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A Niobium Phosphate "Bronze" Closely Related to the $Ba_3Nb_6Si_4O_{26}$ Structure: $Na_6Nb_8P_5O_{35}$

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A new niobium "bronze" $Na_6Nb_8P_5O_{35}$ has been isolated, the structure of which has been determined from a single crystal by X-ray diffraction. This oxide crystallizes in the space group $R32$, $a = 8.9185$ (5) Å and $c = 30.055$ (11) Å. The mixed framework built up from corner sharing NbO_6 octahedra and single PO_4 tetrahedra can be described by the stacking along **c** of tetrahedral $[P_3O_6]_\infty$ layers and $[Nb_8P_2O_{29}]_\infty$ layers. The latters are closely related to the $Ba_3Nb_6Si_4O_{26}$ structure since they present identical $[Nb_6O_{27}]$ units with identical orientations leading to a similar "a" parameter; those units are linked through single PO_4 tetrahedra and NbO_6 octahedra instead of Si_2O_7 groups in the siliconiobate. The similarity with the structure of $K_3Nb_8O_{21}$ is also discussed. Attention is drawn to the existence of wide circular galleries where Na^+ ions can move freely, suggesting possible ionic conductivity. The name of "bronze" for this phase is discussed taking into account the bond valence calculation which suggests a localization of the electrons. © 1991 Academic Press, Inc.

The synthesis of numerous phosphate tungsten bronzes with various structures has shown the possibility of creating cage and tunnel structures with a host lattice built up from octahedra and tetrahedra. These results suggest that the PO_4 tetrahedra should be able to accommodate many other octahedral frameworks involving transition elements. In this respect, niobium is a potential candidate for the formation of bronzes owing to its two oxidation states Nb(V) and Nb(IV). The ability of PO_4 tetrahedra to adapt to NbO_6 octahedra is now demonstrated. A series of niobium phosphate bronzes has indeed been recently isolated corresponding to the formulae: $KNb_3P_3O_{15}$ (*1*) and $[K_3Nb_6P_4O_{24}]_n$ $KNbP_2O_8$ with $n = 1,2$ and ∞ (*2–4*). Those oxides exhibit similarities with the oxygen tungsten bronzes discovered by Magneli and Kihlborgh (5–7). Thus, it appears that the other cage or tunnel structures should be generated by changing the nature of the interpolated cation. For this reason the system Na–Nb–P–O was investigated. Recently a sodium phosphate bronze $Na_4Nb_8P_6O_{35}$ (*8*) whose structure is closely related to that of the diphosphate tungsten bronzes was isolated. We report here on a new bronze, $Na_6Nb_8P_5O_{35}$, whose structure exhibits a similarity with $Ba_3Nb_6Si_4O_{26}$ (*9*).

Synthesis

Single crystals for X-ray structure determination were grown from a mixture of

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TABLE I

Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $Na_6Nb_8P_5O_{35}$

1. Crystal data	
Space group	$R32$
Cell dimensions (Å)	$a = 8.9185$ (5)
	$b = 8.9185$ (5)
	$c = 30.055$ (11)
Volume (Å^3)	$v = 2070$ (1)
Z	3
2. Intensity measurement	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - 2/3\ \theta$
Scan width (°)	$0.9 + 0.35 \tan\theta$
Slit aperture (mm)	$1. + \tan\theta$
Max θ (°)	45°
Standard reflections	3 measured every 3000 sec (no decay)
Reflections with $I > 3\sigma$	598
μ (mm^{-1})	3.578
3. Structure solution and refinement	
Parameters refined	55
Agreement factors	$R = 0.037$, $R_w = 0.038$
Weighting scheme	$W = f(\sin\theta/\lambda)$
Δ/σ_{max}	0.005
$\Delta\rho$	0.4 e/Å^{-3}

nominal composition "$Na_4Nb_8P_4O_{29}$." The synthesis of this latter compound was carried out in two steps: first, the mixture of adequate amounts of Na_2CO_3, H $(NH_4)_2$ 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 niobium was added and the finely ground mixture was sealed in an evacuated silica ampoule and heated up to 1273 K for 9 days. The approximate composition of these crystals was first estimated by microprobe analysis.

Structure Determination

A dark crystal with dimensions 0.060 × 0.048 × 0.024 mm was selected for the structure resolution. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 294 K with a least square refinement based upon 25 reflections with $18 < \theta < 22°$. The systematic absences for $-h + k + l \neq 3n$ are consistent with the space groups $R32$, $R3m$ and $R\bar{3}m$. The Patterson function allowed the noncentrosymmetric group $R32$ to be chosen.

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 niobium atoms were deduced from the Patterson function and the other atoms were located by successive Fourier series.

The final refinement with anisotropic thermal factors for Nb, P, and Na atoms and isotropic factors for the oxygen atoms led to $R = 0.037$ and $R_w = 0.038$ for the atomic coordinates given in Table II.

Description of the Structure and Discussion

The oxide $Na_6Nb_8P_5O_{35}$ represents the second sodium niobium phosphate bronze isolated up to now. The host lattice $[Nb_8P_5O_{35}]_\infty$ consists of two sorts of single PO_4 tetrahedra, P(1) and P(2), and two sorts

TABLE II

Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å^2)
Nb(1)	0.2341(1)	−0.0090(1)	0.06328(3)	0.49(1)
Nb(2)	0.000	0.000	0.23608(5)	0.42(2)
P(1)	0.333	0.667	0.0711(2)	0.57(5)
P(2)	0.4413(4)	0.000	0.500	0.38(7)
Na(1)	0.7862(9)	0.000	0.500	1.4(2)
Na(2)	0.583(2)	0.000	0.000	4.1(3)
O(1)	0.229(1)	0.000	0.000	0.9(1)*
O(2)	0.2526(9)	−0.0364(9)	0.1314(2)	0.7(1)*
O(3)	0.4933(9)	0.140(1)	0.0658(2)	0.8(1)*
O(4)	0.261(1)	−0.2218(9)	0.0514(2)	1.0(1)*
O(5)	0.187(1)	0.171(1)	0.0696(3)	0.7(1)*
O(6)	0.1996(9)	0.1422(9)	0.1897(3)	0.7(1)*
O(7)	0.333	0.667	0.1212(5)	1.0(2)*

Note. Atoms with asters were refined isotropically. Anisotropically refined atoms are given in the isotropic equivalent displacement parameter defined as $B = 4/3\ [\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab \cos\gamma + \beta_{13}ac \cos\beta + \beta_{23}\ bc \cos\alpha]$.

TABLE III

BOND LENGTHS IN THE NbO_6 AND PO_4 POLYHEDRA

Nb(1)–O(1)	1.905(1) Å
Nb(1)–O(2)	2.079(7) Å
Nb(1)–O(3)	2.010(8) Å
Nb(1)–O(4)	2.057(9) Å
Nb(1)–O(5)	1.859(9) Å
Nb(1)–O(5′)	1.999(9) Å
Nb(2)–O(3^{ii})	1.896(8) Å
Nb(2)–O(3^{iii})	1.896(8) Å
Nb(2)–O(3^{iv})	1.896(8) Å
Nb(2)–O(6)	2.111(9) Å
Nb(2)–O(6^{v})	2.111(9) Å
Nb(2)–O(6^{i})	2.111(9) Å
P(1)–O(4^{vi})	1.55(1) Å
P(1)–O(4^{v})	1.55(1) Å
P(1)–O(4^{vii})	1.55(1) Å
P(1)–O(7)	1.50(2) Å
P(2)–O(2^{viii})	1.539(9) Å
P(2)–O(2^{ix})	1.539(9) Å
P(2)–O(6^{viii})	1.536(9) Å
P(2)–O(6^{ix})	1.536(9) Å

of NbO_6 octahedra, Nb(1) and Nb(2), sharing their corners.

The P(1) tetrahedra share three of their corners with the Nb(1) octahedra and have one corner free; consequently they exhibit three normal P–O distances and a shorter one, 1.50 Å, as shown in Table III. The P(2) tetrahedra which are linked to two Nb(2) octahedra and two Nb(1) octahedra are characterized by normal P–O bonds (Table III).

The NbO_6 octahedra are strongly distorted. Each Nb(1) octahedron is linked to three other Nb(1) octahedra, to one Nb(2) octahedron, to one P(1) tetrahedron, and to one P(2) tetrahedron. It is worth pointing out that the Nb(1)–O–Nb(1) bonds are the shortest (1.859 to 1.999 Å), whereas the Nb(1)–O bonds linked to the PO_4 tetrahedra are much longer (2.057 to 2.079 Å) in agreement with the covalent character of phosphorus (Table III). The Nb(2) octahedron is linked to three Nb(1) octahedra and three P(2) tetrahedra; consequently it exhibits three short distances (1.896 Å) corresponding to the Nb(2)–O–Nb(1) bonds and three long distances (2.111 Å) corresponding to the Nb(2)–O–P(2) bonds.

The view of the structure along $\mathbf{a}_H$ (Fig. 1) shows that it consists of two sorts of layers parallel to (001). One indeed observes $[Nb_8P_2O_{29}]_\infty$ layers, the thickness of which determined by two octahedra sharing their corners along **c**, and $[P_3O_6]_\infty$ layers. The tetrahedral layers $[P_3O_6]_\infty$, which ensure the connection between two $[Nb_8P_2O_{29}]_\infty$ layers, are only formed of P(2) tetrahedra. The mixed layers $[Nb_8P_2O_{29}]_\infty$ are built up from octahedral units $[Nb_6O_{27}]$ which consist of 2

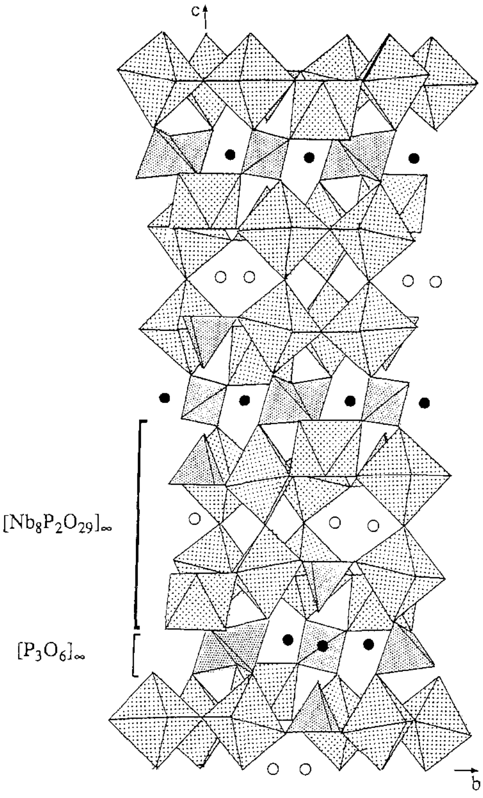

FIG. 1. A view of the structure along $\mathbf{a}_H$.

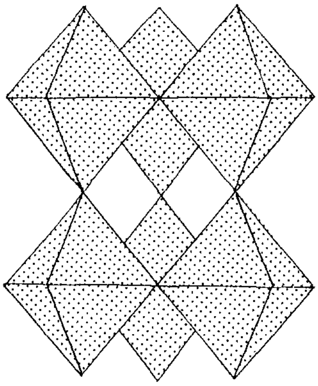

FIG. 2. The [Nb_6O_{27}] unit.

× 3 corner-sharing octahedra (Fig. 2). Laterally, in the (001) plane, the [Nb_6O_{27}] units are linked to each other through single P(1) tetrahedra and Nb(2) octahedra whose ternary axes are parallel to c_H. The projection of those layers onto the (001) plane of the hexagonal cell (Fig. 3a) shows a striking similarity with the structures of $Ba_3Nb_6Si_4O_{26}$ (*9, 10*) (Fig. 3b) and of $K_3Nb_8O_{21}$ (*11, 12*) (Fig. 3c). Both oxides $Ba_3Nb_6Si_4O_{26}$ and $Na_6Nb_8P_5O_{35}$ exhibit identical [Nb_6O_{27}] units with identical relative orientations leading to very similar *a* parameters. In

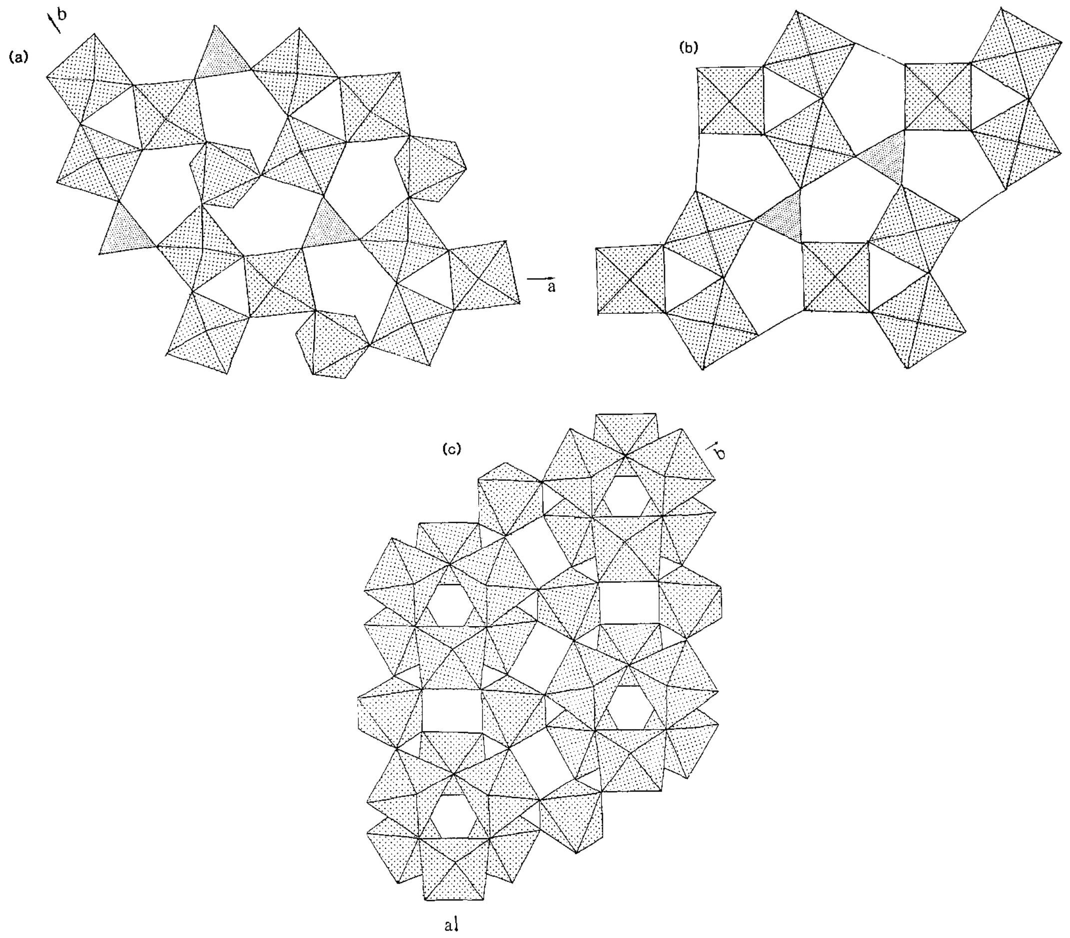

FIG. 3. (a) Projection along **c** of a [$Nb_8P_2O_{29}$]$_x$ layer. (b) Projection along **c** of $Ba_3Nb_6Si_4O_{26}$. (c) Projection along **c** of $K_3Nb_8O_{21}$.

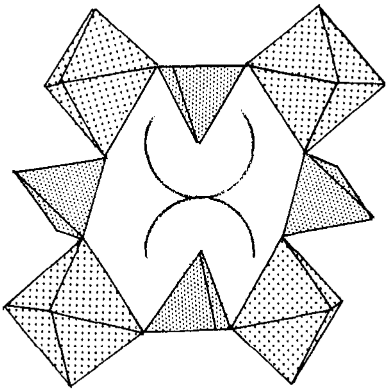

FIG. 4. Stacking of P(1)O_4 tetrahedra in Van der Waals contact.

$Ba_3Nb_6Si_4O_{26}$, the [Nb_6O_{27}] units are linked through disilicate groups whose ternary axes are parallel to **c** (Fig. 3b) whereas in $Na_6Nb_8P_5O_{35}$, half of the Si_2O_7 positions are replaced by single P(1) tetrahedra, the other half being replaced by the Nb(2) octahedra. This latter connection via Nb(2) octahedra is similar to that observed in $K_3Nb_8O_{21}$, which exhibits a two-dimensional accord with the two other structures in the (001) plane; however, in this latter structure the [Nb_6O_{27}] units are replaced by [Nb_6O_{24}] units built up of 2 × 3 edge-sharing octahedra so that their lateral connection in the (001) plane can be ensured by single NbO_6 octahedra only (Fig. 3c).

The original feature of the $Na_6Nb_8P_5O_{35}$ structure deals with the fact that the free corner of each P(1) tetrahedron is directed away from the $[Nb_8P_2O_{29}]_\infty$ layer so that two P(1) tetrahedra belonging to two adjacent layers are facing; consequently two successive $[Nb_8P_2O_{29}]_\infty$ layers are in van der Waals contact via the free apices of the P(1) tetrahedra (Fig. 4).

The $[Nb_8P_5O_{35}]_\infty$ framework delimits two sorts of cages where the Na^+ ions are located. The three narrow cages which surround the P(1)–O··O–P(1) bond (Fig. 4) are occupied by Na(1). The Na(1)–O distances observed for those sites, ranging from 2.35 to 2.53 Å (Table IV), show that this cation is strongly bonded to the surrounding oxygen atoms and especially to the free apices of the P(1) tetrahedra (2.35 Å) and cannot move through the structure in agreement with the low value of their B factor ($B \approx 1.4$ Å^2). In contrast, the Na(2) cations are located in very spacious cages as shown from the Na–O distances greater than 2.60 Å (Table IV). They are indeed located at the intersection of narrow tunnels waving along **c** which are limited by five-sided windows (Fig. 3a), and large circular "galleries" running all around each [Nb_6O_{27}] unit in the (001) plane (Fig. 3a). Such galleries communicate one with the other through very large six-sided windows built up from six NbO_6 octahedra and one PO_4 tetrahedron (Fig. 5). The useful diameter of those windows being much greater than that of Na^+ should allow free

TABLE IV

Na–O DISTANCES LESS THAN 3.20 Å

Na(1)–O(2^{x})	2.53(1) Å
Na(1)–O(2^{xi})	2.53(1) Å
Na(1)–O(6^{viii})	2.50(1) Å
Na(1)–O(6^{ix})	2.50(1) Å
Na(1)–O(7^{viii})	2.35(1) Å
Na(1)–O(7^{ix})	2.35(1) Å
Na(2)–O(4^{xii})	2.60(1) Å
Na(2)–O(4^{xiii})	2.60(1) Å
Na(2)–O(3)	2.66(1) Å
Na(2)–O(3^{xiv})	2.66(1) Å
Na(2)–O(4)	2.98(1) Å
Na(2)–O(4^{xiv})	2.98(1) Å
Na(2)–O(5^{xv})	2.98(1) Å
Na(2)–O(5^{xvi})	2.98(1) Å
Na(2)–O(1)	3.16(2) Å

Note. The symmetry code is (i) $y - x, -x, z$; (ii) $y - \frac{1}{3}, x - \frac{2}{3}, \frac{1}{3} - z$; (iii) $\frac{2}{3} - x, \frac{1}{3} + y - x, \frac{1}{3} - z$; (iv) $x - y - \frac{1}{3}, \frac{1}{3} - y, \frac{1}{3} - z$; (v) $-y, x - y, z$; (vi) $x, 1 + y, z$; (vii) $1 + y - x, 1 - x, z$; (viii) $\frac{2}{3} + y - x, \frac{1}{3} - x; \frac{1}{3} + y$; (ix) $\frac{1}{3} + y, x - \frac{1}{3}, \frac{2}{3} - z$; (x) $\frac{2}{3} + y, \frac{1}{3} + y; \frac{1}{3} + z$; (xi) $\frac{1}{3} + x - y, \frac{1}{3} - y, \frac{2}{3} - z$; (xii) $1 + y - x, -x, z$; (xiii) $y, 1 + x, -z$; (xiv) $x - y, -y, -z$; (xv) $1 - y, x - y, z$; (xvi) $1 - x, y - x, -z$.

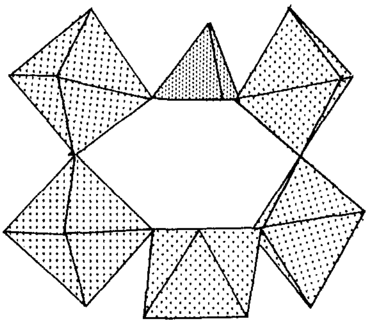

FIG. 5. The six sided window connecting the circular "galleries."

movement of the latter within the $[Nb_8P_2O_{29}]_\infty$ layers. The high *b* factor observed for this cation ($B \approx 4.1$ Å^2) confirms that it is weakly bonded to the surrounding oxygens. These observations suggest that this oxide could be a potential material for ionic conductivity.

The mixed valency Nb(V)–Nb(IV) observed for this phase suggests a possible delocalization of the *d* electrons of niobium in the $[Nb_8P_2O_{29}]_\infty$ layers, which would then justify the name bronze. Nevertheless, the calculation of the valency of niobium using the Brown and Altermatt tables (*13*) shows that the Nb(1) sites corresponding to the $[Nb_6O_{27}]$ units are only occupied by the Nb(V), whereas the Nb(2) sites which correspond to the octahedra with a threefold rotation axis parallel to **c** exhibit the mixed valence Nb(V)/Nb(IV). Consequently, it seems that a tendancy for the localization of electrons should be preferred so that this material would only be a poor *d* electronic conductor and not really a bronze.

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