values of 25 strong reflections in the range 20–30° on an automated Rigaku AFC-5 four-circle diffractometer, are a = 10.653(4) Å, b = 11.647(3) Å, c = 2.9392(6) Å, α = 97.25(3)°, β = 90.00(11)°, γ = 102.44(2)°, and V = 353.15(12) Å^3.

Structure Determination

A small tabular crystal, $0.094 \times 0.094 \times 0.047$ mm^3 in size, was used for the structure analysis. The intensity data were collected by the $2\theta - \omega$ scan method with a scan rate of 1°/min at room temperature on the four-circle diffractometer (operating conditions: 40 kV, 30 mA) using graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å). The fluctuation of the intensities, monitored by examining a set of three standard reflections ((070), $(4\bar{1}0)$, $(0\bar{1}2)$) taken after every 100 observations, was within 1.2%. A total of 3118 independent reflections were obtained within the limit of $2\theta \leqq 70°$, of which 2706 reflections have a criteria of $|F_o| > 3\sigma(|F_o|)$, and were used for the subsequent crystal structure determination. The intensity data were corrected for Lorentz and polarization effects. No absorption and extinction corrections were performed.

Initial positions for one Na atom and five Ti atoms were determined by the direct method using the computer program MULTAN80 system (*8*). A Patterson map showed that this coordination was reasonable. At first, the space group of $P\bar{1}$, confirmed by successful refinement, was adopted. Nine oxygen atoms were located in the subsequent Fourier and difference Fourier syntheses using GSFFR program (*9*). Full-matrix least-squares refinement with anisotropic thermal parameters (isotropic for O(5) and O(8)) using the RFINE-II program (*10*) resulted in convergence with R = 0.097. Then the remaining two sodium atoms were introduced (R = 0.055), though they had large temperature factors (B_{eq} = 7.5 and 3.8 Å^2 for Na(2) and Na(3), respectively). EPMA data for these crystals suggested that the ratio Na : Ti was close to 2 : 4, and much less than 3 : 4. From these facts, the occupancy refinement for three Na sites was performed. The converged site occupancies were 0.97 for Na(1), 0.48 for Na(2), and 0.63 for Na(3), and these give the final formula of $Na_{2.08}Ti_4O_9$. Finally, the structure was refined to R = 0.053 and R_w = 0.065 [$w = 1/\sigma^2(F_o)$] for 2706 reflections, with shift/error for all parameters less than 0.01. A difference Fourier synthesis using the final parameters showed no significant residual peak. The scattering factors for the neutral Na, Ti,

TABLE I

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA OF $Na_2Ti_4O_9$

Space group	$P\bar{1}$
Crystal size (mm)	0.094 × 0.094 × 0.047
a (Å)	10.653(4)
b (Å)	11.647(3)
c (Å)	2.9392(6)
α (°)	97.25(3)
β (°)	90.00(11)
γ (°)	102.44(2)
V (Å^3)	353.15(12)
Chemical formula[a]	$Na_{2.08}Ti_4O_9$
Z	2
Density (calc.) (g/cm^3)	3.606
Maximum 2θ (°)	70
Absorption coefficient for Mo$K\alpha$ (cm^{-1})	44.8
Scan width of 2θ (°)	$1.0 + 0.5 \tan \theta$
Scan speed (°/min)	1
Number of independent reflections	3118
Number of used reflections ($>3\sigma$)	2706
Final R	0.053
Final R_w [$w = 1/\sigma^2(F_o)$]	0.065

[a] Determined by the structure analysis.

and O atoms tabulated by Cromer and Mann (*11*) were used in the calculations. The anomalous dispersion correction factors were taken from the "International Tables for X-ray Crystallography" (*12*). The experimental and crystallographic data are summarized in Table I. The final atomic coordinates and temperature factors are given in Tables II and III. The computations were performed on the FACOM M-380R at our institute.

Description and Discussion of the Structure

The crystal structure of triclinic $Na_2Ti_4O_9$ projected down to the c-axis direction is shown in Fig. 1. The structure consists of single, double and triple rutile-type chains of edge-sharing TiO_6 octahedra that share the vertices to produce a framework containing large tunnels elongated to the c-axis, and three types of sodium atoms are located in the tunnel. The selected interatomic distances (Table IV) and bond angles were calculated using the UMBADTEA program (*13*).

Both Na(1) and Na(3) atoms are surrounded by eight oxygen atoms in the bi-

TABLE II

ATOMIC POSITIONAL PARAMETERS, SITE OCCUPANICES, AND TEMPERATURE FACTORS[a]

Atom	Position	x	y	z	Occupancy	B_{eq} or B
Na(1)	2i	0.5974(3)	0.2731(3)	0.137(1)	0.97(1)	1.13
Na(2)	2i	0.3068(7)	0.1484(6)	0.073(4)	0.48(1)	4.34
Na(3)	2i	0.1041(6)	0.2814(5)	0.640(3)	0.63(1)	4.20
Ti(1)	1a	0.0	0.0	0.0	1.0	0.66
Ti(2)	2i	0.3745(1)	0.4464(1)	0.7232(4)	1.0	0.35
Ti(3)	2i	0.8791(1)	0.4302(1)	0.7151(4)	1.0	0.38
Ti(4)	2i	0.8090(1)	0.1216(1)	0.5609(4)	1.0	0.35
Ti(5)	1d	0.5	0.0	0.0	1.0	1.79
O(1)	2i	0.9394(4)	0.1491(4)	0.075(1)	1.0	0.33
O(2)	2i	0.1233(4)	0.0461(4)	0.523(1)	1.0	0.46
O(3)	2i	0.6947(4)	0.0617(4)	0.030(1)	1.0	0.39
O(4)	2i	0.3186(4)	0.3442(4)	0.172(2)	1.0	0.47
O(5)	2i	0.9918(4)	0.4066(4)	0.204(1)	1.0	0.22[b]
O(6)	2i	0.7812(4)	0.4837(4)	0.242(1)	1.0	0.35
O(7)	2i	0.4878(4)	0.1119(4)	0.555(1)	1.0	0.47
O(8)	2i	0.7829(4)	0.2738(4)	0.637(1)	1.0	0.36[b]
O(9)	2i	0.5528(4)	0.4305(4)	0.715(1)	1.0	0.30

[a] B_{eq} is defined as $\exp[-(h^2\beta_{11} + \cdot \cdot \cdot + 2kl\beta_{23})]$.

[b] Isotropic temperature factors.

TABLE III

ANISOTROPIC TEMPERATURE FACTORS

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na(1)	0.0038(3)	0.0011(2)	0.034(4)	0.0003(2)	−0.0001(8)	0.0009(7)
Na(2)	0.0020(7)	0.0015(6)	0.33(3)	0.0003(5)	−0.001(3)	0.000(3)
Na(3)	0.0038(6)	0.0025(5)	0.28(2)	0.0004(4)	0.000(3)	0.002(2)
Ti(1)	0.0024(1)	0.0016(1)	0.011(2)	0.0015(1)	0.0008(4)	0.0012(3)
Ti(2)	0.00094(9)	0.00073(7)	0.009(1)	0.00030(6)	0.0000(2)	0.0006(2)
Ti(3)	0.00102(9)	0.00090(7)	0.006(1)	0.00001(6)	−0.0002(2)	0.0005(2)
Ti(4)	0.00103(8)	0.00079(7)	0.006(1)	0.00020(6)	0.0000(2)	0.0006(2)
Ti(5)	0.0016(2)	0.0025(1)	0.089(3)	−0.0013(1)	−0.0008(5)	0.0016(5)
O(1)	0.0005(3)	0.0003(3)	0.020(4)	0.0003(2)	0.0000(9)	0.0006(9)
O(2)	0.0004(3)	0.0012(3)	0.016(4)	0.0000(3)	0.0001(9)	0.0005(9)
O(3)	0.0005(3)	0.0007(3)	0.017(4)	−0.0001(2)	0.0000(9)	0.0009(9)
O(4)	0.0015(4)	0.0003(3)	0.018(5)	−0.0001(3)	0.000(1)	0.0005(9)
O(6)	0.0004(3)	0.0011(3)	0.013(4)	0.0006(2)	−0.0002(9)	0.0008(9)
O(7)	0.0013(4)	0.0004(3)	0.018(5)	0.0001(3)	0.000(1)	0.0003(9)
O(9)	0.0006(3)	0.0005(3)	0.010(4)	0.0001(2)	−0.0002(9)	0.0004(9)

capped trigonal prisms (Fig. 2). The average eightfold Na–O distances are 2.549 and 2.624 Å for Na(1) and Na(3), respectively, which are normal for the eightfold Na–O coordination. However, the Na(3)–O(4) distance, about 2.68 Å, is much longer than those of Na(3)–O(1) and Na(3)–O(5) forming a trigonal prism (Table IV). In addition, the bicap angle (O(2)–Na(3)–O(6): 149.9(3)°) is apparently larger than those of O(3)–Na(1)–O(6) (115.7(2)°) and further, O(3)–Na–O(3′) (131.72(5)°) in $NaTi_2O_4$ (*1*), which has a similar bicapped trigonal prism for Na–O coordination. From these facts, oxygen atoms around the Na(3) atom form a distorted bicapped trigonal prism (Fig. 2).

On the contrary, the Na(2) atom is coordinated by six oxygen atoms to form a con-

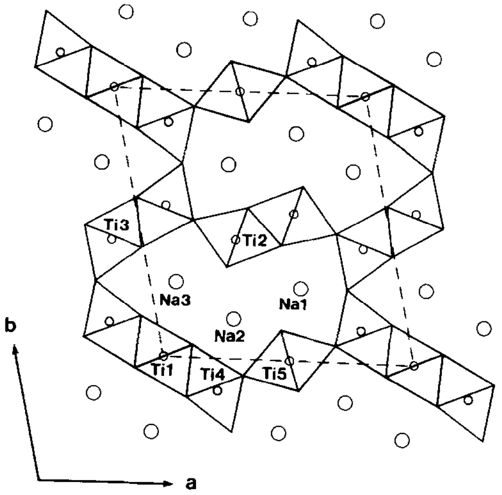

FIG. 1. Crystal structure of $Na_2Ti_4O_9$ viewed along [001]. The TiO_6 unit is illustrated as an octahedron. Ti atoms are shown as small open circles and Na atoms as large open circles.

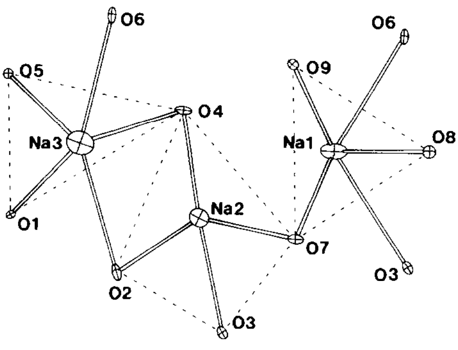

FIG. 2. Na–O coordinations of three types of Na atoms in a large tunnel viewed along [001]. Ellipsoids are scaled to include 75% probability.

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å)

Na(1)–O(3)	2.853(6)		Ti(2)–O(4)	1.898(4)	
–O(6)	2.772(5)		–O(4)	1.899(5)	
–O(7)	2.461(5)		–O(9)	2.075(5)	
–O(7)	2.458(5)		–O(9)	2.075(4)	
–O(8)	2.461(6)	×2	–O(9′)	1.948(5)	
–O(9)	2.463(6)		–O(6)	1.996(5)	
–O(9)	2.462(5)		Mean	1.982	
Mean	2.549				
			Ti(3)–O(6)	1.977(5)	
Na(2)–O(4)	2.238(9)		–O(6)	1.978(5)	
–O(7)	2.532(11)	×2	–O(5)	1.952(5)	
–O(2)	2.523(10)		–O(5)	1.955(5)	
–O(2)	2.526(10)		–O(5′)	2.079(4)	
–O(3)	2.424(9)		–O(8)	1.874(4)	
Mean	2.463		Mean	1.969	
Na(3)–O(4)	2.679(9)		Ti(4)–O(3)	1.939(5)	
–O(4)	2.682(9)		–O(3)	1.937(5)	
–O(1)	2.529(8)		–O(1)	1.998(5)	
–O(1)	2.534(8)		–O(1)	2.001(5)	
–O(2)	2.770(8)		–O(2)	2.209(5)	
–O(5)	2.534(9)		–O(8)	1.839(5)	
–O(5)	2.539(9)		Mean	1.987	
–O(6)	2.724(7)				
Mean	2.624		Ti(5)–O(3)	2.042(4)	×2
			–O(7)	1.982(5)	×2
Ti(1)–O(1)	1.967(5)	×2	–O(7)	1.979(4)	×2
–O(2)	1.966(5)	×4	Mean	2.001	
Mean	1.966				

siderably distorted octahedron (Fig. 2). The Na(2)–O distance varies in the range 2.238–2.532 Å, and the average value is 2.463 Å, which is very consistent with the average sixfold distance of 2.44 Å reported in the literature (*14*).

Both the octahedra of Ti(2)O_6 and Ti(3)O_6 form the double rutile-type chains by the centers of inversion at ($\frac{1}{2}$, $\frac{1}{2}$, 0) and (0, $\frac{1}{2}$, 0), respectively (Fig. 1). The average Ti–O distances are 1.982 and 1.969 Å for the bonds Ti(2)–O and Ti(3)–O, respectively. It can be seen from Figs. 3a and 3b that both of the body diagonal O(6)–Ti(2)–O(9′) and O(5′)–Ti(3)–O(8) angles, the values of which are 162.0(2)° and 172.1(2)°, respectively, are considerably smaller than 180° as in a regular octahedron. Such a distortion of the octahedron is always observed in the double rutile-type compounds, e.g., $NaTi_2O_4$ (*1*), $CaTi_2O_4$ (*7*), and hollandite-type minerals, whose general formula is $A_{0\sim2}Mn_8(O, OH)_{16}$ (A = Ba, K, Pb, Na) (*15*). This may be due to the nature of metal–oxygen octahedra forming a double rutile chain, and may serve to minimize repulsive forces between neighboring titanium cations with their large charges of +3 or +4.

The triple rutile-type chain is formed by the Ti(1)O_6 octahedron located at the origin and the Ti(4)O_6 octahedra sharing a pair of opposite edges of the Ti(1)O_6 octahedron (Fig. 3c). Because the Ti(1) site is located on the center of symmetry, the Ti(1)O_6 octahedron has little distortion (Ti(1)–O distance 1.966–1.967 Å, average 1.966 Å), and the body diagonal O(1)–Ti(1)–O(1) angle is 180°. In contrast, the Ti(4)–O distance ranges largely between 1.839 and 2.209 Å, averaged by 1.987 Å, and the body diagonal O(2)–Ti(4)–O(8) angle (169.9(2)°) is much smaller than 180°. Accordingly, the Ti(4) position is shifted from the center of its coordination octahedra, away from the Ti(1) cation (Fig. 1). A similar shift is observed in the triple chains of $Na_4Mn_4Ti_5O_8$ (*16*) and mineral romanechite (Ba, $H_2O)_2Mn_5O_{10}$ (*17*) and todorokite (Na, Ca, K, Ba, $Sr)_{0.3\text{–}0.7}(Mn, Mg, Al)_6O_{12} \cdot 3.2\text{–}4.5H_2O$ (*18*). As in the case of above-mentioned double chains, this situation serves to minimize electrical repulsive forces between Ti cations in the triple chain.

On the other hand, the Ti(5)O_6 octahedra form a single rutile-type chain (Fig. 3d). The Ti(5) site is situated on the inversion center ($\frac{1}{2}$, 0, 0); the Ti(5)–O distance varies in a short range between 1.979 and 2.042 Å, which gives a mean of 2.001 Å. It must be noted that the Ti(5) site has a considerably larger thermal vibrational ellipsoid toward the c-axis direction (B_{eq} = 1.79 $Å^2$), compared with the other four Ti sites (Fig. 3d). This fact suggests the disordered arrangement of Ti(5) atoms along the c-axis direction. Maybe most of Ti^{3+} ions occupy the Ti(5) site in the stoichiometric compound "$Na_3Ti_4O_9$."

The compound of the formula $Na_2Ti_4O_9$,

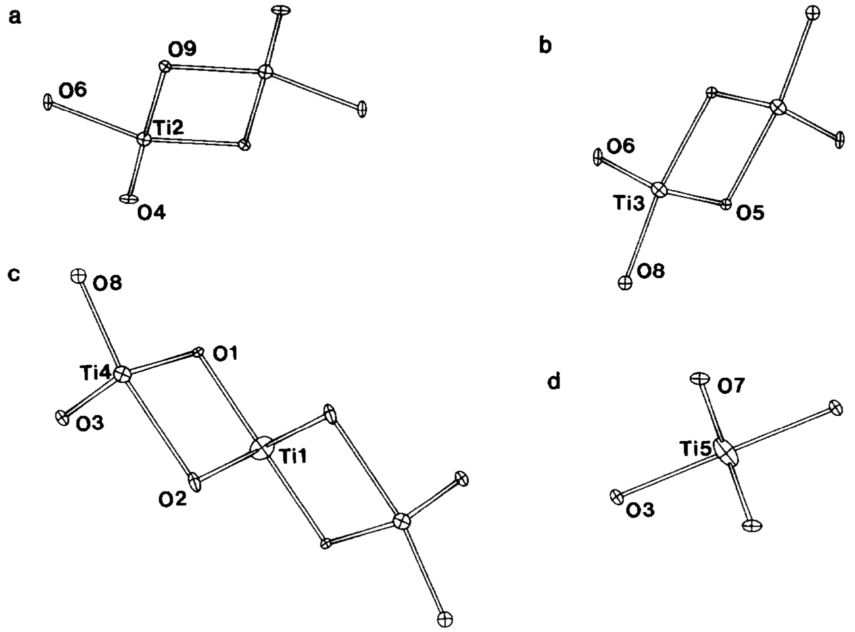

FIG. 3. (a) $Ti(2)O_6$ and (b) $Ti(3)O_6$ double rutile chains; (c) triple rutile chain of $Ti(1)O_6$ and $Ti(4)O_6$ octahedra; and (d) $Ti(5)O_6$ single rutile chain viewed along [001]. Ellipsoids are scaled to include 75% probability.

which has a monoclinic lattice, space group $C2/m$, and lattice constants $a = 17.38(2)$ Å, $b = 3.784(2)$ Å, $c = 11.99(1)$ Å, and $\beta = 106.2(1)°$, was previously obtained by Dion *et al.* (*4*). The basic framework of the monoclinic $Na_2Ti_4O_9$ is built up from four TiO_6 octahedra sharing edges at the same height which combine similar units above and below into zigzag ribbons of octahedra toward the *b*-axis. The ribbons are connected to similar units by sharing vertices to form staggered sheets between which sodium atoms are situated. In contrast, the present triclinic $Na_2Ti_4O_9$ has a large tunnel structure formed by four types of rutile-type TiO_6 chains.

Defects in the Tunnel Structures with Rutile-Type Chains

As described earlier, triclinic $Na_2Ti_4O_9$ has a large tunnel structure built up from the rutile-type chains of the TiO_6 octahedra. The rutile-type linkage of octahedra is often observed in manganese oxide minerals, whose structures can be described as tunnel ones with rutile chains. Pyrolusite (β-MnO_2), which is isostructural to rutile, with single chains of the MnO_6 octahedra, and ramsdellite of double chains have small vacant tunnels, respectively.

The hollandite structure (*15*) is constructed of double chains and todorokite (*18*) of triple chains resulting in frameworks with [2 × 2] and [3 × 3] square tunnels, respectively, where the expression [*m* × *n*] is after Post and Bish (*18*). Further, the double and triple chains in romanechite (*17*) result in [2 × 3] tunnels. These tunnels are occupied by large cations such as Ba^{2+}, K^+, Na^+, Pb^{2+}, and H_2O. The octahedral sites in these minerals can accommodate a large variety of cations with an apparent change in the charge and size, e.g., Mn^{3+} (*15*),

Fe^{3+}, Al^{3+}, Si^{4+}, and Mg^{2+} cations in addition to Mn^{4+}, and as a result, the site occupancy of tunnel cations depends on the average charge of the octahedral cations to preserve the charge neutrality in the hollandite-type and its related minerals. Byström and Byström (*19*) and Post *et al.* (*15*) reported that the occupancy of the tunnel alkali cation sites in hollandite was about 50%. In addition, for most of the todorokite samples the chemical formulae show several kinds of tunnel cations, all with occupancies less than one (*18*). In romanechite, Turner and Post (*17*) reported that the Ba-site occupancy was 33% from the result of chemical analyses.

Similar features can be seen in the synthetic hollandite-type compounds previously reported. In $Ba_xAl_{2x}Ti_{8-2x}O_{16}$, Sinclair *et al.* (*20*) reported a wide range of x, varying from 0.3 to 1.2. Bayer and Hoffman (*6*) reported that nonstoichiometric compounds of hollandite-type K–Al–Ti oxides were found down to about $K_{1.60}(Al_{1.60}Ti_{6.40})O_{16}$, and there were no difficulties in preparing stoichiometric hollandite-type compounds with K and Rb as tunnel cations. However, in the case of Cs, the nonstoichiometric phases $Cs_x(B_xTi_{8-x})O_{16}$ with B = Al, Ti, Cr, Fe, Ga and $Cs_x(B_{x/2}Ti_{8-x/2})O_{16}$ with B = Mg, Co, Ni, Cu, and Zn were only obtained (*6*). The A–A cation distances, corresponding to the repeat distance of the c-axis (about 3.0 Å), were found to be unusually short for the stoichiometric hollandite-type compounds with A = Ba, K, Rb, and Cs. This fact probably causes the electrical repulsive forces between alkali or alkali–earth cations toward the tunnel direction. Accordingly, these cations are partially occupied in the tunnel sites, not only in the hollandite-type and its related minerals but also in the synthetic hollandite-type compounds.

In the present triclinic $Na_2Ti_4O_9$ with rutile-type tunnel structure, the site occupancies for Na(2) and Na(3), both of which are located in the distorted Na–O polyhedra as mentioned above, have significantly small values, 0.48 and 0.63, respectively. The tunnels in the present $Na_2Ti_4O_9$ are wide, like those in the hollandite-type compounds as mentioned above. This would cause an easy migration of Na ions toward the tunnel direction, despite the small ionic radius of Na^+ compared with those of Ba^{2+}, K^+, Rb^+, and Cs^+.

It is known empirically that the Ti^{3+} cation has a strong tendency to change to Ti^{4+} under the oxidizing atmosphere. For example, the surfaces of Ti_2O_3 powder are easily oxidized in air atmosphere, even at room temperature. In the present experiment, a deposition of white powder, which was probably Na_2CO_3, was observed on the surface of "old" $Na_2Ti_4O_9$ crystals. These facts suggest that the as-grown crystals should be richer in Na content and considerable amounts of the Na defects are introduced during storing by oxidation with residual oxygen in Ar atmosphere. The reaction formula by the oxidation together with the Na ion migration to the crystal surface can be described as

$$[Na^+] + [Ti^{3+}] + 1/4O_2 \rightarrow \square + [Ti^{4+}] + 1/2Na_2O,$$

where [ ] means ions in the lattice sites and □ is the Na vacancy.

We have no doubt that the mixed valence state with the stoichiometric composition "$Na_3Ti_4O_9$" could be achieved by controlling the preparation and the following sampling conditions, e.g., by a perfect shielding from air. We are trying to reduce the amount of Na defects in this compound, however, the samples of the stoichiometric "$Na_3Ti_4O_9$" compounds have not been confirmed yet.

Conclusion

We successfully isolated a new polymorph of sodium titanate $Na_2Ti_4O_9$. The present structure analysis revealed that the framework of triclinic $Na_2Ti_4O_9$ is described as a large and distorted tunnel structure, built up from single, double and triple rutile-type chains with sharing vertices. Similar rutile-type chains are observed in some alkali or alkali-earth titanates and manganates, e.g., $NaTi_2O_4$ (*1*), $CaTi_2O_4$ (*7*), $Na_4Mn_4Ti_5O_{18}$ (*16*), $Rb_{0.27}MnO_2$ (*21*), and the hollandite-type and its related minerals (*15, 17, 18*), where the chain size lies between two and five.

The Na defects in $Na_2Ti_4O_9$ are supposed to be introduced by the oxidation reaction after its crystallization. The large tunnel structure in $Na_2Ti_4O_9$ would cause the easy migration of Na ions to the crystal surface and form the sodium-site defects.

In the system Na_2O–Ti_2O_3–TiO_2, further investigation into the preparation of the other compounds is presently being carried out so as to isolate new mixed valence phases and to determine their crystal structures.

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