A REDETERMINATION OF THE STRUCTURE OF Sb_2VO_5, STIBIVANITE, A NEW MINERAL

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ABSTRACT

The crystal structure of synthetic Sb_2VO_5 has been redetermined from 1959 X-ray reflections (1581 observed), collected on a 4-circle diffractometer with Mo $K\alpha$ radiation. The new mineral stibivanite (Kaiman *et al.* 1980) and synthetic Sb_2VO_5 are shown to be identical. The structure of Sb_2VO_5 is monoclinic, space group is $C2/c$, with $a = 17.989(6)$, $b = 4.7924(7)$, $c = 5.500(2)$ Å, $\beta = 95.15(3)°$, and $Z = 4$. The structure is refined to $R = 0.059$ for all data (unweighted) and $R = 0.040$ (weighted). The previous structure of Sb_2VO_5 (Darriet *et al.* 1976) is confirmed; the present refinement, however, has resulted in more precise knowledge of the bond lengths and interbond angles in this mixed oxide phase that contains $Sb(III)$ and $V(IV)$.

Keywords: stibivanite, Sb_2VO_5, X-ray structural refinement, correction of powder pattern.

SOMMAIRE

La structure cristalline de Sb_2VO_5 (synthétique) est redéterminée à partir de 1959 réflexions (dont 1581 observées), recueillies sur diffractomètre à 4 cercles en radiation Mo $K\alpha$. L'identité du nouveau minéral stibivanite (Kaiman *et al.* 1980) avec le composé Sb_2VO_5 est confirmée. La structure est décrite dans le groupe $C2/c$ et la maille a 17.989(6), b 4.7924(7), c 5.500(2) Å, β 95.15(3)°, avec $Z = 4$; l'affinement en a été poussé jusqu'à $R = 0.059$ pour données complètes (non pondérées) et $R = 0.040$ (données pondérées). La structure antérieure (Darriet *et al.* 1976) est confirmée; la précision des longueurs de liaison et les angles entre liaisons, dans cette structure d'oxyde mixte qui contient à la fois Sb (*III*) et V (*IV*), est toutefois nettement améliorée.

(Traduit par la Rédaction)

Mots-clés: stibivanite, affinement roentgenographique, correction du cliché de poudre.

INTRODUCTION

The new mineral stibivanite, Sb_2VO_5, is described in the preceding paper (Kaiman *et al.* 1980). Microprobe analysis of the mineral and of the synthetic material gave identical results and showed the ratio Sb:V to be 2:1, but there was some uncertainty about the oxygen content. A composition $2Sb_2O_3 \cdot V_2O_3$ was suggested, but was not unambiguous (Kaiman *et al.* 1980). In order to determine the composition crystallographically and to provide a complete description of the mineral, a structure determination was undertaken. After the structure had been solved and refined, the composition was shown to be Sb_2VO_5 and not $Sb_4V_2O_9$, as had been proposed originally from the electron-microprobe measurements. It was then discovered that the structure of Sb_2VO_5 had been solved and published (Darriet *et al.* 1976, hereafter DBG), although the powder pattern of DBG was not in the JCPDS file. The DBG refinement was based on 185 reflections and was refined to $R = 8.9\%$. The present refinement is based on 1959 reflections refined to $R = 5.9\%$ overall (weighted $R = 4.0\%$). As the standard deviations of the bond lengths are at least an order of magnitude better than in the DBG refinement, and since there appear to be serious discrepancies in the published cell dimensions and in the powder pattern, publication of the present results seems warranted.

EXPERIMENTAL

A detailed comparison was carried out of the mineral stibivanite and the synthetic material (Kaiman *et al.* 1980). Single-crystal precession photographs showed them to be identical (cell dimensions, space group, intensities). The powder patterns obtained from both materials were the same, as were their physical and optical properties. The synthetic material was used in the structure determination, as the crystal quality was far superior. The synthetic crystals grew as fine laths, elongated along c, up to 2 mm long and up to 0.02 mm wide. Any attempt to cut a crystal normal to the needle resulted in its separation into a multitude of fibres because of the acicular cleavage of the material. Finally, a short single crystal was obtained by

the following technique. A thin-wall quartz capillary was drawn out to provide a tube 0.1 mm in diameter. The end of this was dipped in epoxy resin, and the tip of a long single crystal was embedded in the epoxy. When the resin had set, the excess of the crystal was dissolved in aqua regia, leaving a specimen 0.2 mm long and 0.020 x 0.014 mm in cross-section, embedded in the epoxy.

The crystal was mounted on a 4-circle single-crystal diffractometer in a general orientation, and the cell dimensions were refined (Table 1) by a least-squares technique (Busing 1970) for 10 reflections ($2\theta > 45°$) using the resolved α_1 component of Mo $K\alpha$ radiation. Three segments of data were collected with graphite-monochromated Mo $K\alpha$ radiation to $2\theta = 70°$, and the shell $70 < 2\theta < 90°$ was collected twice. The overall intensity agreement between symmetry-related reflections was 4.4%. Peak backgrounds were estimated with line-profile analysis (Grant & Gabe 1978). Three standard reflections were monitored every fifty measurements. Some instrumental fluctuations were observed and corrected for in the scaling. The data were reduced with the application of Lorentz and polarization factors, but absorption corrections could not be applied because of the indeterminate factors of the silica tube and epoxy resin. Of the 1959 unique reflections measured, 1581 were considered observed on the criterion that $I_{obs} > 1.65\sigma(I)$. Standard deviations were calculated from counting statistics and instrumental uncertainties, and were used throughout in the least-squares refinement.

TABLE 1. CRYSTAL DATA

Stibivanite, Sb_2VO_5

Microprobe Composition: $Sb_{2.01}V_{0.98}O_5$ (based on O=5)

(Kaiman et al. 1980)

Formula Weight: Sb_2VO_5 = 374.44 , Z = 4.

Crystal System: monoclinic

Systematic Absences: hkℓ, h+k = 2n+1

h0ℓ,   ℓ = 2n+1

Space group: C2/c (#15) or Cc (#9)

C2/c confirmed by structure analysis.

Cell dimensions: a=17.989(6), b=4.7924(7), c=5.500(2)Å,

β=95.15(3)°

Linear Absorption Coefficient: $\mu(MoK\alpha)$ = 132.4 cm^{-1}

Density: D_{calc} = 5.267 Mg m^{-3}, density not measured.

Data: 3 segments of data collected to 2θ = 70°

2 segments of data collected 70<2θ<90°

Total data = 1959 reflections, 1581 with I>1.65σ(I)

STRUCTURE DETERMINATION

Normalization of the data was carried out, and the distribution of normalized structure-factors (Es) was examined. This showed a distribution part way between centrosymmetric and noncentrosymmetric. This is usually indicative of a noncentric structure with some centrosymmetric component, e.g., the heavy atoms. The structure was thus solved in the noncentrosymmetric space group Cc (#9) using MULTAN–78 (Main et al. 1978). When refinement was complete it was realized that all the positional coordinates were within 1σ of the requirements for the centrosymmetric space group $C2/c$ (#15). The refinement of anisotropic thermal parameters was extremely ill-conditioned in Cc, with U_{33} negative for O(2) and very large for its (centrosymmetrically) related oxygen O(2'). Other thermal parameters oscillated. Refinement in space group $C2/c$ eliminated all problems and converged to $R = 0.0594$ for all 1959 reflections (weighted $R = 0.0404$). A secondary extinction correction (Larsen 1970), which had to be introduced in the final stages of the refinement, turned out to be substantial. It must be presumed that the magnitudes of the normalized structure-factors (Es) were affected by the nonapplication of absorption corrections and by the presence of extinction, which affects mainly the strong reflections.

The scattering curves used in the refinement were those of the neutral species Sb, V and O, taken from Cromer & Mann (1968); the anomalous dispersion corrections were those of Cromer & Liberman (1970). The final refined parameters, with their standard deviations, are given in Table 2. The observed (F_o) and calculated (F_c) structure factors, together with $\sigma(F_o)$ and an asterisk for unobserved reflections, are given in Table 3 (available at a nominal charge from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2).

DESCRIPTION OF THE STRUCTURE

A detailed description of the structure has been given by Darriet et al. (1976). The atomic fractional coordinates given in Table 2 have been transformed from those used in this refinement to conform with those published by DBG. Sb is coordinated to three oxygens: O(3) at 1.963(5) Å, O(3)⁹ at 2.009(4) Å and O(2) at 2.014(4) Å (for list of symmetry codes, see Table 4). Atoms O(3) and O(3)⁹ link adjacent SbO_3 units along $+z$ and $-z$, whereas

TABLE 2. ATOMIC POSITIONAL AND THERMAL PARAMETERS

Atom	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	8f	.16126(2)	.72028(9)	.15140(7)	119(2)	173(2)	109(2)	10(2)	-35(1)	-9(2)
V	4e	0	.37157(36)	¼	103(6)	231(8)	78(6)	0	-30(5)	0
O(1)	4e	0	.0412(17)	¼	335(43)	219(39)	167(33)	0	22(30)	0
O(2)	8f	.0717(2)	.4956(10)	.0220(7)	99(18)	205(22)	98(17)	-14(17)	-33(14)	5(16)
O(3)	8f	.2062(2)	.4142(11)	.3512(8)	110(19)	246(25)	132(18)	55(18)	5(15)	31(18)

The anisotropic temperature factors are expressed in the form:

$T = \exp[-2\pi^2(U_{11}a^{*2}h^2..+.2U_{12}a^*b^*hk..+.)]$, and the values quoted are $\times 10^4$.

TABLE 4. BOND LENGTHS AND INTERBOND ANGLES, WITH STANDARD DEVIATIONS

1. Coordination of Sb

	d(Å)	O(3)[9]	O(2)	O(3)[13]	O(2)[8]
O(3)	1.963(5)	92.6(2)	94.3(2)	86.4(2)	64.3(2)
O(3)[9]	2.009(4)	-	84.6(2)	70.6(2)	138.9(2)
O(2)	2.014(4)	-	-	155.2(2)	65.2(1)
O(3)[13]	2.561(4)	-	-	-	135.2(2)
O(2)[8]	2.900(4)	-	-	-	-

2. Coordination of V

	d(Å)	O(2)	O(2)[4]	O(2)[8]	O(2)[11]
O(1)	1.583(8)	107.6(1)	108.7(1)	108.7(1)	107.6(1)
O(2)	1.970(4)	-	80.9(2)	88.0(2)	144.9(2)
O(2)[4]	1.990(4)	-	-	142.7(2)	88.0(2)
O(2)[8]	1.990(4)	-	-	-	80.9(2)
O(2)[11]	1.970(4)	-	-	-	-

A two-fold axis through O(1) and V relates O(2) to O(2)[11] and O(2)[4] to O(2)[8].

3. Coordination of O(1)

O(1) is bonded only once, to V (see above). Its closest non-bonded distances are to V, 3.21Å and (2x) 3.39Å, and to Sb, (2x) 3.37Å.

4. Coordination of O(2)

	d(Å)	V	V[4]	Sb[9]
Sb	2.014(4)	119.0(2)	122.6(2)	87.8(1)
V	1.970(4)	-	99.1(2)	141.0(2)
V[4]	1.990(4)	-	-	87.1(1)
Sb[9]	2.900(4)	-	-	-

5. Coordination of O(3)

	d(Å)	Sb[8]	Sb[14]
Sb	1.963(5)	121.6(2)	127.2(2)
Sb[8]	2.009(4)	-	109.4(2)
Sb[14]	2.561(4)	-	-

Superscripts used above, in Fig. 1, and in the text, refer to following equivalent positions:

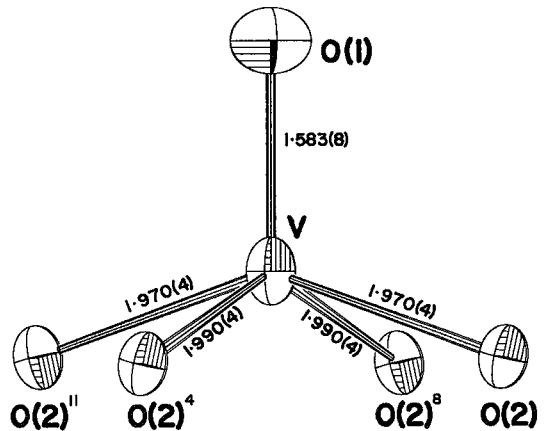|			
4.	$-x$, $1-y$, $-z$	9.	x, $1-y$, $-\frac{1}{2}+z$
8.	x, $1-y$, $\frac{1}{2}+z$	11.	$-x$, y, $\frac{1}{2}-z$
		13.	$\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$
		14.	$\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$

FIG. 1. The coordination of vanadium. A twofold axis of symmetry through V and O(1) relates O(2) to O(2)[11] and O(2)[4] to O(2)[8]. The ellipsoids are drawn at 50% probability (Johnson 1970).

The coordination of vanadium is square pyramidal. Four oxygens form the square base, with vanadium above the mean plane by 0.615 Å. Directly above V lies O(1) at 1.583(8) Å (Fig. 1). Oxygen atom O(1) is not coordinated to anything else; its closest contact is the vanadium in the unit cell related by the translation $y = 1$, at a distance of 3.209(8) Å. A twofold axis through O(1) and V relates O(2) to O(2)[11] and O(2)[4] to O(2)[8]. O(2) and O(2)[11] are bonded to the next vanadium at $x = 0$, $z = -\frac{1}{4}$, whereas O(2)[4] and O(2)[8] are bonded to the next vanadium at $x = 0$, $z = \frac{3}{4}$ (Fig. 2). Structural units are formed of SbO₂–O–VO–O–SbO₂ extending along x, with adjacent units bonded along z through Sb–O(3)–Sb and V–O(2)–V bonds. Ribbons are thus formed with no bonding in y, and only the Sb–O(3)[13] interaction [2.561(4) Å] along x. This accounts for the excellent acicular cleavage of the mineral.

O(2) bridges to vanadium. The angles (Table 4) are close to 90°, which is a fairly typical coordination for Sb(III). Two additional oxygens are found at less than the van der Waals distance from Sb, 2.561(4) and 2.900(4) Å. The former weak bond is the only interaction across the plane at $x = \frac{1}{4}$, where cleavage is presumed to occur.
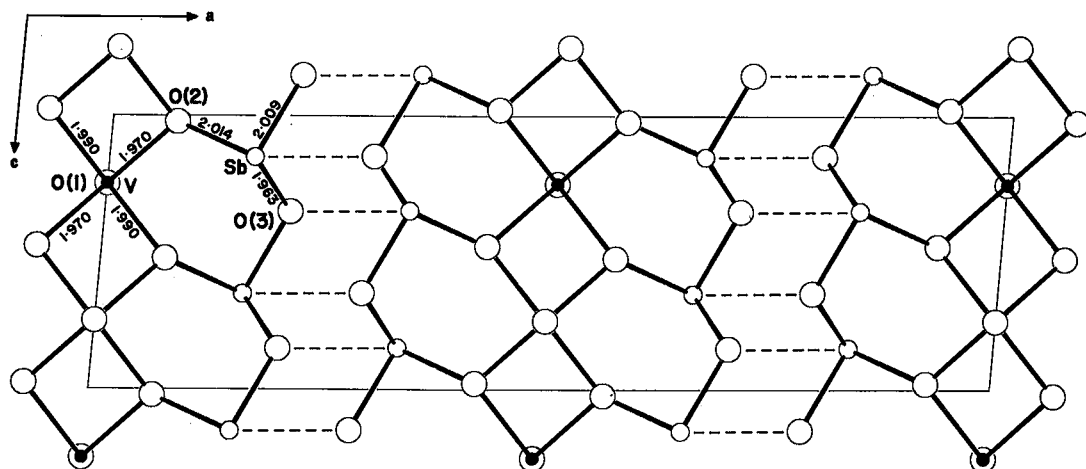
The author is indebted to Professor Guy

FIG. 2. The structure of stibivanite projected on the *a–c* plane. The largest circles are oxygens, smaller ones are antimony, whereas the small solid circles are vanadium. The atoms of the asymmetric unit are labeled. The ribbons of SbO₂–O–VO–O–SbO₂ units extend in the *z* direction from $x = \frac{1}{4}$ to $x = \frac{3}{4}$. The bond lengths are indicated. The weaker Sb–O(3) interactions (2.561 Å) linking adjacent ribbons are shown as dashed lines.

Perrault, who refereed this paper, for the following additional information on the cleavage of stibivanite. Professor Perrault examined crystals of stibivanite on a 2-circle optical goniometer and indexed the following forms:

form	ϕ_{calc}	ϕ_{obs}	remarks
{210}	61° 51′	61.5 – 62.5°	principal
{110}	75° 02′	74 –76°	minor
{110}	0°	∞ 0°	small, indistinct

The {210} cleavage develops at an angle to the *a–c* plane, between adjacent ribbons, one ribbon along *a* and one along *b*. The {110} cleavage implies a step of two ribbons along *a* and one ribbon along *b*. The additional indistinct {100} cleavage is evident in Figure 2. This result was somewhat surprising to the author, but is still consistent with the structure.

DISCUSSION

Darriet *et al.* (1976) considered this material as a vanadyl antimonate, $(VO)^{2+}(Sb_2O_4)^{2-}$, with only weak bonding between the VO group and the SbO₃ units. However, a number of structures have been reported (*e.g.*, Cs₂V₅O₁₄, CsV₂O₅: Waltersson & Forslund 1977a, b) in which the same square pyramidal VO₅ units are found, with very comparable bond lengths and interbond angles, and which are obviously

mixed V(*V*) and V(*IV*) vanadates. It is therefore doubtful whether stibivanite can be considered as vanadyl(*V*) antimonate (*III*), nor is it proven that it is an antimonyl(*III*) vanadate (*IV*). It is probably best to consider it as a mixed oxide phase, without specifying anion or cation. Other aspects of the structure are discussed at some length by Darriet *et al.*

CELL DIMENSIONS AND POWDER PATTERN

Darriet *et al.* refined the cell dimensions from the X-ray powder-diffraction data, having obtained approximate values for indexing purposes from Weissenberg photographs. This procedure, which led to several lines being misindexed, consequently leaves some doubt about their refined cell parameters and their powder pattern. The refined DBG values are *a* 18.03(1), *b* 4.800(20), *c* 5.497(2) Å, *β* 94.58(10)°. Particularly significant is the difference in *β* (0.57°) between the two determinations.

After the structure refinement was complete, the program POWGEN (Hall & Szymański 1975) was run. This program calculates the X-ray powder pattern for a specific wavelength from the final observed and calculated structure factors of the refined structure. Table 5 presents a comparison of the higher-angle half of the DBG published pattern with the POWGEN calculated pattern, which conforms to our observed pattern. It can be seen that there are a

TABLE 5. DARRIET et al. POWDER PATTERN vs. POWGEN AND OBSERVED PATTERNS FOR STIBIVANITE

| | Darriet et al. (1976) | | | | POWGEN and observed values (CoKα) | | | | |
h k ℓ	d_{obs}	d_{cal}	I/I_o	h k ℓ	d_{obs}	d_{cal}	I_{cal}	ΣI	I/I_o
8 0 0	2.24	2.24	10	8 0 0	unobs	2.240	<1	<1	--
2̄ 2 1	2.151	2.151	15	2̄ 2 1	2.151	2.150	8	8	5
2 2 1	2.119	2.120	25	2 2 1	2.114	-	<.1	35	40
4 2 0		2.117		4 2 0		2.113	14		
				6 0 2		2.115	21		
7 1 1	2.036	2.042	20	7 1 1	2.031	2.032	29	29	30
				4 2 1	1.942	1.944	12	12	10
6 0 2	1.947	1.946	10	6 0 2	-	1.934	<3	<3	--
6 2 0	1.873	1.873	15	6 2 0	1.870	1.869	24	24	40
10 0 0	1.792	1.797	30	10 0 0	1.787	1.792	2	36	40
				2 2 2		1.789	16		
				9 1 1		1.788	18		
2 2 2	1.750	1.752	10	2 2 2	1.751	1.748	10	10	5
				1̄ 1 3	1.714	1.712	23	23	30
				9 1 1	1.701	1.701	14	14	30
1 1 3	1.685	1.687	25	1 1 3	1.687	1.685	6	6	5
7 1 2		1.687		7 1 2	-	1.678	2	2	-
8 0 2	1.663	1.662	13	8 0 2	1.661	1.662	14	14	10
8 2 0	1.640	1.640	10	4 2 2	1.639	1.640	17	17	10
				8 2 0		1.636	<1		
8̄ 2 1	1.593	1.597	10	8̄ 2 1	1.594	1.597	1½	9	10
1 3 0		1.593		5 1 3		1.593	5		
				1 3 0		1.591	2		
1̄0 0 2	1.569	1.561	5	1̄0 0 2	1.567	1.565	4	4	5
12 0 0	1.493	1.497	10	3 3 1	1.494	1.494	5	28	30
				12 0 0		1.493	8		
				5 1 3		1.493	15		
3 3 1	1.478	1.479	5	7 1 3		1.478	10	13	not meas
				3 3 1		1.476	3		
				9 1 2		1.471	½		
				11 1 1		1.453	4	22B	not meas
				2̄ 2 3		1.450	3		
				8 2 2		1.447	2		
10 0 2	1.450	1.450	5	10 0 2		1.441	2		
				10 2 0		1.435	6		

POWGEN and observed values scaled to I_{max}=100. I/I_o from Kaiman et al. (1980).

number of indexing discrepancies in the former published pattern; the use of any of these lines in the refinement of the cell parameters would account for the differences observed between the DBG cell and that in the present paper. The full powder pattern for stibivanite is given by Kaiman et al. (1980).

ACKNOWLEDGEMENTS

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