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$Rb_xP_8W_{32}O_{112}$: A Tunnel Structure Built up from ReO_3-Type Blocks and P_2O_7 Groups

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(*Received* 17 *May* 1980; *accepted* 1 *July* 1980)

Abstract

The structure of a $Rb_{1.6}P_8W_{32}O_{112}$ single crystal has been established by X-ray diffraction. The composition of this oxide with general formula $Rb_xP_8W_{32}O_{112}$ ($1.6 \leq x \leq 2$) has been confirmed by a powder work. In a first step, the mean structure was solved in the space group $P2/c$ with $a = 16.194$ (3), $b = 3.7719$ (4), $c = 17.095$ (4) Å, $\beta = 93.89$ (2)°, leading to $R = 0.038$ and $R_w = 0.043$. Examination of the mean structure and the splitting of O atoms suggested the doubling of the b parameter. The actual structure, corresponding to the space group $P2_1/c$ with the cell a, $2b$, c, was confirmed by an accurate X-ray investigation and by electron microscopy. The host lattice of this structure, which is built up from WO_6 octahedra and PO_4 tetrahedra, can be described as ReO_3-type slabs connected through P_2O_7 groups. Several sorts of cages, with a geometry derived from that of perovskite, are formed; these cages are empty. The Rb^+ ions are inserted in tunnels with a strongly distorted hexagonal section, running along [010] and situated at the boundary between two ReO_3-type slabs. The possibility of insertion in this structure and the existence of microphases $Rb_xP_8W_{8n}O_{24n+16}$ are discussed.

Introduction

Few tunnel structures with a tetrahedra and octahedra corner-sharing host lattice are known at present, probably due to the great rigidity of the tetrahedral configuration. The X_2O_7 groups, which are formed of two corner-sharing tetrahedra, can however, sometimes be accommodated in an octahedral framework. This is the case for the siliconiobates and silicotantalates $A_3M_6Si_4O_{26}$ (Shannon & Katz, 1970; Choisnet, Nguyen, Groult & Raveau, 1976) with a pentagonal tunnel structure and for the intergrowths $(A_3M_6Si_4O_{26})_n.A_3M_8O_{21}$ (Nguyen, Studer, Groult, Choisnet & Raveau, 1976; Choisnet, Hervieu, Groult & Raveau, 1977). This ability to form such a framework can be explained by the height of the Si_2O_7 group, which is very close to that of a TaO_6 (or NbO_6) octahedron, allowing the connection of these polyhedra through their corners. In this respect, the P_2O_7 group should be able to accommodate the WO_6 octahedra due to the sizes of P and W which are respectively smaller than Si and Ta (or Nb). The present study describes the behaviour of the P_2O_7 groups and WO_6 octahedra in an oxide $Rb_xP_8W_{32}O_{112}$, characterized by a new tunnel structure.

Experimental

Sample preparation

During the synthesis of the hexagonal rubidium tungsten bronze from a mixture of composition $Rb_{0.20}WO_3$ (Labbé, Goreaud, Raveau & Monier, 1978), in an evacuated silica ampoule at 1173 K, a single crystal of unknown composition was isolated.

The crystallographic data collected from this crystal showed that its structure and probably its composition had nothing to do with the hexagonal tungsten bronze structure. All attempts to obtain such crystals, from the composition $Rb_{0.20}WO_3$, but in a platinum crucible *in vacuo*, were unsuccessful. The reaction of $Rb_{0.20}WO_3$

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Table 1. *Powder pattern of* $Rb_{0.8}P_4W_{16}O_{56}$ *prepared at* 1173 K

Refined parameters: a = 16·200 (5), b = 3·7729 (11), c = 17·093 (4) Å, β = 93·93 (3)°.

$h\ k\ l$	d_o (Å)	d_c (Å)	$h\ k\ l$	d_o (Å)	d_c (Å)
3 0 2	4·419	4·420	0 2 0	1·8859	1·8864
2 0 $\bar{4}$	3·879	3·882	5 0 $\bar{8}$	1·8390	1·8383
0 1 0	3·773	3·773	4 1 $\bar{8}$	1·7253	1·7260
1 1 0	3·676	3·674	5 0 8		1·7260
4 0 2	3·563	3·558	0 2 4		1·7251
3 0 $\bar{4}$	3·463	3·460	4 2 0	1·7081	1·7093
3 1 2	2·868	2·870	1 0 $\overline{10}$		1·7081
1 0 6	2·765	2·767	9 0 $\bar{4}$	1·6960	1·6970
2 1 $\bar{4}$	2·704	2·706	2 2 $\bar{4}$		1·6967
4 1 1		2·702	4 2 1		1·6959
6 0 $\bar{2}$	2·621	2·621	4 2 2	1·6667	1·6667
4 1 2	2·589	2·589	5 1 8	1·5688	1·5695
3 0 $\bar{6}$		2·588	10 0 2		1·5684
3 1 $\bar{4}$	2·551	2·550	1 1 $\overline{10}$	1·5565	1·5561
1 1 6	2·229	2·231	5 0 $\overline{10}$	1·5523	1·5528
6 1 $\bar{2}$	2·153	2·152	5 2 3		1·5521
7 0 4	1·972	1·974	8 1 $\bar{6}$		1·5519
4 0 $\bar{8}$	1·939	1·941	6 2 $\bar{2}$	1·5309	1·5310
3 0 8		1·937			

with the silica tube was thus considered. However, all attempts to prepare a compound corresponding to the observed cell parameters, in the system Rb—Si—W—O, were also unsuccessful. During the structure resolution, the presence of tetrahedral X_2O_7 groups clearly appeared. Among the elements which could be present in the silica of the ampoule, P seemed most likely to be the X atom, due to its size and atomic number, close to those of Si. The study of the system Rb—P—W—O confirmed this point of view. A mixture of $H(NH_4)_2PO_4$, Rb_2CO_3 and WO_3 in appropriate ratios was first heated in air at 1173 K to decompose the phosphate and the carbonate; the resultant product was then mixed with an adequate amount of W and heated in a platinum crucible placed in an evacuated silica ampoule.

A new oxide of composition $Rb_xP_8W_{32}O_{112}$ was then isolated ($1{\cdot}6 \le x \le 2$). Its powder pattern (Table 1) could be indexed in the monoclinic cell determined from the single-crystal study; its identity with the single-crystal structure was confirmed at the end of the structure determination by comparing the observed and calculated intensities of the powder diffraction pattern.

Determination of the mean structure

The crystal selected for the structure determination was an optically transparent plate, limited by the {100}, {010} and {001} forms with the dimensions 18 × 75 × 280 µm. The Laue patterns showed monoclinic symmetry ($2/m$) and the cell parameters, measured on precession and Weissenberg films, were confirmed later by diffractometric techniques with a least-squares refinement based on 25 reflections: a = 16·194 (3), b = 3·7719 (4), c = 17·095 (4) Å, β = 93·89 (2)°. The only systematic absences ($h0l$, $l = 2n + 1$) led to Pc or $P2/c$ space groups. At this stage no evidence of superstructure reflections involving the doubling of b was observed.

The data were collected on a CAD-4 Enraf–Nonius diffractometer with Mo $K\alpha$ radiation filtered with a graphite monochromator. The intensities were measured up to $2\theta = 84°$ by the ω–2θ technique with a maximum scan width of 1·35° and a counter slit aperture of 3·70 mm. The background intensity was measured on both sides of each reflection. A periodic control verified the stability of the sample. Among the 6446 measured reflections, only 3469 had $\sigma(I)/I \le 0{\cdot}333$. These were corrected for Lorentz and polarization effects, then for absorption with a program based on crystal morphology. The minimum and maximum transmission factors were 0·027 and 0·372.

The structure was solved by the heavy-atom method in $P2/c$. All the W atom positions were fixed by the Patterson function and refined by least squares. All Rb and O atoms were then located in the subsequent difference synthesis. From the maps of electron density, three features appeared which were confirmed by the results: the occupation of the d sites by the Rb atoms is only partial, about 40%; the P site is occupied by 0·5P; some O atoms [(2), (6), (7), (8), (9), (10), (11), (12) and (13)] around the Rb and P sites are distributed over two neighbouring positions with an occupancy factor of 0·5, but further O atoms [(1), (3), (4), (5) and (14)] do not seem disturbed. With these hypotheses, the atomic parameters were refined by full-matrix least squares. Scattering factors for W, Rb and P were from Cromer & Waber (1965) corrected for anomalous

Table 2. $Rb_{0.8}P_4W_{16}O_{56}$: *positional parameters and e.s.d.'s*

	Occupation	x	y	z	B (Å^2)
Rb	0·4	$\frac{1}{2}$	0	$\frac{1}{2}$	B_{eq} = 1·42 (10)
P(1)	0·5	0·4316 (4)	0·4062 (15)	0·1456 (3)	0·37 (7)
P(2)	0·5	0·4317 (4)	0·5936 (16)	0·1450 (4)	0·43 (7)
W(1)	1·0	0·15094 (3)	0·48884 (15)	0·21246 (3)	B_{eq} = 0·40 (1)
W(2)	1·0	0·35917 (3)	0·53926 (15)	0·32722 (2)	B_{eq} = 0·39 (1)
W(3)	1·0	0·25863 (3)	0·47253 (18)	0·52189 (2)	B_{eq} = 0·39 (1)
W(4)	1·0	0·05192 (3)	0·50512 (11)	0·40526 (3)	B_{eq} = 0·40 (1)
O(1)	1·0	0	$\frac{1}{2}$	0	0·79 (18)
O(2*A*)	0·5	0·2141 (17)	0·4784 (85)	0·1143 (16)	0·78 (40)
O(2*B*)	0·5	0·2134 (22)	0·5144 (97)	0·1152 (20)	0·90 (54)
O(3)	1·0	0·1635 (6)	0·4991 (34)	0·4613 (6)	1·04 (15)
O(4)	1·0	0·0532 (7)	0·4885 (39)	0·1522 (7)	1·09 (12)
O(5)	1·0	0·1033 (6)	0·4959 (29)	0·3060 (6)	0·83 (11)
O(6*A*)	0·5	0·3273 (11)	0·4602 (63)	0·4248 (9)	0·19 (18)
O(6*B*)	0·5	0·3215 (14)	0·5537 (79)	0·4221 (12)	0·75 (26)
O(7*A*)	0·5	0·3769 (14)	0·4535 (79)	0·0766 (13)	0·55 (24)
O(7*B*)	0·5	0·3766 (16)	0·5472 (88)	0·0778 (15)	0·87 (28)
O(8*A*)	0·5	0·2613 (16)	0·4521 (86)	0·2741 (14)	0·89 (28)
O(8*B*)	0·5	0·2636 (13)	0·5442 (76)	0·2714 (12)	0·49 (23)
O(9*A*)	0·5	0·4117 (15)	0·4418 (77)	0·2228 (14)	1·02 (24)
O(9*B*)	0·5	0·4156 (13)	0·5724 (61)	0·2235 (11)	0·60 (20)
O(10*A*)	0·5	0·4787 (15)	0·4379 (84)	0·3743 (14)	0·92 (26)
O(10*B*)	0·5	0·4806 (12)	0·5449 (69)	0·3730 (11)	0·41 (18)
O(11*A*)	0·5	0·2625 (11)	0·0037 (53)	0·0217 (9)	0·29 (20)
O(11*B*)	0·5	0·2839 (14)	0·0065 (60)	0·0123 (11)	0·67 (23)
O(12*A*)	0·5	0·1706 (13)	−0·0041 (57)	0·2065 (11)	0·60 (22)
O(12*B*)	0·5	0·1483 (13)	−0·0004 (52)	0·2114 (10)	0·46 (22)
O(13*A*)	0·5	0·3845 (13)	0·0139 (62)	0·3179 (11)	0·81 (23)
O(13*B*)	0·5	0·3571 (15)	0·0102 (76)	0·3311 (14)	1·26 (30)
O(14)	1·0	0·0557 (7)	0·0008 (31)	0·4044 (7)	1·18 (14)
O(15)	1·0	0·4112 (13)	0·0042 (66)	0·1537 (13)	1·18 (25)

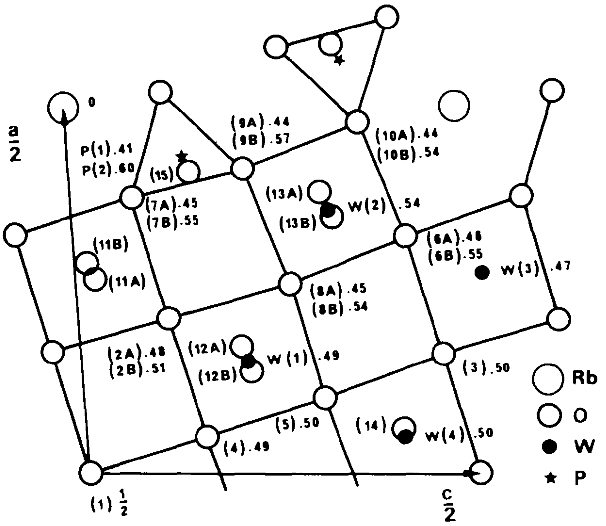

Fig. 1. Projection of the mean structure on to (010).

dispersion (Cromer, 1965) and for O^{2-} from Suzuki (1960). A linear weighting scheme was adjusted according to $\langle w|F_o| - |F_c|\rangle$ in terms of sin θ/λ. The refinement with anisotropic thermal coefficients for W and Rb and isotropic for O and P atoms led to $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0{\cdot}038$ and $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2|^{1/2} = 0{\cdot}043$. Final atomic parameters are given in Table 2. The content of the mean cell is $Rb_{0\cdot8}P_4W_{16}O_{56}$. A schematic projection of atomic positions on to (010) is shown in Fig. 1. All the previous considerations led us to regard the results as those of a mean structure and to consider later the existence of a superstructure.*

The actual structure

The O atoms define tetrahedra and octahedra. Both polyhedra form uninterrupted columns along [010]. Thus face-sharing tetrahedra with unacceptable P—P distances (0·71 Å) appear. This observation, the occupancy factor of the P site and the splitting of O atoms suggest the existence of a superstructure involving the doubling of *b*, which had not been observed.

We consider now the features of the actual structure in the cell *a*, 2*b*, *c*. A projection on to (010) is shown in Fig. 2, where only one layer of octahedra has been drawn, lying from $y = 0$ to $y = 0{\cdot}5$. In the cell, only one ordering is possible for the actual structure due to the position of the bridging O(15) of the P_2O_7 groups and to the direction of rocking for the WO_6 octahedra. In Fig. 2 indeed, the projection of O(15), out of the centre of gravity of the triangle O(7*B*)—O(9*B*)—O(10*A*) or equivalent, allows a choice of tilting for a PO_4 tetrahedron. Two dispositions of the P_2O_7 groups are possible but lead to the same final solution for the actual structure since they correspond to one another through a *c*/2 translation. So, a disposition of a P_2O_7 group being chosen, the tilting of the octahedra is well defined (Fig. 2).

The observed angle P—O—P = 152·9 (16)° seems to fix the amplitude of the tilting for the octahedra. The proximity of the P_2O_7 groups raises this amplitude: the $W(4)O_6$ octahedron is not tilted whereas the inclination of $W(1)O_6$ with respect to the [010] direction is 5·7 (3)°. For $W(3)O_6$, which is linked to one tetrahedron, the value is 5·9 (3)° and for $W(2)O_6$, linked to two tetrahedra, the value is 7·7 (3)°. So, the presence of P_2O_7 groups in the structure creates a gradual distortion with respect to the ideal perovskite framework built up from non-tilted octahedra. It is rather rare that such a feature could be established from an X-ray study without ambiguity. The atomic framework built up in such a manner led to the space group $P2_1/c$ (Fig. 2). An electron-microscopy study has confirmed the existence of the cell *a*, 2*b*, *c*, and the systematic extinctions 0*k*0, $k = 2n + 1$; *h*0*l*, $l = 2n + 1$. The symmetry was thus confirmed. Calculations of structure factors with atomic positions in the actual cell were then undertaken to determine the superstructure reflections whose intensities were the strongest. Thus we retained four reflections, all with $k = 5$: 057, $\bar{9}53$, 355 and 455. $F_c(057)$, which has the highest value, corresponds to 7% of the maximum F_c for the whole structure. So, $I_c(057)$ corresponds to about 5‰ of the maximum I_c. Afterwards, the crystal was mounted again on the CAD-4 goniometer and the super-

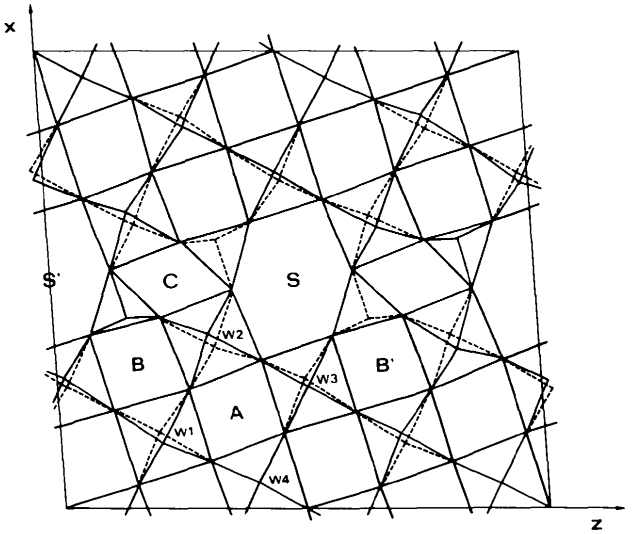

Fig. 2. Projection of the actual structure on to (010) limited to the O-atom framework from $y = 0$ to $y = 0{\cdot}5$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35534 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structure level *h5l* registered with a very slow scanning method. The data collection showed that the measured reflections were those that were expected.

Description of the structure and discussion

The host lattice $P_8W_{32}O_{112}$ (actual cell) is built up from corner-sharing PO_4 tetrahedra and WO_6 octahedra. Three types of octahedra can be distinguished: the $W(1)O_6$ or $W(4)O_6$ octahedra which share their corners with six octahedra, the $W(3)O_6$ octahedra which are linked to five other octahedra and one PO_4 tetrahedron, and the $W(2)O_6$ octahedra which are linked to four octahedra and two PO_4 tetrahedra.

Due to the tilting, each sort of octahedron $W(1)O_6$, $W(2)O_6$ and $W(3)O_6$ corresponds in the actual structure to two different octahedra whereas $W(4)O_6$ is unique. The geometry of every WO_6 group has been studied and the distances W—O and angles are given in Table 3. Except for the $W(4)O_6$ octahedron, whose situation is unique, all the W atoms present either a 4 + 2 or a 3 + 3 coordination, and are off-centred inside their octahedra. The mean W displacement from the centre of gravity of O atoms is 0·14 (2) for W(1) and 0·24 (2) Å for W(2) and W(3), the main direction of these displacements being [100] or [110]. These results can be compared to the values obtained in WO_3, *i.e.* 0·31 Å (Loopstra & Rietveld, 1969), in the bronzes, *i.e.* 0·10 to 0·16 Å for In_xWO_3 (Labbé, Goreaud, Raveau & Monier, 1979), and in other structures (Magnéli, 1956).

These displacements can be related to the mean value of the oxidation state of W, the W^V having a tendency for an ideal octahedral coordination and the W^{VI} for a 4 + 2 coordination. However, consideration of the W—O and P—O distances in the structure (Table 3) shows that a long O—W bond is always opposite a short W—O or P—O bond. W(4) is special because all the bonds O—W(4) are opposite short W—O bonds; so the coordination 4 + 2 is not so apparent in the $W(4)O_6$ octahedra.

Each PO_4 tetrahedron shares one vertex with another tetrahedron, forming a P_2O_7 group. The three other corners are linked to three octahedra. The distances P—O and angles in the P_2O_7 groups are given in Table 4. They agree with values found in the literature, particularly for WOP_2O_7 (Kierkegaard, 1958), $Na_4P_2O_7.10H_2O$ (MacArthur & Beevers, 1957) and α-$Ca_2P_2O_7$ (Calvo, 1968). The distances P—O(15), between a P atom and the O atom connecting two PO_4 tetrahedra, are larger than the other P—O distances. The result is that, in a P_2O_7 group, one observes a repulsion among the P atoms which are slightly off-centred inside their tetrahedra with an opposite displacement of 0·06 (3) and 0·07 (3) Å mainly along the [010] and $[0\bar{1}0]$ directions respectively.

Table 3. *Coordination of* Rb *and* W *atoms in the actual structure*

Interatomic distances are given in Å. Both possible locations are given for Rb.

Bond Neighbour *N*	Rb—*N* (*S* site)	Rb—*N* (*S′* site)	W(1)—*N* (*a*)	W(1)—*N* (*b*)	W(2)—*N* (*a*)	W(2)—*N* (*b*)	W(3)—*N* (*a*)	W(3)—*N* (*b*)	W(4)—*N*
O(1)									1·875 (1)
O(2*A*)			2·02 (3)				1·79 (3)		
O(2*B*)				2·01 (4)				1·80 (3)	
O(3)							1·80 (1)	1·80 (1)	1·99 (1)
O(4)			1·83 (1)	1·83 (1)					1·91 (1)
O(5)			1·82 (1)	1·82 (1)					1·94 (1)
O(6*A*)					1·80 (2)		2·06 (2)		
O(6*B*)						1·77 (2)		2·07 (2)	
O(7*A*)	2 × 2·99 (3)	2 × 3·21 (3)						2·09 (2)	
O(7*B*)	2 × 3·01 (3)	2 × 3·22 (3)					2·08 (3)		
O(8*A*)			2·02 (2)		1·80 (2)				
O(8*B*)				2·03 (2)		1·76 (2)			
O(9*A*)						2·06 (2)			
O(9*B*)					2·05 (2)				
O(10*A*)	2 × 3·02 (3)	2 × 2·71 (3)				2·08 (2)			
O(10*B*)	2 × 2·99 (2)	2 × 2·77 (2)			2·07 (2)				
O(11*A*)							1·80 (2)	1·98 (2)	
O(11*B*)							2·02 (2)	1·86 (2)	
O(12*A*)			1·94 (2)	1·89 (2)					
O(12*B*)			1·85 (2)	1·93 (2)					
O(13*A*)					2·03 (2)	1·85 (2)			
O(13*B*)					1·78 (3)	2·00 (3)			
O(14)									1·87 (1) 1·90 (1)
O(15)		2 × 3·08 (2)							

Table 4. *The* P_2O_7 *group in the actual structure: interatomic distances* (Å) *and angles* (°)

Neighbour *N*	P(2)	O(7*A*)	O(7*B*)	O(9*A*)	O(9*B*)	O(10*A*)	O(10*B*)	O(15)
Bond								
P(1)–*N*	3·065 (9)		1·51 (3)		1·51 (2)	1·52 (3)		1·56 (3)
P(1)–O(15)–*N*	153 (2)							
O(7*B*)–P(1)–*N*					114 (1)	109 (2)		107 (1)
O(9*B*)–P(1)–*N*						113 (1)		106 (1)
O(10*A*)–P(1)–*N*								108 (1)
P(2)–*N*		1·51 (2)		1·50 (3)			1·49 (2)	1·59 (3)
O(7*A*)–P(2)–*N*				114 (1)			108 (1)	107 (1)
O(9*A*)–P(2)–*N*							114 (1)	103 (1)
O(10*B*)–P(2)–*N*								110 (1)

The behaviour of the P_2O_7 group is similar to that of the Si_2O_7 group in $A_{6-x}M_6Si_4O_{26}$ (Choisnet, Nguyen & Raveau, 1977) which shares also six corners with the NbO_6 (or TaO_6) octahedra. The relative orientation of the WO_6 octahedra around a P_2O_7 group is, however, different from that observed for NbO_6 or TaO_6 around a Si_2O_7 group: this orientation is imposed here by the WO_6 octahedra which are more numerous and form slabs of ReO_3-type extending indefinitely along the [010] and [001] directions.

This framework delimits several types of cavities: cages and tunnels. Four sorts of cages are formed, denoted respectively *A*, *B*, *B'* and *C* in Fig. 2. These cages are empty. The *A* cages are not strictly identical among themselves but are delimited by 12 O atoms belonging to the octahedra and very similar to those observed in the ReO_3 structure from which they derive by a slight distortion; they can also be considered as perovskite tunnels running along the [010] direction. The *B* cages are also delimited by 12 O atoms: their geometry, though close to that of the *A* cages, is somewhat different in that they result from the association of six octahedra and one P_2O_7 group (Fig. 3). Every *B* cage shares its faces along [010] with a *B'* cage. The geometry of the *B'* cage which is delimited by 11 O atoms is very close to that of the *B* cage but one O atom is missing due to the absence of the P_2O_7 group at this level (Fig. 3). In the hypothesis of the actual structure, the columns of P_2O_7 groups parallel to [010] are ordered. Then, only one sort of *C* cage is possible, built up from four $W(2)O_6$ octahedra and one P_2O_7 group. Only one O atom belonging to the bridge P—O—P participates in the formation of this cage and consequently the *C* cage is limited by 11 O atoms and communicates with a *B'* cage and a Rb site.

Rings, built up from $W(2)O_6$ and $W(3)O_6$ octahedra (2 × 4 octahedra) and two P_2O_7 groups or by eight WO_6 only, form tunnels with a distorted hexagonal section, running along [010] and where the Rb^+ ions are inserted. Two sites are possible for Rb in the tunnel at the levels $y = 0$ and 0·5. The coordination is different in each case: 8 if the P_2O_7 groups are missing at this level (*S* site), 10 if P_2O_7 groups are present (*S'* site). The calculation of the structure factors for a statistical distribution of Rb ions and for an order of these ions in one type of sites shows that the difference of their contribution is so weak that it is impossible to differentiate. The Rb—O distances, calculated for each of the two possible sites, are given in Table 3. The coordination is more regular and the distances more satisfactory for the *S* site. So, Rb is likely to occupy the sites at the levels *y* where the P_2O_7 groups are missing.

The ideal structure of $Rb_xP_8W_{32}O_{112}$ given in Fig. 2 shows that the host lattice of this compound can be described as ReO_3-type slabs connected through P_2O_7 groups, and thus separated by rows of distorted hexagonal tunnels along the [001] direction (Fig. 4). The extension of the ReO_3-type slabs can be characterized by considering the strings of polyhedra along

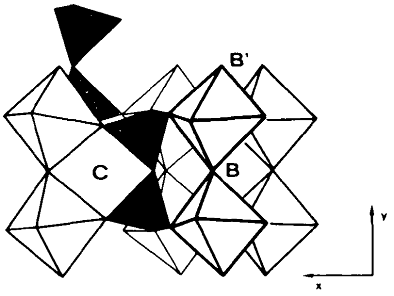


Fig. 3. Association of WO_6 octahedra and P_2O_7 groups showing the *B* and *C* cages.

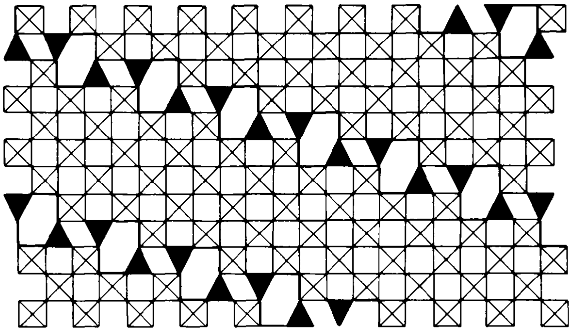
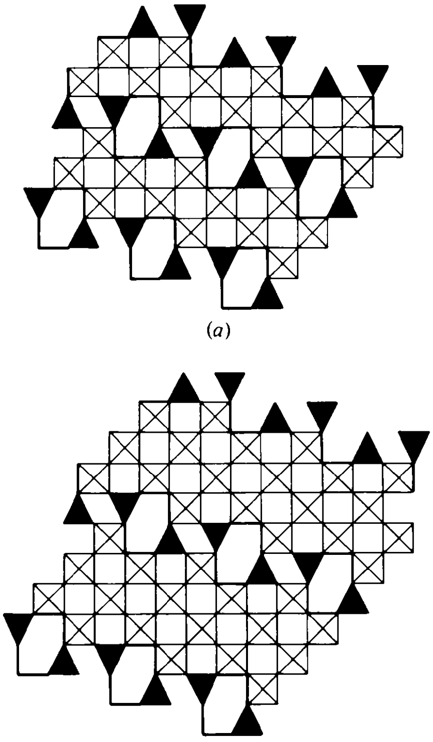


Fig. 4. Projection of the idealized structure of $Rb_xP_8W_{32}O_{112}$ showing the ReO_3-type slabs.



(a)

(b)

Fig. 5. Hypothetical structures of the members (a) $n = 2$ and (b) $n = 3$ of the series $Rb_xP_8W_{8n}O_{24n+16}$.

[201] and $[\bar{1}02]$: along the first direction, strings of four corner-sharing octahedra interrupted by a tetrahedron are observed, while in the second direction, the length of the octahedral strings is doubled, *i.e.* strings with eight octahedra are connected through one tetrahedron. The width of the ReO_3-type slabs can be characterized by the number of octahedra which determines the periodicity of the strings of polyhedra along the [201] direction. A new family of microphases $Rb_xP_8W_{8n}O_{24n+16}$ can thus be predicted where n determines the width of the ReO_3-type slabs, the term $n = 4$ corresponding to the compound described here. Fig. 5 shows as an example the hypothetical structures of the members $n = 2$ and $n = 3$ of such a series. Due to the presence of ReO_3-type slabs, the possibility of insertion of Li and Na in these compounds should also be considered.

Conclusion

The structural study of the oxide $Rb_xP_8W_{32}O_{112}$ shows the ability of the tetrahedral groups P_2O_7 to be accommodated in an octahedral framework, such as that of perovskite. The progressive distortion of the perovskite framework which results from the presence of the P_2O_7 groups is an original feature of this structure. It is rather rare that such an evolution, involving a superstructure characterized by very faint reflections, can be established from an X-ray study without ambiguity. The possibility of double non-stoichiometry opens the way to the synthesis of a large family of compounds: insertion in cages and tunnels, formation of microphases by modification of the width of the perovskite slabs. The mixed valence of W in this oxide, which can be formulated $Rb_xP_8W^{VI}_{24-x}W^{V}_{8+x}O_{112}$, can be compared to the tungsten bronze A_xWO_3. Consequently, the electrical properties of this compound will be investigated.

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