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The Niobium Phosphate Bronze β-$K_2Na_{2-x}Nb_8P_5O_{34}$, Second Form of the First Member of the Series $(K_3Nb_6P_4O_{26})_n$ KNb_2PO_8

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A new niobium phosphate bronze β-$K_2Na_{2-x}Nb_8P_5O_{34}$ has been isolated. Its structure was solved by single crystal X-ray diffraction for $x = 0.27$. It crystallizes in the space group $P\bar{4}m2$ with $a = 10.612$ (1) and $c = 6.384$ (1) Å. This phase is the second form of the first member of the series $(K_3Nb_6P_4O_{26})_n$ KNb_2PO_8. The structural relationships with the other members of this series and especially with $K_7Nb_{14}P_9O_{60}$ ($n = 2$) are discussed. © 1991 Academic Press, Inc.

Introduction

The recent investigation of the K–Nb–P–O system led to the synthesis of several phases (*1–4*) characterized by a mixed valency of niobium Nb(V)–Nb(IV). All these oxides exhibit a great structural similarity with the oxygen tungsten bronzes described by Magneli *et al.* (*5–7*) and for these reasons were called niobium phosphate bronzes. Among them the phosphate bronzes α-$K_4Nb_8P_5O_{34}$ (*4*), $K_7Nb_{14}P_9O_{60}$ (*2*), and $K_3Nb_6P_4O_{26}$ (*3*) belong to the same series $(K_3Nb_6P_4O_{26})_n$ KNb_2PO_8 and can be classified as the members $n = 1$, 2, and ∞, respectively. Their structures are indeeed built up from infinite layers $[Nb_3P_2O_{13}]_\infty$ connected eventually through identical $[Nb_2PO_8]_\infty$ chains. However the $[Nb_3P_2O_{13}]_\infty$ layers exhibit a different geometry from one member to the other, so that these phases cannot be rigorously considered as members of the same structural family. In this respect, the study of the first member of the series, $K_{5-x}Nb_8P_5O_{34}$ (*4*), suggested that besides this first form called α, a second structural β form could be expected. For this reason the K–Na–Nb–P–O was investigated, with carefully controlled experimental conditions, especially temperature. We report here on the synthesis and structure of the niobium phosphate bronze β-$K_2Na_{2-x}Nb_8P_5O_{34}$.

Synthesis

β-$K_2Na_2Nb_8P_5O_{34}$ could be synthesized in the form of powder in two steps. First the stoichiometric mixture of Na_2CO_3, K_2CO_3, $H(NH_4)_2PO_4$, and Nb_2O_5 was heated up to 673 K in order to remove CO_2, NH_3, and H_2O. In the second step, the finely ground

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TABLE I

$K_2Na_2Nb_8P_5O_{34}$: INTERETICULAR DISTANCES

h	k	l	d_{obs}	d_{calc}	I
0	0	1	6.375	6.384	26
1	0	1	5.467	5.470	38
2	0	0	5.304	5.306	17
2	0	1	4.073	4.080	49
2	1	1	3.805	3.809	12
2	2	0	3.748	3.752	6
3	0	0	3.534	3.537	100
3	1	0	3.363	3.356	6
2	2	1	3.231	3.235	6
3	0	1	3.089	3.094	37
1	0	2	3.054	3.056	14
3	1	1	2.966	2.970	16
1	1	2	2.934	2.937	15
2	0	2	2.731	2.735	24
3	2	1	2.671	2.673	23
2	1	2	2.646	2.648	15
3	3	0	2.499	2.501	13
2	2	2	2.430	2.431	12
5	0	0	2.120	2.122	8
4	3	0		2.122	
5	1	0	2.082	2.081	7
5	0	1	2.013	2.014	12
4	3	1		2.014	
5	2	0	1.971	1.971	5
2	1	3	1.939	1.942	6
5	3	0	1.819	1.820	5

TABLE II

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $K_2Na_{2-x}Nb_8P_5O_{34}$

1. Crystal data	
Space group	$P\bar{4}m2(115)$
Cell dimensions	$a = 10.612(1)$ Å $c = 6.384(1)$
Volume	$v = 718.9(2)$ Å^3
Z	1
2. Intensity measurement	
$\lambda(\mathrm{Mo}K\overline{\alpha})$	0.71073 Å
Scan mode	$\omega - \theta$
Scan width (°)	$0.95 + 0.35 \tan \theta$
Slit aperture (mm)	$1 + \tan \theta$
Max θ(°)	45
Standard reflections	Three measured every 3000 s (no decay)
Reflections with $I > 3\sigma$	1518
$\mu(\mathrm{mm}^{-1})$	3.66
3. Structure solution and refinement	
Parameters refined	70
Agreement factors	$R = 0.032$, $R_w = 0.035$

powder mixed with the appropriate amount of niobium, sealed in an evacuated silica ampoule, was heated up to 1353 K for a day.

The single crystals of this phase were obtained at the same temperature (1353 K) but for a longer time (2 days). The structure determination showed for this phase the existence of a sodium nonstoichiometry leading to the formulation $K_2Na_{2-x}Nb_8P_5O_{34}$ ($x \approx 0.27$).

Structure Determination

The X-ray powder diffraction pattern of $K_2Na_2Nb_8P_5O_{34}$ (Table I) was indexed in the tetragonal cell deduced from the single crystal study (Table II).

A dark crystal of the sample with nominal composition $K_2Na_2Nb_8P_5O_{34}$ was selected for the structure determination. The cell parameters reported in Table II were determined by diffractometric techniques at 294 K and refined with a least square refinement method based upon 25 reflections with $18 \leq \theta \leq 25°$.

The intensity of reflections indicated 4/*mmm* as Laue symmetry. No systematic absences were observed. The structure was resolved in the space group $P\bar{4}m2$ (No. 115) accordingly to our model (*4*).

The data were collected on a CAD-4 Enraf–Nonius diffractometer with the parameters reported in Table II.

The reflections were corrected for Lorentz and polarization effects. No absorption corrections were performed.

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	$B(\text{Å}^2)$
Nb(1)	0.500	0.18295(6)	0.20093(9)	0.797(6)
Nb(2)	0.17682(3)	0.177	0.000	0.582(3)
P(1)	0.500	0.500	0.000	0.17(2)
P(2)	0.24040(9)	0.240	0.500	0.52(1)
O(1)	0.500	0.000	0.256(1)	1.1(1)
O(2)	0.3649(3)	0.1753(4)	0.0200(5)	1.02(4)
O(3)	0.3793(3)	0.2155(5)	0.4548(5)	1.36(6)
O(4)	0.500	0.3841(5)	0.151(1)	1.23(8)
O(5)	0.1776(6)	0.000	0.0340(8)	1.32(8)
O(6)	0.1592(3)	0.1978(3)	0.3114(5)	0.83(4)
Na[a]	0.500	0.500	0.500	5.6(2)
K	0.000	0.000	0.500	2.84(6)
K.Na[b]	0.000	0.500	0.2965(7)	3.28(8)

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

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

[a] Position filled 73% by Na.

[b] Position filled 50% by Na and 50% by K.

The positions of niobium and phosphorus atoms deduced from the model were calculated more accurately from Patterson function peaks. The alkali and oxygen atoms were determined by Fourier difference series. Sodium and potassium contents determined from the refinement of the occupancy factors led to the composition $K_2Na_{1.73}Nb_8P_5O_{34}$ in agreement with the last refinement leading to $R = 0.032$ and $R_w = 0.035$. The atomic parameters are reported in Table III.

Description of the Structure and Discussion

This new niobium phosphate bronze represents, like α-$K_4Nb_8P_5O_{34}$ (*4*), the first member of the series $(K_3Nb_6P_4O_{26})_n$ KNb_2PO_8. Like for other phases—α-$K_4Nb_8P_5O_{34}$, $K_7Nb_{14}P_9O_{60}$, and $K_3Nb_6P_4O_{26}$—its structure consists of $[Nb_3P_2O_{13}]_\infty$ layers. Although they are closely related, the geometry of the $[Nb_3P_2O_{13}]_\infty$ layers differs noticeably from one phase to the other. The similarity of the $[Nb_3P_2O_{13}]_\infty$ layers for these four bronzes is shown from Fig. 1. In all cases, one can recognize an infinite chain of corner-sharing octahedra $[NbO_3]_\infty$ running along **c** for α-$K_4Nb_8P_5O_{34}$ (Fig. 1a) and for $K_3Nb_6P_4O_{26}$ (Fig. 1b) and along **b** for $K_7Nb_{14}P_9O_{60}$ (Fig. 1c) and along **a** (or **b**) for β-$K_2Na_{1.73}Nb_8P_5O_{34}$ (Fig. 1c).

In the four oxides, the $[NbO_3]_\infty$ chains are connected through single PO_4 tetrahedra. The remarkable feature of those compounds deals with the fact that β-$K_2Na_{1.73}Nb_8P_5O_{34}$ and $K_7Nb_{14}P_9O_{60}$ exhibit absolutely identical $[Nb_3P_2O_{13}]_\infty$ layers parallel to (100) and (100) or (010), respectively, forming only two sorts of hexagonal windows similar to those observed in hexagonal tungsten bronzes (HTB) and brownmillerite (BM) (Fig. 1c). On the other hand, the edges of

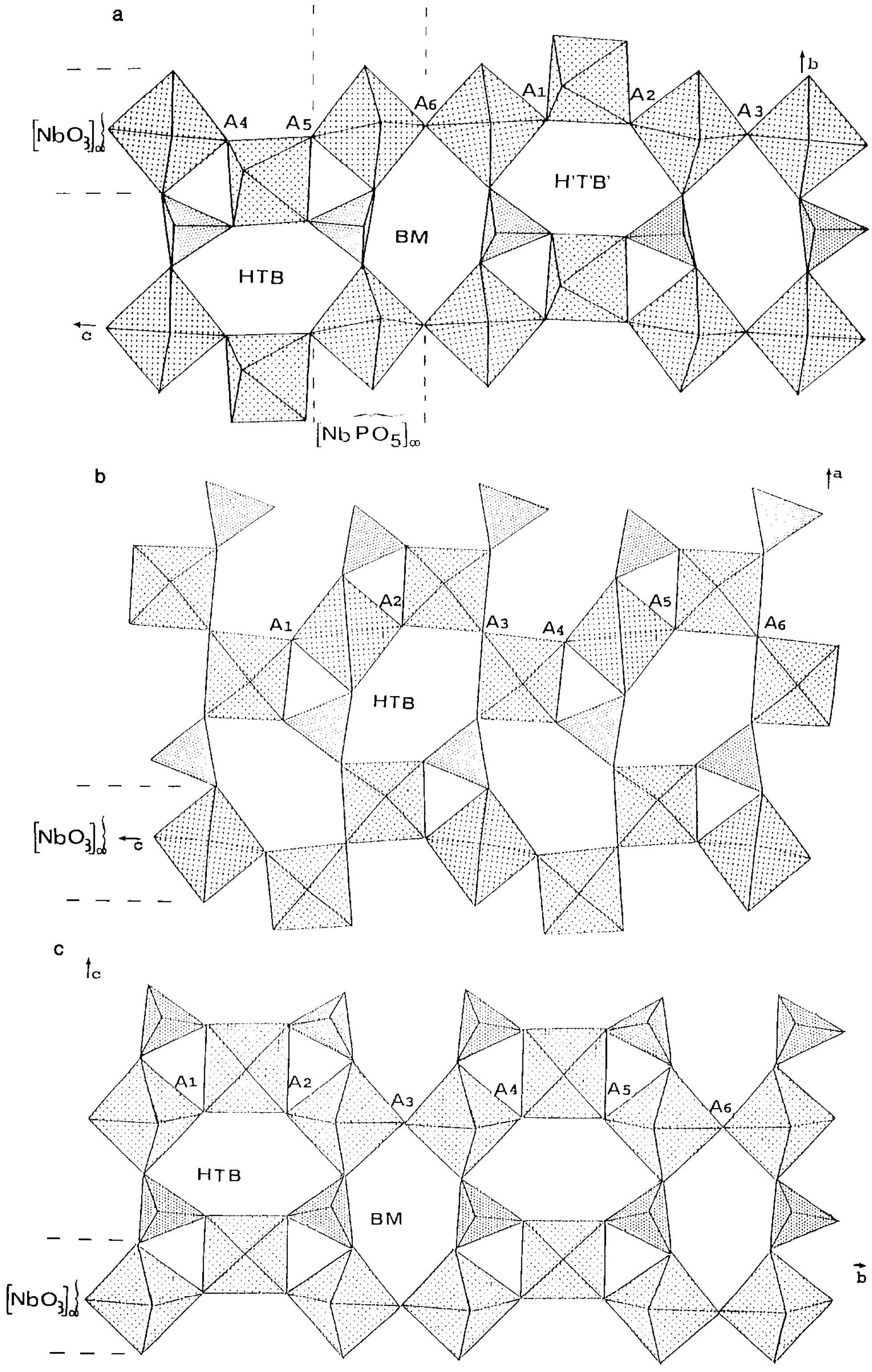

FIG. 1. $[Nb_3P_2O_{13}]_\infty$ layers in (a) α-$K_4Nb_8P_5O_{34}$; (b) $K_3Nb_6P_4O_{26}$; (c) $K_7Nb_{14}P_9O_{60}$ or $K_2Na_{2-x}Nb_8O_{34}$.

the NbO_6 octahedra of the $[NbO_3]_\infty$ chains form different O–O–O angles as well in α-$K_4Nb_8P_5O_{34}$ (Fig. 1a) as in $K_3Nb_6P_4O_{26}$ (Fig. 1b); as a result, one observes different relative positions of the HTB windows for the two latter phases which possess two sorts (HTB and H'T'B') (Fig. 1a) and one sort (HTB) (Fig. 1b) of such windows, respectively.

The second point deals with the assemblage of the $[Nb_3P_2O_{13}]_\infty$ layers. The comparison of the projection of the structure of β-$K_2Na_{1.73}Nb_8P_5O_{34}$ onto the (001) plane (Fig. 2a) with that of α-$K_4Nb_8P_5O_{34}$ onto the (010) plane (Fig. 2b) shows that the two structures are fundamentally different. The first one consists of $[Nb_3P_2O_{13}]_\infty$ layers linked through $[Nb_2PO_8]_\infty$ chains running along **a** or **b**, whereas in the second one the $[Nb_3P_2O_{13}]_\infty$ layers are linked through layers of PO_4 tetrahedra and NbO_6 octahedra alternately.

In fact, β-$K_2Na_{1.73}Nb_8P_5O_{34}$ is very closely related to $K_7Nb_{14}P_9O_{60}$ as shown from the projection of this latter structure into the (001) plane (Fig. 2c). Both structures are built up from identical $[Nb_3P_2O_{13}]_\infty$ layers parallel to (010) connected through identical $[Nb_2PO_8]_\infty$ chains running along **b**. The two structures, β-$K_2Na_{2-x}Nb_8P_5O_{34}$ and $K_7Nb_{14}P_9O_{60}$ differ only by the number of successive $[Nb_3P_2O_{13}]_\infty$ directly connected to each other through the corners of their polyhedra. One can indeed describe the structure of $K_7Nb_{14}P_9O_{60}$ as the stacking along **a** of quadruple $[(Nb_3P_2O_{13})_4]_\infty$ layers with single $[Nb_2PO_8]_\infty$ chains (Fig. 2c), whereas that of the β form consists of stacking along **a** or **b** of identical double $[(Nb_3P_2O_{13})_2]_\infty$ layers with single $[Nb_2PO_8]_\infty$ chains (Fig. 2a). Thus β-$K_2Na_{2-x}Nb_8P_5O_{34}$ and $K_7Nb_{14}P_9O_{60}$ belong rigorously to the same structural family $(K_3Nb_6P_4O_{26})_n$ KNb_2PO_8 and represent the members $n = 1$ and $n = 2$, respectively. Consequently these two structures exhibit the same kinds of tunnels running along **a** and **b** (Figs. 1 and 2). These tunnels which have been previously described (2) (4) are similar to those observed in hexagonal tungsten bronzes and in brownmillerite and called HTB and BM tunnels, respectively.

The geometry of the polyhedra NbO_6 and PO_4 in $K_2Na_{1.73}Nb_8P_5O_{34}$ (Tables IV and V)

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE NbO_6 OCTAHEDRA

Nb(1)	O(1)	O(2)	O(2^{i})	O(3)	O(3^{i})	O(4)
O(1)	1.973(2)	2.791(6)	2.791(6)	2.910(6)	2.910(6)	4.127(6)
O(2)	94.0(2)	1.843(4)	2.868(6)	2.812(6)	3.905(6)	2.769(6)
O(2^{i})	94.0(2)	102.2(3)	1.843(4)	3.905(6)	2.812(6)	2.769(6)
O(3)	91.4(2)	91.0(2)	165.5(2)	2.094(4)	2.560(8)	2.931(7)
O(3^{i})	91.4(2)	165.5(2)	91.0(2)	75.4(2)	2.094(4)	2.931(7)
O(4)	178.1(2)	87.2(2)	87.2(2)	87.2(2)	87.2(2)	2.158(6)
Nb(2)	O(2)	O(2^{ii})	O(5)	O(5^{ii})	O(6)	O(6^{ii})
O(2)	1.999(3)	2.855(7)	2.723(7)	3.886(7)	2.877(5)	2.764(5)
O(2^{ii})	91.2(2)	1.999(3)	3.886(7)	2.723(7)	2.764(5)	2.877(5)
O(5)	88.9(3)	177.0(2)	1.888(7)	2.70(1)	2.753(5)	2.786(6)
O(5^{ii})	177.0(2)	88.9(3)	91.2(4)	1.888(7)	2.786(6)	2.753(5)
O(6)	91.8(2)	87.2(2)	89.8(2)	91.2(2)	2.009(3)	4.017(7)
O(6^{ii})	87.2(2)	91.8(2)	91.2(2)	89.8(2)	178.5(2)	2.009(3)

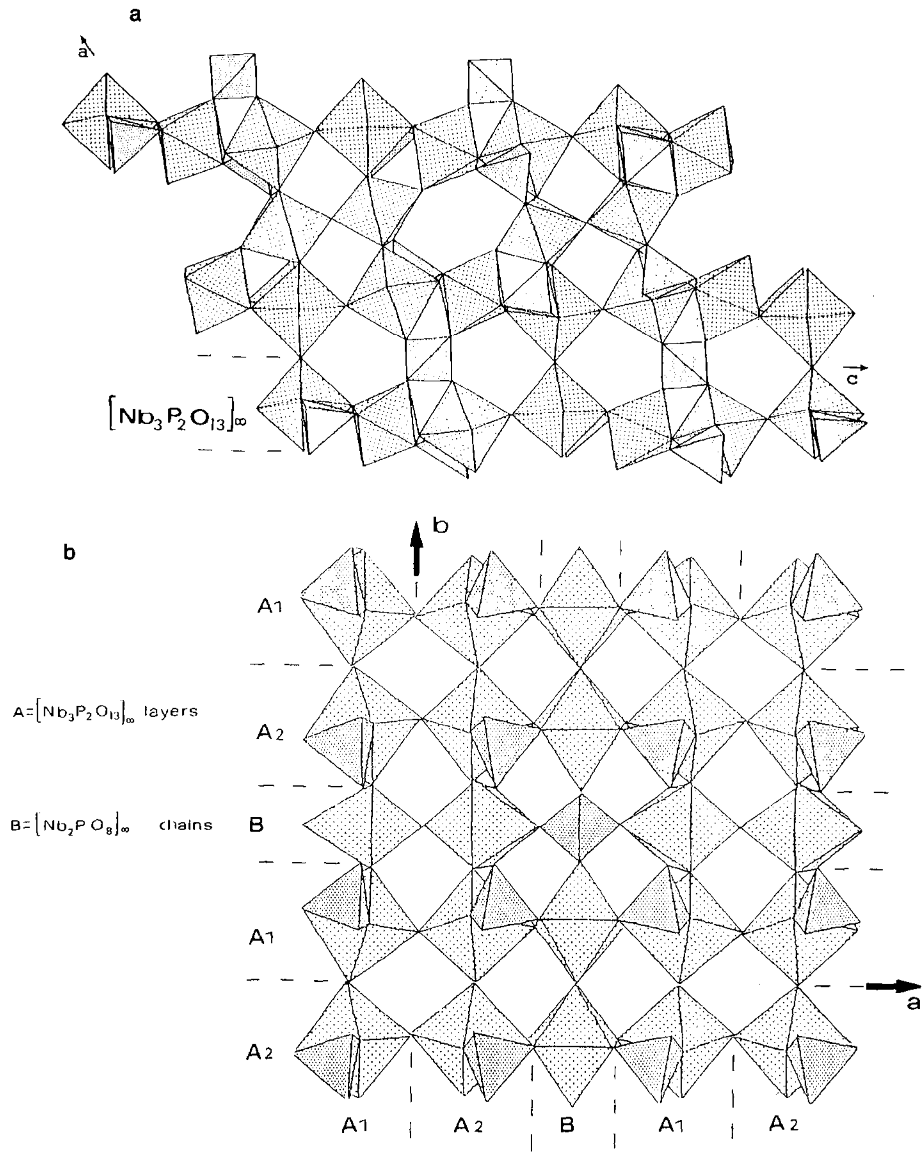

FIG. 2. Projection of the structures of (a) α-$K_4Nb_8P_5O_{34}$ along **b**; (b) $K_7Nb_{14}P_9O_{60}$ along **c**; (c) $K_2Na_{2-x}Nb_8P_5O_{34}$ along **c**.

is quite similar to that of their equivalent polyhedra in the phosphate bronze $K_7Nb_{14}P_9O_{60}$. The Nb (1) octahedron which forms the $[Nb_2PO_8]_\infty$ chains is more distorted than that of Nb (2). The P (1) and P (2) tetrahedra show the values of P–O bonds and O–P–O angles characteristic of almost regular monophosphate groups.

The distribution of sodium and potassium cations is remarkable. One indeed observes three sorts of sites which are occupied in an ordered way by the two alkali ions. A first

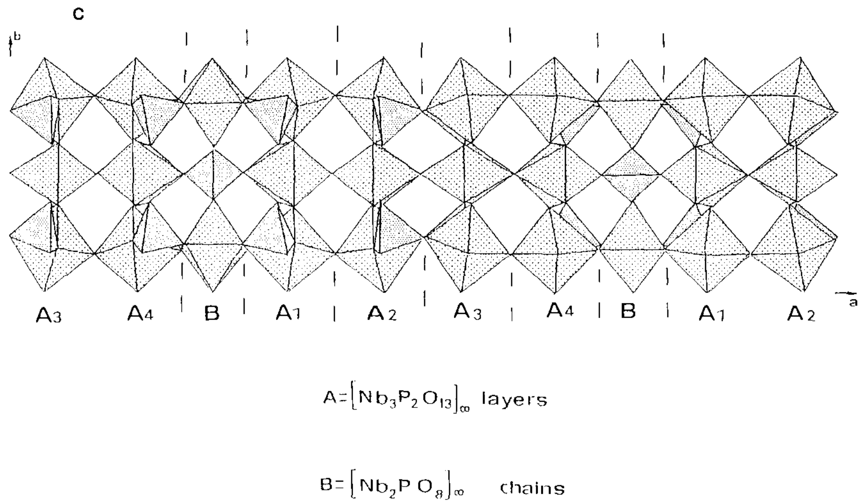

FIG. 2—*Continued*

of sites is only occupied by potassium; in this site, K$^+$ exhibits an eightfold coordination with distances of 2.95 Å (Table VI). The second type of site, located at the intersection of BM and HTB tunnels, is half filled by potassium and half by sodium ions; in this site alkali ions are characterized by a ninefold coordination with distances ranging from 2.85 to 3.10 Å (Table VI). The third site which exhibits cationic vacancies (27%) is only occupied by sodium (73%). In this site, sodium exhibits an elongated tetrahedral coordination with Na–O distances of 2.54 Å (Table VI). It is the size of this latter site which explains the difficulty in obtaining the pure potassium phase β-$K_4Nb_8P_5O_{34}$, owing to the induced constraints by the introduction of potassium on this latter site. Nevertheless, these results suggests that it

TABLE V

DISTANCES (Å) AND ANGLES (°) IN THE PO$_4$ TETRAHEDRA

P(1)	O(4)	O(4^{ii})	O(4^{iii})	O(4^{iv})
O(4)	1.563(6)	2.60(1)	2.46(1)	2.60(1)
O(4^{ii})	112.4(2)	1.563(6)	2.60(1)	2.46(1)
O(4^{iii})	103.7(5)	112.4(2)	1.563(6)	2.60(1)
O(4^{iv})	112.4(2)	103.7(5)	112.4(2)	1.563(6)
P(2)	O(3)	O(3^{iv})	O(6)	O(6^{v})
O(3)	1.525(4)	2.525(9)	2.515(5)	2.508(5)
O(3^{iv})	111.8(4)	1.525(4)	2.508(5)	2.515(5)
O(6)	109.9(2)	109.4(2)	1.548(3)	2.476(7)
O(6^{v})	109.4(2)	109.9(2)	106.3(2)	1.548(3)

TABLE VI

K–O DISTANCES Å

Na–O(4)	2.542(6) × 4
K–O(6)	2.951(3) × 8
K.Na–O(1^{vi})	2.85(1)
K.Na–O(2^{ii})	3.098(5)
K.Na–O(2^{iv})	2.098(5)
K.Na–O(2^{vii})	3.098(5)
K.Na–O(2^{viii})	3.098(5)
K.Na–O(3^{v})	3.064(5)
K.Na–O(3^{vi})	3.064(5)
K.Na–O(3^{ix})	3.064(5)
K.Na–O(3^{x})	3.064(5)

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

should be possible to stabilize the pure potassium phases by eventually creating defects upon the potassium site or by controlling the temperature of synthesis carefully.

The great similarity of these oxides with the oxygen tungsten bronzes—tunnel structure and mixed valency of niobium—explains the possibility of potassium and sodium nonstoichiometry observed for both compounds. The particular tetragonal symmetry of β-$K_2Na_{1.73}Nb_8P_5O_{34}$ is due to the fact that the number of directly connected $[Nb_3P_2O_{13}]_\infty$ layers parallel to (010) is equal to two, leading to the formation of $[Nb_2PO_8]_\infty$ chains at 90°, i.e., parallel to **a** and consequently to identical $[Nb_3P_2O_{13}]_\infty$ layers at 90°, i.e., parallel to (100).

This study confirms the great flexibility of the "Nb–P–O" framework which allows several forms to be synthetized. It suggests the possibility to synthesize upper n members ($n > 2$) by varying not only the experimental conditions of synthesis but by changing the molar ratio Na/K. The electron transport properties of these new bronzes appears most promising.

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