

Structure Determination of $\text{H}_2\text{V}_3\text{O}_8$ by Powder X-Ray Diffraction

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A vanadium oxyhydroxide $\text{H}_2\text{V}_3\text{O}_8$ with a green fibrous shape was hydrothermally synthesized; it was originally formulated as $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$. It has an orthorhombic symmetry: $a = 16.9298(2)$, $b = 9.3589(1)$, $c = 3.64432(4)$ Å, and $Z = 4$. The structure analysis was performed by the Rietveld method using powder X-ray diffraction data. A structure model for the space group $Pnam$ was found to be compatible with the X-ray data leading to $R_p = 0.059$ and $R_{wp} = 0.063$. The structure is described as a layer structure composed of V_3O_8 layers which are made up with VO_6 octahedra ($\text{V}(1)\text{O}_6$ and $\text{V}(2)\text{O}_6$) and VO_5 trigonal bipyramids ($\text{V}(3)\text{O}_5$), where $\text{V}(3)$ was assigned to V^{5+} and $\text{V}(2)$ was likely V^{4+} . The arrangement of VO polyhedra resembles to that in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$. © 1990 Academic Press, Inc.

Introduction

There are a number of crystalline phases in vanadium oxides, oxyhydroxides, and hydrated oxides for the oxidation numbers of vanadium between 4 and 5 and hydrothermal methods are helpful in preparing these compounds. $\text{H}_2\text{V}_3\text{O}_8$ is one of the vanadium oxyhydroxides that is synthesized especially well by hydrothermal methods. The formation of $\text{H}_2\text{V}_3\text{O}_8$ was first reported by Théobald and Cabala (1) as a product of the hydrothermal treatment of mixtures of V_2O_5

and VO_2 . This compound was formulated as a hydrated vanadium oxide $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$. Théobald (2, 3) also performed extensive studies on hydrothermal synthesis in the $\text{VO}_2\text{-VO}_{2.5}\text{-H}_2\text{O}$ system, where he reported several new crystalline phases besides $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ ($\text{H}_2\text{V}_3\text{O}_8$) belonging to the above-mentioned group, for example, $\text{VO}_2(\text{A})$, $\text{VO}_2(\text{B})$, polytypes of $\text{VO}_2 \cdot \text{H}_2\text{O}$ ($\text{VO}(\text{OH})_2$), and $\text{V}_2\text{O}_{4.8} \cdot n\text{H}_2\text{O}$. He showed that $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ had an orthorhombic symmetry ($a = 9.34(4)$, $b = 17.0(1)$ and $c = 3.626(5)$ Å) and a density of $3.26(15)\text{gcm}^{-3}$ (1). However, the structure of $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ ($\text{H}_2\text{V}_3\text{O}_8$) has remained unknown. The present authors have

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already determined the structure of $\text{VO}_2(\text{A})$ by the powder X-ray diffraction data using the Rietveld method (4) and a similar procedure has been employed here to solve the structure of $\text{H}_2\text{V}_3\text{O}_8$.

In the present study, $\text{H}_2\text{V}_3\text{O}_8$ was prepared hydrothermally from VOSO_4 aqueous solutions, which was somewhat different from the preparation method used by Théobald (1, 2). The structure determination by the Rietveld method revealed a layered structure composed of V_3O_8 layers. As mentioned above, this compound was originally formulated as $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$, but the notation of $\text{H}_2\text{V}_3\text{O}_8$ is used in the present paper instead of $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ since it seems that it better represents the structure.

Experimental and Results

Synthesis

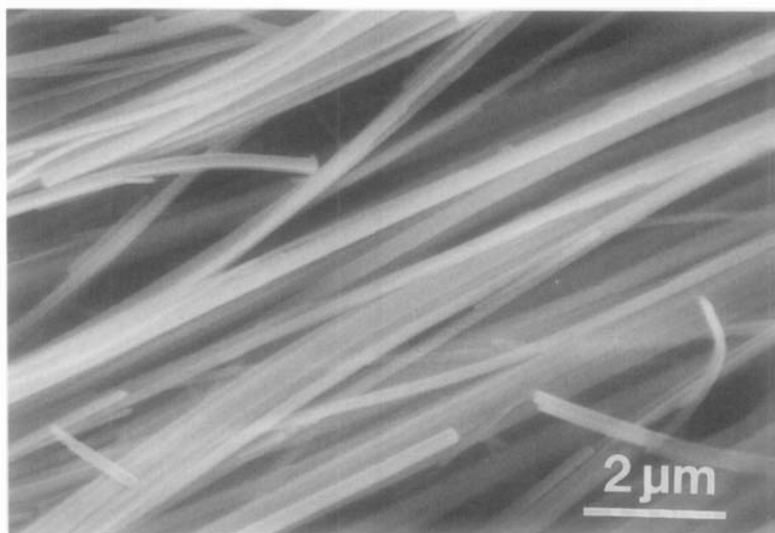
Hydrothermal treatment was conducted as follows. VOSO_4 aqueous solutions with concentrations of 0.1 to 0.2 M were sealed in Pyrex ampules followed by hydrothermal treatment in a Morey-type autoclave at 220°C for 1 to 2 days. The precipitates were separated by filtration and dried in air. The products were of green fibers with a flat surface as shown in the SEM picture of Fig. 1. The powder X-ray diffraction pattern of the products using $\text{CuK}\alpha$ radiation was identical to that of $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ reported by Théobald (1, 2). The oxidation number of vanadium was analyzed to be 4.66(2) by the absorption spectroscopy on the samples dissolved in sulfuric acid solutions. The composition $\text{H}_2\text{V}_3\text{O}_8$ was confirmed by the weight loss in TG-DTA conducted under Ar gas flow at a heating rate of 3°C min^{-1} .

Structure Determination

A powder X-ray diffraction pattern for the Rietveld method was obtained with a Rigaku Corp. Rad-B powder diffraction system equipped with a curved-crystal graphite

monochromator using $\text{MoK}\alpha$ radiation. The data were collected on thoroughly ground powders by the step-scanning method in a 2θ range of 5 to 50° with a step width 0.01° and a step time of 14 sec. The Rietveld method employed in the present study was almost the same as that in the previous study (4) and the details of the method were also described elsewhere (5).

The powder X-ray pattern taken with a $\text{CuK}\alpha$ radiation was indexed by the aid of a computer program for indexing X-ray patterns (6) on the basis of the orthorhombic symmetry with $a = 16.9298(2)$, $b = 9.3589(1)$, and $c = 3.64432(4)\text{\AA}$. Possible space groups were chosen by the results of the electron diffraction study and also of the powder X-ray diffraction. Figure 2 shows an electron diffraction pattern with the incident beam perpendicular to the fiber axis. The pattern represents the a^* plane and has revealed the systematic absence of the $0kl$ reflections with $k + l = 2n + 1$, which is consistent with the extinction rule reported by Théobald and Cabala (1). This led to possible space groups of $Pnam$, $Pna2_1$, $Pnn2$, and $Pnnm$; also, space groups $P2_12_12$ and $P2_12_12_1$ were compatible with the above extinction rule. Among the six possible space groups, $Pnn2$ and $Pnnm$ were excluded because of the clear existence of the 201 peak in the powder X-ray pattern denying the presence of a glide plane perpendicular to the b -axis. Finally, model structures with the composition of V_3O_8 were constructed for $Pnam$ and $Pna2_1$, but could not be derived for $P2_12_12$ and $P2_12_12_1$. The model structures were examined in a preliminary study of the pattern fitting and consequently proved to give satisfactory fitting to the powder X-ray pattern. The two structures were basically the same and thus $Pnam$, with higher symmetry than $Pna2_1$, was adopted in the refinement. The Rietveld refinement was carried out on the structure for $Pnam$ leading to the reliability factors $R_p = 0.059$ and $R_{wp} = 0.063$. The final result of the pattern fitting

FIG. 1. SEM photograph of $\text{H}_2\text{V}_3\text{O}_8$.

is shown in Fig. 3 and the crystallographic data are listed in Table I. It is noted in Fig. 3 that the 200 peak at $2\theta = 4.82^\circ$ was partly taken into the refinement because reliable data were collected for $2\theta \cong 5^\circ$ under our experimental conditions. The positional parameters for V and O atoms are listed in Table II.

TABLE I
CRYSTALLOGRAPHIC DATA FOR $\text{H}_2\text{V}_3\text{O}_8$

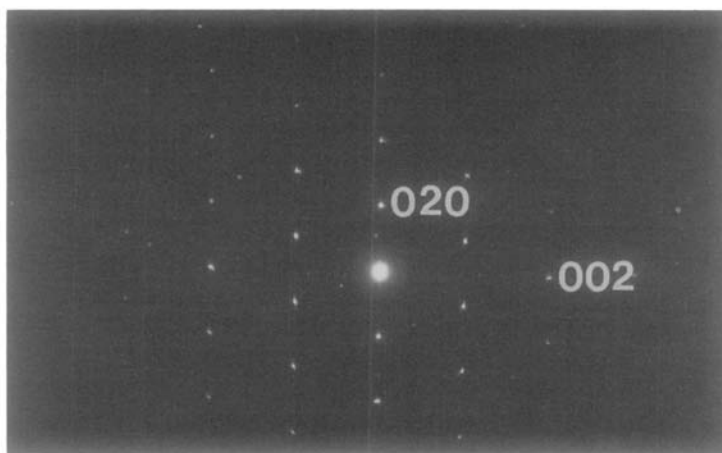
Radiation	MoK α
2θ range ($^\circ$)	5–50
Step scan increment ($2\theta^\circ$)	0.01
Count time (sec/step)	14
Space group	<i>Pnam</i>
a (\AA)	16.9298(2)
b (\AA)	9.3589(1)
c (\AA)	3.64432(4)
Volume(\AA^3)	577.42
Z	4
Calculated density (g/cm^3)	3.253
No. of reflections	592
No. of structural parameters	22
No. of profile parameters	17
R_p	0.059
R_{wp}	0.063

Description of the Structure

The crystal structure of $\text{H}_2\text{V}_3\text{O}_8$ thus determined is illustrated in Fig. 4. The structure is characterized as a nearly two-dimensional framework (V_3O_8 layer) comprised of three kinds of VO polyhedra; two VO_6 octahedra ($\text{V}(1)\text{O}_6$ and $\text{V}(2)\text{O}_6$) and one VO_5 trigonal bipyramid ($\text{V}(3)\text{O}_5$). Units of edge-shared $\text{V}(1)\text{O}_6$ and $\text{V}(2)\text{O}_6$ octahedra are piled up along the c -axis by sharing edges and are connected by two edge-shared $\text{V}(3)\text{O}_5$ trigonal bipyramids along the b -axis, forming a V_3O_8 layer in the a -plane. The V_3O_8 layers are stacked along the a -axis, resulting in a layered structure. It was also observed in the electron diffraction pattern that the $\text{H}_2\text{V}_3\text{O}_8$ fiber elongates along the c -axis. The bond distances and angles in the VO_6 octahedra and the VO_5 trigonal bipyramid are listed in Table III.

Discussion

$\text{H}_2\text{V}_3\text{O}_8$ is a mixed-valence compound composed of V^{5+} and V^{4+} in a ratio of 2 to 1. The valence states of V(1), V(2), and V(3)

FIG. 2. Electron diffraction pattern of $\text{H}_2\text{V}_3\text{O}_8$.

can be determined through the bond strength calculations around vanadium atoms using the following equation proposed by Walterson (7) for vanadium oxide compounds: $s = 21.29d^{-5.0} - 0.153$, where s is bond strength and d is bond distance. The sums of bond strengths for V(1), V(2), and V(3) were obtained as 4.53, 4.19, and 4.94, respectively, indicating that V(3) is V^{5+} and V^{4+} prefers the site of V(2) to that of V(1). It is impossible to determine the positions of hydrogen directly, but the sums of bond strengths for oxygen atoms should

offer a clue to locating hydrogen atoms. Walterson (7) also proposed another equation of $s = 29.29d^{-6.0} + 0.065$ for bond strength calculations around oxygen atoms in vanadium oxides. The sums of bond strengths for O atoms, except for O(6), range from 1.74 for O(1) to 2.04 for O(4),

TABLE II
POSITIONAL PARAMETERS FOR $\text{H}_2\text{V}_3\text{O}_8$

Atom	Position	x	y
V(1)	4c	0.04471(2)	0.12990(3)
V(2)	4c	-0.14834(2)	0.07625(3)
V(3)	4c	0.44654(1)	0.08892(3)
O(1)	4c	-0.02514(5)	-0.06573 (7)
O(2)	4c	0.10014(5)	0.26705(10)
O(3)	4c	0.13340(5)	-0.02263(6)
O(4)	4c	-0.05728(6)	0.21717(9)
O(5)	4c	-0.21875(5)	0.19122(9)
O(6)	4c	-0.22008(3)	-0.10096(10)
O(7)	4c	0.52529(4)	-0.06441(9)
O(8)	4c	0.35948(8)	0.02738(6)

TABLE III
BOND DISTANCES (Å) AND ANGLES (Å) IN VO_6 OCTAHEDRA AND VO_5 TRIGONAL BIPYRAMID

V(1) O_6 octahedron			
V(1)—O(1) ^a	1.9472(9)	V(1)—O(1)	2.179(3)
V(1)—O(2)	1.590(3)	V(1)—O(3)	2.072(3)
V(1)—O(4)	1.910(3)		
O(1) ^a —V(1)—O(1)	69.4(3)	O(1) ^a —V(1)—O(2)	110.5(4)
O(1) ^a —V(1)—O(3)	84.9(3)	O(1) ^a —V(1)—O(4)	88.7(3)
O(1)—V(1)—O(3)	79.3(4)	O(1)—V(1)—O(4)	82.6(4)
O(2)—V(1)—O(3)	97.4(5)	O(2)—V(1)—O(4)	100.8(5)
V(2) O_6 octahedron			
V(2)—O(1)	2.473(3)	V(2)—O(3) ^a	1.9067(7)
V(2)—O(4)	2.029(3)	V(2)—O(5)	1.607(3)
V(2)—O(6)	2.056(3)		
O(3) ^a —V(2)—O(6)	82.3(3)	O(3) ^a —V(2)—O(1)	75.4(3)
O(3) ^a —V(2)—O(4)	94.1(5)	O(3) ^a —V(2)—O(5)	105.9(4)
O(1)—V(2)—O(4)	73.1(5)	O(1)—V(2)—O(6)	93.8(4)
O(5)—V(2)—O(4)	97.4(5)	O(5)—V(2)—O(6)	95.8(4)
V(3) O_5 trigonal bipyramid			
V(3)—O(4) ^b	1.816(2)	V(3)—O(7) ^a	1.8976(7)
V(3)—O(7)	1.959(3)	V(3)—O(8)	1.581(3)
O(7) ^a —V(3)—O(8)	99.8(4)	O(7) ^a —V(3)—O(7)	69.8(3)
O(7) ^a —V(3)—O(4) ^b	97.5(3)	O(8)—V(3)—O(4) ^b	109.3(6)
O(8)—V(3)—O(7)	111.6(6)		

Note. Symmetry code. a, $-x, -y, \frac{z}{2}$; b, $\frac{1}{2} + x, \frac{1}{2} - y, \frac{z}{2}$.

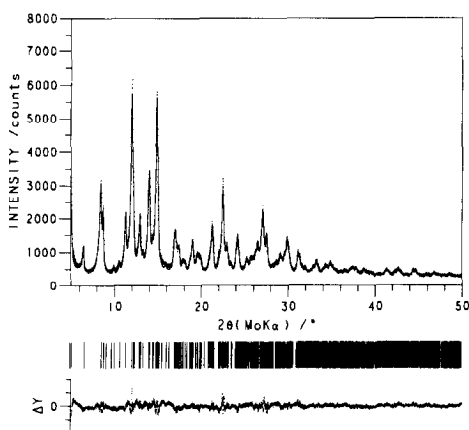


FIG. 3. Rietveld refinement plot of $H_2V_3O_8$. The calculated and observed patterns are shown on the top by the solid line and the dots, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The trace on the bottom is a plot of the difference: observed minus calculated.

which do not deviate significantly from 2, but that for O(6) is 0.45. It is noteworthy that O(6) bonds solely to V(2) at a somewhat longer distance of 2.056 Å. It is speculated at the present stage that one or two hydrogen atoms firmly attach to O(6) and bridge between O(5) and O(6) ($O(5) - O(6) = 2.859$ Å) to hold the V_3O_8 layers.

The structure of $H_2V_3O_8$ is found to be related to those of the vanadium bronzes

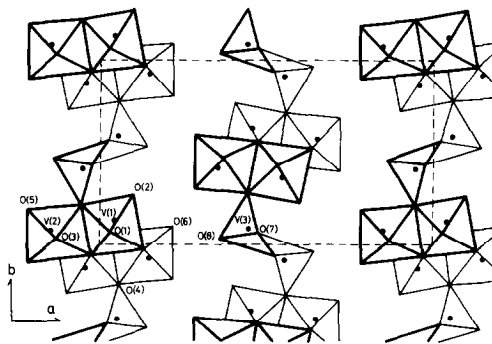


FIG. 4. Crystal structure of $H_2V_3O_8$ viewed along the c -axis.

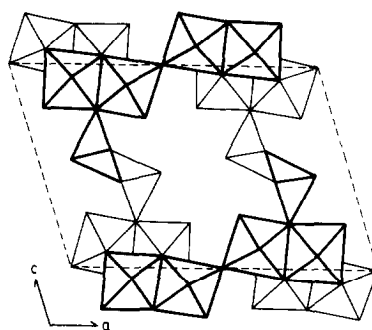


FIG. 5. Framework of VO polyhedra in the structure of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ viewed along the b -axis.

in the arrangement of VO polyhedra, especially to that of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ (8) shown in Fig. 5. It is seen by a comparison of Figs. 4 and 5 that the arrangements of VO polyhedra are almost identical in both structures. There is some dissimilarity between the two structures; the V_3O_8 layers are separated in $H_2V_3O_8$ while they are attached in $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$, forming a tunnel structure along the b -axis where Na ions are located. Therefore this compound may be regarded as a member of the vanadium bronzes from the structural point of view, and in this respect the formulation as $H_2V_3O_8$ is more appropriate than that of $V_3O_7 \cdot H_2O$.

Further studies of the electrical and magnetic properties of $H_2V_3O_8$ as well as the reactivity with other cations are in progress and will be reported in the future.

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