

Structural Study of $P_4W_{14}O_{50}$, a New Odd Member in the Series $(PO_2)_4(WO_3)_{2m}$

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Single crystals of the odd member $m = 7$ of the series of low dimensional tungsten bronzes $(PO_2)_4(WO_3)_{2m}$ have been grown by means of chemical vapor transport technique. The structure has been solved from X-ray diffraction data in the monoclinic space group $P2_1/n$ with the lattice parameters $a = 5.291(1)$ Å, $b = 6.557(2)$ Å, $c = 26.654(8)$ Å, and $\beta = 90.19^\circ$. In contrast to the $m = 5$ compound whose structure has been found as corresponding to the regular intergrowth of the two even members $m = 4$ and $m = 6$, the $m = 7$ compound can be considered as a pure phase whose structure is similar to that of $m = 4$, 6, or 8 members. It can indeed be described by a stacking of WO_6 octahedral slabs of ReO_3 -type, all of the same thickness, connected through PO_4 tetrahedra. The difference about the crystal symmetry between the terms $m = 7$ and $m = 6$ is discussed in terms of tilting of WO_6 octahedra. © 1996 Academic

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INTRODUCTION

After the discovery of the diphosphate tungsten bronzes (1), structural studies from single crystal X-ray diffraction and also from high resolution electron microscopy revealed that a large series of compounds has to be considered (2–6).

The structural basic principle of these new materials consists of rows or columns and mostly layers, built up of corner-sharing WO_6 octahedra, connected through PO_4 tetrahedra or P_2O_7 ditetrahedra. Most of these compounds belong to three “layers” families: diphosphate tungsten bronzes with hexagonal tunnels ($DPTB_h$) with the general formula $A_x(P_2O_4)_2(WO_3)_{2m}$ and monophosphate tungsten bronzes either with hexagonal tunnels ($MPTB_h$) or with pentagonal tunnels ($MPTB_p$) with the general formula $A_x(PO_2)_4(WO_3)_{2m}$ or $(PO_2)_4(WO_3)_{2m}$, respectively. A refers to a cation (Na, K, Rb, Tl, Ba) and m is an integer which is related to the width of the perovskite ReO_3 -type infinite layers of WO_3 composition, all built up of WO_6 octahedra. In the three families indeed, the intergrowth of

octahedral WO_3 layers and diphosphate or phosphate slices can be synthesized as pure phases with different widths of the layers, i.e., with different m values in the range of 4 to 16.

Such a mixed framework consists of WO_3 layers of metallic character, due to the mixed valency of tungsten, interconnected with insulating slices of PO_4 groups and consequently should exhibit anisotropic properties. For six years, the $MPTB_p$ family, i.e., the family whose members crystallize without inserted cations, has been the subject of a particular interest inferred from the structural quasi-two-dimensional electronic properties of all its members, and numerous physical properties were explored with respect to different m values. Thus, electronic instabilities were pointed out from anomalies in the electrical conductivity (7–9): incommensurate charge density waves (CDW) were revealed by X-ray diffuse scattering at low temperature (10–16) and by electron microscopy (17, 18); large magnetoresistance equally at low temperature were attributed to the existence of small electrons and hole pockets on the Fermi surface in the CDW state with large mobilities (19–22); band structure calculations, performed in the two-dimensional approximation, showed three bands crossing the Fermi level (23, 24). A theory called “hidden nesting” or hidden one-dimensionality was proposed based on the presence of infinite ribbons of WO_6 octahedra in three directions of the structure.

The interest of the measurements in the series of compounds $(PO_2)_4(WO_3)_{2m}$ belonging to $MPTB_p$ is enhanced by the fact that the physical properties can be studied for increasing m values and then compared, one with the others, in relation to the structural features. However, it is easier to grow large single crystals as pure phase for small m values than for high m values so the more studied crystals are mostly related to the $m = 4, 6, 7$, and 8 values. Among these compounds, the $m = 4, 6$, and 8 structures are known: they are all of orthorhombic symmetry with successive WO_3 slabs, all of the same width for a given m value (25, 26). Alone, the $m = 7$ structure is unknown and it is of great interest to determine the structure of such a

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crystal with an odd m value. Indeed, up to now, the only odd m with an already published structure, $m = 5$ (27), is monoclinic and consists of a regular intergrowth of $m = 4$ and $m = 6$ WO_3 layers separated by PO_4 tetrahedra. One challenge of this study was to verify whether this phenomenon is general for odd m members, thereby explaining the rather different electron transport behavior of the $m = 7$ member (19) compared to that of the $m = 4$ and 6 members, or to determine if other structural features are involved.

The present paper deals with the crystallographic study of the $m = 7$ member of the series $(\text{PO}_2)_4(\text{WO}_3)_{2m}$, i.e., $\text{P}_4\text{W}_{14}\text{O}_{50}$.

EXPERIMENTAL

1. Preparation

Platelike purple crystals of $\text{P}_4\text{W}_{14}\text{O}_{50}$ ($m = 7$) were prepared by chemical vapor transport technique. As reported elsewhere (25) a mixture of $(\text{NH}_4)_2\text{HPO}_4$ and WO_3 was first heated at 600°C in air for 10 hr to decompose the ammonium phosphate. Then an appropriate amount of metallic tungsten was added before the mixture was heated in an evacuated sealed quartz tube.

For this study, the goal of the experiments being the preparation of single crystals of MPTB_p with sizes large enough to allow physical properties to be investigated, particular attention was paid to the temperature gradient which was maintained along the length of the quartz tube. In a typical experiment a charge of about 5 g of the reactant mixture was packed in a quartz tube of 20 cm long and 2 cm in internal diameter. The tube was inserted in a horizontal furnace having two heating zones 20 cm apart. The temperature of the furnace which was initially set at 600°C was raised to 1200°C for the hot zone and 1000°C for the cold zone at a rate of about $100^\circ\text{C}/\text{hr}$. The reaction was carried out under these conditions for 1 week and then slowly cooled to 600°C . The platelike crystals used in this study were obtained from a stoichiometric mixture corresponding to $m = 6$. They grew in the cold zone of the quartz tube from which they were taken off after being washed with 20% HF for 10 mn.

2. Preliminary Crystal Study

All X-ray diffraction films, realized from a $m = 7$ member, gave the aspect of an orthorhombic crystal with parameters $a \approx 5.3 \text{ \AA}$, $b \approx 6.5 \text{ \AA}$, and $c \approx 26.6 \text{ \AA}$. For most of the samples, the row of the rotating crystal was $[110]$ and it was rather difficult to deduce unambiguously the actual space group. However, some crystals could be oriented with \mathbf{a} parallel to the ϕ axis of the goniometer head and the reciprocal space was registered both with Weissenberg and precession camera. Laue films have been also realized.

The following observations were made, involving the conditions limiting possible reflections: $h00$ ($h = 2n$); $0k0$ ($k = 2n$); $00l$ ($l = 2n$); $0kl$ (no condition); $h0l$ ($h + l = 2n$); $hk0$ ($h + k = 2n$). We will see later that this last condition ($hk0$: $h + k = 2n$) deduced from a film where all the spots were of weak intensity was not actually true but as it corroborated previous deductions of the electron microscopy analysis (28), it has been first taken into consideration. Further, the orthorhombic symmetry was established, according to all the Laue photographs: two space groups were considered, $Pmnn$ (No. 58) and $P2nn$ (No. 34). However if, on one hand, the zero levels indicated no particular anomaly in the diffraction pattern aspect, on the other hand, the upper levels often showed a splitting of some spots first attributed to the poor quality of the crystallization.

A first structural study has been carried out with a crystal which gave rise to a set of 2946 independent reflections of weak intensity on the whole. The result of the atomic parameter refinement in the orthorhombic space group was not satisfying. This was attributed to a lack of information. But one constancy of the diffractometer, whose adjustment was checked by a Si crystal, was to find a β value of about 90.20° when α and γ were both 90.00° in the range of e.s.d.'s. An other crystal with a larger size was examined. The measured β angle was still $\beta = 90.19^\circ$ and then the extinction conditions were again carefully scrutinized. The conditions $h0l$ ($h + l = 2n$) and $0k0$ ($k = 2n$) were maintained, but the condition $hk0$ ($h + k = 2n$) was discarded because of the presence of some reflections, all of weak intensity, which did not fit the constraint. The symmetry appeared clearly monoclinic with the unique space group $P2_1/n$ associated with the (a, b, c) cell, nearly orthorhombic.

3. Structure Determination

The crystal data, the experimental parameters for the intensity data collection, the strategy used for the crystal structure determination, and the results obtained are listed in Table 1. The cell parameters were refined by least-squares fitting the θ values ($\theta > 25^\circ$) of 25 reflections selected after an examination of their profile and their intensity. Scattering factors for W^{6+} , P^{5+} , and O^{2-} and anomalous dispersion corrections were taken from the International Table for X-ray Crystallography (29). The structure was solved by the heavy atom method using the SDP (30) program. The refinement resulted in apparently satisfactory atomic positions toward interatomic distances, but some distortion in the thermal coefficients U_{ij} of the W atoms and rather high B values of the oxygen atoms suggested an anomaly elsewhere. We realized that such a monoclinic crystal, pseudo-orthorhombic with a β value very near to 90° , could be twinned and a careful examina-

TABLE 1
X-Ray Diffraction Data for $P_4W_{14}O_{50}$

Crystal data	
System	Monoclinic
Space group	$P2_1/n$
Lattice parameters	$a = 5.291(1) \text{ \AA}$ $b = 6.557(2) \text{ \AA}$ $c = 26.654(8) \text{ \AA}$ $\beta = 90.19^\circ$
Cell volume	$924.7(4) \text{ \AA}^3$
Z	1
Crystal size	$0.69 \times 0.15 \times 0.075 \text{ mm}^3$
Linear abs. coeff.	461.6 cm^{-1}
Intensity measurements	
Wavelength	$\lambda = 0.71073 \text{ \AA}$
Temperature	294 K
Scan mode	$\omega - 2/3 \theta$
Scan width ($^\circ$)	$1 + 0.35\theta$
Slit aperture (mm)	$1 + \tan \theta$
θ maximal angle	40°
Standard reflections	3 every 3600 s
Nb meas. reflections	12156 ($-9 \leq h \leq 9, 0 \leq k \leq 11, -48 \leq l \leq 48$)
Nb obs. reflections	8427 ($I > 3\sigma(I)$)
Structure solution and refinement	
Nb reflections used in the refinement	4182 ($l \geq 0$)
Nb of refined parameters	88
Twin ratio	42.1(7) %
Agreement factors	$R = 0.057; R_w = 0.067$
Weighting scheme	$w = 0.33$ if $I < 100$

tion of the splitted reflections already observed resulted in a possible mirror perpendicular to c^* , as macroscopic twin element (Fig. 1 and 2). Assuming a macroscopic (usual) twin, the total intensity of the nearly overlapped reflections in the diffraction pattern is the summation of the reflection intensities from individual twin domains. Using the REMOS program (31), the relative domain size was refined together with the structural parameters improving in a significant way the previous results which did not take into account the twin effect. Note that no single crystal was found among the samples that exhibit sufficient diffracted intensity.

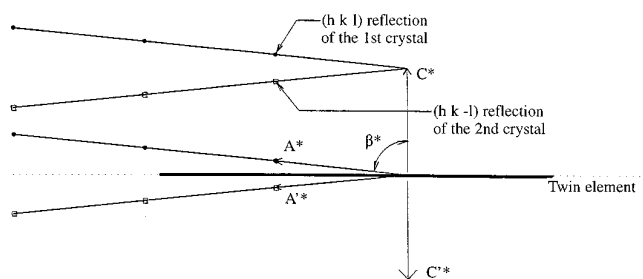


FIG. 1. Schematic drawing of the reciprocal space associated with the twinned crystal for $P_4W_{14}O_{50}$.

The final results are given in Table 2 (atomic positions and B factors) and in Table 3 (interatomic distances). The U_{ij} components of the thermal tensor (Table 4) have been refined with 974 hkl corresponding to the highest θ values. U_{11} coefficients which are rather high compared to U_{22} could be assumed to be due to twinning effect. We tried also to refine both P and O atoms anisotropically, but the results were not satisfactory for some of these atoms and without physical meaning. We thought that the twin effect plays an important role in this fact, the detwinning treatment being probably not perfect since the R values remain a little high. It was judged better to publish only the B_{iso} values of the light atoms.

DISCUSSION

1. Structural Aspect of the New $P_4W_{14}O_{50}$ Member

Like all other even m members of the $MPTB_p$'s, the odd $m = 7$ compound has a structure which can be regarded as a stacking of WO_6 octahedral (001) slabs of ReO_3 -type, all of the same thickness, connected through isolated PO_4 tetrahedra forming layers also parallel to (001). At the junction between two ReO_3 -type slabs, tetrahedra and octahedra form pentagonal tunnels which are empty (Fig. 3). The $m = 7$ value characterizes the thickness of the ReO_3 -

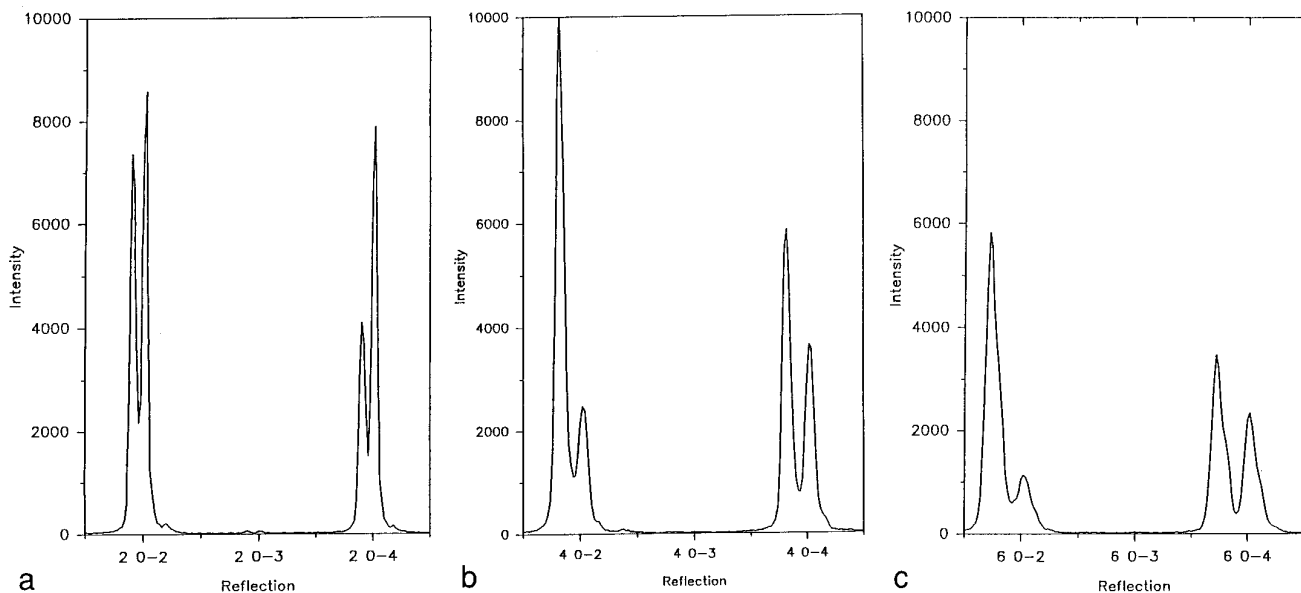


FIG. 2. X-ray profiles of $h0l$ reflections ($h = 2, 4$, and 6) showing the splitting effect due to the twin. Observe that the splitting increases when h increases.

type slabs, for which one observes a herringbone arrangement of the WO_6 octahedral links (Fig. 3). Thus, at a given x level ($x = 0$ or $x = 1/2$), one can observe chevron-shaped strings, built up of links of three and four corner-sharing WO_6 octahedra alternately, bound through a PO_4 tetrahedron. These two types of octahedral links appear also in a same slab, but at a different x level, so that it is easier to visualize the m value by connecting, in a given slab, the

WO_6 octahedra in a direction normal to the link. This number is always 7 in this case.

Moreover, an alternative description of this structure consists in considering it as a succession of identical mixed slices built up of both octahedra and tetrahedra units. Such a slice is constituted from WO_6 octahedra sharing corners as in the perovskite structure bordered on each side by isolated PO_4 tetrahedra which communicate with the **a** and **b** lattice translations. In a perovskite WO_3 framework, a PO_4 tetrahedron is, indeed, easily substituted for a WO_6 octahedron. The synthesis of numerous compounds in the field of the phosphate bronzes has widely proved this feature of a stable mixed polyhedra building. Each lateral

TABLE 2
Refined Atomic Parameters for $\text{P}_4\text{W}_{14}\text{O}_{50}$ with e.s.d's

	x	y	z	$B(\text{\AA}^2)$
W1	0	0.5	0	0.47(1)
W2	0.0075(4)	0.1559(1)	0.11356(2)	0.36(1)
W3	-0.0037(4)	-0.0076(1)	0.32965(2)	0.25(1)
W4	0.0005(4)	0.3276(1)	0.44405(2)	0.45(1)
P	0.482(1)	0.3013(7)	0.2911(1)	0.18(5)
O1	0.5	0	0	0.9(2)
O2	0.495(7)	0.167(2)	0.5600(5)	0.7(2)
O3	0.017(5)	0.155(3)	0.3849(5)	0.9(2)
O4	0.017(6)	-0.006(3)	0.1768(5)	0.6(2)
O5	0.529(4)	0.362(2)	0.2368(5)	0.7(2)
O6	0.285(4)	0.190(3)	0.4681(7)	0.7(2)
O7	0.785(4)	0.145(3)	0.4754(7)	0.7(2)
O8	0.283(4)	0.017(3)	0.0927(6)	0.6(2)
O9	0.786(4)	-0.023(3)	0.0834(6)	0.8(2)
O10	0.231(4)	0.347(3)	0.1512(7)	0.8(3)
O11	0.725(4)	0.310(4)	0.1443(8)	0.9(3)
O12	0.229(4)	0.201(4)	0.2965(7)	0.9(3)
O13	0.701(5)	0.158(4)	0.3050(8)	1.2(3)

TABLE 3
Selected Interatomic Distances (\AA) for $\text{P}_4\text{W}_{14}\text{O}_{50}$ with e.s.d's

	P	W1	W2	W3	W4
O1					1.871(6)
O2		1.94(1)	1.84(1)		
O3				1.82(2)	1.94(2)
O4	1.53(2)		1.99(2)		
O5	1.52(1)			1.97(1)	
O6		1.89(2)			1.87(2)
O7		1.90(2)			1.85(2)
O8			1.81(2)		1.95(2)
O9			1.84(2)		1.95(2)
O10			1.99(2)	1.80(2)	
O11			1.98(2)	1.81(2)	
O12	1.50(2)			2.04(2)	
O13	1.54(3)			2.01(3)	

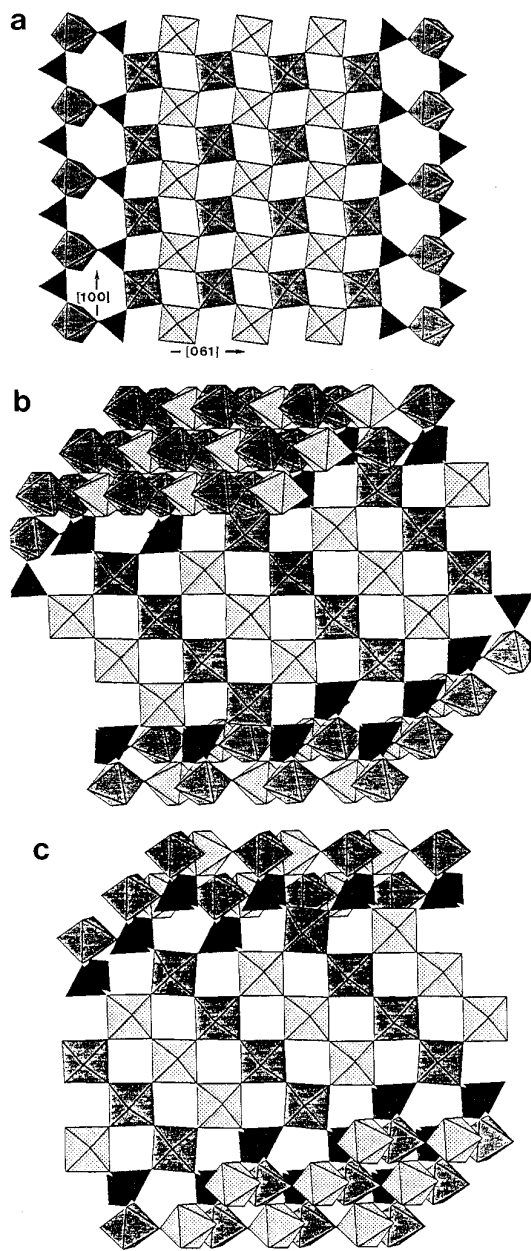


FIG. 4. Projection of the structure along the three axes of the octahedra; (a) along a_p , (b) along b_p , and (c) along c_p (p index referring to the perovskite axes). Note that the tilting of the WO_3 framework occurs only about the a_p direction.

2. Symmetry in the MPTB_p Series

The lattice parameters and the symmetry of the different members of the series $(\text{PO}_2)_4(\text{WO}_3)_{2m}$ studied with X-ray diffraction from single crystals ($2 \leq m \leq 8$) are compared in Table 5; a and b parameters have always about the same value, and the members differ one from the other particularly by the c value. The $m = 5$ member is apart

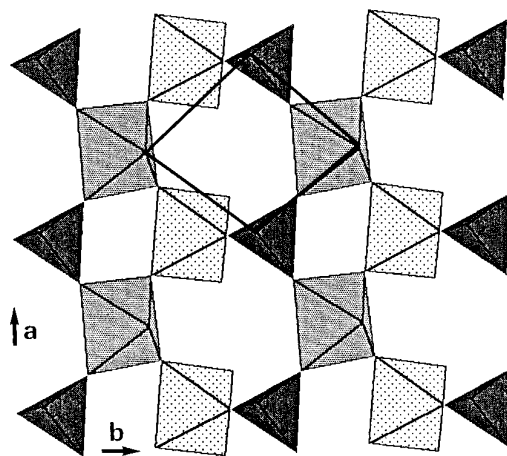


FIG. 5. Structural aspect between two adjacent $[\text{P}_2\text{W}_7\text{O}_{25}]_\infty$. The quadrilateral diamond-shaped formed by four neighbor oxygens is in bold.

because of the intergrowth character of its structure ($m = 4 + m = 6$), the successive slabs being of different widths. All the other members have slabs of the same thickness (Fig. 7), with a basic building principle which is always the same, the links of sharing corners of the WO_6 octahedra being arranged as chevrons in the successive slabs and separated by a PO_4 tetrahedron. The resulting symmetry is orthorhombic for all the m even members, but without center ($P2_1cn$ or $P2_12_12_1$), whereas it appears centrosymmetric in the $m = 7$ odd member, which is discussed here, associated to a monoclinic lattice ($P2_1/n$). This point, which

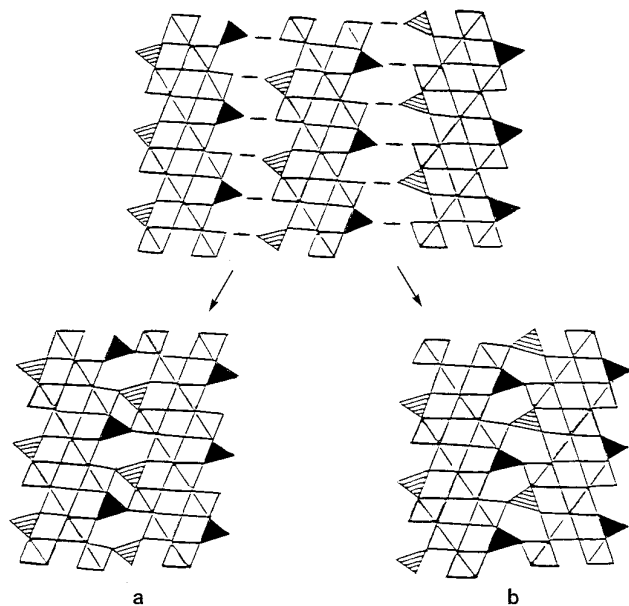
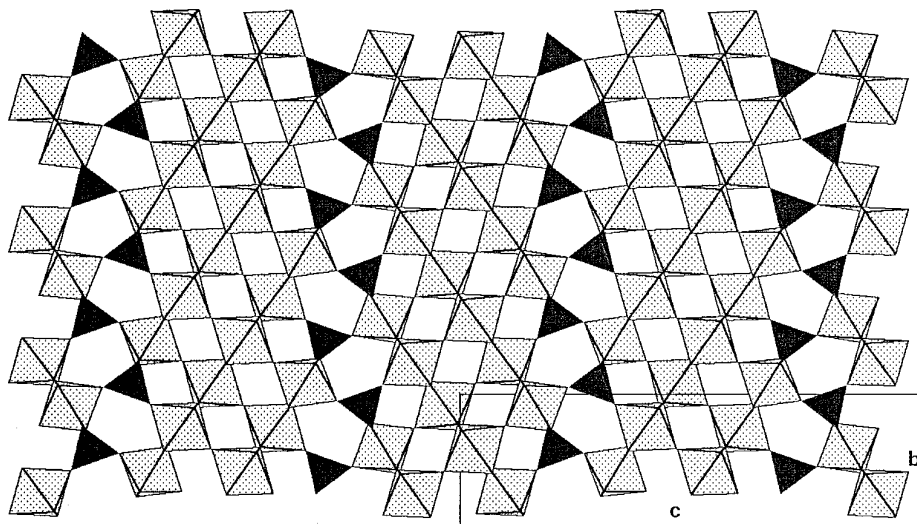


FIG. 6. Projection onto (100) of "elementary" layers whose arrangements lead either to the structure of MPTB_h (a) or to the structure of MPTB_p (b).

FIG. 7. Structure of the $m = 6$ member viewed along $[100]$.

seems rather strange with respect to the similarity of all these structures, can, however, be understood if one considers the tilting of the WO_6 octahedra including some simplified models.

Let us indeed compare the projection along $[100]$ of the idealized models for $m = 6$ (chosen as an even example) (Fig. 8a) and $m = 7$ members (Fig. 8b) for which no tilting of the WO_6 octahedra, supposed regular, has been considered. Some of the edges of the WO_6 octahedra and of the PO_4 tetrahedra are then parallel to the projection plane and some others are perpendicular. The space groups describing the symmetry of these two atomic arrangements are $P2_1/m2_1/c2_1/n$ and $P2/m2_1/n2_1/n$ for $m = 6$ and $m = 7$ members, respectively, therefore both are orthorhombic and centrosymmetric. Between these two groups, there are two major differences: (i) the glide plane c normal to b in $m = 6$ is replaced by a glide plane n in $m = 7$. This change is only due to a $a/2$ translation of the links of three or four WO_6 octahedra in the successive slabs. (ii) The binary axes parallel to a , located in the middle plane of the slabs, are not the same in the two structures: here is the main difference. Indeed, for a $m = 6$ member, the screw axes are located, either along the edges of the octahedra or in holes between octahedra (Fig. 8a), whereas for the $m = 7$ member, the twofold axes run either through the W atoms or through the O atoms in the middle of a four octahedra link (Fig. 8b). Since in both cases a m mirror normal to a is implied, the symmetry centers are located on the binary axes.

Let us now consider a tilting of the WO_6 octahedra, assuming that all the octahedra of the same link are slightly rotated in the same direction. Figure 9 shows clearly that, for the $m = 6$ member, the m mirror perpendicular to a

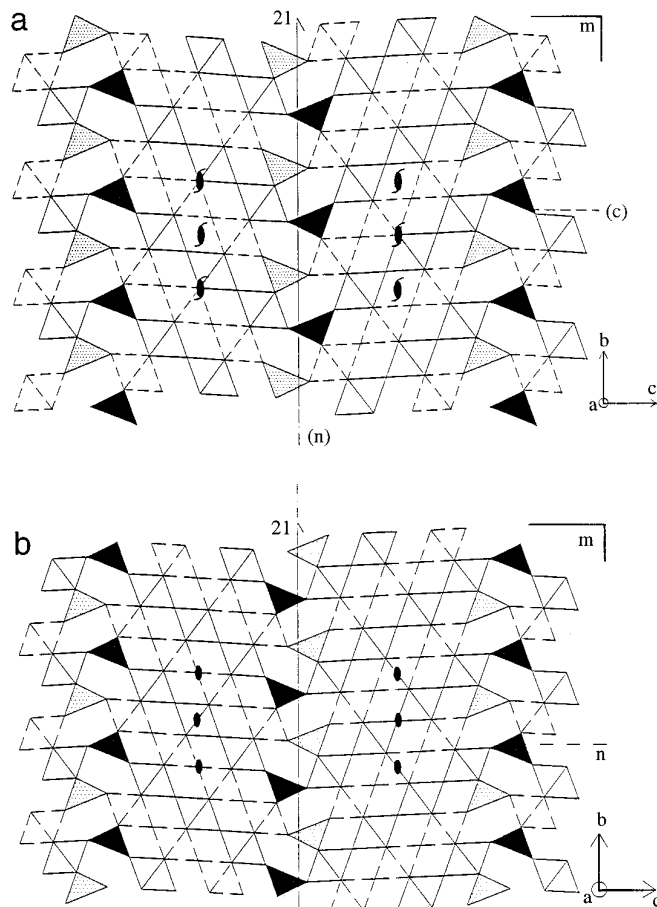
FIG. 8. Projections along $[100]$ of idealized model for $m = 6$ (a) and $m = 7$ (b) members for which no tilting of the WO_6 octahedra has been considered.

TABLE 5
Crystal Parameters for Some Members of the Series $(\text{PO}_2)_4(\text{WO}_3)_{2m}$

Compound	m	a (Å)	b (Å)	c (Å)	Space group	System
$\text{P}_4\text{W}_4\text{O}_{20}$	2	5.23	6.55	11.17	$P2_1cn$	Orthorhombic
$\text{P}_4\text{W}_8\text{O}_{32}$	4	5.28	6.57	17.35	$P2_12_12_1$	Orthorhombic
$\text{P}_4\text{W}_{10}\text{O}_{38}$	5	5.28	6.57	20.57	$P2_1$	Monoclinic
$\text{P}_4\text{W}_{12}\text{O}_{44}$	6	5.29	6.56	23.55	$P2_12_12_1$	Orthorhombic
$\text{P}_4\text{W}_{14}\text{O}_{50}$	7	5.29	6.57	26.65	$P2_1/n$	Monoclinic
$\text{P}_4\text{W}_{16}\text{O}_{56}$	8	5.29	6.55	29.70	$P2_12_12_1$	Orthorhombic

and the symmetry centers are no longer available for the actual structure. In fact, as the 2_1 screw axes subsist, two subgroups of $Pm\bar{c}n$ are now compatible with the new atomic arrangement, $P2_1cn$ and $P2_12_12_1$, both orthorhombic. According to the observed conditions limiting the possible reflections, the group $P2_1cn$ is chosen for the member $m = 2$ (34) and $P2_12_12_1$ for $m = 4, 6$, and 8 (25, 26). The case of the $m = 7$ member is illustrated in Fig. 10: m mirrors normal to \mathbf{a} are suppressed due to the tilting, but also the twofold axes which are no longer available. Only the C symmetry center could subsist. As a result, two possible subgroups $P2_1/n$, one with \mathbf{b} as the unique axis and the other with \mathbf{c} as the unique axis, can be considered: the former is effectively observed. The important point is that the symmetry becomes monoclinic and consequently a monoclinic distortion is certainly possible from the starting orthorhombic atomic arrangement, only due to a tilting of the octahedra which nevertheless maintains the symmetry centers. As expected, the studied monoclinic crystal exhibits locally a noticeable orthorhombic symmetry. Indeed, in the space defined by $0 < x < 1$, $0 < y < 1$, and $0 < z < 1/2$, it is verified that the positions of all the tungsten, phosphorus, and oxygen atoms are slightly deviated from

the more symmetric ones given by the microscopic twin element, a \mathbf{n} glide mirror (001) located at $z = 1/4$.

3. Interatomic Distances

As for the other members of the series $(\text{PO}_2)_4(\text{WO}_3)_{2m}$, and in particular for the $m = 6$ and $m = 8$ compounds, the member $m = 7$ includes, within the octahedral slabs, WO_6 octahedra whose geometry varies from the middle part of the slab to the lateral part where PO_4 tetrahedra are found. In $\text{P}_4\text{W}_{14}\text{O}_{50}$, there are indeed four independent octahedra: W(1) and W(4) are only bound to other octahedra, W(2) is linked to five octahedra and one tetrahedron, and W(3) is surrounded with three octahedra and three tetrahedra. In the three previous mentioned structures, the W–O distances can be distinguished by starting from the middle part of the slab (Fig. 11): the influence of the lateral tetrahedron on the W–O distances is clearly illustrated, involving similar features in the three structures. For $m = 7$, the most regular octahedron is located just in the middle of the slab with 12 O–O distances ranging from 2.69(3) to 2.74(3) Å. The W(1) atom located on a symmetry center has rather a 4 + 2 coordination. In contrast, the furthest octahedron W(3) is very distorted with O–O distances

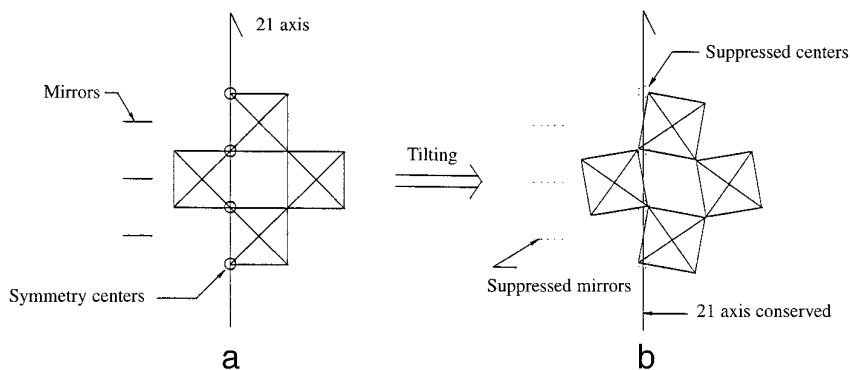


FIG. 9. Schematic representation of the WO_6 octahedra in an idealized structure without tilting (a) and in the actual structure (b) for the $m = 6$ member taken as an even example.

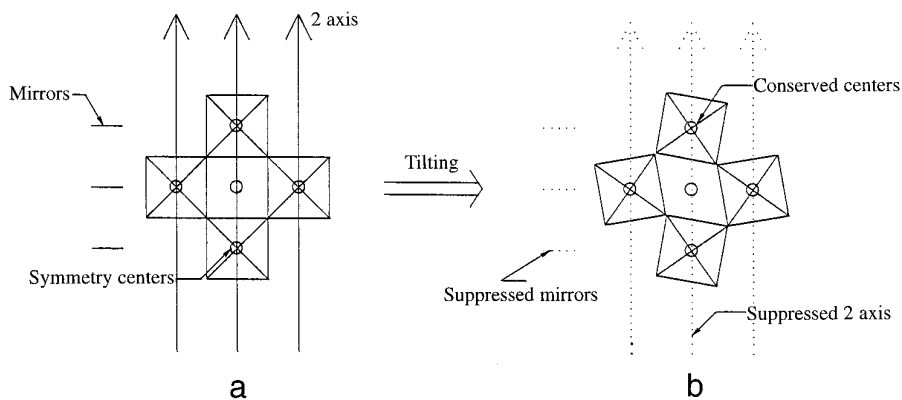


FIG. 10. Schematic representation of the WO_6 octahedra in an idealized structure without tilting (a) and in the actual structure (b) for the $m = 7$ member.

ranging from 2.61(3) to 2.82(3) Å and with a 3 + 3 coordination. Thus, the two intermediate octahedra exhibit intermediate distortion as for $m = 6$ and $m = 8$, and hence one observes a gradual distortion of the WO_6 octahedra both in the O–O and in the W–O distances from the center to the side of the slabs.

The dispersion of the W–O distances can be correlated to the oxidation state of the tungsten atoms calculated from the relation of bond length–bond strength theory (35) as can be seen in Fig. 11. One observes that the formal valence state of W atoms decreases as the distance from the

PO_4 tetrahedra increases, which implies that the electron delocalization mainly occurs in the middle part of the slab.

CONCLUSION

The crystallographic study of the odd $m = 7$ member of the series $(PO_2)_4(WO_3)_{2m}$ showed that its structural properties are very different from that of the $m = 5$ member though the monoclinic symmetry is available for both compounds. Indeed if, on one hand, the $m = 5$ structure $P_4W_{10}O_{38}$ can be described as an intergrowth of the $m =$

		1.80	1.85	1.90	1.95	2.0	2.05			
$m=6$	5.67	W(1)		•••	••	•		6ϕ	5.54	
		W(2)	••	•		•••		$5\phi + 1T$	5.67	
		W(3)	•	••		•	••		$3\phi + 3T$	5.79
$m=7$	5.71	W(1)			••	•		6ϕ	5.58	
		W(4)		••		•••		6ϕ	5.68	
		W(2)	•	••			•••		$5\phi + 1T$	5.75
		W(3)	•••			•	•	•	$3\phi + 3T$	5.85
$m=8$	5.75	W(1)		•	••••	•		6ϕ	5.73	
		W(3)		••	•	•••		6ϕ	5.71	
		W(2)	•	••			•••		$5\phi + 1T$	5.76
		W(4)	•••			•	••	•	$3\phi + 3T$	5.81
			1.80	1.85	1.90	1.95	2.0	2.05		
	Mean oxidation state	Atom	W–O Distances (Å) in the octahedra				Six neighbors polyhedra	Calculated oxidation state		

FIG. 11. Dispersion of the W–O distances observed for three members of the series $(PO_2)_4(WO_3)_{2m}$. The calculated oxidation state of W is reported in the last column.

4 and $m = 6$ members and consequently with successive WO_3 slabs of different widths, on the other hand the new $m = 7$ structure $\text{P}_4\text{W}_{14}\text{O}_{50}$ exhibits successive slabs of the same width, and consequently has exactly the same structural behavior as all the even members of the series, known at the present time. However, the even members are all of orthorhombic symmetry without center, whereas $\text{P}_4\text{W}_{14}\text{O}_{50}$ crystallizes in a centrosymmetric group. This difference is due to the unequal number of WO_6 octahedra in the links which build the slabs in $\text{P}_4\text{W}_{14}\text{O}_{50}$. It results probably in a slight adjustment stress at the junction between the slabs which induces a little monoclinic distortion from the orthorhombic symmetry.

Compared to its $m = 4$ and $m = 6$ parent compounds, which have been more extensively studied in the viewpoint of charge density wave instabilities (15), the odd member $m = 7$ exhibits also, as recently shown (16), two structural transitions at 188 and 60 K, respectively. However, in contrast to $m = 4$ and $m = 6$, the satellite reflections of the upper transition suggest very unusual behaviors like unexpected hysteresis phenomena also observed in resistivity measurements (21). Further studies including X-ray diffuse scattering, electron transport properties, magnetoresistance, and Hall effect measurements have been scheduled in the framework of European Human Capital and Mobility contract to provide more information on the CDW instabilities of these quasi-two-dimensional metallic compounds.

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Note added in proof. The X-ray structure determination of the oxide $(\text{Mo}, \text{W})_9\text{O}_{25}$ has been recently published by O. G. D'Yachenko, V. V. Tabachenko, and M. Sundberg (*J. Solid State Chem.* **119**, 8 (1995)). The results are very close to that described here for $\text{P}_4\text{W}_{14}\text{O}_{50}$ and confirm the weak monoclinic distortion of the lattice ($\beta = 90.2^\circ$).

REFERENCES

- J. P. Giroult, M. Goreaud, Ph. Labbé, and B. Raveau, *Acta Crystallogr. Sect. B* **36**, 2570 (1980).
- B. Raveau, *Indian Acad. Sci.* **96**, 419 (1986); B. Raveau, *Proc. Indian Nat. Sci. Acad. A* **52**(1), 67 (1986).
- M. M. Borel, M. Goreaud, A. Grandin, Ph. Labbé, A. Leclaire, and B. Raveau, *Eur. J. Solid State Inorg. Chem.* **28**, 93 (1991).
- B. Raveau, M. M. Borel, A. Leclaire, A. Grandin, and Ph. Labbé, *Phosphorus Res. Bull.* **1**, 393 (1991).
- B. Domengès, M. Hervieu, B. Raveau, and R. J. D. Tilley, *J. Solid State Chem.* **54**, 10 (1984).
- M. Hervieu, B. Domengès, and B. Raveau, *J. Solid State Chem.* **58**, 233 (1985).
- Z. S. Teweldemedhin, K. V. Ramanujachary, and M. Greenblatt, *Phys. Rev. B* **46**, 7897 (1992).
- E. Wang, M. Greenblatt, E. I. Rachidi, E. Canadell, M. H. Whangbo, and S. Vadlamannati, *Phys. Rev. B* **39**, 12969 (1989).
- C. Schlenker, C. Le Touze, C. Hess, A. Rötger, J. Dumas, J. Marcus, M. Greenblatt, Z. S. Teweldemedhin, A. Ottolenghi, P. Foury, and J. P. Pouget, in "ICSM, Seoul, Korea, Synth. Met." to appear.
- P. Foury, J. P. Pouget, E. Wang, and M. Greenblatt, *Europhys. Lett.* **16**, 485 (1991).
- A. Ottolenghi, P. Foury, J. P. Pouget, Z. S. Teweldemedhin, M. Greenblatt, D. Groult, J. Marcus, and C. Schlenker, *Synth. Met.* **70**, 1301 (1995).
- P. Foury, Thèse de l'université d'Orsay, 1993.
- P. Foury, J. P. Pouget, E. Wang, and M. Greenblatt, *Synth. Met.* **41-43**, 3973 (1991).
- P. Foury, J. P. Pouget, Z. S. Teweldemedhin, E. Wang, and M. Greenblatt, *Synth. Met.* **55-57**, 2605 (1993).
- P. Foury and J. P. Pouget, *Int. J. Mod. Phys. B* **7**, 3973 (1993).
- P. Foury, J. P. Pouget, Z. S. Teweldemedhin, E. Wang, M. Greenblatt, and D. Groult, *J. Phys. IV C* **23**, 133 (1993).
- Y. Yan, M. Kleman, C. Le Touze, J. Marcus, C. Schlenker, and P. A. Buffat, *Europhys. Lett.* **30**, 49 (1995).
- Y. F. Yan, M. Kleman, C. Le Touze, J. Marcus, and C. Schlenker, in "ICEM 13 Paris July 17-22, 1994," p. 909.
- A. Rötger, J. Lehman, C. Schlenker, J. Dumas, J. Marcus, Z. S. Teweldemedhin, and M. Greenblatt, *Europhys. Lett.* **25**, 23 (1994).
- C. Le Touze, G. Bonfait, C. Schlenker, J. Dumas, M. Almeida, M. Greenblatt, and Z. S. Teweldemedhin, *J. Phys. I* **5**, 437 (1995).
- A. Rötger, C. Schlenker, J. Dumas, E. Wang, Z. S. Teweldemedhin, and M. Greenblatt, *Synth. Met.* **55-57**, 2670 (1993).
- J. Lehmann, C. Schlenker, C. Le Touze, A. Rötger, J. Dumas, J. Marcus, Z. S. Teweldemedhin, and M. Greenblatt, *J. Phys. IV C* **2**, 243 (1993).
- M. H. Whangbo, E. Canadell, P. Foury, and J. P. Pouget, *Science* **252**, 96 (1991).
- E. Canadell and M. H. Whangbo, *J. Solid State Chem.* **86**, 131 (1990).
- J. P. Giroult, M. Goreaud, Ph. Labbé, and B. Raveau, *Acta Crystallogr. Sect. B* **37**, 2139 (1981).
- Ph. Labbé, M. Goreaud, and B. Raveau, *J. Solid State Chem.* **61**, 324 (1986).
- A. Benmoussa, Ph. Labbé, D. Groult, and B. Raveau, *J. Solid State Chem.* **44**, 318 (1982).
- B. Domengès, F. Studer, and B. Raveau, *Mater. Res. Bull.* **18**, 669 (1983).
- "International Tables for Crystallography, Vol IV." Kynoch Press, England, 1974.
- B. A. Frenz and Associates Inc., "SDP Structure Determination Package." College Station, Texas, 1982.
- A. Yamamoto, "REMOS. A computer program for the refinement of modulated structures." National Institute for Research in Inorganic Materials, Niiharigun, Ibaraki, Japan.
- Ph. Labbe, in "Diffusionless Phase Transition and Related Structures in Oxides." Ed (C. Boulesteix, Ed.), pp. 293-339. Trans Tech Publication, 1992.
- B. Domengès, M. Hervieu, B. Raveau, and M. O'Keefe, *J. Solid State Chem.* **72**, 155 (1988).
- S. L. Wang, C. C. Wang, and K. H. Lii, *J. Solid State Chem.* **82**, 298 (1989).
- B. Domengès, N. K. McGuire, and M. O'Keefe, *J. Solid State Chem.* **56**, 94 (1985).