

A New Member of Sodium Titanates, $\text{Na}_2\text{Ti}_9\text{O}_{19}$

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A new compound of sodium nonatitanate, $\text{Na}_2\text{Ti}_9\text{O}_{19}$, has been prepared by the hydrothermal reactions of titanium dioxide gel with sodium hydroxide aqueous solution. The crystal has a *C*-centered monoclinic lattice with the unit-cell dimensions $a = 12.2$, $b = 3.78$, $c = 15.3$ Å, and $\beta = 98.0^\circ$. It is expected that the structure consists of a framework different from those in tri-, hexa-, hepta-, and octatitanates.

Introduction

Some compounds which are formed by sodium metal with titanium dioxide are represented as a composition series, $\text{Na}_2\text{O} \cdot n\text{TiO}_2$ ($1 \leq n$). Andersson and Wadsley (1, 2) prepared $\text{Na}_2\text{Ti}_3\text{O}_7$ ($n = 3$) and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ ($n = 6$) crystals by heating mixtures of Na_2CO_3 and TiO_2 , and they examined the relations between chemical compositions and crystal structures. $\text{Na}_2\text{Ti}_7\text{O}_{15}$ ($n = 7$) crystals were prepared by heating a mixture of sodium oxalate, aluminum oxide, and titanium dioxide by Wadsley and Mumme (3), who predicted the decomposition of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ into $\text{Na}_2\text{Ti}_7\text{O}_{15}$ and Na_2O at a sufficiently high temperature without fusing. However, the vaporization of sodium metal from hexatitanate seemed to result in hexatitanate and rutile because of the high stability of the titanate. Also, the production of the sodium titanates with $n \geq 7$ above about 1000°C by the simple expedient of heating the weighed mixture of titanium dioxide and sodium carbonate or oxalate, etc., is disturbed by the easy formation of hexatitanate and rutile. Their preparations should be made at a temperature less than

about 1000°C . For this purpose, hydrothermal syntheses are effective.

In this paper, the hydrothermal growth conditions for a new member of sodium titanate, $\text{Na}_2\text{Ti}_9\text{O}_{19}$, and its crystallographic data are reported. It is expected that nonatitanate has a framework different from those in other titanates among this series.

Experimental

Syntheses of sodium titanates are carried out by hydrothermal reactions of X-ray amorphous titanium dioxide with an aqueous solution of sodium hydroxide. The amorphous titanium dioxide is gel dried at 50°C and contains about 25 wt% water.

The hydrothermal reactions proceed in closed platinum capsules with 5 and 50 mm diameter and length, respectively. The contents in the capsules are 25 mg of gel and 0.25 ml of sodium hydroxide solution. The concentrations of solvents are prepared so that the atomic ratios ($X_{\text{Na}} = \text{Na}/(\text{Na} + \text{Ti})$) are given between 20 and 40%. The gel is packed in the high-temperature side of the capsules. The capsules are placed in Tuttle cold-seal test tubes laid horizontally. The hot

zone is held at a temperature between 400 and 600°C and the growth zone at a temperature about 50°C lower than that of the hot zone. The temperature is measured by thermocouples contacted with the tube wall. The pressures in the test tubes are adjusted to those corresponding to about 55% fill for every run. The durations of reactions are more than a week for each run.

The composition ratios of Ti to Na are measured by electron probe microanalysis (EPMA) using single crystals. The standard specimens are rutile and albite single crystals for Ti and Na, respectively. The electron beam is scanned at 20 $\mu\text{m}/\text{min}$ in order to avoid a decay of X-ray intensities of $\text{NaK}\alpha$. The data were treated according to the Bence-Albee method.

Densities were determined using about 12 mg of the crystals by means of a Berman balance with carbon tetrachloride at 20°C. The crystals have average physical dimensions of $0.3 \times 0.05 \times 0.03$ mm and form radiated or concentric aggregates. The specimens in CCl_4 are placed for 10 min in a desiccator where pressure is diminished in order to exhaust the air from the interstices of the aggregates.

Crystallographic data were obtained by single crystal and powder diffraction methods.

Results and Discussion

When the hot zone is held between 450 and 550°C, the new compound crystals are well transported into the growth zone over the ratio from 0.20 to 0.40. The residual nutrients in the high-temperature side change to light grey powder consisting of the new compound and bronze-type titanium dioxide (4).

The new compound occurs in woolly or radiated aggregates in the growth zone, as shown in Fig. 1. The appearance of the woolly aggregates is quite similar to those of

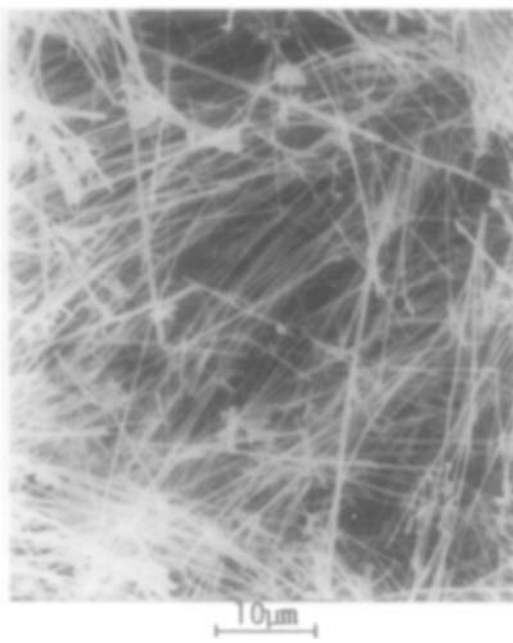


FIG. 1. Typical woolly aggregate of nonatitanate crystals ($X_{\text{Na}} = 0.25$ and 550°C).

hexatitanate. Long colorless needles form the former aggregates when the hot zone is held near 550°C. However, they do not occur in the growth zone held more than 90°C lower than the hot zone. In such a growth zone there occur concentric aggregates of long plate-like crystals. On the other hand, the radiated aggregates consisting of slightly bluish and long plate-like crystals are found in the case of the hot zone held below about 500°C.

In the present preparations, hepta- and octatitanates were not found. But the needle crystals of hexatitanate are transformed very dominantly in the range of 0.25 to 0.40 in X_{Na} when the hot zone is kept at 600°C. The crystals transformed in the ratio from 0.35 to 0.40 are accompanied by trace amounts of the new compound. Trititanate forms in the high-temperature side of the capsules near $X_{\text{Na}} = 0.40$.

The X-ray intensities obtained by EPMA were treated with a chemical formula

$x\text{Na}_2\text{O}\cdot y\text{TiO}_2$ considering the fact that the present crystals form the woolly aggregates characteristic for alkali metal titanates. The ratios y/x and total weight percentages are shown in Table I. From y/x and the unit-cell volume (689.6 \AA^3), the compound has a stoichiometric chemical formula $\text{Na}_2\text{Ti}_9\text{O}_{19}$. The calculated density is in good agreement with the observed one (Table II).

The crystallographic data of nonatitanate are shown in Table II. The crystal has a monoclinic symmetry. The systematic absence is $h+k \neq 2n$ for hkl . The possible space groups are C_m , C_2 , and $C_{2/m}$.

The unit-cell dimensions of nonatitanate suggest that the structure is constructed by a framework different from those in $\text{Na}_2\text{Ti}_3\text{O}_7$ (1), $\text{Na}_2\text{Ti}_6\text{O}_{13}$ (2), $\text{Na}_2\text{Ti}_7\text{O}_{15}$ (3), and $\text{K}_3\text{Ti}_8\text{O}_{17}$ (5). For these titanates, the length of the c axis is approximately equal to the product of an edge of the TiO_6 octahedron ($\sim 3 \text{ \AA}$) and the number of octahedra sharing edges in the linear arrays at the same level parallel to the (010) plane. The lengths of the c and the a axes of nonatitanate correspond to 10 and 4 in the number of octahedra, respectively. The hypothetical frameworks of 10 octahedra are represented by the compositions $(\text{Ti}_5\text{O}_{11})^{2-}$ or $(\text{Ti}_{10}\text{O}_{21})^{2-}$ and those of 4 by $(\text{Ti}_4\text{O}_9)^{2-}$ or $(\text{Ti}_8\text{O}_{17})^{2-}$. If the crystal has the frameworks mentioned above, it should have calculated densities

TABLE I
TOTAL WEIGHT PERCENTAGES AND THE MOLAR RATIOS OF TiO_2 TO Na_2O

Crystal No.	(1)	(2)	(3)
Total (%)	100.3	99.9	99.4
y/x	8.98	8.90	8.88

TABLE II
CRYSTALLOGRAPHIC DATA FOR NONATITANATE

(a) Cell dimensions	(c) X-ray powder pattern				
$a = 12.2 \pm 0.1 \text{ \AA}$	h	k	l	$D_0 (\text{\AA})$	I
$b = 3.78 \pm 0.01 \text{ \AA}$	0	0	1	15.1	15
$c = 5.3 \pm 0.1 \text{ \AA}$	0	0	2	7.56	30
$\beta = 98.0 \pm 0.3^\circ$	0	0	3	5.04	5
	0	0	4	3.78	2
	1	1	0	3.61	4
	2	0	3		
(b) Densities (g cm^{-3})	0	0	5	3.021	100
	0	0	6	2.517	2
$D_0 = 3.67 \pm 0.04$	0	0	7	2.156	36
$D_c = 3.69$	6	0	-1	2.026	2
	0	2	0	1.887	10
	0	0	8		

greater than 4.0 g cm^{-3} or less than 3.4 g cm^{-3} . But the values are appreciably different from the observed one.

The structure analysis is in process in this Institute.

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