A Vanadium(IV) Diphosphate with an Intersecting Tunnel Structure, PbVOP$_2$O$_7$

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

A novel lead vanadophosphate, PbVOP$_2$O$_7$, has been synthesized. This phase crystallizes in the *Pnma* space group with $a = 8.899(1)$ Å, $b = 7.534(1)$ Å, and $c = 9.142(1)$ Å. The $[VP_2O_8]_\infty$ framework consists of ReO$_3$-type $[VO_3]_\infty$ chains running along $\vec{b}$, interconnected through P$_2$O$_7$ groups forming large intersecting tunnels running along $\vec{b}$, $\vec{a}$, and $\vec{c}$, respectively, where the Pb^{2+} cations are located. This is the second lead vanadophosphate, beside Pb(VO)$_3$(P$_2$O$_7$)$_2$, that consists of $[VO_3]_\infty$ chains interconnected by P$_2$O$_7$ groups.   © 2001 Elsevier Science

Previous studies of lead vanadophosphates have shown the great ability of these compounds to display isolated phosphate groups. This is the case with the monophosphate hydrates Pb(VOPO$_4$)$_2$·4H$_2$O which exhibit different forms of layered structures (1, 2), with the hydroxide monophosphate Pb(OH)V(HPO$_4$)$_2$ (3), and with several anhydrous monophosphates Pb$_3$(VO$_{4-x}$P$_x$)O$_4$ (4), PVO$_2$PO$_4$ (5), Pb(VO)$_2$(PO$_4$)$_2$ (6), and Pb$_2$V$_2$VO(PO$_4$)$_4$ (7). In contrast, only two lead vanadodiphosphates are actually known, PbV$_2$(P$_2$O$_7$)$_2$ (8) and Pb(VO)$_3$(P$_2$O$_7$)$_2$ (9). This study is devoted to the crystal growth and the structure determination of a novel vanadium(IV) diphosphate, PbVOP$_2$O$_7$, built up of octahedral $[VO_3]_\infty$ chains interconnected through P$_2$O$_7$ group, forming intersecting tunnels.

CRYSTAL GROWTH

Single crystals of the title compound were grown from a mixture of nominal composition Pb$_2$V$_2$P$_4$O$_{15}$. First PbCO$_3$, H(NH$_4$)$_2$PO$_4$, and V$_2$O$_3$ were mixed in an agate mortar in the ratio 2 : 4 : 1 and heated at 600 K in a platinum crucible to decompose the ammonium phosphate and the carbonate. In a second step the resulting mixture was crushed in an agate mortar and sealed in evacuated silica ampoules, and then heated for 1 day at 773 K cooled at 2 K per hour to 573 K, and finally quenched to room temperature.

Green-blue crystals were extracted from the resulting product. Microprobe analysis of these crystals leads to the "PbVP$_2$" formulation. Many attempts to prepare large amounts of the phase in the form of powder always failed, the yield being less than 10%.

SINGLE CRYSTAL X-RAY DIFFRACTION

A green-blue eight-sided prismatic crystal with dimension of $0.066 \times 0.038 \times 0.034$ mm^3 was selected for the X-ray structure determination. The quality of the crystal was checked by film techniques with a Weissenberg camera. The cell parameters (Table 1) were determined with a least-squares method using the θ and $-\theta$ measured values of 25 reflections carefully centered and with $18° < |\theta| < 22°$.

The data were recorded at room temperature on an Enraf-Nonius CAD-4 diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) isolated with a graphite monochromator. The stability of the X-ray intensity and of the crystal was checked by monitoring three standard reflections every hour. No significant deviations in intensities were observed. The intensity data were corrected for Lorentz, polarization, absorption, and secondary extinction effects. The systematic absences $k + l = 2n + 1$ in $0kl$ and $h = 2n + 1$ in $hk0$ are consistent with the *Pnma* (62) or the *Pn*2$_1$*a* (other setting of the *Pna*2$_1$ (33)) space groups. The Harker line 0V0 observed on the Patterson function is characteristic of the centrosymmetric space group *Pnma*.

The structure was solved with the heavy atom method and subsequent Fourier and difference synthesis. Full-matrix least-squares refinements of the atomic parameters were performed on the F values using a SPARC Station with the Xtal 3.4 system (10) which led to $R = 0.039$ and $R_W = 0.035$ and the atomic parameters listed in Table 2. In the unit cell four vanadium atoms are distributed at random over eight sites. All these positions are only half occupied because the two nearest positions related by a symmetry center are distant by only 0.529(5) Å and are located inside the oxygen octahedron above and under the equatorial plane of the latter.

TABLE 1
Summary of Crystal Data, Intensity Measurement, and Structure Refinement for PbVOP$_2$O$_7$

Chemical formula	PbVP$_2$O$_8$
Molecular weight	448.084 Da
Crystal system	Orthorhombic
Space group	*Pnma* (62)
Cell dimensions	$a = 8.8989(7)$ Å
	$b = 7.5341(7)$ Å
	$c = 9.1420(8)$ Å
Cell volume	612.93(9) Å^3
Z	4
Density	4.856
μ, mm^{-1}	29.48
Secondary extinction	0.14(2)
Measured reflections	2870
Reflections with $I > 3\sigma(I)$	730
Temperature of the data collections	21°C
$R (F_o)$	0.039
R_W	0.035

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The projections of the structure of PbVOP$_2$O$_7$, along $\vec{b}$ (Fig. 1) and along $\vec{a}$ (Fig. 2), show that the framework [VP$_2$O$_8$]$_\infty$ is remarkably simple: it consists of VO$_6$ octahedra and diphosphate groups sharing their apices, in such a way that large tunnels are formed running along $\vec{b}$ and $\vec{a}$, respectively. In fact, the entire [VP$_2$O$_8$]$_\infty$ framework can be described by the assemblage of ReO$_3$-type chains [VO$_3$]$_\infty$, with rows of P$_2$O$_7$ groups running along

TABLE 2
Atomic Positional, Isotropic Displacement, and Site Occupation Parameters

	x/a	y/b	z/c	U	PP
Pb(1)	0.06393(8)	$\frac{1}{4}$	0.09732(8)	*0.0114(2)	
V(1)	0.5000(8)	0.4654(5)	−0.0046(8)	*0.0049(9)	0.5000
P(1)	0.2793(3)	0.5519(4)	0.2769(3)	*0.0076(8)	
O(1)	0.504(1)	$\frac{1}{4}$	−0.036(1)	*0.014(3)	
O(2)	0.6375(8)	0.463(1)	0.1693(8)	*0.007(2)	
O(3)	0.3240(8)	0.460(1)	0.1335(7)	*0.007(2)	
O(4)	0.232(1)	$\frac{3}{4}$	0.228(1)	*0.007(3)	
O(5)	0.4023(8)	0.556(1)	0.3890(9)	0.012(2)	

Anisotropic Displacement Parameters

	U_{11}	U_{22}	U_{33}	U_{13}	U_{13}	U_{23}
Pb(1)	0.0133(3)	0.0125(3)	0.0085(2)	0	0.0002(4)	0
V(1)	0.008(1)	0.005(2)	0.002(1)	0.000(3)	0.001(1)	−0.000(3)
P(1)	0.006(1)	0.008(1)	0.009(1)	−0.000(1)	−0.001(1)	−0.000(1)
O(1)	0.015(6)	0.015(6)	0.010(6)	0	−0.001(5)	0
O(2)	0.008(4)	0.007(4)	0.007(4)	−0.003(3)	−0.003(3)	−0.003(3)
O(3)	0.008(3)	0.010(4)	0.005(3)	−0.000(3)	0.000(3)	−0.000(3)
O(4)	0.010(5)	0.005(5)	0.007(5)	0	0.004(5)	0
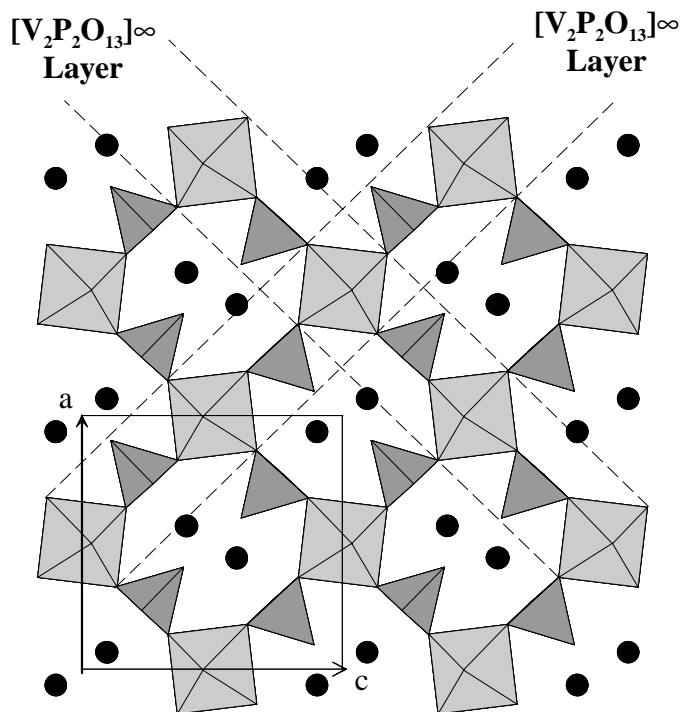
FIG. 1. Projection along $\vec{b}$ of the PbVOP$_2$O$_7$ structure showing the connection between the [VO$_3$]$_\infty$ chains and the P$_2$O$_7$ groups, which delimit large tunnels running along $\vec{b}$.

$\vec{b}$ (Fig. 2). Each P$_2$O$_7$ group interconnects two successive [VO$_3$]$_\infty$ chains along [101] or [10$\bar{1}$], sharing four of its corners with four VO$_6$ octahedra, so that its two remaining apices are free and oriented toward the center of the [010] tunnel (Fig. 1). In fact, this structure is pseudotetragonal and can be described as built up from 90° oriented intersecting
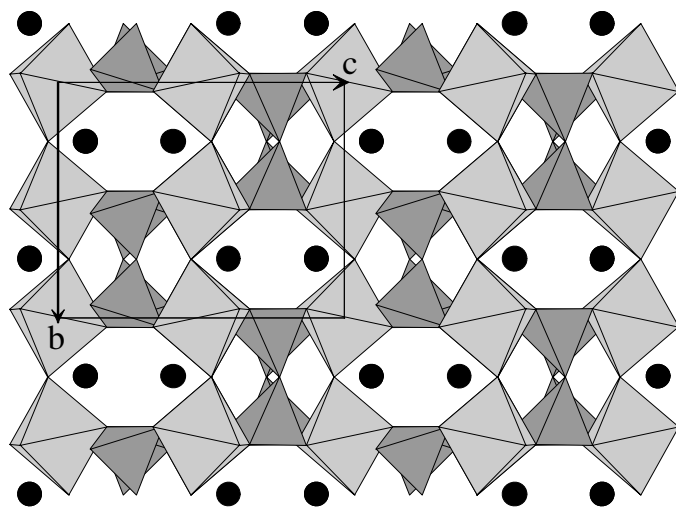

FIG. 2. Projection along $\vec{a}$ of the PVOP$_2$O$_7$ structure showing the second kind of tunnels.
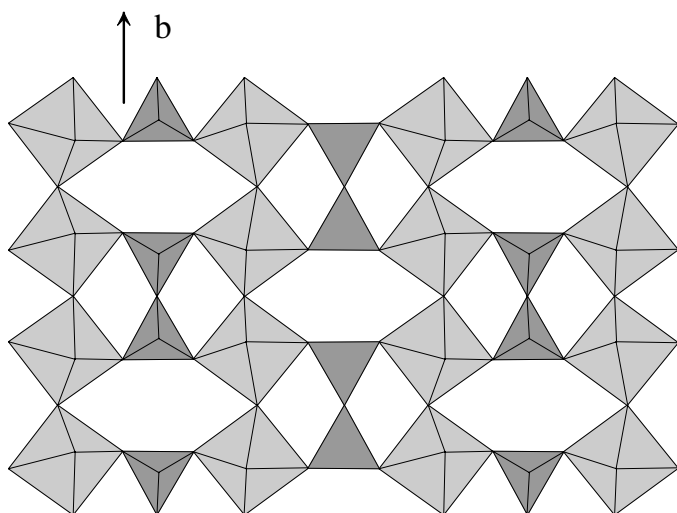
FIG. 3. The $[V_2P_2O_{13}]_\infty$ layer parallel to the (101) crystallographic plane.

$[V_2P_2O_{13}]_\infty$ layers (Fig. 1). In such (101) or (10$\bar{1}$) layers (Fig. 3) the $[VO_3]_\infty$ chains and the rows of P_2O_7 groups form six-sided windows built up of four VO_6 octahedra and two P_2O_7 groups. Note that two successive rows of P_2O_7 groups are shifted by $\vec{b}/2$ with respect to each other in order to allow a better accommodation of the P_2O_7 groups to each $[VO_3]_\infty$ chain. Moreover, the free apices of the P_2O_7 groups of two successive rows are in trans positions with respect to each other, considering the plane of the layer (Figs. 1 and 3).

One original feature of this structure concerns the geometry of the $[VO_3]_\infty$ chains. The VO_6 octahedra exhibit a geometry characteristic of V(IV), with one short vanadyl bond (1.649 Å) opposed to a very long one (2.177 Å) along $\vec{b}$, whereas the four V–O bonds of the basal plane are intermediate, ranging from 2.01 Å to 2.04 Å as shown from the list of interatomic distances (Table 3). The dissymetry of the O–V–O bond along $\vec{b}$ explains the splitting of the vanadium sites along the direction with a half occupancy. These results show that the structure consists of two types of $[VO_3]_\infty$ chains which differ only by the orientation of their vanadyl ions which are oriented at 180° with respect to each other. Thus in the present structure, like in ferroelectrics, we consider that $[VO_3]_\infty$ chains with "up" displacement of vanadium alternate statistically with $[VO_3]_\infty$ chains with "down" displacement of vanadium, so that the possibility to generate structures in which all the vanadium atoms are displaced in the same direction should be considered. A second important feature deals with the tilting of the VO_6 octahedra in each $[VO_3]_\infty$ chain which allows the P_2O_7 groups to be more easily accommodated by the chain.

The eclipsed configuration of the diphosphate groups is rather classical (Table 3): each PO_4 tetrahedron exhibits one longer P–O bond (1.612 Å) corresponding to the bridging

TABLE 3
Bond Distances in PbVOP$_2$O$_7$

Pb(1)–O(3)	2.825(7)
Pb(1)–O(5^{III})	2.418(8)
Pb(1)–O(2^V)	2.748(7)
Pb(1)–O(5^V)	2.722(7)
Pb(1)–O(2^{II})	2.748(7)
Pb(1)–O(5^{II})	2.722(7)
Pb(1)–O(5^{IV})	2.418(8)
Pb(1)–O(3^{VI})	2.825(7)
V(1)–O(1)	1.649(4)
V(1)–O(2)	2.01(1)
V(1)–O(3)	2.01(1)
V(1)–O(1^I)	2.177(4)
V(1)–V(1^I)	0.529(5)
V(1)–O(2^I)	2.01(1)
V(1)–O(3^I)	2.04(1)
P(1)–O(3)	1.533(7)
P(1)–O(4)	1.612(5)
P(1)–O(5)	1.500(8)
P(1)–O(2^{II})	1.511(8)

Symmetry codes. I: $1-x$; $1-y$; $-z$. II: $-\frac{1}{2}+x$; y; $\frac{1}{2}-z$. III: $\frac{1}{2}-x$; $-\frac{1}{2}+y$; $-\frac{1}{2}+z$. IV: $\frac{1}{2}-x$; $-y$; $-\frac{1}{2}+z$. V: $-\frac{1}{2}+x$; $\frac{1}{2}-y$; $\frac{1}{2}-z$. VI: x; $\frac{1}{2}-y$; z.

oxygen between two phosphorus atoms, a shortest one (1.500 Å) corresponding to its free apex, and two intermediate bonds (1.511–1.533 Å) corresponding to P–O–V bonds.

The lead cations are located at the intersection of the tunnels, showing an eight-fold coordination (Table 3, Fig. 4)
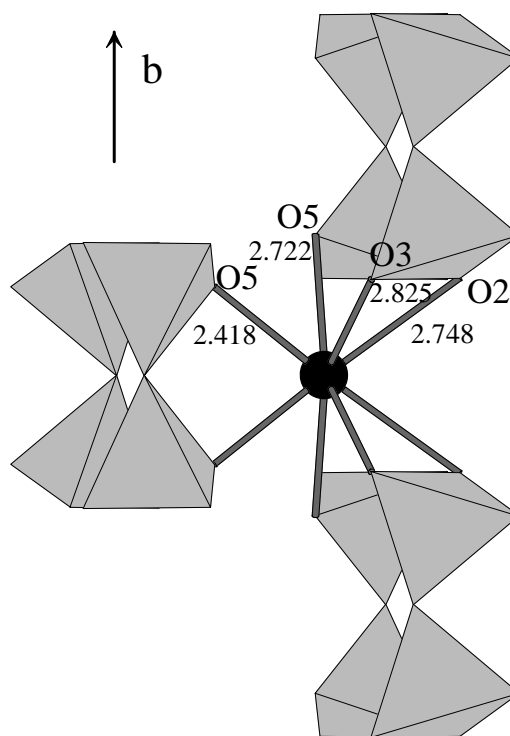

FIG. 4. The surrounding of the Pb ions.

TABLE 4
Electrostatic Bond Valence Distribution in PbVOP$_2$O$_7$

	V	P	Pb	$\sum u$
O1	1.442			1.787
	0.345			
O2	0.537^a	1.323	0.179	2.044
	0.548		0.179	
O3	0.504^a	1.248	0.146	1.915
	0.539		0.146	
O4		1.00814, 1.00814		2.016
O5		1.365	0.437, 0.192	1.994
			0.192, 0.437	
$\sum u +$	3.915	4.944	1.908	

^{a} The respective mean values 0.542 and 0.521 were used to compute the electrostatic valence received by O2 and O3.

It is worth pointing out that each Pb^{2+} cations is linked to four free oxygen atoms (O(5)) of three different P$_2$O$_7$ groups (Fig. 4). Moreover, the shortest Pb–O distances (2.418 Å) correspond also to two of these O(5) oxygen atoms in agreement with the electrostatic valences calculated for the different atoms of the structure (Table 4).

Finally, it must be emphasized that, among all the lead phosphates, Pb(VO)P$_2$O$_7$ is, after Pb(VO)$_3$(P$_2$O$_7$)$_2$ (9), the second structure that exhibits [VO$_3$]$_\infty$ octahedral chains interconnected through P$_2$O$_7$ groups. Remarkably, in Pb(VO)$_3$(P$_2$O$_7$)$_2$ each P$_2$O$_7$ group interconnects three [VO$_3$]$_\infty$ chains against two chains in Pb(VO)P$_2$O$_7$, so that the first one does not exhibit free apices for its P$_2$O$_7$ groups.

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