Synthesis and Crystal Structure of Priderite-Type Barium Vanadium Oxide Ba$_x$V$_8$O$_{16}$ (x = 1.09(1))

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The crystal structure of priderite-type barium vanadium oxide, Ba$_x$V$_8$O$_{16}$ (x = 1.09(1)), was determined. Ba$_{1.09}$V$_8$O$_{16}$: M_r = 813.209, tetragonal, $I4/m$, a = 9.9805(2)Å, c = 2.8755(1) Å, V = 286.43(1) Å^3, Z = 1, D_x = 4.714 Mg m^{-3}, μ = 9.811 mm^{-1}, F(000) = 373.04, T = 295 K, λ(Mo$K\alpha$) = 0.71073 Å, final R = 0.016 for 580 unique observed reflections. Ba$_x$V$_8$O$_{16}$ showed no detectable solid-solution range. © 1995 Academic Press, Inc.

INTRODUCTION

Since the crystal structure of hollandite was determined by Byström and Byström (1, 2), a number of hollandite- or priderite-type phases have been studied extensively. These phases contain both trivalent and tetravalent transition metal cations. V^{3+}–V^{4+} mixed-valent oxides are good objects for studying the character of 3d electrons, which are in a state intermediate between localized and itinerant.

Bouloux *et al.* (3) first synthesized hollandite-type vanadium oxide Ba$_x$VO$_2$ (0.15 ≤ x ≤ 0.17 at 1173 K) corresponding to Ba$_x$V$_8$O$_{16}$ (1.20 ≤ x ≤ 1.36). Single crystals of Ba$_{0.17}$VO$_2$ were prepared by melting a mixture with nominal composition of BaV$_4$O$_9$ at 1423 K and were shown to crystallize in a tetragonal system by Weissenberg photography (3); however, the crystal structure of Ba$_x$VO$_2$ has not been determined yet. Hollandite-type and hollandite-related vanadium oxides K$_2$V$_8$O$_{16}$ (4), A_{2-x}V$_8$O$_{16}$ (A = K, Tl) (5), A_{2-x}V$_{8+2x}$O$_{16+x}$ (A = K, Rb) (6), K$_{3.46}$V$_{40.6}$O$_{68.3}$ (7), Bi$_{1.7}$V$_8$O$_{16}$ (8), and BaV$_{10-x}$O$_{17}$ (9) were prepared and their crystal structures were determined. In this study, tetragonal priderite-type barium vanadium oxide, Ba$_x$V$_8$O$_{16}$ (x = 1.09 ± 0.01), was prepared and its crystal structure was determined by an X-ray single-crystal diffraction study.

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EXPERIMENTAL AND RESULTS

Sample Preparation

V$_2$O$_3$ was obtained by reducing V$_2$O$_5$ (99.9%) under hydrogen at 1073 K. V$_2$O$_4$ was prepared by heating an equimolar mixture of V$_2$O$_5$ and V$_2$O$_3$ in a sealed silica tube at 1273 K for 3 days. BaV$_2$O$_6$ was obtained by heating a mixture of BaCO$_3$ (99.9%) and V$_2$O$_5$ in a 1 : 1 molar ratio at 923 K for 2 days.

Polycrystalline samples with the composition Ba$_x$V$_8$O$_{16}$ were obtained as follows. BaV$_2$O$_6$, V$_2$O$_3$, and V$_2$O$_4$ were mixed in a x:2x:4–3x molar ratio. About 1.5 g of the mixture was placed in a platinum capsule, sealed in an evacuated silica tube, and then heated at 1173 K for 1 day. After cooling to room temperature, the product was ground and examined by X-ray powder diffraction with Cu$K\alpha$ radiation. This procedure was repeated until its X-ray powder pattern changed no longer. Two heating runs (1 and 5 days) were required to reach equilibrium.

Single-crystal samples were prepared as follows. BaV$_2$O$_6$, V$_2$O$_3$, and V$_2$O$_4$ were mixed in a 1.1 : 2.2 : 0.7 molar ratio. About 1.5 g of the mixture was placed in a platinum capsule and sealed in an evacuated silica tube. It was heated at 873 K for 20 hr. The temperature was raised to 1173 K at a rate of 100 K/hr; then the sample was kept at 1173 K for 1 month. After cooling to room temperature, column-shaped black crystals were selected for an X-ray diffraction study. Weissenberg photographs revealed that the phase crystallizes in a body-centered tetragonal system, a = 10.0 and c = 2.9 Å. The size of the specimen for the intensity collection was 0.032 × 0.032 × 0.110 mm (along [110], [1$\bar{1}$0], and [001], respectively).

The Ba$_x$V$_8$O$_{16}$ samples with nominal composition of x = 1.07, 1.08, 1.09, 1.095, 1.10, 1.11, and 1.12 were examined by X-ray powder diffraction. Those with x = 1.095 and 1.10 were single-phased Ba$_x$V$_8$O$_{16}$. Those with x = 1.07–1.09 and 1.11–1.12 were mixtures of Ba$_x$V$_8$O$_{16}$ and V$_2$O$_4$ and mixtures of Ba$_x$V$_8$O$_{16}$ and unidentified phase(s), respectively. Lattice parameters of Ba$_x$V$_8$O$_{16}$ in these specimens were calculated on the basis of the X-ray

TABLE 1
X-Ray Powder Diffraction Pattern of $Ba_{1.09}V_8O_{16}{}^a$
(Tetragonal, $I4/m$, a = 9.9816(2), c = 2.8770(3) Å)

h k l	d_{obs} (Å)	d_{calc} (Å)	I/I_0	h k l	d_{obs} (Å)	d_{calc} (Å)	I/I_0
1 1 0	7.048	7.058	3	4 0 2^b	1.2464	1.2463	<1
2 0 0	4.988	4.991	16	7 2 1	1.2375	1.2377	1
2 2 0	3.527	3.529	27	8 2 0	1.2101	1.2105	1
3 1 0	3.156	3.156	100	6 6 0	1.1763	1.1763	3
1 0 1	2.7643	2.7645	1	7 5 0	1.1603	1.1603	2
4 0 0	2.4956	2.4954	6	7 4 1	1.1373	1.1372	1
2 1 1	2.4182	2.4183	14	8 4 0	1.1158	1.1160	1
4 2 0	2.2321	2.2320	22	9 1 0	1.1024	1.1023	2
3 0 1	2.1758	2.1763	8	6 0 2	1.0882	1.0881	1
3 2 1	1.9951	1.9949	2	8 3 1	1.0823	1.0824	1
5 1 0	1.9574	1.9576	9	9 0 1	1.0350	1.0348	1
4 1 1	1.8522	1.8524	9	7 6 1	1.0131	1.0133	2
4 4 0	1.7642	1.7645	13	5 5 2	1.0076	1.0075	<1
5 3 0	1.7118	1.7118	6	8 6 0	0.9980	0.9982	1
6 0 0	1.6640	1.6636	24	8 5 1	0.9932	0.9930	1
6 2 0	1.5783	1.5782	2	10 2 0	0.9788	0.9788	1
5 2 1	1.5581	1.5582	10	7 3 2	0.9689	0.9688	1
0 0 2	1.4386	1.4385	2	9 4 1	0.9559	0.9559	<1
6 1 1	1.4252	1.4254	2	10 1 1	0.9389	0.9388	1
5 5 0	1.4116	1.4116	3	10 4 0	0.9269	0.9268	1
6 4 0	1.3841	1.3842	2	3 0 3	0.9214	0.9215	<1
5 4 1	1.3707	1.3706	9	6 6 2	0.9107	0.9106	1
6 3 1	1.3215	1.3217	2	7 5 2	0.9032	0.9032	<1
7 3 0	1.3107	1.3107	7	4 1 3	0.8916	0.8916	<1
7 0 1	1.2774	1.2776	1				

^{a} Nominal composition is $Ba_{1.095}V_8O_{16}$.
^{b} From Si (internal standard) free data.

diffraction data collected using Si as an internal standard (Table 1). The lattice parameters showed no significant differences among these samples. X-ray microanalysis was performed on the above-mentioned single-crystal samples using $LaVO_4$ and $BaAl_2O_4$ as standard materials. The Ba:V ratio was determined to be 1.09(1):8. On the basis of the above results, the $Ba_xV_8O_{16}$ phase was concluded to have a unique composition of x = 1.09(1). The homogeneity range, if any, is insignificant. We tried to prepare $Ba_{1.09}V_8O_{16}$ at higher temperatures; however, some X-ray diffraction peaks of $Ba_{1.09}V_8O_{16}$ broaden if it is prepared at 1223 K. $Ba_{1.09}V_8O_{16}$ decomposes above 1273 K.

Crystal Structure Analysis

X-ray single crystal diffraction data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromatized $MoK\alpha$ radiation (λ = 0.71073 Å) by ω–θ scan with $\Delta\omega$ = (0.8 + 0.35 × tan θ)° at 295 K. Lattice parameters were determined from 22 reflections (80° < 2θ < 90°). Both hkl and $\bar{h}kl$ reflections for $0 \le h \le 19$, $0 \le k \le 19$, $0 \le l \le 5$, with $2\theta \le 90°$ were measured. Three standard reflections 600, 060, and $00\bar{2}$ were measured

every 4 hr, and the decrease in intensity was 1.6% during the total exposure time of 105.9 hr. A linear decay correction was applied. An absorption correction was applied with a correction factor for F from 1.167 to 1.210. Among collected 1438 reflections, 168 were unobserved. The 1438 collected reflections were averaged into 671 unique reflections with R_{int} for F = 0.010. Finally, 580 reflections with $I > 1.5 \sigma(I)$ were used for refinement. Atomic scattering factors ($f = f_0 + \Delta f' + i\Delta f''$) for neutral atoms were taken from Ref. (10). Structural parameters were refined by a least-squares method (11) based on F by employing an extinction correction.[2]

An initial structure model with tetragonal $I4/m$ symmetry was quoted from Ref. (1). The occupancy of Ba

TABLE 2

Atomic Positions in Wyckoff Notation, Occupancies (g), Positional Parameters, and Equivalent
Isotropic Thermal Parameters (Å^2) of $Ba_{1.09}V_8O_{16}$ (Tetragonal, $I4/m$, $a = 9.9805(2)$ Å, $c = 2.8755(1)$
Å, $Z = 1$, $B_{eq} = \frac{8}{3}\pi^2 \times (U_{11} + U_{22} + U_{33})$)

Atom	Wyckoff position	g	x	y	z	B_{eq}
Ba(1)	$2b$	0.3841(7)	0	0	1/2	1.250(6)
Ba(2)	$4e$	0.0804^a	0	0	0.3251(5)	0.62(1)
V	$8h$	1	0.35226(2)	0.16964(2)	0	0.548(2)
O(1)	$8h$	1	0.15450(9)	0.19637(9)	0	0.51(1)
O(2)	$8h$	1	0.53879(9)	0.16543(10)	0	0.59(1)

^{a} $g(Ba(2))$ is constrained as follows: $g(Ba(2)) = \{1.09{-}4 \times g(Ba(1))\}/2$.

was fixed to retain the composition $Ba_{1.09}V_8O_{16}$. The R
value converged to as low as 0.039; however, a difference
Fourier synthesis detected a significant residual at a $4e$
position, $(0, 0, z)$. The next refinement was performed on
the assumption that Ba atoms occupy both $2b$ $(0, 0, 1/2)$
and $4e$ $(0, 0, z)$ positions and that the composition is
$Ba_{1.09}V_8O_{16}$. The refinement was successful: the R value
converged to 0.016 and absolute residual electron density
was less than 0.640 e Å^{-3}. Three possible space groups,
$I4/m$, $I4$, and $I\bar{4}$, were tested using unaveraged intensity
data. Neither $I4$ nor $I\bar{4}$ models provided lower R values
than the $I4/m$ model. Therefore, the highest symmetry,
$I4/m$, was selected from the possible space groups. $R =$
0.016, $R_W = 0.027$, $w = 1/\sigma^2(F)$, $\Delta/\sigma < 0.005$ in final
refinement cycle, $-0.609 \le \Delta\rho \le 0.640$ e Å^{-3}.

DISCUSSION

Both $Ba_xVO_2(3)$ and $Ba_{1.09}V_8O_{16}$ crystallize in a body-
centered tetragonal and their lattice parameters are
nearly equal; therefore, they appear to be identical. How-
ever, the Ba : V ratio of the former $(1.20 : 8{-}1.36 : 8)$ is
variable and significantly higher than that of the latter.
This is attributable to the difference in sample prepara-
tion. To obtain Ba_xVO_2, Bouloux et $al.$ (3) sealed the
starting mixture directly into an evacuated vycor-glass
tube. This method allows reactions between the mixture
and the vycor-glass tube. An excess of barium was neces-
sary to compensate for the loss of BaO absorbed by the

tube wall and the product remained single-phased so long
as the tube wall could absorb all the excess barium. In
$Ba_{1.09}V_8O_{16}$ preparation, the reaction between the stoi-
chiometric mixture and the silica tube is prevented by the
platinum capsule which was placed between them. In-
deed, an X-ray microanalysis proved that the Ba : V ratio
of the product (1.09 ± 0.01) is consistent with that of the
starting mixture (1.10).

The atomic fractional coordinates and the equivalent
isotropic thermal parameters of $Ba_{1.09}V_8O_{16}$ are listed in
Table 2. The anisotropic thermal parameters are listed in
Table 3. Interatomic distances in $Ba_{1.09}V_8O_{16}$ are shown
in Table 4. Figure 1 shows the crystal structure of
$Ba_{1.09}V_8O_{16}$ along [001]. The VO_6 octahedra form a dou-
ble chain along [001] through edge-sharing. A large tunnel
along [001] is formed by four chains: two tunnels per unit
cell. Two VO_6 octahedra which belong to different chains
share an octahedral corner. The formal charge of V cat-
ion is $+3.7275$. The $\overline{V{-}O}$ distance of 1.9473 Å (Table 4) is
almost equal to $r(^{VI}V^{4+}) + r(^{IV}O^{2-}) = 1.96$ Å (12).

Both Ba(1) and Ba(2) atoms occupy the center of the
tunnel and are coordinated by eight O(1) atoms. The
Ba(1) is located at the $2b$ position and its occupancy,
0.3841(7), is nearly equal to $5/13 \approx 0.3846$. The Ba(2) is
located at a $4e$ position and its occupancy, 0.0804, is
close to $1/13 \approx 0.0769$. Therefore, the Ba distribution ap-
pears to be explained assuming that each tunnel includes
5 Ba(1) and 2 Ba(2) atoms per 13 c units. As the distance
of 2.8755(1) Å between two adjacent Ba(1) sites is too

TABLE 3
Anisotropic Thermal Parameters of $Ba_{1.09}V_8O_{16}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	0.01019(9)	U_{11}	0.0271(2)	0	0	0
Ba(2)	0.0087(2)	U_{11}	0.0060(4)	0	0	0
V	0.00723(6)	0.00718(6)	0.00642(7)	0.00106(5)	0	0
O(1)	0.0068(3)	0.0069(3)	0.0057(3)	0.0008(2)	0	0
O(2)	0.0049(3)	0.0106(3)	0.0068(3)	0.0006(2)	0	0

TABLE 4
Interatomic Distances (Å) in $Ba_{1.09}V_8O_{16}$

V–O(2)	1.8621(10)	Ba(1)–O(1)^{v,vi,vii,viii,ix,x,xi,xii}	2.8785(8)
V–O(2)^{i,ii}	1.9503(6)		
V–O(1)^{iii,iv}	1.9647(7)	Ba(2)–O(1)^{v,vii,ix,xi}	2.6632(10)
V–O(1)	1.9917(10)	Ba(2)–O(1)^{vi,viii,x,xii}	3.1598(11)
$\overline{V–O}$	1.9473	$\overline{Ba(2)–O}$	2.9115
V–V^{vi}	2.8755(1)		
V–V^{iii}	2.9676(3)		

Note. Symmetry operations: (i) $1/2 - y$, $-1/2 + x$, $1/2 + z$; (ii) $1/2 - y$, $-1/2 + x$, $-1/2 + z$; (iii) $1/2 - x$, $1/2 - y$, $1/2 + z$; (iv) $1/2 - x$, $1/2 - y$, $-1/2 + z$; (v) x, y, z; (vi) $x, y, 1 + z$; (vii) $-x, -y, z$; (viii) $-x, -y, 1 + z$; (ix) $-y, x, z$; (x) $-y, x, 1 + z$; (xi) $y, -x, z$; (xii) $y, -x, 1 + z$.

short for a real Ba–Ba distance, we must assume that they cannot be occupied simultaneously. If we further assume that the Ba^{2+} cations tend to be uniformly distributed within a tunnel, we obtain a possible model of their distribution, as shown in Fig. 2. This Ba configuration allows larger thermal motion along the [001] direction for the Ba(1) atom than the Ba(2) atom, because the adjacent Ba(1)–Ba(1) interatomic distance is longer than both adjacent Ba(1)–Ba(2) and Ba(2)–Ba(2) distances. Indeed, the U_{33} of Ba(1) atom is much larger than that of Ba(2),
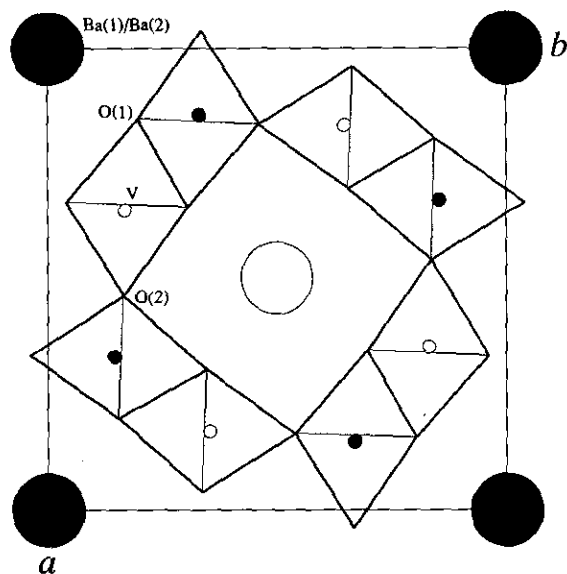

FIG. 1. Projection of the structure of $Ba_{1.09}V_8O_{16}$ onto (001) drawn with ATOMS (Shape Software). Large and small circles indicate Ba and V atoms, respectively. The y coordinates of the open circles are 0 and those of the filled circles are 1/2. Open and hatched tetragons denote coordination octahedra of V atoms, the y coordinates of which are 0 and 1/2, respectively.
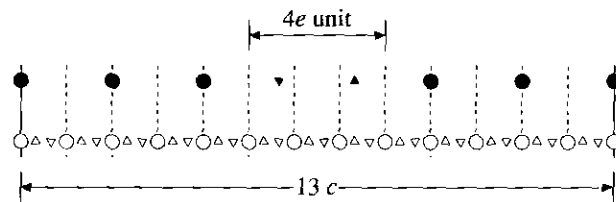

FIG. 2. Ba configuration in the tunnel along [001]. Dashed lines indicate unit-cell boundaries. Circles and triangles show the Ba(1) and Ba(2) sites, respectively. A set of solid circles and triangles shows an example of a possible configuration for occupied Ba sites. According to the space group, $I4/m$ which contains the center of symmetry, numbers of ▲ and ▼ should be equal.

despite that the U_{11} values of the two atoms are nearly equal (Table 3). There is no periodicity about how to locate the $4e$ unit per 13 c units, because no additional line was detected in an oscillation photograph around [001]. This model with 14 Ba atoms in 13 unit cells results in a composition of $Ba_{1.077}V_8O_{16}$. The Ba(1)–O (2.8785 Å) and $\overline{Ba(2)–O}$ (2.9115 Å) distances are slightly longer than $r(^{VIII}Ba^{2+}) + r(^{IV}O^{2-}) = 2.80$ Å (12).

$Ba_{1.09}V_8O_{16}$ becomes unstable above 1223 K and decomposes above 1273 K. On the other hand, the hollandite-related phase, $BaV_{10-x}O_{17}$, was obtained at 1473 K (9). The Ba and O atoms in $BaV_{10-x}O_{17}$ form close-packed layers chhchh. . . of which the c layers contain the Ba atom (9). However, those atoms in $Ba_{1.09}V_8O_{16}$ do not form close-packed layers. The difference in the stabilities of these phases at high temperature appears to be sensitive to the packing of Ba and O atoms.

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