

Synthesis and Crystal Structure of $\text{NaTi}_8\text{O}_{13}$

J. AKIMOTO* AND H. TAKEI

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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A new member of the $\text{Ti}^{3+}/\text{Ti}^{4+}$ mixed-valence sodium titanate family, $\text{NaTi}_8\text{O}_{13}$, was synthesized by the reaction of sodium metal and titanium oxides at high temperatures. It crystallizes in the trigonal system, space group $R\bar{3}$ with hexagonal lattice constants $a = 7.7544(7) \text{ \AA}$, $c = 14.073(3) \text{ \AA}$, $V = 732.9(2) \text{ \AA}^3$, and $Z = 3$. The structure was determined from a single-crystal X-ray diffraction study and refined to the conventional values of $R = 0.033$ and $R_w = 0.031$ for 869 observed reflections. The structure can be described as a cubic closest packing of oxygen atoms, in which the defects of oxygen packing are occupied by sodium ions, and some of the octahedral O_6 interstices are occupied by two types of Ti cations. Sodium ion is surrounded by twelve oxygen ions in a cuboctahedron. © 1991 Academic Press, Inc.

Introduction

During investigations of the system $\text{Na}_2\text{O}-\text{Ti}_2\text{O}_3-\text{TiO}_2$ using sealed iron vessels at high temperatures, we have recently found four members of mixed-valence sodium titanates, NaTi_2O_4 (1), $\text{Na}_{2.08}\text{Ti}_4\text{O}_9$ (2), $\text{Na}_{1.7}\text{Ti}_6\text{O}_{11}$ (3), and $\text{Na}_x\text{Ti}_2\text{O}_4$ ($0.50 \leq x \leq 0.57$) (4), and determined their crystal structures. The average titanium valence states for these new phases, estimated by chemical formulae, lie between 3.38 (3) and 3.98 (2). The framework of these compounds consists of edge-shared rutile-related type TiO_6 chains, with repeat distances of about 3.0 \AA , which form a tunnel structure. This is quite different from those of the other sodium titanates previously reported, e.g., $\text{Na}_2\text{Ti}_3\text{O}_7$ (5), $\text{Na}_2\text{Ti}_5\text{O}_{19}$ (6), and Na_xTiO_2

($0.20 \leq x \leq 0.25$) (7, 8), and a similar rutile-related type linkage of TiO_6 octahedra was observed only in $\text{Na}_4\text{Ti}_5\text{O}_{12}$ (9).

At higher temperatures, above 1600 K, we have examined the system $\text{Na}_2\text{O}-\text{Ti}_2\text{O}_3-\text{TiO}_2$ by the reactions of metallic sodium and titanium oxides using a similar iron vessel so as to separate new crystals with lower valence states of titanium for determining the crystal structures as well as their physical properties. In this paper, we describe the synthesis and crystal structure of a new rhombohedral phase having the formula $\text{NaTi}_8\text{O}_{13}$.

Experimental and Results

Sample Preparation

Starting materials of excess metallic sodium blocks (99%) and TiO_2 (99.9%) and synthesized Ti_2O_3 powder were placed in a sealed iron vessel, heated in a resistance

* Present address: National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305, Japan.

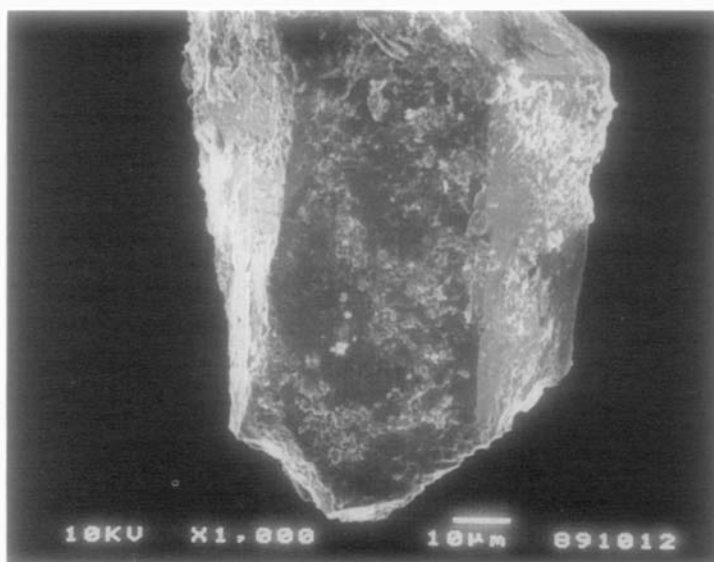


FIG. 1. SEM photograph of well-formed $\text{NaTi}_8\text{O}_{13}$ single crystal.

furnace at 1673 K in an argon gas flow for several hours, and slowly cooled to room temperature. No leakage of sodium vapor was observed during heating. This fact suggests the synthetic conditions of high temperature and high sodium vapor pressure.

Well-formed brownish golden crystals, as shown in Fig. 1, $0.1 \times 0.1 \times 0.05$ mm in average size, were grown on the surface of aggregated mixtures of Ti_2O_3 block crystals and $\text{Na}_{1.7}\text{Ti}_6\text{O}_{11}$ needle-shaped crystals. EPMA showed that the crystals were sodium titanate and were free from iron contamination from the vessel. The chemical formula of this compound determined by the present structure analysis is $\text{NaTi}_8\text{O}_{13}$.

Precession photographs indicate that the crystal belongs to the trigonal system with the possible space group $R\bar{3}$ or $R\bar{3}$. Table I shows the X-ray powder diffraction data of $\text{NaTi}_8\text{O}_{13}$ obtained at a scan rate of $1^\circ/\text{min}$ in 2θ using graphite-monochromatized $\text{CuK}\alpha$ radiation and a Si internal standard. The lattice parameters, determined by a least-squares refinement using the 2θ values of 25

strong reflections in the range $20\text{--}30^\circ$ and $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) on an automated Rigaku AFC-5 four-circle diffractometer, are $a = 7.7544(7) \text{ \AA}$ and $c = 14.073(3) \text{ \AA}$ with hexagonal indices.

Structure Determination

A small tabular crystal, which was $0.109 \times 0.078 \times 0.031$ mm in size, was used for crystal structure determination. All of six possible equivalent sets of diffraction data up to $2\theta = 80^\circ$ were collected by the $2\theta - \omega$ scan method with a scan rate of $1^\circ/\text{min}$ at room temperature on the four-circle diffractometer (operating conditions: 40 kV, 30 mA) using graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), and reduced to structure factors after due correction for Lorentz and polarization effects. Fluctuations of the intensities, monitored by examining a set of the three standard reflections ($(41\bar{5}0)$, $(12\bar{3}8)$, (2243)) taken after every 50 observations, were within 2.2%. Averaging the structure factors resulted in a total of 1013 independent reflec-

TABLE I
X-RAY POWDER DIFFRACTION DATA FOR NaTi₈O₁₃

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{calc} (Å)	<i>d</i> _{obs} (Å)	<i>I</i> / <i>I</i> ₀
1	0	1	6.06	6.08	59
0	1	2	4.858	4.874	5
0	0	3	4.691	4.700	5
1	1	0	3.877	3.887	14
0	2	1	3.266	3.274	34
2	0	2	3.030	3.036	19
1	1	3	2.989	2.994	64
0	1	5	2.596	2.600	12
2	1	1	2.498	2.500	19
1	2	2	2.388	2.391	3
0	0	6	2.345	2.346	28
2	1	4	2.058	2.058	100
3	0	3	2.020	2.020	5
1	0	7	1.926	1.926	2
1	2	5	1.885	1.886	5
1	3	1	1.846	1.845	1
3	1	2	1.801	1.802	3
2	2	3	1.792	1.791	19
0	2	7	1.725	1.725	2
4	0	1	1.667	1.667	3
0	3	6	1.619	1.619	2
2	1	7	1.576	1.575	11
0	0	9	1.564	1.563	7
3	1	5	1.553	1.553	7
4	1	0	1.465	1.465	26
1	1	9	1.450	1.445B	5
1	2	8	1.446		
0	4	5	1.442		
1	3	7	1.366	1.366	3

tions, of which 869 reflections have a criteria or $|F_0| > 3\sigma (|F_0|)$. No absorption and extinction corrections were performed. In the structure analysis that followed, the space group of highest symmetry, $R\bar{3}$, confirmed by successful refinement, was adopted.

Initial positions for two titanium atoms and three oxygen atoms were determined by the direct method using the computer program MULTAN80 system (10). The crystal structure factor F_c was calculated with an overall temperature factor 0.44. The R value was 0.236, showing that the structure model adopted was reasonable. Then, the atomic parameters as well as the scale and temperature factors were refined by the

full-matrix least-squares method using the RFINE-II program (11). The converged R value with isotropic temperature factors was 0.072. At this stage, sodium atoms were introduced, which was revealed by the Fourier and difference Fourier syntheses using the GSFFR program (12). The anisotropically refined thermal parameters for the Na site ($B_{eq} = 5.04 \text{ \AA}^2$) was considerably larger than those of the other sites. From this point of view, a site-occupancy refinement in the 3b position and displacement refinements from the 3b position to the lower site symmetry positions of 6c and 18f with 50% and 16.7% occupancy factors, respectively, were also applied for sodium at the final stage. However, such a treatment did not improve either the R value or the difference Fourier map. Therefore, we continued further refinement using the fixed occupancy of 100% in 3b positions for the sodium site. The large thermal parameter of the Na site will be discussed in the following part, in comparison with the similar cuboctahedral sites in sodium transition metal oxides. Finally, the structure was refined to $R = 0.033$ and $R_w = 0.031$ [$w = 1/\sigma^2(F_0)$] for 869 observed reflections, with shift/error for all parameters less than 0.01.

The scattering factors for neutral atoms tabulated by Cromer and Mann (13) were

TABLE II
EXPERIMENTAL AND CRYSTALLOGRAPHIC DATA
OF NaTi₈O₁₃

Space group	$R\bar{3}$
Crystal size (mm)	$0.109 \times 0.078 \times 0.031$
<i>a</i> (Å)	7.7544(7)
<i>c</i> (Å)	14.073(3)
<i>V</i> (Å ³)	732.9(2)
<i>Z</i>	3
Density (calculated)(g/cm ³)	4.176
Maximum 2θ (°)	80
Absorption coefficient for MoK α (cm ⁻¹)	62.7
Scan width of 2θ (°)	$1.0 + 0.5 \tan \theta$
Scan speed (°/min)	1.0
Number of observed reflections	1013
Number of used reflections	869 ($>3\sigma$)
Final R	0.033
Final R_w [$w = 1/\sigma^2(F_0)$]	0.031

TABLE III
 ATOMIC POSITIONAL PARAMETERS, AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR $\text{NaTi}_8\text{O}_{13}$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Na	3b	0.0	0.0	0.5	5.04
Ti(1)	18f	0.22984(7)	0.02680(7)	0.08112(3)	0.36
Ti(2)	6c	0.0	0.0	0.72759(5)	0.37
O(1)	3a	0.0	0.0	0.0	1.30
O(2)	18f	0.1575(3)	0.2381(3)	0.66147(13)	0.53
O(3)	18f	0.4843(3)	0.1177(3)	0.16088(12)	0.42

used in the calculations. The anomalous dispersion correction factors were taken from "International Tables for X-ray Crystallography" (14). The experimental and crystallographic data are summarized in Table II. The final atomic coordinates and temperature factors are given in Tables III and IV. The computation was performed on FACOM M-380R at ISSP.

Description and Discussion of Structure

Figure 2 shows the crystal structure of $\text{NaTi}_8\text{O}_{13}$ viewed down the *c*-axis direction using a packing expression. As can be seen from this figure, the present $\text{NaTi}_8\text{O}_{13}$ structure can be described as a cubic closest packing of oxygen atoms, in which the defects of oxygen packing are occupied by sodium ions, and some of the octahedral O_6 interstices are occupied by Ti cations. Both the hexagonal axis and the pseudocubic axis directions are shown in Fig. 2. The cubic stacking sequence of oxygen atoms is

ABCABC, while the stacking sequence of the oxygen layers (O) and the sodium containing layers (S) is OSOSOS. The average thickness of the cubic closest packed layer is 2.346 Å, which corresponds to one-sixth of the *c*-axis length (14.073 Å). The value is well consistent with the data of some barium titanates after Tillmanns *et al.* (15).

The interstitial layers between the two closest packed layers in $\text{NaTi}_8\text{O}_{13}$ are drawn with the TiO_6 octahedral representation in Fig 3; (a) $-0.01 < z < 0.18$, and (b) $0.16 < z < 0.34$, respectively. Two types of TiO_6 octahedra are connected with sharing edges, and form a three-dimensional framework structure. The number of the shared edges is seven for $\text{Ti}(1)\text{O}_6$, and six for $\text{Ti}(2)\text{O}_6$ octahedra, respectively. Sodium ions are weakly bound by the electrostatic force with the surrounding twelve oxygen ions from the nature of c.c.p. arrangement. This makes the situation that sodium ions are located in the large cages constructed by twenty-six TiO_6 octahedra. Selected interatomic dis-

TABLE IV
 ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) FOR $\text{NaTi}_8\text{O}_{13}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	377(13)	377	19(2)	188	0	0
Ti(1)	18.1(7)	22.2(8)	4.2(2)	9.7(6)	-0.9(3)	-1.4(3)
Ti(2)	18.5(8)	18.5	5.4(3)	9.3	0	0
O(1)	80(7)	80	13(2)	40	0	0
O(2)	33(3)	21(3)	6.8(7)	10(3)	5(1)	3(1)
O(3)	20(3)	29(3)	4.6(6)	11(3)	-1(1)	-1(1)

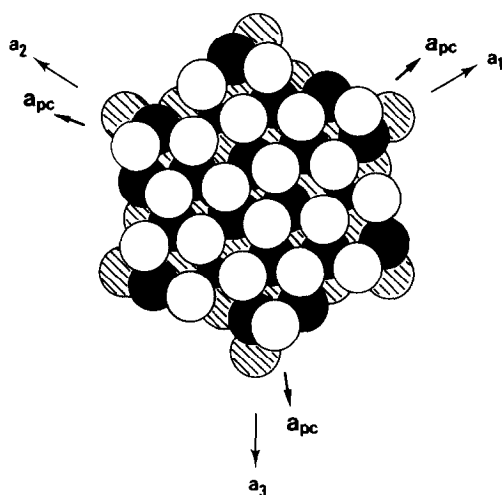


FIG. 2. The cubic closest packing of sodium and oxygen ions in $\text{NaTi}_8\text{O}_{13}$, viewed along the hexagonal [0001] direction, which corresponds to the pseudocubic [111] direction. The oxygen ions are large circles and sodium ions solid small circles. The stacking sequence is represented by line-shaded A(O), solid B(S), and open circles C(O). The three pseudocubic a_{pc} -axis directions are also drawn.

tances and bond angles calculated using the UMBADTEA program (16) are listed in Table V.

The $\text{Ti}(1)\text{O}_6$ octahedron is formed by six

$\text{Ti}-\text{O}$ bonds in a small range from 1.980(2) Å to 2.115(2) Å (Table V). In contrast, the $\text{Ti}(2)\text{O}_6$ octahedron is distorted like a ‘‘3 + 3’’ coordination for titanium with two $\text{Ti}-\text{O}$ distances, 1.874(2) Å and 2.100(2) Å, which give an average value 1.987 Å. The O(1) ion existing at the origin is octahedrally coordinated by six $\text{Ti}(1)$ cations at the distance of 2.0378(6) Å, and six $\text{Ti}(1)\text{O}_6$ octahedra form a tightly bound Ti_6O_{19} block (Fig. 4). Accordingly, the distortion of the $\text{Ti}(2)\text{O}_6$ octahedron is thought to be caused by the edge-shared linkages to the Ti_6O_{19} block. Maybe most of the Ti^{4+} cations in $\text{NaTi}_8\text{O}_{13}$ occupy the $\text{Ti}(2)$ sites preferentially, because the mean $\text{Ti}(2)-\text{O}$ distance is remarkably shorter by 0.060 Å than the mean $\text{Ti}(1)-\text{O}$ distance (Table V), and the latter is quite consistent with the mean $\text{Ti}^{3+}-\text{O}$ distance of 2.048 Å in Ti_2O_3 (17).

Figure 5 shows a side view of the crystal structure of $\text{NaTi}_8\text{O}_{13}$ along one of the three equivalent pseudocubic a_{pc} -axis directions. Interestingly, the NaCl-like edge-shared TiO_6 octahedral arrangements can be recognized when this figure is viewed down along the equivalent three a_{pc} -axis directions.

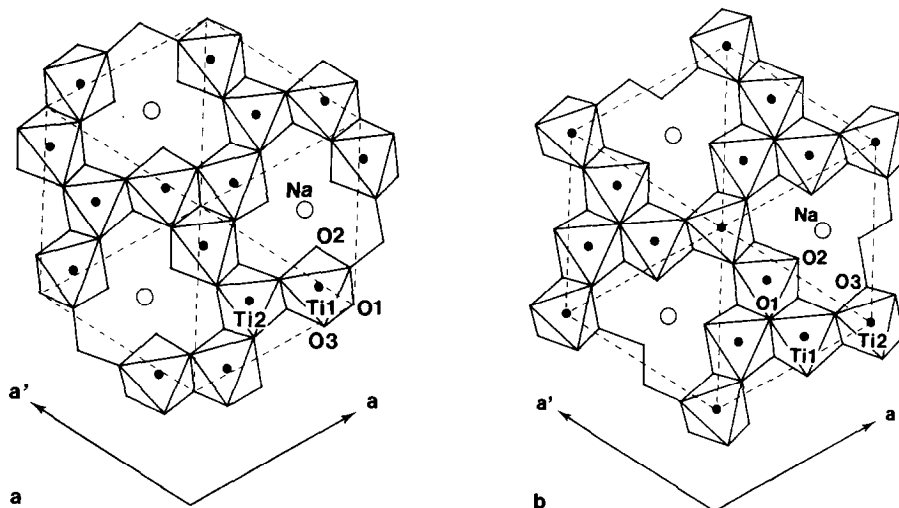


FIG. 3. Cross-sections of the crystal structure of $\text{NaTi}_8\text{O}_{13}$ perpendicular to the c -axis in ranges of (a) $-0.01 < z < 0.18$ and (b) $0.16 < z < 0.34$, which correspond to the thickness of the closest-packed layers. TiO_6 unit is illustrated as an octahedron and sodium atom as an open circle.

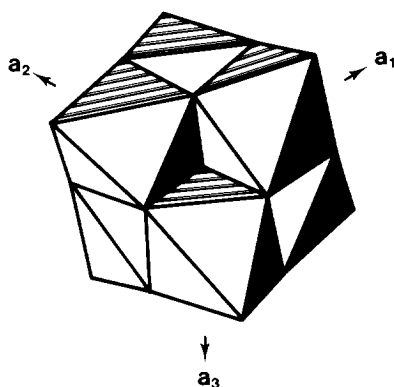


FIG. 4. A Ti_6O_{19} block forming six edge-shared $\text{Ti}(1)\text{O}_6$ octahedra in $\text{NaTi}_8\text{O}_{13}$ viewed along the c -axis.

These arrangements cross one another at the threefold axes (Fig. 5).

The sodium ion, which is located at the site with $\bar{3}$ symmetry, is surrounded by twelve oxygen ions in a cuboctahedron where six of the Na–O distances are 2.794(2) Å and the others are 3.085(2) Å (Fig. 6). It should be noted that the 12-coordinated

sodium site is unusual, but often observed in synthetic sodium transition metal oxides. In $\text{NaV}_6\text{O}_{11}$ (18), sodium atoms occupy similar cuboctahedral sites with an average Na–O distance of 2.797 Å. Marezio *et al.* (19) described the high-temperature and high pressure form of cubic $\text{NaMn}_7\text{O}_{12}$, in which sodium atoms are surrounded by 12 equidistant oxygen atoms with a distance of 2.649 Å. Recently, Kohler and Simon (20) prepared a mixed-valence sodium niobate, $\text{NaNb}_{10}\text{O}_{18}$, having a 12-coordinated Na-site with the mean Na–O distance of 2.892 Å. Moreover, Craig and Stephenson (21) reported four-sided tunnels elongated to the c -axis direction of bronze-type $\text{Na}_{13}\text{Nb}_{35}\text{O}_{94}$, where four types of sodium sites are surrounded by the 12 nearest oxygen atoms. Accordingly, the mean Na–O distance of 2.940 Å in the present $\text{NaTi}_8\text{O}_{13}$ is well consistent with these results.

It should also be noted that the thermal vibrational factors for the sodium sites in the previous oxide containing 12-coordinated sodium ions with transition metal cat-

TABLE V
SELECTED INTERATOMIC DISTANCES (Å) AND
BOND ANGLES (°) FOR $\text{NaTi}_8\text{O}_{13}$

Na–O(2)	2.794(2) × 6	O(1)–Ti(1)–O(2)	90.04(5)
Na–O(3)	3.085(2) × 6	O(1)–Ti(1)–O(2)	92.16(7)
		O(1)–Ti(1)–O(3)	167.86(6)
Mean	2.940	O(1)–Ti(1)–O(3)	87.98(6)
		O(1)–Ti(1)–O(3)	90.24(6)
		O(2)–Ti(1)–O(2)	91.78(2)
Ti(1)–O(1)	2.0378(6)	O(2)–Ti(1)–O(3)	81.30(7)
Ti(1)–O(2)	2.054(2)	O(2)–Ti(1)–O(3)	94.88(8)
Ti(1)–O(2)	1.980(2)	O(2)–Ti(1)–O(3)	176.08(8)
Ti(1)–O(3)	2.064(2)	O(2)–Ti(1)–O(3)	96.58(10)
Ti(1)–O(3)	2.115(2)	O(2)–Ti(1)–O(3)	173.34(8)
Ti(1)–O(3)	2.033(2)	O(2)–Ti(1)–O(3)	92.12(8)
		O(3)–Ti(1)–O(3)	84.31(10)
Mean	2.047	O(3)–Ti(1)–O(3)	97.82(7)
		O(3)–Ti(1)–O(3)	81.22(9)
Ti(2)–O(2)	1.874(2) × 3	O(2)–Ti(2)–O(2)	97.47(8)
Ti(2)–O(3)	2.100(2) × 3	O(2)–Ti(2)–O(3)	164.77(9)
		O(2)–Ti(2)–O(3)	97.18(9)
Mean	1.987	O(2)–Ti(2)–O(3)	84.74(9)
		O(3)–Ti(2)–O(3)	80.03(7)

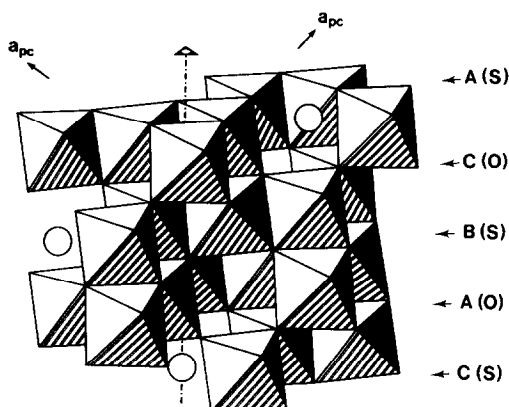


FIG. 5. A side view of the crystal structure of $\text{NaTi}_8\text{O}_{13}$ along one of the three pseudocubic a_{pc} -axis directions. The TiO_6 unit is illustrated as an octahedron and the sodium ion as an open circle. The NaCl-like edge-shared TiO_6 octahedral arrangements toward the pseudocubic a_{pc} -axis direction are clear. The cubic closest stacking sequence of sodium and oxygen ions is also indicated by the notations of A, B, C, (O), and (S), which are referred to the text.

ions are often considerably larger than those for other sites. For example, the Na-site in $\text{NaV}_6\text{O}_{11}$ has an equivalent isotropic temperature factor of $B_{eq} = 2.4 \text{ \AA}^2$ (18). A similar feature can be seen in the present $\text{NaTi}_8\text{O}_{13}$, where the fully occupied Na-site has the value of $B_{eq} = 5.04 \text{ \AA}^2$ (Table III). This fact implies that Na atoms are forced to stay at the inapt cuboctahedral sites with a structural requirement of the framework in which the site is provided as a defect of the cubic closest packing of oxygen ions. Consequently, the large thermal vibrations would be introduced in the Na-sites of $\text{NaTi}_8\text{O}_{13}$.

From the calculation of the valence bond sums using Zachariasen's curve (22), the titanium valence charges in Ti(1) and Ti(2) sites of $\text{NaTi}_8\text{O}_{13}$ are 3.03 and 3.84, respectively. These values strongly support the above-mentioned preferential occupation by Ti^{4+} cations of the Ti(2) sites. On the other hand, the average value of two Ti sites in $\text{NaTi}_8\text{O}_{13}$ is 3.23, which is consistent with the average titanium valency of 3.13 from

an estimation by chemical formula. This value is the lowest recorded in the mixed-valence sodium titanate system (1-4). In the sodium titanate system, the crystal structure of $\text{NaTi}_8\text{O}_{13}$ is quite different from those of other sodium titanate members, e.g., NaTi_2O_4 (1), $\text{Na}_2\text{Ti}_3\text{O}_7$ (5), and $\text{Na}_2\text{Ti}_9\text{O}_{19}$ (6), most of which can be described as sodium tunnel structures. This structural difference in the sodium titanate compounds may be related to the fact that the present $\text{NaTi}_8\text{O}_{13}$ has both the lowest valence charge of titanium and the smallest content of sodium in these sodium titanate compounds.

It is well known that the lower valency titanates have unusual electrical and magnetic properties such as LiTi_2O_4 of an oxide superconductor (23) and a semiconductor-metal transition in Ti_2O_3 (24). From this point of view, physical measurements using the present $\text{NaTi}_8\text{O}_{13}$ samples with a high electrical conductivity are now in progress.

Conclusion

We have succeeded in the synthesis of $\text{NaTi}_8\text{O}_{13}$ single crystals by the reaction of sodium metal and titanium oxides at high temperatures. From the result of X-ray structure analysis, $\text{NaTi}_8\text{O}_{13}$ can be de-

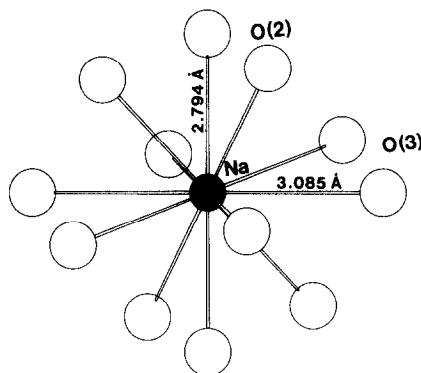


FIG. 6. A cuboctahedral oxygen coordination around sodium atom in $\text{NaTi}_8\text{O}_{13}$.

scribed as a new type sodium titanate bronze having the cubic closest packing of oxygen atoms. On the contrary, rutile, hollandite, and similar rutile-related type structures are considered to be not closest packed, as indicated by Tillmanns *et al.* (15), because they have the corrugated close-packed planes which mutually intersect. Furthermore, the crystal structure of $\text{NaTi}_8\text{O}_{13}$ is quite different from those of the previous rutile-related type mixed-valence sodium titanates, e.g., NaTi_2O_4 (1), $\text{Na}_{1.7}\text{Ti}_6\text{O}_{11}$ (3), and $\text{Na}_x\text{Ti}_2\text{O}_4$ (4). A similar structural arrangement can be seen in the $\text{Na}_2\text{O}-\text{Mn}_2\text{O}_3-\text{MnO}_2$ system. $\text{NaMn}_7\text{O}_{12}$ (19) has a perovskite-like packing that is quite different from those of the compounds previously reported in the $\text{Na}_2\text{O}-\text{Mn}_2\text{O}_3-\text{MnO}_2$ system by Parant *et al.* (25), where most of them have the double rutile-type chains. It is interesting to note that $\text{NaMn}_7\text{O}_{12}$ was prepared in the high-temperature and high-pressure experiments of 80 kbar and 1273 K. The present $\text{NaTi}_8\text{O}_{13}$ crystals were also synthesized at the similar conditions of temperatures above 1623 K and high vapor pressures of sodium.

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