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$Na_{2+x}Nb_6P_4O_{26}$: A Novel Niobium Phosphate Bronze Isotypic of the $m = 3$ Member of the $MPTB_p$ Family

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A new niobium phosphate bronze $Na_{2+x}Nb_6P_4O_{26}$ ($0 \leq x \leq 0.75$) has been isolated. Its structure was solved by single crystal X-ray diffraction. It crystallizes in the orthorhombic system with space group $P2_12_12$. The cell parameters are $a = 19.8050(10)$, $b = 14.3859(7)$, and $c = 5.3960(4)$ Å. The framework is built up from ReO_3-type slabs of NbO_6 octahedra, perpendicular to **a** and linked by isolated PO_4 tetrahedra delimiting pentagonal tunnels running along **c**. The structure of this bronze corresponds to that expected for the hypothetical member $m = 3$ of the series of the monophosphate tungsten bronzes ($MPTB_p$) with pentagonal tunnels $(WO_3)_{2m}(PO_2)_4$. Relationships with other niobium phosphate bronzes are also discussed.

Introduction

The recent investigation of the systems A–Nb–P–O where A = Na, K has allowed several niobium phosphate bronzes to be synthesized. The difference in size between potassium and sodium ions has given rise to a great disparity between the structures of the phases isolated in the two systems. In part, the phases obtained in the K–Nb–P–O system present great similarities with the tungsten bronzes, as shown for instance for $KNb_3P_3O_{15}$ (*1*) related to the tetragonal tungsten bronze (TTB) (*2*), for $K_3Nb_6P_4O_{26}$ (*3*) related to the hexagonal tungsten bronze (HTB) (*4*), and for $K_7Nb_{14}P_9O_{60}$ (*5*), α-$K_{5-x}Nb_8P_5O_{34}$ (*6*), and β-$K_4Nb_8P_5O_{34}$ (*7*) related to the intergrowth tungsten bronzes (ITB) (*8*). On the other hand, the study of the Na–Nb–P–O system has allowed the oxide $Na_4Nb_8P_5O_{35}$ (*9*), whose structure exhibits similarities with the $m = 3$ member of the diphosphate tungsten bronzes with pentagonal tunnels (*10*), to be isolated. The existence of different series of phosphate tungsten bronzes related to the ReO_3-type structure (*11*) should allow a similar behavior to be expected for niobium phosphate bronzes. The synthesis of the bronzoid β-$NbPO_5$ (*12*), isotypic of WPO_5 (*13*), the second member of the monophosphate tungsten bronzes ($MPTP_p$) with pentagonal tunnels $(WO_3)_{2m}(PO_2)_4$, is in agreement with this view. However, in the other members of this series, the valency of tungsten is always greater than five, which makes impossible

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the synthesis of isotypic niobium phosphates. Nevertheless, the size of the empty tunnels in the $MPTB_p$'s is adequate for sodium so that it should be possible to compensate the excess charge with respect to niobium by introducing sodium ions in the tunnels in order to synthesize other members of the niobium phosphate bronze series with composition $Na_x(NbO_3)_{2m}(PO_2)_4$. We report here on the crystal structure of a new niobium phosphate bronze $Na_{2+x}Nb_6P_4O_{26}$, third member of the series of monophosphate bronzes.

Synthesis and Characterization

The limiting compound, with $x = 0$, i.e., the bronzoid $Na_2Nb_6^VP_4O_{26}$, was prepared in air in two steps. First, the appropriate mixture of Na_2CO_3, Nb_2O_5, and $H(NH_4)_2PO_4$ was ground in an agate mortar and heated up to 673 K in order to remove CO_2, H_2O, and NH_3. Then, the mixture was reground and heated in a platinum crucible at 1273 K in air for 1 day. The X-ray powder diffraction pattern of this phase was indexed in an orthorhombic cell in agreement with the parameters obtained from the single crystal study (Table I).

For higher sodium contents, corresponding to the composition $Na_{2+x}Nb_6P_4O_{26}$ with $0 < x < 0.75$, a similar experimental method was used; the appropriate mixtures were heated in air at 673 K in order to decompose Na_2CO_3 and $H(NH_4)_2PO_4$. The necessary amount of niobium was added to that mixture and heated at 1273 K in an evacuated silica ampoule. This method allowed for blue crystals to be grown. The approximate composition of these crystals was determined by microprobe analysis and the structure refinement of the selected crystal converged to the composition $Na_{2.66}Nb_6P_4O_{26}$.

Structure Determination

A dark blue crystal with dimensions 0.077 × 0.059 × 0.045 mm was selected for the structure determination. The cell parameters reported in Table II were determined by diffractometric techniques at 294 K and refined by the least squares method based upon 25 reflections with $18 \leq \theta \leq 25°$.

TABLE I

$Na_2Nb_6P_4O_{26}$: INTERETICULAR DISTANCES

h	k	l	d_{obs}	d_{calc}	I
0	2	0	7.190	7.193	17
3	2	0	4.860	4.864	39
3	0	1	4.168	4.178	48
3	1	1	4.004	4.012	100
3	3	0	3.880	3.880	56
0	4	0	3.601	3.597	50
4	3	0	3.445	3.445	8
3	3	1	3.151	3.150	52
6	2	0	2.999	3.000	2
6	1	1	2.761	2.763	22
2	5	0		2.763	
6	3	0	2.718	2.719	26
0	0	2	2.688	2.698	35
0	5	1	2.538	2.539	30
6	3	1	2.427	2.428	9
9	1	0	2.174	2.175	4
9	3	0	1.999	2.000	8
6	6	0	1.939	1.940	8
6	3	2	1.913	1.915	21
1	7	1		1.912	
9	4	0	1.880	1.877	13
3	7	1	1.843	1.844	4
10	1	1		1.844	
10	2	1	1.800	1.800	9
0	8	0		1.798	

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

The intensity of reflections indicated *mmm* as Laue symmetry. The systematic absences $h + l = 2n + 1$ for $h0l$ are consistent with the space groups $Pmn2_1$ and $Pmnm$ (another setting of $Pmmn$). The first group was finally chosen according to the Patterson peaks. The niobium atoms were located from the Patterson series. Then, the phosphorus, sodium, and oxygen atom co-

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $Na_{2.66}Nb_4P_4O_{26}$

1. Crystal data	
Space group	$P2_12_12$
Cell dimensions	a = 19.805(1) Å b = 14.3859(7) Å c = 5.3960(4) Å
Volume	1537.4(3) $Å^3$
Z	3
2. Intensity measurements	
λ(Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - \theta$
Scan width (°)	$1 + 0.35 \tan \theta$
Slit aperture (mm)	$1 + \tan \theta$
Max θ(°)	45
Standard reflections	3 measured every 3000 sec (no decay)
Reflections with $I > 3\sigma$	1341
3. Structure solution and refinement	
Parameters refined	140
Agreement factors	$R = 0.035$, $R_w = 0.034$

ordinates were obtained by successive difference synthesis calculations. The refinement of the positions of all the atoms led to $R = 0.089$; however, some of the coordinates did not converge. Furthermore, after an isotropic refinement, all the thermal factors became abnormal, either very large or negative.

Subsequently, since the structure was found to be described also in the space group $P2_12_12$ by permuting the cell constants to obtain those indicated in Table II, the isotropic refinement was performed in this group. The reliability factor R decreased to 0.045 and the thermal factor of all atoms became normal. Then, anisotropic refinement including only niobium atoms led to $R = 0.035$ and $R_w = 0.034$, leading to the formula $Na_{2.66}Nb_6P_4O_{26}$ in agreement with microprobe analysis.

The atomic parameters are reported in Table III.

Description of the Structure and Discussion

The $[Nb_6P_4O_{26}]_\infty$ framework is built up from slabs of corner sharing NbO_6 octahedra connected through isolated PO_4 tetrahedra and delimiting pentagonal tunnels parallel to **c** as shown from the projection of the structure along **c** (Fig. 1).

The structure can be described as built up from ReO_3-type slabs parallel to the (010) plane, forming infinite zig-zag chains of corner sharing octahedra along **a** (Figs. 1 and 2). The ReO_3-type slabs are three octahedra

TABLE III

POSITIONAL PARAMTERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	$B(Å^2)$
Nb(1)	0.000	0.000	0.2640(6)	0.77(2)
Nb(2)	0.33090(5)	−0.02029(6)	0.2372(5)	0.71(1)
Nb(3)	0.11669(5)	0.10021(6)	0.7647(4)	0.62(1)
Nb(4)	0.43601(4)	0.09682(6)	0.7459(5)	0.49(1)
Nb(5)	0.77765(6)	0.11139(6)	0.7414(4)	0.65(1)
P(1)	0.2158(1)	0.1654(2)	0.264(1)	0.41(4)[a]
P(2)	0.5369(1)	0.1787(2)	0.253(1)	0.36(4)[a]
P(3)	0.8842(1)	0.1708(2)	0.2332(9)	0.35(4)[a]
Na(1)	0.0587(3)	0.2161(4)	0.242(3)	1.18(9)[a]
Na(2)	0.3779(4)	0.2060(5)	0.246(4)	1.4(1)[a]
O(1)	0.0642(6)	0.0530(8)	0.023(3)	1.2(2)[a]
O(2)	−0.0453(4)	0.1262(6)	0.271(3)	0.9(1)[a]
O(3)	0.0598(5)	0.0459(7)	0.517(2)	0.8(2)[a]
O(4)	0.2595(4)	0.0781(5)	0.273(3)	0.7(1)[a]
O(5)	0.3915(6)	0.0540(7)	0.474(2)	0.9(2)[a]
O(6)	0.2765(6)	−0.0931(6)	0.026(2)	0.7(1)[a]
O(7)	0.4030(5)	−0.1126(6)	0.214(2)	1.1(2)[a]
O(8)	0.3714(5)	0.0546(7)	−0.022(2)	0.9(2)[a]
O(9)	0.2940(5)	−0.0832(7)	0.536(2)	0.7(1)[a]
O(10)	0.0626(4)	0.2218(5)	0.765(3)	0.7(1)[a]
O(11)	0.1737(5)	0.1721(7)	0.493(2)	1.0(2)[a]
O(12)	0.1686(6)	0.1680(7)	0.036(2)	1.1(2)[a]
O(13)	0.1849(4)	0.0094(5)	0.757(4)	0.7(1)[a]
O(14)	0.3910(5)	0.2242(6)	0.712(2)	0.7(1)[a]
O(15)	0.500	0.000	0.780(4)	1.0(2)[a]
O(16)	0.4855(5)	0.1653(7)	0.054(2)	0.7(2)[a]
O(17)	0.5085(5)	0.1655(7)	0.514(2)	1.0(2)[a]
O(18)	0.7627(4)	0.2516(5)	0.725(2)	0.5(1)[a]
O(19)	0.8577(5)	0.1543(6)	−0.024(2)	0.6(1)[a]
O(20)	0.8400(5)	0.1315(7)	0.441(2)	0.8(2)[a]

[a] Isotropically refined. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as

$$B = \frac{4}{3} \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \cdot \beta_{ij}.$$

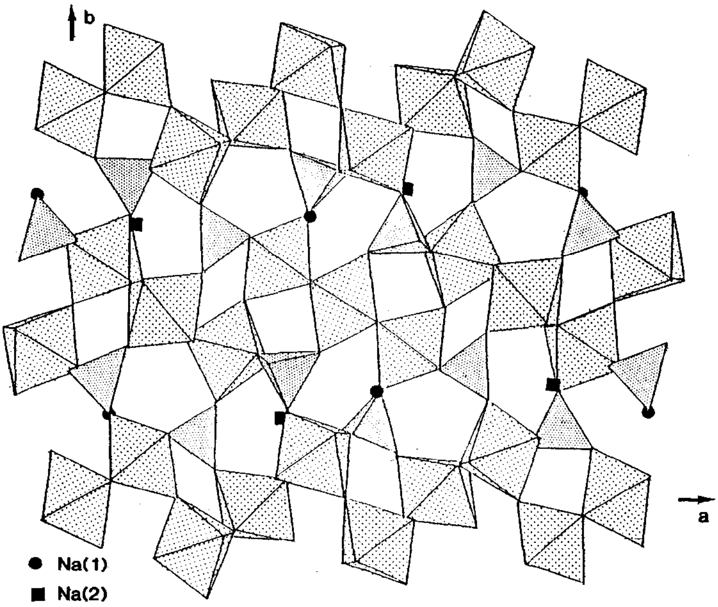

FIG. 1. Projection of the $Na_{2.66}Nb_6P_4O_{26}$ structure along **c**.

wide along the direction [110] and formed of strings of two octahedra alternating with one octahedron along the perpendicular direction [2$\bar{3}$0]. Consequently, this oxide represents the $m = 3$ member of the large family of the monophosphate tungsten bronzes with pentagonal tunnels $(WO_3)_{2m}(PO_2)_4$ which was previously studied (*10*). However, it is worth pointing out that in the case of tungsten bronzes the $m = 3$ member was never observed. The phase $W_{12}P_8O_{52}$ which corresponds to this composition exhibits a

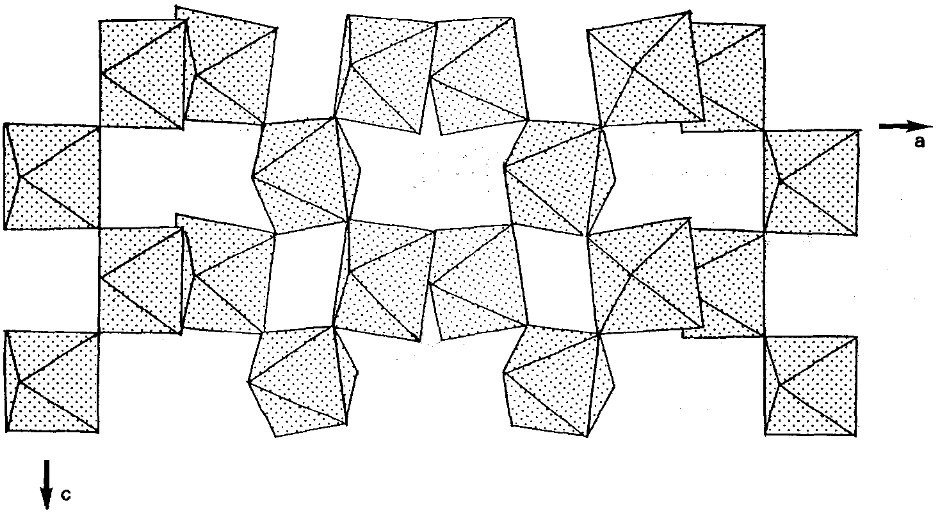

FIG. 2. ReO_3-type slabs parallel to the (010) plane.

TABLE IV

DISTANCES (Å) ANGLES (°) IN THE NbO_6 OCTAHEDRA[a]

Nb(1)	O(1)	O(1^{i})	O(2)	O(2^{i})	O(3)	O(3^{i})
O(1)	1.97(1)	2.96(2)	2.76(2)	2.93(2)	2.66(2)	3.89(2)
O(1^{i})	97.6(6)	1.97(1)	2.93(2)	2.76(2)	3.89(2)	2.66(2)
O(2)	87.2(5)	94.2(5)	2.025(8)	4.05(2)	2.72(1)	2.82(2)
O(2^{i})	94.2(5)	87.2(5)	177.9(7)	2.025(8)	2.82(1)	2.72(2)
O(3)	86.4(5)	175.8(5)	87.3(5)	91.25(3)	1.92(1)	2.71(1)
O(3^{i})	175.8(5)	86.4(5)	91.3(5)	87.3(5)	89.7(5)	1.92(1)

Nb(2)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)
O(4)	2.009(8)	2.85(1)	2.82(1)	3.96(2)	2.75(2)	2.81(1)
O(5)	89.2(4)	2.05(1)	3.94(2)	2.79(1)	2.71(1)	2.78(1)
O(6)	92.7(4)	177.6(4)	1.89(1)	2.72(1)	2.85(1)	2.78(2)
O(7)	177.3(5)	88.1(4)	90.0(4)	1.955(9)	2.79(1)	2.81(1)
O(8)	88.2(5)	85.4(5)	96.2(5)	91.6(4)	1.94(1)	3.92(2)
O(9)	89.2(5)	86.9(5)	91.6(4)	90.7(4)	171.9(5)	1.99(1)

Nb(3)	O(1^{ii})	O(3)	O(10)	O(11)	O(12^{ii})	O(13)
O(1^{ii})	1.87(1)	2.74(2)	2.80(2)	3.98(2)	2.65(2)	2.86(2)
O(3)	92.7(5)	1.92(1)	2.87(1)	2.90(1)	3.95(2)	2.85(2)
O(10)	91.1(5)	92.4(5)	2.051(8)	2.74(2)	2.67(2)	3.90(2)
O(11)	172.1(5)	91.7(5)	82.1(5)	2.12(1)	2.94(2)	2.75(2)
O(12^{ii})	85.3(5)	173.6(4)	81.6(5)	89.8(5)	2.04(1)	2.75(2)
O(13)	99.5(6)	97.1(6)	165.5(3)	86.6(5)	89.2(6)	1.879(8)

Nb(4)	O(5)	O(8^{ii})	O(14)	O(15)	O(16^{ii})	O(17)
O(5)	1.82(1)	2.75(2)	2.76(1)	2.82(2)	3.98(2)	2.83(2)
O(8^{ii})	95.5(5)	1.89(1)	2.86(1)	2.87(1)	2.80(1)	4.02(1)
O(14)	91.2(4)	93.0(4)	2.045(8)	3.90(1)	2.76(1)	2.70(1)
O(15)	98.8(6)	98.8(5)	163.7(3)	1.892(2)	2.82(1)	2.78(2)
O(16^{ii})	172.7(4)	86.8(5)	81.9(4)	87.6(5)	2.17(1)	2.95(2)
O(17)	90.6(5)	170.8(4)	80.1(4)	86.9(5)	86.3(4)	2.15(1)

Nb(5)	O(6^{iii})	O(9^{iv})	O(13^{iv})	O(18)	O(19^{ii})	O(20)
O(6^{iii})	1.89(1)	2.67(2)	2.75(2)	2.91(1)	2.81(1)	3.95(2)
O(9^{iv})	91.2(5)	1.84(1)	2.80(1)	2.86(1)	3.96(1)	2.79(1)
O(13^{iv})	93.4(6)	97.2(5)	1.891(8)	3.90(2)	2.77(1)	2.69(2)
O(18)	95.2(4)	94.6(4)	165.2(3)	2.040(7)	2.71(1)	2.77(1)
O(19^{ii})	88.8(5)	175.7(4)	87.0(5)	81.2(4)	2.12(1)	2.93(2)
O(20)	177.7(5)	91.1(5)	85.9(6)	85.0(4)	89.0(4)	2.06(1)

TABLE IV—*Continued*

Distances (Å) and angles (°) in the PO_4 tetrahedra[b]

P(1)	O(4)	O(11)	O(12)	O(18$^{\mathrm{v}}$)
O(4)	1.526(8)	2.48(1)	2.56(2)	2.45(1)
O(11)	110.3(7)	1.49(1)	2.47(2)	2.39(1)
O(12)	112.7(7)	108.5(6)	1.55(1)	2.55(1)
O(18$^{\mathrm{v}}$)	107.5(4)	105.1(6)	112.5(6)	1.514(8)

P(2)	O(7$^{\mathrm{iv}}$)	O(10$^{\mathrm{vi}}$)	O(16)	O(17)
O(7$^{\mathrm{iv}}$)	1.54(1)	2.48(1)	2.49(1)	2.50(2)
O(10$^{\mathrm{vi}}$)	108.2(5)	1.522(9)	2.43(1)	2.46(2)
O(16)	110.4(7)	107.7(7)	1.49(1)	2.53(2)
O(17)	109.5(7)	107.4(8)	113.4(6)	1.53(1)

P(3)	O(2$^{\mathrm{vii}}$)	O(14$^{\mathrm{vi}}$)	O(19)	O(20)
O(2$^{\mathrm{vii}}$)	1.550(9)	2.50(1)	2.53(2)	2.45(1)
O(14$^{\mathrm{vi}}$)	107.5(5)	1.546(8)	2.51(1)	2.45(1)
O(19)	111.7(7)	111.2(6)	1.50(1)	2.55(2)
O(20)	105.5(7)	105.8(6)	114.7(6)	1.53(1)

Na–O (Å) distances

Na(1)–O(1) : 2.63(2)
–O(2) : 2.44(1)
–O(3) : 2.86(2)
–O(10$^{\mathrm{viii}}$) : 2.58(3)
–O(10) : 2.82(3)
–O(11) : 2.72(2)
–O(12) : 2.54(2)
–O(16$^{\mathrm{ix}}$) : 2.75(2)
–O(17$^{\mathrm{v}}$) : 2.37(2)

Na(2)–O(4) : 2.98(1)
–O(5) : 2.52(2)
–O(8) : 2.62(2)
–O(14) : 2.91(2)
–O(14$^{\mathrm{viii}}$) : 2.54(2)
–O(16) : 2.44(1)
–O(17) : 3.02(2)
–O(18$^{\mathrm{v}}$) : 2.37(1)
–O(19$^{\mathrm{ix}}$) : 2.38(2)
–O(20$^{\mathrm{v}}$) : 2.98(2)

Note. Symmetry code: i: $-x, -y, -z$; ii: $x, y, z + 1$; iii: $1 - x, -y, 1 + z$; iv: $1 - x, -y, z$; v: $x - 1/2, 1/2 - y, -z + 1$; vi: $1/2 + x, 1/2 - y, -z + 1$; vii: $x + 1, y, z$; viii: $x, y, z - 1$; ix: $x - 1/2, 1/2 - y, -z$.

[a] The diagonal terms are Nb–O(i) distances, the terms above the diagonal are O(i)–O(j) distances, and those below are the O(i)–Nb–O(j) angles.

[b] The diagonal terms are the P–O(i) distances, the terms above the diagonal are the O(i)–O(j) distances, and those below are the O(i)–P–O(j) angles.

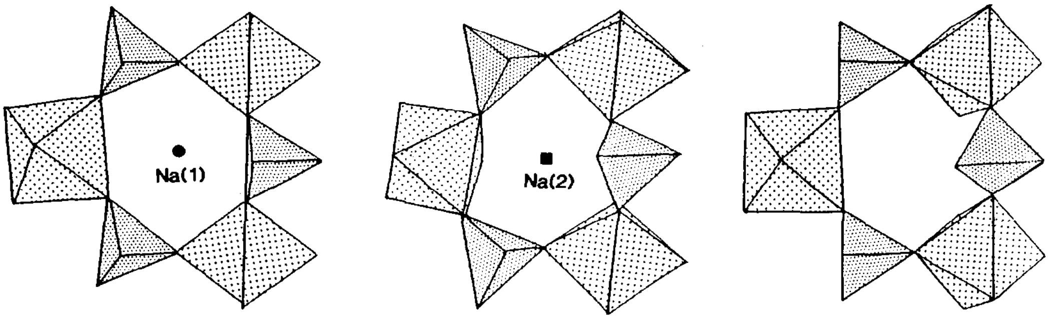

FIG. 3. Hexagonal windows: two of them contain Na(1) and Na(2), the third is empty.

different tunnel structure (*14*) related to $CsW_8P_8O_{40}$ (*15*). This difference can be explained by the fact that for low m values, the ReO_3-type slabs are more distorted in order to accomodate the PO_4 tetrahedra, so that other arrangements can be more stable; this is especially true in the case of tungsten bronzes, where it is well known that the symmetry of the WO_6 octahedra increases as the W(V) content increases.

The significant distortion of the octahedral slabs is easily evidenced from the consideration of the cell parameters. The previous study of the $MPTB_p$'s (*11*) allowed cell parameters to be calculated versus m, based on the parameter of the cubic cell of ReO_3 according to the equations

$$a \approx a_{ReO_3}\sqrt{2},\ b \approx a_{ReO_3}\sqrt{3},\ \text{and}$$

$$c \approx 2\left(K + \frac{m}{2} a_{ReO_3} \cos 35.3^\circ\right).$$

Moreover, two space groups, $P2_12_12_1$ and $Pnn2$, were foreseen for even and odd m, respectively. In the case of this niobium phosphate bronze one observes that the distortion of the ReO_3-type slabs gives rise to the degeneracy of the space groups, with a tripling of the b parameter with respect to the phosphate tungsten bronzes $(WO_3)_{2m}(PO)_4$ ($a_{Nb} \approx 3a_W \approx 3a_{ReO_3}\sqrt{3}$). Note that the additional reflections are as strong as the basic reflections, in agreement with the fact that some of the NbO_6 octahedra are strongly tilted with respect to the ideal ReO_3-type structure.

Though they are distorted, the NbO_6 octahedra exhibit a more regular geometry (Table IV) than the other niobium phosphates. The Nb(1) and Nb(2) atoms exhibit four Nb–O distances smaller than 2 Å (1.92 to 1.97 Å) and two longer ones (2.025 Å) in agreement with the fact that they share their oxygen atoms with four NbO_6 octahedra and two tetrahedra, respectively. In the same way Nb(3), Nb(4), and Nb(5) octahedra are characterized by three short bondlengths, smaller than 2 Å, corresponding to Nb–O—Nb bonds, and three Nb–O distances longer than 2 Å, corresponding the Nb–O–P bonds (Table IV).

The PO_4 tetrahedra which share their four corners with NbO_6 octahedra are regular as generally observed for other niobium phosphates (Table IV).

The sodium atoms are not located on the axis of the pentagonal tunnels (Fig. 1) but at the boundary between two adjacent tunnels along **a**, nearly at the center of the hexagonal windows formed of three octahedra and three tetrahedra (Fig. 3). Only two sites out of three are occupied by sodium. The Na(1) and Na(2) atoms exhibit a 9- and 10-fold coordination, respectively, with Na–O distances ranging from 2.327 to 3.02 Å. In the ideal structure the coordination should be identical for all the sodium atoms; the two sorts of coordination are just due to the distortion of the $[Nb_6P_4O_{26}]_\infty$ framework.

Concluding Remarks

This study shows the possibility of introducing sodium into the host lattice of the monophosphate tungsten bronze-type structure ($MPTB_p$), leading to the formula $Na_x(MO_3)_{2m}(PO_2)_4$. The third member of the series, represented by $Na_{2+x}Nb_6P_4O_{26}$, has been synthesized for the first time, opening the route to the synthesis of other niobium phosphate bronzes with the $MPTB_p$ structure. The existence of mixed valency for niobium Nb(V)/Nb(IV) suggests the possibility of inducing electron transport properties by adjusting the sodium content in the cavities, in agreement with the metallic behavior of the phosphate tungsten bronzes $(WO_3)_{2m}(PO_2)_4$. The investigation of physical properties will be performed in connection with structural evolution and sodium nonstoichiometry.

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