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$BaNb_7P_6O_{33}$: A Niobium Monophosphate with a Tunnel Structure Related to HTBs and ITBs

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Single crystals of a new niobium monophosphate $BaNb_7P_6O_{33}$ have been isolated and their structure determined by X-ray diffraction. This oxide crystallizes in the space group $P\bar{3}1c$, $a = 9.992$ Å, $c = 14.635$ Å. The structure consists of an original framework built up from isolated Nb_6O_{27} octahedral units and isolated NbO_6 octahedra sharing their corners with PO_4 tetrahedra. This host lattice delimits six-sided tunnels derived from the HTBs, where the barium ions are located. Structural relationships between this structure and those of HTBs, ITBs of the phosphate bronze $Ca_{0.5}Cs_2Nb_6P_3O_{24}$, and of the fluoride $CsBaCr_3FeF_{12}$ are discussed.

Introduction

The recent investigations of the system K–Nb–P–O have shown its great ability to form tunnel structures closely related to the pure octahedral tungsten bronzes. Besides the phosphate niobium bronze $KNb_3P_3O_{15}$ (*1*) closely related to the tetragonal tungsten bronze described by Magneli (*2*), several other phosphate bronzes closely related to the hexagonal tungsten bronze (HTB) (*3*) and to the "intergrowth" tungsten bronzes called ITBs (*4, 5*) were isolated. It is indeed the case of the bronzes $(K_3Nb_6P_4O_{26})_n \cdot KNb_2PO_8$ which form a large structural family as shown from the existence of the oxides $A_{4-x}Nb_6P_4O_{26}$ (A = K, Rb, Ba) corresponding to $n = \infty$ (*6, 7*), $K_4Nb_8P_5O_{34}$, the first member of the series (*8*), and $K_7Nb_{14+x}P_{9-x}O_{60}$ corresponding to $n = 2$ (*9*). Barium, because its size is close to that of potassium, is also a potential candidate for the generation of tunnel structures which can be either very similar to the potassium oxides as shown for $BaNb_6P_4O_{26}$ which is isotypic of $K_3Nb_6P_4O_{26}$ (*7*), or original structures like $Ba_{0.15}WO_3$ (*10*), which differs from the potassium tungsten bronzes. For this reason the study of the system Ba–Nb–P–O with reduced Nb was undertaken. The present paper deals with a new niobium phosphate, $BaNb_7P_6O_{33}$, which exhibits an original structure closely related to that of $Ca_{0.5}Cs_2Nb_6P_3O_{24}$ (*11*).

Synthesis

During the investigation of the Ba–Nb–P–O system, black single crystals could be isolated from samples corresponding to three nominal compositions: $Ba_2Nb_8P_6O_{34}$, $BaNb_4P_6O_{25}$, and $BaNb_{14}P_{11}O_{60}$. This crystal growth was performed in two steps. First an adequate mixture of $BaCO_3$,

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$(NH_4)_2$ H PO_4, and Nb_2O_5 was heated to 673 K in air in order to eliminate CO_2, H_2O, and NH_3. In the second step, the resulting finely ground product was mixed with an appropriate amount of niobium and sealed in an evacuated silica ampoule. This sample was then heated to 1273 K for a week and cooled slowly to room temperature.

All the crystals have the same cell dimensions and their composition "$BaNb_7P_6O_{33}$" deduced from the structural determination was confirmed by microprobe analysis.

Subsequent attempts to prepare this phase in the form of pure ceramics were unsuccessful; it was always obtained as a mixture with other compounds.

Structure determination

A dark crystal with dimensions 0.084 × 0.084 × 0.096 mm 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 $18 < \theta < 22°$.

TABLE I

SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $BaNb_7P_6O_{33}$

1. Crystal data	
Space group	$P\bar{3}1c$
Cell dimensions	$a = 9.992(1)$ Å $c = 14.635(3)$ Å
Volume	$v = 1265.4$ Å^3
Z	2
2. Intensity measurement	
λ(Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega - \frac{2}{3}\theta$
Scan width (°)	$1.25 + 0.35 \tan\theta$
Slit aperture (mm)	$1. + \tan\theta$
Max θ(°)	45
Measured reflections	6041
Standard reflections	3 measured every 3000 s (no decay)
Reflections with $I > 3\sigma$	2228
μ (mm^{-1})	4.966
3. Structure solution and refinement	
Parameters refined	73
Agreement factors	$R = 0.058$, $R_w = 0.067$
Weighting scheme	$W = f(\sin\theta/\lambda)$
Δ/σ_{max}	0.005

TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B(Å^2)
Nb(1)	0.42773(7)	0.24017(7)	0.12252(4)	0.589(8)
Nb(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.54(2)
P	0.1507(2)	0.3518(2)	0.1142(1)	0.59(3)
Ba	0.	0.	$\frac{1}{4}$	1.03(1)
O(1)	0.2328(5)	0.0126(6)	0.1368(4)	0.83(9)
O(2)	0.2616(6)	0.2952(6)	0.1461(4)	0.93(9)
O(3)	0.5615(6)	0.1510(6)	0.1044(4)	0.86(9)
O(4)	0.3816(7)	0.1666(6)	0.5118(4)	1.1(1)
O(5)	0.3115(6)	0.4978(6)	0.3328(4)	1.1(1)
O(6)	0.4498(9)	0.2249	$\frac{1}{4}$	0.8(1)

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

The symmetry of the diffraction pattern and the systematic absences $l = 2n + 1$ for $hh\bar{2h}l$ are consistent with the space groups $P\bar{3}1c$ and $P31c$. The structure has been solved and refined in the centrosymmetrical space group $P\bar{3}1c$.

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 and polarization effects; no absorption corrections were performed.

The atoms were located by the heavy atom method. The refinement of the atomic coordinates and the anisotropic thermal factors of all the atoms led to $R = 0.058$ and $R_w = 0.067$ for the results given in Table II.[1]

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

TABLE III

$BaNb_7P_6O_{33}$: DISTANCES (Å) AND ANGLES (°)

Nb(1)	O(1)	O(2)	O(3)	O(3$^{\mathrm{i}}$)	O(4$^{\mathrm{ii}}$)	O(6)
O(1)	2.140(6)	2.696(8)	2.895(8)	3.984(8)	2.833(8)	2.710(7)
O(2)	80.7(2)	2.023(6)	3.968(8)	2.910(8)	2.894(8)	2.769(9)
O(3)	89.7(2)	170.3(2)	1.960(6)	2.743(9)	2.772(8)	2.675(7)
O(3$^{\mathrm{i}}$)	176.5(2)	97.5(2)	92.2(3)	1.846(6)	2.749(8)	2.839(6)
O(4$^{\mathrm{ii}}$)	86.1(2)	91.9(2)	88.7(2)	91.0(3)	2.006(6)	3.884(8)
O(6)	84.2(2)	89.9(3)	87.9(3)	98.8(2)	169.7(2)	1.894(6)

Nb(2)	O(5)	O(5$^{\mathrm{iii}}$)	O(5$^{\mathrm{iv}}$)	O(5$^{\mathrm{v}}$)	O(5$^{\mathrm{vi}}$)	O(5$^{\mathrm{vii}}$)
O(5)	1.999(6)	2.75(1)	2.75(1)	3.08(1)	3.98(1)	2.73(1)
O(5$^{\mathrm{iii}}$)	87.1(3)	1.999(6)	2.75(1)	2.73(1)	3.08(1)	3.98(1)
O(5$^{\mathrm{iv}}$)	87.1(3)	87.1(3)	1.999(6)	3.98(1)	2.73(1)	3.08(1)
O(5$^{\mathrm{v}}$)	100.9(3)	86.0(4)	169.1(3)	1.999(6)	2.75(1)	2.75(1)
O(5$^{\mathrm{vi}}$)	169.1(3)	100.9(3)	86.0(4)	87.1(3)	1.999(6)	2.75(1)
O(5$^{\mathrm{vii}}$)	86.0(4)	169.1(3)	100.9(3)	87.1(3)	87.1(3)	1.999(6)

P	O(1$^{\mathrm{viii}}$)	O(2)	O(4$^{\mathrm{ix}}$)	O(5$^{\mathrm{vii}}$)
O(1$^{\mathrm{viii}}$)	1.535(6)	2.456(8)	2.503(8)	2.515(8)
O(2)	105.7(3)	1.546(6)	2.515(8)	2.506(8)
O(4$^{\mathrm{ix}}$)	110.0(3)	110.2(3)	1.521(6)	2.517(8)
O(5$^{\mathrm{vii}}$)	110.3(3)	109.2(3)	110.2(4)	1.529(6)

Note. Ba–O(1) = 2.807(6) × 6; Ba–O(2) = 3.184(6) × 6. i: $1 - x + y, 1 - x, z$; ii: $x, x - y, \frac{1}{2} - z$; iii: $1 - y, 1 + x - y, z$; iv: $-x + y, 1 - x, z$; v: $1 - y, 1 - x, \frac{1}{2} - z$; vi: $x, 1 + x - y, \frac{1}{2} - z$; vii: $-x + y, y, \frac{1}{2} - z$; viii: $-y, x - y, z$; ix: $y, x, z - \frac{1}{2}$; x: $-x + y, -x, z$; xi: $-y, -x, \frac{1}{2} - z$.

Description of the Structure and Discussion

From the projection of the structure of this oxide along **c** (Fig. 1), it can be seen that the $[Nb_7P_6O_{33}]_\infty$ framework forms six-sided tunnels running along **c**, and that in the mixed framework all the PO_4 tetrahedra and NbO_6 octahedra share their corners. The PO_4 tetrahedra are isolated, i.e., each PO_4 tetrahedron is linked to four NbO_6 octahedra and consequently is characterized by classical P–O distances ranging from 1.52 to 1.54 Å and with O–P–O angles ranging from 106 to 110° (Table III). One can distinguish two sorts of NbO_6 octahedra labeled Nb(1) and Nb(2). Each Nb(1) octahedron is linked to three PO_4 tetrahedra and three other Nb(1) octahedra, and consequently exhibits two sets of Nb(1)–O distances; the three shortest ones (1.85–1.96 Å) correspond to the Nb(1)–O–Nb(1) bonds, whereas the three longest ones (2.00–2.14 Å) correspond to the Nb(1)–O–P bonds (Table III). The Nb(2) octahedron, which has its ternary axis parallel to **c** shares its six corners with PO_4 tetrahedra and consequently exhibits six equal Nb(2)–O distances. Like for Nb(1), the Nb(2) octahedron is distorted, as shown from the O–Nb–O angles ranging from 86 to 101° instead of 90° (Table III).

An interesting characteristic of this structure rests on the presence of Nb_6O_{27} structural units (Fig. 2) built up from six corner-sharing NbO_6 octahedra, as shown from the view of the structure along [210] (Fig. 3). In this respect, the $[Nb_7P_6O_{33}]$ framework is related to those of the TTBs (*2*), HTBs (*3*),

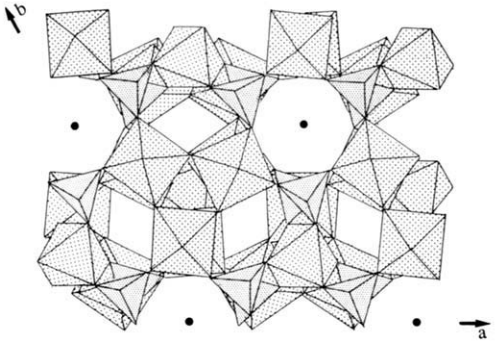


FIG. 1. Projection of the $BaNb_7P_6O_{33}$ structure along **c** showing the tunnels delimited by $[Nb_7Pb_6O_{45}]_\infty$ columns sharing their free corners. The tunnels are filled by barium atoms represented here by a large dot.

and ITBs (*4, 5*) which can be described from the same units. Similar units have also been observed for the phosphate bronzes $Ca_{0.5}Cs_2Nb_6P_3O_{24}$ (*11*) and $Na_6Nb_8P_5O_{35}$ (*12*). Nevertheless, in all the pure octahedral structures, as well as in the mixed frameworks "P–M–O" which have been isolated up to now, the M_6O_{27} units are never isolated, i.e., they always share corners of their octahedra with other octahedra. Thus, the present oxide exhibits a particular behavior, since the Nb_6O_{27} units are absolutely isolated, i.e., they share eighteen corners of their NbO_6 octahedra only with PO_4 tetrahedra.

Consideration of these Nb_6O_{27} units leads us to describe the $[Nb_7P_6O_{33}]_\infty$ host lattice in two different manners. The first description deals with the consideration of double layers of polyhedra, $[Nb_7P_6O_{45}]_\infty$ parallel to (001) (Fig. 4), in which the Nb_6O_{27} units are connected to each other through PO_4 tetrahedra, themselves linked through the Nb(2) octahedra. In these double layers, one recognizes six-sided rings which form tunnels running along **c**; note their similarity with the HTBs rings, from which they can be deduced by replacing one NbO_6 octahedron out of two by one PO_4 tetrahedron. The Nb(2) octahedra are located within these double layers, i.e., they share their six vertices with PO_4 tetrahedra belonging only to the layer. The three-dimensional $[Nb_7P_6O_{33}]_\infty$ framework is then realized by the stacking of identical double layers along **c** (Fig. 3) in such a way that the PO_4 tetrahedra of one layer share their vertices with the NbO_6 octahedra of the adjacent layer and vice versa. In the second description, one can consider the stacking along **c** of Nb_6O_{27} units, with PO_4 tetrahedra and single Nb(2) octahedra successively forming $[Nb_7P_6P_{45}]_\infty$

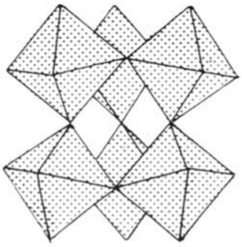


FIG. 2. The Nb_6O_{27} structural unit where one NbO_6 octahedron shares three of its corners with three other NbO_6 octahedra of the unit.

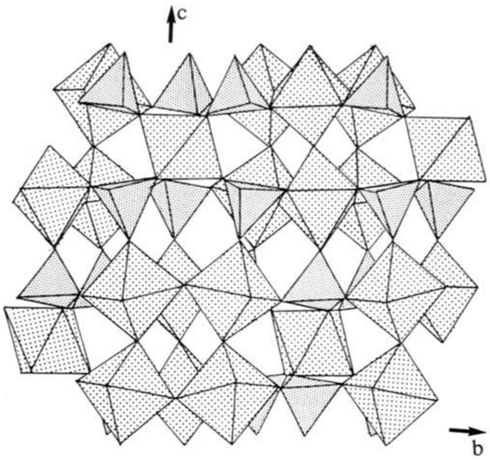


FIG. 3. Projection of the $BaNb_7P_6O_{33}$ structure along [210] showing the stacking of the double layers $[Nb_7P_6O_{45}]_\infty$ parallel to (001) plane. One octahedron of one layer shares its corner with a tetrahedron of the adjacent layer and vice-versa.

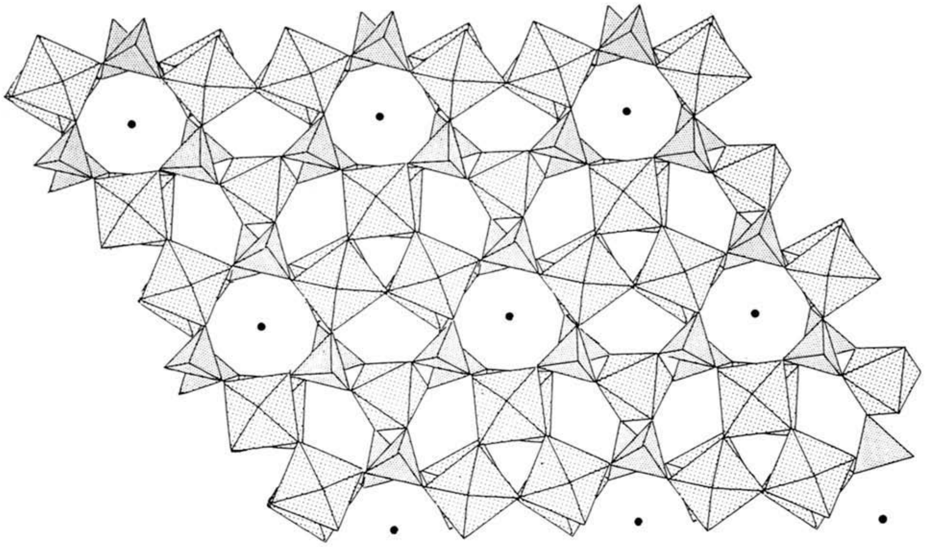
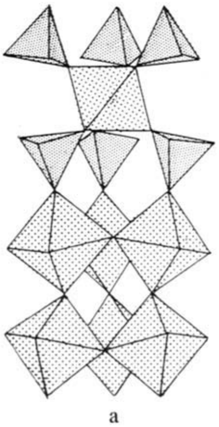


FIG. 4. Double layer $[Nb_7P_6O_{45}]_\infty$ parallel to (001) projected along c. The groups of the three corner-sharing octahedra represent the Nb_6O_{27} units (the three other octahedra located below are almost wholly hidden). The PO_4 tetrahedra have their apical corner directed outside of the layer, the three upper pointing up and the three below pointing down.

columns running along **c** (Fig. 5a); laterally in the (001) plane these columns share all their free vertices (Fig. 1) leading to the host lattice $[Nb_7P_6O_{33}]_\infty$. This description shows the similarity of this structure to that of $Ca_{0.5}Cs_2Nb_6P_3O_{24}$, which also exhibits six-sided tunnels but built up from rings of four NbO_6 octahedra and two tetrahedra Fig. 6). The main difference between $BaNb_7P_6O_{33}$ and $Ca_{0.5}Cs_2Nb_6P_3O_{24}$ comes from the nature of the columns running along **c**. The latter host lattice can indeed be described by $[Nb_{12}P_6O_{66}]_\infty$ columns running along **c** (Fig. 5b), which are deduced from the $[Nb_7P_6O_{45}]_\infty$ columns by replacing the Nb(2) single octahedra by Nb_6O_{27} units.



a

FIG. 5a. The $[Nb_7P_6O_{45}]_\infty$ column in $BaNb_7P_6O_{33}$.

The relative positions of the Nb_6O_{27} units are remarkable. Consideration of the position of these groups in two successive $[Nb_7P_6O_{45}]_\infty$ layers (Figs. 3 and 4) shows that the elimination of PO_4 tetrahedra and of Nb(2) octahedra, followed by a translation of one layer out of two of one height of an Nb_6O_{27} unit along **c**, would lead to the hypothetical structure "BaM_6O_{18}" (Fig. 7) closely related to that of the ITBs and especially to $Sb_2Mo_{10}O_{31}$ (*13*); the topology of

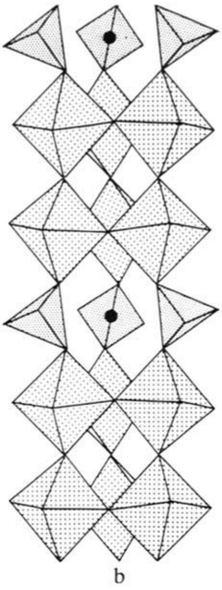


FIG. 5b. The $[Nb_{12}P_6O_{66}]_\infty$ column in $Ca_{0.5}Cs_2Nb_6P_3O_{24}$.

oxygen in the basal planes of NbO_6 octahedra corresponds to a rare case of a plane net described by O'Keeffe and Hyde (*14*). In this respect this structure is closely related to that of the fluoride $CsBaCr_3FeF_{12}$ (*15*), whose CrF_4 layers are the unique example of pure octahedra framework exhibiting this geometry.

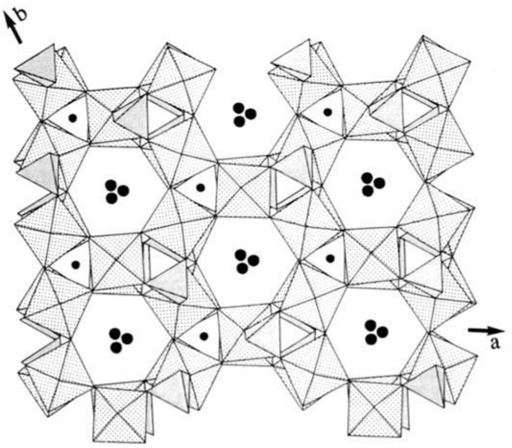


FIG. 6. Projection of the $Ca_{0.5}Cs_2Nb_6P_3O_{24}$ structure along **c** showing the six-sided tunnels.

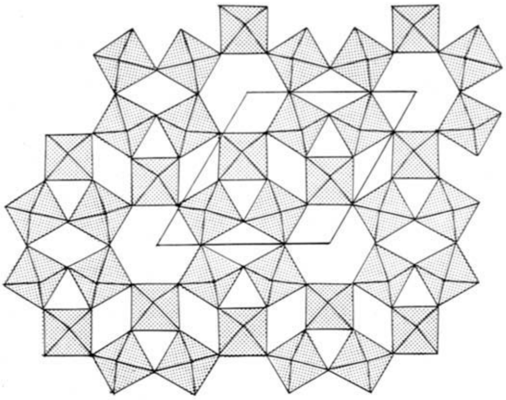


FIG. 7. Hypothetical structure "BaM_6O_{18}" deduced from $BaNb_7P_6O_{33}$ by elimination of the PO_4 tetrahedra and the $Nb(2)O_6$ octahedra followed by a translation of one layer out of two of one Nb_6O_{27} unit height.

This study shows, like for $BaNb_6P_4O_{26}$ (*7*), that although not so easily as potassium barium can stabilize structures with hexagonal tunnels. In the six-sided tunnels, barium exhivits a 12-fold coordination with six shorter Ba–O bonds (2.807 Å) and six longer ones (3.184 Å) (Table III).

This niobium phosphate exhibits, like niobium phosphate bronzes, the mixed valency Nb (IV)/Nb(V). Nevertheless it cannot be considered as a bronze, since differently from other niobium phosphates it does not exhibit infinite chains of corner-sharing NbO_6 octahedra, but "isolated" Nb_6O_{17} units and isolated NbO_6 octahedra. The Nb–O bond lengths (Table III) suggest a localization of Nb(V) in the Nb_6O_{27} units and Nb(IV) in the Nb octahedra in agreement with the charge balance leading to the formula $BaNb^{V}_{6}Nb^{IV}P_6O_{33}$.

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