Na$_x$P$_4$W$_{14}$O$_{50}$: The Sodium m = 7 Member of the Monophosphate Tungsten Bronze Series A_x(PO$_2$)$_4$(WO$_3$)$_{2m}$

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The structure of Na$_{1.7}$P$_4$W$_{14}$O$_{50}$ was established by single crystal X-ray analysis. The compound is the m = 7 member of the family of monophosphate tungsten bronzes with hexagonal tunnels, Na$_x$(PO$_2$)$_4$ (WO$_3$)$_{2m}$, characterized by ReO$_3$-type slabs of various widths connected through PO$_4$ tetrahedra. In order to compare with other members of the MPTB$_h$ family, a cell symmetry A$\bar{1}$ has been chosen with a = 6.575(2), b = 5.304(1), c = 27.076(3) Å, α = 89.62(1), β = 96.17(1), and γ = 90.26(1)°. The refinement has led to R = 0.040 and R_w = 0.036 for 6634 reflections with $\sigma(I)/I \leq 0.333$. A comparative study is carried out concerning the behavior of the alkaline ions in that sort of framework and especially their coordination state in the O$_{18}$ cages. © 1987 Academic Press, Inc.

Introduction

During the investigation of the P–W–O and A–P–W–O systems (A = Na, K, Rb, Cs, Tl), several series of bronzes called "phosphate-bronzes" were isolated whose structures are built up from ReO$_3$-type slabs connected through phosphate planes. Among these oxides, the monophosphate tungsten bronzes with hexagonal tunnels (MPTB$_h$) A_x(PO$_2$)$_4$(WO$_3$)$_{2m}$, which are closely related to the structure of η-Mo$_4$O$_{11}$ described by Kihlborg (*1*), appear to be stabilized by ions of intermediate size such as Na$^+$ and K$^+$. Contrary to the monophosphate bronzes with pentagonal tunnels MPTB$_p$, (PO$_2$)$_4$(WO$_3$)$_{2m}$, or to the diphosphate tungsten bronzes DPTB, A$_x$(P$_2$O$_4$)$_2$

(WO$_3$)$_{2m}$, only four MPTB$_h$ compounds were known up to the present: A_xP$_4$W$_8$O$_{32}$ (m = 4) with A = K and Na (2, 3), Na$_x$P$_4$ W$_{12}$O$_{44}$ (m = 6) (*3*), and K$_x$P$_4$W$_{14}$O$_{50}$ (m = 7) (*4*). What is more, the sodium bronzes exhibit a symmetry different from that of the potassium bronzes, although they are both monoclinic.

The present paper deals with a new sodium member, Na$_x$P$_4$W$_{14}$O$_{50}$ (m = 7), which is triclinic, and with the influence of the A ion, sodium or potassium, on the distortion of the ReO$_3$-type framework.

Experimental

A mixture of Na$_2$CO$_3$, (NH$_4$)$_2$HPO$_4$, and WO$_3$ in appropriate ratios was first heated in air at 773 K in an alumina crucible to decompose the carbonate and the phosphate. An adequate amount of metallic W

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TABLE I

EXPERIMENTAL DATA AND STRUCTURE
REFINEMENT PARAMETERS FOR $Na_{1.7}P_4W_{14}O_{50}$

Crystal shape and size	Triclinic sample 216 × 192 × 96 μm limited by {100}, {$\bar{1}$00}, {110}, {$\bar{1}\bar{1}$0}, {$\bar{1}$10}, {1$\bar{1}$0}, {001}, and {00$\bar{1}$}
Lattice parameters (Å, °)	a = 6.575(2)
	b = 5.304(1)
	c = 27.076(3)
	α = 89.62(1)
	β = 96.17(1)
	γ = 90.26(1)
Conditions limiting possible Space Group	No condition
Possible Space Group	A$\bar{1}$ or A1 (see text)
Data collection technique	CAD 4 Enraf–Nonius ω–θ scan
(sin θ/λ) max	0.941
Standard reflections and their intensity variation	3 reflections with ($\Delta I/I$) max = 0.04
Number of reflections measured	10,390 (0 < h < 12, $-10 < k < 10$, $-54 < l < 54$)
Number of reflections used in the refinement	6634 with $\sigma(I)/I$ < 0.333
Absorption correction	Based on the crystal morphology Program AGNOSTC (5, 6)
Linear absorption coefficient, μ(AgKα)	121.6 cm^{-1}
Max and min values of the transmission factor	0.50 and 0.33
Method used to solve the structure	Patterson and Fourier methods. Use of F magnitude in least-squares refinement
Atomic scattering factors, f' and f'' values	International Tables (7)
R, R_w	0.040, 0.036

was then added to obtain the composition $Na_xP_4W_{14}O_{50}$ and the sample was heated for 3 days at 1173 K in an evacuated silica ampoule. The sample was formed by dark-red triclinic crystals (Table I).

A crystal was adjusted on an Enraf–Nonius goniometer and studied with MoKα radiation. The triclinic lattice parameters suspected on X-ray films were then confirmed although the intensity distribution was not far from the monoclinic symmetry. The chosen coordinate system would involve an easy comparison with $K_xP_4W_{14}O_{50}$ (4) of $A2/m$ symmetry: this compound has a = 6.660(2), b = 5.3483(3), c = 27.06(5) Å, and β = 97.20(2)°. An axial orientation was fixed (Table I) and a data collection was registered with approximately the same values for the lattice parameters, α and γ angles close to 90°, and an unusual A-centered cell. Unfortunately, this set of intensities gave results of poor quality whatever corrections were used, and in particular, some factors of thermal vibration β_{ii} became negative for heavy atoms. It was thought that absorption certainly played a part (μ_l(MoKα) = 212 cm^{-1}) and we decided to collect a new set of intensities using AgKα radiation. The major experimental data and structure parameters are listed in Table I. The refinement was made assuming the centrosymmetric group. The results (Table II) were obtained using a linear weighting scheme $\langle w|\Delta F|\rangle$ in terms of (sin θ/λ). The composition in Na$^+$ obtained during the refinement gives the formula $Na_{1.7(2)}P_4W_{14}O_{50}$.

Description of the Structure and Discussion

These results confirm that $Na_{1.7}P_4W_{14}O_{50}$ belongs to the monophosphate tungsten bronze series MPTB$_h$ $A_x(PO_2)_4(WO_3)_{2m}$ previously described for A = K and Na (2–4). However, the structure of this bronze is characterized by a triclinic symmetry and appears to be a distortion of the usual monoclinic structure of MPTB$_h$. A projection onto (010) of the unusual A cell is drawn in Fig. 1.

The dispersion of the cation–oxygen distances is generally slightly larger than in the

TABLE II

POSITIONAL AND THERMAL PARAMETERS WITH e.s.d.'s FOR $Na_{1.7}P_4W_{14}O_{50}$

	x	y	z	B (Å^2)
W(1)	0	0	0	B_{eq} = 0.323(7)
W(2)	0.69794(5)	0.49951(5)	0.054473(9)	B_{eq} = 0.285(9)
W(3)	0.39771(4)	0.99115(5)	0.111453(9)	B_{eq} = 0.274(5)
W(4)	0.08628(4)	0.49454(4)	0.167629(8)	B_{eq} = 0.268(3)
P	0.2046(2)	0.5227(3)	0.29191(6)	0.32(1)
O(1)	0.192(1)	−0.006(1)	0.0597(2)	0.71(4)
O(2)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.58(6)
O(3)	0.8225(8)	0.7865(9)	0.0327(2)	0.65(3)
O(4)	0.8654(7)	0.2810(8)	0.0237(2)	0.53(3)
O(5)	0.5209(7)	0.7085(8)	0.0927(2)	0.54(3)
O(6)	0.5639(8)	0.2117(9)	0.0834(2)	0.64(4)
O(7)	0.901(1)	0.495(1)	0.1139(2)	0.82(5)
O(8)	0.2204(8)	0.7774(8)	0.1523(2)	0.60(3)
O(9)	0.2654(8)	0.2775(9)	0.1459(2)	0.60(3)
O(10)	0.585(1)	0.000(1)	0.1779(3)	0.94(5)
O(11)	0.2500(9)	0.490(1)	0.2380(2)	0.73(4)
O(12)	0.1208(9)	0.792(1)	0.2965(2)	0.76(4)
O(13)	0.055(1)	0.316(2)	0.3042(3)	1.25(7)
Na	0.330(3)	0.012(3)	0.2368(6)	1.4(2)

U_{ij}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	0.0040(1)	0.00430(9)	0.00407(9)	−0.00014(6)	0.00097(6)	0.00040(6)
W(2)	0.00361(7)	0.00384(7)	0.00346(6)	−0.00008(4)	0.00066(5)	0.00016(4)
W(3)	0.00340(8)	0.00389(7)	0.00318(6)	0.00016(4)	0.00042(5)	0.00012(4)
W(4)	0.00375(6)	0.00387(6)	0.00265(6)	0.00005(4)	0.00071(4)	0.00007(3)

Note. The values of the thermal coefficients were obtained from $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}a_ia_j$ and $U_{ij} = (1/2\pi^2)\beta_{ij}a_ia_j$ (Å^2).

other members of the series (Table III). The distances of P or W from the center of gravity G of the surrounding oxygen atoms are generally larger than in the previously studied compounds if one excepts the case of W(1) which is located at the center of symmetry and gives an almost regular octahedron with homogeneous W–O distances. As we have previously observed, the coordination of the tungsten atoms is not as regular for the WO$_6$ octahedra connected to PO$_4$ tetrahedra as W(3) which shares its corners with one PO$_4$ tetrahedron or W(4) which is connected to three tetrahedra (Fig. 1). The W–G distances are 0.205(4) and 0.215(5) Å, respectively, whereas they are

shorter in $K_xP_2W_4O_{16}$ and $Na_xP_4W_8O_{32}$ (0.08 and 0.16 Å in both cases) or in $Na_xP_4W_{12}O_{44}$ (0.15 and 0.16 Å). Nevertheless the values observed in $K_{1.4}P_4W_{14}O_{50}$ (4) are close to those described here for $Na_{1.7}P_4W_{14}O_{50}$ and the comparison of the W–O distances in the two oxides shows very small differences in the coordination of W. The octahedral coordination of the W(1) atoms is almost regular in both cases with a tendency toward 4 + 2 coordination, and we have noted that, in $Na_{1.7}P_4W_{14}O_{50}$, the O–W(1)–O angles are very close to the theoretical values (88.6(2) to 91.4(2) and 180°). As for W(1), the W(2)O$_6$ octahedra are linked only to other octahedra. They are
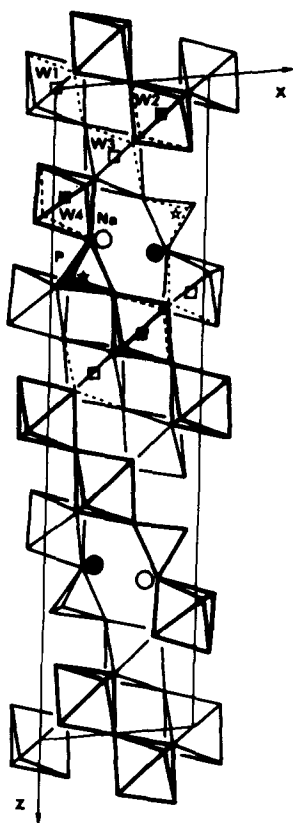
FIG. 1. $Na_{1.7}P_4W_{14}O_{50}$: projection of the structure onto (010). The polyhedra with dark and light outlines, respectively, lie at levels $y = \frac{1}{2}$ and 0. Na^+ ions lie at $y \sim 0$ (open circles) and $y \sim 0.5$ (filled circles).

hedra and from about 2.4 to 2.6 Å in the tetrahedra.

From the projection onto (010) (Fig. 1) it is easy to compare the host lattice of this bronze to that of $K_{1.4}P_4W_{14}O_{50}$ previously described (4). Both frameworks are built up from corner-sharing WO_6 octahedra and PO_4 tetrahedra forming hexagonal tunnels where the Na^+ or K^+ ions are located. Thus, the structure can be regarded as ReO_3-type slabs connected through "phosphate planes." The width of these slabs is determined, as for $K_{1.4}P_4W_{14}O_{50}$, by chains of alternately three and four octahedra limited at each end by one tetrahedron and running approximately along [301]. A slight rotation of the octahedra around the mean axis [301] with respect to those of $K_{1.4}P_4W_{14}O_{50}$ is observed. This rotation occurs in opposite directions for the adjacent chains, or for successive chains of three and four octahedra (Fig. 1). However, the position of the P atoms with respect to the heavy atoms is identical to that observed in the potassium members of the series. The four W atoms involved in the W–O–P bonds form a tetrahedron including the P atom which is located at 0.652(2) Å from the center of the corresponding W_4 tetrahedron, compared to 0.60 Å in $K_{0.4}P_2W_4O_{16}$ (2) and 0.61 Å in $K_{1.4}P_4W_{14}O_{50}$ (4).

The main difference between the bronzes $Na_{1.7}P_4W_{14}O_{50}$ and $K_{1.4}P_4W_{14}O_{50}$ concerns the geometry of the O_{12} perovskite cages. The projection of a structural layer along [301] shows that the perovskite tunnels running along this direction exhibit a diamond-shaped section (Fig. 2) whereas the two other directions, about [58$\bar{1}$] and [$\bar{5}$81], are characterized by square perovskite tunnels. The behavior is different from that of $K_{1.4}P_4W_{14}O_{50}$ which exhibits square tunnels along the three directions as in the ideal perovskite structure. In a perovskite cage formed by WO_6 octahedra exclusively, the calculated distances G–O from the center of gravity of the O_{12} group to the oxygen

nearly regular with a tendency toward $3 + 3$ coordination as in $K_{1.4}P_4W_{14}O_{50}$. For the W atoms connected to PO_4 tetrahedra, the coordination is $3 + 3$, well marked in the case of $Na_{1.7}P_4W_{14}O_{50}$. The $W(3)O_6$ and $W(4)O_6$ units seem to be equally distorted with W–$G \sim 0.21$ Å and O–W–O angles ranging from 79.8(2) to 96.1(2)°, and 168.8(2) to 171.2(2)° for $W(3)O_6$. For $W(4)O_6$ the values are 82.2(3) to 98.5(2) and 168.3(2) to 171.7(3), and the W–O distances (Table III) show a more pronounced $3 + 3$ coordination: indeed W(4) is linked to three PO_4 tetrahedra by the longest W(4)–O distances. In all cases, the O–O distances are usual, ranging from about 2.6 to 2.8 Å in the octa-

TABLE III

$Na_{1.7}P_4W_{14}O_{50}$ Interatomic Distances (Å)

	Na[a]	P	W(1)	W(2)	W(3)	W(4)
G^b	1.19(2)	0.063(6)	0	0.092(3)	0.205(4)	0.215(5)
O(1)			2 × 1.944(6)		1.837(6)	
O(2)				1.8593(4)		
O(3)			2 × 1.904(5)	1.848(5)		
O(4)			2 × 1.889(5)	1.862(5)		
O(5)				1.985(5)	1.809(4)	
O(6)				1.959(5)	1.816(5)	
O(7)				1.976(6)		1.796(6)
O(8)	2.64(2)				2.028(5)	1.806(5)
O(9)	2.82(2)				2.035(5)	1.797(5)
O(10)	2.43(2)	1.536(7)			2.068(7)	
O(11)	⎧2.59(2)⎫ ⎨2.77(2)⎬ ⎩2.82(2)⎭	1.533(6)				2.085(5)
O(12)	2.51(2)	1.546(6)				2.094(6)
O(13)	2.81(2)	1.528(9)				2.070(9)

[a] Next neighbors are beyond 3.16 Å.

[b] G is the center of gravity of O_{18}, O_4, and O_6 polyhedra.

atoms show a large variation for $Na_{1.7}P_4W_{14}O_{50}$ (2.48 to 2.93 Å) and a homogeneous distribution in $K_{1.4}P_4W_{14}O_{50}$ (2.67 to 2.75 Å). The difference appears as a common feature to all the members of the MPTB$_h$ series: $K_xP_4W_8O_{32}$ exhibits only square perovskite tunnels whereas $Na_xP_4W_8O_{32}$ and $Na_xP_4W_{12}O_{44}$ (3) have diamond-shaped tunnels along one direction and square tunnels along the two others. Thus it appears that the ReO_3-type slabs of the potassium bronzes are built up from corner-sharing idealized octahedral units "W_4O_{20}" characterized by angles of 90° as in the cubic perovskite, while the sodium bronzes form diamond-shaped windows along one direction with angles tending toward 60 and 120° (Fig. 7) as in some other perovskite-type structures.

It must be pointed out that the compounds with diamond-shaped tunnels do not exhibit a greater distortion of the WO_6
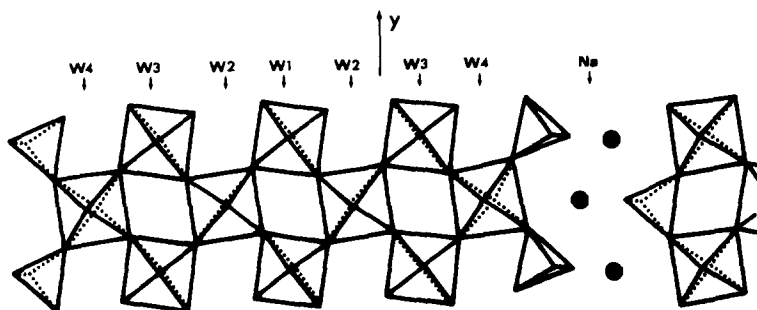

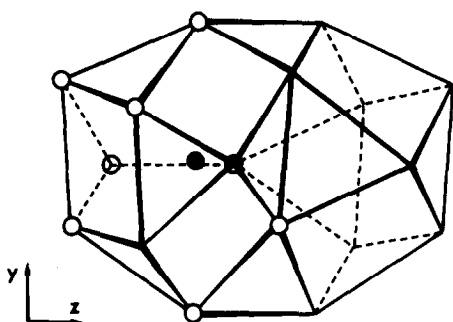Fig. 2. Projection along [301] of a structural layer.

FIG. 3. A cage bounded by 18 oxygen atoms drawn from a projection along [100]. The filled circle is Na^+ and the open circles are the 8 first oxygen neighbors.

in both oxides, i.e., about $6.8 \times 6.6 \times 5.3$ (Å) between O atoms along the three main directions, whatever the m value and the nature of the A ion (sodium or potassium) may be. The O_{18} cage in $Na_{1.7}P_4W_{14}O_{50}$ is drawn in Fig. 3 from a projection along [100]. Owing to the large size of that sort of cage, the alkali ion is widely off-centered: its distance from the center of gravity of the O_{18} cage is 1.19(2) Å for Na^+ in the present oxide, 1.06 Å in $Na_xP_4W_8O_{32}$, 1.04 Å in $Na_xP_4W_{12}O_{44}$, and 0.95 Å for the K compounds. We can infer that the difference observed between the Na^+ and K^+ oxides is due to the difference between the sizes of these ions.

The surroundings of sodium and potassium can be compared in Fig. 4 where Na of the present oxide and K in $K_{1.4}P_4W_{14}O_{50}$ are represented with their eight nearest oxygen neighbors in the orientation of Fig. 3. The disposition of these atoms with respect to the hexagonal tunnels appears by projection onto (010) in Fig. 5. The distribution of the A–O distances in the phosphate tungsten bronzes (Fig. 6) shows a gathering of the K–O distances in the range of 2.6–3.1 Å when Na–O distances range from about 2.4 to 3.2 Å. Nevertheless it is obvious that the Na–O distances are divided in two groups, the first one containing four first neighbors
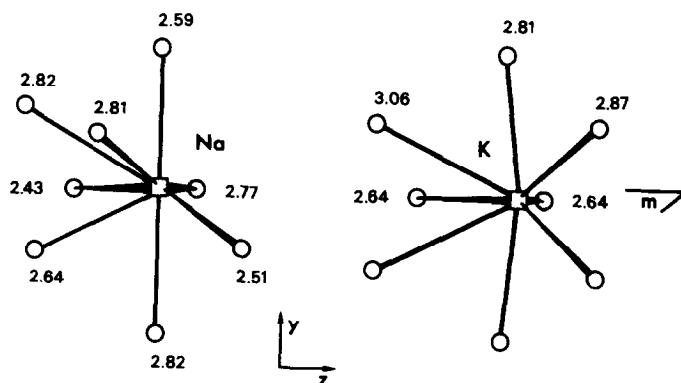
octahedra but result from a tilting of their octahedra with respect to the ideal perovskite. In spite of this difference between sodium and potassium phosphate-bronzes, the mean distances G–O are practically the same in the perovskite cages, i.e., 2.69(1) and 2.71(1) Å, respectively. Although these distances are compatible with the presence of Na^+ or K^+ in the perovskite cages, it must be pointed out that these cages are always empty in the phosphate tungsten bronzes. Thus the Na^+ ion, in spite of its small size, is preferentially located in the O_{18} cages forming the hexagonal tunnels.

The O_{18} cages have exactly the same size

FIG. 4. The eight nearest oxygen neighbors of Na^+ in $Na_{1.7}P_4W_{14}O_{50}$ and of K^+ in $K_{1.4}P_4W_{14}O_{50}$. Projections along [100].
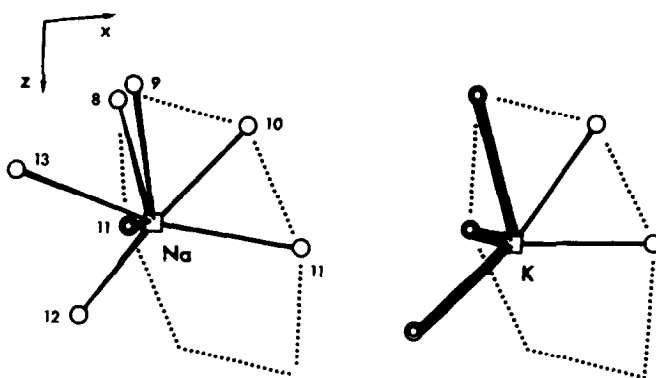
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FIG. 5. The eight nearest oxygen neighbors of the alkali ions and the hexagonal tunnels in $Na_{1.7}P_4W_{14}O_{50}$ and $K_{1.4}P_4W_{14}O_{50}$. Projections onto (010).

from about 2.4 to 2.7 Å which can be regarded as a tendency toward tetrahedral coordination (see Na in Fig. 4). Moreover, the projections in Fig. 5 show that the alkali ions in the $MPTB_h$ have very anisotropic coordinations: a plane perpendicular to the figure and containing an alkali ion can be oriented so that there is only one O atom on one side and all the other neighbors on the other side. This asymmetrical coordination is often observed for Na^+ in layer oxides or in tunnels and cages structures. For instance, in $Na_2Ti_3O_7$ (8) Na^+ is coordinated to nine O atoms with eight neighbors on the same side; in $Na_{14}Fe_6O_{16}$ (9) the six-coordinated Na^+ ion has an environment very similar to that of our phosphate-bronze.

Thus, it appears that sodium tends to take the same coordination as potassium in the $MPTB_h$. The presence of sodium does not seem to influence the geometry of the WO_6 octahedra, but it induces a tilting of the octahedra, leading, for $Na_{1.7}P_4W_{14}O_{50}$, to a triclinic distortion and to diamond-shaped windows in the perovskite cages. It seems that the tilting of the octahedra can be explained by the attraction of oxygen atoms of the O_{18} cage by the Na^+ ion in order to realize the shorter Na–O distances, compared to K–O.

Nevertheless, if the presence of Na^+ ions

in the host lattice can explain the rotations of the octahedral chains, it must be emphasized that these ions play exactly the same role in the present triclinic structure $Na_{1.7}P_4W_{14}O_{50}$ as in the other two $MPTB_h$'s, $Na_xP_4W_8O_{32}$ and $Na_xP_4W_{12}O_{44}$, which however are both monoclinic, $P2_1/a$. The explanation lies in the fact that the last two structures, corresponding to an even value of m ($m = 4$ and $m = 6$), have ReO_3-type layers built up from octahedral chains of the same length. In the same layer, two of these chains are related through a twofold axis or through the lattice translation $\vec{c}$. In two successive layers, two chains are related through a glide plane (a) or through a sym-
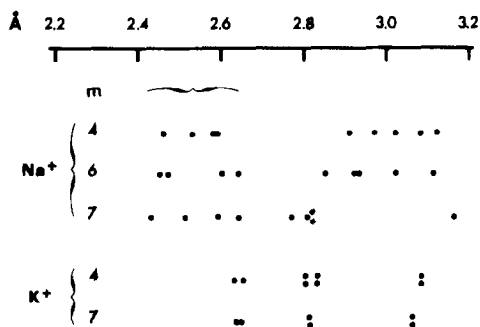

FIG. 6. Distribution of the A–O distances in the $MPTB_h$ family $A_x(PO_2)_4(WO_3)_{2m}$, limited to 3.2 Å (A = Na, K).
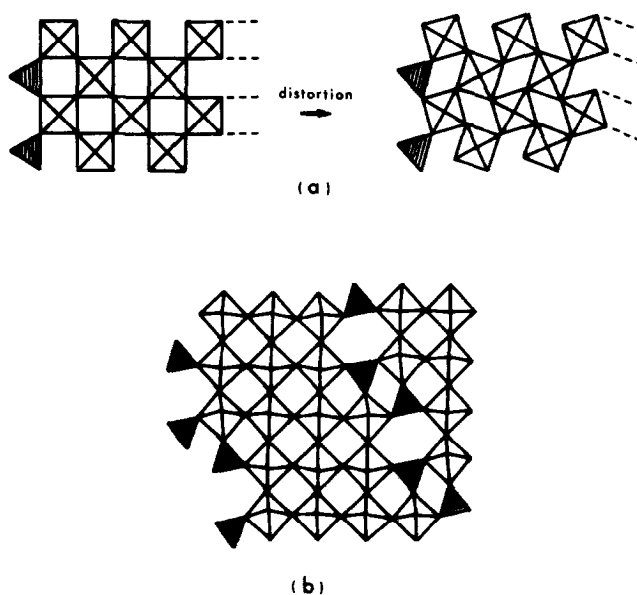
(a)

(b)

FIG. 7. View of the "perovskite planes." (a) Parallel to (2 0 11). The distortion is possible with formation of diamond-shaped windows. (b) Parallel to the hexagonal rings. The tetrahedra are bound by three corners and the distortion is impossible.

metry center. These operations of symmetry do not exist in $Na_{1.7}P_4W_{14}O_{50}$ which corresponds to an odd value of m ($m = 7$) and whose layers contain octahedral strings of unequal length. Only the symmetry centers can be present here. The same result is obtained from the observation of the structure of $K_{1.4}P_4W_{14}O_{50}$ ($m = 7$) whose space group is $A2/m$ (see Fig. 1 of Ref. (4)). Taking into account a slight rotation of the octahedral chains, it is obvious that the distortion removes the mirror planes and the twofold axes but can preserve the symmetry centers.

The fact that the perovskite planes nearly parallel to (2 0 1$\overline{1}$) can easily be distorted, but not the (3 3 $\overline{10}$) and ($\overline{3}$ 3 10) planes, is illustrated in Fig. 7. In the first case (Fig. 7a) the PO_4 tetrahedra are bound by only two corners to the octahedra of the layer, the two other corners being connected with the two adjacent layers. Then the distortion is possible with formation of diamond-shaped windows. In the second case (Fig.

7b) the PO_4 tetrahedra have three corners in common with the WO_6 octahedra of the layer. Then, a small rotation of the octahedra as in Fig. 7a induces unacceptable O–O distances. Consequently the constraint explains the rigidity of the layer and the fact that the perovskite cages' windows keep a square shape. This point can be easily verified by means of a model. The geometry of the perovskite layers is determined by the presence of three-corners linked tetrahedra and by the relative value of the O–O distances in the WO_6 octahedra and PO_4 tetrahedra. More generally, this geometric feature can explain the topography of mixed frameworks built up from polyhedra of various kinds.

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