

Bronzes with a Tunnel Structure $\text{Rb}_x\text{P}_8\text{W}_{8n}\text{O}_{24n+16}$
III. $\text{Rb}_x\text{P}_8\text{W}_{28}\text{O}_{100}$: a Member Corresponding to a Non-Integral n Value $n = 3.5$

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Abstract

The member $n = 3.5$ of the series $\text{Rb}_x\text{P}_8\text{W}_{8n}\text{O}_{24n+16}$ has been studied by X-ray diffraction. The structure of a single crystal with the composition $\text{Rb}_{1.74}\text{P}_8\text{W}_{28}\text{O}_{100}$ has been established. The mean structure was solved in the space group $P2/c$ with $a = 15.723$ (4), $b = 3.764$ (3), $c = 17.118$ (4) Å, $\beta = 113.42$ (2)°, leading to $R = 0.030$ and $R_w = 0.033$ for 1512 reflections with $I \geq 0.005I_{\text{max}}$ and $\sigma(I)/I \leq 0.333$. The actual structure can be described with the cell a , $2b$, c , space group $P2_1/c$. The host lattice of this compound is built up from ReO_3 -type slabs connected through P_2O_7 groups. It can also be described as an ReO_3 -type framework in which P_2O_7 groups replace two octahedra in an ordered manner. A comparison is made between this non-integral member of the series and the integral members $n = 3$ and $n = 4$, especially concerning the distortion of the framework.

Introduction

Our previous studies (Giroult, Goreaud, Labbé & Raveau, 1980, 1981) describe the structure of two members, $n = 3$ and $n = 4$, of a series of oxides with the general formula $\text{Rb}_x\text{P}_8\text{W}_{8n}\text{O}_{24n+16}$. These compounds exhibit, like the $A_x\text{WO}_3$ bronzes (Magnéli, 1949), a tunnel structure and a metallic behaviour (Giroult, Goreaud, Labbé, Provost & Raveau, 1981); however, they differ from $A_x\text{WO}_3$ in that their host lattice is built up from both octahedra and tetrahedra. The structure of these phases can indeed be described as ReO_3 -type slabs connected through rows of P_2O_7 groups forming distorted hexagonal tunnels where the Rb^+ ions are located. This description allows one to predict a series of closely related microphases, which differ only one from the other by the number n of octahedra determining the width of the ReO_3 -type slabs. In consequence, besides the insertion non-stoichiometry, a possibility of non-stoichiometry by intergrowth of two 'integral members' n_1 and n_2 , leading to non-integral n values, can be considered.

However, the great adaptability of the P_2O_7 groups to the ReO_3 -type framework lets us anticipate other arrangements of the WO_6 octahedra and P_2O_7 groups which could render an account of non-integral n values. Thus, the present work deals with the structural study of the bronze $\text{Rb}_x\text{P}_8\text{W}_{28}\text{O}_{100}$ which corresponds to $n = 3.5$.

Experimental

Sample preparation

In a first step, a mixture of $(\text{NH}_4)_2\text{HPO}_4$, Rb_2CO_3 and WO_3 in appropriate ratios was heated in air at 900 K to decompose the phosphate and carbonate. Then, after addition of the theoretical amount of tungsten to obtain the composition $\text{Rb}_2\text{P}_8\text{W}_{28}\text{O}_{100}$, the mixture was heated for seven days at 1270 K in an evacuated silica ampoule. Crystals were selected from the final sample after examination by X-ray powder diffraction.

Determination of the mean structure

The crystal selected for the structure determination was a b -axis needle limited by $\{100\}$, $\{010\}$ and $\{001\}$ with dimensions $10 \times 28 \times 156$ μm. The Laue patterns showed monoclinic symmetry and the cell parameters (see *Abstract*) were deduced from a least-squares refinement based on 25 reflections. The systematic absences ($h0l$, $l = 2n + 1$) led to Pc or $P2/c$ and no superstructure reflections were observed.

The intensities were collected on a CAD-4 Enraf-Nonius diffractometer. The parameters of the data collection were fixed after a profile analysis of three reflections. The stability of the sample was verified by a periodic control. A total of 6054 reflections within a quarter of the reciprocal sphere of radius $\sin \theta/\lambda = 0.995$ Å⁻¹ were measured, using Mo $K\alpha$ radiation filtered with a graphite monochromator. The background intensity was recorded on both sides of each reflection. Lorentz-polarization corrections were applied for 1512 independent reflections with $I \geq$

0.005 I_{\max} and $\sigma(I)/I \leq 0.333$. The absorption correction ($\mu_t = 471 \text{ cm}^{-1}$) based on the crystal morphology led to transmission factors lying between 0.265 and 0.640.

The structure was solved by the heavy-atom method in $P2/c$. The W-atom positions, fixed by the Patterson function, were refined by least squares. The Rb and O atoms were then located in the subsequent difference synthesis.

A study of the maps of electron density of Rb and P showed that the occupation of the corresponding sites is only partial, about 40% for Rb and 50% for P, as in $\text{Rb}_x\text{P}_8\text{W}_{32}\text{O}_{112}$ (Giroult *et al.*, 1980). The atoms O(2), O(4), O(6), O(12) and O(13) are distributed over two neighbouring positions with an occupancy factor of 0.5 while the electron density contours appear to be almost spherical for the other atoms. As examples, the maps for O(4) and O(13) are given in Fig. 1. So, we have introduced split positions only for O(2), O(4), O(6), O(12) and O(13) and have refined the coordinates of all the atoms by full-matrix least squares. Scattering factors for W^{6+} , Rb^+ and P were from Cromer & Waber (1965) corrected for anomalous 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 $\sin \theta/\lambda$. Refinement with anisotropic thermal coefficients for W and Rb atoms led to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.030$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.033$. Final atomic parameters for the mean cell of content $\text{Rb}_{0.87}\text{P}_4\text{W}_{14}\text{O}_{50}$ are given in Table 1* and the projec-

* Lists of structure factors and anisotropic thermal parameters, and a complete list of distances and angles, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36859 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

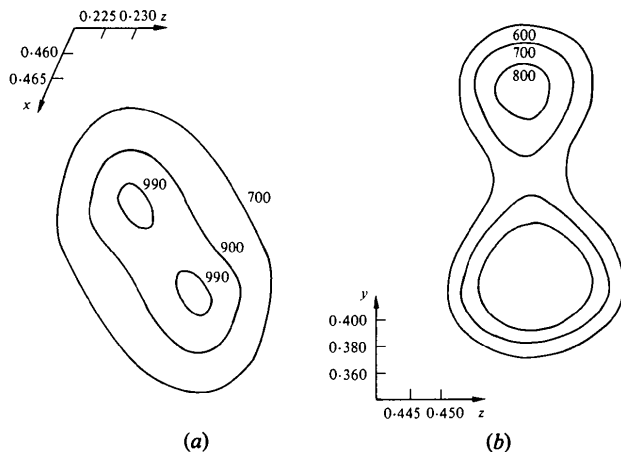


Fig. 1. Maps of electron density (a) for the O(4) atom, (b) for the O(13) atom. The levels of contour lines are given on an arbitrary scale.

Table 1. Positional parameters with e.s.d.'s for $\text{Rb}_x\text{P}_8\text{W}_{28}\text{O}_{100}$

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

Occupation	x	y	z	B (\AA^2)
Rb	0.44 (2)	0	0	1.3 (2)
W(1)	1	0.27014 (4)	0.5094 (2)	0.21 (1)
W(2)	1	0.15670 (5)	0.4596 (2)	0.27 (1)
W(3)	1	0.38745 (6)	0.5026 (3)	0.31 (1)
W(4)	1	↓	0.4910 (4)	0.42 (2)
P(1)	0.5	0.078 (1)	0.403 (3)	0.3 (2)
P(2)	0.5	0.078 (1)	0.596 (3)	0.5 (2)
O(1)	1	0.254 (1)	0*	0.3 (1)
O(2A)	0.5	0.119 (2)	0*	0.6 (3)
O(2B)	0.5	0.168 (3)	0*	1.6 (6)
O(3)	1	0.391 (1)	0*	0.3 (1)
O(4)	0.5	0.487 (3)	0*	1.9 (6)
O(5)	0.5	0.101 (2)	0.013 (12)	0.8 (2)
O(6)	0.5	0.499 (3)	0.577 (5)	-0.2 (1)†
O(7)	1	0.021 (1)	0.531 (7)	1.1 (2)
O(8)	1	0.195 (1)	0.543 (7)	0.7 (2)
O(9)	1	0.375 (1)	0.502 (8)	0.3 (2)
O(10)	1	0.445 (1)	0.481 (7)	0.3 (2)
O(11)	1	0.266 (1)	0.497 (10)	0.6 (2)
O(12A)	0.5	0.093 (3)	0.563 (10)	0.1 (4)
O(12B)	0.5	0.099 (3)	0.427 (11)	0.5 (5)
O(13A)	0.5	0.142 (2)	0.423 (6)	-0.3 (2)†
O(13B)	0.5	0.140 (3)	0.568 (12)	0.9 (5)
O(14)	1	0.318 (1)	0.464 (8)	0.6 (3)

* Non-convergent parameter which oscillates about zero during the refinement.

† Negative value due to the distribution of the atom over two neighbouring positions in the mean structure.

tion on to (010) is drawn in Fig. 2. Two features must be mentioned from these results: during the refinement, the y values of some O atoms oscillated about zero but did not converge; in this case, therefore, y has been fixed at zero. A negative value appeared for the B thermal coefficient of O(6) and O(13A): this phenomenon is occasionally observed in the case of split positions. Here, one can note that the refined O(6) and O(13A) split positions do agree with the values deduced from the electron density maps, and that the values for B obtained without splitting, were generally up to 3 \AA^2 .

The actual structure

The splitting of some O atoms, as shown by the electron density contours in the mean structure, is

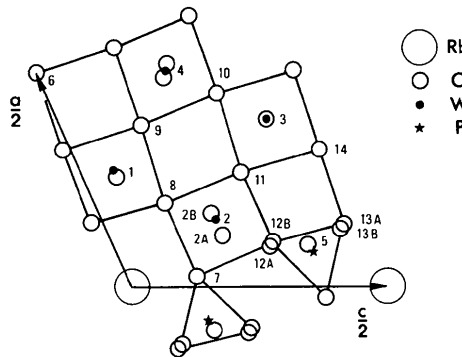


Fig. 2. Projection of the mean structure on to (010).

abnormal. In the same way, the distribution observed for the P atoms in this mean structure is not possible because it would involve the existence in the **b** direction of files of P_2O_7 groups enclosing face-sharing tetrahedra. Two interpretations of these observations can be made: the first by considering that the position of the P_2O_7 group as a whole is disordered, and the second by considering the existence of a superstructure involving the doubling of *b*, though no superstructure reflections were observed. A structure factor calculation for the superstructure reflections showed that the strongest would be 0.43% of the maximum intensity of the whole spectrum and thus they cannot give significant measures. However, the existence of the superstructure appears to be the most appropriate hypothesis for two reasons. First, the superstructure has been previously observed and weak reflections have been measured in the case of the members $n = 3$ and $n = 4$ (Giroult *et al.*, 1980, 1981) and, secondly, it seems impossible to conceive a disordered arrangement of the P_2O_7 groups in the **b** direction which abides by the following conditions: the occupancy factor of the P sites is 0.50 in the mean structure and two successive P_2O_7 groups cannot have a common face. Then the only possible arrangement of the P_2O_7 groups is as shown in Fig. 3. If we consider the actual structure with the cell *a*, 2*b*, *c*, a choice must be made concerning the location of the O atoms which appear to be split in the mean structure. The P(1) and P(2) atoms being located, a calculation of the O—O distances allows one to choose from the O(12A)—O(12B), O(13A)—O(13B) and O(2A)—O(2B) atoms, the positions giving distances too short being rejected. The best solution is then described by Fig. 3 which shows the deformation of the ReO_3 -type framework imposed by the presence of the P_2O_7 groups. This deformation appears to be localized to the neighbouring O atoms, contrary to the term $n = 4$ of the series where the deformation of the ideal perovskite framework is gradual. One can observe that the movement of the O(12) and O(13) atoms from the ideal

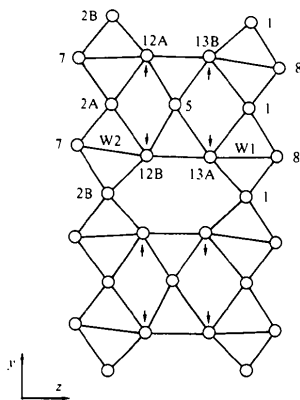


Fig. 3. Partial projection on to (100) showing the adjustment of the P_2O_7 group in the framework.

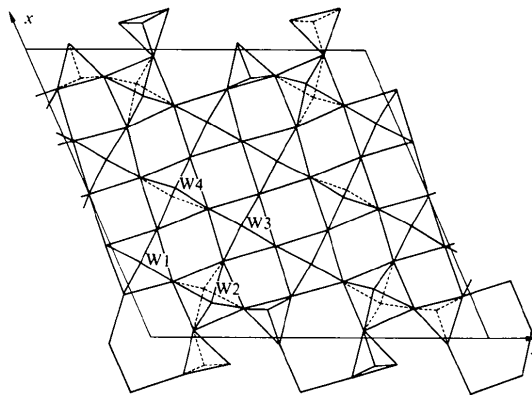


Fig. 4. Projection of the actual structure on to (010) limited to the oxygen framework from $y = 0$ to $y = 0.5$.

positions, noted by the arrows on Fig. 3, corresponds to a distortion of the W(1) and W(2) octahedra, but not to their tilting.

Concerning O(4) and O(6), consideration of interatomic distances does not allow one to choose between the two possible positions. The splitting appeared clearly in the mean structure, due to the existence of a twofold axis and of a centre of symmetry, but we have no data to consider any space group other than $P2/c$ for this mean structure. The splitting of atoms located far from the P_2O_7 groups was not observed in the terms $n = 3$ and $n = 4$ of the series, so we have no explanation and we represent in Fig. 4 the projection of the actual structure with an arbitrary choice for the location of O(4) and O(6).

Description of the structure and discussion

As shown in Fig. 5, the structure of $\text{Rb}_x\text{P}_8\text{W}_{28}\text{O}_{100}$ is closely related to those of the integral members $\text{Rb}_x\text{P}_8\text{W}_{24}\text{O}_{88}$ and $\text{Rb}_x\text{P}_8\text{W}_{32}\text{O}_{112}$. The host lattice of such compounds can be described as ReO_3 -type slabs connected through P_2O_7 groups which form distorted hexagonal tunnels with the WO_6 octahedra located at the boundary of the slices. The extension of these slabs is characterized by the number *n* of octahedra which form the strings directed approximately along the [403] direction of the $\text{Rb}_x\text{P}_8\text{W}_{28}\text{O}_{100}$ cell. For the compound described here, the width of the slab is not constant since the value $n = 3.5$ corresponds to the succession along the [001] direction of strings built up alternately from three and four WO_6 octahedra (Fig. 5*b*). These results show that this structure does not correspond to an intergrowth of the members $n = 3$ and $n = 4$ which would involve a succession alternately of layers three and four octahedra wide (Fig. 5*d*). The distinctive feature of a non-integral member, compared to an integral one, is that the rows of tunnels are shifted one with respect to the other in the [001] direction (Fig. 5).

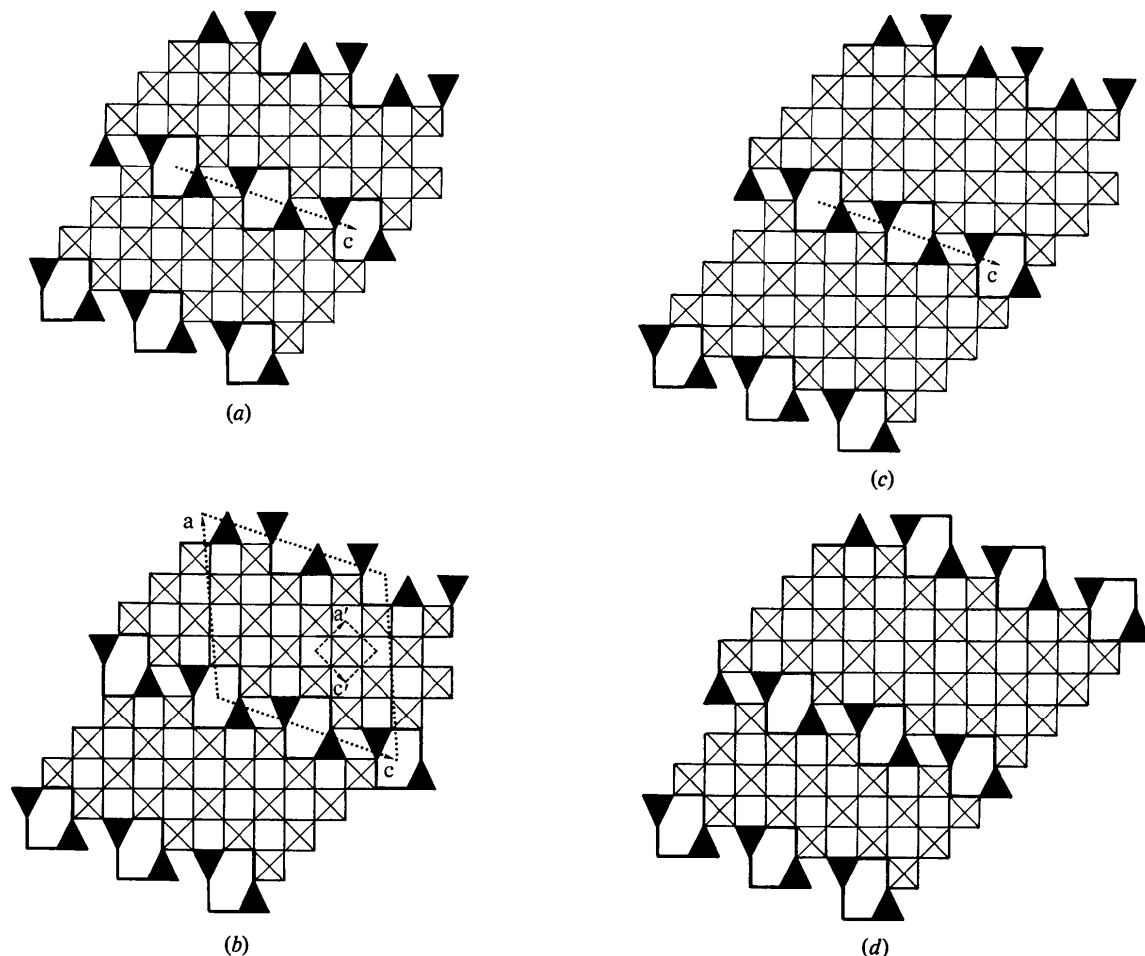


Fig. 5. Projection of the idealized structure (a) for the member $n = 3$, (b) for the member $n = 3.5$. The vectors a' and c' belong to the perovskite cell (c) for the member $n = 4$ of the series $\text{Rb}_x\text{P}_8\text{W}_{8n}\text{O}_{24n+16}$, (d) for the theoretical intergrowth of the members $n = 3$ and $n = 4$.

Another description of this structural family can be obtained by considering the strings of polyhedra directed along the $[100]$ direction of the cubic perovskite cell and which are transversal with respect to the rows of tunnels (Fig. 5). One observes distorted ReO_3 -type strings in which one WO_6 octahedron (O) is periodically replaced by a PO_4 tetrahedron (T), leading to the following sequences: $(O)_3T$ for $n = 3$, $(O)_4T$ for $n = 4$ and $(O)_3T(O)_4T$ for $n = 3.5$ (Fig. 5). Thus it appears that these oxides can be described as ReO_3 -type frameworks in which P_2O_7 groups replace groups of two octahedra in an ordered manner and play the role of ordered structural defects. The connection between these strings of polyhedra in the member $n = 3.5$ is different from that observed in the integral members as shown in Fig. 6. That could be at the origin of the differences observed for the deformation of the host lattice of $\text{Rb}_x\text{P}_8\text{W}_{28}\text{O}_{100}$ ($n = 3.5$) with regard to the integral members $n = 3$ and $n = 4$.

In the actual structure of $\text{Rb}_x\text{P}_8\text{W}_{28}\text{O}_{100}$, there are two possibilities of coordination for each W atom of Table 1, except for W(4) which is located on the twofold axis. The distances W—O listed in Table 2 show that the coordination for W(4) is near to a regular six octahedral coordination with O—W—O angles close

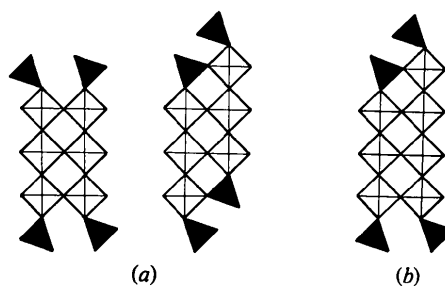


Fig. 6. Connection between the strings of polyhedra (a) in the integral term $n = 3$, (b) in the member $n = 3.5$.

Table 2. *Coordination of Rb and W atoms in the actual structure*

Interatomic distances are given in Å.

Bond	Rb—N	W(1)—N	W(2)—N	W(2')—N	W(3)—N	W(4)—N
Neighbourhood N						
O(1)		{1.936 (3) 1.866 (3)				
O(2A)			2.12 (1)	1.83 (1)		
O(2B)			1.743 (7)	2.045 (6)		
O(3)					{1.893 (2) 1.873 (2)	
O(4)						{1.858 (4) 1.926 (4)
O(5)						
O(6)					{1.89 (3) or 1.87 (3)	
O(7)	{2 × 2.80 (2) 2 × 2.95 (2)		2.08 (2)	2.08 (2)		
O(8)		2.06 (2)	1.79 (2)	1.79 (2)		
O(9)		1.79 (1)				2 × 1.98 (1)
O(10)					1.85 (3)	2 × 1.90 (3)
O(11)			1.77 (1)	1.77 (1)	1.99 (1)	
O(12A)				2.08 (5)		
O(12B)			2.06 (6)			
O(13A)	2 × 2.96 (3)	{2.03 (2) or 2.13 (4)				
O(13B)	2 × 3.03 (5)					
O(14)		1.79 (2)			2.02 (2)	

to 90 and 180° and a W(4) atom displacement of 0.01 (2) Å from the centre of gravity of O neighbours: so we can consider that W(4) is perfectly centred in its octahedron. A 4 + 2 coordination appears for the W(1) atoms with a displacement of 0.22 (2) Å, and for the W(3) atoms in spite of a weak displacement of 0.03 (2) Å [or 0.10 (2) Å for the second sort of W(3)] from the centre of gravity. The W(2) atoms, which are linked to two P_2O_7 groups, are the most disturbed: their coordination is 3 + 3 and the displacement is 0.24 (3) or 0.31 (3) Å from the centre, the most important we have observed now in that structural type. Thus, the WO_6 octahedra of the $\text{P}_8\text{W}_{28}\text{O}_{100}$ framework are more distorted than those of the members $n = 3$ and $n = 4$. On the other hand, no tilting of the octahedra is observed for $n = 3.5$ contrary to the members $n = 3$ and $n = 4$.

The distances and angles concerning the P_2O_7 group are given in Table 3. This group does not appear to be geometrically different from those observed in the integral members (Giroult *et al.*, 1980, 1981). The only difference concerns the steric effect of the P_2O_7 group which is somewhat more important in the member $n = 3.5$ than in the integral members $n = 3$ and $n = 4$. The O—O distances between two different tetrahedra are given in Fig. 7 and show that the distance between the O(7) atoms (3.76 Å) is much larger in the member $n = 3.5$ than in $n = 3$ and $n = 4$. This corresponds to greater distances between O(7) and the bridging oxygen atom in $n = 3.5$ (2.59 and 2.69 Å) than in the integral members (close to 2.50 Å) and shows a certain

adaptability of the P_2O_7 group in spite of its apparent rigidity.

The cages and tunnels are similar in both structural types but the location of Rb^+ in the distorted hexagonal tunnels merits discussion. The solution we retained for the integral members was deduced from the observed symmetry and from the tilting of the WO_6 octahedra: the structural configuration led us to consider that P_2O_7 groups on both sides of the pseudohexagonal tunnel are lying at the same level y , the most probable Rb^+ site being at the level where the P_2O_7 groups are missing. These features do agree for the member $n = 3.5$ with Rb^+ on a centre of symmetry, with an 8 coordination and suitable distances (Table 2). However, in $n = 3.5$ the WO_6 octahedra are distorted but not tilted, and we cannot reject a second hypothesis where, on each side of a pseudohexagonal tunnel, the P_2O_7 groups are

Table 3. *The P_2O_7 group in the actual structure: interatomic distances (Å) and angles (°)*

P(1)—P(2)	3.04 (2)	O(5)—P(1)—O(12A)	104 (2)
P(1)—O(5)	1.52 (5)	O(5)—P(1)—O(13B)	111 (3)
P(1)—O(7)	1.55 (3)	O(7)—P(1)—O(12A)	104 (2)
P(1)—O(12A)	1.53 (5)	O(7)—P(1)—O(13B)	105 (2)
P(1)—O(13B)	1.46 (4)	O(12A)—P(1)—O(13B)	111 (3)
P(2)—O(5)	1.61 (5)	O(5)—P(2)—O(7)	112 (2)
P(2)—O(7)	1.52 (3)	O(5)—P(2)—O(12B)	108 (3)
P(2)—O(12B)	1.46 (6)	O(5)—P(2)—O(13A)	109 (2)
P(2)—O(13A)	1.63 (3)	O(7)—P(2)—O(12B)	113 (2)
P(1)—O(5)—P(2)	153 (3)	O(7)—P(2)—O(13A)	104 (2)
O(5)—P(1)—O(7)	122 (2)	O(12B)—P(2)—O(13A)	110 (2)

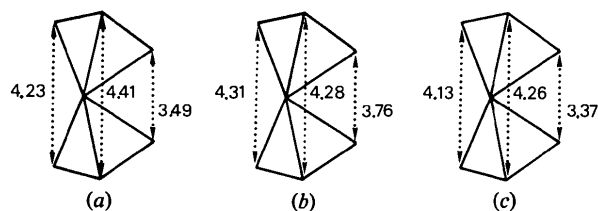


Fig. 7. Steric effect of the P_2O_7 group (a) in the member $n = 3$, (b) in the member $n = 3.5$, (c) in the member $n = 4$ of the series $Rb_xP_8W_{8n}O_{24n+16}$.

shifted each with respect to the other by the \mathbf{b} vector. Then Rb^+ could be located near the y level of $O(5)$ and should present a 7 coordination. The hypothesis where Rb^+ could be located at the same y level as $O(7)$ and $O(13)$ is unlikely because two $Rb-O$ distances would be too short.

Conclusion

This structural study shows the existence of non-integral members in the series of oxides with the general formula $Rb_xP_8W_{8n}O_{24n+16}$. The oxides $Rb_xP_8W_{28}O_{100}$

($n = 3.5$) are not formed by the intergrowth of two integral members but by a variation in the number of WO_6 octahedra (alternately three and four) which build up the perovskite slabs of the framework. The cages, the tunnels and the location of Rb^+ appear to be similar to those of the integral members $n = 3$ and $n = 4$. Nevertheless, the deformation of the ideal perovskite framework, due to the presence of P_2O_7 groups, is localized and different from the progressive distortion by tilting which was observed in $Rb_xP_8W_{24}O_{88}$ and $Rb_xP_8W_{32}O_{112}$.

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Structure du Tétrafluorure de Zirconium, $ZrF_4 \alpha$

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Abstract

α - ZrF_4 , the high-temperature polymorph of zirconium tetrafluoride, crystallizes with tetragonal symmetry, space group $P4_2/m$, and $a = 7.896(1)$, $c = 7.724(1)$ Å, $Z = 8$, $D_m = 4.55$, $D_x = 4.61$ g cm $^{-3}$, $\mu(\text{Mo } K\alpha) = 44$ cm $^{-1}$. Its structure has been solved by single-crystal X-ray analysis and refined to a conventional $R = 0.030$ ($R_w = 0.031$) for 1335 independent reflexions recorded on a four-circle automatic diffractometer. The structure is a three-dimensional framework of triangular ZrF_8 dodecahedra sharing corners along Ox and Oy axes, and edges and corners alternately along Oz . An alternative approach is to consider it as a stacking of three atomic

layers: a $3^2.4.3.4$ planar network of Zr atoms, a $[(3.5.4.5)^2, 3.5.3.5]$ and a distorted $[(4.6.8)^2, 6.8^2]$ planar network of F atoms. Its relationship to the monoclinic β - ZrF_4 structure as well as to the ReO_3 type is described and discussed.

Introduction

Quatre variétés polymorphiques du tétrafluorure de zirconium ZrF_4 sont connues à ce jour: une variété amorphe et trois variétés cristallines: α , γ et β (Gaudreau, 1965).

Seule la variété β de symétrie monoclinique, thermodynamiquement stable à température et pression ordinaires – les trois autres variétés se transforment irréversiblement en la variété β par chauffage plus ou

* Auteur auquel toute correspondance doit être adressée.