JOURNAL OF SOLID STATE CHEMISTRY 79, 212–217 (1989)

Synthesis and Crystal Structure of $NaTi_2O_4$: A New Mixed-Valence Sodium Titanate

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Received September 26, 1988; in revised form December 27, 1988

A new sodium titanate, $NaTi_2O_4$, is black in color, has a needle shape, and crystallizes in the orthorhombic calcium ferrite-type structure, space group *Pnam* with $a = 9.2615(10)$ Å, $b = 10.7357(7)$ Å, $c = 2.9556(3)$ Å, and $Z = 4$. The structure was determined from a single-crystal X-ray study and refined to the conventional values $R = 0.029$ and $R_w = 0.034$ for 1856 observed reflections. The framework structure is built up from "double rutile" chains, and two types of Ti sites are randomly occupied by Ti^{3+} and Ti^{4+} ions. © 1989 Academic Press, Inc.

Introduction

Recently, a number of physical and chemical properties on sodium titanate bronze Na_xTiO_2 ($0.20 \leqq x \leqq 0.25$) have been reported (*1–3*). The framework structure of this compound, determined by Andersson and Wadsley (*4*), is slightly different from those of other Na_2O–TiO_2 compounds. Reid and Sienko (*5*) reported that Na_xTiO_2 gave an electronic spectral absorption supporting delocalization of *d* electrons of Ti^{3+}. On the other hand, in Na TiO_2, originally described by Hagenmuller *et al.* (*6*), all titanium ions are expected to be in trivalent state. However, a single-crystal study of this compound has not been made yet. No sodium titanate containing Ti^{3+} is known except for the above-mentioned two compounds.

We examined the system Na_2O–Ti_2O_3–TiO_2 and prepared single crystals of a new type of sodium titanate compound, Na Ti_2O_4. In this paper, the synthesis and crystal structure of $NaTi_2O_4$ are reported.

Experimental

Sample Preparation

A mixture of TiO and Ti_2O_3 was prepared by a solid-state reaction of Ti metal powder (99.9%) and TiO_2 (rutile + anatase, 99.9%) powder at 1773–1873 K in a vacuum. The mixture was blended with excess amorphous Na_2O (reagent, 98%) and placed in a sealed iron vessel. The vessel was heated in a resistance furnace at 1473 K in argon gas flow for several hours and then slowly cooled to room temperature. In many cases, the samples were partially oxidized on heating runs because of the reaction

$$Na_2O + Ti_2O_3 \rightarrow 2Na\uparrow + 2TiO_2.$$

In fact, leakage of excess Na gas from the vessel was observed. Black needle-type single crystals (maximum length 5 mm with 0.5 mm maximum diameter) together with colorless crystals were grown. The latter crystals were identified to be $Na_8Ti_5O_{14}$ (JCPDS 28-1155) by the X-ray powder diffraction method.

0022-4596/89 $3.00

Electron microprobe analyses showed that the black crystals were sodium titanate and were free from iron contamination from the vessel. A molar ratio of Na/Ti was approximately 1.0/2.1; however, the analytical values of 12 points varied widely from point to point. Table I shows the X-ray powder diffraction data of this compound obtained on a powder diffractometer at a scan rate of 1°/min in 2θ using graphite-monochromatized Cu$K\alpha$ radiation (λ = 1.5405 Å) and Si internal standard. Precession photographs indicate that the crystals belong to the orthorhombic system, space group *Pnam* or $Pna2_1$. The lattice parameters are very similar to those of $NaScTiO_4$ (*7*), which has the calcium ferrite $CaFe_2O_4$-type structure. These data lead us to the chemical formula $NaTi_2O_4$. The lattice parameters, determined by a least-squares refinement using the 2θ values of 25 strong reflections in the range 49–66° on an automated Rigaku AFC-5 four-circle diffractometer, are a = 9.2615(10) Å, b = 10.7537(7) Å, c = 2.9556(3) Å, V = 294.36(5) Å^3.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $NaTi_2O_4$

$h\ k\ l$	d_{calc}	d_{obs}	I/I_0
0 2 0	5.377	5.39	16
1 2 0	4.650	4.65	100
2 0 0	4.631		
2 2 0	3.509	3.51	7
3 1 0	2.967	2.971	2
0 1 1	2.850	2.840	1
0 4 0	2.688	2.689	91
3 2 0	2.677		
2 0 1	2.494	2.495	45
1 2 1	2.491		
2 1 1	2.427	2.431	4
3 3 0	2.339	2.344	1
0 3 1	2.280	2.284	5
4 1 0	2.264	2.263	5
1 3 1	2.214	2.214	17
4 2 0	2.127	2.128	10
1 5 0	2.095	2.094	19
3 1 1	2.094		
2 3 1	2.046	2.044	3
3 2 1	1.984	1.982	2
4 3 0	1.945	1.945	9
1 4 1	1.944		
2 4 1	1.827	1.825	36
5 1 0	1.825		
4 0 1	1.823		
4 1 1	1.797	1.798	6
0 6 0	1.792	1.790	9
1 6 0	1.760	1.760	6
4 4 0	1.754	1.752	7
5 2 0	1.751		
4 2 1	1.726	1.726	1
3 4 1	1.672	1.673	12
4 3 1	1.625	1.625	2
3 6 0	1.550	1.550	13
6 0 0	1.544	1.544	16
4 4 1	1.509	1.508	36
5 2 1	1.507		
0 0 2	1.478	1.478	6
2 6 1	1.455	1.455	7
6 4 0	1.340	1.340	6
1 8 0	1.330	1.330	4
6 2 1	1.326	1.327	3

Structure Determination

A small block crystal, 0.124 × 0.122 × 0.090 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 the four-circle diffractometer (operating conditions: 40 kV, 30 mA) using graphite-monochomatized Mo$K\alpha$ radiation (λ = 0.71069 Å). The fluctuation of the intensities, monitored by examining a set of three standard reflections ((080), (600), (002)) taken after every 100 observations, was within 1.4%. A total of 2101 independent reflections were obtained within the limit of $2\theta \leqq 110°$, of which 1856 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 made.

The Patterson maps showed that the arrangement of the atoms in $NaTi_2O_4$ is very similar to that in $NaScTiO_4$ (*7*). Therefore, the space group *Pnam*, confirmed by successful refinement, was adopted. The crystal structure factor F_c was calculated by GSFFR program (*8*) using the atomic coordinates of $NaScTiO_4$. The *R* value was 0.155, showing that the model was reasonable. Then, the atomic parameters and scale and temperature factors were refined by the full-matrix least-squares method using the program RFINE2 (*9*).

Site occupancy refinement was also applied for sodium at the final stage, however, which did not produce any improvement in the *R* value. Therefore, we proceeded in the structural refinement using the fixed occupancy (100%) for sodium site.

The least-squares refinements with the anisotropic temperature factors yielded the final $R = 0.029$ and weighted $R_w = 0.034$ [$w = 1/\sigma^2(F_o)$] for 1856 reflections. The maximum shift of the atomic parameters in the last cycles was less than 0.01 times the corresponding standard deviation. A difference Fourier synthesis using the final atomic parameters showed no significant residual peak. The scattering factors for the neutral Na, Ti, and O atoms tabulated by Cromer and Mann (*10*) were used in the calculations. The anomalous dispersion correction factors were taken from the "International Tables for X-Ray Crystallography" (*11*). The experimental conditions and crystallographic data are summarized in Table II. The final atomic coordinates and temperature factors are given in Table III.[1] The computations were performed on FACOM M-380R at ISSP.

TABLE II

CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA

Space group	*Pnam*
Crystal size (mm)	0.124 × 0.122 × 0.090
a (Å)	9.2615(10)
b (Å)	10.7537(7)
c (Å)	2.9556(3)
V (Å^3)	294.36(5)
Chemical formula	$NaTi_2O_4$
Z	4
Density (calc.) (g/cm^3)	4.126
Maximum 2θ (°)	110
Absorption coefficient for Mo*Kα* (cm^{-1})	53.4
Scan width of 2θ (°)	$1.0 + 0.5 \tan \theta$
Scan speed (°/min)	1
Number of independent reflections	2101
Number of used reflections	1856 (>3σ)
R	0.029
R_w	0.034

Description of the Structure and Discussion

The crystal structure of $NaTi_2O_4$ projected down the *c*-axis direction is shown in Fig. 1. The basic unit of the structure is the "double rutile" chain (*12*), in which a pair of or double edge-shared TiO_6 octahedra pile up along the *c*-axis with sharing edges (Fig. 2a). Four chains are linked by sharing vertices to form a three-dimensional framework structure and produce a single tunnel elongated to the *c*-axis. The sodium atoms are located in the tunnels, bonded weakly to four chains by the electrostatic force. The selected interatomic distances and bond angles calculated using UMBADTEA (*13*) are listed in Table IV.

Both Ti1 and Ti2 atoms are octahedrally coordinated by six oxygen atoms. The coordination environments of oxygen atoms around the Ti1 and Ti2 atoms are very similar. The Ti–O distance varies in the short range of 1.932–2.051 Å, which gives an average value 2.014 Å. However, the O3–Ti1–O4′ and O1–Ti2–O2′ angles, the val-

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[1] For a table of observed and calculated structure factors, see NAPS Document No. 04659 for 14 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $3.00 for each additional page. All orders must be prepaid.

TABLE III

ATOMIC POSITIONAL PARAMETERS[a] AND ANISOTROPIC TEMPERATURE FACTORS ($\times 10^5$)[b]

Atom	x	y	β_{11}	β_{22}	β_{33}	β_{12}	B_{eq} ($Å^2$)[c]
Na	0.24363(12)	0.34683(11)	198(10)	181(8)	226(11)	−4(7)	0.77
Ti1	0.06624(4)	0.10964(4)	102(3)	76(2)	141(3)	−13(2)	0.40
Ti2	0.08209(4)	0.60455(4)	113(3)	67(2)	117(3)	−2(2)	0.37
O1	0.2884(2)	0.6512(2)	108(12)	144(10)	159(14)	−14(9)	0.53
O2	0.3875(2)	0.9803(2)	107(12)	79(9)	131(13)	3(8)	0.40
O3	0.4795(2)	0.2177(2)	173(13)	64(8)	142(13)	−30(9)	0.46
O4	0.0801(2)	0.9304(2)	165(13)	81(9)	132(13)	21(9)	0.47

[a] All atoms in point position 4c, $\pm(x, y, \frac{1}{4})$, $\pm(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{4})$.

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

[c] B_{eq} is defined as $\frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$.

ues of which are 160.40° and 167.83°, respectively, are considerably smaller than 180° as in a regular octahedron (Table IV). Therefore, both Ti1–O and Ti2–O octahedra are apparently distorted. A similar distortion of metal–oxygen octahedra is observed in $CaFe_2O_4$-type compounds and $CaTi_2O_4$ (*14*), in which double-rutile chains are connected by sharing vertices in another way.

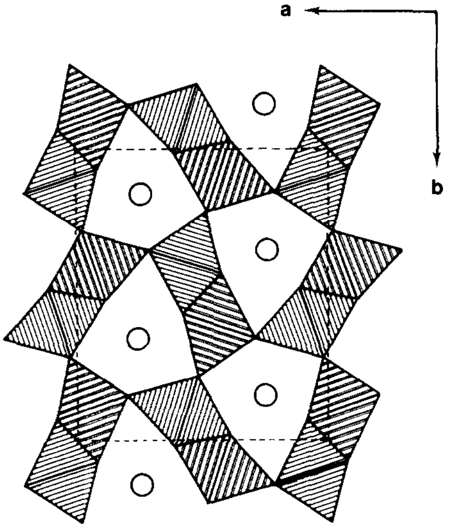

FIG. 1. Crystal structure of $NaTi_2O_4$ viewed along [001]. TiO_6 coordination octahedra are illustrated as octahedra shaded with double lines. Na atoms are shown as open circles.

The sodium atom is surrounded by eight oxygen atoms in a bicapped trigonal prism at an average of 2.481 Å. This coordination type is normal for sodium atoms. The ninth oxygen (Na–O1′ in Table IV; distance, 3.299 Å) in the same tunnel is too far away to be bonded.

The Ti^{3+}/Ti^{4+} ratio in $NaTi_2O_4$ is required to be 1 : 1 by the charge compensation. We note that the average Ti^{3+}–O distance in

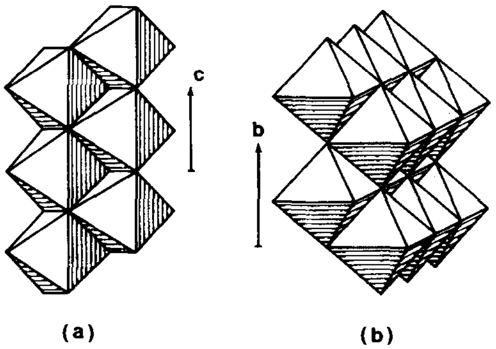

FIG. 2. (a) $Ti(1)O_6$ octahedral representation of "double rutile" chain in $NaTi_2O_4$. Repeat distance along the c-axis is 2.9556 Å. (b) Idealized TiO_6 octahedral representation of "zigzag ribbon" in $Na_2Ti_3O_7$ (*20*). Repeat distance along the b-axis is 3.804 Å.

TABLE IV

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Na–O1	2.588(2)	×2	O1–Ti1–O1	92.93(7)
–O2	2.392(2)	×2	O1–Ti1–O3	93.50(6)
–O3	2.588(2)		O1–Ti1–O4	87.72(5)
–O3′	2.543(2)		O1–Ti1–O4′	100.02(6)
–O4	2.378(2)	×2	O3–Ti1–O4	85.99(6)
–O1′	3.299(2)		O3–Ti1–O4′	160.40(7)
			O4–Ti1–O4	92.22(7)
Ti1–O1	2.049(1)	×2	O4–Ti1–O4′	80.47(6)
–O3	2.023(2)			
–O4	2.051(1)	×2		
–O4′	1.932(2)		O1–Ti2–O2	91.91(6)
Mean	2.026		O1–Ti2–O2′	167.83(7)
			O2–Ti2–O3	96.98(6)
Ti2–O1	1.975(2)		O2–Ti2–O2	94.55(7)
–O2	2.012(1)	×2	O2–Ti2–O2′	79.90(6)
–O2′	2.020(2)		O2–Ti2–O3	84.31(5)
–O3	1.997(1)	×2	O3–Ti2–O2′	91.18(6)
Mean	2.002		O3–Ti2–O3	95.44(7)

Ti_2O_3 (*15*) and $CaTi_2O_4$ (*14*) is 2.05 Å, while Ti^{4+}–O distances in rutile (*16*), ilmenite (*17*), perovskite (*18*), titanite (*19*), and sodium titanates (*20–22*) center around 1.97 Å. The average of these two (2.05 and 1.97 Å) is 2.01 Å, which is identical with the average Ti–O distance in $NaTi_2O_4$ (2.014 Å). In addition, the difference of the average Ti1–O distance (2.026 Å) from the average Ti2–O distance (2.002 Å) is 0.024 Å, which is remarkably smaller than the difference of the effective ionic radii, 0.06 Å, between Ti^{3+} (0.67 Å) and Ti^{4+} (0.61 Å) (*23*). These facts suggest that both types of Ti sites in $NaTi_2O_4$ are randomly occupied by Ti^{3+} and Ti^{4+} ions.

In the crystal structures of most sodium titanates elucidated, the length of the *b*-axis is about 3.8 Å (e.g., 3.804 Å in $Na_2Ti_3O_7$ (*20*), 3.784 Å in $Na_2Ti_4O_9$ (*24*), and 3.745 Å in $Na_2Ti_6O_{13}$ (*21*)), which corresponds to the diagonal length of the Ti–O octahedra (Fig. 2b). The basic frameworks of the above sodium titanates are built up from three or four Ti–O octahedra with sharing edges at the same height which combine similar units above and below into zigzag ribbons of the 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.

On the contrary, the length of the *c*-axis in $NaTi_2O_4$ is about 3.0 Å, which corresponds to the length of the Ti–O octahedral edge, that is, the oxygen–oxygen contact length as shown in Fig. 2a. Similar chains of Ti–O octahedra are also observed in rutile ($c = 2.959$ Å) and "double rutile"-type Ca Ti_2O_4 ($c = 3.136$ Å).

Acknowledgment

The authors thank Dr. I. Nakai, Department of Chemistry, the University of Tsukuba, for his help in X-ray intensity data collection and structure analysis.

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