

Growth and Structure Analysis of Nonstoichiometric Single Crystal Na_xTiO_2 ($x \sim 0.5$) with the $\alpha\text{-NaFeO}_2$ -Type Structure

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Single crystals of Na_xTiO_2 ($x \sim 0.5$) with the rhombohedral $\alpha\text{-NaFeO}_2$ -type structure were successfully prepared from high-temperature solutions of sodium metal and titanium dioxide. The structure refinement by a single crystal X-ray diffraction study confirmed a triangular lattice outstanding two-dimensionality of $\text{Na}_{0.54}\text{TiO}_2$ and the space group $R\bar{3}m$ with the final $R = 5.7\%$ ($R_w = 5.1\%$) for 170 independent observed reflections. The lattice parameters of the present $\text{Na}_{0.54}\text{TiO}_2$ crystal are $a = 2.9791(6)$ Å, $c = 16.928(3)$ Å, and $V = 130.11(5)$ Å³. These crystals are strongly attacked by air atmosphere, and a remarkable lattice contraction toward the c -axis direction in the trigonal lattice was observed when the Na contents were decreased. The most highly contracted lattice constants for the compound with the chemical formula $\text{Na}_{0.3}\text{TiO}_2$ are $a = 2.9665(5)$ Å, $c = 15.755(9)$ Å, and $V = 120.07(8)$ Å³. © 1990 Academic Press, Inc.

Introduction

NaTiO_2 was originally described by Hagemmüller *et al.* (1). They prepared powder samples using a redox reaction of metal sodium and titanium dioxide at 1173 K, and revealed from the result of X-ray powder diffraction that this compound had a rhombohedral unit cell and the $\alpha\text{-NaFeO}_2$ -type structure with the hexagonal lattice constants of $a = 3.02$ and $c = 16.2$ Å (JCPDS 16-251).

Hirakawa *et al.* (2) first pointed out that NaTiO_2 and LiNiO_2 were promising candidates of two-dimensional triangular lattice antiferromagnet with $S = 1/2$. To clarify the physical properties of NaTiO_2 , Hirakawa *et al.* (2) successfully prepared NaTiO_2 powder samples using the reaction of Na_2O with Ti_2O_3 at 1273 K under high-pressure Ar gas atmosphere.

Recently, Maazaz *et al.* (3) examined the structures of the Na_xTiO_2 system ($0.46 \leq x \leq 1$) by the electrochemical deintercalation from the stoichiometric NaTiO_2 powder. They reported Na_xTiO_2 ($0.94 \leq x \leq 1$) crystallized in the rhombohedral system, while Na_xTiO_2 ($0.71 \leq x \leq 0.87$) had the monoclinic lattice parameters, $a = 5.157$, $b = 2.977$, $c = 6.652$ Å, and $\beta = 122.4^\circ$. In addition, the further deintercalation yielded the irreversible rhombohedral Na_xTiO_2 phase in the range of $0.46 \leq x \leq 0.67$. In order to investigate the more precise structural and physical properties, single crystals of the compounds in the Na_xTiO_2 system ($x \leq 1$) were needed.

During investigations of the system $\text{Na}_2\text{O-Ti}_2\text{O}_3\text{-TiO}_2$, we have recently synthesized new members of sodium titanates, CaFe_2O_4 -type NaTi_2O_4 (4), $\text{Na}_2\text{Ti}_4\text{O}_9$ (5), and $\text{Na}_{1.7}\text{Ti}_6\text{O}_{11}$ (6) by the reactions of Na,

Na_2O , TiO_2 , Ti_2O_3 , and TiO at 1273–1473 K using sealed iron vessels. On the other hand, Brohan *et al.* (7) produced stoichiometric small platelet-like crystals of bronze-type $\text{Na}_{0.25}\text{TiO}_2$ using a similar method where the soaking temperature was 1600 K and a nickel tube sealed under vacuum was used. We have examined the system Na_2O – Ti_2O_3 – TiO_2 by reactions of metal sodium and titanium oxides at high temperatures between 1473 and 1673 K so as to synthesize large single crystals of lower valency sodium titanates and to determine crystal and magnetic structures. In this paper, we describe the crystal growth and crystal structure of the nonstoichiometric $\text{Na}_{0.54}\text{TiO}_2$, and, further, we discuss the decrease of the intersheet distance with the Na defects in comparison with the Na_xTiO_2 system ($0.46 \leq x \leq 1$) previously reported (3).

Experimental and Results

Single Crystal Growth

Starting materials were TiO_2 powder (99.9%), which was composed of rutile and anatase and was dried at 673 K before preparation, and excess sodium metal blocks with 99% purity. They were placed in a sealed iron vessel, heated in a resistance furnace at 1473–1673 K in an argon gas flow for several hours, and slowly cooled to room temperature. In many cases, no apparent leakage of sodium vapor from the vessel was observed. After cooling, the vessel was opened by sawing in air. Then, the products of black crystal grains were taken out as soon as possible, and were kept in a vacuum.

The black Na_xTiO_2 crystals having a violet tinge with a maximum size of $5 \times 3 \times 3$ mm were grown together with needle-shaped NaTi_2O_4 crystals. Under air atmosphere, the bubbling caused by a reaction with moisture, oxygen, or CO_2 gas was ob-

served on the surfaces of the Na_xTiO_2 crystals, and white powder which was supposed to be NaOH or Na_2CO_3 was precipitated on the crystal surfaces. For this reason, special care was required for the sampling conditions. The selections of Na_xTiO_2 crystals for the subsequent single-crystal X-ray study and the SEM observation were performed in a dehydrated paraffin liquid (Merck, for spectroscopy) under a microscope, and the specimens were transferred for storage in a vacuum, as soon as possible.

Figure 1 is a SEM photograph of the as-grown Na_xTiO_2 crystal indicating that it grows with a developed (0001) habit. The data of EPMA represented that the bulk composition of the block crystals was almost uniform with an approximate molar ratio $\text{Na}/\text{Ti} = 0.5/1.0$ ($x = 0.5$). This result suggested that the crystals contained a considerable amount of Na defect.

Small crystals of $\text{Na}_{0.5}\text{TiO}_2$ were held in evacuated glass capillaries of 0.3 mm diameter with 0.01 mm thickness, and were used for the following X-ray diffraction study. Laue and precession photographs indicate that the crystal belongs to the trigonal system with the possible space group $R32$, $R3m$, or $R\bar{3}m$ and has the hexagonal cell parameters $a = 3.0$ and $c = 16.9 \text{ \AA}$, which were close to those of the $\text{Na}_{0.94}\text{TiO}_2$ specimen derived by Maazaz *et al.* (3). The relation between the lattice parameters and sodium content was carefully investigated using a precession camera, a four-circle diffractometer, and SEM–EPMA. The results will be described in the following chapter. Magnetic measurements using the present crystals are now in progress.

Structure Determination

A small block crystal with the approximate chemical formula of $\text{Na}_{0.5}\text{TiO}_2$, $0.15 \times 0.10 \times 0.05$ mm in size, which was held in an evacuated glass capillary, was used for the crystal structure determination. Two of

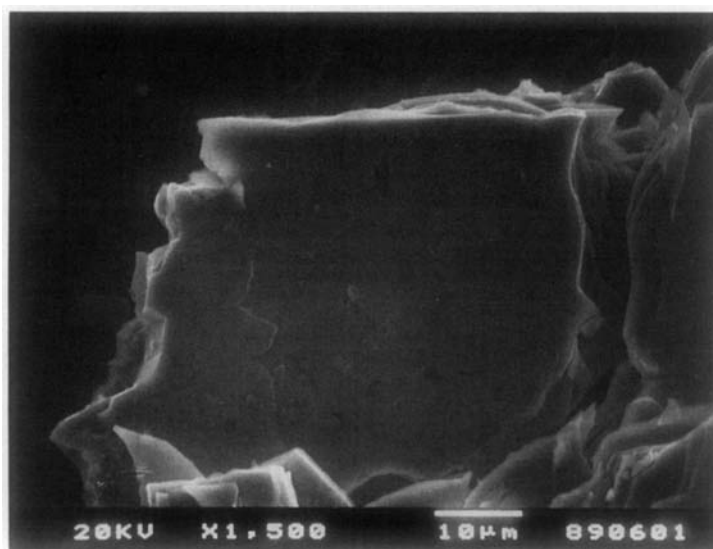


FIG. 1. SEM photograph of single crystal Na_xTiO_2 ($x \sim 0.5$), where the developed surface is (0001).

12 possible equivalent sets of diffraction data up to $2\theta = 90^\circ$ were collected by the 2θ - ω scan method with a scan rate of $1^\circ/\text{min}$ at room temperature on an automated Rigaku AFC-5 four-circle diffractometer (operating conditions: 40 kV, 30 mA) using a graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and reduced to structure factors after due correction for Lorentz and polarization effects. The fluctuation of the intensities, monitored by examining a set of three standard reflections ((11 $\bar{2}$ 0), (01 $\bar{1}$ 8), (10 $\bar{1}$ 7)) taken after every 50 observations, was within 1.8%. Averaging the structure factors resulted in a total of 170 independent reflections which have a criteria of $|F_o| > 3\sigma(|F_o|)$. No absorption and extinction corrections were performed.

For the determination of the lattice parameters, 24 2θ values between 20 and 30° were measured on the four-circle diffractometer before and after the intensity data collection. The difference between two pairs of the lattice parameters was within their estimated standard deviations. Then, the final lattice parameters of this crystal,

listed in Table I, were determined by the least-squares method using a wavelength of $\text{MoK}\alpha$ and the averaged 24 2θ values.

In the structure analysis that followed, the space group of highest symmetry $R\bar{3}m$, confirmed by successful refinement, was adopted. The refinement was initiated with the atomic coordinates specified by Hagenmuller *et al.* (1). The sodium site occupancy was also refined at the final stage. A

TABLE I
EXPERIMENTAL AND CRYSTALLOGRAPHIC DATA OF
 $\text{Na}_{0.54}\text{TiO}_2$ WITH THE α - NaFeO_2 -TYPE STRUCTURE

Space group	$R\bar{3}m$
Crystal size (mm)	$0.15 \times 0.10 \times 0.05$
a (\AA)	2.9791(6)
c (\AA)	16.928(3)
V (\AA^3)	130.11(5)
Z	3
Density (calcd)(g/cm^3)	3.536
Maximum 2θ ($^\circ$)	90
Absorption coefficient for $\text{MoK}\alpha$ (cm^{-1})	45.5
Scan width of 2θ ($^\circ$)	$1.0 + 0.5 \tan \theta$
Scan speed ($^\circ/\text{min}$)	1.0
Number of independent reflections ($>3\sigma$)	170
Final R	0.057
Final R_w [$w = 1/\sigma^2(F_o)$]	0.051

TABLE II
 ATOMIC POSITIONAL PARAMETERS, SITE OCCUPANCY, AND TEMPERATURE
 FACTORS FOR $\text{Na}_{0.54}\text{TiO}_2$

Atom	Position	z	Occupancy	β_{11}	β_{33}	B_{eq} (\AA^2)
Na	3a	0.0	0.54(1)	0.28(3)	0.0015(4)	5.48
Ti	3b	0.5	1.0	0.021(1)	0.00111(5)	0.79
O	6c	0.2294(3)	1.0	0.022(4)	0.0009(1)	0.73

full-matrix least-squares refinement using the computer program RFINE-II (8) with isotropic temperature factors converged to $R = 8.6\%$ ($R_w = 6.9\%$). Further refinements with anisotropic temperature factors converged to $R = 5.7\%$ and $R_w = 5.1\%$ [$w = 1/\sigma^2(F_o)$] for 170 observed reflections with shift/error for all parameters less than 0.01. The final difference Fourier map using the GSFFR program (9) showed no significant residual electron density, and the sodium site occupancy with the equivalent isotropic temperature factor of 5.48 was refined to 0.54(1) which is well consistent with the value from chemical analysis. The experimental and crystallographic data are summarized in Table I. The final atomic parameters are given in Table II. The scattering factors for 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 "International Tables for X-ray Crystallography" (11). The computation was performed on FACOM M-380R at ISSP.

Description and Discussion of the Structure of $\text{Na}_{0.54}\text{TiO}_2$

The crystal structure of $\text{Na}_{0.54}\text{TiO}_2$, as shown in Figs. 2 and 3, is a typical layer structure of Na, Ti, and O atoms. The interatomic distances were calculated using a program UMBADTEA (12). Na atom is octahedrally coordinated by six oxygen atoms with the Na–O bond distance of 2.460(3) \AA ,

which is well consistent with the average six-fold distance of 2.44 \AA reported in the literature (13). The arrangement of oxygen ions is divided by the sodium layers into the two close-packed oxygen layers surrounding Ti cations (Fig. 3). The shortest O–O distance across the Na layer is 3.916(8) \AA , which is much longer than the O–O distance of the average value 2.856 \AA forming

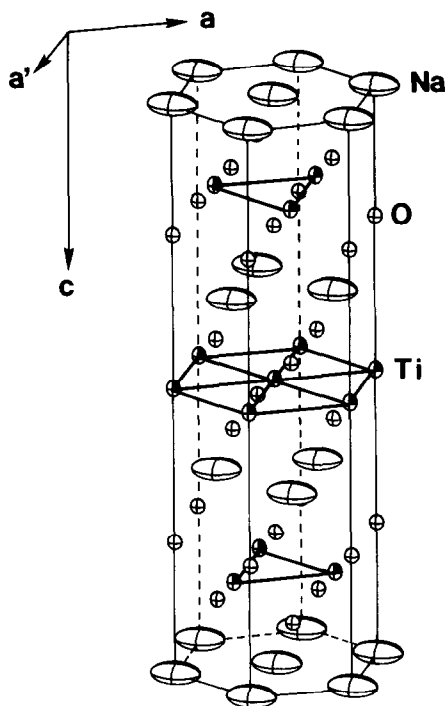


FIG. 2. An ORTEP drawing of $\text{Na}_{0.54}\text{TiO}_2$. The Ti–Ti interactions forming regular triangles are indicated by the bold lines. Ellipsoids are scaled to include 75% probability.

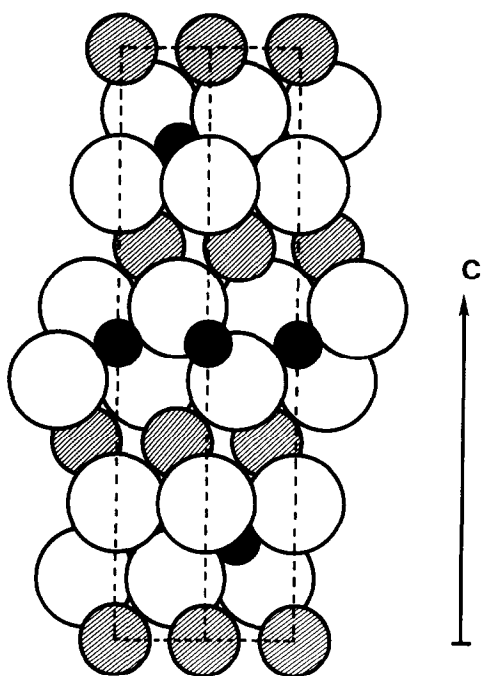


FIG. 3. A packing drawing of $\text{Na}_{0.54}\text{TiO}_2$ viewed along $[10\bar{1}0]$. The sodium ions are hatched circles, the titanium cations black circles, and the oxygen ions large circles.

a TiO_6 octahedron. In addition, the thermal ellipsoids for the Na site with an occupancy 0.54 are spread out over the (0001) plane (Fig. 2). Accordingly, the long distance between the oxygen layers across the Na layer would provide an easy migration of Na ions to the crystal surface through the gap between the two oxygen layers.

The TiO_6 octahedra are connected to each other by sharing of the six edges in the (0001) plane, and form a sheet structure. The shared O–O distance is $2.733(7)$ Å. The intrasheet Ti–Ti distance is 2.9791 Å, while the intersheet distance, which is equal to one-third of the c -axis length, is 5.643 Å. Moreover, the shortest intersheet Ti–Ti distance is $5.899(1)$ Å, which is expected to be too far to interact with each other (Fig. 3). This means that Ti cations in $\text{Na}_{0.54}\text{TiO}_2$ form the triangular lattice outstanding two-

dimensionality. The sixfold Ti–O distance is $2.021(2)$ Å. From the calculation of the valence bond sums using Zachariasen's curve (14), the valence charge of titanium is 3.3, which is well consistent with the result of average titanium valency, 3.5, from an estimation by the chemical formula with the sodium site occupancy of 0.54.

The Lattice Contraction with Na Defects

Microscopic observation revealed that the clean crystal surface of the present $\text{Na}_{0.5}\text{TiO}_2$ was stable only for a few minutes in air atmosphere; it was then covered with the vigorous bubbling of, probably, H_2 gas. The bulk part of $\text{Na}_{0.5}\text{TiO}_2$ crystal is, however, stable in air for several hours. The precession photographs of this bulk crystal held in the evacuated capillary represented the lattice parameters $a = 3.0$ and $c = 16.9$ Å. A prolonged exposure to air for more than several days changed the chemical composition of the bulk part to $\text{Na}_{0.3}\text{TiO}_2$, as determined by EPMA analyses. The Laue and precession photographs showed that the trigonal symmetry of the $\text{Na}_{0.3}\text{TiO}_2$ crystal remained unchanged, with lattice parameters of $a = 3.0$ and $c = 15.8$ Å. No obvious changes in both chemical composition and the lattice parameters were observed with further exposures to air.

The lattice contraction process with decreasing Na content was continuously monitored by the automated four-circle diffractometer ($\text{MoK}\alpha$ radiation) using a small crystal of $\text{Na}_{0.5}\text{TiO}_2$ in air, after the determination of crystal orientation. No other reflections, indicating a possible distortion from the trigonal symmetry, were observed using the peak search method every 20 hr. A total of 51 cycles of peak refinements was performed for several days using 15 to 24 strong reflections, those are $(11\bar{2}3)$, $(10\bar{1}7)$, $(01\bar{1}8)$, $(11\bar{2}0)$, and their equivalent reflections. The typical lattice parameters, determined by the least-squares method, were

TABLE III
LATTICE PARAMETERS OF Na_xTiO_2 CRYSTALS WITH THEIR EXPOSURE
TIME TO AIR ATMOSPHERE

Time (hr)	a (Å)	c (Å)	V (Å ³)	x values ^a
0	2.9791(6)	16.928(3)	130.11(5)	0.54
15	2.9786(8)	16.900(5)	129.83(6)	—
18	2.9777(5)	16.836(9)	129.28(7)	—
25	2.9749(5)	16.662(9)	127.70(7)	—
39	2.9744(5)	16.335(7)	125.16(6)	—
46	2.9737(5)	16.215(8)	124.17(7)	—
50	2.9727(4)	16.189(9)	123.89(6)	—
69	2.9723(4)	16.045(9)	122.76(7)	—
91	2.9714(4)	15.973(9)	122.13(7)	—
137	2.9702(4)	15.844(10)	121.36(8)	—
>1000	2.9665(5)	15.755(9)	120.07(8)	0.3

^a The x value of 0.54 was determined by the structure analysis and that of 0.3 was by the chemical analysis.

listed in Table III with their exposure time to air atmosphere. The chemical composition of each specimen could not be determined because of their rapid lattice contractions. The most contracted lattice parameters with the chemical formula $\text{Na}_{0.3}\text{TiO}_2$ are $a = 2.9665(5)$ Å, $c = 15.755(9)$ Å, and $V = 120.07(8)$ Å³.

The intrasheet Ti–Ti distance in Na_xTiO_2 crystals, which is identical to the a -axis length, decreases with decreasing Na content from 2.9791 Å ($x = 0.54$) to 2.9665 Å ($x = 0.3$) (Table III). This can be explained by a decrease in the ionic radius of titanium with the changing of the oxidation state from 3+ to 4+, because of decreasing Na content. A similar feature was observed in the Na_xTiO_2 powder specimens (3), as in the cases of Na_xMO_2 , where M is Ni, Cr, or Co (15, 16). On the other hand, the intersheet distance of 5.643 Å in the present $\text{Na}_{0.54}\text{TiO}_2$ crystal, which is equal to one-third of the c -axis length, is much longer than 5.408 Å in the stoichiometric NaTiO_2 powder (3). It is interesting to note that the intersheet distance of 5.643 Å in the present $\text{Na}_{0.54}\text{TiO}_2$ crystal was close to 5.617 Å in the monoclinically distorted Na_xTiO_2 speci-

mens ($0.71 \leq x \leq 0.87$) reported by Maazaz *et al.* (3). The increase in the intersheet distance with decreasing Na content is also observed in other Na_xMO_2 systems with deintercalation (15, 16).

A remarkable lattice contraction of about 1.2 Å in the c -axis with a decrease in the Na content from $x = 0.54$ to 0.3 was observed in the present Na_xTiO_2 crystals (Table III). Similar features were described by Maazaz *et al.* (3) in the Na_xTiO_2 powder specimens from 16.73 Å ($x = 0.94$) to 15.41 Å ($x = 0.46$), while the monoclinic form with $0.71 \leq x \leq 0.87$ was also discussed. In the present Na_xTiO_2 crystals with the range of $0.3 \leq x \leq 0.54$, the monoclinically distorted form was not confirmed.

Maazaz *et al.* (3) reported that the powder diffraction patterns of the Na_xTiO_2 specimens with $0.46 \leq x \leq 0.67$ were indexed with a rhombohedral symmetry, and that the intensities of the diffraction lines were considerably modified. Consequently, they supposed that some titanium ions would migrate from the TiO_2 layer to the intersheet space through a triangular oxygen window in the Na_xTiO_2 specimens with $0.46 \leq x \leq 0.67$, and the presence of high

valence cations in the sodium layer would lead to a strong contraction of the intersheet distance, i.e., the c -axis length.

The present rhombohedral lattice contraction process of Na_xTiO_2 crystal with the range of $0.3 \leq x \leq 0.54$, monitored using the four-circle diffractometer, revealed that the intensities of all reflections decreased together with the Na content. This suggests that some structural damage occurred during the exposure to air atmosphere. In addition, changes in diffraction intensities of the (10 $\bar{1}$ 7), (0003), and (0006) reflections between $\text{Na}_{0.54}\text{TiO}_2$ and $\text{Na}_{0.3}\text{TiO}_2$ crystals were considerably large in comparison with those of the corresponding (10 $\bar{1}$ 4) reflections. This tendency resembles the difference in the previous powder diffraction patterns between NaTiO_2 (JCPDS 16-251) and $\text{Na}_{0.46}\text{TiO}_2$ (JCPDS 37-354). Moreover, a similar feature was reported by Vidyasagar and Gopalakrishnan (17) in the Li_xVO_2 system, where the intensity of the (0003) line decreased steadily with decreasing lithium content. We are trying to undertake more precise structural analyses of Na_xTiO_2 with low values of x using the single crystal specimens.

Conclusion

We have succeeded in the preparation of the nonstoichiometric Na_xTiO_2 ($x \sim 0.5$) single crystals from high-temperature solutions of sodium metal and titanium dioxide. The triangular lattice of titanium cations' outstanding two-dimensionality in $\text{Na}_{0.54}\text{TiO}_2$ was confirmed from the single crystal X-ray structure analysis. However, these crystals are strongly attacked by the moisture, oxygen, or CO_2 in air atmosphere. This causes a decrease in the Na contents from $x = 0.5$ to 0.3 with a remarkable lattice contraction of about 1.2 Å towards the c -axis direction in the rhombohedral Na_xTiO_2 crystals. Similar results were

reported by Maazaz *et al.* (3) using the deintercalated powder samples. We are trying to synthesize Na_xTiO_2 crystals with $x \leq 1$ of the different sodium contents by controlling the growth conditions, in order to determine their precise structural and magnetic properties.

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