Na$_{1.7}$Ti$_6$O$_{11}$: A New Mixed-Valence Nonstoichiometric Sodium Titanate with a Tunnel Structure

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From the high-temperature reaction of sodium metal and titanium oxide, a new member of Ti^{3+}/Ti^{4+} mixed valence sodium titanates, Na$_{1.7}$Ti$_6$O$_{11}$, was prepared. It is black in color and crystallizes in the tetragonal system, space group $P4_2/mnm$ with lattice constants $a = 11.7456(10)$ Å, and $c = 2.9866(8)$ Å, $V = 412.03(12)$ Å^3, and $Z = 2$. The structure was determined from a single-crystal X-ray diffraction study and refined to values of the conventional R factors of $R = 0.038$ and $R_w = 0.025$ for 783 observed reflections. The basic units of the structure are built up from six edge-shared TiO$_6$ octahedra, and they are linked along the c-axis by sharing edges to form rutile-type chains, as in the case of CaFe$_2$O$_4$-type NaTi$_2$O$_4$ and Na$_2$Ti$_4$O$_9$. Sodium atoms are located in the tunnels with an occupancy factor of 0.84(1), and two types of Ti sites are randomly occupied by Ti^{3+} and Ti^{4+} cations. © 1990 Academic Press, Inc.

Introduction

During investigations of the system Na$_2$O–Ti$_2$O$_3$–TiO$_2$, we have found two members of mixed-valence sodium titanates, CaFe$_2$O$_4$-type NaTi$_2$O$_4$ (*1*) and Na$_2$Ti$_4$O$_9$ (*2*), and determined their crystal structures. The framework of these compounds consists of edge-shared rutile-type TiO$_6$ chains with repeat distances of about 3.0 Å, which form a tunnel structure. This is quite different from those of the other sodium titanates previously reported, e.g., Na$_2$Ti$_3$O$_7$ (*3*), Na$_2$Ti$_9$O$_{19}$ (*4*), and bronze-type Na$_x$TiO$_2$ (0.20 ≤ x ≤ 0.25) (*5, 6*). Similar tunnel structures with rutile-type chains are observed in some mixed valence alkali or alkaline-earth titanates and manganates, e.g., Na$_x$MnO$_2$ (x ≤ 1) (*7*), Na$_4$Mn$_4$Ti$_5$O$_{18}$ (*8*), and hollandite-type compounds (*9–11*).

We have examined the system Na$_2$O–Ti$_2$O$_3$–TiO$_2$ by the reactions of metallic sodium and titanium oxides at high temperatures between 1173 and 1723 K so as to separate some new crystals with Ti^{3+}/Ti^{4+} mixed-valence states for determining the crystal structures as well as their physical properties. In this paper, we describe the synthesis and crystal structure of a new nonstoichiometric tetragonal phase having the formula Na$_{1.7}$Ti$_6$O$_{11}$.

Experimental and Results

Sample Preparation

Excess metallic sodium blocks with 99% purity and Ti$_2$O$_3$ powder synthesized by the reaction of Ti and TiO$_2$ were placed in a sealed iron vessel, heated in a resistance furnace at 1473 K in an argon gas flow for

several hours, and slowly cooled to room temperature at a rate of about 15°C/hr. A considerable leakage of excess sodium vapor from the vessel was often observed.

Some black, electrically conductive crystals with tabular shape, $0.1 \times 0.1 \times 0.03$ mm in maximum size, were found on the surface of aggregated Ti_2O_3 grains. At the same time, very small TiO crystals, $0.03 \times 0.03 \times 0.01$ mm in size, were commonly observed as golden particles in the Ti_2O_3 powder. Electron microprobe analyses showed that the black crystals were sodium titanate and that they were free from iron contamination from the vessel. The chemical formula of the new phase derived from the present structure analysis is $Na_{1.68(1)}Ti_6O_{11}$.

Precession photographs indicate that the crystals belong to the tetragonal system with possible space group $P\bar{4}n2$, $P4_2nm$, or $P4_2/mnm$. The X-ray powder diffraction data of this phase, obtained on a powder diffractometer at a scan rate of 1°/min in 2θ using graphite-monochromatized $CuK\alpha$ radiation and Si internal standard, was listed in Table I. The lattice parameters, determined by a least-squares refinement using the 2θ values of 25 strong reflections in the range of 20–30° on an automated Rigaku AFC-5 four-circle diffractometer, are $a = 11.7456(10)$ Å, $c = 2.9866(8)$ Å, and $V = 412.03(12)$ Å^3. Details of the crystal structure will be presented in a later section.

To synthesize more stoichiometric and larger crystals, further experiments were carried out by the reactions of metallic sodium and a mixture of TiO_2 and Ti_2O_3 powder using similar iron vessels at 1173–1723 K. At soaking temperatures below 1273 K, only $NaTi_2O_4$ needle crystals with Ti_2O_3 powder were obtained. At temperatures between 1473 and 1673 K, three phases, $NaTi_2O_4$, Ti_2O_3, and $Na_{1.7}Ti_6O_{11}$, were always found, and a single phase of $Na_{1.7}Ti_6O_{11}$ could not be realized under these conditions. EPMA revealed that the crystals of

TABLE I

X-Ray Powder Diffraction Data for $Na_{1.7}Ti_6O_{11}$

$h\ k\ l$	d_{calcd} (Å)	d_{obsd} (Å)	I/I_0
1 1 0	8.31	8.35	6
2 0 0	5.873	5.890	47
2 1 0	5.253	5.253	100
2 2 0	4.153	4.152	89
3 1 0	3.714	3.720	33
3 2 0	3.258	3.260	10
4 1 0	2.849	2.849	92
3 3 0	2.768	2.768	40
4 2 0	2.626	2.628	12
2 1 1	2.596	2.594	36
3 0 1	2.375	2.376	15
4 3 0	2.349	2.349	35
5 1 0	2.304	2.305	13
3 2 1	2.201	2.200	30
5 2 0	2.181	2.180	11
4 4 0	2.076	2.077	16
4 1 1	2.061	2.054	17
3 3 1	2.030	2.027	100
5 3 0	2.014	2.014	18
6 0 0	1.958	1.963	3
6 1 0	1.931	1.933	4
5 0 1	1.846 ⎫		
4 3 1	1.846 ⎭	1.846	12
5 4 0	1.834	1.834	19
5 2 1	1.761	1.762	3
6 3 0	1.751	1.751	7
5 3 1	1.670 ⎫		
5 5 0	1.661 ⎬	1.663	6
7 1 0	1.661 ⎭		
6 4 0	1.629	1.628	12
6 1 1	1.622	1.621	23
6 2 1	1.577	1.578	7
5 4 1	1.563	1.563	8
7 3 0	1.542	1.542	2
6 3 1	1.510	1.510	2
0 0 2	1.493	1.494	15
8 0 0	1.468	1.467	9
7 0 1	1.463	1.463	13
7 4 0	1.457 ⎫		
8 1 0	1.457 ⎭	1.458	12
5 5 1	1.452 ⎫		
7 1 1	1.452 ⎭	1.451	20
2 0 2	1.447	1.447	7
7 2 1	1.420	1.419	9
2 2 2	1.405	1.403	4
3 1 2	1.386 ⎫		
6 6 0	1.384 ⎭	1.385	4
7 3 1	1.370	1.370	6

$Na_{1.7}Ti_6O_{11}$ were almost uniform in chemical composition, and neither more nor less sodium-deficient samples could be prepared. The nonstoichiometry in $Na_{1.7}Ti_6O_{11}$ may be decided by the sodium vapor pressure in the vessel, which maintains the lower valency sodium titanate melt at high temperatures.

The $Na_{1.7}Ti_6O_{11}$ crystals were commonly grown in a needle shape with an average size of $0.1 \times 0.005 \times 0.005$ mm, as shown in Fig. 1. Large crystals of $Na_{1.7}Ti_6O_{11}$, $0.50 \times 0.50 \times 0.10$ mm in maximum size, were occasionally obtained at 1723 K. These crystals were, however, contaminated by a small amount of impurities such as Si, Mn, and Rh, which were supposed to come from the partially melted iron vessel. Even in these specimens, iron contamination from the vessel was scarcely observed.

$Na_{1.7}Ti_6O_{11}$ crystals are stable in air at room temperature. This fact shows a sharp contrast to the mixed-valence sodium titanate crystals, such as rhombohedral $Na_x TiO_2$ $(x \sim 0.5)$ (12) and $Na_2Ti_4O_9$ (2), where the oxidation reaction together with in-creasing Na defects occurred vigorously in air.

Structure Determination

A small tabular crystal, which was free from impurities and $0.093 \times 0.093 \times 0.025$ mm 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 a four-circle diffractometer (operating conditions: 40 kV, 30 mA) using graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.71069$ Å). The fluctuation of the intensities, monitored by examining a set of three standard reflections ((800),(450),(002)) taken after every 50 observations, was within 1.5%. A total of 1003 independent reflections were obtained within the limit of $2\theta \leq 90°$, of which 783 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 or extinction corrections were performed.
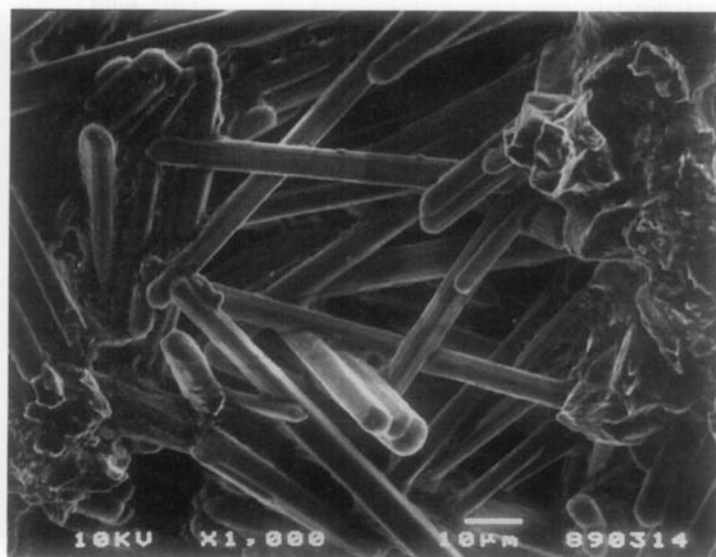

FIG. 1. SEM photograph of typical needle-shaped $Na_{1.7}Ti_6O_{11}$ crystals.

TABLE II

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA
OF $Na_{1.68}Ti_6O_{11}$

Space group	$P4_2/mnm$
Crystal size (mm)	$0.093 \times 0.093 \times 0.025$
a (Å)	11.7456(10)
c (Å)	2.9866(8)
V (Å^3)	412.03(12)
Z	2
Density (calcd) (g/cm^3)	4.050
Maximum 2θ (°)	90
Absorption coefficient for MoKα (cm^{-1})	56.4
Scan width of 2θ (°)	$1.0 + 0.5 \tan \theta$
Scan speed (°/min)	1
Number of independent reflections	1003
Number of used reflections	783 ($>3\sigma$)
Final R	0.038
Final R_w [$w = 1/\sigma^2(F_o)$]	0.025

Initial positions for two titanium atoms were determined by the direct method using the computer program MULTAN80 system (13). At first, the space group of highest symmetry $P4_2/mnm$, confirmed by successful refinement, was adopted. Fourier and difference Fourier syntheses using the GSFFR program (14) revealed the positions of oxygen and sodium atoms. The crystal structure factors F_c were calculated with an overall temperature factor 0.77. The R value was 0.195, showing that the structure model adopted was reasonable. Then, the atomic parameters, scale, and temperature factors were refined by the full-matrix least-squares method using

RFINE-II program (15). The converged R values with isotropic and anisotropic temperature factors were 0.066 and 0.046, respectively. However, a difference Fourier map showed significant residual electron density at the sodium position, despite a large thermal parameter, $B_{eq} = 3.5$ Å^2. Subsequent site occupancy refinement indicated that the occupancy of Na site was close to 0.84 with a temperature factor $B_{eq} = 2.2$ Å^2, and the residual peak in the difference Fourier map had completely disappeared. Finally, the structure was refined to $R = 0.038$ and $R_w = 0.025$ [$w = 1/\sigma^2(F_o)$] for 783 reflections, with shift/error for all parameters less than 0.01.

The scattering factors for neutral atoms tabulated by Cromer and Mann (16) were used in the calculations. The anomalous dispersion correction factors were taken from "International Tables for X-ray Crystallography" (17). The experimental and crystallographic data are summarized in Table II. The final atomic coordinates and temperature factors are given in Table III and IV. The computations were performed on FACOM M-380R at ISSP.

Description and Discussion of the Structure

The crystal structure of $Na_{1.68}Ti_6O_{11}$ projected down the c-axis direction is shown in

TABLE III

ATOMIC POSITIONAL PARAMETERS, SITE OCCU-
PANCY, AND EQUIVALENT ISOTROPIC TEMPERATURE
FACTORS[a]

Atom	Position	x	y	z	Occupancy	B_{eq}
Na	4g	0.6935(1)	−0.6935	0.0	0.84(1)	2.23
Ti(1)	8i	0.46108(4)	0.19115(4)	0.0	1.0	0.66
Ti(2)	4g	0.91664(4)	−0.91664	0.0	1.0	0.56
O(1)	8i	0.2102(2)	0.0206(2)	0.0	1.0	0.60
O(2)	8i	0.6066(2)	0.1117(2)	0.0	1.0	0.71
O(3)	4f	0.3291(2)	0.3291	0.0	1.0	0.88
O(4)	2b	0.5	0.5	0.0	1.0	0.52

[a] B_{eq} is defined as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12})]$.

TABLE IV

ANISOTROPIC TEMPERATURE FACTORS[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}
Na	0.0021(1)	0.0021	0.123(4)	−0.0008(1)
Ti(1)	0.00136(3)	0.00142(3)	0.0128(4)	−0.00030(2)
Ti(2)	0.00111(2)	0.00111	0.0132(6)	−0.00025(3)
O(1)	0.0009(1)	0.0012(1)	0.018(2)	−0.00017(8)
O(2)	0.0013(1)	0.0015(1)	0.018(2)	0.00044(8)
O(3)	0.0019(1)	0.0019	0.015(2)	−0.0003(1)
O(4)	0.0010(1)	0.0010	0.013(3)	−0.0001(2)

[a] $\beta_{13} = \beta_{23} = 0$.
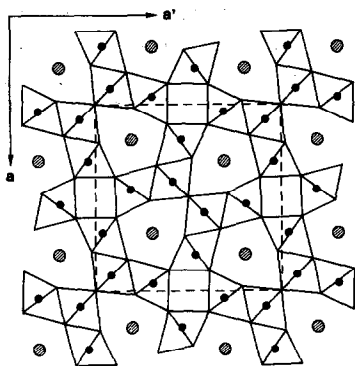
FIG. 2. Crystal structure of $Na_{1.68}Ti_6O_{11}$ viewed along [001]. The TiO_6 unit is illustrated as an octahedron. Ti and Na atoms are represented as small black and large line-shaded circles, respectively.

Fig. 2. The basic units of the structure consist of six TiO_6 octahedra sharing edges and vertices (Fig. 3). The units are linked along the c-axis by sharing edges, and connected with each other by sharing vertices to form a three-dimensional framework structure. As a result, four tunnels parallel to the c-axis are produced in the unit cell, and sodium atoms are located in the tunnels. On the fourfold axes, $(\frac{1}{2},0,z)$ and $(0,\frac{1}{2},z)$, small square tunnels are formed by four TiO_6 octahedra shared vertices (Fig. 2). These tunnels are identical with those in the rutile structure (18) except for a small distortion
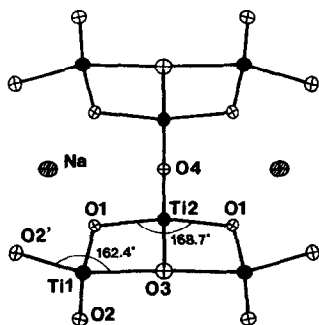
of the surrounding octahedra. Selected interatomic distances and bond angles calculated using the UMBADTEA program (19) are listed in Table V.

The $Ti(1)O_6$ octahedron is formed by five shorter bonds ranging from 1.947 to 2.015 Å with one additional longer $Ti(1)-O(3)$ bond at 2.242 Å (Fig. 3). As a result of this longer bond, the body diagonal $O(2')-O(3)$ distance is about 4.2 Å, which is considerably longer than the distance of about 3.8 Å in the regular TiO_6 octahedron. In contrast, the $Ti(2)-O$ distance varies in a smaller range of 1.926–2.085 Å, which gives an average value of 2.016 Å.

The sodium atom is surrounded by eight oxygen atoms in a bicapped trigonal prism which is similar to those around Ca and/or Na ions in the $CaFe_2O_4$-type compounds (20). The average Na–O distance (2.566 Å) is normal for eightfold coordination. The site occupancy for the Na atom is 0.84(1) for this crystal. The charge imbalance originating from the sodium defects is compensated by the oxidation of Ti^{3+} to Ti^{4+} in the octahedral chains.

From the calculation of the valence bond sums using Zachariasen's curve (21), the titanium valence charge in $Na_{1.68}Ti_6O_{11}$ is

FIG. 3. The basic unit of $Na_{1.68}Ti_6O_{11}$ viewed along [001], where each ellipsoid is scaled to include 75% probability.

TABLE V

SELECTED INTERATOMIC DISTANCES (Å) AND
BOND ANGLES (°)

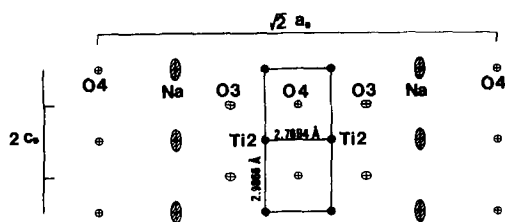|			
Na–O(1)	2.528(2) ×4	O(1)–Ti(1)–O(1)	95.62(8)
–O(2)	2.506(2) ×2	O(1)–Ti(1)–O(2)	83.10(6)
–O(3)	2.702(2) ×2	O(1)–Ti(1)–O(2')	88.35(6)
		O(1)–Ti(1)–O(3)	79.90(6)
Mean	2.566	O(2)–Ti(1)–O(2)	97.46(9)
		O(2)–Ti(1)–O(2')	97.91(9)
		O(2)–Ti(1)–O(3)	93.66(6)
Ti(1)–O(1)	2.015(1) ×2	O(2')–Ti(1)–O(3)	162.40(7)
–O(2')	1.947(2)		
–O(2)	1.987(1) ×2		
–O(3)	2.242(1)		
		O(1)–Ti(2)–O(1)	168.70(11)
Mean	2.032	O(1)–Ti(2)–O(3)	86.06(5)
		O(1)–Ti(2)–O(4)	93.84(4)
Ti(2)–O(1)	1.926(2) ×2	O(3)–Ti(2)–O(3)	91.50(6)
–O(3)	2.085(1) ×2	O(3)–Ti(2)–O(4)	87.09(3)
–O(4)	2.0365(4) ×2	O(4)–Ti(2)–O(4)	94.32(2)
Mean	2.016		

FIG. 4. The atomic arrangement on the (110) plane, where each ellipsoid is scaled to include 75% probability.

3.31, which is consistent with the average titanium valency of 3.39 from an estimation by the chemical formula with sodium site vacancy. On the other hand, the difference between the mean Ti(1)–O distance 2.032 Å and the mean Ti(2)–O distance 2.016 Å is 0.016 Å, which is smaller than the difference of the effective ionic radii, 0.065 Å, between Ti^{3+} (0.670 Å) and Ti^{4+} (0.605 Å) (22). This smallness is one of the important keys for providing the suggestion that both Ti sites in $Na_{1.68}Ti_6O_{11}$ are randomly occupied by Ti^{3+} and Ti^{4+} ions, as in the case of $NaTi_2O_4$ (1).

Figure 3 shows that both of the O(2')–Ti(1)–O(3) and O(1)–Ti(2)–O(1) angles, the values of which are 162.40 and 168.70°, respectively, are considerably smaller than 180° as in the regular octahedron. This fact becomes understandable in terms of electrical repulsive forces between Ti–Ti cations through the shared edge in the rutile-type chain (Fig. 3). As a result, the Ti(1)–Ti(2) distance through the shared O(1)–O(3) edge is 3.0849(5) Å, which is longer than the repeat distance of the c-axis (2.9866 Å). Such a distortion of the octahedron or a shift of metal position from the center of octahedron is observed in double and triple rutile-type compounds, $NaTi_2O_4$ (1), $Na_2Ti_4O_9$ (2), $Na_4Ti_5O_{12}$ (23), $Na_4Mn_4Ti_5O_{18}$ (8), and hollandite and its related minerals (24–26).

The Ti(2)–Ti(2) distance through the shared edge is 2.7694(7) Å (Fig. 4), which is considerably shorter than the repeat dis-

tance, 2.9866 Å, of the c-axis. The shortness may be caused by the distortion of the TiO_6 octahedra in the rutile-type chain (Fig. 3). Such a short Ti–Ti distance is also observed in the lower valency titanium oxides, i.e., Ti_2O_3 (2.579 Å) (27) and Ti_3O_5 (2.61 Å) (28).

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