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$V_3P_5SiO_{19}$, a Vanadosilicophosphate Built Up from V_2O_9 Octahedra Clusters

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A new vanadium(III) silicophosphate $V_3P_5SiO_{19}$ has been isolated. Its structure was solved from a single-crystal study in the space group $P6_3$ and the parameters $a = 14.4671(11)$ Å, $c = 7.4605(2)$ Å, $Z = 4$. The three-dimensional framework of this oxide is built up from corner-sharing PO_4 tetrahedra, disilicate groups Si_2O_7 and octahedral V_2O_9 clusters. The vanadium clusters consist of two face-sharing octahedra. The relationships of this structure with that of the Mo(IV) silicophosphates $AMo_3P_{5.8}Si_2O_{25}$ are studied; it is shown that both structures are closely related to each other by the existence of tetrahedral units $P_6Si_2O_{25}$. The possibility of nonstoichiometry in the $V_3P_5SiO_{19}$ oxide is discussed.

Introduction

The consideration of oxides characterized by a mixed framework built up from octahedra and tetrahedra shows that phosphorus can participate to the edification of many structures, e.g., molybdenophosphates (*1–7*), phosphate tungsten bronzes (*8–17*), and vanadophosphates (*18–27*). On the other hand, the ability of silicon to form such networks seems to be more limited and depends on the nature of the ions in octahedral coordination: silicon forms some heteropolyanions with molybdenum (*28, 29*), but prefers tantalum and niobium for building three-dimensional networks as shown, for instance, for $Ba_3Nb_6Si_4O_{26}$, $K_6Nb_6Si_4O_{26}$, and different intergrowths of those oxides with the $A_3M_8O_{21}$ structure (*30–34*). The recent investigation of the systems A–P–Si–Mo has shown the possibility to synthesize oxides $AMo_3P_{5.8}Si_2O_{25}$ and $AM_3P_6Si_2O_{25}$ (*35*) for A = K, Rb, Tl whose host lattice is formed of PO_4 and SiO_4 tetrahedra and of MoO_6 octahedra. The participation of silicon to the three-dimensional mixed frameworks seems to be favored by the formation of tetrahedral units $Si_2P_6O_{25}$ in which the disilicate group shares its six corners with PO_4 tetrahedra, similar to those observed in $Si_3P_6Si_2O_{25}$ (*36*). To determine the role of such tetrahedral units in the stability of three-dimensional silicophosphate networks, the study of the system V–P–Si–O was undertaken. We describe here the structure of an original vanadosilicophosphate $V_3P_5SiO_{19}$ in which V(III) exhibits a distorted octahedral coordination.

Experimental

Synthesis. The synthesis of the vanadosilicophosphate $V_3P_5SiO_{19}$ in the form of

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microcrystalline powder was carried out in two steps using two different methods.

In the first method the oxides V_2O_5, SiO_2 and the phosphate $(NH_4)_2HPO_4$ were mixed in adequate proportions and heated at 773 K in air to eliminate ammonia and water. Then, in a second step metallic vanadium was added to the resulting products. The mixture was homogenized by crushing and introduced into a platinum crucible which was placed in an evacuated silica ampoule. The mixture was heated at 1273 K, then at 1473 K for 12 hr. The samples were quenched at room temperature.

In the second method, the oxides V_2O_5, SiO_2, the phosphate $(NH_4)_2HPO_4$, and metallic vanadium were mixed in stoichiometric ratios, and heated at 1073 K under purified argon for 24 hr. The resulting product was then introduced in a platinum crucible, placed in an evacuated silica ampoule, and heated at 1473 K for 12 hr. In both methods, a greenish scarcely sintered powder was obtained.

Single crystals were grown in the following way: mixtures of V_2O_5 and $(NH_4)_2HPO_4$ were first heated at 773 K in air as in the first method; the resulting mixture was mixed with metallic vanadium and heated directly in an evacuated silica ampoule, without adding SiO_2, at 1573 K. The crystals grew on the walls of the silica tube in the form of greenish plates.

Determination of the structure. A green crystal with dimensions 0.196 × 0.216 × 0.024 mm was selected for the structure determination. The Laue patterns showed hexagonal symmetry ($6/m$). The cell parameters, initially measured on precession films and later refined by diffractometric techniques at 21°C with a least-squares refinement based on 25 reflections are: $a = b = 14.4671(11)$ Å, $c = 7.4605(2)$ Å, $Z = 4$ formula units $V_3P_5SiO_{19}$.

TABLE I

Positional Parameters

Atom	x	y	z	B_{eq}[a]
V(1)	0.3450(1)	0.3210(1)	0.056136[b]	0.53(3)
V(2)	0.3393(1)	0.3248(1)	0.4445(2)	0.46(3)
P(1)	0.2119(1)	0.4334(1)	0.2492(5)	0.46(3)
P(2)	0.5163(1)	0.0961(1)	0.2608(4)	0.40(3)
P(3)	0.2334(1)	0.0841(1)	0.2505(5)	0.49(3)
P(4)	0	0	0.2911(6)	0.82(2)
Si(1)	$-\frac{1}{3}$	$\frac{1}{3}$	0.2177(4)	0.26(2)
Si(2)	$\frac{1}{3}$	$-\frac{1}{3}$	0.2975(4)	0.41(3)
O(1)	0.3043(3)	0.2070(3)	0.2510(12)	0.64(9)
O(2)	0.4599(3)	0.3974(3)	0.2532(13)	0.67(8)
O(3)	0.2664(3)	0.3654(3)	0.2452(11)	0.53(9)
O(4)	0.2449(7)	0.0415(6)	0.0741(12)	1.40(20)
O(5)	0.2475(6)	0.0319(6)	0.4169(10)	1.07(18)
O(6)	0.2672(6)	−0.1423(6)	0.0838(11)	1.10(17)
O(7)	0.2688(5)	−0.1571(5)	0.4231(10)	0.79(14)
O(8)	0.4587(6)	0.0742(5)	0.0866(13)	1.56(18)
O(9)	0.4489(5)	0.0504(4)	0.4227(10)	0.91(14)
O(10)	0.2449(3)	−0.3063(3)	0.2223(6)	0.54(8)
O(11)	−0.4227(3)	0.2194(3)	0.2975(7)	0.86(10)
O(12)	0	0	−0.0019(49)	6.20(23)
O(13)	0.1185(3)	0.0677(3)	0.2527(26)	3.20(18)
O(14)	$-\frac{1}{3}$	$\frac{1}{3}$	0.0080(15)	1.11(7)

[a] $B_{eq} = \frac{4}{3}\Sigma\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

[b] Value used to fix the cell origin.

The systematic absences led to $P6_3/m$ or $P6_3$ space groups. The structure refinement could only be performed in the non centrosymmetric group $P6_3$. The data were collected on a CAD 4 Enraf-Nonius diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities were measured up to $\theta = 45°$ with a ω–θ scan of $(1 + 0.35 \text{ tg } \theta)°$ and a counter slit aperture of $(1 + \text{tg } \theta)$ mm, all determined after a study of some reflections in the $\omega\theta$ plane. The background intensity was measured on both sides of each reflection. A periodic control of three reflections verified the stability of the sample. The 2837 reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization effect; absorption corrections were performed with the program AGNOST (*37*).

Atomic coordinates of the vanadium atoms and of the corresponding coordinating oxygen atoms were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and

TABLE II

ANISOTROPIC THERMAL PARAMETERS

$F_J = F_{J0} * \exp(-(\beta_{11} * h^2 + \beta_{22} * k^2 + \beta_{33} * l^2 + 2 * \beta_{12} * h * k + 2 * \beta_{13} * h * l + 2 * \beta_{23} * k * l))$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V(1)	0.00099(6)	0.00106(7)	0.00205(17)	0.00068(5)	0.00006(9)	0.00000(10)
V(2)	0.00091(6)	0.00089(6)	0.00140(15)	0.00052(5)	−0.00028(9)	−0.00007(9)
P(1)	0.00055(5)	0.00070(5)	0.00267(19)	0.00031(5)	0.00016(20)	−0.00058(19)
P(2)	0.00060(5)	0.00057(5)	0.00182(23)	0.00021(5)	0.00028(15)	0.00013(14)
P(3)	0.00059(5)	0.00059(5)	0.00311(21)	0.00026(5)	−0.00030(20)	0.00055(19)
P(4)	0.00057(6)	0.00057(6)	0.00786(8)	0.00029(6)	0.00000(0)	0.00000(0)
Si(1)	0.00043(7)	0.00043(7)	0.00115(0)	0.00022(7)	0.00000(0)	0.00000(0)
Si(2)	0.00096(8)	0.00096(8)	0.00009(36)	0.00048(8)	0.00000(0)	0.00000(0)
O(1)	0.00119(17)	0.00091(16)	0.00263(53)	0.00049(14)	0.00000(0)	0.00000(0)
O(2)	0.00075(16)	0.00089(16)	0.00299(53)	0.00003(13)	0.00015(60)	−0.00013(60)
O(3)	0.00111(17)	0.00103(16)	0.00202(60)	0.00079(15)	−0.00135(48)	−0.00121(48)
O(4)	0.00320(42)	0.00190(34)	0.00660(120)	0.00184(32)	−0.00115(59)	−0.00193(55)
O(5)	0.00378(46)	0.00119(29)	0.00059(73)	0.00128(31)	−0.00024(47)	0.00052(38)
O(6)	0.00171(32)	0.00178(32)	0.00483(111)	0.00083(26)	0.00093(45)	0.00101(44)
O(7)	0.00152(28)	0.00133(26)	0.00351(93)	0.00094(22)	−0.00151(40)	−0.00175(39)
O(8)	0.00198(32)	0.00160(32)	0.01159(141)	0.00106(28)	−0.00260(56)	−0.00108(57)
O(9)	0.00155(27)	0.00138(29)	0.00281(84)	0.00042(23)	0.00183(37)	0.00131(37)
O(10)	0.00107(18)	0.00093(17)	0.00212(0)	0.00063(15)	−0.00109(26)	−0.00105(25)
O(11)	0.00149(22)	0.00088(19)	0.00333(61)	0.00019(17)	0.00113(30)	0.00013(29)
O(12)	0.01387(82)	0.01387(82)	0.00534(0)	0.00694(82)	0.00000(0)	0.00000(0)
O(13)	0.00031(18)	0.00125(21)	0.3816(204)	0.00023(16)	0.00201(136)	−0.00132(148)
O(14)	0.00200(25)	0.00200(25)	0.00372(0)	0.00100(25)	0.00000(0)	0.00000(0)

their isotropic thermal motion by full matrix least squares and a linear weighting scheme $\omega = f(\sin \theta/\lambda)$ adjusted using the program POND of LECLAIRE (*38*) led to $R = 0.063$ and $R_\omega = 0.056$. Refinement including anisotropical thermal motion led to $R = 0.047$ and $R_\omega = 0.042$ but some of the β_{ij} of 3 oxygen atoms had no physical signification; refinements were repeated by fixing the non physical β_{ij} to their initial values deduced from the isotropical B using the method previously described by Catti *et al.* (*39*). This refinement led to $R = 0.047$ and $R_\omega = 0.042$ and to the atomic parameters of Table I and temperature factors of Table II. Scattering factors for V, O, P, and Si were taken from the "International Tables for X-ray Crystallography" (*40*) corrected for anomalous dispersion. Important distances and angles may be found in Table III.

Description of the Structure and Discussion

The three-dimensional view of the structure (Fig. 1) shows that the framework of the oxide $V_3P_5SiO_{19}$ can be described as being formed of PO_4 tetrahedra, disilicate groups Si_2O_7, and pairs of face-sharing VO_6 octahedra forming V_2O_9 units.

For P(1), P(2), and P(3) each PO_4 tetrahedron shares three corners with three different V_2O_9 units, and the fourth one with a Si_2O_7 group (Fig. 2) for P(1) and P(2) and with another PO_4 tetrahedron for P(3). With O–O distances ranging from 2.40 to 2.56 Å (Table II), the PO_4 tetrahedra appear as rather regular. However, the examination of the P–O distances and O–P–O angles shows that the phosphorus atom is slightly off centered in its tetrahedron, namely,

TABLE III

Distances (Å) and angles (°)[a]

V(1)	O(1)	O(2)	O(3)	O(5^{i})	O(7^{i})	O(9^{i})
O(1)	2.052(7)	2.541(4)	2.610(7)	2.992(11)	2.882(11)	3.916(9)
O(2)	76.0(2)°	2.076(7)	2.600(6)	3.977(11)	2.975(11)	2.844(11)
O(3)	77.8(2)°	76.9(2)°	2.104(7)	2.863(10)	4.035(11)	2.932(10)
O(5^{i})	97.4(3)°	166.6(3)°	90.3(3)°	1.929(10)	2.901(13)	2.789(13)
O(7^{i})	92.1(3)°	95.2(3)°	168.4(3)°	96.8(3)°	1.952(8)	2.825(8)
O(9^{i})	166.3(3)°	91.4(3)°	94.2(3)°	93.7(3)°	94.6(3)°	1.892(7)
V(2)	O(1)	O(2)	O(3)	O(4^{ii})	O(6^{ii})	O(8^{ii})
O(1)	2.093(7)	2.541(4)	2.610(6)	3.007(12)	2.813(12)	4.080(12)
O(2)	74.9(2)°	2.085(7)	2.600(6)	4.022(12)	2.964(11)	3.021(12)
O(3)	77.6(2)°	77.4(2)°	2.071(7)	2.881(11)	3.953(10)	2.987(12)
O(4^{ii})	95.6(3)°	166.3(3)°	91.0(3)°	1.966(11)	2.835(14)	2.886(13)
O(6^{ii})	89.2(3)°	95.7(3)°	166.3(3)°	94.0(4)°	1.911(8)	2.968(8)
O(8^{ii})	168.1(3)°	95.1(3)°	94.1(3)°	93.1(4)°	98.4(3)°	2.009(8)
P(1)	O(3)	O(6^{iii})	O(7^{iii})	O(10^{iii})		
O(3)	1.537(5)	2.495(9)	2.532(9)	2.455(7)		
O(6^{iii})	109.4(4)°	1.519(8)	2.542(11)	2.456(10)		
O(7^{iii})	113.2(4)°	114.9(4)°	1.496(8)	2.504(9)		
O(10^{iii})	104.2(2)°	105.1(4)°	109.2(4)°	1.575(5)		
P(2)	O(2^{iv})	O(8)	O(9)	O(11^{v})		
O(2^{iv})	1.551(3)	2.503(10)	2.487(9)	2.494(7)		
O(8)	110.8(5)°	1.490(9)	2.525(12)	2.496(8)		
O(9)	110.1(5)°	116.2(4)°	1.484(7)	2.400(7)		
O(11^{v})	106.2(3)°	109.3(3)°	103.6(3)°	1.569(9)		
P(3)	O(1)	O(4)	O(5)	O(13)		
O(1)	1.546(3)	2.481(10)	2.558(9)	2.423(4)		
O(4)	109.2(4)°	1.497(10)	2.562(11)	2.441(15)		
O(5)	113.1(4)°	116.3(5)°	1.520(9)	2.494(14)		
O(14)	102.7(3)°	106.1(7)°	108.3(7)°	1.557(5)		
P(4)	O(12^{i})	O(13)	O(13^{iii})	O(13^{vi})		
O(12^{i})	1.54(4)	2.36(3)	2.36(3)	2.36(3)		
O(13)	100.9(7)°	1.517(5)	2.580(6)	2.580(6)		
O(13^{iii})	100.9(7)°	116.5(4)	1.517(5)	2.580(6)		
O(13^{vi})	100.9(7)°	116.5(4)°	116.5(4)°	1.517(5)		
Si(1)	O(11)	O(11^{vii})	O(11^{viii})	O(14)		
O(11)	1.616(4)	2.603(6)	2.603(6)	2.631(10)		
O(11^{vii})	107.2(3)°	1.616(4)	2.603(6)	2.631(10)		
O(11^{viii})	107.2(3)°	107.2(3)°	1.614(4)	2.631(10)		
O(14)	111.6(2)°	111.6(2)°	111.6(2)°	1.564(11)		
Si(2)	O(10)	O(10^{ix})	O(10^{x})	O(14^{xi})		
O(10)	1.615(5)	2.623(7)	2.623(7)	2.614(10)		
O(10^{ix})	108.6(2)°	1.615(5)	2.623(7)	2.614(10)		
O(10^{x})	108.6(2)°	108.6(2)°	1.615(5)	2.614(10)		
O(14^{xi})	110.3(2)	110.3(2)	110.3(2)	1.570(11)		

[a] The diagonal indicates the X–O bond length (Å). The values above the diagonal are the O---O lengths (Å) and the values below are the O–X–O angles (°).

SYMMETRY CODE

i	$x - y$	x	$z - 0.5$
ii	$x - y$	x	$z + 0.5$
iii	$-y$	$x - y$	z
iv	$1 - y$	$x - y$	z
v	$1 + x$	y	z
vi	$y - x$	$-x$	z
vii	$-y$	$1 + x - y$	z
viii	$y - x - 1$	$-x$	z
ix	$-y$	$x - y - 1$	z
x	$1 + y - x$	$-x$	z
xi	$-x$	$-y$	$z + 0.5$

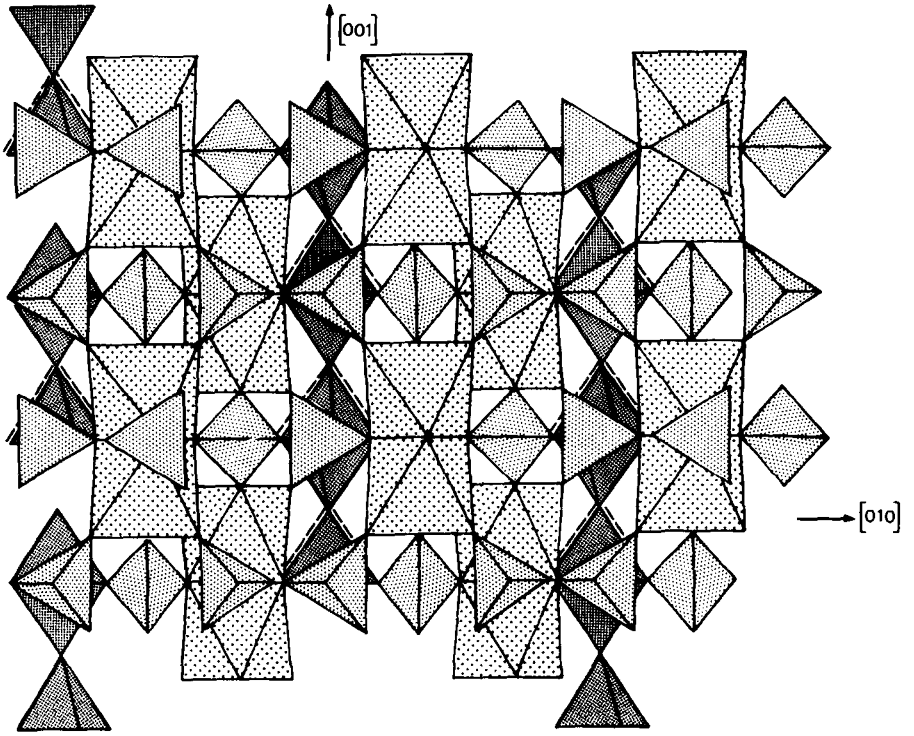

FIG. 1. Idealized projection of the structure along |120|. ∴, VO_6 or MoO_6 octahedra; ⁖, PO_4 tetrahedra; ▦, SiO_4 tetrahedra.

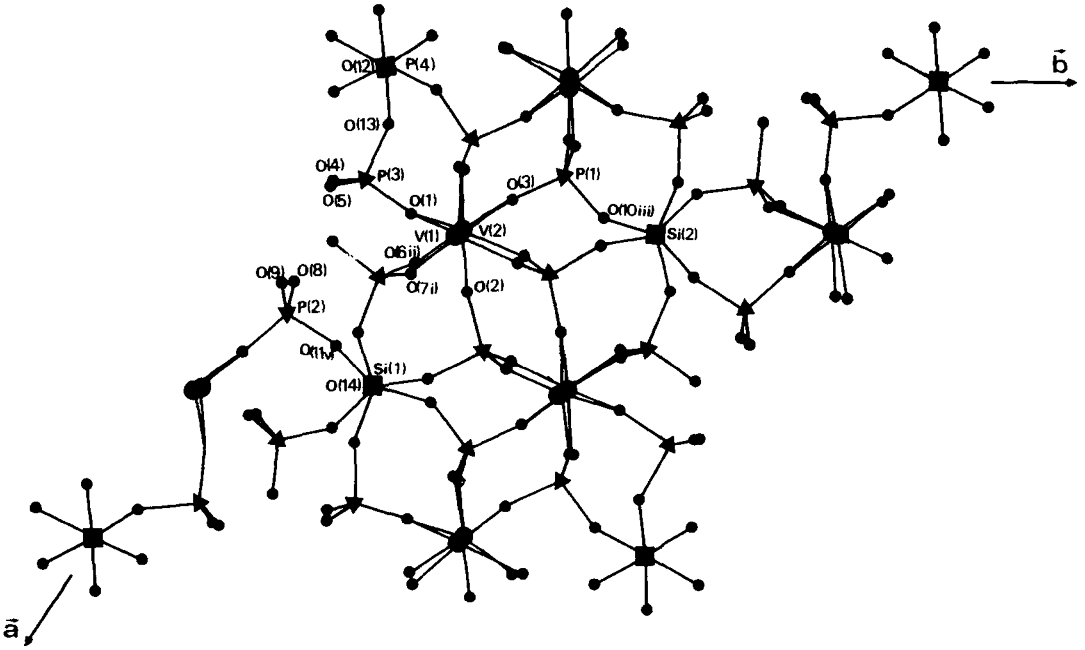

FIG. 2. Projection of the structure on to the (*ab*) plane.

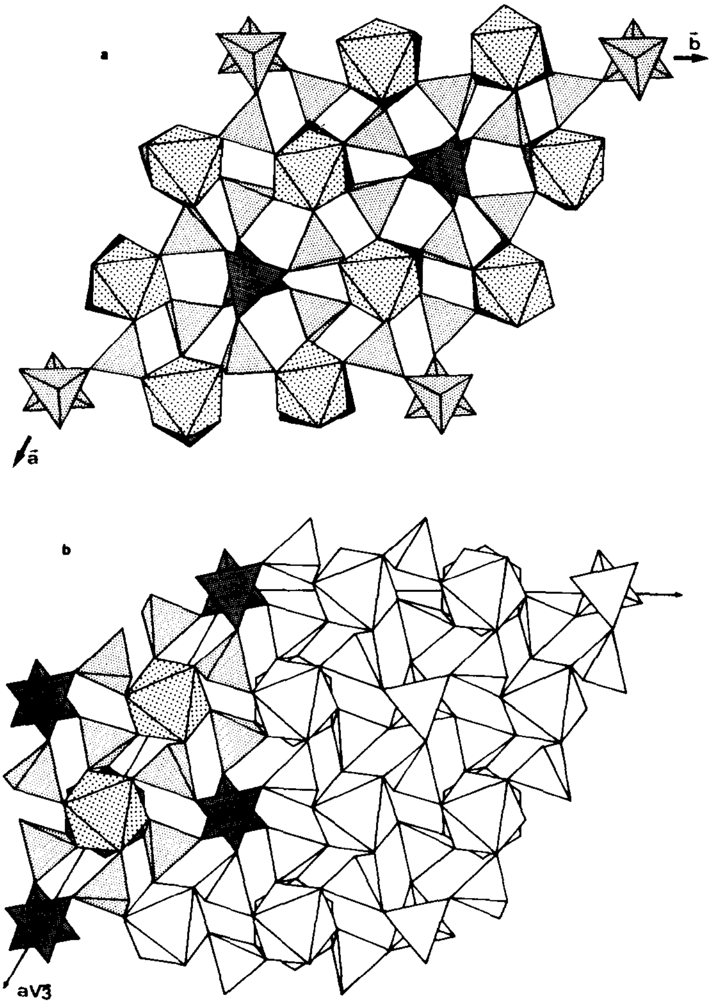

FIG. 3. Framework of (a) $V_3P_5SiO_{19}$ and (b) $RbMo_3P_{5.8}Si_2O_{25}$ seen along *c*. (only the polyhedra of the unit cell are shaded with the same shading as in Fig. 1).

0.090, 0.086, and 0.095 Å for P(1), P(2), and P(3), respectively. The distribution of the P–O distances in each tetrahedron is in agreement with the nature of the polyhedra linked to the PO_4 tetrahedra. The longest P–O distance is observed for the oxygen atom common to the PO_4 and SiO_4 tetrahedra. If one considers the P–O–V bonds, one observes that the two P–O distances which correspond to the oxygen atoms common to one PO_4 tetrahedron and one VO_6 octahedron are close to each other (1.484 to 1.52 Å) and shorter than the P–O distance which corresponds to the oxygen atom common to one PO_4 tetrahedron and two VO_6 octahedra (1.537 to 1.551 Å) in agreement with the theory developed by Brown and Wu (*41*).

The P(4) atom exhibits a rather dissymetric tetrahedron with three very short O–O distances (2.36 Å) and three normal O–O distances (2.58 Å). The P–O distance which corresponds to the free oxygen atom seems to be longer than the three other distances;

however, the low accuracy on this particular distance shows that this difference cannot be considered as significant.

The SiO_4 tetrahedra are almost regular: O–O distances are close to 2.60 Å, and O–Si–O angles are close to the ideal value 109°. The examination of the Si–O distances shows that the silicon atom is displaced towards the bridging oxygen of the disilicate group. This type of displacement of the silicon atoms has often been observed in disilicate groups.

The angles P–O–P or Si–O–P involving an oxygen atom bridging two tetrahedra range from 134.9(2) to 151.1(4)°.

The O–O distances, ranging from 2.54 to 3.00 Å, show that the VO_6 octahedra are strongly distorted owing to their connection through their faces. For the same reason, the vanadium ions exhibit three short V–O distances (mean value 1.94 Å) and three longer ones (mean value 2.08 Å). Although the vanadium ions are off-centered by about 0.22 Å in their octahedra, mainly along the *c* direction, the V–V distances in the V_2O_9 clusters remain rather short, close to 2.90 Å.

The projection of the structure on to the (001) plane (Fig. 3a) shows that it is closely related to the framework of $AMo_3P_{5.8}Si_2O_{25}$ (Fig. 3b) previously described (*28*). Both frameworks exhibit tetrahedral units $P_6Si_2O_{25}$ which form columns running along the |001| direction. These tetrahedral units are both characterized by a Si_2O_7 group but differ from each other by the relative orientation of the PO_4 tetrahedra owing to the fact that the disilicate group exhibits a semi-eclipsed configuration in $V_3P_5SiO_{19}$ (Fig. 3a) and a staggered configuration in $AMo_3P_{5.8}Si_2O_{25}$ (Fig. 3b). In the two structures the VO_6 and MoO_6 octahedra have their ternary axis parallel to *c* and form with the PO_4 tetrahedral files parallel to this latter direction (Fig. 4). These tetrahedral units are linked to each other through MoO_6 and VO_6 octahedra whose ternary axis is parallel to *c*. Each MoO_6 octahedron is replaced by two face-sharing VO_6 octahedra. It results that the infinite files $|V_2P_3O_{15}|_\infty$ (Figs. 4a,b) in $V_3P_5SiO_{19}$ are substituted by the strings $|MoP_2O_{15}|_3$ in $AMo_3P_{5.8}Si_2O_{25}$ (Fig. 4c) along **c**. The relative positions of the tetrahedral columns and of the octahedral files are similar in the two structures (Fig.

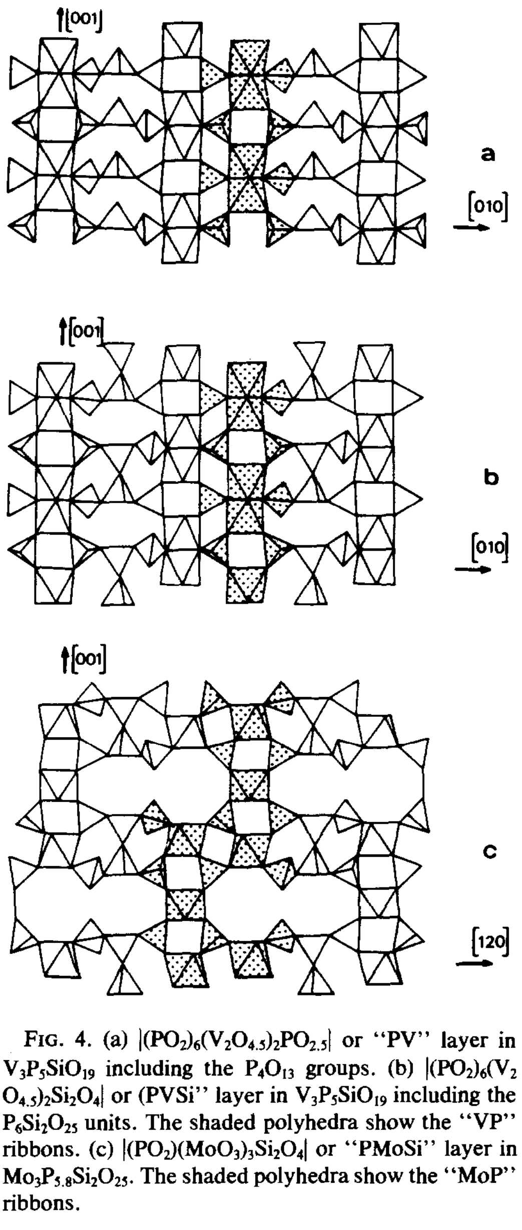

FIG. 4. (a) $|(PO_2)_6(V_2O_{4.5})_2PO_{2.5}|$ or "PV" layer in $V_3P_5SiO_{19}$ including the P_4O_{13} groups. (b) $|(PO_2)_6(V_2O_{4.5})_2Si_2O_4|$ or (PVSi" layer in $V_3P_5SiO_{19}$ including the $P_6Si_2O_{25}$ units. The shaded polyhedra show the "VP" ribbons. (c) $|(PO_2)(MoO_3)_3Si_2O_4|$ or "PMoSi" layer in $Mo_3P_{5.8}Si_2O_{25}$. The shaded polyhedra show the "MoP" ribbons.

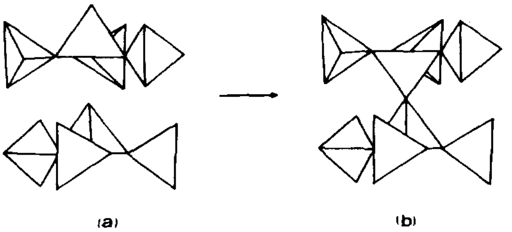

FIG. 5. (a) P_4O_{13} unit in $V_3P_5SiO_{19}$. (b) P_8O_{25} obtained from the condensation of two P_4O_{13} units.

3) in agreement with the parametric relation: $a_{V_3P_5SiO_{19}} \simeq a_{AMo_3P_{5.8}Si_2O_{25}} \cdot \sqrt{3}$. The vanadosilicophosphate differs from the molybdosilicophosphate by the existence of P_4O_{13} units built up from four corner-sharing PO_4 tetrahedra. The geometry of these tetrahedral units (Fig. 5a) is very similar to that of the $P_6Si_2O_{25}$ units. The condensation of two P_4O_{13} units would lead to a P_8O_{25} unit with an identical configuration to $P_6Si_2O_{25}$. Moreover, the stacking of the P_4O_{13} units along *c* (Fig. 5a) shows that the very simple migration of one central phosphorus atom out of two in the file would lead to the formation of the P_8O_{25} unit (Fig. 5b). Thus, it appears, that the possibility of replacement of the central phosphorus atom in the P_4O_{13} unit by silicon should allow the formation of $P_6Si_2O_{25}$ units in those positions, and would lead to the hypothetical compound $V_{12}P_{18}Si_6O_{75}$. In such a structure, all the tetrahedral columns would be identical. As a result, the "*a*" parameter could be similar and close to that of $AMo_3P_{5.8}Si_2O_{25}$.

The similarity of this structure with the $Mo_3P_{5.8}Si_2O_{25}$ framework can also be shown by considering the layers of polyhedra perpendicular to |100|. The $V_3P_5SiO_{19}$ structure can be described by the stacking along |100|* of two types of layers: the "PVSi" layers which can be formulated: $|(PO_2)_6(V_2O_{4.5})_2Si_2O_4|_\infty$ (Fig. 4b) built up from corner-sharing PO_4 tetrahedra, Si_2O_7 groups and V_2O_9 clusters, and the "PV" layers, formulated: $|(PO_2)_6(V_2O_{4.5})_2PO_{2.5}|_\infty$ (Fig. 4a) built up from corner-sharing PO_4 tetrahedra and V_2O_9 clusters. These layers are stacked along |100|* according to the sequence $(PVSi)_2$–PV. The framework of $AMo_3P_{5.8}Si_2O_{25}$ is described by the stacking along |100| of only one type of layers, called "PMoSi" layers, formulated $|(PO_2)_6(MoO_3)_3Si_2O_4|_\infty$ (Fig. 4c).

Both are formed of columns built up from Si_2O_7 groups and PO_4 tetrahedra running along [001], and of mixed strings containing VO_6 or MoO_6 octahedra and PO_4 tetrahedra running along the same directions. However, one observes infinite ribbons (shaded polyhedra in Fig. 4b), ribbons characterized by V_2O_9 clusters in the "VPSi" layers whereas zigzag chains (shaded polyhedra in Fig. 4c) built up from angle MoO_6 octahedra and PO_5 tetrahedra are observed in the "MoPSi" layers.

The comparison of the "PVSi" layers with the crystal structure of the V(IV) phosphate $VOHPO_4$, $0.5H_2O$ (Fig. 6) shows a great similarity with this structure. Both oxides exhibit "V_2O_9" clusters formed of face-sharing VO_6 octahedra; moreover one observes identical connection of these clusters with PO_4 tetrahedra characterized by oxygen atoms common to three polyhedra in both oxides. It results that the extension of the $|(V_2O_{4.5})_2(PO_2)_2|_\infty$ ribbons in the (001) plane leads to the $VOHPO_4$,$0.5H_2O$ struc-

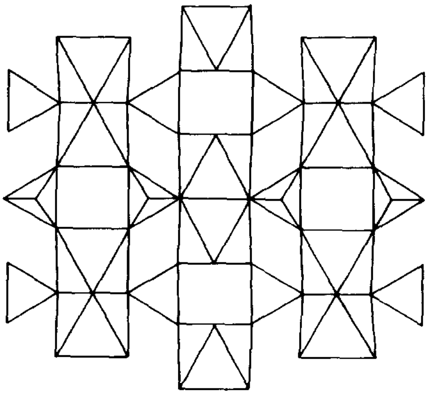

FIG. 6. $VOHPO_4$, $0.5H_2O$ structure.

ture. This ability of three polyhedra to share the same oxygen atom appears as a feature characteristic of vanadophosphates such as γ-$VOPO_4$ and $(VO)_2P_2O_7$ (*26–27*). However, these latter structures differ from those of $V_3P_5SiO_{19}$ by the fact that the VO_6 octahedra share their edges instead of their faces.

The structural analysis of the vanadosilicophosphate $V_3P_5SiO_{19}$ shows that this structure offers the possibility of a rather wide nonstoichiometry range. A defect of oxygen could be introduced by substitution of silicon for phosphorus leading to the hypothetical limit $V_{12}P_{18}Si_6O_{75}$ whose framework would only be built of $P_6Si_2O_{25}$ units. In the same way an excess of oxygen could be introduced by replacement of silicon by phosphorus leading to the hypothetical limit $V_6P_{12}O_{39}$. However, it is worth noting that no oxide belonging to this structural type was isolated in the V–P–O system. Nevertheless, the possibility of formation of vanadosilicophosphates $V_6P_{12-x}Si_xO_{39}$ should be considered.

The presence in the V_2O_9 clusters of vanadium(III) characterized by a d^2 configuration lets us think that this oxide should exhibit interesting magnetic properties.

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