Langbeinite, a Host Lattice for "V₃O" Clusters: The Trivalent Vanadium Phosphate $K_{11}V_{15}P_{18}O_{73}$

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During the study of the K–V–P–O system, crystals of a new phase, $K_{11}V_{15}P_{18}O_{73}$, were isolated. This phase crystallizes in the space group $P2_13$ with $a = 9.896(1)$ Å. Its structure was refined from single-crystal X-ray data, using 561 reflections, leading to agreement factors $R = 0.030$ and $R_w = 0.034$. It consists of a langbeinite-type framework, $[V_{12}P_{18}O_{72}]_x$, whose cages are occupied by K^+ ions and "V₃O" clusters according to the formulation $K_{11}(V_3O)(V_{12}P_{18}O_{72})$. In these cages, the six K(1) sites of the classical langbeinite structure are fully occupied by potassium, whereas one K(2) site out of six is replaced by an oxygen atom O(5). Three vanadium atoms are then inserted around this additional oxygen, forming three additional VO_6 octahedra sharing this common O(5) oxygen. Moreover, each of these additional VO_6 octahedra shares one edge with a PO_4 tetrahedron, and one face and one edge with two VO_6 octahedra, respectively, of the $[V_{12}P_{18}O_{72}]_x$ host lattice. The interatomic distances are discussed. © 1992 Academic Press, Inc.

Introduction

During the study of the K–V–P–O system, single crystals of a new phase were isolated beside the vanadium phosphates KVP_2O_7 (1), $K_6V_2P_4O_{16}$ (2), and $KVPO_5$ (3). A preliminary X-ray single crystal study showed that its symmetry was cubic and that it was closely related to the langbeinite-type structure $K_{2-x}Ti_2P_3O_{12}$ (4).

These observations suggested the possibility of the existence of a langbeinite-type structure for vanadium phosphate with a similar composition, i.e., characterized by a mixed valency V(III)–V(IV). However, analysis of the previous vanadium phosphates (1–3), shows that in those structures,

where the VO_n polyhedra are isolated by PO_4 tetrahedra, V(IV) does not exhibit octahedral coordination, but presents a pyramidal coordination. If this phenomenon is generalized to all vanadium phosphates involving isolated VO_n polyhedra, langbeinite which exhibits only isolated octahedra should not contain V(IV). In order to understand this particular formation of a langbeinite-type structure, we determined the structure of these crystals. We report here on this new compound, which proved to be a trivalent phosphate $K_{11}V_{15}P_{18}O_{73}$ closely related to langbeinite.

Synthesis

The new oxide $K_{11}V_{15}P_{18}O_{73}$ is regularly obtained as a minor phase, during the syn-

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thesis of KVP_2O_7 at high temperature. Well-formed black crystals of the new phase are generally observed in the green polycrystalline powder of KVP_2O_7.

All attempts to prepare it as a pure phase, starting with the nominal composition $K_{11}V_{15}P_{18}O_{73}$, were unsuccessful. They always led to a mixture, suggesting that this oxide is metastable, in agreement with the particular character of the structure, as will be discussed later.

Determination of the Structure

A black pyramidal crystal of dimensions $0.13 \times 0.13 \times 0.07$ mm was selected for the data collection performed on a CAD4 Enraf–Nonius diffractometer, with the parameters in Table I. The micropobe analysis of a second crystal indicated the presence of only vanadium, phosphorus, and potassium.

The amount of vanadium was found to be slightly higher and that of potassium slightly lower than that corresponding to the ideal formula, "$K_2V_2P_3O_{12}$," of langbeinite. The cell parameters reported in Table I were de-

termined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18° < \theta < 22°$. The data were corrected for Lorentz and polarization effects; no absorption corrections were performed.

The Patterson function of the vanadium compound was almost identical to that of $K_2Ti_2P_3O_{12}$ (4). Thus, the refinements were started using the ideal formula $K_2V_2P_3O_{12}$. After several cycles the thermal factor B_{eq} of $K(2)$ was found to be much higher than that of $K(1)$. The multiplicity factor of the $K(2)$ site was then refined, leading to the potassium-deficient formula $K_{1.88}V_2P_3O_{12}$. A difference synthesis showed an additional atom at the positions "0.47, 0.17, 0.59." At this point, we noticed that this atom was surrounded by five oxygen atoms located at distances ranging from 2 to 2.40 Å and by one $K(2)$ site located at 1.99 Å. These results, and the fact that the occupancy factor of the $K(2)$ site was smaller than 1.0, suggested that the additional atom was vanadium and that potassium was partly replaced by oxygen in the $K(2)$ site, leading to an octahedral coordination for this additional vanadium. In a first step, the multiplicity factor of the additional vanadium atom was refined, leading to a significant decrease of the reliability factor $R = 0.031$ and $R_w = 0.035$. The formula deduced from this refinement was then $K_{3.768}V_5O_{24}$. Finally we considered that one oxygen atom $O(5)$ for three additional vanadium atoms was replacing potassium on the $K(2)$ sites or very close to them. Such a hypothesis led to a number of 34.3 electrons at the $K(2)$ sites, very close to that obtained from the refinement of this site (33.6 electrons), the small difference coming from the fact $K(2)$ and $O(5)$ are not located exactly at the same positions. The refinement of the structure with the corresponding formula, $K_{3.666}V_5P_6O_{24.333}$, i.e., $K_{11}V_{15}P_{18}O_{73}$, leads to $R = 0.030$ and $R_w = 0.034$ for the atomic parameters given in Table II.

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $K_{11}V_{15}P_{18}O_{73}$

1. Crystal data	
Space group	$P2_13$
Cell dimensions	$a = 9.896(1)$ Å
Volume	$v = 969.1(4)$ Å^3
Z	$\frac{2}{3}$
2. Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - \theta$
Scan width (°)	$1.25 + 0.35 \tan \theta$
Slit aperture (mm)	$1.1 + \tan \theta$
Maximum θ (°)	45°
Standard reflections	Three measured every 3000 sec (no decay)
Reflections with $I > 3\sigma$	561
3. Structure solution and refinement	
Parameters refined	70
Agreement factors	$R = 0.030, R_w = 0.034$

Atom	Occupancy	x	y	z	B (Å^2)
P	1.	0.4804(1)	0.7101(1)	0.3753(1)	0.66(1)
V(1)	1.	0.66315(8)	—	—	0.841(5)
V(2)	1.	0.39579(9)	—	—	0.882(5)
V(3)	$\frac{1}{6}$	0.4674(5)	0.1742(5)	0.5895(5)	0.85(7)
K(1)	1.	0.1812(2)	—	—	2.45(1)
K(2)	$\frac{5}{6}$	0.9562(2)	—	—	2.10(1)
O(1)	1.	0.5993(5)	0.8337(4)	0.7494(5)	2.09(8)
O(2)	1.	0.4552(5)	0.3018(4)	0.2300(4)	1.86(7)
O(3)	1.	0.4905(4)	0.5632(4)	0.3288(4)	1.39(6)
O(4)	1.	0.5599(5)	0.7336(4)	0.5061(4)	1.88(7)
O(5)	$\frac{1}{6}$	−0.016(3)	—	—	2.7(9)^a

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

^{a} Atom was refined isotropically.

Description of the Structure and Discussion

The vanadium phosphate $K_{11}V_{15}P_{18}O_{73}$ is characterized by the presence of only V(III) and exhibits a host lattice $[V_{12}P_{18}O_{72}]_\infty$ similar to the langbeinite-type titanophosphate $K_{2-x}Ti_2P_3O_{12}$ (Fig. 1), i.e., built up of VO_6 octahedra and PO_4 tetrahedra sharing their corners. The V(1) and V(2) octahedra and P tetrahedra are almost regular (Table II) as in $K_{2-x}Ti_2P_3O_{12}$ (4). This langbeinite framework delimits voluminous double cages where potassium and V_3O clusters are located. In each double cage, one site less voluminous, labeled K(1), is fully occupied by potassium, whereas the adjacent one is $\frac{5}{6}$ occupied by potassium K(2) and $\frac{1}{6}$ by V_3O groups (V(3) and O(5) sites).
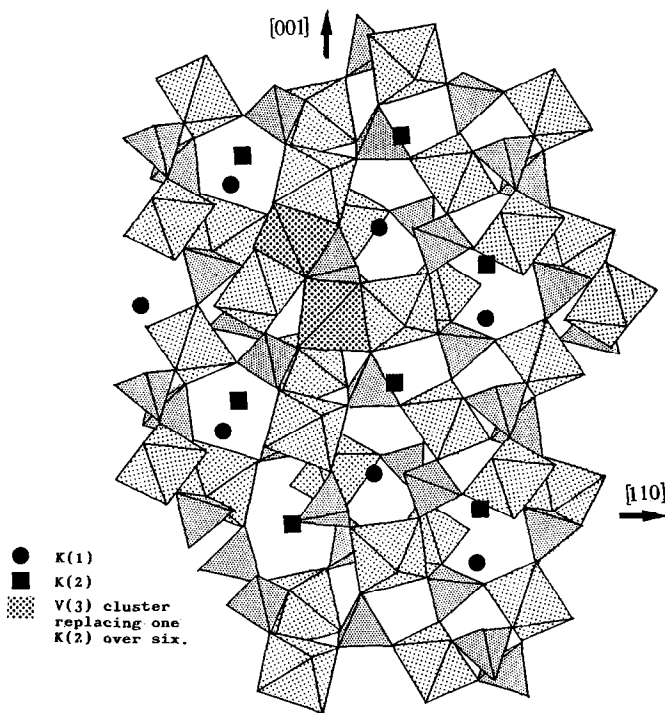

FIG. 1. Partial projection of the structure along [1$\bar{1}$0], showing a double cage containing a V_3O cluster and the potassium K(1), and a double cage containing the K(1) and K(2) ions.

TABLE III

Distances (Å) and Angles (°) in the Coordination Polyhedra

			VO_6 octahedra			
V(1)	O(1)	$O(1^i)$	$O(1^{ii})$	O(4)	$O(4^i)$	$O(4^{ii})$
O(1)	1.994(4)	2.878(7)	2.878(7)	2.632(6)	2.867(5)	3.974(7)
$O(1^i)$	92.4(2)	1.994(4)	2.878(7)	3.974(7)	2.632(6)	2.867(5)
$O(1^{ii})$	92.4(2)	92.4(2)	1.994(4)	2.867(5)	3.974(7)	2.632(6)
O(4)	82.8(2)	173.5(2)	92.2(2)	1.986(4)	2.881(6)	2.881(6)
$O(4^i)$	92.2(2)	82.8(2)	173.5(2)	93.0(2)	1.986(4)	2.881(6)
$O(4^{ii})$	173.5(2)	92.2(2)	82.8(2)	93.0(2)	93.0(2)	1.986(4)
V(2)	O(2)	$O(2^i)$	$O(2^{ii})$	O(3)	$O(3^i)$	$O(3^{ii})$
O(2)	1.976(4)	2.789(7)	2.789(7)	2.787(5)	3.990(7)	2.804(5)
$O(2^i)$	89.8(2)	1.976(4)	2.789(7)	2.804(5)	2.787(5)	3.990(7)
$O(2^{ii})$	89.8(2)	89.8(2)	1.976(4)	3.990(7)	2.804(5)	2.787(5)
O(3)	88.6(2)	89.3(2)	178.1(2)	2.015(4)	2.908(7)	2.908(7)
$O(3^i)$	178.1(2)	88.6(2)	89.3(2)	92.3(2)	2.015(2)	2.908(7)
$O(3^{ii})$	89.3(2)	178.1(2)	88.6(2)	92.3(2)	92.3(2)	2.015(4)
V(3)	$O(1^{iii})$	$O(1^{iv})$	$O(2^{ii})$	$O(3^{ii})$	$O(4^{iv})$	$O(5^v)$
$O(1^{iii})$	2.339(6)	2.878(7)	3.249(6)	3.035(6)	2.867(5)	4.26(2)
$O(1^{iv})$	74.9(2)	2.393(6)	2.508(6)	4.213(7)	2.632(6)	3.29(2)
$O(2^{ii})$	91.9(2)	66.3(2)	2.180(6)	2.787(5)	3.991(7)	3.01(2)
$O(3^{ii})$	87.3(2)	142.9(3)	82.4(2)	2.049(5)	3.874(7)	3.14(2)
$O(4^{iv})$	80.3(2)	71.4(2)	137.6(3)	138.0(3)	2.101(6)	2.83(2)
$O(5^v)$	168.5(3)	98.1(9)	96.6(7)	103.5(6)	88.9(3)	1.94(2)

		PO_4 tetrahedron		
	P	$O(1^{vi})$	$O(2^{vii})$	O(3)	O(4)
$O(1^{vi})$	1.526(4)	2.508(6)	2.521(2)	2.475(5)
$O(2^{vii})$	110.7(2)	1.522(4)	2.491(5)	2.437(5)
O(3)	111.2(2)	109.5(2)	1.528(4)	2.528(5)
O(4)	108.0(2)	105.9(2)	111.4(2)	1.533(4)

K–O distances $\leq$ 3.35 Å

K(1)–O(1) = 2.861(4) ×3	K(2)–O(2) = 3.021(4) ×3
K(1)–O(2) = 3.002(4) ×3	K(2)–O(3) = 2.847(4) ×3
K(1)–O(3) = 3.205(5) ×3	K(2)–O(4) = 3.114(4) ×3
K(1)–O(4) = 3.067(5) ×3	

Note. Symmetry code: (i) z, x, y; (ii) y, z, x; (iii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $1 - z, x - \frac{1}{2}, \frac{3}{2} - y$; (v) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (vi) $y - \frac{1}{2}, \frac{3}{2} - z, 1 - x$; (vii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The O(5) oxygen atom is located on the ternary axis of the cubic cell, whereas the three V(3) atoms forming the V_3O group are related to each other by this ternary axis. They are located in such a way that they form, with O(5) and other oxygen atoms of the $[V_{12}P_{18}O_{72}]_\infty$ framework, three VO_6 octahedra labeled V(3), sharing the same oxygen atom, O(5) (Fig. 2). This group of three V(3) octahedra is wrapped by two rings of six corner-sharing polyhedra (three VO_6 octahedra V(1) or V(2) + three PO_4 tetrahedra)
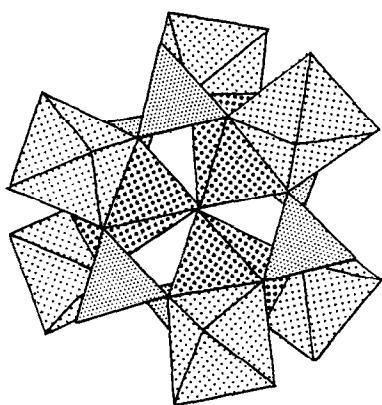
FIG. 2. The $V_9P_3O_{41}$ cluster.

belonging to the $[V_{12}P_{18}O_{72}]_\infty$ host lattice (Fig. 2). It results in a close-packed cluster of polyhedra, $V_9P_3O_{41}$, in which each V(3) octahedron shares one edge with one P tetrahedron, one face with one V(1) octahedron of one ring, and one edge with one V(2) octahedron of the second ring. It is remarkable that we observe in such a cluster both the V_2O_9 units of face-sharing octahedra characteristic of $V_3P_4SiO_{19}$ (5) and of $V_4P_6O_{21}$ (6), the V_2O_{10} units of edge-sharing octahedra characteristic of $V_2P_2O_7$ (7) and the VPO_8 units of an octahedron sharing its edge with a tetrahedron previously observed in $NaV_3P_3O_{12}$ (8) and in $K_6V_2P_4O_{16}$. (2).

Another remarkable feature deals with the fact that the introduction of such clusters does not induce any distortion of the langbeinite framework. On the other hand, the V(3) octahedra are strongly distorted with O–V(3)–O angles ranging from 66.3° to 103.5° instead of 90° and from 137.6° to 168.5° instead of 180° (Table III), and with V–O bonds ranging from 1.942 to 2.393 Å. Note also that the V–V distances between two face-sharing octahedra of 2.77 Å are close to that observed for $V_4P_6O_{21}$ (2.774 Å) (6) and smaller than that of $V_3P_4SiO_{19}$ (2.90 Å) (5). In the same way, the V–V distances of 2.99 Å between two edge-sharing octahedra are similar to that of $V_2P_2O_9$ (3.14 Å)

(7), whereas the V–P distance of 2.683 Å is similar to those of $K_2V_2P_4O_{16}$ (2.669–2.290 Å) (2).

Concluding Remarks

These results show the great ability of the langbeinite structure to accept foreign elements, tending toward a more close-packed structure without any distortion of its framework. There is no doubt that such a structure is difficult to stabilize owing to the short V–V distances; this may explain the difficulty in synthesizing it as a pure phase. The fact that an oxygen atom replaces a potassium ion in the structure can be compared with the pyrochlore structure for which the M_2O_6 host lattice can accept either a large univalent cation like potassium or an oxygen atom. This coexistence of octahedral clusters and potassium in the same cages is very similar to the existence of groups of WO_6 octahedra replacing Rb partially in rubidium tungstate, $Rb_{20+x}(W_4O_6)_{1/3+x/12}W_{32}O_{108}$ (9), derived from the pyrochlore structure.

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