

A New Mixed-Valence Vanadium Phosphate with an Intersecting Tunnel Structure: $KV_3P_4O_{17}$

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A new mixed-valence vanadium phosphate $KV_3P_4O_{17}$ was isolated and its structure was determined from single-crystal X-ray diffraction data. This mixed valence phase crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 7.8654(5)$ Å, $b = 10.0104(7)$ Å, $c = 16.2715(8)$ Å, $V = 1281.2(2)$ Å³, $Z = 4$, $R = 0.053$, and $R_w = 0.062$ for 701 unique reflections with $I > 3\sigma(I)$. The structure can be described as built from ReO_3 -type infinite chains running along **a**. Laterally, in the (001) plane, chains are linked by P_2O_7 diphosphate groups, to form a three-dimensional framework. This host lattice delimits six-sided tunnels running along **a**, intersecting with brownmillerite zig-zag tunnels running along **b**. The potassium cations are located at the intersection of the two types of tunnels. Structural relationships with other mixed framework, and especially with diphosphate tungsten bronzes with hexagonal tunnels, are discussed. © 1992 Academic Press, Inc.

Introduction

The exceptionally rich structural chemistry of the vanadium phosphorus oxides is due to the great flexibility of the VO_n polyhedra which can exhibit V–O distances ranging from 1.6 to 2.6 Å. This property, associated to the ability of vanadium to exhibit several oxidation states, V(V), V(IV), and V(III), has allowed numerous vanadium phosphates to be synthesized. Many pentavalent (1–3) and tetravalent (4–18) vanadium phosphates have been isolated, several of them being studied for their catalytic properties (19). Recent investigations have allowed several trivalent vanadium phosphates (20–24) to be isolated. To the contrary, very few mixed-valent vanadium phosphates have been isolated, so far in spite of the existence of the well known va-

niadium bronzes characterized by the mixed-valence V(V)–V(IV) (25). Two examples of such mixed framework involving the valence V(V)–V(IV) are given by the oxides $RbV_3P_4O_{17+x}$ (26) and $Rb_6V_6P_6O_{31}$ (27). We report here on the synthesis and crystal structure of a new vanadium phosphate $KV_3P_4O_{17}$ involving the mixed-valence V(V)–V(IV).

Synthesis

Green crystals of $KV_3P_4O_{17}$ were crystallized as a minor product in a mixture of composition “ $KV_2P_3O_{12}$ ” in the following way. First, an adequate mixture of K_2CO_3 , $H(NH_4)_2PO_4$, and V_2O_5 was heated up to 653 K in air, in order to eliminate CO_2 , H_2O , and NH_3 . In the second step, the finely ground product was mixed with an appro-

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $KV_3P_4O_{17}$

| | |
|-----------------------------------|---|
| Crystal data | |
| Space group | $P2_12_12_1$ |
| Cell dimensions | $a = 7.8654(5) \text{ \AA}$ $b = 10.0104(7) \text{ \AA}$ $c = 16.2715(8) \text{ \AA}$ |
| Volume | $1281.2(2) \text{ \AA}^3$ |
| Z | 4 |
| Intensity measurement | |
| λ (CuK α) | 1.54056 \AA |
| Scan mode | $\omega - \frac{2}{3}\theta$ |
| Scan width ($^\circ$) | $1 + 0.14 \text{ tg } \theta$ |
| Slit aperture (mm) | $1 + \text{tg } \theta$ |
| Max θ ($^\circ$) | 78 |
| Standard reflections | 3 measured every 3000s |
| Reflections with $I > 3\sigma$ | 701 |
| μ (mm^{-1}) | 2.65 |
| Structure solution and refinement | |
| Parameters refined | 227 |
| Agreement factors | $R = 0.053$, $R_w = 0.062$ |
| Weighting scheme | $w = f(\sin \theta/\lambda)$ |

appropriate amount of vanadium and sealed in an evacuated silica ampoule. This sample was then heated at 923 K for 1 week.

Structure Determination

A green crystal with dimensions $0.038 \times 0.038 \times 0.026$ mm was selected for the structure determination. The cell parameters (Table I) were determined and refined by diffractometric techniques at 294 K with a least squares refinement based upon 25 reflections with $36^\circ < \theta < 44^\circ$. The systematic absences led to the $P2_12_12_1$ space group. 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 and polarization effects; no absorption corrections were performed.

Atomic coordinates of the first vanadium atom were deduced by direct method, and

the other atoms located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.053$ and $R_w = 0.062$, and to the atomic parameters reported in the Table II.

Description of the Structure

The host lattice $[V_3P_4O_{17}]_\infty$ of this vanadophosphate is built up from corner-sharing VO_6 octahedra and P_2O_7 diphosphate groups. One observes ReO_3 -type chains

TABLE II
POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

| Atom | x | y | z | B (\AA^2) |
|-------|-----------|-----------|-----------|----------------------|
| V(1) | 0.7880(7) | 0.3222(4) | 0.1529(2) | 0.91(6) |
| V(2) | 0.2910(6) | 0.2473(5) | 0.4940(3) | 0.70(6) |
| V(3) | 0.2846(7) | 0.3185(4) | 0.1521(3) | 0.93(6) |
| P(1) | 0.1912(8) | 0.6357(5) | 0.1860(3) | 0.22(8) |
| P(2) | 0.1997(9) | 0.5614(5) | 0.4655(3) | 0.30(8) |
| P(3) | 0.1902(9) | 0.1368(6) | 0.3143(3) | 0.42(9) |
| P(4) | 0.192(1) | 0.0607(6) | 0.0367(3) | 0.54(9) |
| K(1) | 0.504(1) | 0.4553(6) | 0.3214(3) | 1.42(9) |
| O(1) | 0.998(3) | 0.332(1) | 0.1631(8) | 1.0(3) |
| O(2) | 0.729(2) | 0.248(2) | 0.2660(9) | 0.8(3) |
| O(3) | 0.486(3) | 0.312(1) | 0.1442(8) | 0.6(3) |
| O(4) | 0.760(2) | 0.137(2) | 0.111(1) | 0.8(3) |
| O(5) | 0.717(3) | 0.503(2) | 0.198(1) | 1.1(3) |
| O(6) | 0.777(3) | 0.382(2) | 0.042(1) | 1.0(3) |
| O(7) | 0.313(3) | 0.327(2) | 0.5958(9) | 0.7(3) |
| O(8) | 0.258(2) | 0.084(2) | 0.552(1) | 0.8(3) |
| O(9) | 0.483(3) | 0.229(2) | 0.464(1) | 1.4(3) |
| O(10) | 0.254(2) | 0.414(2) | 0.447(1) | 0.8(3) |
| O(11) | 0.177(2) | 0.173(2) | 0.406(1) | 0.6(3) |
| O(12) | 0.274(3) | 0.502(2) | 0.200(1) | 0.8(3) |
| O(13) | 0.223(3) | 0.390(2) | 0.040(1) | 0.9(3) |
| O(14) | 0.266(2) | 0.247(2) | 0.265(1) | 0.6(3) |
| O(15) | 0.228(2) | 0.135(2) | 0.115(1) | 1.2(3) |
| O(16) | 0.002(3) | 0.621(2) | 0.2156(9) | 0.7(3) |
| O(17) | 0.003(4) | 0.560(2) | 0.481(1) | 1.7(3) |

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as

$$B = \frac{4}{3} \sum_i \sum_j a_i \cdot a_j \cdot \beta_{ij}$$

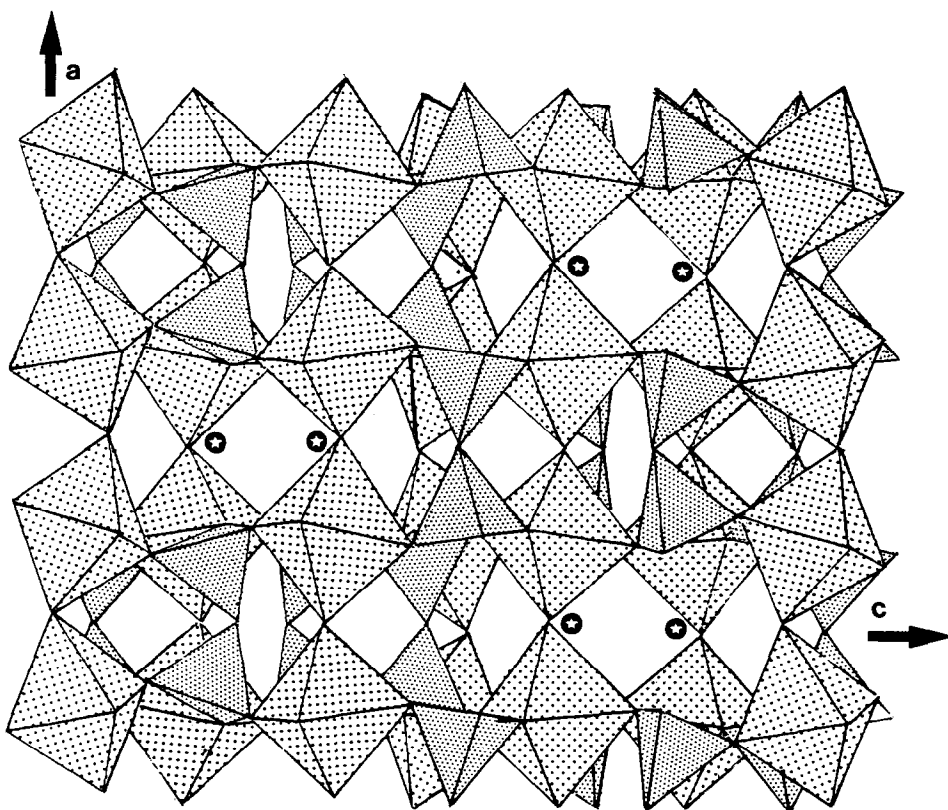


FIG. 1. Projection of the structure along *b*.

$[\text{VO}_3]_\infty$ running along *a* (Fig. 2) linked one to the other by P_2O_7 groups (Fig. 1). This framework delimits six-sided tunnels running along *a* where potassium ions are located (Fig. 2).

In the structure, each P_2O_7 group links its six corners with VO_6 octahedra, and each VO_6 octahedron shares four corners with PO_4 tetrahedra and two corners with two other VO_6 octahedra of the ReO_3 -type chain. In spite of this very simple arrangement, all the octahedra and all the tetrahedra do not correspond to equivalent sites.

Four independent P atoms exist in the framework. Each of them exhibits one long P–O distance (1.56–1.60 Å) characteristic of the bridging oxygen of the P_2O_7 groups; the three other P–O distances are almost

equal in $\text{P}(1)\text{O}_4$, $\text{P}(3)\text{O}_4$, and $\text{P}(4)\text{O}_4$ tetrahedra ranging between (1.50–1.51 Å), (1.49–1.55 Å), and (1.51–1.55 Å), respectively, characteristic of regular PO_4 tetrahedra, whereas the $\text{P}(2)\text{O}_4$ tetrahedron is less regular regarding its three other P–O distances, which range between (1.44–1.56 Å) (Table III).

One observes three crystallographically independent vanadium atoms, which are located in regular oxygen octahedra. There exist two sorts of octahedral chains running along *a*: chains built up of identical V(2) octahedra and chains in which one V(1) octahedron alternates with one V(3) octahedron. In all these octahedra, the vanadium atom is displaced from the basal plane, along *a*, so that an abnormally short V–O bond,

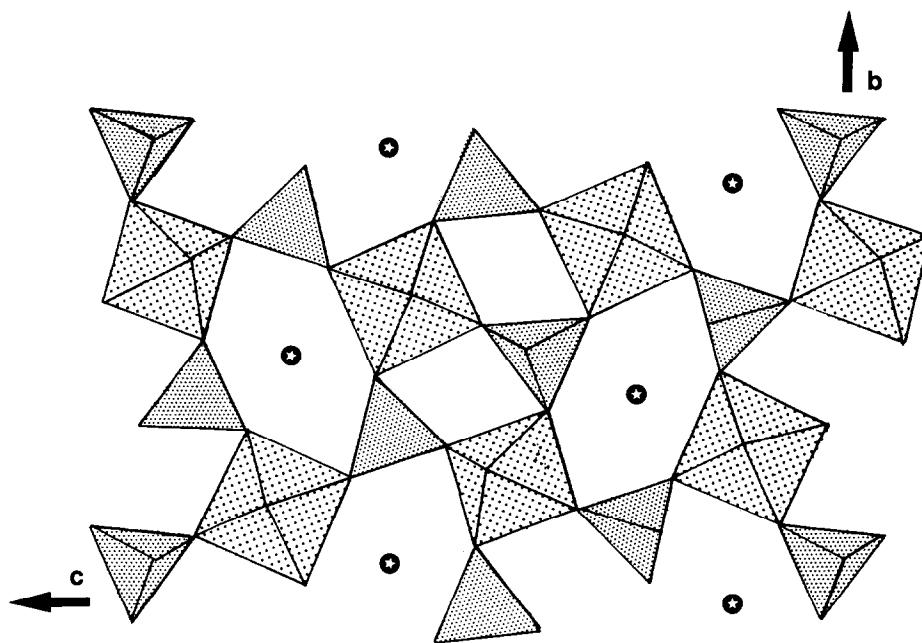


FIG. 2. Projection of the structure along *a*.

1.59 to 1.67 Å, alternates with an abnormally long one, 2.26 to 2.52 Å, as shown in Table IV. This behavior can be interpreted as the result of the ability of V(IV) and V(V) to form vanadyl ions, leading to the formulation $K(\text{VO})_3(\text{P}_2\text{O}_7)_2$. To the contrary, the equatorial V–O bonds in (100) plane are characterized by intermediate distances ranging from 1.84 to 2.04 Å (Table IV). Such a chemical bonding has previously been observed in several vanadophosphates, e.g., $(\text{VO})_2\text{P}_2\text{O}_7$ (9).

Along *b* or *c* the framework shows brownmillerite windows $\text{V}_4\text{P}_2\text{O}_{26}$ (Fig. 1) built up from two tetrahedra and four octahedra. These windows are stacked in such a way that they delimit zig-zag tunnels running along *b* in the (100) plane. At the intersection of the two types of large tunnels potassium ions are located with K–O distances ranging from 2.65 to 3.25 Å (Table V).

Discussion

The chemical composition of this vanadium diphosphate shows the mixed valence

V(IV)–V(V) according to the formula $\text{KV}^{\text{V}}\text{V}_2^{\text{IV}}\text{P}_4\text{O}_{17}$. The calculation of vanadium valency using Brown and Altermatt tables (28) leads for V(1) and V(3) sites which belong to the same ReO_3 -type chains to an occurrence of tetravalent vanadium, whereas the V(2) chains would be mainly occupied by pentavalent vanadium. This suggests that no electronic delocalization appears in the structure, since V(V) chains alternate with V(IV) chains in the framework.

Located on the axis of the large hexagonal tunnels, potassium ions are surrounded by 10 oxygen atoms which delimit a bicapped rectangular prism. The eight oxygen atoms of the rectangular prism lie at 2.65–2.95 Å from the potassium ion, the two other oxygen atoms being more distant (3.22–3.25 Å) (Table V).

It is worth pointing out that three vanadophosphates, α - and β - $\text{K}_2\text{V}_3\text{P}_4\text{O}_{17}$ (15, 16) and $\text{KV}_3\text{P}_4\text{O}_{17}$ were isolated with an identical chemical formulation $[\text{V}_3\text{P}_4\text{O}_{17}]_\infty$ of the host lattice. However, their frameworks are very different. In the β - $\text{K}_2\text{V}_3\text{P}_4\text{O}_{17}$ structure the

TABLE III
DISTANCES (Å) AND ANGLES (°) IN THE PO₄
TETRAHEDRA

| P(1) | O(2 ⁱⁱⁱ) | O(7 ^{iv}) | O(12) | O(16) |
|------------------------|-----------------------|---------------------|---------------------|------------------------|
| O(2 ⁱⁱⁱ) | 1.51(2) | 2.46(2) | 2.52(3) | 2.48(3) |
| O(7 ^{iv}) | 109.2(9) | 1.51(2) | 2.50(2) | 2.48(2) |
| O(12) | 114(1) | 111.8(9) | 1.50(2) | 2.46(3) |
| O(16) | 107.8(9) | 107(1) | 106.4(9) | 1.57(2) |
| P(2) | O(4 ⁱⁱⁱ) | O(10) | O(13 ^v) | O(17) |
| O(4 ⁱⁱⁱ) | 1.49(2) | 2.42(2) | 2.48(2) | 2.51(3) |
| O(10) | 105.3(9) | 1.56(2) | 2.48(2) | 2.52(3) |
| O(13 ^v) | 116(1) | 111(1) | 1.44(2) | 2.42(3) |
| O(17) | 110(1) | 107(1) | 107(1) | 1.57(3) |
| P(3) | O(5 ^{vi}) | O(11) | O(14) | O(16 ^{vii}) |
| O(5 ^{vi}) | 1.54(2) | 2.55(2) | 2.51(2) | 2.55(3) |
| O(11) | 111.6(9) | 1.55(2) | 2.51(2) | 2.49(2) |
| O(14) | 112(1) | 111.8(9) | 1.49(2) | 2.48(3) |
| O(16 ^{vii}) | 109(1) | 104.6(9) | 106.9(2) | 1.60(2) |
| P(4) | O(6 ^{viii}) | O(8 ^{ix}) | O(15) | O(17 ^{viii}) |
| O(6 ^{viii}) | 1.55(2) | 2.55(2) | 2.58(2) | 2.48(3) |
| O(8 ^{ix}) | 112(1) | 1.52(2) | 2.42(2) | 2.46(3) |
| O(15) | 116(1) | 106(1) | 1.51(2) | 2.51(3) |
| O(17 ^{viii}) | 106(1) | 106(1) | 110(1) | 1.56(3) |

two crystallographically independent vanadium atoms are located in pure square pyramidal sites; in the α form one of the three independent vanadium atoms exhibits a square pyramidal coordination, and the two other vanadium atoms present the octahedral coordination, whereas in the title compound the three vanadium atoms present only the octahedral configuration. So the examination of these three structures shows the possibility of a progressive transition from a pure square pyramidal coordination to an octahedral configuration.

To the contrary, this new phase exhibits structural relationships with many other oxides. Its six-sided tunnels are built up from rings of three octahedra sharing their corners with three tetrahedra, leading to an arrangement related to that observed in the

TABLE IV
DISTANCES (Å) AND ANGLES (°) IN THE VO₆
OCTAHEDRA

| V(1) | O(1) | O(2) | O(3) | O(4) | O(5) | O(6) |
|---------------------|---------------------|----------|----------|--------------------|---------|---------|
| O(1) | 1.67(2) | 2.83(3) | 4.05(3) | 2.84(3) | 2.86(3) | 2.68(3) |
| O(2) | 99.1(7) | 2.04(2) | 2.83(2) | 2.77(2) | 2.78(2) | 3.91(3) |
| O(3) | 177.5(6) | 79.1(6) | 2.38(2) | 2.83(2) | 2.78(3) | 2.92(3) |
| O(4) | 101.6(7) | 86.9(7) | 80.1(6) | 1.99(2) | 3.95(3) | 2.70(2) |
| O(5) | 100.6(8) | 86.2(7) | 77.6(7) | 157.5(8) | 2.04(2) | 2.87(2) |
| O(6) | 97.1(8) | 163.7(8) | 84.8(7) | 87.6(7) | 93.2(7) | 1.91(2) |
| V(2) | O(7) | O(8) | O(9) | O(9 ^o) | O(10) | O(11) |
| O(7) | 1.85(2) | 2.57(2) | 2.70(2) | 2.83(3) | 2.61(2) | 3.61(3) |
| O(8) | 86.5(7) | 1.91(2) | 2.70(3) | 2.87(3) | 3.72(3) | 2.61(2) |
| O(9) | 103.3(9) | 100.2(9) | 1.60(2) | 4.12(3) | 2.60(3) | 2.65(3) |
| O(9 ^o) | 79.1(9) | 79.6(9) | 177.6(9) | 2.52(2) | 2.94(3) | 2.77(3) |
| O(10) | 89.5(2) | 162.4(2) | 97.3(9) | 82.8(9) | 1.86(2) | 2.58(2) |
| O(11) | 156.2(9) | 88.4(2) | 100.5(9) | 77.1(9) | 88.3(8) | 1.84(2) |
| V(3) | O(1 ⁱⁱ) | O(3) | O(12) | O(13) | O(14) | O(15) |
| O(1 ⁱⁱ) | 2.26(2) | 3.85(2) | 2.82(3) | 2.73(3) | 2.81(3) | 2.78(3) |
| O(3) | 178.9(7) | 1.59(2) | 2.68(2) | 2.78(2) | 2.70(2) | 2.73(2) |
| O(12) | 82.7(7) | 96.3(8) | 2.00(2) | 2.86(2) | 2.77(2) | 3.94(3) |
| O(13) | 79.1(7) | 100.4(8) | 90.9(7) | 2.02(2) | 3.95(3) | 2.83(2) |
| O(14) | 82.8(6) | 97.6(7) | 88.2(7) | 161.9(8) | 1.98(2) | 2.70(2) |
| O(15) | 81.8(7) | 99.2(8) | 164.0(9) | 90.0(7) | 85.9(7) | 1.98(2) |

Note. The diagonal terms are the M-O(i) distances, the terms above the diagonal are the O(i)-O(j) distances and those below are the O(i)-M-O(j) angles.

TABLE V

Oxygen atoms surrounding K⁺ with
K-O < 3.35 Å

| | | |
|--------|----------------------------|--------------------|
| | K(1)-O(2) | 2.87(9) |
| | K(1)-O(3) | 3.22(2) |
| | K(1)-O(4 ⁱⁱⁱ) | 2.97(6) |
| | K(1)-O(5) | 2.65(5) |
| | K(1)-O(8 ^x) | 2.90(5) |
| | K(1)-O(9) | 3.25(2) |
| | K(1)-O(10) | 2.87(5) |
| | K(1)-O(12) | 2.72(5) |
| | K(1)-O(14) | 2.94(8) |
| | K(1)-O(15 ⁱⁱⁱ) | 2.95(7) |
| | Symmetry code | |
| (i) | $-\frac{1}{2} + x$ | $\frac{1}{2} - y$ |
| (ii) | $-1 + x$ | y |
| (iii) | $1 - x$ | $\frac{1}{2} + y$ |
| (iv) | $\frac{1}{2} - x$ | $1 - y$ |
| (v) | $\frac{1}{2} - x$ | $1 - y$ |
| (vi) | $1 - x$ | $-\frac{1}{2} + y$ |
| (vii) | $-x$ | $-\frac{1}{2} + y$ |
| (viii) | $-\frac{1}{2} + x$ | $\frac{1}{2} - y$ |
| (ix) | $\frac{1}{2} - x$ | $-y$ |
| (x) | $\frac{1}{2} + x$ | $\frac{1}{2} - y$ |

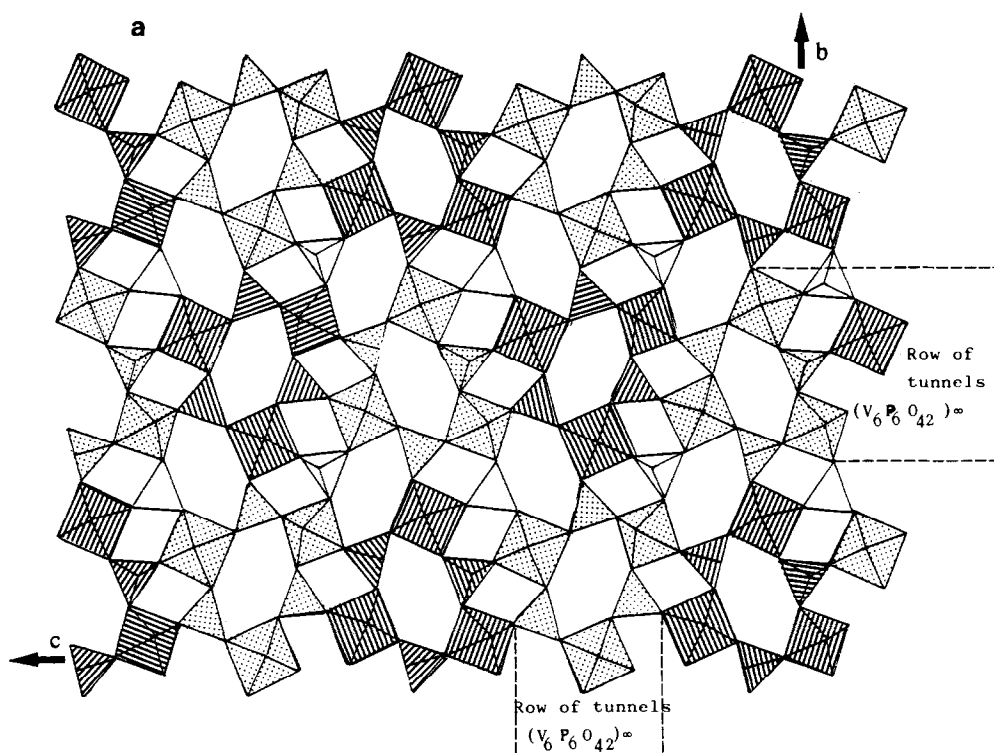


FIG. 3. (a) Rows of tunnels $[V_6P_6O_{42}]_\infty$ running along **b** and **c**; (b) rows of pure octahedral ITB's tubes $[M_{12}O_{50}]_\infty$ in $Sb_2Mo_{10}O_{31}$; (c) rows of $(M_8P_4O_{46})_\infty$ in $(DPTB_H)$.

hexagonal tungsten bronzes (HTB) (29) and in the intergrowth tungsten bronzes (ITB) (30, 31). One indeed observes rows of tunnels $[V_6P_6O_{42}]_\infty$ running along **b** and **c** (Fig. 3a), which can be deduced from the rows of pure octahedral tubes $[M_{12}O_{50}]_\infty$ observed in the $Sb_2Mo_{10}O_{31}$ structure (Fig. 3b) by replacing three octahedra out of six by PO_4 tetrahedra. In the same way they present a great similarity with diphosphate tungsten bronzes $K_xP_2O_7(WO_3)_{2m}$ with hexagonal tunnels (DPTB_H) (32, 33), for which one observes rows of hexagonal tunnels built up from two PO_4 tetrahedra and four WO_6 octahedra sharing the corners of their polyhedra (Fig. 3c). Note the formation of four-sided tunnels related to the perovskite involving two PO_4 tetrahedra and two VO_6

octahedra also observed for DPTB_H's, as well as in $(VO)_2P_2O_7$ (9). The main difference between $KV_3P_4O_{17}$ and these oxides deals with the disposition of hexagonal tunnels along **b**, which form zig-zag chains along this direction (Fig. 2). As in DPTB_H's, the adaptability of P_2O_7 groups to ReO_3 -type chains is remarkable. Moreover it must be emphasized that for each zig-zag row of tunnels parallel to **b**, all the P_2O_7 groups are at the same level along **a**; on the other hand, in each row of tunnels parallel to **c**, two successive tunnels have then P_2O_7 groups shifted of **a**/2.

Though they contain only monophosphate groups, the niobium phosphate bronzes $(K_3Nb_6P_4O_{26})_nKNbP_2O_8$ (34) are also related to $KV_3P_4O_{17}$. They also form

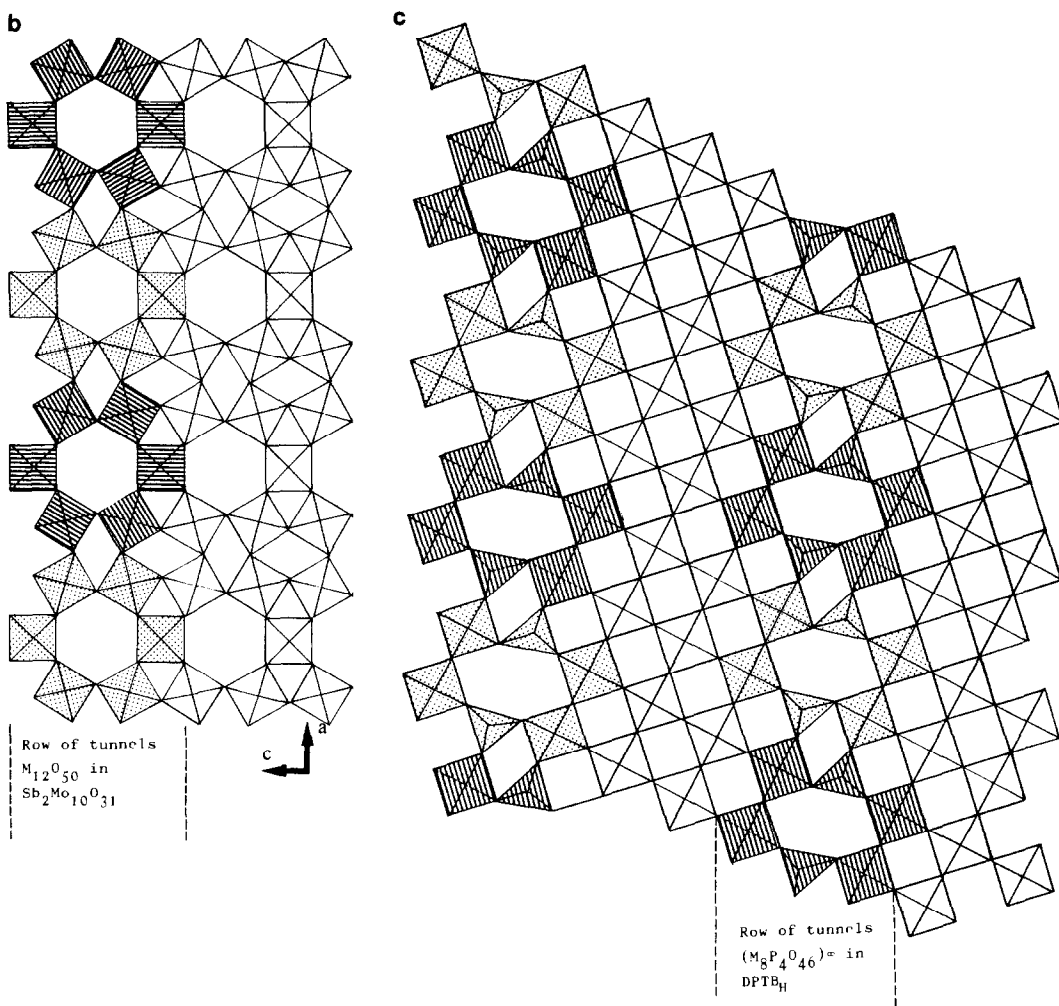


FIG. 3—Continued

six-sided tunnels closely related to HTB's, but the latter's are built up from rings of four NbO_6 octahedra and two PO_4 tetrahedra, as shown for instance from the different types of $[Nb_3P_2O_{13}]_{\infty}$ layers forming the framework of these bronzes (Fig. 4). Moreover, one observes in the latter's brownmillerite tunnels built up from two PO_4 tetrahedra and four NbO_6 octahedra (Figs. 4a and 4c), where zig-zag tunnels involving brownmillerite rings are also observed in the $KV_3P_4O_{17}$ structure (Fig. 1).

Concluding Remarks

These results confirm the great adaptability of VO_6 octahedra and P_2O_7 groups and open the route to the synthesis of new mixed-valent vanadium phosphates. The existence of intersecting tunnels suggests the possibility of ion exchange properties and of ionic conductivity. The magnetic and electric properties of this phase, which exhibits a unidimensional character of the octahedral arrangement, should also be investigated.

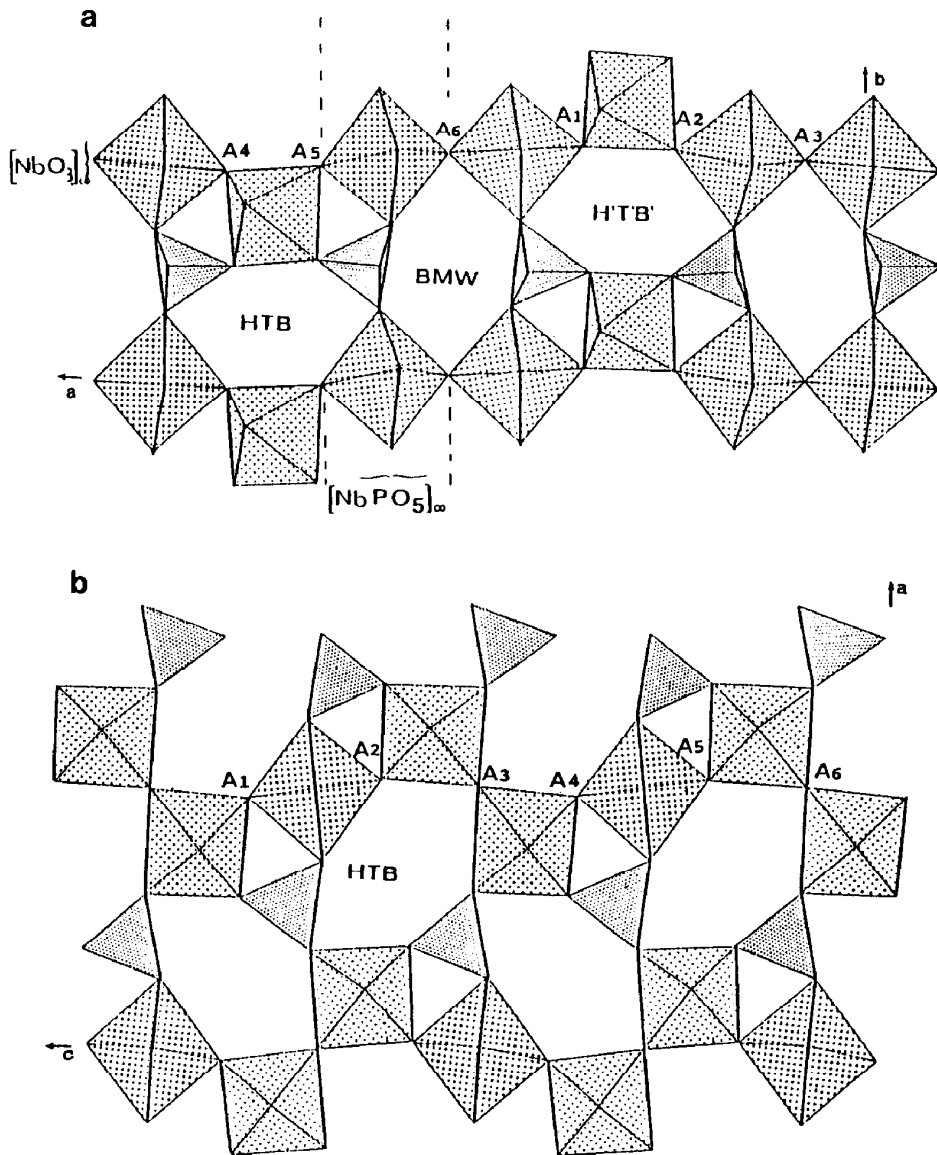


FIG. 4. $[\text{Nb}_3\text{P}_2\text{O}_{13}]_x$ layers in (a) $\text{K}_4\text{Nb}_8\text{P}_5\text{O}_{34}$, (b) $\text{K}_3\text{Nb}_6\text{P}_4\text{O}_{26}$, and (c) $\text{K}_7\text{Nb}_{14}\text{P}_9\text{O}_{60}$.

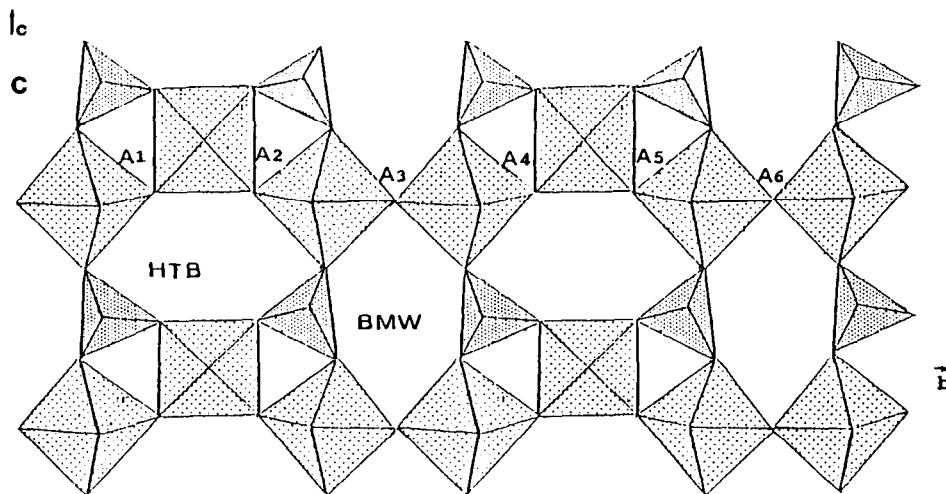


FIG. 4—Continued

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