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Crystal Structure of $Na_xTi_2O_4$ with $0.50 \leqq x \leqq 0.57$

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A new member of Ti^{3+}/Ti^{4+} mixed-valence sodium titanate, $Na_xTi_2O_4$ with $x \approx 0.6$, was prepared by the reaction of sodium metal and titanium oxides at a high temperature of 1723 K. It crystallizes in the orthorhombic system, space group *Pnam*, and is isostructural with $Na_xFe_xTi_{2-x}O_4$ ($0.90 > x > 0.75$). The framework is built up from the rutile-related type Z-shaped chains with the repeat distance of about 3.0 Å. The homogeneity range of $Na_xTi_2O_4$ was determined to be $0.50 \leqq x \leqq 0.57$, from the results of single-crystal X-ray structure analyses of two specimens; as-grown $Na_{0.57}Ti_2O_4$ and $Na_{0.50}Ti_2O_4$ derived by air oxidation at room temperature. A considerable change in the lattice parameters is observed in the $Na_xTi_2O_4$ structure when the Na-content is decreased from $x = 0.57$ to $x = 0.50$. © 1991 Academic Press, Inc.

Introduction

Mumme and Reid (*1*) previously prepared intrinsically nonstoichiometric $Na_xFe_xTi_{2-x}O_4$ ($x = 0.9$) crystals by melting the composition $NaFeTiO_4$ at 1493 K and by the subsequent slow cooling with a loss of sodium. They also confirmed the homogeneity range of $0.90 > x > 0.75$ in $Na_xFe_xTi_{2-x}O_4$ by preparations of the powder samples. $Na_xFe_xTi_{2-x}O_4$ ($0.90 > x > 0.75$) and $NaFeTiO_4$ (*2*), isotypic to $CaFe_2O_4$, have the same space group of *Pnma* as well as similar lattice parameters. Mumme and Reid (*1*) assumed that $Na_xFe_xTi_{2-x}O_4$ and $NaFeTiO_4$ might be regarded as structurally related polymorphs with $x < 0.90$ in the one and $x = 1$ in the other.

Recently, we have succeeded in the preparation of $NaTi_2O_4$ single crystals with the $CaFe_2O_4$ structure (*3*). In $NaTi_2O_4$, two types of octahedral sites are randomly occupied by Ti^{3+} and Ti^{4+} cations. The Ti^{3+} cations in $NaTi_2O_4$ play an essential role in structure determination like Fe^{3+} cations do in $NaFeTiO_4$ as a (Fe^{3+}, Ti^{4+}) solid solution system (*2*). A similar titanium end-member or a substitution of Ti^{3+} for Fe^{3+} in $Na_xFe_xTi_{2-x}O_4$ has been presumed.

We have examined the system Na_2O–Ti_2O_3–TiO_2 by the reactions of metallic sodium and titanium oxides at higher temperatures so as to separate some new crystals with Ti^{3+}/Ti^{4+} mixed-valence states for determining the crystal structures as well as their phase relationships. In this paper, we describe the preparation and crystal structure analysis of a new nonstoichiometric

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compound having the formula $Na_xTi_2O_4$ with $0.50 \leqq x \leqq 0.57$.

Experimental and Results

Sample Preparation

Starting materials of metallic sodium blocks (99%), TiO_2 (99.9%), and synthesized Ti_2O_3 powder were placed in a sealed iron vessel, heated in a resistance furnace at 1723 K in an argon gas flow for several hours, and slowly cooled to room temperature.

Small black $Na_xTi_2O_4$ crystals, 0.5 × 0.2 × 0.2 mm^3 in maximum size, were precipitated together with the other four phases, $NaTi_2O_4$ (*3*), $Na_{1.7}Ti_6O_{11}$ (*4*), Ti_2O_3, and $NaTi_8O_{13}$ (*5*), and some of them were contaminated by small amounts of impurities such as Si, Mn, and Rh, which were supposed to come from the iron vessel. However, EPMA analyses showed that $Na_xTi_2O_4$ crystals had no major impurities, and had the approximate molar ratio Na/Ti = 0.6/2.0, which means $x = 0.6$.

Under air atmosphere, $Na_xTi_2O_4$ crystals were very reactive, and a remarkable change in the lattice parameters was observed on the four-circle diffractometer, together with a decrease in the Na contents. From this fact, special care was required for the sampling conditions. Small crystals of the as-grown $Na_xTi_2O_4$ were held in evacuated glass capillaries of 0.3-mm diameter with 0.01-mm thickness and were used for the following X-ray study.

Precession photographs indicate that the as-grown crystal belongs to the orthorhombic system with the possible space group $Pna2_1$ or *Pnam*, and is isostructural with $Na_xFe_xTi_{2-x}O_4$[1] (*1*). The lattice parameters, determined by a least-squares refinement using 2θ values of 25 strong reflections between 20° and 30° and Mo$K\alpha$ radiation (λ = 0.71069 Å) on an automated Rigaku AFC-5 four-circle diffractometer, were a = 9.486(2) Å, b = 11.307(3) Å, c = 2.9450(8) Å, and V = 315.9(1) $Å^3$. The chemical formula of this crystal, determined by the present structure analysis was $Na_{0.57}Ti_2O_4$.

Homogeneity Range

After the exposure of $Na_xTi_2O_4$ ($x \approx 0.6$) crystals to an air atmosphere for a week, precession photographs were taken using Mo$K\alpha$ radiation. The photographs indicate that the derived $Na_xTi_2O_4$ crystal with a slight decrease in the Na content has a similar orthorhombic cell that remained unchanged. The lattice parameters, determined by a least-squares refinement using 2θ values of the similar reflections on the four-circle diffractometer, were a = 9.616(3) Å, b = 11.134(5) Å, c = 2.9541(11) Å, and V = 316.3(2) $Å^3$. The chemical formula, determined by the structure analysis that follows, changed to $Na_{0.50}Ti_2O_4$. No obvious change in both the chemical composition and the lattice parameters was observed with further exposure to air. From these results, the homogeneity range of $Na_xTi_2O_4$ was confirmed to $0.50 \leqq x \leqq 0.57$ in this study. The more stoichiometric $Na_xTi_2O_4$ specimens may be produced by an improvement of preparation at high temperatures, because the Na defects in $Na_xTi_2O_4$ are supposed to be introduced at the cooling process from 1723 K after its crystal growth, as in the case of nonstoichiometric $Na_{1.7}Ti_6O_{11}$ crystals (*3*). A remarkable change in the lattice parameters with decreasing Na content is discussed from a structural view in the following section, in comparison with the case of $Na_xFe_xTi_{2-x}O_4$ ($0.90 > x > 0.75$) (*1*).

Structure Determination

$Na_{0.57}Ti_2O_4$. A small crystal with the approximate chemical formula of $Na_{0.6}Ti_2O_4$,

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[1] Mumme and Reid (*1*) and Reid *et al.* (*2*) described both $NaFeTiO_4$ and $Na_xFe_xTi_{2-x}O_4$ as space group *Pnma*, while other $CaFe_2O_4$ isotypes have been described as *Pnam*. In accordance with the most common rule for the unit-cell determination, we selected *Pnam* as the space group of $Na_xTi_2O_4$.

$0.15 \times 0.10 \times 0.09$ mm^3 in size, was held in an evacuated glass capillary, and was used for the crystal structure determination. 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 condition: 40 kV, 30 mA) using graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å). Fluctuations of the intensities, monitored by examining a set of the three standard reflections ((440), (071), (002)) taken after every 50 observations, were within 2.1%. A total of 1469 independent reflections were obtained within the limit of $2\theta \leqq 90°$, of which 1040 have a criteria of $|F_o| > 3\sigma|(F_o)|$ and were used for the subsequent structure analysis. The intensity data were corrected for Lorentz and polarization effects. No absorption and extinction corrections were performed.

At first, the space group of the highest symmetry, ***Pnam***, confirmed by a successful refinement, was adopted. Initial positions for two titanium atoms and four oxygen atoms were taken from those of $Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$ reported by Mumme and Reid (*1*). The crystal structure factor F_c was calculated with an overall temperature factor of 0.80. The R value was 0.202, showing that the structure model adopted was reasonable. Then, the atomic parameters and the scale and temperature factors were refined by the full-matrix least-squares method using the RFINE-II program (*6*). The R value with isotropic temperature factors converged to 0.118. Then, an Na(1) atom at (0.095, 0.595, 0.25) was introduced, which was revealed by Fourier and difference Fourier syntheses using the GSFFR program (*7*). The converged R factor with anisotropic temperature factors was 0.067. At this stage, the Na(1) site with the occupancy factor of 0.57(1) had a very large thermal anisotropy toward the c-axis direction with B_{eq} = 12.8 Å^2. Fourier and difference Fourier syntheses indicated a significant residual electron density at the position of (0.403, 0.066, 0.25). Therefore, we adopted a disorder model for the sodium tunnel with two sodium sites. The R value with isotropic temperature factors for two Na sites and their occupancy factors of 0.37 and 0.20 converged to R = 0.058. A subsequent sodium site occupancy refinement indicated that the occupancies for Na(1) and Na(2) were 0.34(1) and 0.23(1), respectively, and equivalent isotropic temperature factors of them were B_{eq} = 2.31 Å^2 and 6.74 Å^2, respectively. The final difference Fourier map showed no significant residual electron density. Finally, the structure was refined to R = 0.054 and R_w = 0.042 [$w = 1/\sigma^2(F_o)$] for 1040 reflections, with shift/error for all parameters less than 0.01. The total sodium site occupancy of 0.57 is very consistent with the EPMA results.

$Na_{0.50}Ti_2O_4$. A small crystal, which was derived from the air oxidation of an $Na_{0.6}Ti_2O_4$ crystal for more than one week, $0.16 \times 0.08 \times 0.08$ mm^3 in size, was used for the crystal structure analysis. The method of intensity data collection was the same as that of $Na_{0.57}Ti_2O_4$. Fluctuations of the intensities, monitored by examining a set of the three standard reflections ((440), (071), (002)) taken after every 50 reflections, were within 2.3%. A total of 1453 independent reflections were obtained within the limit of $2\theta \leqq 90°$, of which 1223 reflections have a criteria of $|F_o| > 3\sigma|(F_o)|$, and were used for the subsequent structure analysis.

The same space group as that of $Na_{0.57}Ti_2O_4$, *Pnam*, confirmed by successful refinement, was adopted. The Patterson maps showed that the arrangement of all atoms in $Na_{0.50}Ti_2O_4$ is very similar to those in $Na_{0.57}Ti_2O_4$. Therefore, the refinement was initiated using the final atomic parameters of $Na_{0.57}Ti_2O_4$. The converged R factors with anisotropic temperature factors were R = 0.047 and R_w = 0.047 [$w = 1/\sigma^2(F_o)$] for 1223 observed reflections, with shift/error less than 0.01. The refined occupancy factors for Na(1) and Na(2) sites

TABLE I

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA OF $Na_xTi_2O_4$

Chemical formulae	$Na_{0.57}Ti_2O_4$	$Na_{0.50}Ti_2O_4$
Space group	*Pnam*	*Pnam*
a (Å)	9.486(2)	9.616(3)
b (Å)	11.307(3)	11.134(5)
c (Å)	2.9450(8)	2.9541(11)
V (Å^3)	315.9(1)	316.3(2)
Z	4	4
Density (calculated) (g/cm^3)	3.637	3.598
Maximum 2θ (°)	90	90
Absorption coefficient for Mo$K\alpha$ (cm^{-1})	49.2	49.0
Scan width of 2θ (°)	$1.1 + 0.5 \tan \theta$	$1.1 + 0.5 \tan \theta$
Scan speed (°/min)	1	1
Number of independent reflections	1469	1453
Number of used reflections ($>3\ \sigma$)	1040	1223
Final R	0.054	0.047
Final R_w [$w = 1/\sigma^2(F_o)$]	0.042	0.047

were 0.33(1) and 0.17(1), respectively, and the equivalent isotropic temperature factors of them were 5.14 and 2.89 Å^2, respectively. The final difference Fourier map showed no significant residual electron density.

The scattering factors for neutral atoms tabulated by Cromer and Mann (*8*) were used in the calculations. The anomalous dispersion correction factors were taken from "International Tables for X-Ray Crystallography," Vol. IV (*9*). The experimental and crystallographic data for both $Na_{0.57}Ti_2O_4$ and $Na_{0.50}Ti_2O_4$ are summarized in Table I. The final atomic coordinates and temperature factors are given in Tables

TABLE II

ATOMIC POSITIONAL PARAMETERS, SITE OCCUPANCY, AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR $Na_{0.57}Ti_2O_4$

Atom	x	y	z	Occupancy	B_{eq}
Na(1)	0.0914(9)	0.6059(8)	0.25	0.34(1)	2.31
Na(2)	0.3958(15)	0.0672(14)	0.25	0.23(1)	6.74
Ti(1)	0.26365(10)	0.83821(9)	0.25	1.00	0.77
Ti(2)	0.02034(9)	0.12121(8)	0.25	1.00	0.56
O(1)	0.3696(4)	0.6921(3)	0.25	1.00	0.81
O(2)	0.1421(4)	0.4074(3)	0.25	1.00	0.70
O(3)	0.3635(4)	0.2706(3)	0.25	1.00	0.55
O(4)	0.1033(3)	0.9608(3)	0.25	1.00	0.56

TABLE III

ANISOTROPIC TEMPERATURE FACTORS[a] FOR $Na_{0.57}Ti_2O_4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}
Na(1)	0.0042(9)	0.0014(6)	0.14(2)	0.0007(5)
Na(2)	0.0043(16)	0.0036(13)	0.49(9)	−0.0019(11)
Ti(1)	0.00144(7)	0.00261(7)	0.0133(8)	0.00059(6)
Ti(2)	0.00103(6)	0.00142(5)	0.0167(8)	0.00003(5)
O(1)	0.0020(3)	0.0022(3)	0.016(4)	0.0008(2)
O(2)	0.0013(3)	0.0022(3)	0.014(3)	0.0005(2)
O(3)	0.0013(3)	0.0012(2)	0.015(3)	−0.0001(2)
O(4)	0.0008(3)	0.0015(2)	0.017(3)	0.0004(2)

[a] $\beta_{13} = \beta_{23} = 0$.

II and III for $Na_{0.57}Ti_2O_4$ and in Tables IV and V for $Na_{0.50}Ti_2O_4$.

Description and Discussion of Structures

The present $Na_xTi_2O_4$ ($0.50 \leqq x \leqq 0.57$) is isostructural with $Na_xFe_xTi_{2-x}O_4$ ($0.90 > x > 0.75$) (*1*). Figure 1 shows the crystal structure of $Na_{0.57}Ti_2O_4$ projected on the (001) plane. As required by space group *Pnam*, all atoms lie in the planes at $z = \frac{1}{4}$ or $z = \frac{3}{4}$, the repeat distance of 2.9450 Å to the *c*-axis direction being both the oxygen–oxygen edge length of TiO_6 octahedra and, necessarily, the metal–metal distance to the *c*-axis direction. The basic unit of the structure, as in $NaTi_2O_4$ (*3*) and other $CaFe_2O_4$-type isomorphs is a pair, or double block, of edge-shared octahedra with their axes normal to the *c*-axis. In the present structure, however, the double blocks are further condensed by edge sharing, giving a distorted Z-shaped group of four TiO_6 octahedra, as viewed in the projection on the (001) plane (Fig. 2). This Z-shaped group extends as an infinite ribbon in the *c*-axis direction, and is linked by sharing vertices to four other Z groups reversed with respect to it. As a result of the corner-joining of four Z groups, large tunnels elongated along the *c*-axis are produced in the structure. Sodium atoms are located in the tunnels, bonded weakly to four Z groups by the electrostatic force. Selected interatomic distances and

TABLE IV

ATOMIC POSITIONAL PARAMETERS, SITE OCCUPANCY, AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR $Na_{0.50}Ti_2O_4$

Atom	*x*	*y*	*z*	Occupancy	B_{eq}
Na(1)	0.0803(11)	0.6048(10)	0.25	0.33(1)	5.14
Na(2)	0.4103(18)	0.0752(13)	0.25	0.17(1)	2.89
Ti(1)	0.25850(9)	0.83690(8)	0.25	1.00	0.86
Ti(2)	0.02124(8)	0.12408(7)	0.25	1.00	0.63
O(1)	0.3682(4)	0.6899(3)	0.25	1.00	0.84
O(2)	0.1500(3)	0.4044(3)	0.25	1.00	0.80
O(3)	0.3683(3)	0.2670(3)	0.25	1.00	0.72
O(4)	0.0995(3)	0.9573(3)	0.25	1.00	0.64

TABLE V

ANISOTROPIC TEMPERATURE FACTORS[a] FOR $Na_{0.50}Ti_2O_4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}
Na(1)	0.0095(16)	0.0068(11)	0.24(4)	0.0020(10)
Na(2)	0.0053(19)	0.0015(10)	0.17(5)	−0.0008(11)
Ti(1)	0.00207(7)	0.00227(6)	0.0197(8)	0.00060(5)
Ti(2)	0.00154(6)	0.00127(4)	0.0198(7)	−0.00001(4)
O(1)	0.0027(3)	0.0016(2)	0.021(3)	0.0010(2)
O(2)	0.0023(3)	0.0018(2)	0.019(3)	0.0007(2)
O(3)	0.0020(3)	0.0015(2)	0.020(3)	0.0000(2)
O(4)	0.0016(3)	0.0014(2)	0.017(3)	0.0003(2)

[a] $\beta_{13} = \beta_{23} = 0$.

bond angles calculated using the UMBADTEA program (*10*) are listed in Table VI for $Na_{0.57}Ti_2O_4$ and Table VII for $Na_{0.50}Ti_2O_4$.

One Z group consists of two types of octahedra, $Ti(1)O_6$ and $Ti(2)O_6$. The average octahedral Ti(1)–O and Ti(2)–O distances are 1.980 and 2.008 Å for $Na_{0.57}Ti_2O_4$, and 1.978 and 2.001 Å for $Na_{0.50}Ti_2O_4$, respectively. The differences between the average Ti(1)–O and Ti(2)–O distances in both $Na_{0.57}Ti_2O_4$ and $Na_{0.50}Ti_2O_4$ are within 0.028 and 0.023 Å, respectively, which are smaller than the difference of the effective ionic radii, 0.065 Å, between Ti^{3+} (0.670 Å) and Ti^{4+} (0.605 Å) tabulated by Shannon (*11*). This fact suggests that all Ti sites are randomly occupied by Ti^{3+} and Ti^{4+} cations in both $Na_{0.57}Ti_2O_4$ and $Na_{0.50}Ti_2O_4$, as in the cases of $NaTi_2O_4$ (*3*) and $Na_{1.7}Ti_6O_{11}$ (*4*). On the other hand, the average Ti–O distances in $Na_xTi_2O_4$ decrease with decreasing the Na-content, in agreement with the fact that the mean oxidation state of titanium increases as well.

A distortion of the octahedron or a shift of metal position from the center of the octahedron is always observed in double and triple rutile-type compounds, e.g., $NaTi_2O_4$

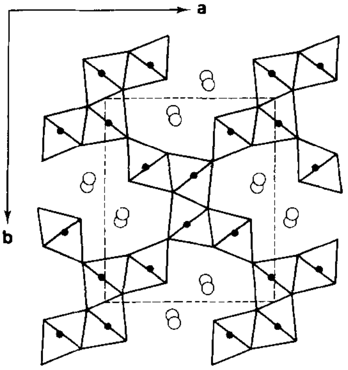

FIG. 1. Crystal structure of $Na_{0.57}Ti_2O_4$ viewed along [001]. TiO_6 unit is illustrated as an octahedron. Ti and Na atoms are represented as small black and large open circles, respectively.

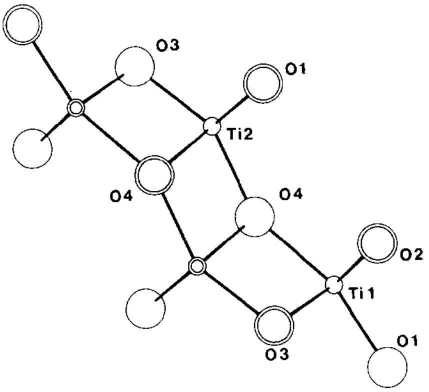

FIG. 2. The Z-shaped group formed by four TiO_6 octahedra in $Na_{0.57}Ti_2O_4$ viewed along [001]. Single circles show sites at $z = \frac{1}{4}$ and double circles show sites at $z = \frac{3}{4}$.

TABLE VI

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $Na_{0.57}Ti_2O_4$

Na(1)—O(1)	2.813(9)	O(1)—Ti(1)—O(3)	89.28(13)
Na(1)—(1′)	3.106(9)	O(1)—Ti(1)—O(2)	96.13(13)
Na(1)—O(2)	2.665(7) ×2	O(1)—Ti(1)—O(4)	163.65(15)
Na(1)—O(2′)	2.295(9)	O(3)—Ti(1)—O(3)	91.78(14)
Na(1)—O(3)	2.413(7) ×2	O(3)—Ti(1)—O(2)	82.69(11)
		O(3)—Ti(1)—O(4)	79.41(12)
Mean	2.624	O(2)—Ti(1)—O(2)	102.24(17)
		O(2)—Ti(1)—O(4)	94.06(13)
Na(2)—O(1)	3.241(13) ×2		
Na(2)—O(2)	2.359(13) ×2		
Na(2)—O(2′)	2.354(14)		
Na(2)—O(3)	2.321(16)		
Na(2)—O(4)	3.025(15)	O(1)—Ti(2)—O(1)	96.40(16)
		O(1)—Ti(2)—O(3)	98.66(13)
Mean	2.700	O(1)—Ti(2)—O(4)	87.22(10)
		O(1)—Ti(2)—O(4′)	99.33(13)
		O(3)—Ti(2)—O(4′)	152.86(15)
Ti(1)—O(1)	1.933(4)	O(4)—Ti(2)—O(4′)	79.45(12)
Ti(1)—O(3)	2.051(3) ×2	O(3)—Ti(2)—O(4)	81.31(12)
Ti(1)—O(2)	1.892(2) ×2	O(4)—Ti(2)—O(4)	89.15(13)
Ti(1)—O(4)	2.058(4)		
Mean	1.980		
Ti(2)—O(1)	1.975(2) ×2		
Ti(2)—O(3)	1.926(4)		
Ti(2)—O(4)	2.098(2) ×2		
Ti(2)—O(4′)	1.977(4)		
Mean	2.008		

(*3*), $Na_{2.08}Ti_4O_9$ (*12*), $Na_4Ti_5O_{12}$ (*13*), $Na_4Mn_4Ti_5O_{18}$ (*14*), and hollandite and its related minerals (*15–17*). A similar feature can be seen in the present $Na_xTi_2O_4$. The O(1)–Ti(1)–O(4) and the O(3)–Ti(2)–O(4′) angles are 163.65(15)° and 152.86(15)° for $Na_{0.57}Ti_2O_4$, and 164.03(14)° and 151.57(14)° for $Na_{0.50}Ti_2O_4$, respectively. These values are much smaller than the 180° found in the regular octahedron. This fact becomes understandable by an explanation in terms of electrically repulsive forces between Ti–Ti cations through the shared edge in the rutile-type chain (Fig. 2). As a result, the Ti(1)–Ti(2) and Ti(2)–Ti(2) distances through the shared O–O edges are 3.104(1) and 3.135(2) Å for $Na_{0.57}Ti_2O_4$, and 3.099(1) and 3.159(2) Å for $Na_{0.50}Ti_2O_4$, respectively, which are longer than the repeat distances of the *c*-axis, 2.9450 Å for $Na_{0.57}Ti_2O_4$ and 2.9541 Å for $Na_{0.50}Ti_2O_4$.

In the large tunnel in $Na_xTi_2O_4$, the poor occupation by sodium ions enables a coexistence of the two types of sodium sites with the very short Na(1)–Na(2) distance of about 1.5 Å along the *c*-axis direction. It is interesting to note that the oxygen coordination environment in the tricapped trigonal prismatic forms around the Na(1) and Na(2) sites resemble each other (Fig. 3). The long distances of Na(1)–O(4) and Na(2)–O(1′) in $Na_xTi_2O_4$ result in the actual sevenfold

TABLE VII

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $Na_{0.50}Ti_2O_4$

Na(1)—O(1)	2.926(12)	O(1)—Ti(1)—O(3)	90.17(12)
Na(1)—O(1′)	3.064(11)	O(1)—Ti(1)—O(2)	94.74(12)
Na(1)—O(2)	2.664(10) ×2	O(1)—Ti(1)—O(4)	164.03(14)
Na(1)—O(2′)	2.329(11)	O(3)—Ti(1)—O(3)	91.19(13)
Na(1)—O(3)	2.385(9) ×2	O(3)—Ti(1)—O(2)	82.24(10)
		O(3)—Ti(1)—O(4)	78.73(11)
Mean	2.631	O(2)—Ti(1)—O(2)	103.85(16)
		O(2)—Ti(1)—O(4)	95.09(12)
Na(2)—O(1)	3.314(15) ×2	O(1)—Ti(2)—O(1)	97.69(15)
Na(2)—O(2)	2.477(12) ×2	O(1)—Ti(2)—O(3)	100.40(12)
Na(2)—(2′)	2.316(17)	O(1)—Ti(2)—O(4)	86.02(10)
Na(2)—O(3)	2.173(15)	O(1)—Ti(2)—O(4′)	98.20(11)
Na(2)—O(4)	3.264(17)	O(3)—Ti(2)—O(4′)	151.57(14)
Mean	2.762		
Ti(1)—O(1)	1.947(3)	O(4)—Ti(2)—O(4′)	78.83(11)
Ti(1)—O(3)	2.068(2) ×2	O(3)—Ti(2)—O(4)	81.20(11)
Ti(1)—O(2)	1.876(2) ×2	O(4)—Ti(2)—O(4)	90.18(13)
Ti(1)—O(4)	2.034(3)		
Mean	1.978		
Ti(2)—O(1)	1.962(2) ×2		
Ti(2)—O(3)	1.906(3)		
Ti(2)—O(4)	2.086(2) ×2		
Ti(2)—O(4′)	2.004(3)		
Mean	2.001		

Na–O coordination in both sites (Tables VI and VII). From these facts, it is possible to say that both of the sodium sites are energetically stable in the tunnel space, and are occupied only in the case of a small Na content. This occupation feature for the tunnel space has not been observed in the case of $Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$ (*1*), because of the high occupancy value of 0.9. With decreasing the Na content in $Na_xTi_2O_4$ from $x = 0.57$ to $x = 0.50$, the occupancy factors of the Na(1) site are almost uniformly unchanged; 0.34(1) for $x = 0.57$ and 0.33(1) for $x = 0.50$, whereas those of the Na(2) site decrease from 0.23(1) for $x = 0.57$ to 0.17(1) for $x = 0.50$. However, the thermal vibrations toward the tunnel direction increase in the Na(1) site from $\beta_{33} = 0.14(2)$ to 0.24(4), together with a decrease in Na content. These results suggest an easy migration of Na ions toward the tunnel direction at room temperature, together with the oxidation of Ti cations.

The basic arrangements of atoms in $Na_xTi_2O_4$ are not changed in the homogeneity range of $0.50 \leqq x \leqq 0.57$. In contrast, a considerable change in the lattice parameters is observed with decreasing the Na content from $x = 0.57$ to $x = 0.50$ (Table I). The *a*-axis length of $Na_{0.50}Ti_2O_4$ is longer by

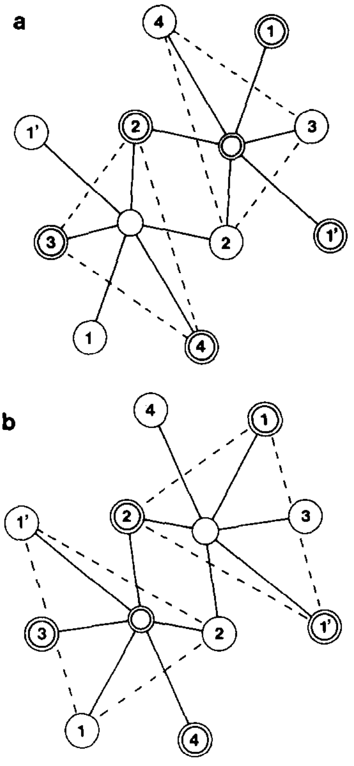

FIG. 3. The Na–O coordination environment around (a) Na(1) and (b) Na(2) sites in $Na_{0.57}Ti_2O_4$. Single circles show sites at $z = \frac{1}{4}$ and double circles show sites at $z = \frac{3}{4}$. The number of oxygen atoms is in accordance with Table VI.

0.13 Å than that of $Na_{0.57}Ti_2O_4$, while the b-axis length of $Na_{0.50}Ti_2O_4$ is smaller by 0.17 Å than that of $Na_{0.57}Ti_2O_4$. The difference in the c-axis length is, however, less than 0.01 Å. As a result, the unit cell volume in $Na_xTi_2O_4$ ($0.50 \leqq x \leqq 0.57$) is almost constant. Similar tendency has been observed in $Na_xFe_xTi_{2-x}O_4$ ($0.90 > x > 0.75$), although the degree of lattice parameter change was very slight (*1*).

In the tunnel structure of $Na_xTi_2O_4$, sodium ions in the tunnel space probably play a role in keeping the framework structure, connecting the surrounding Z groups. With a decrease of sodium content from 0.57 to 0.50, the effective charges in the tunnel space decrease. This causes an increase in the oxygen–oxygen repulsion between the Z groups. Therefore, to minimize the repulsive forces, the Z groups have a tendency to rotate around the inversion center to the direction parallel to the a-axis in the manner of maintaining the $Na_xTi_2O_4$ structure. By this rotation of the Z groups, the average sevenfold Na–O distances for both Na(1) and Na(2) sites in $Na_xTi_2O_4$ increase by 0.007 Å and 0.062 Å, respectively, with decreasing the Na-content from $x = 0.57$ to $x = 0.50$ (Tables VI and VII). This brings a slight increase in the tunnel volume.

Conclusion

We have succeeded in the preparation of $Na_xTi_2O_4$ crystals with $x \approx 0.6$, which are isostructural with the previously reported structure $Na_xFe_xTi_{2-x}O_4$ ($0.90 > x > 0.75$) (*1*), by the reactions of sodium metal and titanium oxides at the high temperature of 1723 K. From the results of single crystal X-ray structure analyses of two specimens, as-grown $Na_{0.57}Ti_2O_4$ and $Na_{0.50}Ti_2O_4$ derived by air oxidation, the intrinsical homogeneity range of $Na_xTi_2O_4$ at room temperature has been confirmed to be $0.50 \leqq x \leqq 0.57$ in this study.

In our recent study, three members of the mixed-valence sodium titanates, $NaTi_2O_4$ (*3*), $Na_{2.08}Ti_4O_9$(*12*), and $Na_{1.7}Ti_6O_{11}$ (*4*), have been originally synthesized. All of them belong to the rutile-related-type sodium tunnel structure, which is characterized by the short cell constant of about 3.0 Å, which is the length of the TiO_6 octahedral edge. The present $Na_xTi_2O_4$ with large tunnel spaces which consist of TiO_6 octahedral chains can be classified into this structure group in the Na_2O–Ti_2O_3–TiO_2 system.

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