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The Molybdenotungsten Monophosphate $MoWO_3(PO_4)_2$: An Original Three-Dimensional Framework Built Up of "MPO_8" Chains (M = Mo, W)

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A new molybdenotungsten monophosphate $(Mo_xW_{2-x})O_3(PO_4)_2$ has been synthesized for $0 \le x \le 1.25$. The crystal structure of the phase $MoWO_3(PO_4)_2$ has been determined. This phase crystallizes in the $P2_1/m$ space group with $a = 7.827(1)$ Å, $b = 12.538(1)$ Å, $c = 7.833(1)$ Å, $\beta = 92.36(1)°$. The structure can be described from the assemblage of two kinds of $[MPO_8]_\infty$ chains running along b, with a *cis* and *trans* orientation of the PO_4 tetrahedra. Another description which consists of the stacking of two different sorts of $[M_2P_2O_{15}]_\infty$, layers along b is also presented that involves two sorts of bioctahedral units "M_2O_{11}" with the perovskite and HTB configurations, respectively. © 1997 Academic Press

INTRODUCTION

The association of molybdenum and tungsten in the same matrix of transition metal phosphates has allowed original mixed frameworks to be generated, different from the non-substituted molybdenum or tungsten phosphates. This has been shown for the phosphates $Na_x(MoW)_2O_3(PO_4)_2$ (1), $Na_{1+x}(MoW)_2O_5PO_4$ (2), $K_6Mo_3W_9PO_{40} \cdot 13H_2O$ (3), and $K_{6.6}Mo_{2.26}W_{3.74}P_4O_{31}$ (4). In this respect, it is of interest to study the substitution of molybdenum for tungsten in the tungsten phosphate $W_2O_3(PO_4)_2$ (5). Such an investigation is all the more interesting since only a structural model could be proposed for the latter tungsten phosphate.

The present paper deals with the study of the phase $Mo_xW_{2-x}O_3(PO_4)_2$, with $0 \le x \le 1.25$, whose structure determination for $x = 1$ shows that it exhibits an original three dimensional framework, different from the structural model proposed for $W_2O_3(PO_4)_2$.

CHEMICAL SYNTHESIS AND CRYSTAL GROWTH

The chemical synthesis of the phase $Mo_xW_{2-x}O_3(PO_4)_2$ was performed by heating stoichiometric mixtures of MoO_3, WO_3, and $H(NH_4)_2PO_4$ in air in a platinum crucible at 1070 K for 12 h. In these conditions a pure solid solution was obtained for $0 \le x \le 1.25$. Beyond $x = 1.25$, the samples were melt and amorphous. Attempts to extend this solid solution by working at lower temperature led to a mixture of WO_3 and $(MoO_2)_2P_2O_7$ (6).

Two different methods were used for crystal growth of the phase $MoWO_3(PO_4)_2$, that both involve a doping of the crystals with Mo(V).

In a first method, the stoichiometric mixture of $H(NH_4)_2PO_4$, WO_3, and MoO_3 in the ratio 2 : 1 : 1 was heated at 600 K in a platinum crucible to decompose the ammonium phosphate. The resulting mixture was then heated at 873 K in an evacuated silica ampoule. A green powder with some green crystals on the silica ampoule were obtained. The microprobe analysis of the single crystals confirmed their cationic composition "$MoWP_2$," and the X-ray single crystal investigation evidenced a monoclinic cell similar to that observed for $W_2O_3(PO_4)_2$ (5).

The second method, starting from a mixture of nominal composition $Li_{0.25}MoWP_2O_{11}$, allowed larger crystals of good quality to be grown. In a first step, the adequate mixture of $H(NH_4)_2PO_4$, Li_2CO_3, MoO_3, and WO_3 in the ratio 2 : 0.125 : 0.96 : 1 was heated similarly at 600 K in a platinum crucible in order to decompose the ammonium phosphate and the carbonate. Then the resulting mixture was added to the required amount of molybdenum metal (0.04 mole), sealed in a evacuated silica ampoule, heated for 100 h at 873 K, cooled at 1 K/h down to 773 K, and finally quenched at room temperature. Green, plate-like crystals mixed with a brown powder were obtained. The microprobe analysis of these crystals, as well as their crystal study, confirmed their cation composition "$MoWP_2$" and their monoclinic cell similar to that obtained by the first method.

The powder X-ray pattern of the $x = 1$ composition of the solid solution synthesized at 1070 K could be perfectly indexed in the monoclinic cell deduced from the single crystal X-ray study (Table 1).

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TABLE 1
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $MoWO_3(PO_4)_2$

Crystal data	
Space group	$P2_1/m$
Cell dimensions	$a = 7.827(1)$ Å, $b = 12.538(1)$ Å, $c = 7.833(1)$ Å
	$\alpha = 90.0°$, $\beta = 92.36(1)°$, $\gamma = 90.0°$
Volume	768.1(1) Å^3
Z	2
Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	ω–θ
Scan width (°)	$1.15 + 0.35 \tan \theta$
Slit aperture (mm)	$1.15 + \tan \theta$
Max θ (°)	45
Standard reflections	3 every h
Reflections measured	6812
Reflections with $I > 3\sigma$	1935
μ (mm^{-1})	17.1
Structure solution and refinement	
Parameters refined	157
Agreement factors	$R = 0.027$ $R_w = 0.025$
Weighting scheme	$w = 1/\sigma^2$
Δ/σ max	< 0.01

TABLE 2
Positional Parameters and Their Estimated Standard Deviations for $MoWO_3(PO_4)_2$

Atom	x	y	z	B(Å^2)
M(1)	0.14929(4)	0.49729(8)	0.69218(4)	0.78(1)
M(2)	0.3591(1)	0.25	0.2021(1)	0.57(3)
M(3)	0.3608(1)	0.75	0.1898(1)	0.68(3)
P(1)	0.2526(2)	0.4946(3)	0.1173(2)	0.62(3)
P(2)	0.2494(3)	0.75	0.6037(3)	0.50(5)
P(3)	0.0741(3)	0.25	0.8468(4)	0.70(5)
O(1)	0.3309(6)	0.4761(5)	0.5881(7)	1.7(2)
O(2)	0.0	0.5	0.5	1.1(2)
O(3)	0.1694(7)	0.6534(5)	0.6903(8)	1.4(2)
O(4)	0.2622(5)	0.5050(8)	0.9228(6)	1.1(1)
O(5)	0.1016(7)	0.3473(5)	0.7355(8)	1.2(1)
O(6)	− 0.0767(6)	0.5311(5)	0.8295(7)	1.4(2)
O(7)	0.2080(9)	0.25	− 0.005(1)	1.4(3)
O(8)	0.3761(6)	0.4034(5)	0.1754(8)	0.8(1)
O(9)	0.204(1)	0.25	0.346(1)	1.4(2)
O(10)	0.5662(9)	0.25	0.017(1)	1.0(2)
O(11)	0.555(1)	0.25	0.356(1)	1.8(3)
O(12)	0.1011(9)	0.75	0.077(1)	1.4(2)
O(13)	0.3254(8)	0.5949(5)	0.2039(8)	1.3(2)
O(14)	0.220(1)	0.75	0.413(1)	1.0(2)
O(15)	0.548(1)	0.75	0.308(1)	1.4(2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3 \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \beta_{ij}$. $M(1) = W_{0.55}Mo_{0.45}$, $M(2) = W_{0.47}Mo_{0.53}$, $M(3) = W_{0.35}Mo_{0.65}$.

STRUCTURE DETERMINATION

A green plate-like crystal with $0.130 \times 0.058 \times 0.013$ mm dimensions was selected from the "$Li_{0.25}MoWP_2O_{11}$" mixture for the structure determination. The cell parameters reported in Table 1 were determined and refined by diffractometric technique at 294 K with least squares refinement based upon 25 reflections in the range $18° < \theta < 25°$. They are similar to those obtained by Kierkegaard (5) for $W_2O_3(PO_4)_2$. The systematic absences $k = 2n + 1$ for $0k0$ are consistent with the space groups $P2_1$ and $P2_1/m$. The refinement of the structure was successful in the centrosymetric group $P2_1/m$. As seen before by Kierkegaard for $W_2O_3(PO_4)_2$, the k odd reflections are very weak in whole space, so that a pseudo-translation 0 1/2 0 should be involved. The structure was solved by the heavy atom method. The Mo and W atoms were first distributed at random in the three metallic M sites. The refinement of the occupancy of the sites led to a preferential occupation of M(1) by tungsten (55% W, 45% Mo), whereas the two other sites were preferentially occupied by molybdenum with 47% W and 53% Mo for M(2) and 35% W and 65% Mo for M(3) (Table 2). Such a distribution of the metallic atoms leads to the formulation $Mo_{1.04}W_{0.96}O_3(PO_4)_2$ which is in perfect agreement with the microprobe analysis of the crystals. The oxygen and phosphorus sites were deduced from Fourier differences series. The refinement of all the atomic parameters and anisotropic thermal factors with a full matrix least squares method led to $R = 0.027$ and $R_w = 0.025$ and to the parameters in Table 2. One should emphasize that the (Mo, W) and oxygen sites, and half of the phosphorus sites are related by a pseudo-translation 0 1/2 0; only the remaining phosphorus atoms destroy this pseudo-translation. This fact is consistent with the dramatic weakening of the k odd reflections.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

These results confirm the atomic positions determined for tungsten and three quarters of phosphorus by Kierkegaard (5) for $W_2O_3(PO_4)_2$, and show that the oxygen and the last quarter of phosphorus sites are different from the structural model proposed by this author. Such a difference could be expected since the latter model did not take into account the k odd reflections, leading to a b parameter of 6.72 Å instead of 12.54 Å.

The projection of the structure of this phase along **b** (Fig. 1) shows that the $[M_2P_2O_{11}]_\infty$ framework consists of bioctahedral units M_2O_{11} connected through single PO_4 tetrahedra. Each octahedral unit is formed of two corner-shared Mo_6 octahedra, but two kinds of M_2O_{11} units are observed: in the first, corresponding to the M(1) sites, the two octahedra form O–O–O angles of 90° as in perovskite, whereas in the second, the two octahedra M(2) and M(3)

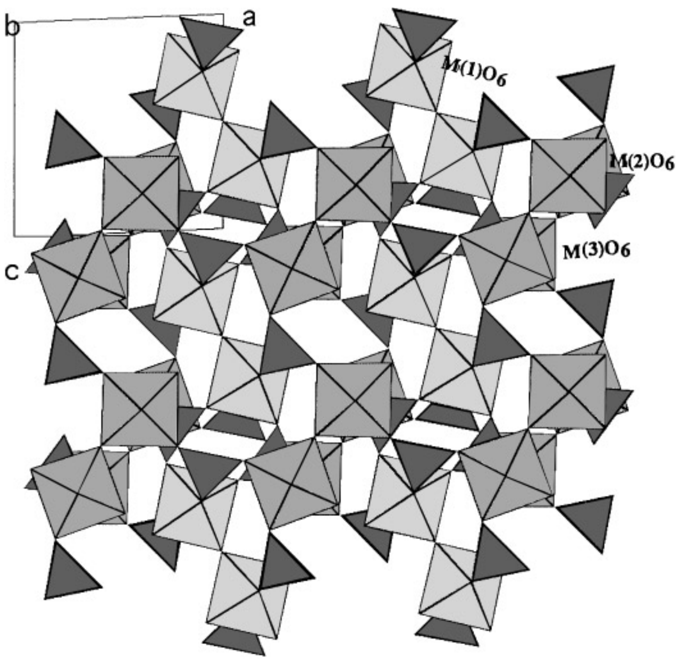

FIG. 1. The projection of the structure of $MoWO_3(PO_4)_2$ along **b**.

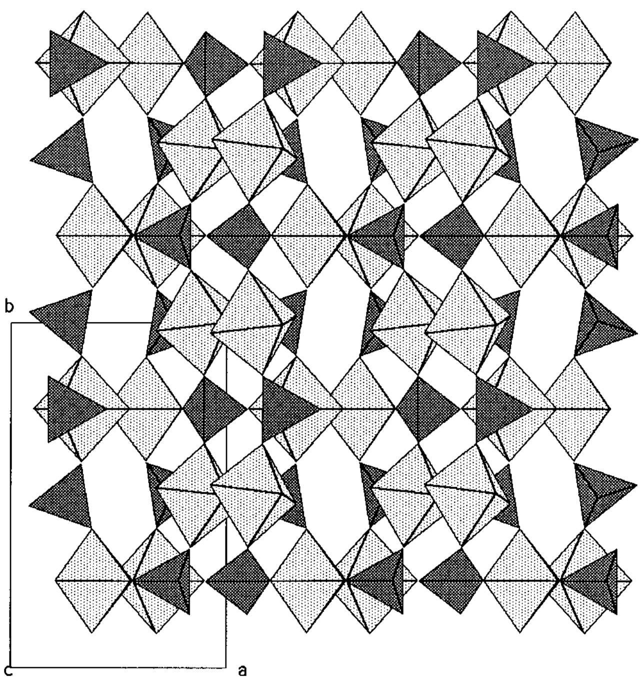

FIG. 2. The projection of the structure of $MoWO_3(PO_4)_2$ along **c**.

form O–O–O angles of 60°–120°, like in the hexagonal tungsten bronze (HTB) structure.

In this three-dimensional framework, each PO_4 tetrahedron shares its four apices with four MO_6 octahedra and exhibits P–O distances (Table 3) characteristic of monophosphate groups. Each MO_6 octahedron is linked along **b** to two PO_4 tetrahedra and in the (0 1 0) plane to the two other PO_4 tetrahedra. Thus a pecularity of the MO_6 octahedra deals with the fact that they exhibit one free equatorial apex. The $M(1)$ and $M(2)$ octahedra that are about half occupied by tungsten (or molybdenum) exhibit a similar geometry (Table 3), with one shorter M–O bond (1.688–1.691 Å) corresponding to the free apex (O(1) and O(9), respectively), four intermediate M–O distances (1.860–1.980 Å), and one abnormally long M–O bond (2.150–2.221 Å) corresponding to the equatorial oxygen O(6) or O(10) that is opposed the free apex. The $M(3)$ octahedra that are preferentially occupied by molybdenum are also strongly distorded. The two shortest $M(3)$–O bonds of 1.701 and 1.737 Å correspond to the free oxygen atom O(15) and to the O(10) atom forming the $M(3)$–O(10)–$M(2)$ bond, respectively, whereas the two longer bonds, $M(3)$–O(14) (2.101 Å) and $M(3)$–O(12) (2.181 Å), are opposed to the two shortest $M(3)$–O bonds in the basal plane of these octahedra; the two intermediate $M(3)$–O distances of 1.968 Å correspond to the apical P–O–Mo–O–P bonds along **b**.

The view of this structure along **c** (Fig. 2) shows that the whole structure can be described by the assemblage of $[MPO_8]_\infty$ chains running along **b** in which one MO_6 octahedron alternates with one PO_4 tetrahedron along **b**; thus, the octahedra of one chain share one apex with the MO_6 octahedra or with the PO_4 tetrahedra of the adjacent chain, forming the $[MoWP_2O_{11}]_\infty$ framework. A three-dimensional framework built up of $[MPO_8]_\infty$ chains was also proposed in the structural model of $W_2O_3(PO_4)_2$ (5), but the relative orientation of the PO_4 tetrahedra and octahedra within the chains and from one chain to the other are fundamentally different for the actual structure. In fact, two kinds of $[MPO_8]_\infty$ chains must be distinguished according to the relative orientation of the PO_4 tetrahedra with respect to each other in the same chain (Fig. 3). In the first type of chain, two successive PO_4 tetrahedra exhibit a *trans* orientation with respect to each other (Fig. 3a) with the periodicity "$M(1)$–P(2)–$M(1)$–P(3)–$M(1)$." In contrast, the second kind of chain is characterized by a *cis* geometry of the orientation of the PO_4 tetrahedra (Fig. 3b) according to the sequence "$M(1)$–P(1)–$M(3)$–P(1)–$M(1)$." Note that in the *cis* chain, one observes a pseudo-translation 0 1/2 0 for all the heavy atoms and for almost all the oxygen atoms, whereas for the *trans* chain, only the (Mo, W) atom and some oxygen atoms respect this translation. Two identical *cis* chains or *trans* chains share the apices of their MO_6 octahedra forming two sorts of $[M_2P_2O_{14}]_\infty$ double chains delimiting browmillerite-like windows, that are about 90° oriented with respect to each other (Fig. 3c). Note also that a *trans* chain and a *cis* chain are linked in the following way: the PO_4 tetrahedra of one chain share one apex with the MO_6 octahedra of the other.

TABLE 3
Distances (Å) and Angles (°) in Polyhedra for $MoWO_3(PO_4)_2$

M(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	**1.688(5)**	2.671(5)	2.696(8)	2.721(7)	2.708(8)	3.836(7)
O(2)	97.2(2)	**1.868(1)**	2.742(6)	3.824(4)	2.753(6)	2.701(5)
O(3)	94.8(3)	91.3(2)	**1.964(6)**	2.681(9)	3.894(8)	2.724(8)
O(4)	95.5(2)	167.2(2)	85.7(3)	**1.980(4)**	2.739(9)	2.741(6)
O(5)	95.9(3)	92.3(2)	168.1(3)	88.3(3)	**1.950(6)**	2.806(8)
O(6)	177.3(3)	84.2(2)	82.8(3)	83.1(2)	86.3(2)	**2.150(5)**

M(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(8^{i})
O(7)	**1.971(8)**	2.700(8)	2.752(9)	2.798(9)	3.843(9)	2.700(8)
O(8)	87.3(2)	**1.940(6)**	2.729(8)	2.757(8)	2.739(8)	3.847(8)
O(9)	97.3(4)	97.3(2)	**1.691(9)**	3.91(1)	2.75(1)	2.729(8)
O(10)	83.7(3)	82.8(2)	179.0(4)	**2.221(8)**	2.66(1)	2.757(8)
O(11)	163.5(4)	90.6(2)	99.2(4)	79.8(3)	**1.914(9)**	2.739(8)
O(8^{i})	87.3(2)	165.0(3)	97.3(2)	82.8(2)	90.6(2)	**1.940(6)**

M(3)	O(12)	O(13)	O(14)	O(15)	O(10^{ii})	O(13^{ii})
O(12)	**2.181(7)**	2.775(8)	2.752(9)	3.87(1)	2.739(9)	2.775(8)
O(13)	83.8(2)	**1.968(6)**	2.690(8)	2.713(9)	2.759(8)	3.889(8)
O(14)	79.9(3)	82.7(2)	**2.101(8)**	2.73(1)	3.82(1)	2.690(8)
O(15)	170.9(4)	95.1(2)	91.0(4)	**1.701(9)**	2.65(1)	2.713(9)
O(10^{ii})	87.8(8)	96.0(2)	167.7(3)	101.3(4)	**1.737(8)**	2.759(8)
O(13^{iii})	83.8(8)	162.3(3)	82.7(2)	95.1(2)	96.0(2)	**1.968(7)**

P(1)	O(8)	O(13)	O(4^{iv})	O(6^{v})
O(8)	**1.554(7)**	2.446(9)	2.489(9)	2.483(7)
O(13)	105.1(3)	**1.527(7)**	2.504(8)	2.513(8)
O(4^{iv})	107.3(4)	109.8(5)	**1.534(5)**	2.514(7)
O(6^{v})	109.0(2)	112.7(4)	112.3(3)	**1.490(5)**

P(2)	O(3)	O(14)	O(11^{vi})	O(3^{iii})
O(3)	**1.534(6)**	2.537(9)	2.51(1)	2.420(8)
O(14)	113.1(3)	**1.505(8)**	2.47(1)	2.537(9)
O(11^{vi})	109.2(3)	108.2(5)	**1.547(9)**	2.51(1)
O(3^{iii})	104.2(4)	113.1(3)	109.2(3)	**1.534(6)**

P(3)	O(5)	O(7^{vii})	O(12^{viii})	O(5^{i})
O(5)	**1.521(6)**	2.481(9)	2.517(8)	2.441(8)
O(7^{vii})	109.0(3)	**1.529(8)**	2.463(9)	2.481(8)
O(12^{viii})	112.1(3)	107.9(5)	**1.517(8)**	2.517(8)
O(5^{i})	106.8(4)	109.0(3)	112.1(3)	**1.520(6)**

Symmetry codes

i : $x; 1/2-y; z$	v : $-x; 1-y; 1-z$
ii : $-x; -y; -z$	vi : $-1-x; -1-y; -1-z$
iii: $x; 3/2-y; z$	vii : $x; y; 1+z$
iv: $-x; y; -z$	viii: $-x; -1-y; -1-z$

The structure of the monophosphate $MoWO_3(PO_4)_2$ can also be described in a very simple way by considering the stacking along **b** of two kinds of layers of polyhedra labeled *A* and *B* (or *B*′), respectively. All of them have the same formulation $[M_2P_2O_{15}]_\infty$ but exhibit a different structure. The *A* layers consist of disconnected infinite chains $[M_2P_2O_{15}]_\infty$ running along **c** (Fig. 4). In such chains the *M*(1) bioctahedra, that exhibit the "perovskite configuration" are bridged by two PO_4 tetrahedra. The *B* (or *B*′) layers are built up of the HTB bioctahedral units *M*(2)*M*(3)

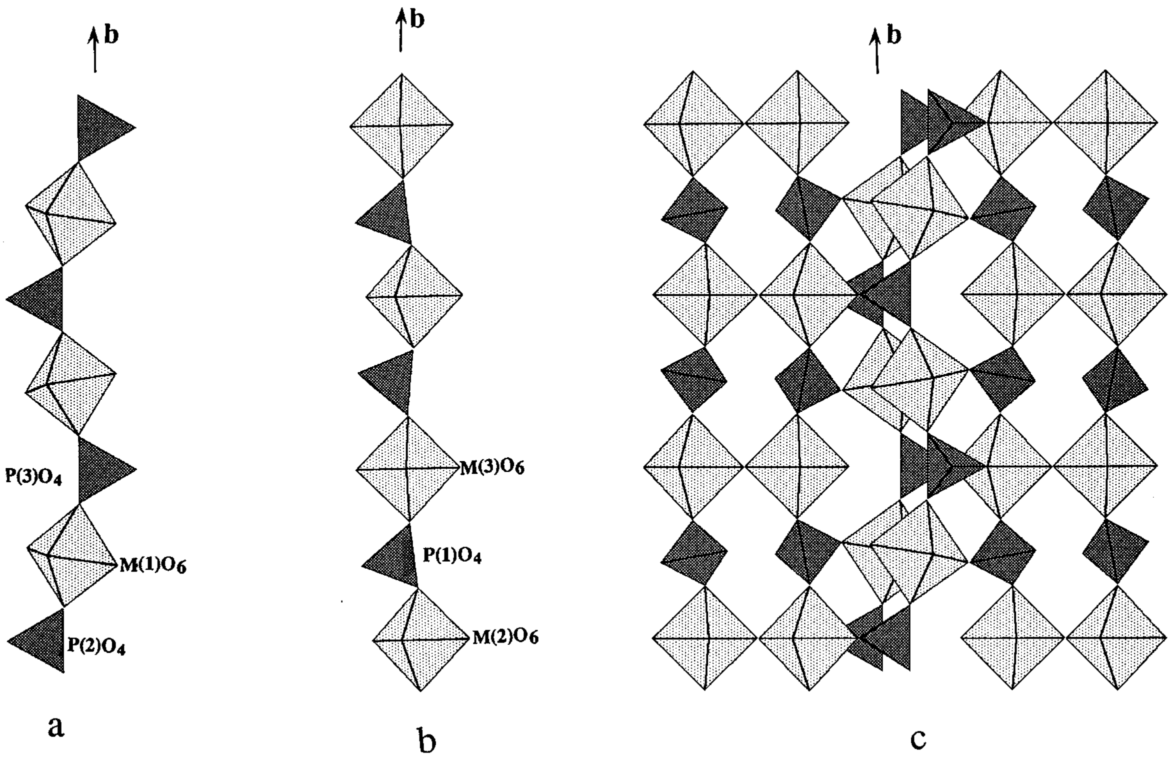

FIG. 3. The $[MPO_8]_\infty$ chains. (a) *trans* orientation of the PO_4 tetrahedra; (b) *cis* orientation of the PO_4 tetrahedra; (c) the assemblage of the $[MPO_8]_\infty$ chains leading to the browmillerite window.

interconnected through P(2) and P(3) tetrahedra forming a bidimensional framework (Fig. 5). This *B* layer can be described as $[M_2PO_{13}]_\infty$ chains running along **c** interconnected along **a** through PO_4 tetrahedra. In fact, two successive *B* layers exhibit two different orientations with respect to each other: they are turned by 180° with respect to each other due to the 2_1 screw axis, so that they can be named *B* and *B′*, respectively. Thus, the $[MoWP_2O_{11}]_\infty$ framework can be described by the stacking along **b** of these two kinds of layers according to the sequence "*ABAB′*," in

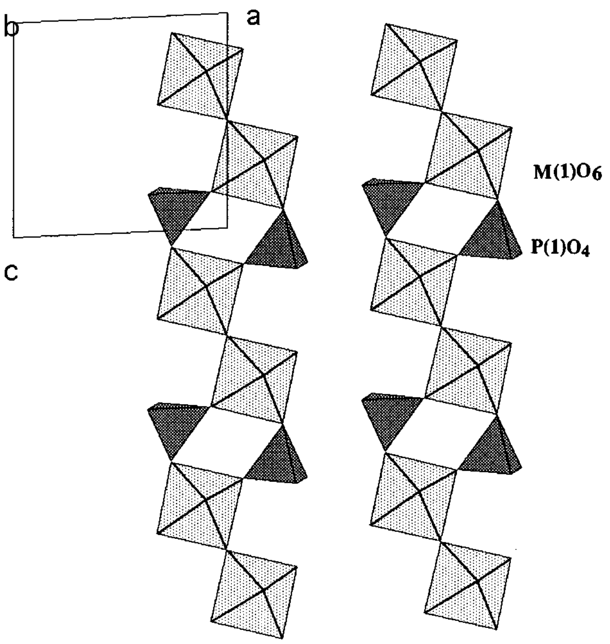

FIG. 4. The *A* layer $[M_2P_2O_{15}]$.

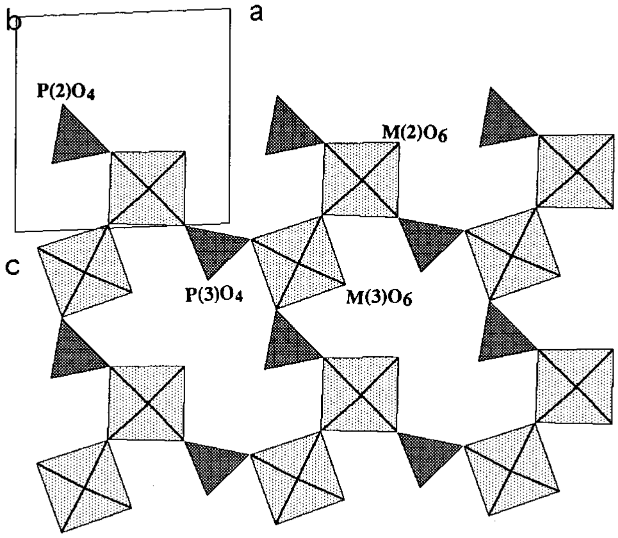

FIG. 5. The *B* layer $[M_2P_2O_{15}]$.

such a way that the tetrahedra of one layer is linked to the octahedra of the next.

As a conclusion, this study has allowed a new structural type of be evidenced and shows that an important substitution of molybdenum for tungsten in the tungsten monophosphate $W_2O_3(PO_4)_2$ can be performed without any significant modification of the structure. The green color of the crystal suggests that the octahedral sites are doped with Mo(V) in agreement with the method of growth; the existence of some oxygen vacancies is most likely but of course cannot be detected due to their very low concentration.

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