

Na_{4-x}Nb₇P₄O₂₉: A Phosphate Niobium Bronze Intergrowth of the Members $m = 3$ and $m = 4$ of the MPTB's Series Na_x(NbO₃)_{2m}(PO₂)₄

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A new niobium phosphate bronze Na_{4-x}Nb₇P₄O₂₉ ($0 \leq x \leq 1$) has been isolated. It crystallizes in the space group *C2/c* with $a = 32.850(4)$, $b = 5.3484(4)$, and $c = 13.252(2)$ Å and $\beta = 97.79(1)^\circ$. The structure was solved by X-ray diffraction on a twinned crystal with an (100) twinning plane. This oxide is an intergrowth of the $m = 3$ and $m = 4$ members of the series of the monophosphate tungsten bronzes with pentagonal tunnels (MPTB_p), corresponding to the formulation Na_x(NbO₃)_{2m}(PO₂)₄. The ReO₃ slabs alternate parallel to (100) and are linked by isolated PO₄ tetrahedra delimiting pentagonal tunnels running along **b**. Relationships with other niobium phosphate bronzes are also discussed.

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Introduction

The systematic study of tungsten phosphates, started in the 1980s, allowed a great number of phosphate tungsten bronzes with various structures to be isolated (1–2). These phases were classified into four series: the monophosphate and the diphosphate tungsten bronzes with hexagonal tunnels noted (MPTB_H and DPTB_H, respectively) and those with pentagonal tunnels (MPTB_p and DPTB_p). More recently, the synthesis of the bronzoid phosphate β-NbPO₅ (3), isotypic of WPO₅ (4), second member of the MPTB_p family (WO₃)_{2m}(PO₂)₄, has allowed a similar behavior to be expected for niobium phosphate bronzes. However, in the other members of this family, the valency of tungsten is always greater than 5, so that the synthesis of other

niobium phosphates, with formulation (NbO₃)_{2m}(PO₂)₄, is not possible for $m > 2$. Nevertheless the fact that the MPTB_p's exhibit empty pentagonal tunnels suggests that cations of intermediate size such as sodium could be inserted into the structure, allowing the synthesis of bronzes with the general formula Na_x(NbO₃)_{2m}(PO₂)₄ to be considered. The recent synthesis of the monophosphate niobium bronzes Na_{2+x}Nb₆P₄O₂₆ (5) and Na₄Nb₈P₄O₃₂ (6), corresponding to the members $m = 3$ and $m = 4$ of this family, respectively, confirms this viewpoint and opens the road to the research of a complete series of monophosphate niobium bronzes with the MPTB_p structure. We report here on the crystal structure of the bronze Na_{4-x}Nb₇P₄O₂₉, which corresponds to $m = 3.5$, intergrowth of the members $m = 3$ and $m = 4$.

Synthesis and Characterization

The bronzes $\text{Na}_{4-x}\text{Nb}_7\text{P}_4\text{O}_{29}$ were prepared in two steps. First the adequate mixture of Na_2CO_3 , Nb_2O_5 , and $\text{H}(\text{NH}_4)_2\text{PO}_4$ was ground in an agate mortar and heated up to 673 K. Then, the appropriate amount of niobium was added to the intermediate composition and the mixture was sealed in an evacuated silica ampoule and heated at 1343 K during 3 days, allowing dark blue crystals to be grown and a pure phase to be prepared.

The limit phase, $x = 1$, which corresponds to the bronzoid $\text{Na}_3\text{Nb}_7\text{P}_4\text{O}_{24}$, was prepared by a similar method but entirely in air. The first step of the reaction was performed at the same temperature of 673 K. Then the mixture was reground and heated in a platinum crucible at 1373 K in air for 1 day. Under these conditions, the bronzoid is absolutely pure. Its X-ray powder pattern was indexed in a monoclinic cell

in agreement with the parameters obtained from the single crystal study (Table I).

Structure Determination

All the crystals obtained from the preparation were found to be twinned. A dark blue crystal of dimensions $0.103 \times 0.077 \times 0.025$ mm was selected for the structure determination.

A careful study of the (010)* reciprocal levels, registered with a Weissenberg camera, led to the following results.

—This twinned crystal was likely constituted of two components as suggested by electron microscopy investigations on several samples. The relative disposition of the reflections issued from the two twin components is illustrated in Fig. 1, taking as an example the $h2l$ level.

—For each component, the $2/m$ Laue

TABLE I
 $\text{Na}_3\text{Nb}_7\text{P}_4\text{O}_{29}$ —POWDER PATTERN

hkl	d_{obs}	d_{calc}	I	hkl	d_{obs}	d_{obs}	I
4 0 0	8.155	8.137	28	2 2 0	2.638	2.638	36
4 0 -2	5.480	5.486	12	12 0 -2		2.636	
4 0 2	4.807	4.801	33	3 1 4		2.636	
3 1 0		4.797		11 1 0	2.589	2.589	79
6 0 -2	4.494	4.492	66	10 0 -4	2.485	2.486	13
1 1 -2	4.160	4.158	69	11 1 1		2.485	
1 1 2	4.070	4.069	85	12 0 4	1.964	1.964	24
8 0 0		4.068		11 1 -5		1.964	
3 1 -2	3.990	3.989	100	13 1 3	1.916	1.919	26
6 0 2	3.928	3.928	71	8 2 -4		1.915	
3 1 2	3.767	3.767	43	6 2 4	1.883	1.883	20
8 0 -2	3.687	3.690	40	2 2 -5		1.882	
5 1 -2	3.642	3.641	60	1 3 0	1.778	1.780	43
5 1 2	3.371	3.369	52	1 1 -7		1.780	
8 0 2	3.264	3.265	32	11 1 -6		1.779	
4 0 -4	3.204	3.198	37	7 1 6		1.777	
10 0 -2	3.087	3.088	18	5 3 1	1.694	1.697	32
7 1 2	2.970	2.971	15	10 2 -5		1.696	
1 1 4	2.761	2.760	37	4 2 -6		1.694	
8 0 -4	2.746	2.743	27	0 2 -6		1.693	
0 2 0	2.676	2.674	64				

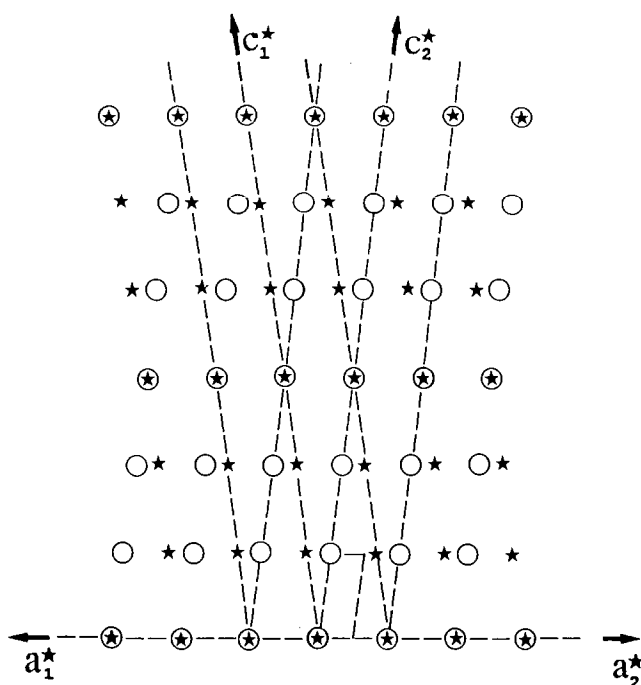


FIG. 1. The reciprocal plane $(h2l)^*$. (★) First component, (○) second component.

symmetry is involved. Besides main reflections, $l = 2n$, weak reflections, $l = 2n + 1$, were observed; they are indicative of a superstructure of the second order along the c axis. Two space groups, Cc and $C2/c$, are consistent with conditions $h + k = 2n$ for hkl and $l = 2n$ for $h0l$.

—The correspondence between the two crystalline components can be described either from a (100) symmetry plane or from a $[001]$ twofold axis.

—The reflections $l = 3n$ were found to be quite superimposed (see Fig. 1), owing to the values of the a, c , and β parameters of the monoclinic unit cell; the relative deviation $(3c \cdot \cos \beta^* - a^*)/a^*$ is about 0.01. These reflections exhibit a symmetry very close to the upper orthorhombic symmetry.

—The α proportion of the smallest component was estimated from the intensity measurement of 50 strong pairs of nonoverlapped reflections; the dispersion of the re-

sults is small, $\alpha = 0.393(8)$, bearing out the twinning hypothesis.

The data of one of the components were collected on a CAD-4 Enraf-Nonius diffractometer, the parameters of the monoclinic unit cell (Table II) refined by least squares from the θ measurements of 25 nonoverlapped reflections ($18^\circ \leq \theta \leq 25^\circ$); the nearly perfect superimposition of the reflections $l = 3n$ was confirmed from an ω - θ profile study. The reflections were corrected for Lorentz and polarization effects. No absorption corrections were performed.

According to the features of the Patterson series, the space group is $C2/c$. The structure was solved using in a first step the 1666 nonoverlapped reflections. The positions of the niobium atoms were determined from the Patterson peaks and the other atoms located from subsequent Fourier difference series. The refinements, carried out with anisotropic thermal parameters for Nb and P

TABLE II
SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND
STRUCTURE REFINEMENT PARAMETERS FOR $\text{Na}_{3.04}\text{Nb}_7\text{P}_4\text{O}_{29}$

1. Crystal data		
Space group	$C2/c$	
Cell dimensions	$a = 32.850(4) \text{ \AA}$	
	$b = 5.3484(4) \text{ \AA}$	
	$c = 13.252(2) \text{ \AA}$	
	$\beta = 97.79(1)^\circ$	
Volume	$v = 2307(1) \text{ \AA}^3$	
Z	4	
2. Intensity measurements		
λ (MoK α)	0.71073 \AA	
Scan mode	ω - θ	
Scan width ($^\circ$)	$1 + 0.35 \tan \theta$	
Slit aperture (mm)	$1 + \tan \theta$	
Max θ ($^\circ$)	45 $^\circ$	
Standard reflections	3 measured every 3600 s (no decay)	
Reflections with $I > 3 \sigma$	2655	
3. Structure solution and refinement		
Parameters refined	202	
Agreement factors	$R = 0.052$ $R_w = 0.069$	
Weighting scheme	$w = 1$	
Δ/σ max	0.007	

atoms and isotropic ones for the other atoms, led to the reliability factors $R = 0.044$ and $R_w = 0.067$.

In a second step, the superimposed reflections (989) were considered. The intensities of such reflections have generally to be corrected for the twinning effect from the relations (7):

$$J_1 = I_1 + \frac{\alpha}{1 - 2\alpha}(I_1 - I_2);$$

$$J_2 = I_2 - \frac{\alpha}{1 - 2\alpha}(I_1 - I_2).$$

I_1 and I_2 are the observed intensities of the superimposed reflection pairs of the two components of the twin, the indices of which are, respectively, hkl and $(-h + 2l/3), k, l$ with $l = 3n$; J_1 and J_2 are the corrected intensities, i.e., the intensities which would be observed from a single crystal of the same

total volume. Since the intensities I_1 and I_2 are nearly equal, no correction was applied to this group of reflections. The refinements were carried out with all the reflections using the CLINUS program (8) and introducing different scale factors for the superimposed and nonoverlapped reflections. The final reliability factors are $R = 0.052$ and $R_w = 0.069$. The atomic parameters are reported in Table III. The refinement of the multiplicity of Na sites shows that Na(1) was fully occupied and Na(2) only partially occupied, leading to the formula $\text{Na}_{3.04}\text{Nb}_7\text{P}_4\text{O}_{29}$.

Description of the Structure and Discussion

This study shows that a regular intergrowth of the members $m = 3$ and $m = 4$ of the series MPTB_p 's has been obtained

TABLE III
POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Nb(1)	0.000	0.000	0.000	0.73(2)
Nb(2)	0.31831(3)	0.5011(4)	0.02287(7)	0.43(1)
Nb(3)	0.22724(3)	0.4785(3)	0.32190(8)	0.48(1)
Nb(4)	0.04595(2)	0.4973(4)	0.17911(7)	0.50(1)
P(1)	0.14822(8)	0.487(1)	0.1205(2)	0.47(4)
P(2)	0.42169(7)	0.503(1)	0.1525(2)	0.39(3)
Na(1)	0.1318(2)	0.507(2)	0.3634(4)	1.28(9)
Na(2)	-0.0976(4)	0.009(4)	-0.0995(9)	2.0(2)
O(1)	-0.0468(3)	-0.025(3)	0.0780(8)	1.6(2)
O(2)	0.0270(4)	-0.286(2)	0.0731(9)	1.2(2)
O(3)	0.0299(4)	0.207(2)	0.1076(8)	1.2(2)
O(4)	0.3791(3)	0.459(2)	0.0956(8)	1.1(2)
O(5)	0.3066(3)	0.730(2)	0.1235(8)	0.8(2)
O(6)	0.3024(3)	0.227(2)	0.0847(7)	0.6(1)
O(7)	0.2710(3)	0.564(2)	-0.0695(7)	0.7(1)
O(8)	0.3401(3)	0.278(2)	-0.0883(7)	0.8(1)
O(9)	0.3482(3)	0.821(2)	-0.0378(7)	1.0(2)
O(10)	0.1737(3)	0.562(2)	0.2216(8)	1.0(2)
O(11)	0.2478(3)	0.291(2)	0.2264(7)	0.9(1)
O(12)	0.000	0.515(5)	0.250	1.6(3)
O(13)	0.1029(3)	0.480(3)	0.1375(7)	1.2(2)
O(14)	0.0722(4)	0.798(2)	0.2645(9)	1.4(2)
O(15)	0.0755(4)	0.264(2)	0.3037(8)	1.1(2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \gamma)*B(1,2) + ac(\cos \beta)*B(1,3) + bc(\cos \alpha)*B(2,3)]$.

in the form of a pure phase for the first time. $(\text{WO}_3)_{2m}(\text{PO}_2)_4$, but only for an integral *m* value (*m* = 5), i.e., $\text{P}_4\text{W}_{10}\text{O}_{38}$ (10) intergrowth of the members *m* = 4 and *m* =

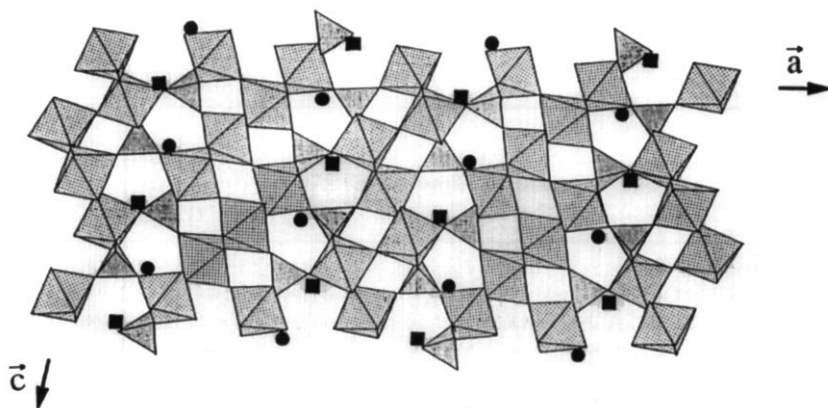


FIG. 2. Projection of the $\text{Na}_{4-x}\text{Nb}_7\text{P}_4\text{O}_{29}$ structure along **b**. (●) Na(1) and (■) Na(2).

TABLE IV
DISTANCES (Å) AND ANGLES (°) IN THE NbO₆ AND PO₄ POLYHEDRA AND MAIN Na–O DISTANCES

Nb(1)	O(1)	O(1 ⁱ)	O(2)	O(2 ⁱ)	O(3)	O(3 ⁱ)
O(1)	1.97(1)	3.94(2)	2.80(2)	2.75(2)	2.79(2)	2.77(2)
O(1 ⁱ)	180.0(7)	1.97(1)	2.75(2)	2.80(2)	2.77(2)	2.79(2)
O(2)	91.2(6)	88.8(6)	1.96(1)	3.92(2)	2.68(2)	2.86(2)
O(2 ⁱ)	88.8(6)	91.2(6)	180.0(7)	1.96(1)	2.86(2)	2.68(2)
O(3)	90.4(5)	89.6(5)	86.2(5)	93.8(5)	1.96(1)	3.92(2)
O(3 ⁱ)	89.6(5)	90.4(5)	93.8(5)	86.2(5)	180.0(7)	1.96(1)
Nb(2)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)
O(4)	2.108(9)	2.85(1)	2.79(1)	3.95(1)	2.77(1)	2.72(1)
O(5)	91.0(4)	1.89(1)	2.74(1)	2.81(1)	3.97(1)	2.73(2)
O(6)	91.1(4)	96.2(5)	1.79(1)	2.81(1)	2.76(1)	3.96(1)
O(7)	165.5(4)	96.6(4)	100.3(4)	1.873(9)	2.77(1)	2.87(1)
O(8)	82.4(4)	170.8(4)	90.3(4)	88.5(4)	2.09(1)	2.98(2)
O(9)	78.9(4)	84.1(4)	169.9(4)	89.7(4)	88.4(4)	2.18(1)
Nb(3)	O(5 ⁱⁱ)	O(6 ⁱⁱⁱ)	O(7 ^{iv})	O(10)	O(11)	O(11 ⁱⁱⁱ)
O(5 ⁱⁱ)	1.93(1)	2.70(1)	2.78(1)	2.72(1)	2.87(2)	3.91(1)
O(6 ⁱⁱⁱ)	83.1(4)	2.14(1)	2.85(1)	2.72(1)	3.94(1)	2.79(2)
O(7 ^{iv})	92.9(4)	89.6(4)	1.905(9)	3.99(1)	2.82(1)	2.82(1)
O(10)	84.8(4)	79.9(4)	169.5(4)	2.104(9)	2.83(1)	2.85(1)
O(11)	99.7(5)	171.4(4)	98.4(4)	92.1(4)	1.82(1)	2.74(1)
O(11 ⁱⁱⁱ)	166.6(5)	84.6(4)	92.3(4)	87.9(4)	91.8(5)	2.00(1)
Nb(4)	O(2 ^v)	O(3)	O(12)	O(13)	O(14)	O(15)
O(2 ^v)	1.86(1)	2.75(2)	2.82(2)	2.82(2)	2.80(2)	4.04(2)
O(3)	95.2(5)	1.86(1)	2.78(2)	2.79(2)	3.93(2)	2.83(1)
O(12)	97.8(6)	96.0(8)	1.885(2)	3.88(2)	2.80(2)	2.82(2)
O(13)	92.9(5)	91.8(6)	166.1(3)	2.02(1)	2.68(2)	2.74(2)
O(14)	90.1(5)	171.7(5)	89.5(7)	81.6(5)	2.09(1)	2.90(2)
O(15)	173.2(5)	88.5(5)	87.5(6)	81.2(5)	85.6(4)	2.19(1)
P(1)	O(8 ^{vi})	O(9 ^{vii})	O(10)	O(13)		
O(8 ^{vi})	1.55(1)	2.54(2)	2.54(1)	2.48(2)		
O(9 ^{vii})	112.1(6)	1.52(1)	2.52(1)	2.46(2)		
O(10)	110.8(6)	111.6(6)	1.53(1)	2.48(1)		
O(13)	107.3(7)	107.1(7)	107.6(6)	1.54(1)		
P(2)	O(1 ^{viii})	O(4)	O(14 ^{ix})	O(15 ^x)		
O(1 ^{viii})	1.53(1)	2.48(1)	2.53(2)	2.48(2)		
O(4)	108.8(6)	1.52(1)	2.43(1)	2.48(1)		
O(14 ^{ix})	110.9(8)	105.4(6)	1.54(1)	2.54(2)		
O(15 ^x)	109.0(8)	109.9(6)	112.7(6)	1.51(1)		

Note. The Nb–O or P–O distances are on the diagonal. Above it are the O(i) ... O(j) distances and below it are the O(i)–Nb–P–O(j) or O(i)–O(j) angles. Na(1)–O(4ⁱⁱ) = 3.01(1) Å; Na(2)–O(1) = 2.70(2) Å; Na(1)–O(4ⁱⁱⁱ) = 2.51(1) Å; Na(2)–O(2ⁱ) = 2.74(2) Å; Na(1)–O(5ⁱⁱ) = 2.50(1) Å; Na(2)–O(3ⁱ) = 2.52(2) Å; Na(1)–O(6ⁱⁱⁱ) = 2.47(1) Å; Na(2)–O(4^{iv}) = 2.81(2) Å; Na(1)–O(9ⁱⁱ) = 2.52(1) Å; Na(2)–O(8^{ix}) = 2.41(2) Å; Na(1)–O(10) = 2.49(1) Å; Na(2)–O(9^{ix}) = 2.65(2) Å; Na(1)–O(13) = 3.02(1) Å; Na(2)–O(13ⁱ) = 2.66(3) Å; Na(1)–O(14) = 2.70(1) Å; Na(2)–O(13^{ix}) = 2.78(3) Å; Na(1)–O(15) = 2.31(1) Å; Na(2)–O(14^v) = 2.65(3) Å.

Symmetry code. i: $-x, -y, -z$; vi: $\frac{1}{2} - x, \frac{1}{2} - y, -z$; ii: $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; vii: $\frac{1}{2} - x, \frac{3}{2} - y, -z$; iii: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; viii: $\frac{1}{2} + x, \frac{1}{2} + y, z$; iv: $x, 1 - y, \frac{1}{2} + z$; ix: $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; v: $x, 1 + y, z$; x: $-x, 1 - y, -z$.

6. In contrast, intergrowths corresponding to nonintegral m values were only observed by HREM in microcrystals of tungsten phosphates but could not be isolated in a quantitative manner. Thus the framework of the niobium bronze phosphate $\text{Na}_{4-x}\text{Nb}_7\text{P}_4\text{O}_{29}$ (Fig. 2) is built up from the same kind of ReO_3 -type slabs as those previously observed in $\text{Na}_{2+x}\text{Nb}_6\text{P}_4\text{O}_{26}$ (5) and Na_4

$\text{Nb}_8\text{P}_4\text{O}_{32}$ (6). These slabs are, respectively, three and four corner-sharing octahedra wide oriented approximately along the direction $[104]$ for the former and $[103]$ for the latter. The junction between these slabs is ensured by slices of isolated PO_4 tetrahedra, giving rise to pentagonal tunnels running along b .

The geometry of NbO_6 octahedra is quite

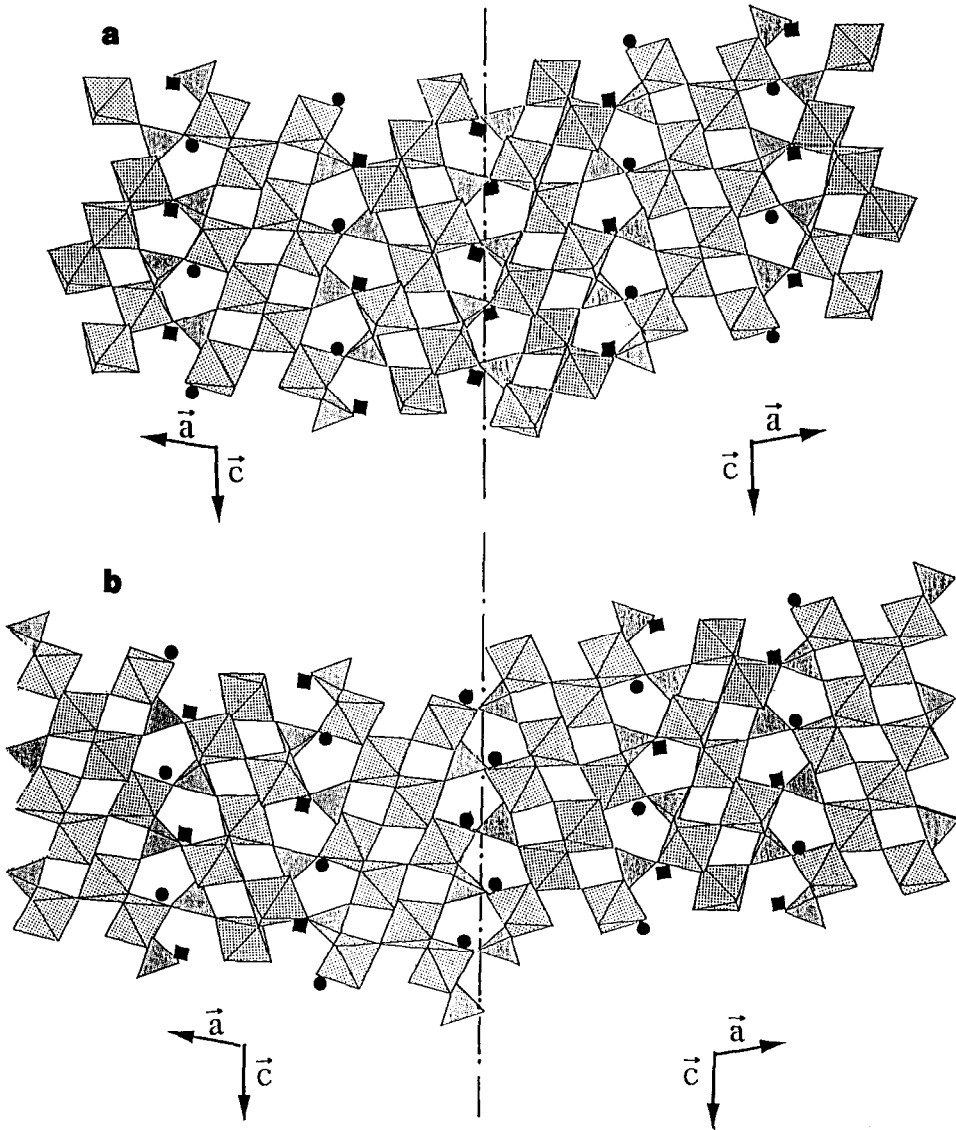


FIG. 3. The two twin components with the glide plane parallel to (100) situated between (a) two blocks of three octahedra and (b) two blocks of four octahedra.

similar to that of the other members of this series, $\text{Na}_{2+x}\text{Nb}_6\text{P}_4\text{O}_{26}$ (4) and $\text{Na}_4\text{Nb}_8\text{P}_4\text{O}_{32}$ (5). In both structures, the octahedra located at the border of the ReO_3 slabs are more distorted than the octahedra disposed inside the same block (Table IV). For example, in this structure the Nb–O distances range from 1.96 to 1.97 Å for Nb(1) and from 1.82 to 2.14 Å for Nb(3); moreover the disparity between the Nb–O distances of the corresponding octahedra in the same block is more pronounced, ranging from 1.86 to 2.19 Å for Nb(4) and from 1.79 to 2.18 Å for Nb(2). The distortion of each NbO_6 octahedron increases with the number of PO_4 tetrahedra sharing its corners. The PO_4 tetrahedra are nearly regular as in other phosphate bronzes. These results confirm again that the PO_4 tetrahedra, more rigid, impose a rather strong distortion to the octahedral framework in order to realize such structures. The comparison of the geometry of NbO_6 octahedra with that of WO_6 octahedra in the various members of the series $(\text{WO}_3)_{2m}(\text{PO}_2)_4$ (9–11) is in agreement with this viewpoint. One indeed observes for the latter the same kind of distortion of the WO_6 octahedra at the border and inside the ReO_3 -type slabs. However, the variation of the amplitude of the distortion is smaller for the WO_6 octahedra than for the NbO_6 octahedra, owing to the larger size of niobium compared to tungsten. This difference of size seems to be at the origin of the inability of niobium to form diphosphate niobium bronzes similar to those of tungsten.

The sodium atoms have the same environment as that of the previous members of this series. They are located approximately at the center of the hexagonal windows situated at the boundary between two adjacent tunnels and formed of three octahedra and three tetrahedra. The two sodium sites are ninefold coordinated to oxygen atoms.

The great tendency of this phase to be twinned is explained by the existence of a local pseudo-symmetry described by a glide plane n parallel to (100) located at $x = \frac{1}{8}$, with a translation part of $c/4$ along c .

Examples of such twinning planes are shown in Fig. 3; such models show that the twinning takes place at the level of the rows of pentagonal tunnels, i.e., at the level of the slices of PO_4 tetrahedra which border the ReO_3 -type slabs.

Concluding Remarks

This study confirms the existence of series of monophosphate niobium bronzes with pentagonal tunnels, with the general formula $\text{Na}_x(\text{NbO}_3)_{2m}(\text{PO}_2)_4$, belonging to the MPTB_p 's structural family. The electron transport properties of these materials will be investigated.

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