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Structure of Dibismuth Vanadate Bi₂VO_{5.5}

BY MARCEL TOUBOUL*

Laboratoire de Réactivité et de Chimie des Solides, URA CNRS 1211, Université de Picardie, 33 rue Saint-Leu, 80039 Amiens CEDEX, France

JAN LOKAJ

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinskeho 9, 81237 Bratislava, Czechoslovakia

LAURENT TESSIER

Laboratoire de Réactivité et de Chimie des Solides, URA CNRS 1211, Université de Picardie, 33 rue Saint-Leu, 80039 Amiens CEDEX, France

VIKTOR KETTMAN

Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojarov 10, 81234 Bratislava, Czechoslovakia

AND VIKTOR VRABEL

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinskeho 9, 81237 Bratislava, Czechoslovakia

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Abstract. Bi₂VO_{5.5}, $M_r = 556.9$, orthorhombic, $Aba2$, $a = 5.598$ (2), $b = 15.292$ (9), $c = 5.532$ (2) Å, $V = 473.6$ Å³, $Z = 4$, $D_m = 7.6$, $D_x = 7.808$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 75.75$ mm⁻¹, $F(000) = 932$, $T = 293$ K, $R = 0.038$ for 396 unique observed reflections. Owing to a very short Bi—O bond (1.89 Å), the structure may be described by alternating Bi₂O_{2.75}⁵⁺ layers of very irregular corner-sharing BiO₄ tetrahedra and by VO_{2.75}⁵⁻ layers of distorted corner-sharing VO₆ octahedra. This structure is slightly different from that of well known oxides of the Aurivillius family and especially of Bi₂XO₆ com-

pounds ($X = \text{Mo, W}$) containing Bi₂O₂²⁺ layers of edge-sharing BiO₄ square pyramids.

Introduction. In a previous work, Touboul & Vachon (1988) investigated a large part of the Bi₂O₃–V₂O₅ system which was being studied at almost the same time by Zhou (1988) and by Blinovskov & Fotiev (1987). Numerous compounds were found but it was sometimes difficult to assign them a correct formula. It would be interesting to determine their structure in order to explain their physical properties, especially their ferroelectricity, as was found by Bierlein & Sleight (1975) for BiVO₄. Single crystals of several

* Author to whom all correspondence should be addressed.

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

	x	y	z	B_{eq}
Bi	4293 (1)	1689 (0)	0	1.49 (1)
V	0	0	508 (6)	2.20 (9)
O(1)	2423 (32)	2494 (7)	3064 (20)	2.74 (23)
O(2)	2450 (23)	4943 (8)	3520 (23)	2.89 (23)
O(3)	-174 (37)	1226 (9)	1170 (25)	2.44 (31)

$$B_{\text{eq}} = (4/3) \sum_i \beta_{ij} a_i^2.$$

compositions were obtained by slow cooling of the melt. They were often twinned, however, as indicated by Sleight, Chen, Ferretti & Cox (1979) for the best known of bismuth vanadates, BiVO_4 . After numerous attempts, one of the single crystals was found to be adequate for studying its structure and this led to the results described in this paper.

Experimental. Single crystals were obtained by slow cooling of a $2\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5$ melt from 1273 K, using a platinum crucible. A red-brown plate-shaped crystal, with dimensions $0.4 \times 0.35 \times 0.2$ mm, was used for data collection; D_m measured by liquid displacement pycnometry; systematic absences hkl for $k+l$ odd, $0kl$ for k odd and $h0l$ for h odd, from Weissenberg photographs; Syntex $P2_1$ diffractometer; accurate unit-cell parameters by least-squares refinement of 18 reflections, $12 < \theta < 25^\circ$; intensity data (up to $2\theta = 65^\circ$) by θ - 2θ scan technique, variable rate 4.9 – $29.3^\circ \text{ min}^{-1}$ in 2θ , background to scan-time ratio 1.0, scan width 2° plus α_1 - α_2 dispersion, Mo $K\alpha$ radiation filtered by graphite monochromator; $0 \leq h \leq 8$, $0 \leq k \leq 22$, $0 \leq l \leq 8$; two standards measured every 98 reflections, no systematic variation; 461 unique reflections, 396 with $I \geq 2\sigma(I)$ considered observed and included in the refinement; no equivalent reflections measured; intensities corrected for Lorentz and polarization effects and for absorption using the empirical absorption correction procedure based on ten reflections measured in ψ scan (North, Phillips & Mathews, 1968), calculated transmission-factor range 0.61–1.0; structure solved by the heavy-atom method and refined anisotropically by full-matrix least squares, origin along the polar axis fixed by $z(\text{Bi}) = 0$, occupation factor of O(3) fixed at 0.75 (it showed a slight tendency to go beyond this value when relieved in the refinement); in final cycle $R = 0.038$, $wR = 0.044$ for observed reflections only, $S = 2.89$; maximum shift/e.s.d. = 0.22, function minimized $\sum w(\Delta F)^2$, where $w = 1$ if $|F_o| < 160$ and $w = 160/|F_o|$ if $|F_o| \geq 160$ in order to obtain $w\Delta^2$ values approximately independent of $|F_o|$ and $\sin\theta/\lambda$; maximum and minimum heights in final $\Delta\rho$ synthesis 1.35 and 1.13 e \AA^{-3} ; scattering factors for uncharged atoms and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974,

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Bi—O(1 ⁱ)	1.89 (1)	V—O(2 ^{iv}) (2 ×)	1.76 (1)
—O(3 ⁱ)	2.29 (1)	—O(3) (2 ×)	1.91 (1)
—O(1)	2.34 (1)	—O(2 ^v) (2 ×)	2.20 (1)
—O(1 ⁱⁱ)	2.47 (2)	O(2)—O(3 ⁱⁱⁱ)	2.58 (2)
—O(3)	2.68 (2)	O(1)—O(3 ⁱⁱⁱ)	2.60 (2)
—O(1 ⁱⁱⁱ)	2.74 (2)	O(1)—O(3)	2.64 (2)
		O(2)—O(3 ⁱⁱ)	2.64 (2)
O(1 ⁱ)—Bi—O(3 ⁱ)	77.7 (6)	O(1 ⁱⁱ)—Bi—O(3)	159.2 (5)
—O(1)	80.9 (5)	—O(1 ⁱⁱⁱ)	64.0 (4)
—O(1 ⁱⁱ)	78.7 (5)	O(3)—Bi—O(1 ⁱⁱⁱ)	124.6 (5)
—O(3)	80.5 (6)	O(2 ^{iv})—V—O(3) (2 ×)	102.0 (7)
—O(1 ⁱⁱⁱ)	112.2 (5)	—O(2 ^v) (2 ×)	88.0 (5)
O(3 ⁱ)—Bi—O(1)	158.4 (5)	—O(2 ^{vi})	102.7 (6)
—O(1 ⁱⁱ)	66.1 (5)	—O(3 ^{vii}) (2 ×)	91.8 (5)
—O(3)	110.1 (5)	—O(2 ^{viii}) (2 ×)	169.3 (7)
—O(1 ⁱⁱⁱ)	125.2 (5)	O(3)—V—O(2 ^v) (2 ×)	85.8 (6)
O(1)—Bi—O(1 ⁱⁱ)	112.4 (5)	—O(3 ^{viii})	157.9 (7)
—O(3)	63.0 (5)	—O(2 ^{ix}) (2 ×)	77.5 (6)
—O(1 ⁱⁱⁱ)	66.3 (5)	O(2 ^v)—V—O(2 ^{viii})	81.3 (6)

Symmetry code: (i) $\frac{1}{2} - x, y, z - \frac{1}{2}$; (ii) $1 - x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (iv) $x, y - \frac{1}{2}, z - \frac{1}{2}$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (vi) $-x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $-x, -y, z$; (viii) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Vol. IV); all calculations performed with a local version of the *NRC* system (Ahmed, Hall, Pippy & Huber, 1973). Atomic coordinates are listed in Table 1,* bond distances and angles in Table 2. Projections of the half unit-cell contents down **b** are shown in Figs. 1 and 2.

Discussion. A $\text{Bi}_2\text{VO}_{5.5}$ or $\text{Bi}_4\text{V}_2\text{O}_{11}$ compound has been noted for its ferroelectric property by Bush, Koshelayeva & Venetsev (1985), who first gave the parameters in an orthorhombic lattice. Since then, several other studies have been published on $\text{Bi}_4\text{V}_2\text{O}_{11}$ alone and in mixtures with other ferroelectric compounds such as Bi_2GeO_5 or Bi_2WO_6 (Borisov, Avakyan, Osipyan & Poplavko, 1989; Savchenko, Elbakyan, Osipyan & Arutyunyan, 1989; Abraham, Debrouille-Gresse, Mairesse & Nowogrocki, 1988; Borisov, Poplavko, Avakyan & Osipyan, 1988; Zhou, 1988; Osipyan, Savchenko, Elbakyan & Avakyan, 1987; Bush & Venetsev, 1986). While writing this paper, Varma, Subbanna, Guru Row & Rao (1990) have published the structure of $\text{Bi}_2\text{VO}_{5.5}$ studied by the Rietveld refinement of X-ray powder diffraction data [space group $B2cb$, $a = 5.543$ (1), $b = 5.615$ (1), $c = 15.321$ (3) \AA , 37 reflections, $R_i = 0.09$]. There are some discrepancies if one compares their results with our data (Table 1) but it is reasonable to consider that our results from 396 reflections are more precise (no e.s.d.'s for the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54918 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0318]

refined atomic coordinates and no interatomic distances were given). Starting from the known structure of Bi₂WO₆, which belongs to the Aurivillius family of oxides (Aurivillius, 1950), Varma *et al.* (1990) have described Bi₂VO_{5.5} as the V analog: it consists of Bi₂O₂²⁺ layers separated by layers of corner-sharing VO₆ octahedra. For the same reason (analogy with Bi₂WO₆) this description was also made by Abraham *et al.* (1988) and by Bush *et al.* (1985), but Zhou (1988) claimed that selected-area electron diffraction (SAED) patterns and high-resolution electron microscopy (HREM) images of Bi₄V₂O₁₁ showed an image contrast different to that expected from Bi₂WO₆ and he thought that Bi₂O₂²⁺ layers certainly did not exist in the structure. As developed below, our results agree with this observation.

From Table 2, Fig. 1 and Fig. 2, we can see that, along **b**, four O(1) atoms at the same height are close to a Bi atom and also four O(2) atoms at the same height are close to a V atom; O(3) atoms are between these two O planes. In Bi₂VO_{5.5}, a very short Bi—O bond exists (1.89 Å) and a possible description of the structure might be given considering isolated BiO⁺

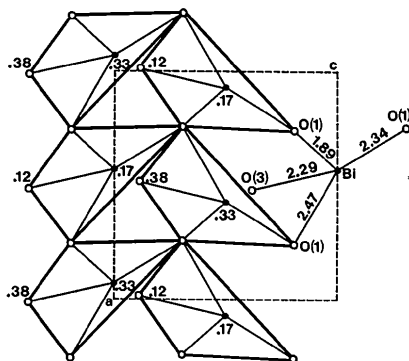


Fig. 1. Projection along **b** showing very distorted corner-sharing BiO₄ tetrahedra which form Bi₂O_{2.75}^{0.5+} layers. O(1) atoms are at $y = 0.25$; bond lengths in Å.

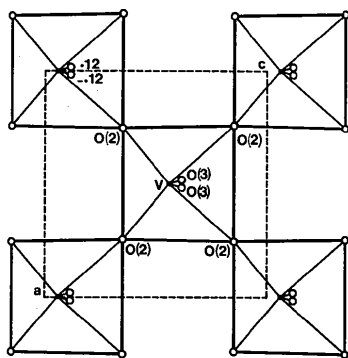


Fig. 2. Projection along **b** showing a corner-sharing VO₆ octahedra layer; V and O(2) atoms are at $y = 0$.

groups between layers of corner-sharing VO₆ octahedra (Fig. 2); the structural formula of the compound would be 2(BiO⁺) VO_{3.5}²⁻ because only O(1) is linked to a Bi atom and the V atom is surrounded by four O(2) which belong to two V atoms, and by two O(3) with an occupancy factor equal to 0.75. However, this description with isolated BiO⁺ is unsatisfactory because there are other O atoms close to Bi atoms with Bi—O bonds comparable to those existing in other Bi compounds.

The simplest oxides of the Aurivillius family are Bi₂XO₆ with $X = \text{Mo, W}$. Their main crystallographic features are: for γ -Bi₂MoO₆, $a = 5.4822$, $b = 16.1986$, $c = 5.5091$ Å, space group $Pna2_1$ (Buttrey, Jefferson & Thomas, 1986; Teller, Brazdil, Grasselli & Jorgensen, 1984; van den Elzen & Rieck, 1973); for Bi₂WO₆, $a = 5.457$, $b = 5.436$, $c = 16.427$ Å, space group $B2cb$ (Varma *et al.*, 1990; Osipyan, Shebanov & Freidenfel'd, 1983; Wolfe, Newnham & Kay, 1969). In these compounds, the structure consists of alternating Bi₂O₂²⁺ layers and of layers of corner-sharing XO₆ octahedra whose formula is XO₄²⁻; Bi lies at the apex of a square pyramid with four O atoms and these units are linked by sharing edges to form continuous Bi₂O₂ sheets. With Bi₂WO₆, there are four O atoms in the Bi₂O₂ layer with Bi—O lengths at 2.21, 2.28, 2.36 and 2.42 Å, and a fifth O atom 2.49 Å from WO₆ octahedra (Ramanan, Gopalakrishnan & Rao, 1985; Wolfe *et al.*, 1969); with Bi₂MoO₆, Bi—O lengths are between 2.10 and 2.56 Å (Teller *et al.*, 1984). It is tempting to describe the structure of Bi₂VO_{5.5} in the same manner: there are also four O atoms O(1) which form an almost regular square, but one Bi—O(1) bond (2.74 Å) is much longer than the others and longer than two Bi—O(3) bonds (Table 2). Another description may be proposed by taking only O atoms surrounding a Bi atom with Bi—O bonds shorter than the shortest O—O bond which exists in this compound, 2.58 Å (Table 2); in Bi₂MoO₆, Teller *et al.* (1984) found that the shortest O—O contact distance is 2.59 Å, close to that found in Bi₂VO_{5.5}. Four O atoms surround a Bi atom and form a very irregular tetrahedron; these tetrahedra are corner-sharing linked to form a Bi₂O_{2.75}^{0.5+} layer (Fig. 1). Around a Bi atom, there are three O(1) atoms each shared by three Bi atoms, and one O(3) atom (0.75 occupancy factor) which maintains the linkage with a VO₆ octahedron; the formula of the BiO₄ tetrahedra is BiO_{2.25}^{0.25+} and the two tetrahedra form the unit of the Bi₂O_{2.75}^{0.5+} layer. Therefore, Bi is coordinated by four O atoms in what may be described as a strongly distorted tetrahedron and not as having a pseudotrigonal bipyramidal geometry, as found recently in BaBiO_{2.5} by Lightfoot, Hriljac, Pei, Zheng, Mitchell, Richards, Dabrowski, Jorgensen & Hinks (1991). The very distorted VO₆ octahedra always form a

layer (Fig. 2) but the formula has changed because O(3) atoms also belong to the coordination sphere of Bi; the formula of the layer of the corner-sharing VO₆ octahedra is thus VO_{2.75}^{0.5-}.

According to Zhou (1988), in the Bi₂VO_{5.5} structure there are no Bi₂O₂²⁺ layers and this compound cannot be included in the Aurivillius family of oxides. The structure of Bi₂VO_{5.5} contains alternating Bi₂O₂²⁺ layers formed by very irregular corner-sharing BiO₄ tetrahedra and VO_{2.75}^{0.5-} layers of corner-sharing distorted VO₆ octahedra.

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Structure of Sn_{0.854}Mo₆S₈

BY L. LE LAY

Applied Superconductivity Center, University of Wisconsin-Madison, Madison, WI 53706, USA

D. R. POWELL

Chemistry Department, University of Wisconsin-Madison, Madison, WI 53706, USA

AND T. C. WILLIS

Applied Superconductivity Center and Materials Science and Engineering Department, University of Wisconsin-Madison, Madison, WI 53706, USA

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Abstract. Molybdenum tin sulfide, Sn_{0.854}Mo₆S₈, $M_r = 933.5$, trigonal, $R\bar{3}$, $a_R = 6.5100$ (10) Å, $\alpha_R = 89.47$ (2)°, $V_R = 275.86$ (7) Å³, $Z = 1$, $D_x = 5.619$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 9.777$ mm⁻¹, $F(000) = 422.70$, $T = 295$ K, $R = 0.0401$ for 517 observed reflections. The title compound is isostructural to SnMo₆S₈, but displays a cation non-stoichiometry.

Introduction. In the series of large-cation sulfide Chevrel phases (MMo₆S₈ where M is a metallic cation), it is generally believed that non-stoichiometry, if any, occurs on the 2(c) sulfur sites along the rhombohedral axis. This issue has been addressed previously, theoretically (Hughbanks & Hoffmann, 1983) and experimentally – powder neutron diffraction showed that partial S-atom substitution by O