Oxovanadium(IV) Diphosphatomonosilicate

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Abstract. $VO(P_2SiO_8)$, tetragonal, $P4/ncc$; $a=8\cdot723$ (1), $c=8\cdot151$ (1) Å; $Z=4$, $D_{calc}=3\cdot05\pm0\cdot1$ g cm^{-3}. The vanadyl bond length is $1\cdot590$ (3) Å. The structure contains chains of distorted VO_6 octahedra lying on fourfold axes bridged by PO_4 groups. Layers are formed by eight-membered rings containing alternately VO_6 and PO_4 groups. These layers are bridged by SiO_4 groups corner sharing with oxygen atoms, as found by Rice, Robinson & Tofield [*Inorg. Chem.* (1976), **15**, 345–348].

Introduction. Tofield, Crane, Bridenbaugh & Sherwood (1975) prepared crystals of $VO(P_2SiO_8)$ by vapor transport in I_2 starting with $VO(PO_3)_2$ and SiO_2. They reviewed the sparse occurrence of P^V substitution for Si^{IV} in silicate minerals. Our interest in this system was whetted by the extensive studies of semiconducting vanadium phosphate glasses reviewed by Adler (1971) and the catalytic properties of vanadium phosphate systems (Escardino, Sola & Ruiz, 1973). Blue crystals were obtained accidentally about three years ago from a V_2O_5–P_2O_5 mix heated to around 900°C in an evacuated sealed silica tube. These crystals had cross-sections of up to about 3 mm and heights, parallel to c, of up to about 0·3 mm. Crystals yielding the same diffraction pattern, but colored green, were obtained more recently from a V_2O_5–P_2O_5 mix heated in an open VitreoSil crucible.

A single blue crystal was ground to a sphere of radius 0·125 mm and used to collect the intensity of 571 symmetry-independent reflections, with Laue group

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$4/mmm$, within a sphere defined by $2\theta_{max}=65°$. Mo $K\alpha$ graphite-monochromatized radiation was used in a θ–2θ mode with variable scan rates and a scintillation counter to determine integrated peak and background intensities. Only reflections whose estimated intensities were positive were considered. The data were corrected for Lorentz, polarization and absorption effects (although $\mu\langle R\rangle=0\cdot3$). The space group was chosen from the systematic extinctions ($hk0$, $h+k=2n$; $0kl$, $l=2n$; hhl, $l=2n$) to be $P4/ncc$. V, Si, P and the vanadyl oxygen atom were found from the Patterson function to be on the special positions with 4, $\bar{4}$, 2 and 4 symmetry respectively. The remaining oxygen atom positions were determined from a difference Fourier synthesis.

The structure consists of layers parallel to the *ab* net and related by the *c* glide plane. The layers consist of VO_6 octahedra, distorted axially, bonded by corner-sharing oxygen atoms with PO_4 groups thus forming interconnected eight-membered rings (Fig. 1). Two phosphate groups in one layer and two in the adjacent layer share O atoms with the SiO_4 groups. This model readily refined, by full-matrix least-squares methods, to an $R=0\cdot032$ and $wR=(\sum w|F_o-F_c|^2/\sum w|F_o|^2)^{1/2}=0\cdot026$. Weights,

$$[0\cdot62-0\cdot0175|F|+0\cdot000315|F|^2+775(\sigma/F)^2]^{-1},$$

were chosen so that $w\Delta F^2$ was independent of F_o.

Atomic scattering curves (corrected for anomalous dispersion) for O, P, Si and V were taken from Cromer & Mann (1968) and secondary extinction corrections were made following procedures indicated by Zachariasen (1963) and Larson (1967). The final atomic positional and anisotropic thermal parameters are in Table 1.

Table 1. *Positional and thermal parameters of* $VO(P_2SiO_8)$

All values (multiplier and fractions excepted) are multiplied by 10^4; standard deviations are given within parentheses. U_{ij} in Å^2 are obtained from $\beta_{ij}=2\pi^2b_ib_jU_{ij}$, where $T=\exp(-\beta_{11}h^2-\ldots-2\beta_{12}hk-\ldots)$ is the thermal factor in the structure factor expression.

	Multiplier	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V	0·249 (1)	$\frac{1}{2}$	0	3529·8 (7)	60 (3)	U_{11}	92 (2)	0	0	0
P	0·498 (1)	·1790·1 (9)	x	$\frac{1}{4}$	61 (3)	U_{11}	85 (2)	4 (2)	0	0
Si	0·249 (1)	0	0	0	80 (4)	U_{11}	68 (3)	0	0	0
O(1)	$\frac{1}{4}$	$\frac{1}{2}$	0	5480 (3)	134 (12)	U_{11}	113 (9)	0	0	0
O(2)	1·0	6523 (2)	1620 (2)	3077 (2)	89 (6)	74 (5)	174 (5)	−23 (4)	−8 (5)	46 (5)
O(3)	1·0	6390 (2)	4392 (2)	3889 (2)	105 (5)	126 (5)	113 (5)	3 (4)	27 (5)	−33 (5)

Table 2. *Lattice parameters for* $VO(P_2SiO_8)$

a	c	Reference
8·723 (1)	8·151 (1)	This work
8·697 (8)	8·119 (8)	Tofield *et al.* (1975)
8·747 (2)	8·167 (2)	Rice *et al.* (1976)
8·733 (2)	8·185 (3)	*

* This compound was recently prepared by reduction of VPO_5 under N_2 at 800°C. The resulting mixture was melted and recrystallized under vacuum in a sealed quartz tube. Square, green crystals were found embedded on the surface of a glass matrix. These crystals had identical diffraction patterns to $VO(P_2SiO_8)$.

Since it is possible that our crystals were non-stoichiometric with some V^{5+} at any of the cation sites and/or Si and P intermixed, the multiplicities of the atoms were varied in the final run. No significant variation from that required by the formula was found and thus the discrepancy between the present lattice parameters and those reported by Tofield *et al.* (1975) [$a = 8·697$ (8), $c = 8·119$ (8) Å], and Rice, Robinson & Tofield (1976) [$a = 8·747$ (2), $c = 8·167$ (2) Å], shown in Table 2, is not understood. The unit-cell parameters were derived by least-squares methods from 42 pairs of 2θ values, both positive and negative, lying between 31 and 60° using $\lambda_{\alpha 1}$ (= 0·70926 Å).†

Discussion. In addition to the corner sharing of PO_4 and SiO_4 groups, the layers of the structure are also bonded by the weak interaction *trans* to the vanadyl group. The bond distances and angles are in Table 3.

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31837 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
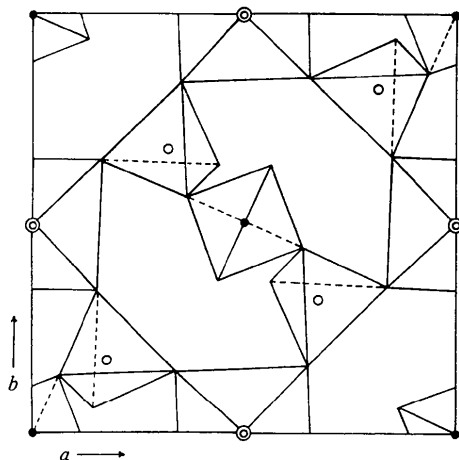

Fig. 1. A half-cell projection of the structure of $VO(P_2SiO_8)$. The remainder of the cell can be generated by a c glide plane parallel to the face diagonal. The Si, P and V are shown as filled, open and doubled circles respectively. O atoms lie at the corners of the outlined polyhedra.

The VO_6 group is distorted from regularity by a 0·4 Å displacement of the V from the plane of the equatorial O atoms in order to form a vanadyl bond while the O atom *trans* to this group moves away by less than 0·1 Å. An ideal octahedron with $V–O = 1·97$ Å was used for comparison. The strongly and weakly bonded equatorial oxygens lie 2·757 and 2·871 Å from the axial O atom respectively.

Table 3. *Bond angles* (°) *and distances* (Å) *in* $VO(P_2SiO_8)$

VO_6 group

V–O(1)^i	1·590 (3)		O(1)^i—V–O(2)^i	100·77 (18)
–O(1)^v	2·486 (3)		O(2)^i—V–O(2)^{xii}	79·23 (13)
–O(2)	1·974 (2)	(4×)	O(2)^i—V–O(2)^{ii}	158·45 (7)
			V——O–P	146·56 (4)

SiO_4 group

Si–O(3)	1·604 (2)	(4×)	O(3)^{xiii}–Si–O(3)^{xiv}	111·23 (18)
			–O(3)^{xv}	108·60 (17)
			Si——O–P	142·39 (6)

PO_4 group

P–O(2)	1·483 (2)	(2×)	O(2)^{xii}–P–O(2)^{xiv}	113·23 (19)
–O(3)	1·571 (2)	(2×)	–O(3)^{xii}	110·52 (18)
			–O(3)^{xiv}	109·47 (18)
			O(3)——P–O(3)	103·17 (17)

Symmetry code

(i)	x	y	z	(iv)	$\frac{1}{2}+x$	$\frac{1}{2}+y$	$-z$
(ii)	$-x$	$-y$	z	(x)	$\frac{1}{2}+y$	$\frac{1}{2}-x$	z
(iii)	$-y$	x	z	(xi)	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
(iv)	y	$-x$	$-z$	(xii)	$\frac{1}{2}-y$	$\frac{1}{2}+y$	z
(v)	$-x$	y	$\frac{1}{2}+z$	(xiii)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(vi)	x	$-y$	$\frac{1}{2}+z$	(xiv)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}-z$
(vii)	y	x	$\frac{1}{2}-z$	(xv)	$\frac{1}{2}-y$	$\frac{1}{2}-x$	$\frac{1}{2}-z$
(viii)	$-y$	$-x$	$\frac{1}{2}-z$	(xvi)	$\frac{1}{2}+y$	$\frac{1}{2}+x$	$\frac{1}{2}+z$

The SiO_4 group is slightly squashed parallel to the c axis with the Si–O bond length in the range expected from silicate structures. The phosphate group has two unique P–O distances. That the shorter involves an O atom shared with V^{4+} is consistent with the Pauling-type valency arguments. The longer involves O(3) which is shared with Si^{4+}. The P–O distances differ by 0·088 Å, although based upon Baur's (1970) linear relationship between bond order and distance, they would be expected to differ by only 0·036 Å. The valency sums following Brown & Shannon (1973) are: $V^* = 4·19$ v.u., $P = 5·01$ v.u., $Si = 4·01$ v.u., where those for P and Si were calculated with parameters based upon distance corrected for oxygen coordination. The major angular distortion of the phosphate group involves those oxygens shared with the VO_6 group. The geometry here is essentially the same as that reported by Rice *et al.* (1976) except that their value of Si–O(3) is 1·610 (1), P–O(2) is 1·492 (1) Å and O(3)^{xiii}–Si–O(3)^i is 111·58 (7)°. The anisotropic thermal parameters are not indicative of any substitutional disorder or non-stoichiometry but those of Rice *et al.* (1976) are con-

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* The parameters in $S = S_o(R_o/R)^n$ for V^{4+} have recently been derived by Brown.

sistently and substantially lower than the present values. The difference in these bond lengths suggests some V substitution at the Si site and either Si or V at the P site. Since these tetrahedrally coordinated vanadium ions are normally 5+ the former substitution is preferred in order to avoid the need for V^{3+} as charge compensation at the octahedral site. Further studies would be necessary to determine whether this is the source of the unit-cell parameter and molecular-geometry discrepancies.

This structure has considerable similarities with that of the isostructural α-VPO_5 (Jordan & Calvo, 1973) and α-VSO_5 (Longo & Arnott, 1970). All have layers generated by the fourfold axis and the n glide plane. The SiO_4 group in the present structure leads to a substantially more open structure as is indicated by the density. The geometry of the $V^{4+}O_6$ group in α-VSO_5 is similar to that in the present case. Both are axially distorted with the vanadyl group lying on the fourfold axis with the V and the equatorial VO bonds slightly shorter here.

This crystal is of some interest with regard to the structure of vanadium phosphate glasses. The present crystal's composition could be represented as M_4O_9 where the average oxidation state of M(=V,P) is 4·5. The stable form of V_4O_9 has a mixture of V^{4+} and V^{5+} in octahedral and square-pyramidal configurations (Wilhelmi & Waltersson, 1970). In the present case with M=V, one quarter of the vanadium ions would be trivalent since tetrahedrally coordinated V^{4+} is not expected. Harper & McMillan (1974) prepared mixtures of $(1+x)V_2O_5$ and $(1-x)P_2O_5$ with $-0\cdot8 < x < 0\cdot818$ and x incremented in steps of about 0·2. Oxygen was lost in almost direct proportion to the number of P atoms in the glass. The glass richest in V also lost P which suggests that this glass differs in structure from that of the remaining glasses, or at least is a mixture of an α-VPO_5-like glass (Jordan, 1975) and one based on a V_2O_5-like structure.

The composite EPR spectra showed three signals near $g=1\cdot96$, but with different line widths. Signal A was found in glasses with $0 \le x \le 0\cdot818$ and was attributed by Harper & McMillan (1974) to V^{4+}. Signal B appeared in glasses with $-0\cdot4 \le x \le 0$ while signal C occurred in those glasses with $-0\cdot8 \le x \le 0\cdot4$. The latter signal was attributed to either V^{3+} or V^{2+} while signal B was associated with either V^{3+}, which would be consistent with the present structure, or a second V^{4+} site.

The radial distribution function (RDF) of the $x= -0\cdot4$ glass was imperfectly, but suggestively, fitted to an α-VPO_5-like model, with the composition suitably adjusted (Jordan, 1975). He concluded that the glass should have a layer-like structure basically like that of α-VPO_5, as he had found for glasses with $0 \le x \le 0\cdot6$. The experiments of Harper & McMillan (1974) support an α-VPO_5-like model for glasses with $x > 0$, a mixture of α-VPO_5-like and $VO(P_2SiO_8)$-like glasses for $x=0$ and a $VO(P_2SiO_8)$-like glass for $-0\cdot4 < x < 0$. Near $x = -0\cdot4$, a new phase appears, together with a $VO(P_2SiO_8)$-like glass, which is stable for $x < -0\cdot6$. The interpretation of the $x=0$ glass as a single phase (Jordan, 1975) may be in error despite the excellent fit of the RDF, and the glass should be examined by EPR techniques. Harper & McMillan's (1974) interpretation of the peak on the low-energy side of the K absorption in the X-ray absorption spectrum as being a measure of the number of V atoms with non-centrosymmetric environments is not consistent with these proposals, however.

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