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$Bi_{1.7}V_8O_{16}$: The First Bi-Hollandite-Type Compound

F. Abraham and O. Mentre

Laboratoire de Cristallochimie et Physcochimie du Solide, URA CNRS 452, ENSCL, Université des Sciences et Technologies de Lille, BP 108, 59652 Villeneuve d'Ascq Cedex, France

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$Bi_{1.7}V_8O_{16}$ was synthesized by high temperature solid state reaction between Bi_2O_3, V_2O_5, and V_2O_3. The compound crystallizes with tetragonal symmetry, space group *I4/m*. The structure refinement using single crystal data confirms that the compound belongs to the hollandite family. It is the first hollandite-type compound containing bismuth in the large tunnels of the V_8O_{16} framework. The bismuth atom forms a very flat BiO_4 square pyramid with the skeleton oxygen atoms. $Bi_{1.7}V_8O_{16}$ is oxidized to $BiVO_4$ and V_2O_5 at 400°C in air, as evidenced by TGA and DSC.

INTRODUCTION

The Bi_2O_3–V_2O_5 system has been investigated by several authors (1–6). Among the isolated compounds, two in particular have been studied: the ferroelastic $BiVO_4$ (7) and $Bi_4V_2O_{11}$ (8–14) which is the first term of a series of anionic conductors named BIMEVOX (15–20). The structure of these conductors is built of $Bi_2O_2^{2+}$ layers, and they belong to the Aurivillius family. In an attempt to synthesize $Bi_4V_3O_{12}$, an hypothetic $n = 3$ member of the Aurivillius family analogous to $Bi_4Ti_3O_{12}$, Ramanan *et al.* (21) obtained $Bi_{1.33}V_2O_6$ or $Bi_2V_3O_9$, a compound in which vanadium is present in the +4 state and which adopts a distorted pyrochlore structure with an orthorhombic cell $a = 7.04$ (3), $b = 7.55$ (3), and $c = 10.70$ (2) Å, as determined from powder diffraction patterns. More recently, Varma *et al.* (11) indexed the X-ray powder pattern of this compound with different orthorhombic parameters: $a = 7.622$, $b = 6.977$, and $c = 23.35$ Å. High-resolution electron microscopy images showed that the unit cell consists, along c, of recurrent intergrowths of two subunits of 7 and 16 Å. The authors suggested the possibility of a layered structure somewhat similar to that of ThV_2O_7.

During attempts to grow single crystals of this compound we isolate a new phase which belongs to the hollandite family. We report in this paper its crystal structure and the solid state preparation of powder samples.

PREPARATION

The compound $Bi_{1.33}V_2O_6$ was prepared according to the previously described method (21) from a mixture of Bi_2O_3–V_2O_5–V_2O_3 in the proportions 4:3:3 heated at 800°C for 6 days in a silica tube sealed under primary vaccum. The X-ray pattern of the powder was identical to that of $Bi_{1.33}V_2O_6$ (JCPDS 39.0105). The powder sample was reheated in a sealed evacuated silica tube at about 1050°C for a few hours and then cooled by cutting off the furnace.

The product thus obtained was not homogeneous; it contained a powder phase and a few black needle-shaped single crystals. The X-ray powder pattern of the product showed, in addition to the reflections of $Bi_{1.33}V_2O_6$, a small amount of $BiVO_4$.

Astonishingly, structure determination of the black single crystal from X-ray diffraction led, not to $Bi_{1.33}V_2O_6$, but to $Bi_{1.625}V_8O_{16}$! Pure phase of composition $Bi_{1.7}V_8O_{16}$ was obtained by reaction of the appropriate amounts of Bi_2O_3, V_2O_5, and V_2O_3 at 850°C for 72 h, in a sealed evacuated silica tube.

STRUCTURE DETERMINATION

A single crystal was mounted with the greatest dimension of the needle as the rotation axis. Preliminary oscillation and Weissenberg photographs indicated 4/*m* Laüe symmetry. Systematic absences ($hk\bar{l}$: $h + k + l = 2n + 1$) were consistent with space groups $I\bar{4}$, $I4/m$, $I4$. The intensity data were collected with a Philips PW 1100 automated diffractometer. Conditions for data collection are given in Table 1. The intensity of each reflection was corrected for background and for Lorentz and polarization effects.

Possible space groups and lattice dimensions suggested a hollandite-type structure for this new compound. Refinement in the $I4/m$ space group with bismuth and vanadium coordinates given by Byström and Byström (22) for hollandite structures failed. In fact, calculation of the Patterson function showed that bismuth atoms are lo-

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TABLE 1
Crystal Data, Intensity Measurement, and Structure Refinement Parameters for $Bi_{1.625}V_8O_{16}$

Crystal data	
Crystal symmetry	Tetragonal
Space group	*I4/m*
Cell dimension (Å)	a = 9.930 (4)
	c = 2.914 (1)
Volume (Å^3)	287.3
Z	1
Data collection	
Equipment	Philips PW 1100
λ (Mo$K\alpha$ (graphite monochromator))	0.7107 Å
Scan mode	$\omega - 2\theta$
Scan width (°)	1.4
θ range (°)	2–30
Standard reflections	101, 310, 141 measured every 2 hr (no decay)
Recording reciprocal space	$-13 \le h \le 13$, $-13 \le k \le 13$, $0 \le l \le 4$
Number of measured reflections	913
Number of reflections $I > 3\sigma(I)$	799
Number of independent reflections	206
μ(cm^{-1}) (for λ $K\alpha$ = 0.7107 Å)	317.7
Limiting faces and distances (mm) from an arbitrary origin	001 00$\bar{1}$ 0.16 1$\bar{1}$0 $\bar{1}$10 0.24 110 $\bar{1}\bar{1}$0 0.16
Transmission factor range	0.43–0.61
Merging R factor	0.058
Refinement	
Number of refined parameters	18
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.022
$R_w = [\Sigma_w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma F_o^2]^{1/2}$	0.027
With $\omega = 1/\sigma(F_o)$	

cated in a (2*a*) site (0, 0, 0) rather than a (2*b*) site (0, 0, ½). However, a Fourier difference synthesis calculated with vanadium and bismuth atoms indicated significant residual peaks along the *c*-axis on both sides of the origin. Consequently the Bi atom was split into a (4*e*) site (0, 0, *z*; 0, 0, $\bar{z}$). A subsequent difference synthesis showed oxygen atoms in two (8*h*) sites with coordinates in accordance with Byström and Byström model. At this stage, isotropic temperature factors for V and O atoms were negative; refinement of the occupancy factor of Bi site to a value of 0.429(6) remedied this problem and led to the chemical formula $Bi_{1.72}V_8O_{16}$. Then absorption corrections were performed using the analytic method of De Meulenaer and Tompa (23). In the last cycles of refinement U_{ij} thermal parameters were introduced for Bi and V atoms. Refinement of secondary extinction coefficient and introduction of a weighting scheme reduced the occupancy factor of Bi site to 0.406(2) and gave the results reported in Table 2.

Scattering factors were taken from (24). The anomalous dispersion corrections were made according to Cromer and Liberman (25). The full matrix least-squares refinements were performed with a local modification of SFLS-5 (26).

DISCUSSION

The analysis of the data indicates that the chemical composition of the product is close to $Bi_{1.6-1.7}V_8O_{16}$. It belongs to the large group of hollandite-type phases. Mineral hollandite with the formula $[(Ba,Pb,Na,K)_{\approx 1}$ $(Mn,Fe,Al)_8$ $(O,OH)_{16}]$ is one member of an entire family of natural and artificial isostructural compounds of the general formula $A_xM_8O_{16}$. In these compounds the *A* cation may be monovalent or divalent (*A* = Na,K,Rb,Cs,Tl,Sr, Ba,Pb), and the smaller *M* cation may be a combination of two metals, the less abundant being of lower valence (Mg,Al,Ni,Zn,Co,Cr,Fe,Mn,Ga,Cu, ...) than the other (Ti,Sn,Ru,Ge,Si,Sb), or one metal being present at two different oxidation states (Mn,V,Cr,Ti,Ru,Mo). This family has been extensively studied for several reasons; (i) sanidine feldspar $KAlSi_3O_8$ is transformed at 120 kbars and 900°C to the high-density hollandite structure (27) and this form has been proposed as a major phase of the earth's mantle; (ii) manganese oxide hollandite-type minerals (hollandite, cryptomelane, priderite, ...) are constituents of manganese deposits; (iii) some hollandite-type oxides are known as 1-D fast ion conductors for alkali ions (28, 29); (iv) $Ba_x(Al^{3+}Ti^{4+})_8O_{16}$ hollandite is used as a host for the immobilization of radioactive wastes in the

TABLE 2
Positional Parameters and Coefficients of the Anisotropic Thermal Factors for $Bi_{1.625}V_8O_{16}$

Atom	Site	Occupancy factor	Positional Parameters (×10^5) x	y	z	B or B_{eq}(Å^2)[a]
Bi	4*e*	0.406(2)	0	0	10449(28)	1.62(3)
V	8*h*	1	35504(8)	17023(8)	0	0.54(2)
O(1)	8*h*	1	15302(36)	19406(36)	0	0.59(6)
O(2)	8*h*	1	54078(36)	16439(36)	0	0.64(6)

Atom	Anisotropic Temperature Coefficients (×10^4)[b] U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	147(3)	$=U_{11}$	322(9)	0	0	0
V	58(4)	58(4)	90(5)	2(3)	0	0

[a] The B_{eq} are defined by $B_{eq} = \frac{1}{3}\Sigma_i\Sigma_j\beta_{ij}a_ia_j$.

[b] The anisotropic temperature factor is defined by $U = \exp(-2\pi^2 \Sigma_i\Sigma_j a_i^* a_j^* U_{ij})$.

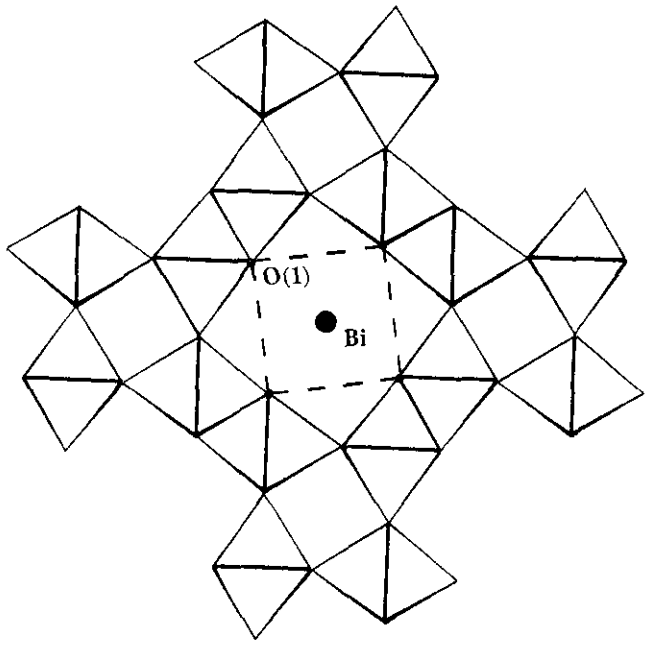

FIG. 1. The hollandite structure projected along the tetragonal *c*-axis.

mineral assemblage known as SYNROC (30); (v) titanates with the hollandite structure exhibit photoelectrochemical properties (31).

The hollandite structure first reported by Byström and Byström (22) can be described as a $[M_8O_{16}]$ host lattice which consists of infinite rutile chains parallel to the *c*-axis sharing edges to form double strings that are connected at their corners, forming large channels (2 × 2 octahedra) with square cross-section and rutile-type channels (1 × 1 octohedra) in equal numbers along the *c*-axis (Fig. 1). The *A* cations occupy the large channels.

The resolution of the structure of $Bi_xV_8O_{16}$ confirms the classical $[M_8O_{16}]$ framework. Only three vanadium compounds have been reported as adopting the hollandite-type structure: $K_2V_8O_{16}$, $K_{1.8}V_8O_{16}$, and $Tl_{1.74}V_8O_{16}$ (32). In these oxides the mean oxidation state of vanadium is about 3.75; in the Bi-hollandite, it is significantly lower (3.36). However the average V–O distances within an octahedron are, for the four compounds, nearly equal (1.954, 1.945, 1.948, and 1.957 Å, respectively) although the ionic radius of V^{4+} is appreciably smaller than that of V^{3+} (33). These average distances are nevertheless higher than that calculated for VO_2 (1.940 Å) (34). Despite these nearly equal average values, the V–O distances within an octahedron are somewhat different (Table 3); in particular, V–O(1)(2×) distances are longer in Bi-hollandite than in K- or Tl-hollandite, whereas V–O(2)(1×) is smaller; otherwise V–O distances in Bi-hollandite vary from 1.845 to 2.020 Å, while those in K- and Tl-hollandite vary from 1.876 to 2.00 Å, and those in VO_2 from 1.763 to 2.064 Å. Moreover, bond-length bond-strength calculations using the method of Brown and Shannon (35), and the data of Brown and Altermatt (36) for V^{4+} (r_0 = 1.784, B = 0.37) lead, for the K_2–, $K_{1.8}$–, and $Tl_{1.74}$–V hollandite compounds, to the average valency of 3.80, 3.90, and 3.86 respectively; these values agree quite well with the average charge calculated from the stoichiometry (3.75, 3.79, 3.78). In contrast, the average charge calculated for the Bi-hollandite from the stoichiometry based on the refined site occupation factor is only 3.39; this value can be obtained from the bond valence parameters calculation using V^{3+}, (r_0 = 1.743, B = 0.37) instead of V^{4+}, data.

In the ideal hollandite structure, the *A* cations are located in the (2*b*) site of the *I*4/*m* space group and are coordinated by eight equivalent O(1) oxygen atoms at the vertices of a tetragonal prism. Relatively small cations are displaced from the special (2*b*) position, toward the base plane of the tetragonal prism, to a more stable (4*e*) site, which is approximately located at a distance from the nearest O(1) atoms equal to the sum of the ionic radii. For instance, in mineral hollandite, although Ba occupies the (2*b*) site, Pb^{2+} is displaced from the (2*b*) to the (4*e*) position (0, 0, *z*) with z = 0.30, leading to four Pb–O distances of 2.65 Å (37). The Bi^{3+} ion is smaller than Pb^{2+} and is displaced nearest the O(1) plane (z = 0.10), leading to a practically square plane coordination with four Bi–O distances of 2.473 Å and an O(1)–Bi-O (1) angle of 166°. In the flat BiO_4 pyramid, the Bi^{3+} ion is only 0.30 Å above the square O_4 base. BiO_4 pyramids are found in the $Bi_2O_2^{2+}$ layers characteristic of the Aurivillius family, but in these compounds they are not so flat (Fig. 2).

Galy and Enjalbert (38) reported that the center Es of the sphere of influence of the Bi^{3+} lone pair is at 0.98 Å from the Bi^{3+} cation center; on the basis of their results, the Es center occupies in our compound a (0, 0, *z*) positions with $z \simeq 0.44$, and is located near the (2*b*) site leading to Es–O(1) distances of 2.77 Å.

In hollandite-type compounds it is sometimes difficult to get the actual location of the *A* cation; in hollandite with fully occupied tunnel sites, the cation is located in the (2*b*) position and the anisotropic thermal ellipsoid is

TABLE 3
Vanadium–Oxygen Distances in the Different Vanadium Hollandite Compounds

	$K_2V_8O_{16}$	$K_{1.8}V_8O_{16}$	$Tl_{1.74}V_8O_{16}$	$Bi_{1.62}V_8O_{16}$
V–O(1) (1×)	1.972(4)	1.990(7)	2.00(1)	2.020(4)
(2×)	1.966(3)	1.947(6)	1.95(1)	1.986(2)
V–O(2) (1×)	1.896(4)	1.876(7)	1.89(1)	1.845(4)
(2×)	1.958(3)	1.954(6)	1.95(1)	1.953(2)
Average	1.954	1.945	1.948	1.957

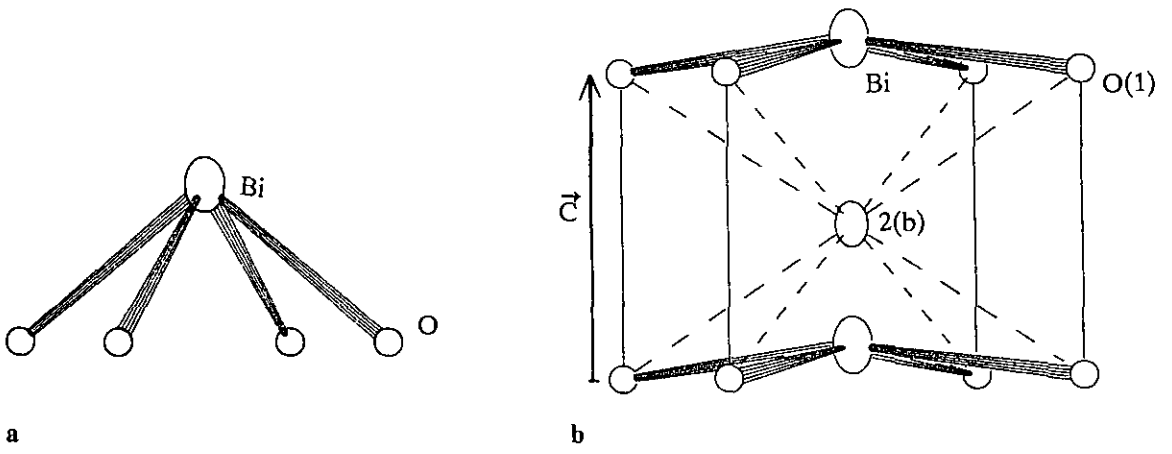

FIG. 2. The BiO_4 pyramid in (a) the $Bi_2O_2^{2+}$ layers of the Aurivillius family compounds and (b) the hollandite $Bi_{1.7}V_8O_{16}$.

slightly elongated along the [001] direction; on the contrary, in $A_{2-x}M_8O_{16}$ compounds, if the cation is randomly distributed in the (2*b*) site, the root mean square amplitude of the anisotropic vibration is high along the tetragonal *c*-axis (about 0.5 Å), and lower rms values can be obtained with an *A* cation occupying two positions on both sides of the (2*b*) site in the *c* direction (39). In our compound bismuth atoms are located on a (4*e*) site on both sides of the (2*a*) position with a rms in the [001] direction of 0.18 Å, compared with 0.12 Å in the perpendicular plane. A refinement carried out with bismuth in (0, 0, 0) instead of (0, 0, *z*) leads to a larger anisotropic vibration along [001] (rms = 0.41 Å) and to higher reliability factors (R = 0.069 and R_w = 0.102); these results indicate that, in the Bi-hollandite, the location of the bismuth in the channel is not ambiguous.

Moreover, the nonstoichiometric phases frequently exhibit commensurate or incommensurate superlattice ordering of the tunnel cation (40–45). Conversely, in our compound, crystal rotation diagrams ([001] rotation axis) based on long exposure times do not show any superstructure reflection or diffuse streaking between the Bragg spots.

Pure powder bismuth hollandite was obtained from the starting composition corresponding to $Bi_{1.7}V_8O_{16}$. For all other compositions two-phase mixtures were obtained. The unit cell parameters refined using data collected with a Siemens D5000 Diffractometer (CuKα radiation) equipped with a monochromotor, and corrected for $K\alpha_2$ contribution, confirm the single-crystal results (a = 9.9331(7), c = 2.9116(4) Å) (Table 4). The intensities of powder diffraction lines calculated using single-crystal results are compared with peak intensities observed on both Guinier–De Wolff and diffractometer patterns. It is obvious that these intensities are highly affected by orientation effects.

Figure 3 shows the TGA and DSC curves of $Bi_{1.7}V_8O_{16}$ powder heated at 0.5°C/min to 550°C in air for TGA, and 10°C/min to 640°C for DSC. It is seen that the 9.8% weight gain begins at 300°C and finishes at 480°C. The powder changes color from black to orange on heating. X-ray analysis shows that the orange powder consists of $BiVO_4$ and V_2O_5. The behavior observed on the DSC curve is more complicated: the oxidation proceeds by two steps and is followed by V_2O_5 melting. Thus the ther-

TABLE 4
Observed and Calculated X-Ray Powder Diffraction Pattern for $Bi_{1.7}V_8O_{16}$

h k l	$2\theta_{obs}$	$2\theta_{cal}$	I_{cal}	I_{obs}[a]	I_{obs}[b]
1 1 0	12.620	12.627	26.7	26.7	23.2
2 0 0	17.879	17.879	5.7	7.7	5.8
2 2 0	25.370	25.375	30.1	49.2	30.8
3 1 0	28.425	28.425	100	100	100
1 0 1	32.041	32.041	17.4	8.5	26.2
2 1 1	36.919	36.916	56.6	18.3	76.2
3 3 0	38.461	38.452	1.7	3.9	3.5
4 2 0	40.618	40.619	24.0	22.9	29.6
3 2 1	45.322	45.314	11.1	4.3	18.0
5 1 0	46.620	46.619	8.3	7.8	11.0
4 1 1	49.081	49.074	21.1	9.2	25.0
4 4 0	52.073	52.074	5.5	6.4	9.9
5 3 0	53.802	53.802	6.4	5.4	7.0
6 0 0	55.496	55.493	15.8	15.0	15.1
5 0 1, 4 3 1	56.017	56.026	24.0	11.3	27.3
6 2 0	58.784	58.776	2.3	3.1	3.5
5 2 1	59.286	59.290	14.8	6.4	15.1
7 1 0, 5 5 0	66.548	66.542	3.1	4.4	5.7
5 4 1	68.504	68.511	8.2	4.1	11.0
7 3 0	72.426	72.433	6.1	4.8	7.7

[a] From Siemens D5000 Goniometer.
[b] From Guinier–De Wolff spectrum.

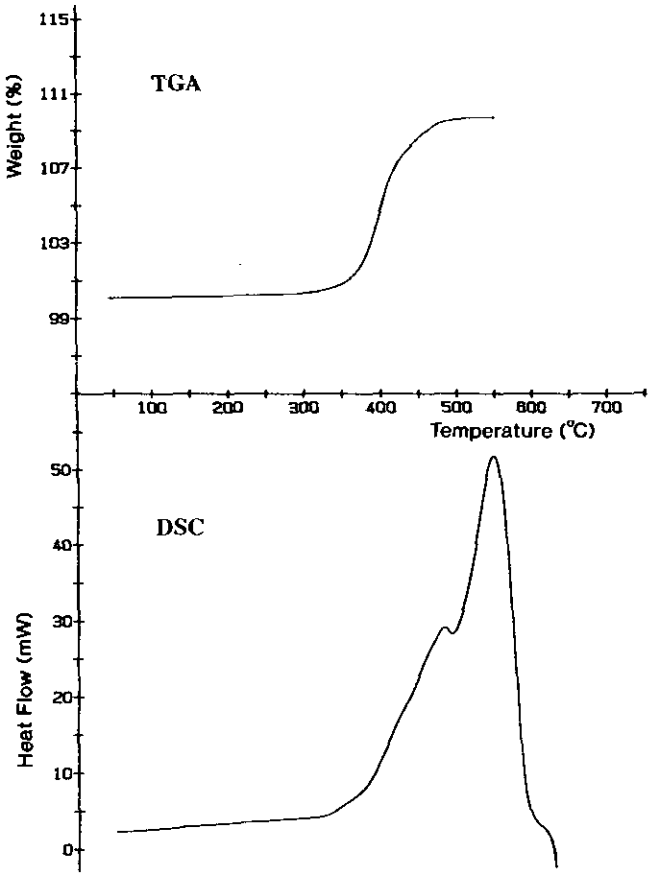

FIG. 3. TGA and DSC curves obtained from $Bi_{1.7}V_8O_{16}$ heated in air.

mal change is due to the oxidation

$$Bi_{1.7}V_8O_{16} + 3.275\ O_2 \rightarrow 1.7\ BiVO_4 + 3.15\ V_2O_5.$$

The weight gain of 9.8% observed is approximately equal to the calculated gain of 10.3% based on the above equation. Accordingly, $Bi_{1.7}V_8O_{16}$ in air cannot persist at temperatures higher than 300°C.

Figure 4 shows the X-ray pattern obtained for the composition $Bi_{1.33}V_2O_6$. It is obvious from this pattern that $Bi_{1.33}V_2O_6$ contains the Bi-hollandite phase. The other reflections (phase *X*) observed can be readily indexed in the tetragonal system and a body-centered cell with refined parameters $a = 3.8767(5)$ and $c = 15.337(5)$ Å.

Thus $Bi_{1.33}V_2O_6$ seems to be a two-phase mixture. The second component would pertain to the Aurivillius family and would be a room-temperature stabilized γ-$Bi_4V_2O_{11}$-type compound. For comparison, the pattern of $Bi_4V_{1.7}Ti_{0.3}O_{10.85}$ is given together with that obtained from the composition $Bi_4V_3O_{12}$ which contains metallic bismuth. Identification and preparation of this second component is under investigation. Perhaps in the future it will be possible to give some explanation for the electron diffraction patterns and the high-resolution images observed for some crystals obtained from the composition $Bi_{1.33}V_2O_6$ (11). Table 5 reports the X-ray pattern and the two-phase indexation of both our $Bi_{1.33}V_2O_6$ sample and JCPDS data.

CONCLUSION

$Bi_{1.7}V_8O_{16}$ is the first bismuth hollandite; in this compound bismuth atoms occupy original positions within the channel in a rather strange quasi-square planar coordination. (Recently another hollandite-related compound

TABLE 5
X-Ray Pattern of $Bi_{1.33}V_2O_6$

$2\theta_{obs}$[a]	$2\theta_{cal}$[a]	*h k l* Bi-hollandite	Phase *X*	$2\theta_{obs}$[b]	$2\theta_{cal}$[c]	$2\theta_{cal}$[d]	*h k l*[b]
11.555	11.529		0 0 2	11.634	11.492	11.71	0 1 0
12.619	12.598	1 1 0		12.635	12.578	12.56	1 0 0
17.864	17.853	2 0 0					
23.663	23.653		1 0 1	23.579	23.657	23.55	0 2 0
25.364	25.352	2 2 0		25.281	25.311	25.28	2 0 0
28.416	28.404	3 1 0		28.309	28.357	28.06	1 2 1
28.879	28.880		1 0 3	28.927	28.853	28.92	0 2 2
31.995	31.998	1 0 1		31.936	31.952	31.64	1 2 2
32.642	32.640		1 1 0	32.655	32.654	32.65	2 1 2
34.715	34.725		1 1 2	34.882	34.725		
35.083	35.075		0 0 6		34.960		
36.881	36.878	2 1 1		36.867	36.823	36.92	1 2 3
37.373	37.352		1 0 5				
38.443	38.435	3 3 0					
40.595	40.603	4 2 0		40.566	40.535	40.21	3 1 0
45.287	45.283	3 2 1		45.067	45.211	45.05	2 3 1
46.604	46.606	5 1 0		46.483	46.528	46.27	3 0 3
46.841	46.832		2 0 0	46.788	46.851	46.30	3 2 1
48.380	48.397		2 0 2	48.375	48.406	48.17	0 4 0
48.639	48.665		1 1 6				
49.051	49.046	4 1 1					
52.068	52.064	4 4 0					
53.142	53.121		2 1 1	53.143	53.141	53.28	3 1 4
53.793	53.793	5 3 0					
55.480	55.485	6 0 0		55.367	55.389	55.17	2 4 0
56.008	56.003	5 0 1, 4 3 1		55.953	55.910	56.39	0 3 5
58.762	58.771	6 2 0					
59.268	59.271	5 2 1		59.219	59.170	59.32	2 1 6
59.821	59.832		2 0 6	59.767	59.772	59.81	4 1 3
66.544	66.541	5 5 0, 7 1 0					
68.485	68.498	5 4 1		68.423	68.377	68.42	4 2 4

Note. Refined unit cell parameters:

Bi-hollandite	$a = 9.9287(5)$	$c = 2.9125(5)$	our sample
Phase *X*	$a = 3.8767(5)$	$c = 15.337(5)$	
Bi-hollandite	$a = 9.944(5)$	$c = 2.916(3)$	from JCPD 39-0105
Phase *X*	$a = 3.875(3)$	$c = 15.39(3)$	

[a] Our sample.
[b] JCPDS 39-0105.
[c] Calculated with Bi-hollandite or phase *X* unit cell.
[d] Calculated with orthorhombic unit cell.

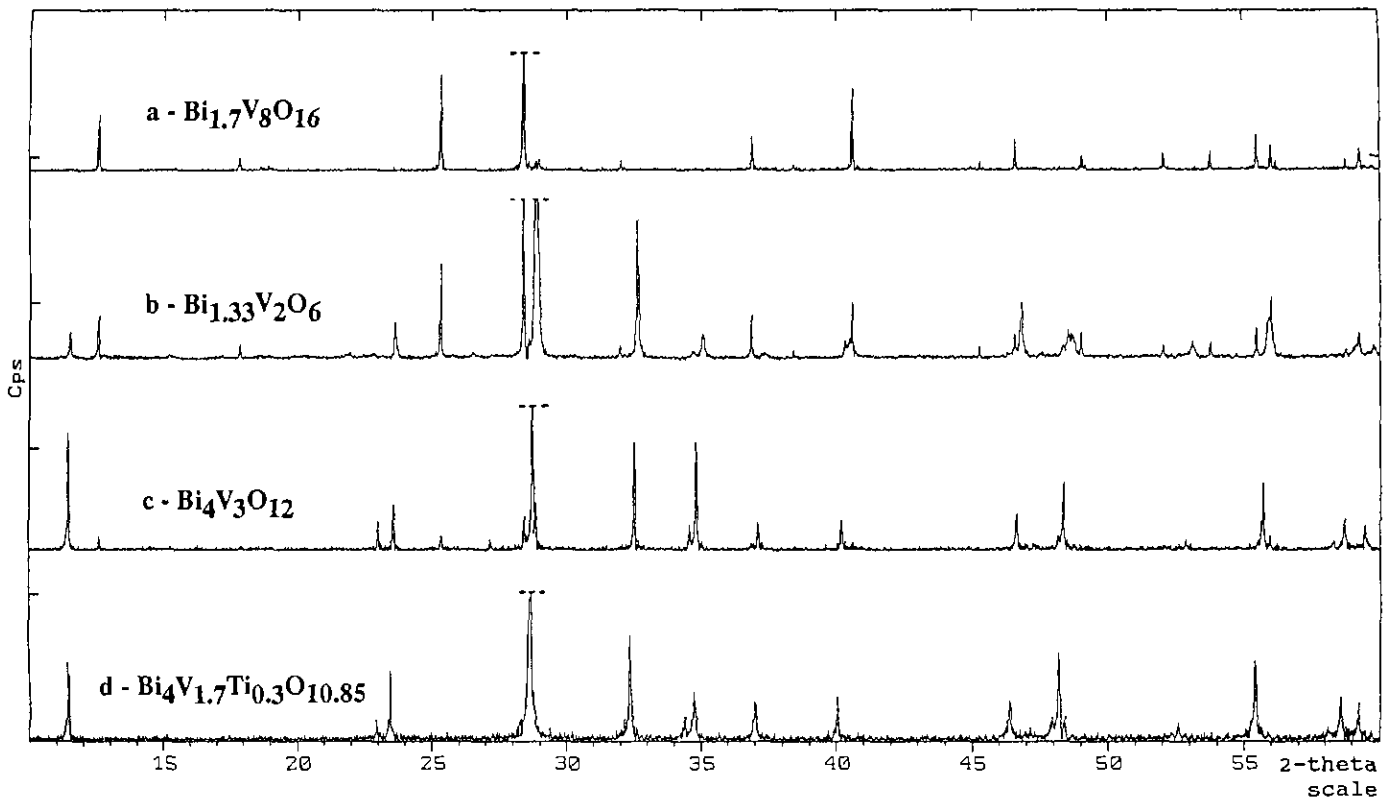

FIG. 4. X-ray pattern of (a) $Bi_{1.7}V_8O_{16}$, (b) $Bi_{1.33}V_2O_6$, (c) $Bi_4V_3O_{12}$ composition, and (d) $Bi_4V_{1.7}Ti_{0.3}O_{1.85}$.

containing a trivalent cation has been reported: $La_{1.16}Mo_8O_{16}$ (46).) It is also the first vanadium hollandite prepared by standard high temperature solid state chemistry; other vanadium hollandites have been prepared by high pressure–high temperature techniques (32, 47) or by electrolysis of molten salt (48). Formation conditions for other bismuth hollandites are being studied; physical property measurements (in particular conductivity) are also planned.

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