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$BaV_2P_2O_{10}$, a New Tetravalent Vanadium Phosphate with a Tunnel Structure

A. GRANDIN, J. CHARDON, M. M. BOREL, A. LECLAIRE, AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT-ISMRA, Boulevard du Maréchal Juin, 14050 Caen Cedex, France

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A new vanadium (IV) phosphate, $BaV_2P_2O_{10}$, with a tunnel structure has been isolated. Its structure was solved by single crystal X-ray diffraction. It crystallizes in the monoclinic system with the space group $P2_1/c$. The cell parameters are a = 5.2204(3), b = 9.1702(7), c = 16.3247(9) Å; β = 92.757(5)°; V = 780.6(3) Å^3; Z = 4; Dm = 3.93(6); D_x = 3.92; R = 0.031 and R_w = 0.035 for 4039 unique reflections with $I > 3\sigma(I)$. The three-dimensional framework $[V_2P_2O_{10}]_\infty$ can be described as the assemblage of $[P_2VO_9]$ rows formed of VO_5 pyramids and PO_4 tetrahedra, linked to each other through VO_6 octahedra. The existence of $[V_2O_{10}]$ units involving one VO_5 pyramid and one VO_6 octahedron, already observed in other V(IV) phosphates is also considered, as well as the existence of $[V_2P_2O_{14}]$ units corresponding to the association of one $[V_2O_{10}]$ unit with two PO_4 tetrahedra and which allow the whole structure to be described. This host lattice delimits large elliptic tunnels running along **a** where double rows of barium cations are located. The particular coordination of vanadium (IV), which corresponds to the existence of vanadyl ion as well in VO_5 pyramids, as in VO_6 octahedra (coordination "5 + 1") is emphasized.

Introduction

The studies performed these last years on transition-metal phosphates have shown a very promising field of investigation for the generation of new structures (*1*). In this respect the chemistry of vanadium phosphates is very rich. Many vanadium (V) phosphates, especially hydrated phosphates and hydrogen phosphates, are known. However few vanadium (IV) phosphates, exempt of OH groups, have been isolated up to now. They can be classified in two series, the vanadium (IV) monophosphates $AVPO_5$ (A = Li, K) (*2, 3*), and the vanadium (IV) diphosphates $A_2VP_2O_8$ (A = K, Rb, Cs) (*4, 5*) and $A_2V_3P_4O_{17}$ (A = K, Rb, Cs) (*6–9*).

A common feature to all these compounds is the ability of V(IV) to form an abnormally short V–O bond of about 1.60 Å, leading for V(IV) either to a pyramidal coordination or to an octahedral coordination, the vanadium atom being off-centered inside its octahedron. This particular behavior of V(IV) suggests a great adaptability of these polyhedra to PO_4 tetrahedra, encouraging the investigation of new systems involving vanadium (IV) phosphates. For this reason, the system Ba–P–V–O for which only one V(III) phosphate is known, $BaV_2P_4O_{14}$ (*10*), was investigated. We report here on the crystal structure of a new tetravalent vanadium phosphate, $BaV_2P_2O_{10}$.

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Synthesis

The synthesis of $BaV_2P_2O_{10}$ was performed in two steps. First an adequate mixture of $BaCO_3$, $H(NH_4)_2PO_4$, and V_2O_5 was heated up to 653 K in air in order to eliminate H_2O, CO_2, and NH_3. In the second step the finely ground product was mixed with an appropriate amount of vanadium and sealed in an evacuated silica ampoule. This sample was heated up to 923 K for 2 months and quenched at room temperature. In these conditions a pure phase is obtained, whose powder X-Ray diffraction pattern (Table I) is indexed in a monoclinic cell deduced from the single crystal study.

Single crystals of this phase were grown from a sample of nominal composition "$Ba_3V_8P_6O_{32}$." The method of preparation was identical to that described above for the quantitative synthesis of the powder. The chemical composition of this phase deduced from the structural determination; $BaV_2P_2O_{10}$ was confirmed by microprobe analysis. The measured volumic mass $\rho = 3.93(6)$ g cm^{-3} agrees with calculated one $\rho = 3.92$ g cm^{-3}.

TABLE I

$BaV_2P_2O_{10}$ INTERRETICULAR DISTANCES

h	k	l	d_{obs}	d_{calc}	I
0	2	0	4.595	4.585	22
$\bar{1}$	1	1	4.436	4.415	13
$\bar{1}$	1	2	4.051	4.034	100
1	1	2	3.910	3.893	17
0	1	4	3.735	3.725	15
1	2	0	3.450	3.443	21
$\bar{1}$	2	1	3.391	3.391	35
$\bar{1}$	0	4	3.292	3.289	15
1	0	4	3.144	3.139	19
$\bar{1}$	1	4	3.108	3.096	41
0	3	1	3.015	3.000	27
1	1	4	2.976	2.970	30
1	2	3	2.871	2.868	52
0	0	6	2.718	2.718	11
$\bar{1}$	2	4	2.671	2.673	19
$\bar{1}$	3	1	2.615	2.613	12
1	3	1	2.593	2.593	11
2	0	2	2.452	2.449	11
$\bar{2}$	1	2	2.430	2.429	7
$\bar{1}$	2	5	2.406	2.406	4
$\bar{1}$	1	6	2.373	2.375	7
0	4	0	2.293	2.293	6
0	4	1	2.271	2.270	12
2	1	3	2.237	2.238	15
1	3	4	2.190	2.190	7
$\bar{1}$	2	6	2.168	2.167	11
2	1	4	2.092	2.093	17
0	2	7	2.077	2.077	17
2	2	3	2.060	2.061	11
$\bar{1}$	4	2	2.042	2.042	15
0	4	4	1.998	1.998	11
2	2	4	1.948	1.946	9
$\bar{1}$	0	8	1.931	1.930	6
1	2	7	1.901	1.901	5

Determination and Refinement of the Structure

A green crystal of $BaV_2P_2O_{10}$ with dimensions $0.126 \times 0.105 \times 0.086$ mm was selected for the structure determination. The cell parameters reported in Table II were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18 \leq \theta \leq 22°$.

The systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ are consistent only with space group $P2_1/c$ *(14)*. The data were collected on a CAD-4 Enraf–Nonius diffractometer with the data collection parameters reported in Table II. The reflections were corrected for Lorentz polarization, absorption, and secondary extinction effects.

The coordinates of the barium atom were determined from a Patterson syntheses. The vanadium, phosphorus, and oxygen atoms were located by subsequent Fourier syntheses. The refinement of the coordinates and the anisotropic thermal factors of all the atoms led to $R = 0.031$, $R_w = 0.035$ and to the atomic parameters of Table III. The scattering factors are taken from "International Tables for X-ray Crystallography" *(11)*.

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS AND STRUCTURE REFINEMENT PARAMETERS

Crystal data	
Space group	$P2_1/c$
Cell dimensions	$a = 5.2204(3)$
	$b = 9.1702(7)$ $\beta = 92.757(5)°$
	$c = 16.3247(9)$ Å
Volume	$V = 780.6(3)$ Å^3
Z	4
Intensity measurements	
$\lambda(\text{Mo}K\alpha)$	0.71073 Å
Monochromator	Graphite
Scan mode	ω-θ
Scan width(°)	$1.10 + 0.35 \tan \theta$
Slit aperture(mm)	$1.09 + \tan \theta$
Max scan time	60 sec
Max θ(°)	45
Standard reflections	3 measured every 3600 sec (no decay)
Nb reflections	6832
Reflections with $I > 3\sigma$	4039
$\mu(\text{mm}^{-1})$	7.71
Structure solution and refinement	
Parameters refined	137
Agreement factors	$R = 0.031$ $R_w = 0.035$
Weighting schema	$w = f(\sin \theta/\lambda)$
ESD	1.006
Δ/σ	<0.004

Description of the Structure and Discussion

The projection of the structure into the (010) plane (Fig. 1) shows that the tridimensional framework $[V_2P_2O_{10}]_\infty$ is built up from corner-sharing VO_5 pyramids, VO_6 octahedra and single PO_4 tetrahedra. This framework delimits tunnels with an elliptic section running along **a** (Fig. 2).

This host lattice can be described in a simple way as built up from identical $[P_2VO_9]_\infty$ rows of corner-sharing VO_5 pyramids and PO_4 tetrahedra running along **a** (Fig. 2) and linked to each other through VO_6 octahedra. Each VO_6 octahedron V(2),

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B(Å^2)
Ba	0.00266(3)	0.20027(2)	0.18004(1)	0.807(2)
V(1)	0.11936(7)	0.81937(5)	0.06397(3)	0.474(4)
V(2)	0.45604(8)	0.04678(5)	0.34292(3)	0.469(4)
P(1)	0.3913(1)	0.29316(8)	0.02522(4)	0.469(7)
P(2)	0.3826(1)	0.40559(7)	0.32798(4)	0.429(7)
O(1)	0.1600(4)	0.6711(3)	0.1149(2)	0.96(3)
O(2)	−0.1538(3)	0.8087(3)	−0.0244(1)	0.72(2)
O(3)	−0.1409(4)	0.9291(3)	0.1232(2)	0.89(3)
O(4)	0.3531(4)	0.7907(3)	−0.0267(1)	0.88(2)
O(5)	0.3701(4)	0.9440(3)	0.1233(2)	0.87(3)
O(6)	0.1927(4)	−0.0234(3)	0.3055(2)	1.01(3)
O(7)	0.3921(4)	0.2488(2)	0.2952(1)	0.85(3)
O(8)	0.6551(4)	0.0132(3)	0.2440(1)	0.77(2)
O(9)	0.6229(4)	−0.1272(2)	0.3918(1)	0.82(2)
O(10)	0.3646(4)	0.1072(3)	0.4514(1)	0.90(3)

Note. Anisotropically refined atoms are given in the isotropic equivalent displacement parameter defined as $B = \frac{4}{3}[\beta_{11} a^2 + \beta_{22} b^2 + \beta_{33} c^2 + \beta_{12} ab \cos \gamma + \beta_{13} ac \cos \beta + \beta_{23} bc \cos \alpha]$.

ensures the junction between three $[P_2VO_9]_\infty$ rows; two of its corners are shared with PO_4 tetrahedra of one row, a third corner is shared with the VO_5 pyramid of the same row, whereas its two other apices are shared with the PO_4 tetrahedra of the two other adjacent rows, the sixth corner being free. In this V(2) octahedron one observes (Table IV) a very short V–O bond (1.611 Å) corresponding to a vanadyl group, the oxygen of which is not shared with other polyhedra, four intermediate V–O distances (1.937–2.034 Å), and a very long one (2.379

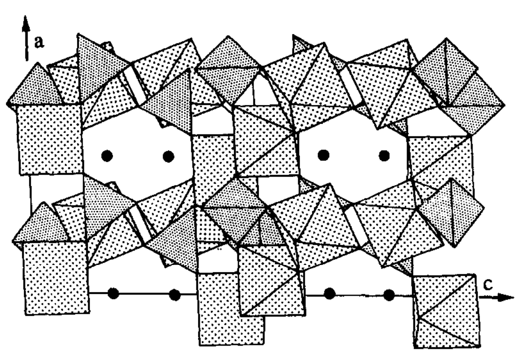

FIG. 1. Projection of the structure along **b** (●Ba).

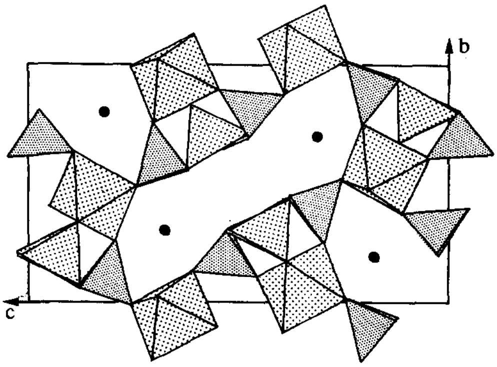

FIG. 2. Projection of the structure along **a** (●Ba).

Å). The "O_6" octahedron is almost regular (Table IV) but the O–V–O angles range from 78° to 102.6° due to the fact that the vanadium atom is strongly off-centered in the octahedron so that its coordination can be considered as pyramidal or at least "5 + 1."

Each VO_5 pyramid V(1) shares its apical oxygen with the VO_6 octahedron V(2), whereas its four corners of the basal plane are shared with PO_4 tetrahedra. Consequently it exhibits one abnormally short V–O bond (1.603 Å) corresponding to the apical oxygen, and four medium V–O distances (1.958–1.981 Å) distributed in the basal plane. As a result, the V(1)–O–V(2) bond is nonlinear (angle of 130°2), and dissymetric, i.e., the oxygen of this bridge is strongly bonded to V(1) (1.603 Å) and weakly bonded to V(2) (2.379 Å).

The great adaptability of the vanadium polyhedra allows the PO_4 tetrahedra to be almost regular (Table IV), as observed in the monophosphates of transition elements. One also recognizes in this framework the presence of $[V_2O_{10}]$ units built up from one VO_5 pyramid and one VO_6 octahedron sharing one corner corresponding to the apical oxygen of the VO_5 pyramid. Similar groups have already been observed in the phosphates $A_2V_3P_4O_{17}$ (A = K, Rb, Cs) (*6–9*). But the structure can better be understood by considering units of four polyhedra $[V_2P_2O_{14}]$ involving the association of one VO_5 pyramid, the neighboring VO_6 octahedron, and two PO_4 tetrahedra all sharing their corners (Fig. 3). Then the whole structure can be described by the association of such units, through the corners of their polyhedra. In the (010) plane, each unit shares the corners of its VO_6 octahedron and two corners of its PO_4 tetrahedra with those of the PO_4 tetrahedra and the VO_6 octahedron of adjacent units respectively. It results that six such units form an elliptic ring whose large axis is parallel to [011] or [01$\bar{1}$[(Fig. 2). Along **a** the $P_2V_2O_{14}$ units are associated in such a way that the VO_5 pyramid of one unit shares two of its apices with the PO_4 tetrahedra of the adjacent unit (Fig. 1). Thus the $[V_2P_2O_{10}]_\infty$ framework can also be described as the stacking along **a** of six-sided rings of $[V_2P_2O_{14}]$ units forming the elliptic tunnels running along **a**. Another view of the structure, along **b** (Fig. 1) is also interesting, since it shows the existence of much smaller tunnels running along this direction intersecting the elliptic tunnels.

The barium cations are located in the elliptic tunnels running along **a**, forming a double row in each tunnel. Each barium sits at the intersection of the two sorts of tunnels, i.e., the elliptic tunnels and those running along [010]. It exhibits an eightfold coordination (Fig. 4) with Ba–O distances ranging from 2.69 to 3.046 Å, giving for barium a

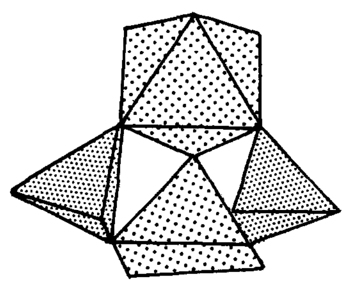

FIG. 3. The $V_2P_2O_{14}$ unit.

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE VO_5 SQUARE PYRAMIDS, VO_6 OCTAHEDRA AND PO_4 TETRAHEDRA AND Ba-O DISTANCES LESS THAN 3.05 Å.

V(1)	O(1)	O(2)	O(3)	O(4)	O(5)
O(1)	1.603(2)	3.015(3)	2.847(3)	2.791(3)	2.733(3)
O(2)	114.1(1)	1.981(3)	2.647(3)	2.653(3)	3.768(3)
O(3)	104.7(1)	83.9(1)	1.980(2)	3.854(3)	2.671(3)
O(4)	101.8(1)	84.1(1)	153.4(1)	1.981(2)	2.821(3)
O(5)	99.8(1)	146.0(1)	85.4(1)	91.5(1)	1.958(2)

V(2)	O(1^{i})	O(6)	O(7)	O(8)	O(9)	O(10)
O(1^{i})	2.379(2)	3.983(3)	2.793(3)	2.849(3)	2.965(3)	2.817(3)
O(6)	173.1(1)	1.611(2)	2.713(3)	2.680(3)	2.762(3)	2.776(3)
O(7)	78.2(1)	95.6(1)	2.032(2)	2.713(3)	3.956(3)	2.871(3)
O(8)	81.0(1)	95.7(1)	85.0(1)	1.986(2)	2.747(3)	3.873(3)
O(9)	85.5(1)	100.5(1)	163.0(1)	88.0(1)	1.968(2)	2.741(3)
O(10)	80.8(1)	102.6(1)	92.7(1)	161.7(1)	89.2(1)	1.937(2)

P(1)	O(2^{ii})	O(4^{iii})	O(9^{iv})	O(10^{v})
O(2^{ii})	1.552(2)	2.578(3)	2.419(3)	2.484(3)
O(4^{iii})	113.0(1)	1.539(2)	2.487(3)	2.518(3)
O(9^{iv})	102.7(1)	107.5(1)	1.544(2)	2.565(3)
O(10^{v})	108.3(1)	111.1(1)	114.0(1)	1.514(2)

P(2)	O(3^{vi})	O(5^{i})	O(7)	O(8^{iv})
O(3^{vi})	1.540(2)	2.557(3)	2.529(3)	2.412(3)
O(5^{i})	113.1(1)	1.525(2)	2.521(3)	2.493(3)
O(7)	110.7(1)	111.0(1)	1.536(2)	2.516(3)
O(8^{iv})	103.2(1)	108.9(1)	109.8(1)	1.540(2)

Ba–O(2^{ii})	2.698
Ba–O(7)	2.738
Ba–O(8^{vii})	2.740
Ba–O(3^{viii})	2.746
Ba–O(6^{ix})	2.746
Ba–O(9^{iv})	2.814
Ba–O(6)	3.032
Ba–O(4^{ii})	3.046

Note. Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-x, 1 - y, -z$; (iii) $1 - x, 1 - y, -z$; (iv) $1 - x, \frac{1}{2} - y, \frac{1}{2} - z$; (v) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vi) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (vii) $x - 1, y, z$; (viii) $x, y - 1, z$; (ix) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

sum of electrostatic valence of 1.99 with the Brown and Altermatt curves (*12*), which agrees with the formal charge +2 of this cation. In the same way the calculated sum of the electrostatic valences leads to a tetravalent state for each of the two independent vanadium atoms.

Concluding Remarks

A new vanadium (IV) phosphate with an original tunnel structure has been isolated. The synthesis of this new phase confirms, if needed, the great ability of tetravalent vanadium to form vanadyl ions, characterized

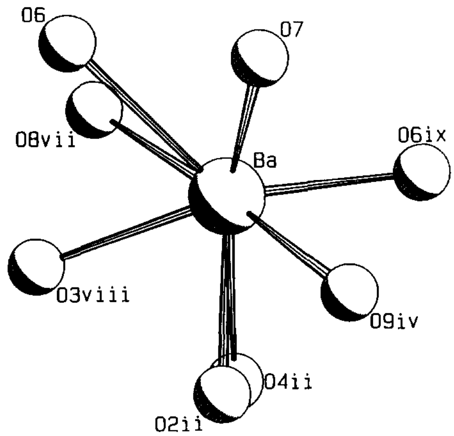

FIG. 4. Ba^{2+} cation environment.

either by VO_5 pyramids or by "off-centered" VO_6 octahedra. Contrary to all other vanadium (IV) phosphates with a three-dimensional framework such as $AVPO_5$ (A = Li, K) (*2, 3*) and $A_2V_3P_4O_{17}$ (A = K, Rb, Cs) (*6–9*), the structure of $BaV_2P_2O_{10}$ does not exhibit ReO_3-type rows of VO_6 octahedra. Nevertheless, it is characterized like the phosphates $A_2V_3P_4O_{17}$ by the existence of $[V_2O_{10}]$ units in which the VO_6 octahedron and the VO_5 pyramid can be considered as weakly bonded by their bridging oxygen. The spacious character of the tunnels suggest the possibility to generate in these phosphates new zeolithic compounds with larger cavities using soft chemistry and hydrothermal synthesis.

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