

A Niobium Phosphate Bronze Closely Related to the Tungsten Phosphate Bronzes Family: $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$

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A new niobium phosphate bronze $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$ has been isolated. Its structure was solved by single crystal X-ray diffraction. It crystallizes in the orthorhombic system with the space group *Pbam*. The cell parameters are $a = 8.4992(7)$ Å, $b = 15.3390(8)$ Å, and $c = 10.5913(9)$ Å. The framework $[\text{Nb}_8\text{P}_6\text{O}_{35}]_\infty$ consists of $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers, sharing the corners of their octahedra and forming $[\text{Nb}_6\text{P}_4\text{O}_{31}]_\infty$ bilayers. The latter bilayers are linked along \vec{c} through $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units, built up themselves of two edge-sharing NbO_6 octahedra connected to two PO_4 tetrahedra. The $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers are very closely related to the structure of the diphosphate tungsten bronzes with pentagonal tunnels (DPTB_p's) and can be described as derived from the $m = 3$ member of the series $(\text{PO}_2)_4(\text{WO}_3)_{2m}$. The relationships with other niobium phosphate bronzes is also discussed as well as the great distortion of the different polyhedra of the structure. © 1990 Academic Press, Inc.

Introduction

The recent investigation of the K–Nb–P–O system has allowed a new series of anisotropic niobium phosphate bronzes to be isolated. These phases present a great similarity with the oxygen tungsten bronzes A_xWO_3 . For instance the bronze $\text{KNb}_3\text{P}_3\text{O}_{15}$ (1) is closely related to the tetragonal tungsten bronze (TTB) described by Magneli (2), whereas the bronzes $\text{K}_7\text{Nb}_{14}\text{P}_9\text{O}_{60}$ (3), $\text{K}_{5-x}\text{Nb}_8\text{P}_5\text{O}_{34}$ (4), and $\text{K}_3\text{Nb}_6\text{P}_4\text{O}_{26}$ (5) are related to the hexagonal tungsten bronze family (HTB) (6) and the intergrowth of HTBs with the

ReO_3 -type structure called ITBs (7). The behavior of niobium is in this respect very different from that of tungsten, for which a huge family of tungsten phosphate bronzes was also discovered (8, 9) but which are always closely related to the perovskite. Nevertheless a bronzoid NbPO_5 (10) isotopic of WPO_5 (11) first member of the series of monophosphate tungsten bronzes (MPTB_p) was synthesized. Clearly the nature and the size of the interpolated cation play an important role in the stabilization of the various host lattices. In order to understand all those relationships, the investigation of the Na–Nb–P–O system was undertaken. We report here $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$ in which niobium exhibits a lower oxida-

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tion state than the other niobium phosphate bronzes characterized up to now.

Synthesis

Single crystals for X-ray resolution of structure were taken into the sample of nominal composition of $\text{NaNb}_2\text{P}_2\text{O}_{10}$. The synthesis of $\text{NaNb}_2\text{P}_2\text{O}_{10}$ was carried out in two steps. First, the mixture of the adequate amount of Na_2CO_3 , $\text{H}(\text{NH}_4)_2\text{PO}_4$, and Nb_2O_5 was ground and heated up to 673 K in air to eliminate CO_2 , H_2O , and NH_3 . In the second step the appropriate quantity of niobium was added and the finely ground mixture was sealed in an evacuated ampoule and heated at 1173 K for a month.

The approximate composition of these crystals was first estimated by microprobe analysis.

Structure Determination

A dark crystal with dimensions $0.096 \times 0.048 \times 0.024 \text{ mm}^3$ was selected for the structure determination. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18 < \theta < 22^\circ$.

The systematic absences $k = 2n + 1$ for $0kl$ and $h = 2n + 1$ for $h0l$ are consistent with the space groups $Pbam$ (No.55) and $Pba2$ (No.32). The structure was solved and refined in the centrosymmetrical space group $Pbam$.

The data were collected on a CAD-4 Enraf-Nonius diffractometer with the data collection parameters reported in Table I. The reflections were corrected for Lorentz polarization effects. No absorption correction was performed.

Atomic coordinates of the niobium atoms were deduced from the Patterson

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$

	1. Crystal data
Space group	<i>Pbam</i>
Cell dimensions	$a = 8.4992(7) \text{ \AA}$ $b = 15.3390(8)$ $c = 10.5913(9)$
Volume	$v = 1380.8(3) \text{ \AA}^3$
Z	2
	2. Intensity measurement
$\lambda(\text{MoK}\alpha)$	0.71073 \AA
Scan mode	$\omega - \theta$
Scan width($^\circ$)	$1 + 0.35 \tan \theta$
Slit aperture (mm)	$1 + \tan \theta$
Max θ ($^\circ$)	45 $^\circ$
Standard reflections	3 measured every 3000 sec (no decay)
Reflections with $I > 3 \sigma$	979
$\mu (\text{mm}^{-1})$	3.602 mm^{-1}
	3. Structure solution and refinement
Parameters refined	108
Agreement factors	$R = 0.036, R_w = 0.031$
Weighting scheme	$w = 1/\sigma^2(F)$
$\Delta/\sigma_{\text{max}}$	0.005

function and the other atoms were located by successive Fourier series. The structure was first refined with isotropic thermal factors for all the atoms. This led to $R = 0.098$ and $R_w = 0.093$ ($w = 1/\sigma^2(F)$). At this stage, the B factor of Nb(3) atom was much higher than those of other Nb atoms, and the B factor of some oxygen atoms was about 4.5. These atoms are linked to the Nb(1) and Nb(3) atoms and all are approximately located in the same plane. It was observed that after refinement their anisotropic thermal factors β_{11} , β_{22} , or β_{12} were 10 times greater than the other components. This led us to think to a splitting of each of these atoms in two positions. A subsequent Fourier difference confirmed our hypothesis. The Nb(3) and O(6) atoms were split out of the twofold axis and the other oxygen atoms distributed over two

TABLE II
 POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (\AA^2)
Nb(1)	0.09915(9)	0.10776(5)	0.18127(7)	0.76(1)
Nb(2)	0.0776(1)	0.42436(8)	0.500	0.95(2)
Nb(3)	-0.0016(3)	0.4877(1)	0.1735(1)	0.60(2)
P(1)	0.1972(4)	0.0928(2)	0.500	0.95(6)
P(2)	0.2122(3)	0.3218(2)	0.2336(2)	1.08(4)
Na(1)	0.4102(8)	0.2916(4)	0.500	2.4(1)
Na(2)	0.441(1)	0.2103(6)	0.000	5.6(2)
O(1)	0.075(1)	0.1178(5)	0.000	0.9(1) ^a
O(2)	0.1074(7)	0.1223(4)	0.3809(5)	1.1(1) ^a
O(3a)	0.200(1)	0.2237(7)	0.184(1)	0.8(2) ^a
O(3b)	0.133(1)	0.2460(8)	0.177(1)	1.2(2) ^a
O(4a)	0.391(1)	0.3158(7)	0.209(1)	1.0(2) ^a
O(4b)	0.372(1)	0.3510(8)	0.207(1)	1.8(3) ^a
O(5a)	0.285(1)	0.0484(7)	0.176(1)	1.2(2) ^a
O(5b)	0.316(1)	0.0890(7)	0.179(1)	1.2(2) ^a
O(6)	0.036(1)	-0.0073(8)	0.1976(9)	0.7(2) ^a
O(7)	0.000	0.500	0.3571(8)	1.5(2) ^a
O(8)	0.364(1)	0.1384(6)	0.500	1.2(2) ^a
O(9)	0.1761(7)	0.3292(4)	0.3744(6)	1.3(1) ^a
O(10)	0.221(1)	-0.0066(6)	0.500	1.0(1) ^a
O(11)	0.000	0.500	0.000	1.9(3) ^a
O(12a)	0.087(2)	0.3736(8)	0.163(1)	1.8(2) ^a
O(12b)	0.141(1)	0.4025(7)	0.162(1)	1.2(2) ^a

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as

$$B_{\text{eq}} = \frac{4}{3} [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (ab \cos \gamma) \beta_{12} + (ac \cos \beta) \beta_{13} + (bc \cos \alpha) \beta_{23}]$$

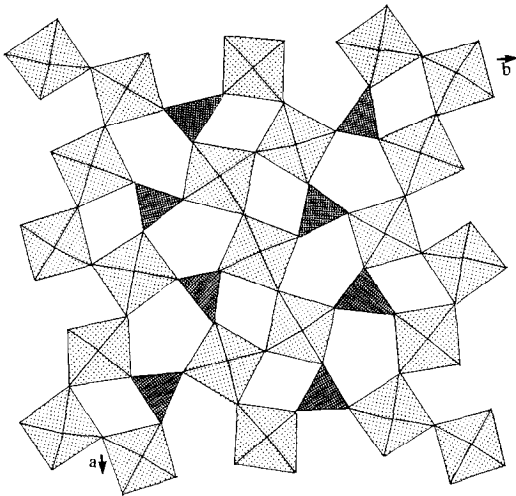
^a Refined isotropically.

neighboring positions which had after refinement the same multiplicity of 0.5. This splitting allowed the reliability factor to be lowered to $R = 0.060$ and $R_w = 0.050$. The final refinement with anisotropic thermal factors for the Nb, P, and Na atoms and isotropic factors for the oxygen atoms led to $R = 0.036$ and $R_w = 0.031$ for the atomic coordinates given in Table II.¹

¹ List of structure factors and anisotropic thermal motion parameters are available on request to the authors.

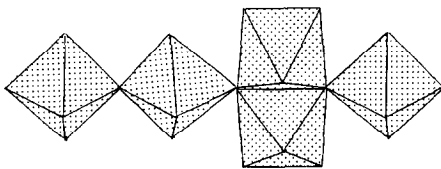
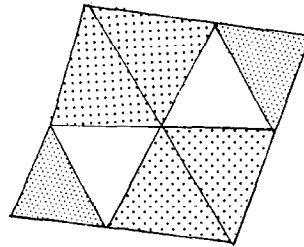
Description of the Structure and Discussion

The oxide $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$ represents the first sodium niobium phosphate bronze isolated up to now. Its $[\text{Nb}_8\text{P}_6\text{O}_{35}]_\infty$ framework consists of two sorts of octahedral chains. The first type of chain $[\text{NbO}_3]_\infty$, running along \vec{a} , can also be described as ReO_3 -type ribbons which are three octahedra wide along $[720]$ (Fig. 1). These ribbons or chains form diamond-shaped windows, where O-O-O angles are close to 60 and 110°, respectively. The second type of chain,

FIG. 1. The $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layer.

$[\text{Nb}_4\text{O}_{11}]_\infty$, running along \vec{c} , results from the association of two corner-sharing octahedra, with a bioctahedron built up of two edge-sharing octahedra (Fig. 2). These two kinds of octahedral chains are linked through single PO_4 groups. One characteristic feature of this host lattice deals with the $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units (Fig. 3) in which two PO_4 tetrahedra share two of their corners with the same bioctahedron.

The remarkable feature of this tridimensional host lattice concerns its possible description from $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers (Fig. 1) parallel to (0 0 1) which are closely related to those observed in the diphosphate tungsten bronzes with pentagonal tunnels (12) $(\text{P}_2\text{O}_4)_2(\text{WO}_3)_{2m}$ (Fig. 4a). Such layers can indeed be described as built up from ReO_3^-

FIG. 2. The $[\text{Nb}_4\text{O}_{11}]_\infty$ chain running along \vec{c} .FIG. 3. The $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units.

type slabs, three NbO_6 octahedra wide, connected through rows of PO_4 tetrahedra running along \vec{a} , forming in both cases rows of pentagonal rings. This oxide differs from the $m = 3$ member of DPTBs, by the stacking along \vec{c} of the $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers. In the niobium phosphate bronze $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$, the corners of the PO_4 tetrahedra of two successive layers lie in opposite directions along \vec{c} , so that such layers share only the corners of their NbO_6 octahedra forming $[\text{Nb}_6\text{P}_4\text{O}_{31}]_\infty$ bilayers (Fig. 5). In contrast, in the DPTB_p's, two successive layers share both the corners of their WO_6 octahedra and those of their tetrahedra forming P_2O_7 groups (Fig. 4b). Moreover in $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$, the $[\text{Nb}_6\text{P}_4\text{O}_{31}]_\infty$ bilayers are connected between them along \vec{c} by $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units (Fig. 5). This stacking leads to the formation of pentagonal tunnels running along \vec{c} (Fig. 1) whereas brownmillerite (BMT) and new hexagonal tunnels (HT) formed of three PO_4 tetrahedra and three NbO_6 octahedra are running along \vec{a} (Fig. 5).

An interesting similarity with the other phosphate niobium bronzes deals with the fact that the host lattice of the latter— $\text{K}_7\text{Nb}_{14}\text{P}_9\text{O}_{60}$ (3), $\text{K}_3\text{Nb}_6\text{P}_4\text{O}_{26}$ (5), and $\text{K}_{5-x}\text{Nb}_8\text{P}_5\text{O}_{34}$ (4)—can also be described by the stacking of $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$, i.e., characterized by an identical composition. However, the arrangement of the tetrahedra and octahedra in those layers is very different leading to the formation of hexagonal tunnels, i.e., a geometry similar to that observed in HTBs and ITBs. Thus it appears

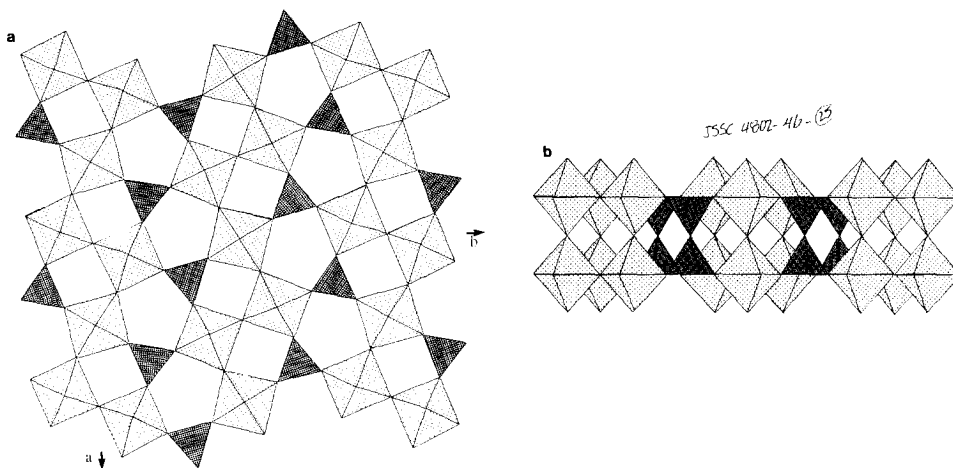


FIG. 4. (A) The $(\text{P}_2\text{O}_4)_2(\text{WO}_3)_6$ layer. (b) The stacking of two successive $(\text{P}_2\text{O}_4)_2(\text{WO}_3)_6$ layers forming bilayers containing P_2O_7 units.

that $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$ is much more closely related to the diphosphate tungsten bronze with pentagonal tunnels than to the other phosphate niobium bronzes synthesized up to now. From a more general point of view it can be stated that the phosphate niobium bronzes $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$ and $\text{KNb}_3\text{P}_3\text{O}_{15}$ are related to the TTBs, whereas the other phosphate niobium bronzes $(\text{K}_3\text{Nb}_6\text{P}_4\text{O}_{26})_n$

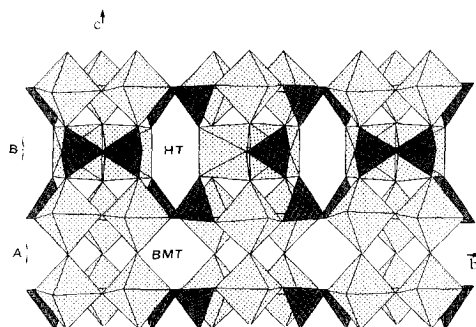


FIG. 5. The projection of $\text{Na}_4\text{Nb}_8\text{P}_6\text{O}_{35}$ along \vec{a} showing the $[\text{Nb}_6\text{P}_4\text{O}_{31}]$ bilayers (A) connected via $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units (B) which delimit BMT and HT tunnels.

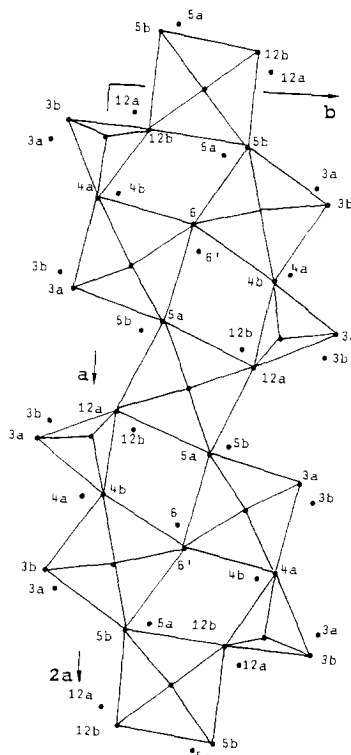


FIG. 6. The splitting of several atomic positions due to the regular tilting of the polyhedra along \vec{a} .

TABLE III
DISTANCES (Å) AND ANGLES (°) IN THE NbO₆ OCTAHEDRA

Nb(1)	O(1)	O(2)	O(3a)	O(4a ⁱ)	O(5a)	O(6 ⁱⁱ)
O(1)	1.937(1)	4.04(1)	2.75(1)	2.90(1)	2.80(1)	2.86(1)
O(2)	168.6(2)	2.127(5)	2.72(1)	2.75(1)	2.87(1)	2.90(1)
O(3a)	89.3(4)	83.0(4)	1.97(1)	2.70(1)	2.79(1)	3.88(1)
O(4a ⁱ)	90.3(3)	80.3(3)	82.1(4)	2.14(1)	3.96(1)	2.79(1)
O(5a)	96.0(5)	93.0(4)	94.4(4)	172.7(5)	1.82(1)	2.81(2)
O(6 ⁱⁱ)	95.1(3)	90.8(3)	167.4(4)	86.1(4)	96.9(4)	1.93(1)
Nb(1)	O(1)	O(2)	O(3b)	O(4b ⁱ)	O(5b)	O(6)
O(1)	1.937(1)	4.04(1)	2.76(1)	2.83(1)	2.83(1)	2.86(1)
O(2)	168.6(2)	2.127(5)	2.88(1)	2.75(1)	2.83(1)	2.84(1)
O(3b)	85.2(4)	84.9(4)	2.14(1)	2.69(2)	2.87(1)	3.98(1)
O(4b ⁱ)	90.4(5)	82.4(4)	79.6(5)	2.05(1)	3.90(1)	2.78(1)
O(5b)	96.0(5)	89.8(4)	91.2(4)	168.6(6)	1.87(1)	2.80(1)
O(6)	97.9(3)	91.0(3)	169.9(4)	90.6(5)	98.0(4)	1.85(1)
Nb(2)	O(7)	O(7 ⁱⁱⁱ)	O(8 ⁱ)	O(9)	O(9 ^{iv})	O(10 ^v)
O(7)	2.018(6)	3.03(1)	2.851(7)	3.023(5)	4.15(1)	2.818(7)
O(7 ⁱⁱⁱ)	97.2(3)	2.018(6)	2.851(7)	4.15(1)	3.023(5)	2.818(7)
O(8 ⁱ)	88.9(1)	88.9(1)	2.053(7)	3.008(8)	3.008(8)	4.07(1)
O(9)	93.1(2)	169.7(2)	91.5(2)	2.146(5)	2.66(1)	2.982(9)
O(9 ^{iv})	169.7(2)	93.1(2)	91.5(2)	76.7(3)	2.146(5)	2.981(9)
O(10 ^v)	88.6(2)	88.6(2)	176.2(3)	91.5(2)	91.5(2)	2.017(8)
Nb(3)	O(5a ^v)	O(5a ⁱ)	O(7)	O(11)	O(12a)	O(12a ^{vi})
O(5a ^v)	2.07(1)	3.95(1)	2.75(1)	2.72(1)	2.90(2)	2.84(2)
O(5a ⁱ)	170.0(3)	1.90(1)	2.75(1)	2.72(1)	2.84(2)	2.90(2)
O(7)	86.2(4)	91.1(5)	1.954(7)	3.78(1)	2.92(1)	2.92(1)
O(11)	87.8(4)	93.0(5)	168.6(2)	1.847(1)	2.70(1)	2.70(1)
O(12a)	93.6(6)	96.4(5)	98.2(4)	92.0(4)	1.91(1)	4.15(1)
O(12a ^{vi})	82.1(4)	88.2(4)	87.6(4)	81.8(4)	172.5(5)	2.25(1)
Nb(3)	O(5b ^v)	O(5b ⁱ)	O(7)	O(11)	O(12b)	O(12b ^{vi})
O(5b ^v)	2.22(1)	4.16(1)	2.81(1)	2.81(1)	2.89(1)	2.77(1)
O(5b ⁱ)	172.0(5)	1.95(1)	2.81(1)	2.81(1)	2.77(1)	2.89(1)
O(7)	84.4(4)	92.0(4)	1.955(8)	3.78(1)	2.82(1)	2.82(1)
O(11)	87.1(4)	95.6(5)	168.6(2)	1.847(1)	2.58(1)	2.58(1)
O(12b)	91.8(5)	95.0(5)	97.5(5)	90.3(5)	1.79(1)	3.83(1)
O(12b ^{vi})	80.7(5)	92.1(6)	89.0(4)	82.2(4)	169.6(6)	2.06(1)

Note. Symmetry codes:

- (i): $x - 1/2; -y + 1/2; z$.
- (ii): $-x; -y; z$.
- (iii): $-x; -y + 1; -z + 1$.
- (iv): $x; y; -z + 1$.
- (v): $-x + 1/2; y + 1/2; z$.
- (vi): $-x; -y + 1; z$.

TABLE IV
 DISTANCES (Å) AND ANGLES (°) IN THE PO_4 TETRAHEDRA

P(1)	O(2)	O(2 ^{iv})	O(8)	O(10)
O(2)	1.542(5)	2.52(1)	2.532(8)	2.535(8)
O(2 ^{iv})	109.7(4)	1.542(5)	2.532(8)	2.535(8)
O(8)	108.3(3)	108.3(3)	1.582(8)	2.54(1)
O(10)	110.8(3)	110.8(3)	108.8(4)	1.536(9)
P(2)	O(3a)	O(4b)	O(9)	O(12a)
O(3a)	1.60(1)	2.45(2)	2.59(1)	2.50(1)
O(4b)	106.7(7)	1.46(1)	2.45(1)	2.49(2)
O(9)	112.3(5)	110.7(6)	1.527(5)	2.46(1)
O(12a)	106.5(6)	113.2(7)	107.5(5)	1.52(1)
P(2)	O(3b)	O(4a)	O(9)	O(12b)
O(3b)	1.47(1)	2.47(1)	2.47(1)	2.47(2)
O(4a)	109.7(6)	1.55(1)	2.54(1)	2.56(1)
O(9)	111.2(5)	111.4(4)	1.527(5)	2.53(1)
O(12b)	104.6(6)	110.2(6)	109.5(5)	1.57(1)

Note. Symmetry codes are given in the footnote to Table III.

KNb_2PO_8 are related the HTBs and ITBs. The splitting of several atomic positions, although remarkable, is not new in this type of phase and has been observed in several phosphate tungsten bronzes (8, 9). Considering only the $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers it can be explained by the fact that the perfectly ordered bronze should exhibit a doubling of the a parameter $a' = 2a$, due to the regular tilting of the polyhedra along \vec{a} as shown in Fig. 6. However, the $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers are connected via $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units so that they can be shifted at random of $a/2$ with respect to each other without affecting the $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units. This is possible because the oxygen atoms shared by the $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units and the $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers are not tilted, since they lie on the rotation axis of the tilting operation. The absence of superstructure reflections involving a doubling of the “ a ” parameter agrees with this statistical shifting of the $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers. This splitting of some oxygen atoms leads us also

to consider two sorts of polyhedra for Nb(1), Nb(3), and P(2), respectively (Tables III and IV). It is worth pointing out that these Nb(1) and Nb(3) octahedra with Nb–O distances ranging from 1.82 to 2.25 Å (Table III) are strongly distorted in order to decrease the strains in the structure. In contrast the Nb(2) octahedra which belong to the $(\text{Nb}_2\text{P}_2\text{O}_{14})$ units are much less distorted as shown from their Nb–O distances ranging from 2.01 to 2.14 Å. The calculation of the valency of niobium using the Brown and Altermatt tables (13) shows that the Nb(2) sites are only occupied by Nb(IV), whereas the Nb(1) and Nb(3) sites are mainly occupied by Nb(V). These results are absolutely coherent with the distortion of the octahedra, since Nb(V) allows a greater distortion of those polyhedra, owing to its d^0 character; moreover the occupation of the edge-sharing Nb(3) octahedra of the $[\text{Nb}_2\text{P}_2\text{O}_{14}]$ units by Nb(IV) allows a smaller coulombic repulsion than by Nb(V). This latter “localization” of the charges in

that oxide raises the issue of the electronic conductivity in these materials. This study shows also the rather great flexibility of the PO_4 tetrahedra, especially of the P(2) tetrahedra which belong to the $[\text{Nb}_3\text{P}_2\text{O}_{17}]_\infty$ layers for which a rather great distortion is observed characterized by P–O distances ranging from 1.46 to 1.60 Å (Table 4).

The sodium cations which are located at the intersection of the tunnels are surrounded by oxygen atoms and exhibit Na–O distances ranging from 2.38(1) to 3.13(1) Å as usually observed.

These results suggest the possible existence of a large family of niobium phosphate bronzes with general formula $\text{Na}_x(\text{PO}_2)_4(\text{NbO}_3)_{2m}$, similar to the tungsten phosphate bronzes isolated previously. The issue of the “bronze” nature of these phases should also be studied. A systematic investigation of these systems involving niobium and phosphorus oxides will be carried out from the structural point of view and for their electron transport properties.

References

1. A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **80**, 12 (1989).
2. A. MAGNELI, *Ark. Kemi* **1**, 213 and 269 (1949).
3. A. LECLAIRE, A. BENABBAS, M. M. BOREL, A. GRANDIN, AND B. RAVEAU, *J. Solid State Chem.* **83**, 245 (1989).
4. A. BENABBAS, M. M. BOREL, A. GRANDIN, A. LECLAIRE, AND B. RAVEAU, *J. Solid State Chem.* **87**, 360 (1990).
5. A. BENABBAS, M. M. BOREL, A. GRANDIN, A. LECLAIRE, AND B. RAVEAU, *J. Solid State Chem.* **84**, 365 (1990).
6. A. MAGNELI, *Acta Chem. Scand.* **7**, 315 (1953).
7. A. HUSSAIN AND L. KIHNBORG, *Acta Crystallogr., Sect. A* **32**, 551 (1976).
8. B. RAVEAU, *Proc. Indian Acad. Sci. Acad. A* **52**, 67 (1986).
9. B. RAVEAU, *Proc. Indian Acad. Sci. (Chem. Sci.)* **96**, 419 (1986).
10. A. LECLAIRE, H. CHAHBOUN, D. GROULT, AND B. RAVEAU, *Z. Kristallogr.* **177**, 277 (1986).
11. S. L. WANG, C. C. WANG, AND K. H. LII, *J. Solid State Chem.* **82**, 298 (1989).
12. M. HERVIEU, B. DOMENGES, AND B. RAVEAU, *J. Solid State Chem.* **58**, 223 (1985).
13. I. D. BROWN AND D. ALTERMATT, *Acta Crystallogr., Sect. B* **41**, 244 (1985).