

## Crystal Structure of $\beta\text{VPO}_5$

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$\beta\text{VPO}_5$  crystallizes as an orthorhombic crystal with  $a = 7.770(3)$ ,  $b = 6.143(3)$ ,  $c = 6.965(3)$  Å and  $Z = 4$  in space group  $Pnma$ . The structure was refined, by full matrix least squares, from the coordinates of the isostructural  $\beta\text{VSO}_5$  with 772 nonequivalent reflections measured on a General Electric quarter circle diffractometer. The final  $R$  value is 0.047. The structure consists of chains of distorted  $\text{VO}_6$  groups with V-O bond lengths parallel to the chain of 1.566 and 2.591 Å. The equatorial V-O bond lengths range from 1.849 to 1.902 Å. The  $\text{PO}_4$  group, which shares oxygen atoms with separate  $\text{VO}_6$  groups in three separate chains, has the P-O bond lengths ranging from 1.519 to 1.540 Å.

### Introduction

Brown and Hummel (1) have indicated that a crystalline phase of  $\text{VPO}_5$  exists but to date the crystal structure of this compound has not been reported. Considerable interest has been generated by the study of  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glass systems (2, 3). The electrical and magnetic properties of these glasses indicate that the amount of  $\text{V}^{4+}$  varies in proportion to the fractional amount of  $\text{P}_2\text{O}_5$  present in the glass. Since structural data on  $\text{VPO}_5$  were not available these properties have been interpreted in terms of the structure of  $\text{V}_2\text{O}_5(2)$ .

This form of  $\text{VPO}_5$  is isostructural with  $\beta\text{VSO}_5(4)$  and thus allows a comparison of the vanadium environment when the formal oxidation state changes from 4+ to 5+. These systems feature an irregular near neighbor environment to the vanadium ion with five strong bonds and the ubiquitous long sixth interaction.

### Experiments

Crystals of  $\text{VPO}_5$  were grown from a mix containing an excess of about 1%  $\text{H}_3\text{PO}_4$  in  $\text{V}_2\text{O}_5$ . The slurry was dried at temperatures slightly above 100°C, then heated in an open silica crucible to 900°C and slowly cooled to room temperature. Small yellow-green crystals of  $\text{VPO}_5$  were extracted for study from a nonuniform-looking mass.

Preliminary photographic studies indicated that the crystals were orthorhombic with space group  $Pnma$  or  $Pn2_1a$  since the  $hk0$  and  $0kl$  reflections were extinct when  $h$  and  $k+l$  were odd, respectively. Accurate parameters were derived from a least-squares refinement of 16( $2\theta$ ) values measured with filtered  $\text{MoK}\alpha$  radiation ( $\lambda_{\alpha_1} = 0.70926$  Å). The parameters obtained are  $a = 7.770(3)$ ,  $b = 6.143(3)$  and  $c = 6.965(3)$  Å with errors set at  $3\times$  the standard deviations derived from the least squares. The calculated density for  $z = 4$  is 3.238 g/cm<sup>3</sup>. The density of the crystals were not measured because a sufficient number were not available. A crystal measuring  $0.07 \times 0.07 \times 0.05$  mm, the largest available, was used to collect data with a General Electric quarter circle automatic diffractometer using filtered  $\text{MoK}\alpha$  radiation and a scintillation counter detector. 1620 reflections were scanned using a scanning range dependent upon the  $2\theta$  value. Each peak was scanned at 2° per min using a  $\theta/2\theta$  scan while the background was counted on either side of the peak at a fixed orientation for 20 sec. The estimated standard deviations,  $\sigma$ , were assigned on the basis of counting statistics and an unobserved limit set at  $3\sigma$ . Reflections whose intensity calculated negative were left out of the refinement. 772 symmetry independent reflections of which 254 were observable were included in the final data set. These data were corrected for Lorentz and polarization effects

but not absorption. Since the crystal average  $\mu R$  was 0.5 the average error in the structure factors over the angular range studied was estimated to be 2%.

The structure was refined with the coordinates determined for  $\beta\text{VSO}_5(4)$  as initial values. The centrosymmetric space group assigned to this latter compound was chosen. Scattering curves for V, P and O were taken from Cromer and Waber (5) and corrected for dispersion using the tabulated values in the "International Tables for X-ray Crystallography" (6). The structure was refined using a full matrix least-squares program written by J. S. Stephens for the CDC 6400. Weights were chosen so that the local average discrepancy between the observed and calculated structure factors would be independent of the magnitude of the structure factors. The derived weighting function was  $w = \{1.50 + 0.59|F_o| + 0.0037|F_o|^2\}^{-1}$ . Unobserved structure factors whose calculated values were less than the local unobserved limit were given zero weight in that cycle of refinement, otherwise  $\Delta = F_{calc} - 0.9F_{min}$ , where  $F_{min}$  is the estimated maximum possible value for an unobserved reflection in that region of reciprocal space. Initially independent isotropic thermal parameters were used and the  $R$  value obtained was 0.075. In the final cycles of refinement the anisotropic thermal components of the atoms were varied independently. The  $R$  value dropped to 0.047 and although the ratio of observed structure factors (254) changed from 17:1 to 8.5:1 the improvement is significant. The final value of

$$R_w = \left( \frac{\sum w ||F_o| - |F_c||^2}{\sum w |F_o|^2} \right)^{\frac{1}{2}}$$

was 0.068 when the calculated shifts were all less than  $0.2\sigma$ . Both  $R$  values include all 772 reflec-

tions. Table I contains the final coordinates and the calculated and observed structure factors are available.<sup>1</sup>

### Description of the Structure

The structure of  $\text{VPO}_5$  is isostructural with that of  $\beta\text{VSO}_5(4)$  and thus consists of corner sharing irregular  $\text{VO}_6$  groups arrayed parallel to the  $a$  axis with no additional direct bonding between these groups. Both the shortest and longest V-O bonds lie at small angles to the chain direction and in each case involves O(4). Both the  $\text{MO}_n$  groups contain crystallographic mirror planes. The  $\text{PO}_4$  group shares its oxygen atoms with four separate  $\text{VO}_6$  groups in three separate chains and of the oxygen atoms only O(4) is not shared between a phosphorus and vanadium atom. The structure contains sheets composed of  $\text{VO}_6$  chains as shown in Fig. 1 with neighboring chains related by the  $a$  glide plane. The pseudo four fold axes are tilted by  $30^\circ$  from paralleling the  $c$  axis as a result of the  $\text{PO}_4$  group bridging across adjacent  $\text{VO}_6$  groups in a chain. This feature distorts the packing sufficiently to prevent a rational description of the structure in terms of close packing. Adjacent sheets, generated by the centers of symmetry, are joined through corner sharing of O(1) between  $\text{PO}_4$  groups in one sheet with  $\text{VO}_6$  groups in the next.

<sup>1</sup> A table of observed and calculated structure factors from this analysis has been deposited as Document No. NAPS-01852 with the ASIS National Auxiliary Publications Service, c/o CCM Information Corp., 909 Third Avenue, New York, N.Y. 10022. A copy may be secured by citing the document number and by remitting \$5.00 for photocopies or \$2.00 for microfiche. Advance payment is required. Make check or money order payable to ASIS-NAPS.

TABLE I  
POSITIONAL AND THERMAL PARAMETERS FOR  $\beta\text{VPO}_5$

Atom	Site	$x$	$y$	$z$	$U_{11}^a$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
V	4(C)	0.1735(2)	$\frac{1}{4}$	0.2307(2)	0.0119(8)	0.0090(6)	0.0115(5)	—	-0.0010(6)	
P	4(C)	0.8831(3)	$\frac{1}{4}$	0.8783(3)	0.0126(10)	0.0083(9)	0.0070(7)	—	0.0088(8)	
O(1)	8(d)	0.1228(6)	0.5494(8)	0.2511(6)	0.020(2)	0.010(2)	0.012(2)	0.002(1)	-0.001(2)	0.003(2)
O(2)	4(C)	0.7235(9)	$\frac{1}{4}$	0.0091(9)	0.015(3)	0.016(3)	0.012(2)	—	0.005(2)	
O(3)	4(C)	0.0469(8)	$\frac{1}{4}$	-0.0030(9)	0.013(3)	0.015(3)	0.011(2)	—	0.006(2)	
O(4)	4(C)	0.3594(9)	$\frac{1}{4}$	0.1442(10)	0.017(4)	0.016(3)	0.015(2)	—	0.004(2)	

<sup>a</sup>  $U_{ij}$ 's in  $\text{\AA}^2$  are computed from  $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$  where  $T = \exp(-\beta_{11}h^2 + 2\beta_{12}hk + \dots)$  appears in the structure factor expression and  $b_j$  are reciprocal lattice vectors.

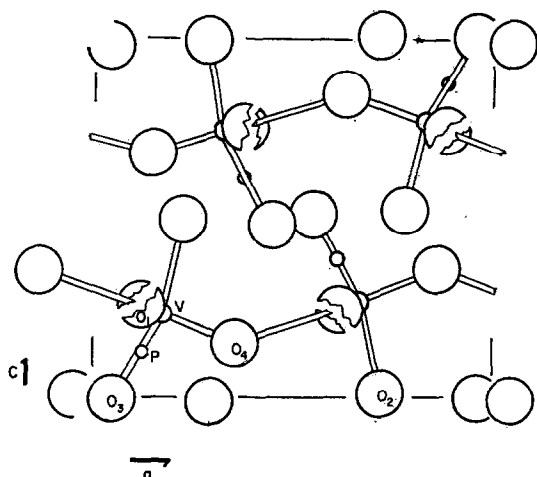


FIG. 1. The structure of  $\beta$ VPO<sub>5</sub> is shown projected onto the *ac* plane. The oxygen atoms are shown as the largest circles and those related by the mirror plane are split. The phosphorus atom is indicated by the smallest circles while the next larger circles represent vanadium ions. The phosphorus position is related to that of Table I by transformation  $-x, -y, -z$ .

The VO<sub>6</sub> group is distorted from a regular octahedron primarily as a result of the displacement of the V atom from the center of the octahedron towards one of the O(4) atoms by about 0.5 Å. The two axial V–O(4) interactions are

1.556(7) and 2.591(7) Å in length. The equatorial V–O bond lengths are 1.886(5) Å for the mirror plane related pair of O(1) atoms, 1.849(7) Å for O(2) and 1.902(7) Å for O(3). The separation of these oxygen atoms in the equatorial plane are either 2.499 Å between O(1) and O(2) or 2.620 Å between O(1) and O(3). The separation of these oxygen atoms from the axial atom involved in the vanadyl ion are 2.705, 2.631 and 2.636 Å to O(1), O(2) and O(3), respectively. The remaining O(4) atom has interactions of 2.846, 2.980 and 2.892 Å with the equatorial O(1), O(2) and O(3). These latter two sets of values suggest an additional distortion of the octahedron involving a displacement of O(4) by about 0.1 Å from the center. Further deviations from ideality are small. These bond lengths and angles for VPO<sub>5</sub> are collected in Table II.

The average PO bond length is 1.526 Å a value slightly smaller than commonly found value of 1.54 Å(7). The individual PO values range from 1.519(5)–1.540(7) Å but do not differ significantly from each other. The angles also show modest distortions from regularity.

## Discussion

One of the more interesting aspects of this structure results from a comparison of the

TABLE II  
BOND LENGTHS AND ANGLES IN  $\beta$ VPO<sub>5</sub>

VO <sub>6</sub> group						
distance		(Å)	angle	(°)	angle	(°)
V–O(1a)	2×	1.886(5)	O(1a)–V–O(19)	154.3(2)	O(2b)–V–O(3a)	161.0(3)
–O(2b)		1.849(7)	–O(2b)	88.3(2)	–O(4a)	100.5(3)
–O(3a)		1.902(7)	–O(3a)	87.5(2)	–O(4b)	82.5(3)
–O(4a)		1.566(7)	–O(4a)	102.8(2)	O(3a)–V–O(4a)	98.5(3)
–O(4b)		2.591(7)	–O(4b)	77.2(2)	–O(4b)	78.5(3)
			O(4a)–V–O(4b)	177.0(3)		
distance		(Å)	angle	(Å)	angle	(°)
O(1a)–O(19)		2.465(7)	O(19)–O(2b)	2.498(7)	O(3a)–O(4a)	2.636(9)
–O(2b)		2.663(6)	–O(3a)	2.499(7)	–O(4b)	2.893(9)
–O(3a)		2.619(7)	O(2b)–O(4a)	2.981(10)		
–O(4a)		2.705(7)	–O(4b)	2.632(9)		
–O(4b)		2.846(7)	–O(3a)	2.514(9)		
PO <sub>4</sub> group						
distance		(°)	angle	(°)	angle	(°)
P–O(1c)	2×	1.528(5)	O(1c)–P–O(1e)	107.6(3)	O(2a)–P–O(3a)	110.3(2)
–O(2a)		1.540(7)	–O(2a)	109.1(2)		
–O(3a)		1.519(7)	–O(3a)	110.6(2)		

$a$ -h, represent:  $x, y, z; x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z; -x, \frac{1}{2} + y, -z; \frac{1}{2} - x, -y, \frac{1}{2} + z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z; x, \frac{1}{2} - y, z; \frac{1}{2} + x, y, \frac{1}{2} - z$ .

individual V–O bond lengths with those of  $\beta\text{VSO}_5$ , where vanadium has the formal oxidation state of 4+. The vanadyl ion is 1.59(2) Å long in this case while the remaining V–O(4) bond length is 2.28(2) Å. The average equatorial V–O bonds are 2.03 Å long in  $\beta\text{VSO}_5$ , as compared to 1.881 Å in the present case. These bond length changes are consistent with the difference in the valency of the vanadium as calculated from the relationship

$$d_n = d_1 + 2k \log n$$

introduced by Pauling (8), where  $d_n$  is the bond length for a  $n$ th-order bond while  $k$  is an empirical constant. Evans (9) derived a value of 1.81 for  $d_1$  and 0.39 for  $k$  while Wilhemi, Waltersson and Kihlberg (10) prefer 1.789 and 0.390, respectively. From the latter values the total  $n$  of V adds up to 5.19 and 4.21 for the phosphate and sulfate compounds, respectively.

A second common feature concerns the shortened bonds in the tetrahedral groups. The average S–O bond length is 1.43 Å in  $\beta\text{VSO}_5$  and represents a decrease of 0.06 Å from the expected value. The individual P–O bonds should be 1.54 Å from Baur's correlation between bond lengths and electrostatic valency. However since the existence of the vanadyl ion weakens the equatorial V–O bond yielding an average bond order of 0.76 the P–O bonds would be expected to be shortened an average of 0.026 Å, from Baur's correlation. In actual fact the shortening should be in the order P–O(2), P–O(1) and P–O(3) as it is in fact found. Unfortunately the errors are too high to regard this agreement alone as being significant.

Finally it would have been of considerable interest to study the conductivity of  $\text{VPO}_5$  with slightly reduced vanadium perhaps by doping with  $\text{SO}_4^{2-}$  ions. Unlike other vanadium oxygen systems studies where the structure is unknown, as in the  $\text{V}_2\text{O}_5$ – $\text{P}_2\text{O}_5$  glasses (2, 3, 10), or where

there are more than one conductivity path for a "hopping" mechanism, as in  $\text{V}_2\text{O}_5$  (11) and  $\text{M}_x\text{V}_2\text{O}_5$  (12), only one such path exists in  $\text{VPO}_5$ . The change in conductivity with pressure would then give a relationship between the conductivity and the V=O...V distance. Unfortunately efforts at growing large crystals in air gave only black glasses while attempts at vacuum growth in Vycor containers gave two forms of blue-green crystals. One of these appears to be related to the structure of  $\alpha\text{VSO}_5$ , where the oxygen atoms show a close packing but with a complex disordering and variable stoichiometry.

### Acknowledgment

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*Note added in proof:* Yellow crystals of  $\text{VPO}_5$  isotopic with  $\alpha\text{VSO}_5$  have been prepared and their crystal structure is under investigation.

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