

Structure Analysis of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ by 1 MV High-Resolution Electron Microscopy

BY YOSHIO BANDO, MAMORU WATANABE AND YOSHIZO SEKIKAWA

National Institute for Researches in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan

(Received 27 December 1978; accepted 14 March 1979)

Abstract

The crystal structure of disodium nonatitanate(IV), $\text{Na}_2\text{Ti}_9\text{O}_{19}$, has been determined on the basis of 1 MV structure images, in which each of the Ti and Na atom sites is resolved. The crystal has monoclinic symmetry with $a = 12.2$, $b = 3.78$, $c = 15.3$ Å and $\beta = 98^\circ$. The space group of the crystal is either $C2/m$ or $C2$. The nonatitanate has a framework of a new type which is different from those of tri-, hexa- and heptatitanates. The structure consists of titanium dioxide bronze-type units interleaved with bridging TiO_6 octahedra.

Introduction

The Na–Ti–O system contains several compounds of sodium titanates and sodium titanium dioxide bronze. The sodium titanates can be represented by a composition series $\text{Na}_2\text{O} \cdot n\text{TiO}_2$ ($n \geq 1$). The crystal structures of $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_7\text{O}_{15}$ were determined by Andersson & Wadsley (1961, 1962*a*) and Wadsley & Mumme (1968). They clarified the relationships between crystal structure and chemical composition in this system. These structures are constructed from sheets of composition $(\text{Ti}_3\text{O}_7)^{2-}$ held together by sodium ions. Each sheet consists of zigzag ribbons of TiO_6 octahedra joined by a corner-sharing scheme to form cubic interstitial positions. In $\text{Na}_2\text{Ti}_3\text{O}_7$, the number of cubic interstitial positions is four in each unit cell and all are fully occupied by sodium ions; in $\text{Na}_2\text{Ti}_6\text{O}_{13}$, this number is reduced to three, and only two are occupied by sodium ions. The structure of $\text{Na}_2\text{Ti}_7\text{O}_{15}$ is considered as an ordered intergrowth at the unit-cell level of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and hypothetical sodium octatitanate, $\text{Na}_2\text{Ti}_8\text{O}_{17}$. Andersson & Wadsley (1962*b*) determined the crystal structure of sodium titanium dioxide bronze, $\text{Na}_x\text{Ti}_4\text{O}_8$ (x approximately 0.8); the nonstoichiometric $\text{Na}_x\text{Ti}_4\text{O}_8$ has a framework different from those of sodium titanates.

Crystals of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ are easily formed in this system. The titanates with $n > 7$ had not been prepared until Watanabe, Bando & Tsutsumi (1979) succeeded in synthesizing sodium nonatitanate, $\text{Na}_2\text{Ti}_9\text{O}_{19}$, by the hydrothermal technique. Because it

formed as small fibrous crystals, it was difficult to analyse its crystal structure by the single-crystal X-ray diffraction technique.

The high-voltage electron microscope (Hitachi, 1250 kV) constructed in this Institute has a resolving power near 2.0 Å at an accelerating voltage of 1 MV with axial illumination and a goniometer stage (Horiuchi, Matsui & Bando, 1976). Such a high resolution enables one to determine the framework of the crystal structure on the basis of structure images taken along two or more directions. Horiuchi, Kikuchi & Goto (1977) have determined the crystal structure of $\text{Bi}_2\text{Ti}_4\text{NbO}_{21}$ on the basis of structure images. Bando, Watanabe, Sekikawa, Goto & Horiuchi (1979) determined the new layered structure of $\text{Bi}_2\text{W}_2\text{O}_9$ and deduced the point group of the crystal directly from the structure images in which each cation site was well resolved. Bando, Saeki, Sekikawa, Matsui, Horiuchi & Nakahira (1979) determined the superstructure of $\text{TiS}_{1.46}$ by directly observing the images of the S atoms and metal vacancies and comparing them with the calculated images.

In the Na–Ti–O system, the compounds mentioned above have closely related frameworks, consisting of TiO_6 octahedra, and b axes of approximately the same length (in the range 3.7 to 3.9 Å). This means that it is very probable that the framework of the presently studied $\text{Na}_2\text{Ti}_9\text{O}_{19}$ can be determined on the basis of a finely resolved structure image projected along the b axis.

In the present study, the framework of the crystal structure of sodium nonatitanate, $\text{Na}_2\text{Ti}_9\text{O}_{19}$, has been determined by 1 MV high-resolution electron microscopy. It is shown that the Ti and Na atom sites are resolved as dark dots and white spots respectively. The possible models for polytypes of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ are discussed.

Experimental procedures

The new compound, $\text{Na}_2\text{Ti}_9\text{O}_{19}$, was prepared by hydrothermal reactions (Watanabe, Bando & Tsutsumi, 1979). The X-ray amorphous titanium dioxide gel and sodium hydroxide solution were enclosed in a platinum capsule. The capsule was placed in a

horizontal Tuttle cold-seal test tube. The high-temperature zone was kept at 783 K and the growth zone 50 K lower. The pressure was kept at 1.013×10^8 Pa. The duration of the reaction was more than one month. The crystals obtained were bluish and consisted of fibrous aggregates which were only a few microns thick.

The chemical composition of the product was determined by electron-probe microanalysis. The molar ratio of Ti to Na was then calculated to be 4.5 ± 0.05 . The density of the specimen was measured to be $3.67 \pm 0.04 \text{ Mg m}^{-3}$ by means of the Berman balance method.

The polycrystals were picked from the aggregates and crushed in an agate mortar to fragments several hundred ångströms in diameter. They were placed on a holey carbon supporting film and observed by a 1 MV electron microscope. The astigmatism of the objective lens was corrected by observing the granular image of a carbon supporting film. The objective aperture size corresponded to about 0.5 \AA^{-1} in reciprocal space. The image contrast obtained at an underfocus between 500 and 1000 Å was interpreted by analogy with other sodium titanate samples of known structure. The direct magnification was 2.5×10^5 times.

Results and interpretation

Many electron diffraction patterns were taken from $\text{Na}_2\text{Ti}_9\text{O}_{19}$ crystal fragments. Two are shown in Fig. 1(a) and (b). They indicate that the crystal has monoclinic symmetry with the lattice parameters $a = 12.2$, $b = 3.78$, $c \cong 15.3 \text{ \AA}$ and $\beta = 98^\circ$, which are in good agreement with those found in the previous X-ray diffraction study (Watanabe *et al.*, 1979). The systematically absent reflexions are hkl with $h + k = 2n + 1$. The possible space groups for the crystal are therefore $C2$, Cm and $C2/m$. The crystallographic data for $\text{Na}_2\text{Ti}_9\text{O}_{19}$ are shown in Table 1.

Fig. 2 shows a structure image obtained from a $\text{Na}_2\text{Ti}_9\text{O}_{19}$ crystal. The incident electron beam is parallel to the $[010]$ direction. The corresponding diffraction pattern is shown in Fig. 1(a), in which the size and position of the objective aperture are outlined. About 70 waves were used for imaging. The image contrast can be viewed as sheets with dark dots and grey dots which alternate along the c axis. They are

designated here as B and D . Sheet D consists of connected dark dots along the a axis in a dark zigzag shape, while sheet B consists of isolated grey dots. They are ordered in the sequence $\dots BDDDB \dots$ along the c axis with a repeating period of 15.3 \AA . In the previous observation of $\text{Bi}_2\text{W}_2\text{O}_9$ crystals (Bando, Watanabe, Sekikawa, Goto & Horiuchi, 1979), it was shown that each cation site could be resolved as a dark dot. Based on this analogy the dark and grey dots were assigned as the sites of the Ti atoms. The arrangement of the Ti atoms is shown schematically by solid circles in the inset to Fig. 2. The approximate separation of two adjoining Ti atoms within sheet D is either 2 or 3

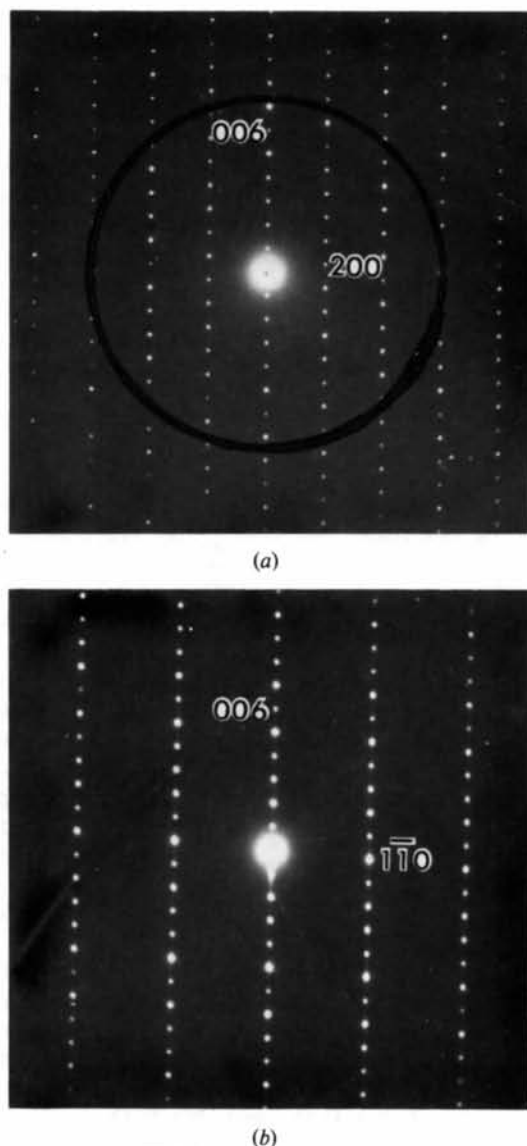


Fig. 1. Electron diffraction patterns from $\text{Na}_2\text{Ti}_9\text{O}_{19}$ crystal fragments (1 MV electron microscope). The incident electron beam is parallel (a) to the $[010]$ and (b) to the $[110]$ directions. The position of the objective aperture is outlined.

Table 1. Crystallographic data for $\text{Na}_2\text{Ti}_9\text{O}_{19}$

Monoclinic	
$a = 12.3 \text{ \AA}$	$D_c = 3.71 \text{ Mg m}^{-3}$
$b = 3.78$	$D_o = 3.67$
$c = 15.3$	$Z = 2$
$\beta = 98^\circ$	
Systematically absent reflexions hkl with $h + k = 2n + 1$	
Possible space groups $C2$, Cm and $C2/m$	

Å. The Ti–Ti distance between neighbouring *D* sheets is about 4 Å. These separations can be accounted for on the basis of the known structures of $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, $\text{Na}_2\text{Ti}_7\text{O}_{15}$ and $\text{Na}_x\text{Ti}_4\text{O}_8$.

Fig. 3 shows various arrays of TiO_6 octahedra found in the titanates and titanium dioxide bronze. The metal-to-metal distances are approximately 3 and 2 Å when two octahedra share an edge at the same level as shown in Fig. 3(a) and at a different level as shown in Fig. 3(b), respectively. On the other hand, the Ti–Ti distance between the corner-shared TiO_6 octahedra shown in Fig. 3(c) is about 4 Å. Thus it is understood that the Ti–Ti distances in Fig. 2 correspond to those of edge- or corner-shared TiO_6 octahedra.

Fig. 4 shows a structure image taken with the incident electron beam parallel to the [110] direction. The corresponding diffraction pattern is shown in Fig. 1(b). In this projection, each Ti atom site is resolved more clearly than in the previous projection (Fig. 2). It is found that the image contrast of the dark dots in sheet *B* is about half as strong as that in sheet *D*. This means that the numbers of superposing Ti atoms in sheet *B* are half as many as those in sheet *D* in the projected plane.

It is important to note in Fig. 2 that a twofold axis along *b* is present. The space group of the crystal can

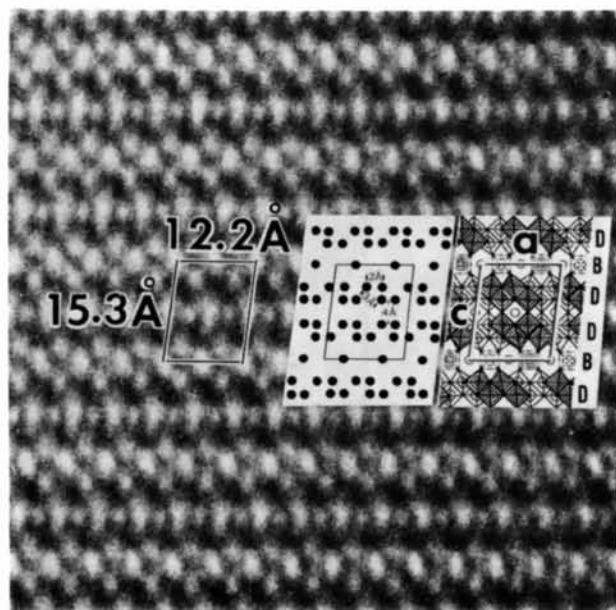


Fig. 2. A structure image of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ (1 MV high-resolution electron microscope). The incident electron beam is parallel to the [010] direction. The two types of sheets are indicated *B* and *D*. The schematic arrangement of the dark dots is shown as solid circles in the inset, in which the separations of the adjoining dark dots are indicated. The structure model is also shown as an inset. The heavy squares indicate TiO_6 octahedra at $y = 0$, and the light ones TiO_6 octahedra at $y = \frac{1}{4}$. The dashed squares show bridging TiO_6 octahedra at $y = \frac{1}{4}$ and $\frac{3}{4}$. The open circles show Na atoms.

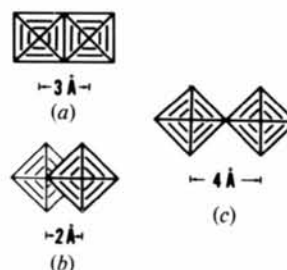


Fig. 3. Three types of arrays of TiO_6 octahedra, as viewed along the *b* axis, which are found in known titanates and titanium dioxide bronze. The Ti–Ti distances are indicated. (a), (b) Two octahedra sharing an edge at the same and different levels respectively. (c) Two octahedra sharing a corner.

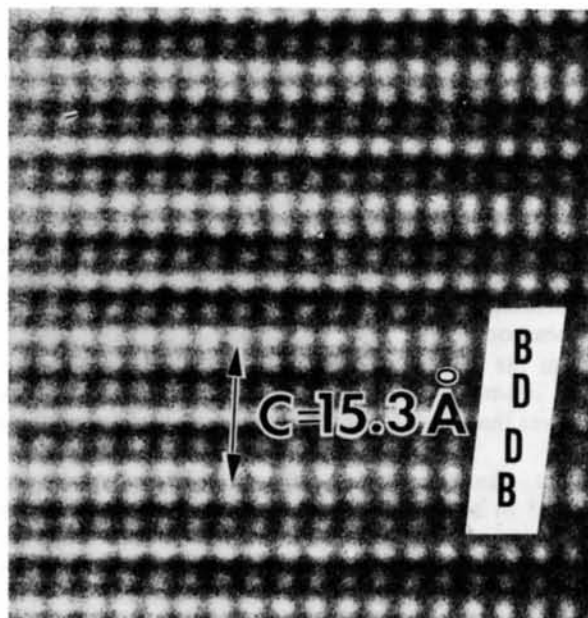


Fig. 4. A structure image of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ taken with the incident electron beam parallel to the [110] direction. The structure is constructed from the sheet sequence of ...*B**D**D**B*... along the *c* axis with a repeating period of 15.3 Å.

then be considered to be either $C2$ (noncentrosymmetric) or $C2/m$ (centrosymmetric).

Description and discussion

The proposed crystal structure of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ projected on to the (010) plane is shown in Fig. 5. The positions of the O atoms are speculated from the observations of the Ti atoms. The structure consists of TiO_6 octahedra and enclosed sodium ions. Each octahedron shares an edge with another at the same level, forming a group of four-linking octahedra. Each group is connected by the edge-sharing scheme to another, which sits at a different level as viewed along the *b* axis, to form a sheet, which is indicated as *D*. Two sheets thus formed

are linked to each other by the corner-sharing scheme to form a double sheet DD . The double sheet is the framework of the crystal structure in titanium dioxide bronze, $\text{Na}_x\text{Ti}_4\text{O}_8$, in which it contains infinite DD chains (Andersson & Wadsley, 1962*b*). Therefore, it is called hereafter a bronze-type unit. In $\text{Na}_2\text{Ti}_9\text{O}_{19}$, the bronze-type units are interleaved with bridging TiO_6 octahedra, the rows of which are indicated as B . The structure is thus constructed from the stacking of sheets in the sequence ... $BDDDB$... along the c axis.

As a result of the arrangement of TiO_6 octahedra, four types of holes are formed, as shown in Fig. 5. Two holes are located within the bronze-type unit. They are small and large square-shaped holes as viewed along the b axis. The former is as small as about 2 Å and the latter is as large as about 3 Å. The remaining two types of holes are formed between the bronze-type units. These two holes are of hexagonal and trigonal shape in projection and their diameters are approximately 4 and 2 Å respectively. The arrangements of the white spots in Fig. 2 correspond well to those of all the holes.

The positions of Na atoms are assigned on the basis of a crystal-chemical consideration. As seen in Fig. 5, the structure contains two types of large holes (large square and hexagonal shaped) as long as one looks at the structure along the b axis. They are large enough to accommodate Na ions. Therefore it is reasonable to assign the positions of Na atoms to these large holes. The chemical composition of the present crystal requires that these holes should be occupied fully by Na ions.

The arrangement of TiO_6 octahedra can be described in terms of the centrosymmetric space group $C2/m$ as well as the noncentrosymmetric $C2$. The space group of the present crystal, however, could be selected on the basis of the determination of the y

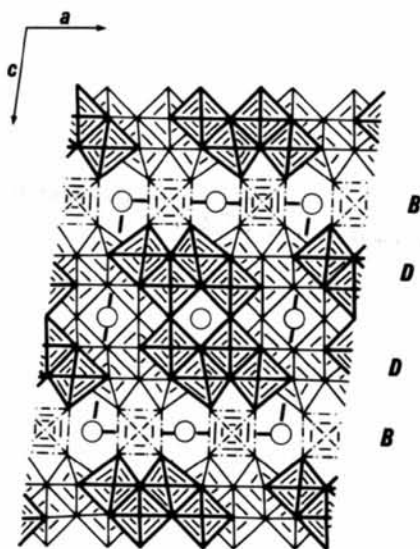


Fig. 5. A crystal structure model of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ projected on to the (010) plane. The symbols are as in Fig. 2.

coordinates of the Na atoms. If Na atoms were at the position $y = 0$ or $\frac{1}{2}$, the space group would be $C2/m$. On the other hand, if they were at $y = \frac{1}{4}$ or $\frac{3}{4}$, the space group would be $C2$. Because of the difficulty of determination of the y positions of Na atoms from structure images, the space group of the crystal could not be determined uniquely in the present case.

The TiO_6 octahedra bridging the bronze-type unit are characteristic in the present crystal for their edges are not shared by other octahedra. The bridging octahedron is considered to be distorted. However, the distortion could only be determined accurately by the X-ray refinement of the crystal structure.

In the region marked F in Fig. 6, the arrangement of the sheet is different from that in the matrix. Its schematic representation is shown in the inset. The sheet sequence in this region is ... $B\bar{D}DBDB$... along the c axis, where \bar{D} is a sheet which can be derived by rotating D 180° about the b axis. New basic units such as ... $B\bar{D}DB$... and ... BDB ... were observed in this defect region. Therefore it is possible to construct a hypothetical crystal structure model consisting of the new basic units. The compositions of the former and the latter are $\text{Na}_2\text{Ti}_9\text{O}_{19}$ and $\text{Na}_2\text{Ti}_{10}\text{O}_{21}$ respectively.

Here, possible models for polytypes of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ are considered for the case of those having a c axis which is about twice as large as that of the parent crystal. Four types of basic units are introduced. They show the stacking sequences ... $BDDDB$..., ... $B\bar{D}DB$..., ... $B\bar{D}DB$... and ... $B\bar{D}DB$..., which are here represented as M , \bar{M} , O and \bar{O} respectively. The basic units M

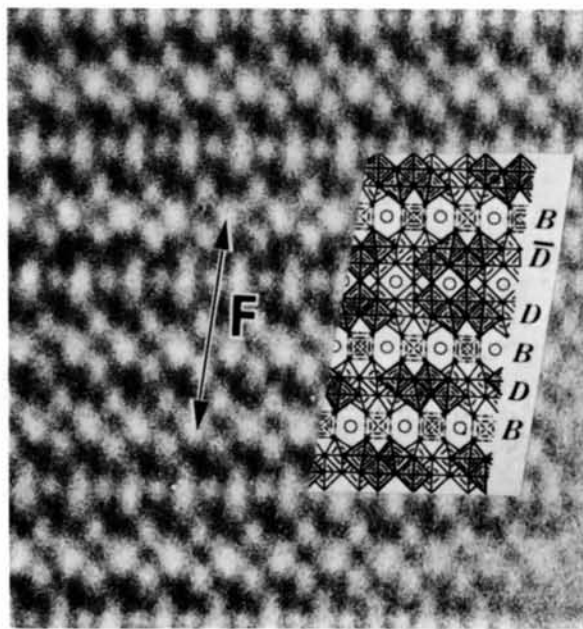


Fig. 6. A defect region observed in $\text{Na}_2\text{Ti}_9\text{O}_{19}$. A schematic representation of the arrangement of TiO_6 octahedra is shown as an inset, in which \bar{D} indicates a sheet which is derived by rotating D 180° about the b axis.

Table 2. Possible models for polytypes of $\text{Na}_2\text{Ti}_9\text{O}_{19}$

The basic units M , \bar{M} , O and \bar{O} show the stacking sequences $\dots BDD\bar{B}\dots$, $\dots \bar{B}\bar{D}\bar{D}\bar{B}\dots$, $\dots B\bar{D}\bar{D}\bar{B}\dots$ and $\dots B\bar{D}\bar{D}\bar{B}\dots$ respectively.

Model	Stacking sequence
$M\bar{M}$	$\dots BDD\bar{B}\bar{D}\bar{D}\bar{B}\dots$
$O\bar{O}$	$\dots \bar{B}\bar{D}\bar{D}\bar{B}\bar{D}\bar{B}\dots$
MO	$\dots BDD\bar{B}\bar{D}\bar{D}\bar{B}\dots$
$M\bar{O}$	$\dots BDD\bar{B}\bar{D}\bar{D}\bar{B}\dots$
$\bar{M}O$	$\dots \bar{B}\bar{D}\bar{D}\bar{B}\bar{D}\bar{B}\dots$
$\bar{M}\bar{O}$	$\dots \bar{B}\bar{D}\bar{D}\bar{B}\bar{D}\bar{B}\dots$

and \bar{M} indicate a monoclinic arrangement along the c axis, where \bar{M} means a basic unit which is obtained by rotating M 180° about the b axis. On the other hand, the basic units O and \bar{O} show an orthorhombic arrangement. Six models, $M\bar{M}$, $O\bar{O}$, MO , $M\bar{O}$, $\bar{M}O$ and $\bar{M}\bar{O}$, are derived and shown in Table 2. They are ordered intergrowths of the basic units at unit-cell level. The models MO and $M\bar{O}$ are equivalent to $\bar{M}\bar{O}$ and $\bar{M}O$ respectively. Among them, the only model $M\bar{M}$ which has the stacking sequence $\dots BDD\bar{B}\bar{D}\bar{D}\bar{B}\dots$ can be described in terms of unit-cell twinning or poly-synthetic twinning in monoclinic $\text{Na}_2\text{Ti}_9\text{O}_{13}$, as observed in enstatite (Iijima & Buseck, 1975) and wollastonite (Wenk, 1969). In fact, we have recently obtained an orthorhombic $\text{Na}_2\text{Ti}_9\text{O}_{19}$ crystal which seems to be constructed by the $M\bar{M}$ model.

The authors would like to express their deep gratitude to Dr S. Kimura for valuable discussions and for correcting the manuscript. They also thank Dr S. Horiuchi and Mr Y. Matsui for their support in the experiments.

References

- ANDERSSON, S. & WADSLEY, A. D. (1961). *Acta Cryst.* **14**, 1245–1249.
- ANDERSSON, S. & WADSLEY, A. D. (1962a). *Acta Cryst.* **15**, 194–201.
- ANDERSSON, S. & WADSLEY, A. D. (1962b). *Acta Cryst.* **15**, 201–206.
- BANDO, Y., SAEKI, M., SEKIKAWA, Y., MATSUI, Y., HORIUCHI, S. & NAKAHIRA, M. (1979). To be published.
- BANDO, Y., WATANABE, A., SEKIKAWA, Y., GOTO, M. & HORIUCHI, S. (1979). *Acta Cryst.* **A35**, 142–145.
- HORIUCHI, S., KIKUCHI, T. & GOTO, M. (1977). *Acta Cryst.* **A33**, 701–703.
- HORIUCHI, S., MATSUI, Y. & BANDO, Y. (1976). *Jpn. J. Appl. Phys.* **15**, 2483–2484.
- IJIMA, S. & BUSECK, P. R. (1975). *Am. Mineral.* **60**, 758–770.
- WADSLEY, A. D. & MUMME, W. G. (1968). *Acta Cryst.* **B24**, 392–396.
- WATANABE, M., BANDO, Y. & TSUTSUMI, M. (1979). *J. Solid State Chem.* In the press.
- WENK, H.-R. (1969). *Contrib. Mineral. Petrol.* **22**, 238–247.

Acta Cryst. (1979). **B35**, 1545–1550

Redétermination de la Structure du Sulfate de Vanadyle Pentahydraté $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$

PAR MICHEL TACHEZ ET FRANÇOIS THÉOBALD

Université de Franche-Comté, Laboratoire de Chimie-Physique, 32 rue Mégevand, 25030 Besançon CEDEX, France

KENNETH J. WATSON*

Department of Physical Chemistry, Chemical Laboratory IV, University of Copenhagen, Copenhagen, Denmark

ET RENÉ MERCIER

Université de Franche-Comté, Laboratoire de Chimie-Physique, 32 rue Mégevand, 25030 Besançon CEDEX, France

(Reçu le 4 septembre 1978, accepté le 5 mars 1979)

Abstract

The structure of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ has been determined by single-crystal X-ray techniques. The cell is monoclinic,

space group $P2_1/c$, unit-cell parameters $a = 6.976$ (2), $b = 9.716$ (5), $c = 12.902$ (4) Å, $\beta = 110.90$ (3)°; $V = 816.9$ Å³, $D_x = 2.06$ Mg m⁻³, $Z = 4$. The structure consists of molecular units built up of an $[\text{SO}_4]$ tetrahedron and a $[\text{VO}_6]$ octahedron sharing one apex. The asymmetric units are linked by hydrogen bonds. Four water molecules are coordinated with the vanadium,

* Adresse actuelle: Department of Physics, The University of Western Australia, Nedlands, Western Australia.