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α-$V_{1\cdot08}P_{0\cdot92}O_5$ at 22°C

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Abstract. α-$V_{1\cdot08(1)}P_{0\cdot92}O_5$, tetragonal, $P4/n$; $a=6\cdot011$ (4), $c=4\cdot452$ (4) Å; $Z=2$, $D_{\text{calc}}=3\cdot39$ g cm^{-3}, 147 independent reflexions. The structure was refined by full-matrix least-squares methods, $R=0\cdot076$, with scintillation counter-measured intensities and monochromatized Mo $K\alpha$ radiation. The composition was determined by varying the occupancy of the tetrahedral site. The vanadyl bond length is 1·578 (9) Å. Unlike stoichiometric α-VPO_5 no evidence of positional disorder was found.

Introduction. Crystals were grown in a Pt crucible in an attempt to produce large single crystals by the Czochralski procedure. The present crystals grew at the interface with the crucible and at the surface of the charge. Crystals of β-VPO_5 and some as yet unidentified crystals were found near the centre of the crucible.

A crystal with dimensions 0·5 × 0·5 × 0·05 mm was used for data collection with a Syntex $P\bar{1}$ diffractometer. The data, corrected for Lorentz–polarization and absorption, were used together with the parameters of disordered α-VPO_5 (Jordan & Calvo, 1973) to refine the structure. Convergence of the least-squares refinement yielded an R of 0·12 with residual peaks in the difference Fourier map that indicated that the compound was non-stoichiometric. Subsequent refinements, with weights set as $w^{-1}=0\cdot9+0\cdot20F+0\cdot005F^2$, and with the extinction parameter varied indicated that 8 (1)% of the tetrahedral sites were occupied by V. The final parameters are compared with those of α-VPO_5 in Table 1.*

Some intensity measurements were made on the present crystal near liquid N_2 temperatures with a cryotip apparatus (Air Products Inc.) using the Joule–Thomson effect. Precession photographs of α-VPO_5 were taken with this apparatus for temperatures below room temperature; for those above room temperature a heated air stream was used.

Discussion. The bond lengths and angles for the present structure are compared with those for the stoichiometric crystal in Table 2. The size of the estimated standard deviations precludes a definitive statement concerning the difference between the present structure and that of α-VPO_5. The tetrahedrally coordinated cation–oxygen bond length should be larger by about 8% of the difference between the average tetrahedral V–O and P–O bond length, or about 0·014 Å. No significant change is seen. Many of the bond distances and angles differ by about 2σ. The thermal parameters of the heavy scatterers are about 50% larger in the present structure and decrease to about those of α-VPO_5 at −100°C. No evidence of disorder was found in the present structure and the measured inten-

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31831 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic and thermal parameters* (× 10^4) *for* α-$V_{1\cdot08}P_{0\cdot92}O_5$ *with standard errors in parentheses*

Thermal parameters were obtained from $\exp[-2\pi^2(h^2b_1b_1U_{11}+\ldots+2hkb_1b_2U_{12}+\ldots)]$, Where the b_i's are the reciprocal lattice parameters. Values of the free parameters of α-VPO_5 are in square brackets.

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	2500	2500	2165 (5)	100 (30)	U_{11}	280 (20)	–	–	–
			[2139 (5)]	[19 (14)]		165 (11)			
M*	2500	7500	5000	140 (30)	U_{11}	290 (20)	–	–	–
				[30 (18)]		189 (16)			
O(1)	2500	2500	8620 (20)	270 (80)	U_{11}	170 (40)	–	–	–
			[8580 (20)]	[110 (50)]		[180 (40)]			
O(2)	1965 (7)	9448 (7)	2970 (10)	130 (30)	100 (20)	310 (30)	−0 (20)	20 (20)	−0 (20)
	[1965 (13)]	[9522 (12)]	[2987 (17)]	[120 (30)]	[90 (30)]	[227 (30)]	[−10 (30)]	[−20 (30)]	[20 (30)]

* M consists of 0·92 P and 0·08 (1) V.

Table 2. *Bond lengths and angles in* α-$V_{1.08}P_{0.92}O_5$, *with estimated standard errors in parentheses*

Values in square brackets correspond to α-VPO_5.

VO_6 group			
V–O(1)	1·578 (9) Å	O(1)–V–O(2)	4× 101·1 (5)°
	[1·580 (11)]		[101·6 (2)]
V–O(2)	4× 1·868 (4)	O(2)–V–O(2)	4× 87·9 (3)
	[1·858 (7)]		[87·7 (3)
V–O(1)*a*	2·874 (10)	O(2)–V–O(2)	2× 157·9 (2)
	[2·853 (11)]		[156·7 (4)]
PO_4 group			
P–O(2)	4× 1·536 (4) Å	O(2)–P——O(2)	108·0 (5)°
	[1·541 (8)]		[109·1 (4)]
		P——O(2)–V	146·3 (1)

sities returned to the previous values upon reheating to room temperature.

The structure consists of layers with VO_5 groups sharing equatorial oxygen atoms with four separate XO_4 groups (Fig. 1). The former lie on fourfold axes and the latter on $\bar{4}$ axes. Nearest VO_5 groups are related by *n* glide planes such that the vanadyl bonds are antiparallel. The layers are held together by the weak bond *trans* to the vanadyl group and the length of this bond is limited by the oxygen–oxygen repulsion between adjacent tetrahedral groups.

Non-stoichiometry has been reported in $VMoO_5$ (Eich & Kihlborg, 1966) involving both cation sites. Brown & Hummel (1965) indicated that an excess of 10% V would dissolve in their form of VPO_5 which, according to the reported powder pattern, corresponds to β-VPO_5 (Gopal & Calvo, 1972). The structure of V_2O_5–VO_2–P_2O_5 glasses has been interpreted in terms of α-VPO_5-like layers with deviations from the molal equivalent of P and V related to the substitution of V at the tetrahedrally coordinated cation site (Jordan & Calvo, 1976*a*). This quasi-crystalline model for the glass leads naturally to a correct prediction for the density (Calvo & Jordan, 1976), the Seebeck coefficient behaviour as functions of x and the degree of reduction (Jordan & Calvo, 1976*a*) and the value and invariance of polaron–polaron coordination number with a change in V:P (Jordan & Calvo, 1976*b*).

Photographic studies of α-VPO_5 between −100°C and 100°C show a progressive development of a mirror plane parallel to [110]. Further studies varying composition, temperature and perhaps pressure are needed to resolve the apparent lack of disorder in the present crystal near room temperature.

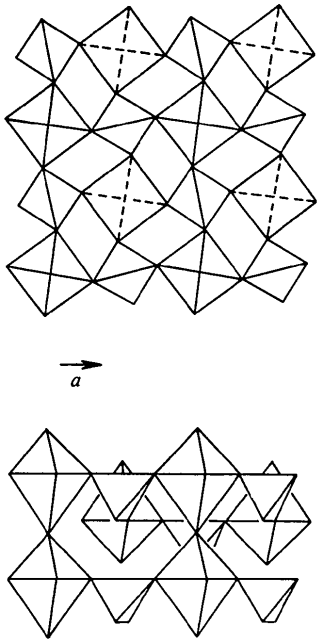

Fig. 1. View of the structure of α-VPO_5. Oxygen atoms are at the corners of the polyhedra. The dotted lines indicate a vanadyl group directed parallel to −**c**.

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