

Crystal Structure of $\text{As}_2\text{V}_4\text{O}_{13}$

BY R. ENJALBERT, P. LECANTE AND J. GALY

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse CEDEX, France

(Received 12 February 1986; accepted 18 June 1986)

Abstract. Diarsenic(V) tetravanadium(IV) oxide, $M_r = 561.6$, triclinic, $P1$, $a = 4.9441(5)$, $b = 4.990(1)$, $c = 8.8156(8)$ Å, $\alpha = 90.12(1)$, $\beta = 100.57(1)$, $\gamma = 80.72(1)^\circ$, $V = 210.9(1)$ Å³, $Z = 1$, $D_x = 4.422$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 12$ mm⁻¹, $F(000) = 262$, $T = 292$ K, $R = 0.020$ for 2531 unique observed reflections and 170 variable parameters. The structure consists of a cubic close-packed oxygen atom array with four crystallographically independent tetravalent vanadium atoms distributed in octahedra sharing edges and corners, and with pentavalent arsenic atoms located in two independent tetrahedral sites sharing corners with VO_6 octahedra.

Introduction. The ternary system As–V–O exhibits glassy regions in which vanadium and arsenic may coexist under two oxidation states. Data have been reported concerning specifically the pseudo-binary system As_2O_3 – V_2O_5 , in which a wide range of semi-conducting glasses has been observed (Culea & Nicula, 1984). We also observed glass formation in the systems As_2O_3 – V_2O_5 and As_2O_5 – V_2O_4 , and in the ternary systems As_2O_5 – V_2O_5 – V_2O_4 and As_2O_5 – V_2O_4 – As_2O_3 (Enjalbert, Mosset, Lecante & Galy, 1985). It has been possible to isolate a crystalline phase of the well defined $1\text{As}_2\text{O}_3$ – $2\text{V}_2\text{O}_5$. Its crystal structure is of fundamental importance, since it is located close to the barycentre of these mixed-valence glassy systems, in view of solving the problem of the atomic architecture of the amorphous families: $\text{As}_2^5 + \text{V}_4^4 + \text{V}_{2x}^{5+} \text{O}_{13+5x}$ with $x < 1$ and $\text{As}_2^5 + \text{As}_{2y}^{3+} + \text{V}_4^4 + \text{O}_{13+3y}$ with $y < 1$.

Experimental. Crystal growth obtained from carefully dehydrated powder mixture of As_2O_3 and V_2O_5 (molar ratio 1:2), introduced in a quartz tube, sealed under vacuum, heated at 833 K for 24 h and cooled to room temperature at a rate of 1 K min⁻¹. Chosen crystal: black faceted regular block (ca $0.10 \times 0.15 \times 0.15$ mm) (Fig. 1). Preliminary crystallographic study performed using a precession camera: triclinic system, space groups $P1$ or $P\bar{1}$. Intensity measurements: CAD-4 Enraf–Nonius diffractometer; graphite-monochromated Mo $K\alpha$; take-off angle: 3.3° ; 25 reflections with $6 < \theta < 20^\circ$ used for measuring lattice parameters; $\theta_{\text{max}} = 40^\circ$; θ – 2θ scan mode; $\Delta\theta = 0.85^\circ + 0.35^\circ \tan\theta$; prescan speed: $10^\circ \text{ min}^{-1}$; final scan: $\sigma(I)/I$ 0.018, max. time = 100 s; standard reflections: $400/32\bar{6}/23\bar{2}$ with measuring frequencies: 3600 s; intensity variations $< 0.6\%$; 2598 unique reflections measured; range of hkl : h 0→8, k –9→9, l –15→15; correction for Lorentz–polarization; numeric absorption corrections: range of transmission coefficient 0.21–0.39. Structure determination using Patterson method; refinement with 2531 observations with $I > 3\sigma(I)$ and 170 refined parameters. Full-matrix least-squares refinement based on F magnitude; function minimized: $\sum w(\Delta F)^2$. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). $R = 0.020$; $wR = 0.029$; $w = 1$; $S = 0.74$; extinction coefficient: 8.09×10^{-6} ; $(\Delta/\sigma)_{\text{max}} = 0.01$; max. height in final difference synthesis: $1.5 \text{ e } \text{Å}^{-3}$. Calculations made with *SDP* (Enraf–Nonius, 1979) and illustrations with *ORTEP* (Johnson, 1976) using a DEC VAX/11-730 computer. Fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1.* Interatomic distances and bond angles are given in Table 2.

Discussion. The choice of $P1$, a non-centrosymmetric space group, is based on a careful analysis of data and on the final structure determination. Among 2598 hkl

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43155 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey square, Chester CH1 2HU, England.

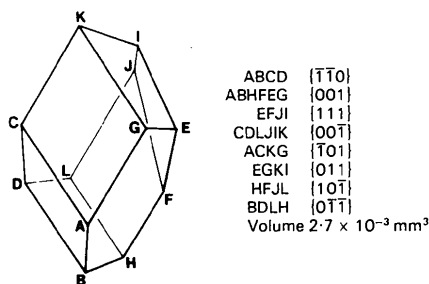


Fig. 1. Drawing of the crystal.

Table 1. Positional parameters and their e.s.d.'s

$$B_{eq} = \frac{4}{3} \sum_i \sum_j (\mathbf{a}_i \cdot \mathbf{a}_j) \beta_{ij}$$

	x	y	z	B _{eq} (Å ²)
As(1)	*0.000	0.000	0.000	0.309 (4)
As(2)	0.75608 (8)	0.56610 (8)	0.58753 (5)	0.237 (4)
V(1)	0.5484 (1)	0.5478 (1)	-0.05821 (7)	0.283 (7)
V(2)	0.2606 (1)	0.0457 (1)	0.68320 (7)	0.263 (7)
V(3)	0.4367 (1)	0.2328 (1)	0.30307 (7)	0.282 (7)
V(4)	0.1057 (1)	0.7989 (1)	0.35768 (7)	0.307 (7)
O(1)	0.1916 (6)	-0.1581 (6)	-0.1275 (3)	0.52 (4)
O(2)	-0.0866 (6)	0.3286 (6)	-0.0479 (4)	0.58 (4)
O(3)	0.2143 (6)	-0.0208 (6)	0.1791 (3)	0.41 (3)
O(4)	-0.2715 (6)	-0.1466 (6)	0.0190 (3)	0.55 (4)
O(5)	0.8780 (6)	0.2423 (6)	0.6377 (4)	0.52 (4)
O(6)	0.5203 (6)	0.5638 (6)	0.4191 (3)	0.44 (4)
O(7)	0.0226 (6)	0.7274 (6)	0.5632 (3)	0.44 (4)
O(8)	0.5865 (6)	0.7303 (6)	0.7196 (3)	0.37 (3)
O(9)	0.4635 (6)	0.4311 (6)	0.0973 (3)	0.58 (4)
O(10)	0.3984 (7)	0.2819 (7)	-0.2141 (4)	0.61 (4)
O(11)	0.3076 (6)	0.0756 (6)	0.4701 (3)	0.44 (3)
O(12)	0.7489 (6)	0.0511 (6)	0.3158 (3)	0.51 (4)
O(13)	0.0588 (6)	0.5094 (6)	0.2743 (3)	0.57 (4)

* Fixed coordinates giving the cell origin.

registered only 62 have the status 'weak' and 2531 have $I > 3\sigma(I)$. Statistical distribution tests have been performed using all 2598 reflections (Table 3). The zero-moment test clearly indicates a non-centrosymmetric space group (Howells, Phillips & Rogers, 1950). Two refinements carried out with the two enantiomorphic forms give significantly different values of R , 0.037 and 0.025. In the last refinement cycle, there is no correlation order above 0.56. All temperature factors, distances and angles exhibit no anomalous discrepancies.

An orthogonal projection of the crystal structure of As₂V₄O₁₃ onto the (010) plane is given in Fig. 2. The arsenic atoms are pentavalent since they are located in regular oxygen tetrahedra (As³⁺ generally is one-side coordinated to three oxygen atoms only). This implies that all the vanadium atoms are in the tetravalent state. As⁵⁺-O distances (Table 2) compare well with those of other structures, e.g. 2H₃AsO₄·H₂O (As-O = 1.663 Å) (Worzala, 1968) and As₂O₅· $\frac{3}{2}$ H₂O (As-O = 1.693 Å) (Jost, Worzala & Thilo, 1966), but differ from As³⁺-O distances, e.g. As₂O(SO₄)₂ (As-O = 1.75 Å) (Mercier & Douglade, 1982).

Vanadium atoms V(1), V(2), V(3) and V(4) are octahedrally coordinated and characterized by one short V-O distance, typical of the vanadyl group VO²⁺, V-O = 1.647 Å. The short bond is opposite to the long V-O distance, implying that vanadium atoms are slightly displaced towards one of the summits of the octahedron which is conventional in such structures (Bouloux & Galy, 1976). The mean of V-O further confirms the tetravalence of the vanadium atoms as discussed by Galy & Hardy (1965) for LiV₂O₅, Galy & Carpy (1975) for K₂V₃O₈, Carpy & Galy (1971) for α'-NaV₂O₄F, Carpy & Galy (1975) for α'-NaV₂O₅,

Andersson, Galy & Wilhelmi (1970), and Waltersson, Forslund, Wilhelmi, Andersson & Galy (1974) for V₃O₇.

Table 2. Interatomic distances (Å) and bond angles (°) in AsO₄ tetrahedra and VO₆ octahedra

Symmetry code: (i) x, 1 + y, z; (ii) x, -1 + y, z; (iii) 1 + x, y, z; (iv) -1 + x, y, z; (v) x, y, 1 + z; (vi) x, y, -1 + z; (vii) 1 + x, 1 + y, z; (viii) -1 + x, 1 + y, z.

As(1)	O(1)	O(2)	O(3)	O(4)		
O(1)	1.712 (4)	109.2 (2)	107.7 (2)	113.4 (2)		
O(2)	2.750 (6)	1.661 (4)	106.1 (2)	113.3 (2)		
O(3)	2.775 (5)	2.707 (5)	1.726 (4)	106.8 (2)		
O(4)	2.802 (6)	2.732 (6)	2.720 (5)	1.663 (4)		
					⟨As(1)-O⟩	1.691
As(2)	O(5)	O(6)	O(7 ⁱⁱⁱ)	O(8)		
O(5)	1.661 (4)	105.9 (2)	109.7 (2)	112.5 (2)		
O(6)	2.693 (5)	1.713 (4)	111.6 (2)	107.9 (2)		
O(7 ⁱⁱⁱ)	2.745 (5)	2.819 (5)	1.696 (4)	109.2 (2)		
O(8)	2.789 (5)	2.754 (5)	2.762 (5)	1.693 (4)		
					⟨As(2)-O⟩	1.691
V(1)	O(1 ⁱ)	O(2 ⁱⁱⁱ)	O(4 ^{vii})	O(8 ^{vi})	O(9)	O(10)
O(1 ⁱ)	2.099 (4)	162.0 (2)	85.1 (2)	72.8 (1)	98.2 (2)	91.7 (2)
O(2 ⁱⁱⁱ)		1.940 (4)	89.3 (2)	89.4 (2)	99.7 (2)	87.1 (2)
O(4 ^{vii})	2.740 (6)	2.732 (6)	1.948 (4)	80.7 (2)	102.4 (2)	157.9 (2)
O(8 ^{vi})	2.560 (5)	2.928 (5)	2.701 (5)	2.212 (4)	170.3 (2)	77.5 (2)
O(9)	2.840 (5)	2.743 (6)	2.802 (5)		1.638 (4)	99.7 (2)
O(10)	2.967 (6)	2.740 (6)		2.662 (6)	2.818 (6)	2.035 (4)
					⟨V(1)-O⟩	1.979
V(2)	O(1 ^v)	O(5 ^{iv})	O(7 ⁱⁱ)	O(8 ⁱⁱ)	O(10 ^v)	O(11)
O(1 ^v)	2.063 (4)	93.0 (2)	79.9 (2)	77.2 (2)	94.2 (2)	153.9 (2)
O(5 ^{iv})	2.916 (5)	1.956 (4)	77.8 (2)	160.2 (2)	96.8 (2)	92.8 (2)
O(7 ⁱⁱ)	2.789 (5)	2.669 (5)	2.274 (4)	83.4 (2)	171.7 (2)	76.6 (1)
O(8 ⁱⁱ)	2.560 (4)		2.877 (5)	2.042 (4)	101.0 (2)	89.2 (2)
O(10 ^v)	2.731 (6)	2.701 (6)		2.856 (6)	1.645 (4)	110.3 (2)
O(11)		2.823 (5)	2.625 (5)	2.798 (5)	2.950 (6)	1.943 (4)
					⟨V(2)-O⟩	1.987
V(3)	O(3)	O(6)	O(9)	O(11)	O(12)	O(13)
O(3)	2.003 (4)	159.2 (2)	89.4 (2)	82.2 (2)	98.6 (2)	86.0 (2)
O(6)		2.002 (4)	89.4 (2)	94.0 (2)	102.1 (2)	73.3 (2)
O(9)	2.889 (5)	2.887 (5)	2.102 (4)	164.7 (2)	92.6 (2)	81.0 (2)
O(11)	2.581 (5)	2.871 (5)		1.923 (4)	101.2 (2)	85.7 (2)
O(12)	2.775 (5)	2.846 (5)	2.727 (5)	2.762 (5)	1.644 (4)	172.1 (2)
O(13)	2.806 (5)	2.458 (5)	2.736 (5)	2.746 (6)		2.111 (4)
					⟨V(3)-O⟩	1.964
V(4)	O(3 ⁱ)	O(6)	O(7)	O(11 ⁱ)	O(12 ^{viii})	O(13)
O(3 ⁱ)	2.010 (4)	91.0 (2)	162.3 (2)	80.3 (2)	87.9 (2)	97.3 (2)
O(6)	2.979 (4)	2.165 (4)	91.7 (2)	79.9 (2)	172.7 (2)	78.9 (2)
O(7)		2.972 (5)	1.975 (4)	82.9 (2)	87.3 (2)	100.4 (2)
O(11 ⁱ)	2.581 (5)	2.672 (5)	2.625 (5)	1.992 (4)	92.8 (2)	158.6 (2)
O(12 ^{viii})	2.762 (5)		2.722 (5)	2.868 (5)	1.969 (4)	108.4 (2)
O(13)	2.758 (5)	2.458 (5)	2.794 (5)		2.942 (5)	1.651 (4)
					⟨V(4)-O⟩	1.954

Table 3. Zero-moment test for centre of symmetry

N(Z) test for 2598 reflections in the range $0 < 2\theta < 80^\circ$.

	Z												
	Shell Number	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0		
1	351	12	22	29	37	41	45	49	54	60	64		
2	423	5	14	23	30	37	43	48	54	59	62		
3	433	7	15	23	30	36	43	48	52	56	60		
4	433	5	13	18	27	34	41	48	53	60	64		
5	436	8	15	24	30	39	44	51	54	58	63		
Average values		7	16	23	31	37	43	49	53	59	63		
Acentric distribution		10	18	26	33	39	45	50	55	59	63		
Centric distribution		25	35	42	47	52	56	60	63	66	68		

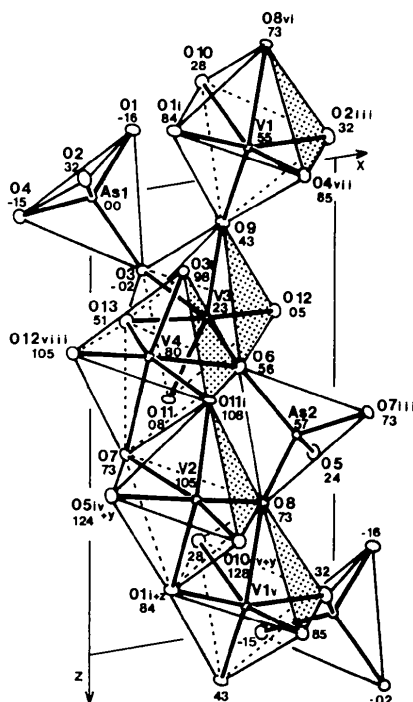


Fig. 2. Orthogonal projection of the atomic arrangement of $\text{As}_2\text{V}_4\text{O}_{13}$ on the (010) plane (y atomic coordinates $\times 10^2$).

The VO_6 octahedra sharing edges and corners build up as two chains along the [010] direction sharing corners and held together by AsO_4 tetrahedra. The distribution of the cations As^{5+} and V^{4+} within the network of oxygen atoms forming cubic close packing is complicated.

We have started the investigation of the glassy architecture of the 'AsVO' system using the knowledge

of the structure of $\text{As}_2\text{V}_4\text{O}_{13}$ and the assumptions by Galy, Meunier, Andersson & Åström (1975) and Galy & Enjalbert (1982) that the lone pairs in AsO_3E may be substituted by AsO_4 or VO_4 tetrahedra in oxide networks.

References

- ANDERSSON, S., GALY, J. & WILHELMI, K. A. (1970). *Acta Chem. Scand.* **24**, 1473–1474.
- BOULOUX, J.-C. & GALY, J. (1976). *J. Solid State Chem.* **16**, 385–391.
- CARPY, A. & GALY, J. (1971). *Bull. Soc. Fr. Minér. Cristallogr.* **94**, 24–29.
- CARPY, A. & GALY, J. (1975). *Acta Cryst.* **B31**, 1481–1482.
- CULEA, E. & NICULA, AL. (1984). *Solid State Commun.* **50**, 929–932.
- ENJALBERT, R., MOSSET, A., LECANTE, P. & GALY, J. (1985). *Proc. Ninth Eur. Crystallogr. Meeting*. Torino, Sept. 1985, pp. 534–535.
- Enraf-Nonius (1979). *Structure Determination Package*. Enraf-Nonius, Delft.
- GALY, J. & CARPY, A. (1975). *Acta Cryst.* **B31**, 1794–1795.
- GALY, J. & ENJALBERT, R. (1982). *J. Solid State Chem.* **44**, 1–23.
- GALY, J. & HARDY, A. (1965). *Acta Cryst.* **19**, 432–435.
- GALY, J., MEUNIER, G., ANDERSSON, S. & ÅSTRÖM, A. (1975). *Acta Cryst.* **13**, 142–159.
- HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–214.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- JOST, K. H., WORZALA, H. & THILO, E. (1966). *Acta Cryst.* **21**, 808–813.
- MERCIER, R. & DOUGLADE, J. (1982). *Acta Cryst.* **B38**, 1731–1735.
- WALTERSSON, K., FORSLUND, B., WILHELMI, K. A., ANDERSSON, S. & GALY, J. (1974). *Acta Cryst.* **B30**, 2644–2652.
- WORZALA, H. (1968). *Acta Cryst.* **B24**, 987–991.

Acta Cryst. (1986). **C42**, 1467–1469

A Refinement of the Structure of V_2O_5

BY RENÉE ENJALBERT AND JEAN GALY

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse CEDEX, France

(Received 12 February 1986; accepted 16 May 1986)

Abstract. Vanadium pentoxide, $M_r = 181.88$, orthorhombic, $Pm\bar{m}n$, $a = 11.512(3)$, $b = 3.564(1)$, $c = 4.368(1)$ Å, $V = 179.2(1)$ Å³, $Z = 2$, $D_x = 3.37$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 4.94$ mm⁻¹, $F(000) = 172$, $T = 292$ K, $R = 0.020$, $wR = 0.027$ for 334 unique reflections collected up to $\theta = 36^\circ$ and 24 variable parameters. V_2O_5 , a layered structure, built up

from VO_5 square pyramids sharing edges and corners, with V_2O_5 sheets held together *via* weak vanadium–oxygen interaction, $\text{V}–\text{O} = 2.791(3)$ Å. The structural investigation is confirmed and made more precise, showing a slight difference in the description of VO_5 polyhedra (square pyramid instead of trigonal bipyramid).

0108-2701/86/111467-03\$01.50

© 1986 International Union of Crystallography