

# Synthesis and Crystal Structure of Na<sub>2</sub>TiO<sub>3</sub>

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**ABSTRACT** The crystal structure of a sodium titanium oxide Na<sub>2</sub>TiO<sub>3</sub> obtained by high temperature solid state reaction method was determined from single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic system, space group C2/c,  $M_r = 141.88$ ,  $a = 9.885(1)$ ,  $b = 6.4133(8)$ ,  $c = 5.5048(7)$  Å,  $\beta = 115.50(3)^\circ$ ,  $V = 314.99(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.992$  g/cm<sup>3</sup>,  $\lambda = 0.71073$  Å,  $\mu = 27.80$  cm<sup>-1</sup>,  $F(000) = 272$ ,  $T = 295$  K,  $R = 0.0189$  and  $wR = 0.0512$  for 30 variables and 370 contributing unique reflections. The three-dimensional structure in Na<sub>2</sub>TiO<sub>3</sub> is constructed by the TiO(1)<sub>4</sub>O(2) and NaO(1)<sub>3</sub>O(2)<sub>2</sub> groups. The titanium atoms are grouped in the form of trigonal bipyramid and arranged along the  $c$  axis by sharing the edges. The structure is compared with other structures of related A<sub>2</sub>BO<sub>3</sub> compounds.

**Keywords:** synthesis, crystal structure, X-ray diffraction

## 1 INTRODUCTION

Titanates have received much attention because of their wide applications as ferroelectric materials<sup>[1]</sup>. Previous work on sodium titanates compounds has been focused on their synthesis and structural characterizations<sup>[2-4]</sup> due to their extensive applications in the synthesis of other titanates like BaTiO<sub>3</sub><sup>[5]</sup>. In previous reports, NaTiO<sub>3</sub> was synthesized normally by high temperature ( $T > 900$  °C) solid-state reaction<sup>[6, 7]</sup>.

X-ray powder diffraction patterns of as-obtained products were indexed to several different symmetries. Nalbandyan has got Na<sub>2</sub>TiO<sub>3</sub> in rhombohedral symmetry  $R\bar{3}$  (148) with  $a = 13.927$  and  $c = 7.676$  Å when prepared by solid-state synthesis at 900 °C<sup>[6]</sup>. Hill *et al.* have got two kinds of Na<sub>2</sub>TiO<sub>3</sub>. One was prepared by annealing the high temperature phase  $\alpha$ -Na<sub>2</sub>O-TiO<sub>2</sub> or  $\gamma$ -Na<sub>2</sub>O-TiO<sub>2</sub> for 3 h at 800 °C. In this case, the crystal is of face-centered monoclinic with  $a = 13.021$ ,  $b = 13.922$ ,  $c = 9.526$  Å and  $\beta =$

95.539°. As for the other kinds, a mixture of Na<sub>2</sub>CO<sub>3</sub> and TiO<sub>2</sub> (anatase) in molar proportion was heated in a P crucible in an electric furnace at 1200 °C for 1 h, and then cooled in air. In this method, the Na<sub>2</sub>TiO<sub>3</sub> belongs to the monoclinic system with  $a = 9.064$ ,  $b = 6.457$ ,  $c = 5.54$  Å,  $\beta = 97.923^\circ$ <sup>[4]</sup>. However, the single-crystal structure determination of this compound has not been made yet.

In this work, the system NaOH-TiO<sub>2</sub> is studied and single crystals of Na<sub>2</sub>TiO<sub>3</sub> as reported in JCPDS 37-0346<sup>[7]</sup> have been obtained by the solid-state reaction at a lower temperature ( $T = 500$  °C). The crystal structure of Na<sub>2</sub>TiO<sub>3</sub> determined by single-crystal X-ray diffraction is described, which is compared with other structures of related A<sub>2</sub>BO<sub>3</sub> compounds.

## 2 EXPERIMENTAL

### 2.1 Synthesis of Na<sub>2</sub>TiO<sub>3</sub>

A mixture of NaOH (96%, Sinopharm Chemical

Reagent Co., Ltd) and TiO<sub>2</sub> (98%, China Medicine (Group) Shanghai Chemical Reagent Corporation) in molar ratio of 3:1 was placed in an Al<sub>2</sub>O<sub>3</sub> crucible, heated for 12 h in an electric furnace at 500 °C, and then slowly cooled to room temperature. Well-formed crystals were obtained by leaching and filtering the products.

## 2.2 Structure determination

X-ray powder diffraction pattern (Rigaku D/max-

RC) of manually selected crystals agreed well with that calculated from the single-crystal data and also matched the data of Na<sub>2</sub>TiO<sub>3</sub> (JCPDS 37-0346), as shown in Fig. 1. The chemical composition confirmed by a chemical semi-quantitative energy dispersive X-ray diffraction analysis (LEO1530, Oxford Instruments) showed the atomic ratio of Na/Ti/O is approximately 1.04/1/4.39.

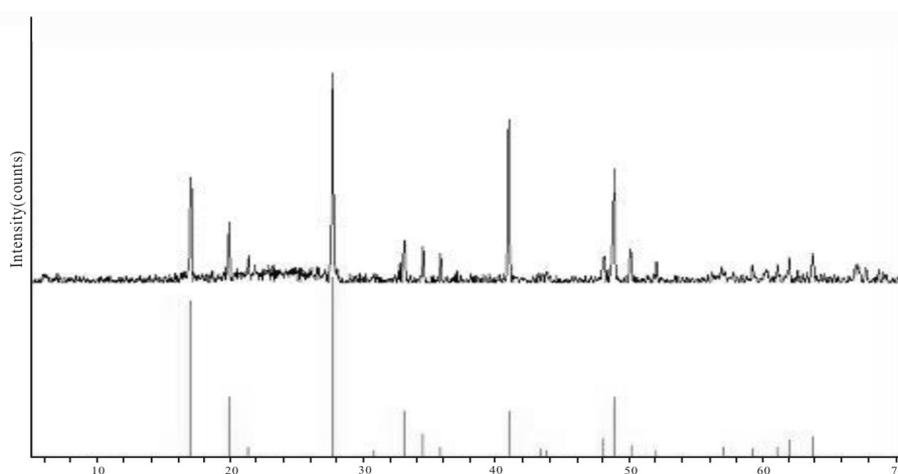


Fig. 1. Comparison of experimental X-ray powder diffraction pattern (upper) of Na<sub>2</sub>TiO<sub>3</sub> compound with the JCPDS card 37-0346

A single crystal with dimensions of 0.15mm × 0.11mm × 0.06mm was mounted on a Bruker Apex CCD diffractometer equipped with a graphite-monochromatic MoK $\alpha$  radiation at 295(2) K. Crystallographic data for the title compound are summarized in Table 1. A total of 892 reflections were taken from  $3.91 < \theta < 28.10^\circ$ , yielding 370 unique reflections ( $R_{\text{int}} = 0.0228$ ) including 367 observed ones ( $I > 2\sigma(I)$ ). The intensity data were corrected for  $Lp$  factors, and absorption correction was made in the final refinement ( $T_{\text{min}}/T_{\text{max}} = 0.8747$ ). The anomalous-dispersion coefficients were taken into account during the data processing. Systematic absence led to the space

groups  $C2/c$  or  $Cc$  (International Tables for Crystallography, 1983, Vol. A). The structure was solved in space group  $C2/c$  and confirmed by the full-matrix least-squares refinement on  $F^2$  using SHELXL 97<sup>[8]</sup>. 30 Variables including anisotropic displacement parameters were refined to  $R = 0.0187$  and  $wR = 0.0512$  ( $w = 1/[\sigma^2(F_o^2) + (0.0141P)^2 + 0.4656P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ) considering 370 contributing unique reflections with  $F_o > 4\sigma(F_o)$ ,  $S = 1.180$  and  $(\Delta/\sigma)_{\text{max}} = 0.000$ . The final residual electron density was  $+0.299$  ( $-0.317$ )  $e/\text{\AA}^3$ ,  $0.92(1.19)$   $\text{\AA}$  from the titanium atoms. The important bond distances are shown in Table 2.

$${}^b wR2 = \left[ \frac{\sum_{hkl} w(F_o^2 - F_c^2)^2}{\sum_{hkl} wF_o^4} \right]^{\frac{1}{2}}$$

$${}^a R1 = \frac{\sum_{hkl} ||F_o| - |F_c||}{\sum_{hkl} |F_o|}$$

**Table 1. Crystallographic Data for Na<sub>2</sub>TiO<sub>3</sub>**

Formula	Na <sub>2</sub> TiO <sub>3</sub>
Formula weight/amu	141.88
Space group	C2/c
Z	4
a/Å	9.885(1)
b/Å	6.4133(8)
c/Å	5.5048(7)
β	115.50(3)
V/Å <sup>3</sup>	314.99(7)
D <sub>c</sub> /g·cm <sup>-3</sup>	2.992
Linear absorption coefficient μ/cm <sup>-1</sup>	27.80
Temperature/K	293(2)
Radiation, monochromator	MoKα graphite
Crystal shape, color	Prism, colorless
2θ range/°	7.82~56.20
Total reflections	892
Unique reflections	370
hkl ranges	-13 ≤ h ≤ 12, -8 ≤ k ≤ 4, -7 ≤ l ≤ 7
Number of parameters	30
F(000)	272
<sup>a</sup> R, <sup>b</sup> wR (I > 2σ(I))	0.0187, 0.0512
<sup>a</sup> R, <sup>b</sup> wR (all data)	0.0187, 0.0512
Goodness-of-fit on F <sup>2</sup>	1.181
Residual peaks (hole)/e·Å <sup>-3</sup>	0.299 (-0.317)
Software	Shelxl-97 <sup>[8]</sup>

**Table 2. Important Bond Distances of Na<sub>2</sub>TiO<sub>3</sub>**

Atom 1	Atom 2	Distance (Å)
Ti(1)	O(2)	1.7475(17)
	O(1) <sup>a</sup>	1.8797(13)
	O(1) <sup>b</sup>	1.8797(13)
	O(1)	2.0164(12)
	O(1)	2.0164(12)
	O(1)	2.0164(12)
Na(2)	O(1) <sup>c</sup>	2.3065(16)
	O(2) <sup>d</sup>	2.3090(14)
	O(2) <sup>e</sup>	2.3104(8)
	O(1) <sup>b</sup>	2.3643(14)
	O(1) <sup>e</sup>	2.3737(15)

a: x, -y+1, z +1/2; b: -x+1, -y+1, -z; c: -x+1, y, -z +1/2; d: -x+1/2, -y+1/2, -z; e: x - 1/2, y+1/2, z

### 3 RESULTS AND DISCUSSION

For the reaction between NaOH and TiO<sub>2</sub>,



At the temperature from 600 to 1200 K, all above reactions can take place automatically, but the

when the molar ratio of NaOH and TiO<sub>2</sub> is not lower than 3, the following reactions may happen:

thermodynamical tendency of reaction 1) is the biggest<sup>[5]</sup>, and the system of NaOH-TiO<sub>2</sub> in our

synthesis favors the formation of  $\text{Na}_2\text{TiO}_3$  crystal. This is in agreement with the X-ray powder

diffraction pattern of our product, a mixture of  $\text{NaOH}$  and  $\text{Na}_2\text{TiO}_3$ .

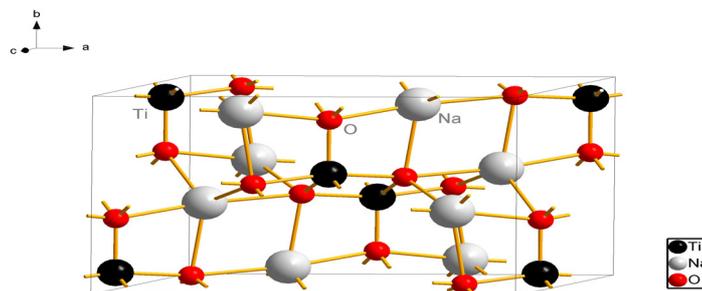


Fig. 2. Three-dimensional network in the  $\text{Na}_2\text{TiO}_3$  structure presented in one unit cell

The structure of  $\text{Na}_2\text{TiO}_3$  is displayed in Fig. 2, which shows that the titanium atoms are bonded to five oxygen atoms grouped in the form of a trigonal bipyramid. They are arranged along the  $c$  direction by sharing edges (Fig. 3). The sodium atoms are surrounded by five oxygen atoms, too. They serve as a bridge between  $\text{TiO}(1)_4\text{O}(2)$  and  $\text{NaO}(1)_3\text{O}(2)_2$  groups thus developing a three-dimensional structure in  $\text{Na}_2\text{TiO}_3$  (Fig. 2). In  $\text{Na}_2\text{TiO}_3$ , the  $\text{Na}-\text{O}$  bond distances are quite regular (from 2.31 to 2.37 Å); however, the  $\text{Ti}-\text{O}$  bond distances fall in a relatively wider range (1.75 ~ 2.02 Å). Both titanium and sodium atoms have five coordination numbers. In the crystal structures of most sodium titanates

elucidated, most  $\text{Ti}-\text{O}$  units are in octahedral group<sup>[9~11]</sup>. In the crystal structures of compounds  $\text{Li}_2\text{TiO}_3$ <sup>[12]</sup> and  $\text{Li}_2\text{SnO}_3$ <sup>[12]</sup>, the coordination number of  $\text{Li}^+$  is six with average  $\text{Li}-\text{O}$  bond distance of 2.13 (from 1.87 to 2.39 Å) for  $\text{Li}_2\text{TiO}_3$  and 2.20 (in the range of 2.18 ~ 2.24 Å) for  $\text{Li}_2\text{SnO}_3$ . The coordination numbers of  $\text{Ti}$  or  $\text{Sn}$  atoms are also six, and the average  $\text{Ti}/\text{Sn}-\text{O}$  bond distance is 1.95 (ranging from 1.91 to 1.99 Å) for  $\text{Li}_2\text{TiO}_3$  and 2.07 (in the range of 2.06 ~ 2.08 Å) for  $\text{Li}_2\text{SnO}_3$ . The cell volumes of  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_2\text{SnO}_3$  are 425.22 and 480.24 Å<sup>3</sup>, respectively, consistent with the bigger radius of  $\text{Sn}^{4+}$  than  $\text{Ti}^{4+}$  and  $\text{Na}^+$  than  $\text{Li}^+$ .

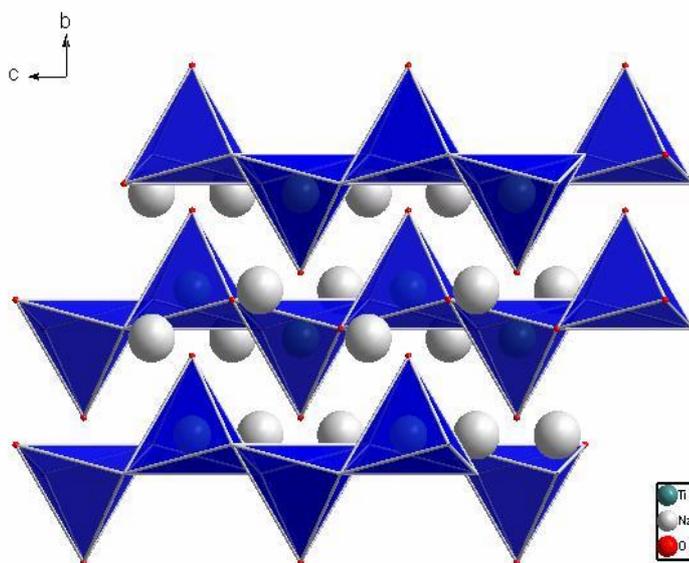


Fig. 3. Structure of  $\text{Na}_2\text{TiO}_3$  viewed along  $\langle 100 \rangle$  direction

The crystal of compound  $\text{Rb}_2\text{TiO}_3$  belongs to orthorhombic symmetry, space group  $Cmca$ , with  $a = 6.0150$ ,  $b = 11.9360$ ,  $c = 13.3660 \text{ \AA}$ ,  $V = 959.61 \text{ \AA}^3$  and  $Z = 8$ . The titanium atoms are bonded to four oxygen atoms forming slightly distorted tetrahedra arranged along the  $c$  axis. As regards  $\text{K}_2\text{SnO}_3$ , its crystal is of orthorhombic symmetry, space group  $Pnma$ , with  $a = 5.7400$ ,  $b = 10.3400$ ,  $c = 7.1400 \text{ \AA}$ ,  $V = 423.77 \text{ \AA}^3$  and  $Z = 4$ . The tin atom is bonded to

five oxygen atoms. No connection between potassium and oxygen atoms is found due to the bigger cation radius of  $\text{K}^+$  in  $\text{K}_2\text{SnO}_3$  than that of  $\text{Na}^+$  in  $\text{Na}_2\text{TiO}_3$ . Fig. 4 is the schematic presentation of cell volume per unit formula for related  $\text{A}_2\text{BO}_3$  compounds (A: Li, Na, K Rb; B: Ti, Sn), showing the dependence of cell volume per unit formula on the radius of  $\text{A}^+$  cation.

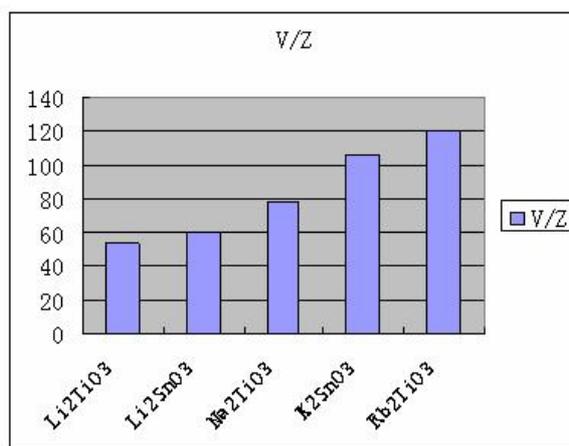


Fig. 4. Comparison of  $V/Z$  of some  $\text{A}_2\text{BO}_3$  compounds shown in histogram

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