$K_xP_2W_2O_{16}$: A Bronze with a Tunnel Structure Built Up From PO_4 Tetrahedra and WO_6 Octahedra

J. P. GIROULT, M. GOREAUD, PH. LABBE, AND B. RAVEAU

Laboratoire de Cristallographie et Chimie du Solide, LA 251, Institut des Sciences de la Matière et du Rayonnement, Université de Caen, 14032 Caen Cedex, France

The structure of a $K_xP_2W_4O_{16}$ ($x \simeq 0.4$) crystal was established by X-ray analysis. The solution in the cell of symmetry $P2_1/m$, with $a = 6.6702(5)$, $b = 5.3228(8)$, $c = 8.9091(8)$ Å, $\beta = 100.546(7)°$, $Z = 1$, has led to $R = 0.033$ and $R_w = 0.036$ for 2155 reflections with $\sigma(I)/I \leq 0.333$. This structure can be described as two octahedra-wide ReO_3-type slabs connected through "planes" of PO_4 tetrahedra. A new structural family $K_xP_2W_{2n}O_{6n+4}$ can be foreseen which is closely related to the orthorhombic $P_4W_8O_{32}$ and the monoclinic $Rb_xP_8W_{8n}O_{24n+16}$ series.

Introduction

The recent investigation of the systems P–W–O and Rb–P–W–O proved to be fruitful. Three structural types were indeed synthesized: the $Rb_xP_8W_{8n}O_{24n+16}$ family, characterized by ReO_3-type slabs connected through P_2O_7 groups and forming distorted hexagonal tunnels (*1–3*), the $P_4W_{4n}O_{12n+8}$ series, whose framework is also built up of ReO_3-type slabs, but connected through single PO_4 tetrahedra forming pentagonal tunnels (*4*), and the oxide $P_8W_{12}O_{52}$ (*5*), whose host lattice consists of WO_6 octahedra and P_2O_7 groups forming both sorts of tunnels, pentagonal and distorted hexagonal. Moreover, these compounds exhibit a metallic conductivity (*3*) like the tunnel tungsten bronzes of Magnéli (*6*). An electron microscopy study (*7*) of the series $A_xP_8W_{8n}O_{24n+16}$ (A = K, Rb) has shown the close structural relations between the two families. However, a new phase was observed with potassium for $n = 2$ and the present work deals with the struc-ture of this compound which corresponds to the composition $K_xP_2W_4O_{16}$.[1]

Experimental

Sample preparation. Mixtures of $(NH_4)_2HPO_4$, WO_3, and K_2CO_3 in appropriate ratios were first heated in air at 873K to decompose the phosphate and the carbonate. Then adequate amounts of metallic tungsten were added to obtain the composition $K_xP_2W_4O_{16}$ and the samples were heated for 4 days at 1250K in evacuated silica ampoules. The domain of the phase

TABLE I

POWDER PATTERN OF $K_{0.5}P_2W_4O_{16}$ PREPARED AT 1250K (REFINED PARAMETERS: $a = 6.673(7)$, $b = 5.327(7)$, $c = 8.909(7)$ Å, $\beta = 100.54(7)°$; d_{obs} AND d_{calc} ARE GIVEN IN Å)

h k l	d_{obs}	d_{calc}	I/I_0	h k l	d_{obs}	d_{calc}	I/I_0
0 0 1	8.77	8.759	38	2 2 $\bar{3}$	1.789	1.787	15
1 0 0	6.577	6.560	7	0 0 5	1.7509	1.7517	3
1 0 1	4.845	4.843	45	3 1 2	1.7292	1.7285	23
0 0 2	4.381	4.379	9	1 2 $\bar{4}$	1.6969	1.6969	20
1 1 $\bar{1}$	3.924	3.918	100	2 0 4	1.6850	1.6844	11
1 1 1	3.587	3.583	2	3 1 $\bar{4}$	1.6313	1.6297	17
1 0 2	3.369	3.369	72	2 2 3	1.6017	1.6025	10
1 1 $\bar{2}$	3.200	3.196	34	4 1 $\bar{2}$	1.5661	1.5652	12
2 0 $\bar{2}$	2.895	2.891	20	4 0 $\bar{3}$	1.5540	1.5567	16
2 1 0	2.795	2.793	31	1 1 5	1.5495	1.5501	14
0 2 0	2.664	2.664	16	3 1 3	1.5454	1.5449	13
0 1 3	2.560	2.560	61	2 3 1	1.5142	1.5147	9
2 0 $\bar{3}$	2.412	2.411	15	1 2 5	1.4773	1.4772	4
1 2 1	2.333	2.334	6	0 0 6	1.4605	1.4598	6
3 0 $\bar{1}$	2.222	2.219	13	1 3 3	1.4474	1.4482	3
2 1 2	2.203	2.204	10	4 2 1	1.3474	1.3469	4
1 2 2	2.088	2.089	12	4 2 $\bar{3}$	1.3443	1.3440	3
0 1 4 ⎫ 3 1 0 ⎭	2.025	2.025 ⎫ 2.023 ⎭	4	2 3 $\bar{4}$ ⎫ 5 0 $\bar{2}$ ⎭	1.3261	1.3272 ⎫ 1.3253 ⎭	12
2 0 3	2.005	2.006	12	4 0 $\bar{5}$	1.3228	1.3242	9
2 2 $\bar{2}$	1.960	1.959	23	0 2 6	1.2798	1.2801	3
1 1 4	1.849	1.849	6	1 1 $\bar{7}$	1.2379	1.2378	4
3 1 $\bar{3}$	1.815	1.813	15	4 1 4	1.1805	1.1806	12

$K_xP_2W_4O_{16}$ ranges from $x = 0.5$ to $x = 1.5$. Crystals were selected from the preparation of nominal composition $K_{0.5}P_2W_4O_{16}$. The corresponding powder patterns showed a pure phase and were indexed in the monoclinic cell deduced from a preliminary single-crystal study (Table I). The only systematic absences $0k0$, $k = 2n + 1$, led to the space groups $P2_1$ or $P2_1/m$.

Structure determination. The crystal used for the structure determination was a b axis copper-colored needle with a hexagonal section limited by $\{100\}$ and $\{001\}$. Its dimensions were $30 \times 50 \times 290$ μm. The monoclinic cell parameters deduced from Weissenberg photographs were confirmed by diffractometric techniques with a least-squares refinement based on 25 reflections: $a = 6.6702(5)$, $b = 5.3228(8)$, $c = 8.9091(8)$ Å, $\beta = 100.546(7)°$. The data were collected with a CAD 4 Enraf–Nonius diffractometer using $MoK\alpha$ monochromatized radiation. The intensities were measured up to $2\theta = 90°$ by the $\omega - 2\theta$ technique, with a maximum scan width of 1°. The background intensity was measured on both sides of each reflection. A periodic control verified the stability of the sample. Among 2702 reflections within a quarter of the reciprocal sphere, 2155 which had $\sigma(I)/I \leq 0.333$ were retained and corrected for Lorentz and polarization effects, then for absorption with a program based on crystal morphology. The minimum and maximum transmission factors were 0.119 and 0.338 for $\mu l = 393$ cm^{-1}.

The structure was solved by the heavy-atom method in $P2_1/m$. The W atom positions were fixed by the Patterson function and refined by least squares. P, O, and K atoms were then located in the subsequent difference synthesis. The determination of

the K composition by refinement is not accurate owing to a strong correlation between the K composition and the thermal coefficient. The occupancy of the K sites would be 20 ± 5%, the content of the cell being then $K_{0.4}P_2W_4O_{16}$, slightly different from the preparation stoichiometry $K_{0.5}$ $P_2W_4O_{16}$. The atomic parameters were refined by full-matrix least squares. Scattering factors for P^0, K^+, and W^{6+} were from Cromer and Waber (8), corrected for anomalous dispersion (9), and for O^{2-} from Suzuki (10). A linear weighting scheme was adjusted according to $\langle w|F_0| - |F_c|\rangle$ in terms of $\sin\theta/\lambda$. The refinement with anisotropic thermal coefficients for W and isotropic for P, O, and K led to $R = \Sigma||F_0|-|F_c||/\Sigma|F_0| = 0.033$ and $R_w = [\Sigma_w(|F_0|-|F_c|)^2/\Sigma_w|F_0|^2]^{1/2} = 0.036$. Final atomic parameters are given in Table II and a projection of atomic positions onto (010) is shown in Fig. 1.

Description of the Structure and Discussion

The host lattice of the bronze $K_xP_2W_4O_{16}$ is built up from corner-sharing WO_6 octahe-
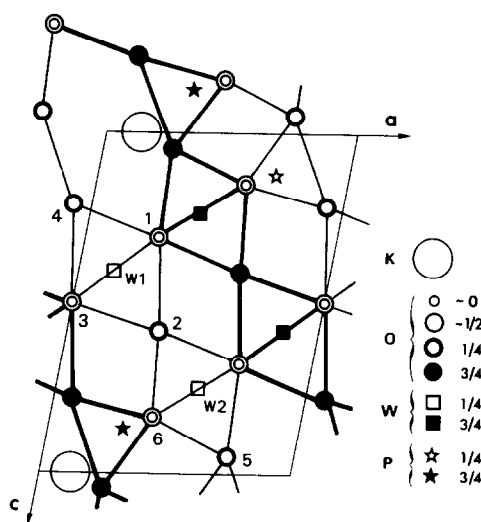

Fig. 1. $K_xP_2W_4O_{16}$: projection of the structure onto (010). The polyhedra with dark and light outlines lie at the level $y = \frac{3}{4}$ and $\frac{1}{4}$, respectively.

dra and PO_4 tetrahedra. Although it does not belong to the structural family $P_4W_{4n}O_{12n+8}$ (4), this structure exhibits a great similarity with the second member of this series, $P_4W_8O_{32}$. Like that of $P_4W_8O_{32}$, the framework can be described by the association of chains of octahedra and tetra-

TABLE II

$K_{0.4}P_2W_4O_{16}$: POSITIONAL AND THERMAL PARAMETERS AND esd's

	Position	x	y	z	B (Å²)
K	(2e)	0.138(2)	$\frac{1}{4}$	−0.0001(12)	1.4(2)[a]
P	(2e)	0.7113(3)	$\frac{1}{4}$	0.1296(2)	0.31(2)
W(1)	(2e)	0.13897(4)	$\frac{1}{4}$	0.41163(3)	B_{eq} = 0.26(1)
W(2)	(2e)	0.56375(4)	$\frac{1}{4}$	0.74928(3)	B_{eq} = 0.22(1)
O(1)	(4f)	0.2827(7)	−0.0026(9)	0.3119(5)	0.67(4)
O(2)	(2e)	0.3643(9)	$\frac{1}{4}$	0.5764(7)	0.54(5)
O(3)	(2c)	0	0	$\frac{1}{2}$	0.68(6)
O(4)	(2e)	−0.072(1)	$\frac{1}{4}$	0.2223(8)	0.82(7)
O(5)	(2e)	0.7344(9)	$\frac{1}{4}$	0.9608(7)	0.56(6)
O(6)	(4f)	0.3982(8)	−0.013(1)	0.8368(6)	0.97(5)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W(1)	0.00136(3)	0.00230(5)	0.00081(2)	0	−0.00007(2)	0
W(2)	0.00136(3)	0.00716(5)	0.00065(2)	0	−0.00001(2)	0

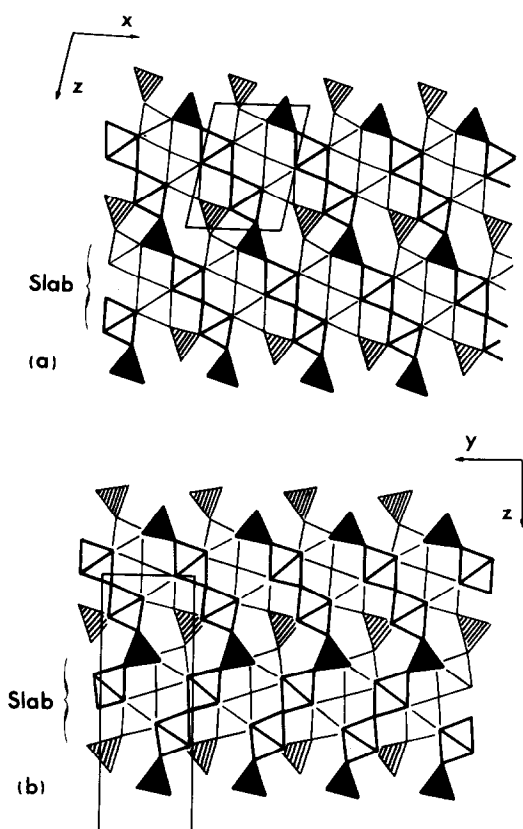[a] The occupation of the corresponding site obtained by refinement is 21(2)%.

FIG. 2. Projection onto (010) of (a) the idealized K_x $P_2W_4O_{16}$ structure and (b) the idealized $P_4W_8O_{32}$ structure.

hedra parallel to the [101] direction and lying at the levels $y = \frac{1}{4}$ and $\frac{3}{4}$ (Figs. 1 and 2a). Each of these periodic chains is built up from strings of two octahedra and one tetrahedron within the period in such a way that each PO_4 tetrahedron shares its corners with four WO_6 octahedra (W(1) + 3W(2)) whose centers are located at the apices of an almost regular W_4 tetrahedron: the distance of P from the center of gravity on this tetrahedron is 0.60 Å. The environment of the WO_6 octahedra is also very similar to that observed for $P_4W_8O_{32}$. Each $W(1)O_6$ octahedron shares its corners with one tetrahedron and five octahedra whose centers (P + 2 W(1) + 3 W(2)) are located at the apices of an almost regular octahedron, the

distance between W(1) and the center of gravity of this octahedron being equal to that observed in $P_4W_8O_{32}$, i.e., 0.13 Å. In the same way, the $W(2)O_6$ octahedra are linked to three PO_4 tetrahedra and three octahedra whose centers (3P + 3W (1)) form an octahedron; the distance from the center of gravity of this octahedron to W(2) is, however, greater for $K_xP_2W_4O_{16}$ (0.25 Å) than for $P_4W_8O_{32}$ (0.13 Å), involving three W(2)–W(1) long distances and three W(2)–P short distances. The bond distances and angles (Table III) show that the geometry of the polyhedra PO_4, $W(1)O_6$, and $W(2)O_6$ are almost identical to those observed in $P_4W_8O_{32}$ (4). The W(2) atom is indeed characterized by a 3 + 3 coordination with three longer W(2)–O bonds corresponding to the three oxygen atoms linked to the P atoms; the displacement of W(2) off the center of gravity of this octahedron (0.16 Å) is not very different from that observed in $P_4W_8O_{32}$ (0.11 Å). As for $P_4W_8O_{32}$, the $W(1)O_6$ octahedra and the PO_4 tetrahedra are almost regular and the W(1) and P atoms are only shifted, respectively, 0.08 and 0.04 Å from the center of gravity of their polyhedra.

Figure 2a shows the projection of the idealized structure onto the (010) plane. It can be seen that this structure can be described, like that of $P_4W_8O_{32}$, as two octahedra-wide ReO₃-type slabs connected through "planes" of PO_4 tetrahedra. In spite of all these similarities, the framework of this phase is different from that of $P_4W_8O_{32}$ in that it delimits distorted hexagonal tunnels parallel to [010], while pentagonal tunnels are observed in $P_4W_8O_{32}$ (Fig. 2b). This difference comes from the relative orientation of the PO_4 tetrahedra which limit the strings of two octahedra in both structures. Two successive PO_4 tetrahedra in a string are disposed, one with respect to the other, in an eclipsed configuration in $K_xP_2W_4O_{16}$, while they are in a staggered configuration in $P_4W_8O_{32}$. We thus observe straight chains

TABLE III

COORDINATION OF K, P, AND W ATOMS IN $K_xP_2W_4O_{16}$ (INTERATOMIC DISTANCES ARE GIVEN IN Å)

	Bond			
Neighbor N	K–N	P–N	W(1)–N	W(2)–N
O(1)	2 × 3.08(1)		2 × 1.956(5)	2 × 1.813(3)
O(2)			1.899(6)	1.842(6)
O(3)			2 × 1.875(1)	
O(4)	2.63(1)	1.528(7)	1.989(6)	
O(5)	{ 2.65(1) { 2 × 2.797(4)	1.540(7)		2.015(6)
O(6)	2 × 2.83(1)	2 × 1.513(6)		2 × 2.026(6)

made of octahedra and tetrahedra running along the [101] direction in $K_xP_2W_4O_{16}$ (Fig. 2a), and zigzag chains built up of the same units (two octahedra + one tetrahedron) in $P_4W_8O_{32}$ (Fig. 2b). Correlatively, two successive slabs of WO_6 octahedra in the c direction are symmetric with respect to a (001) plane in the orthorhombic structure (Fig. 2b), but present the same orientation in $K_xP_2W_4O_{16}$, leading to a monoclinic deformation (Fig. 2a).

Both structures $K_xP_2W_4O_{16}$ and $P_4W_8O_{32}$ must be compared with those of the two forms, respectively, monoclinic (Fig. 3) and orthorhombic (Fig. 4), of the oxide Mo_4O_{11} established by Kihlborg (11) and Magnéli (12). We observe in these oxides, respectively, the same rows of distorted hexagonal and pentagonal tunnels, formed by almost identical planes of MoO_4 tetrahedra. Very similar slabs of ReO_3 type are also observed, but with a different width corresponding to three octahedra. Thus, $P_4W_8O_{32}$ and γ-Mo_4O_{11} can be considered as the members $n = 2$ and $n = 3$ of an orthorhombic series $T_4M_{4n}O_{12n+8}$ (T = P, Mo; M = W, Mo). In the same way, K_x $P_2W_4O_{16}$ and η-Mo_4O_{11} also correspond to the members $n = 2$ and $n = 3$ of a monoclinic family which can be formulated A_x $T_4M_{4n}O_{12n+8}$ (A = K or vacancy) with a cell content which can be a submultiple of that

formula. From these observations, it appears that the possibility of existence of a series of monoclinic phases $K_xP_2W_{2n}O_{6n+4}$ corresponding to ReO_3-type slabs of various widths should be considered.

The comparison of these results with our previous works (1, 2) shows that the behavior of rubidium is different from that of potassium, the oxides $Rb_xP_8W_{8n}O_{24n+16}$ also being characterized by ReO_3-type slabs but connected through P_2O_7 groups exclusively. Potassium gives both sorts of structures, built up from PO_4 and P_2O_7 units. Nevertheless, the presence in $K_xP_2W_4O_{16}$
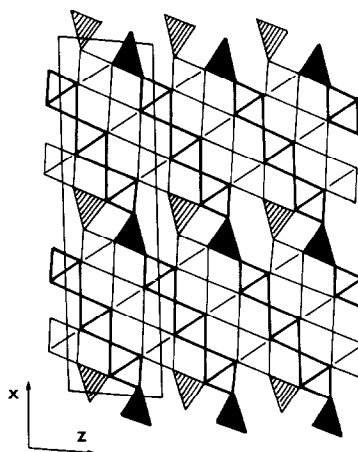

FIG. 3. Projection onto (010) of the idealized monoclinic Mo_4O_{11} structure from Kihlborg (11).
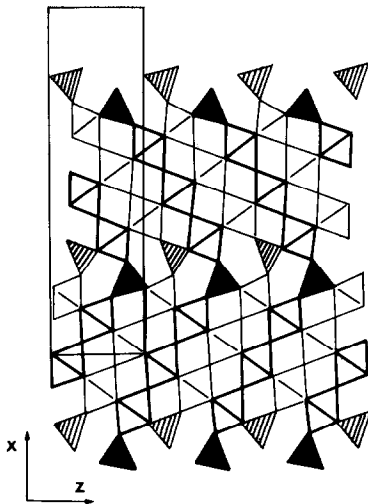
FIG. 4. Projection onto (010) of the idealized orthorhombic Mo_4O_{11} structure from Magnéli (12).

of distorted hexagonal tunnels led us to examine the relation of its framework with those of the bronzes $Rb_xP_8W_{8n}O_{24n+16}$ (1, 2). The tunnels can be described as a stacking along b of hexagonal rings built up of two tetrahedra and four octahedra (Fig. 5). These rings are strongly inclined with respect to the axis of the tunnel, i.e., about 50° with respect to b, their mean plane being approximately parallel either to ($\bar{4}43$) or to ($44\bar{3}$), owing to the fact that the tetrahedron of a ring shares two of its corners with the octahedra of the adjacent tunnel. These rings are very similar to those forming the distorted hexagonal tunnels in the Rb_x $P_8W_{8n}O_{24n+16}$ family (1, 2), but in this family the stacking is different, with the mean planes normal to the tunnel axis (b axis) and the successive rings being oriented in such a way that the tetrahedra are connected to form P_2O_7 groups.

The examination of a layer of polyhedra parallel to the mean plane of a hexagonal ring shows that the structure of $K_xP_2W_4O_{16}$ is in fact closely related to that of the oxides $Rb_xP_8W_{8n}O_{24n+16}$, and especially to the member $n = 2$, i.e., $Rb_xP_8W_{16}O_{64}$, that we are investigating at the present time. Its hy-

pothetical structure (H) has been deduced from the study of the members $n = 3$ and $n = 4$ (1, 2) and depicted by the projection of a layer in Fig. 6a. The comparison with a one-octahedron-thick layer parallel to a hexagonal ring in $K_xP_2W_4O_{16}$ (Fig. 6b) shows clearly that in both cases we find rows of identical pseudohexagonal rings separated by a double string of octahedra. The only difference concerns the orientation of the fourth apices of the PO_4 tetrahedra: for the two tetrahedra of a ring, they are directed on the same side of the mean plane of the L_1 layer in $Rb_xP_8W_{16}O_{64}$ (Fig. 6a), while they are alternately directed on either side of the mean plane of the L_2 layer in $K_xP_2W_4O_{16}$ (Fig. 6b). Thus the structure of $K_xP_2W_4O_{16}$ can be described as a stacking of such identical L_2 layers approximately along the [$23\bar{1}$] or [$\bar{2}31$] direction. Two adjacent layers correspond to one another in projection through the translation T_1 or T_2 (Fig. 6b), whose modulus is, respectively, equal to the diagonal or twice the edge of an octahedron. This disposition of two adjacent layers differs from that of $Rb_xP_8W_{16}O_{64}$ by the fact that two tetrahedra of different layers are never connected. The structure of $Rb_xP_8W_{16}O_{64}$ is obtained by stacking alternately one layer L_1 with one layer deduced from L_1 by a rotation of 180° (Fig. 6a). It is noteworthy that, stacking al-
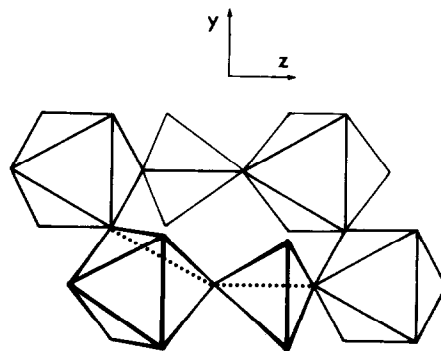

FIG. 5. $K_xP_2W_4O_{16}$: a pseudohexagonal ring drawn from a projection onto (100). The tetrahedra point on both sides of the mean plane of the ring.
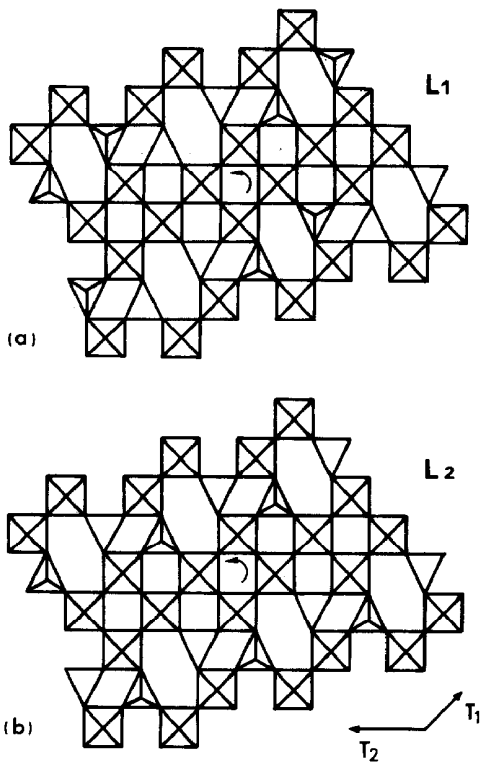
FIG. 6. Schematic representation of a layer of polyhedra parallel to the mean plane of a hexagonal ring (a) in the monoclinic $Rb_xP_8W_{16}O_{64}$ and (b) in $K_xP_2W_4O_{16}$.

involve the possibility of intergrowth of the two structural types.

Two sorts of cages are observed in $K_x P_2W_4O_{16}$ which can be compared to those of $P_4W_8O_{32}$ and $Rb_xP_8W_{8n}O_{24n+16}$. The first type consists of perovskite cages built up of seven octahedra and one tetrahedron and which are almost identical to those observed in $P_4W_8O_{32}$. Like $P_4W_8O_{32}$ and the rubidium oxides, $K_xP_2W_4O_{16}$ is characterized by cages bound by 18 oxygen atoms. These cages, located in the distorted hexagonal tunnels, are formed by eight octahedra and four tetrahedra (Fig. 8). Geometrically they are very close to those of $P_4W_8O_{32}$ (4) but different in $Rb_xP_8W_{8n}$ $O_{24n\pm16}$, where they correspond to the S' sites (1) bound by P_2O_7 groups. The K^+ ion is off-centered inside the "O_{18}" cage (Fig. 8), the displacement being 0.95 Å from the center of gravity, so as to avoid too short distances (2.15 Å between the center of gravity and O(6) atoms). The size of the "O_{18}" cage should be considered as intermediate between that of $P_4W_8O_{32}$ and that of rubidium compounds as shown from the K–O distances of Table III. This can ex-
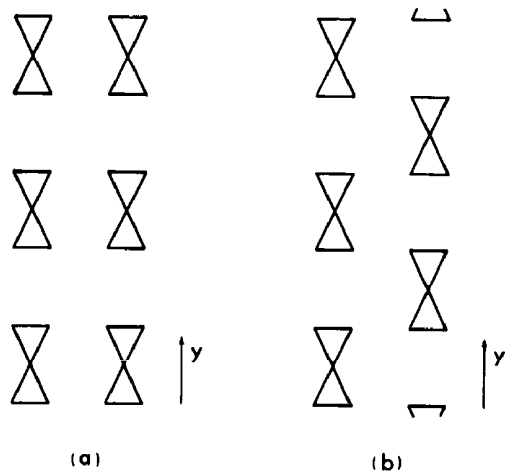
ternately one layer L_2 of $K_xP_2W_4O_{16}$ with one layer deduced from L_2 by a rotation of 180° (Fig. 6b), we would obtain a hypothetical structure H' very close to H. The only difference between H and H' is the relative positions of the P_2O_7 group along b: two P_2O_7 forming a distorted hexagonal tunnel are at the same level in H, while they are situated at different levels in H' (Fig. 7). On account of the results obtained for the terms $n = 3$ and $n = 4$ of the Rb_x $P_8W_{8n}O_{24n+16}$ series, it appears that the H structure is more probable for the term $n = 2$; nevertheless, the study of the term $n = 5$ (13) and of a nonintegral member $n = 3.5$ (14) allows us to consider H' as a possible framework. Whatever it may be, it must be pointed out that these close structural relations between the Rb and K oxides could

FIG. 7. Schema of the relative disposition of the P_2O_7 groups bounding a pseudohexagonal tunnel (a) in the hypothetical H structure and (b) in the hypothetical H' structure.
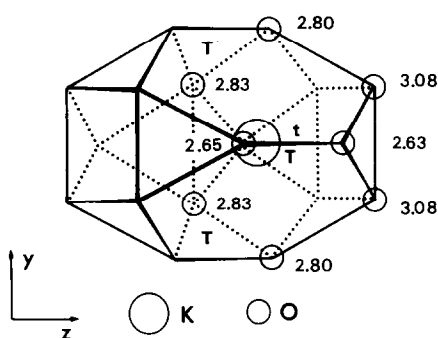
FIG. 8. A "O_{18}" cage drawn from a projection onto (100). T and t are, respectively, a face and an edge of a tetrahedron. The neighboring O atoms for K are given with the K–O distances in Å.

plain that such a structure is stabilized by K^+, whose size is smaller than that of Rb^+, Tl^+, or Cs^+.

It is worthy of note that perovskite tunnels running along the [101] direction are obtained, so that the framework of $K_x P_2 W_4 O_{16}$ can also be described as an intersecting-tunnels host lattice.

Conclusion

The structural study of the $K_x P_2 W_4 O_{16}$ bronze confirms the great ability of the PO_4 tetrahedra to accommodate an octahedral framework. A new structural family $K_x P_2 W_{2n} O_{6n+4}$, closely related to the two previous series, is observed. The possibility of formation either of other microphases or of intergrowths of these different structural types should be considered. A great number of the cavities of this structure are

empty, so that the possibility of intercalation of cations such as lithium or sodium will be investigated. Moreover, the great similarity of this phase with ReO_3 and the mean oxidation state of tungsten close to 5.4 let us foresee a metallic conductivity. Nevertheless, the presence of "planes" of PO_4 tetrahedra should involve an anisotropy.

References

1. J. P. GIROULT, M. GOREAUD, PH. LABBE, AND B. RAVEAU, Acta Crystallogr. Sect. B 36, 2570 (1980).
2. J. P. GIROULT, M. GOREAUD, PH. LABBE, AND B. RAVEAU, Acta Crystallogr. Sect. B 37, 1163 (1981).
3. J. P. GIROULT, M. GOREAUD, PH. LABBE, J. PROVOST, AND B. RAVEAU, Mater. Res. Bull. 16, 811 (1981).
4. J. P. GIROULT, M. GOREAUD, PH. LABBE, AND B. RAVEAU, Acta Crystallogr. Sect. B 37, 2139 (1981).
5. B. DOMENGES, M. GOREAUD, PH. LABBE, AND B. RAVEAU, Acta Crystallogr. Sect. B 38, 1724 (1982).
6. A. MAGNÉLI, Ark. Kemi 1, 213, 269 (1949); 1, 513 (1950).
7. M. HERVIEU AND B. RAVEAU, J. Solid State Chem., in press (1982).
8. D. T. CROMER AND J. T. WABER, Acta Crystallogr. 18, 104 (1965).
9. D. T. CROMER, Acta Crystallogr. 18, 17 (1965).
10. T. SUZUKI, Acta Crystallogr. 13, 279 (1960).
11. L. KIHLBORG, Ark. Kemi 21(35), 365 (1963).
12. A. MAGNÉLI, Acta Chem. Scand. 2, 861 (1948).
13. D. OUACHEE, Private communication.
14. J. P. GIROULT, M. GOREAUD, PH. LABBE, AND B. RAVEAU, Acta Crystallogr., in press (1982).