JOURNAL OF SOLID STATE CHEMISTRY **80**, 12–16 (1989)

A Niobium Phosphate Bronze with a Tunnel Structure: $KNb_3P_3O_{15}$

A. LECLAIRE, M. M. BOREL, A. GRANDIN, AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT, ISMRa, Campus 2, Boulevard du Maréchal Juin, 14032 Caen Cedex, France

Received October 18, 1988; in revised form January 11, 1989

A new niobium monophosphate $KNb_3P_3O_{15}$ has been isolated. Its structure was solved from a single-crystal X-ray study in the space group *Pnnm* with the cell parameters: $a = 13.3085(9)$, $b = 14.7382(10)$, $c = 6.4615(2)$ Å, and $Z = 4$. The refinement by full-matrix least-squares calculations led to $R = 0.029$ with 3184 independent reflections. The structure is built up from corner-sharing NbO_6 octahedra and PO_4 tetrahedra which delimit five-sided tunnels containing the K ions and empty square and triangular tunnels. These tunnels are like those observed in the tetragonal tungsten bronzes. © 1989 Academic Press, Inc.

Introduction

The great flexibility of the perovskite structure (*1*) has allowed mixed frameworks built up from octahedral slices connected through monophosphate or diphosphate groups to be synthesized. It is indeed the case of the phosphate tungsten bronzes (*2*) which form a very large family of anisotropic metal-like phases owing to the delocalization of the electrons resulting from the final mixed-valence W(VI)/W(V) over the tungsten–oxygen framework. Niobium, because of its ability to form octahedral frameworks similar to those observed for tungsten oxides, such as perovskite or tetragonal tungsten bronze-type oxides, is a potential candidate for the synthesis of mixed-host lattices formed of NbO_6 octahedra and PO_4 tetrahedra. Moreover, the possibility for niobium to present two oxidation states, Nb(IV) and Nb(V), suggests that the formation of bronzes with an anisotropic character should be considered. For these reasons, the investigation of the system K–Nb–P–O was undertaken. The present study reports the structure of a new phosphate niobium bronze $KNb_3P_3O_{15}$, whose structure is closely related to that of the tetragonal tungsten bronze (TTB) structure described by Magneli (*3*).

Synthesis

The preparation was performed in two steps. $(NH_4)_2HPO_4$, Nb_2O_5, and K_2CO_3 were mixed in an agate mortar in a mole ratio to obtain the stoichiometric $KNb_{2.802}P_3O_{15}$ and heated at 600 K to decompose the potassium carbonate and the ammonium phosphate. The resulting mixture was then added to the required amount of niobium and placed in an evacuated silica ampoule. This mixture heated for several days at 1373 K allowed the $KNb_3P_3O_{15}$ to be isolated. Black crystals were obtained. The composition was confirmed by microprobe analysis.

0022-4596/89 $3.00

Determination and Refinement of the Structure

A black crystal of $KNb_3P_3O_{15}$ with dimensions 0.168 × 0.096 × 0.072 mm was selected for the structure determination. The Laue patterns showed orthorhombic symmetry (*mmm*). The systematic absences $h + l = 2n$ in $h0l$ and $k + l = 2n$ in $0kl$ are consistent with the space groups *Pnn*2 or *Pnnm*. The structure was solved and refined in the centrosymmetrical space group *Pnnm*. The cell parameters, initially measured on Weissenberg films and later refined by diffractometric techniques at 294 K, with a least-squares refinement based on 25 reflections are $a = 13.3085(9)$, $b = 14.7382(10)$, $c = 6.4615(2)$ Å, with $Z = 4$ formula units of $KNb_3P_3O_{15}$. The data were collected on a CAD-4 Enraf–Nonius diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The intensities were measured out to $\theta = 45°$ with a $\omega - \theta$ scan of $(1. + 0.35 \tan\theta)°$ and a counterslit aperture of $(1. + \tan\theta)$mm, all determined after a study of some reflections in the $\omega - \theta$ plane. The background intensities were measured on both sides of each reflection. A periodic measurement of three reflections verified the stability of the apparatus. The 3184 reflections with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effect; no absorption corrections were performed.

Atomic coordinates of the niobium atoms were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.029$, $R_w = 0.034$, and to the atomic parameters of Table I.[1]

TABLE I

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B (Å^2)
Nb(1)	0.43757(2)	0.38721(2)	0.000	0.424(3)
Nb(2)	0.69285(2)	0.27711(2)	0.000	0.408(3)
Nb(3)	0.35872(2)	−0.02661(2)	0.000	0.393(3)
K	0.0086(3)	0.3233(3)	0.089(1)	9.6(1)
P(1)	0.27237(7)	0.20218(6)	0.000	0.44(1)
P(2)	0.37506(7)	0.37936(6)	0.500	0.43(1)
P(3)	0.20613(7)	0.50253(6)	0.000	0.41(1)
O(1)	0.500	0.500	0.000	1.08(6)
O(2)	0.2999(3)	0.4445(3)	0.000	1.43(5)
O(3)	0.3624(3)	0.2660(2)	0.000	1.25(5)
O(4)	0.5659(2)	0.3256(2)	0.000	1.01(4)
O(5)	0.4418(2)	0.3866(2)	0.3084(3)	0.83(2)
O(6)	0.7709(3)	0.3966(2)	0.000	1.40(5)
O(7)	0.6348(2)	0.1539(2)	0.000	0.76(4)
O(8)	0.8316(2)	0.2169(2)	0.000	0.90(4)
O(9)	0.7046(2)	0.2799(2)	0.3106(3)	0.96(3)
O(10)	0.2958(2)	0.4533(2)	0.500	0.97(4)
O(11)	0.3129(3)	0.1058(2)	0.000	1.08(4)
O(12)	0.1404(2)	0.4788(2)	0.1878(3)	0.97(3)
O(13)	0.500	0.000	0.000	0.80(5)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(\frac{4}{3}) * [a^2 * \beta(1,1) + b^2 * \beta(2,2) + c^2 * \beta(3,3) + ab(\cos\gamma) * \beta(1,2) + ac(\cos\beta) * \beta(1,3) + bc(\cos\alpha) * \beta(2,3)]$.

Description of the Structure and Discussion

The host lattice of this compound, which consists of NbO_6 octahedra and PO_4 tetrahedra sharing their corners, delimits pentagonal tunnels where the potassium ions are located (Fig. 1). All niobium and phosphorus atoms lie in (001) planes at $z = 0$ and 0.5. In those planes, the NbO_6 octahedra share their corners forming double zigzag chains running along **b**; these octahedral ribbons are connected to PO_4 tetrahedra forming rows parallel to **b**. Each PO_4 tetrahedron shares its corners with four NbO_6 octahedra, the Nb atoms of which form a Nb_4 tetrahedron (Fig. 2), whereas each NbO_6 octahedron is linked to four PO_4 tetrahedra and to two other NbO_6 octahedra.

---

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

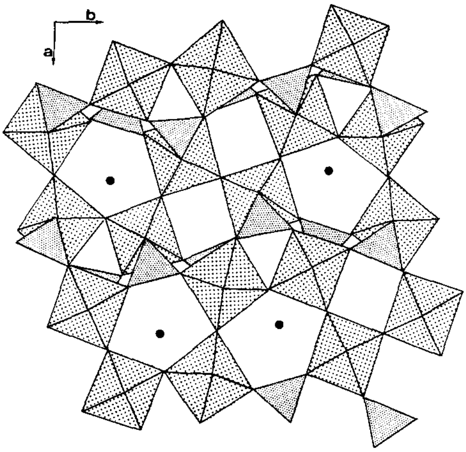

FIG. 1. Structure of $KNb_3P_3O_{15}$ projected along *c* onto the *ab* plane.

TABLE II

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

P(1)	O(3)	O(9^{v})	O(9^{vi})	O(11)
O(3)	1.523(3)	2.523(3)	2.523(3)	2.452(4)
O(9^{v})	110.7(1)	1.544(2)	2.448(3)	2.534(3)
O(9^{vi})	110.7(1)	104.9(1)	1.544(2)	2.534(3)
O(11)	107.3(2)	111.6(1)	111.6(1)	1.520(2)
P(2)	O(5)	O(5^{vii})	O(8^{v})	O(10)
O(5)	1.527(2)	2.476(3)	2.451(3)	2.505(3)
O(5^{vii})	108.3(1)	1.527(2)	2.451(3)	2.505(3)
O(8^{v})	106.5(1)	106.5(1)	1.532(2)	2.554(3)
O(10)	110.7(1)	110.7(1)	113.8(1)	1.517(2)
P(3)	O(2)	O(6^{viii})	O(12)	O(12^{i})
O(2)	1.513(3)	2.524(4)	2.496(3)	2.496(3)
O(6^{viii})	112.8(2)	1.517(3)	2.498(3)	2.498(3)
O(12)	109.9(1)	109.8(1)	1.536(2)	2.427(3)
O(12^{i})	109.9(1)	109.8(1)	104.4(1)	1.536(2)

Note. For symmetry code, see note to Table IV.

The PO_4 tetrahedra are characterized by a classical geometry with four P–O distances almost equal and ranging from 1.52 to 1.54 Å, and angles O–P–O ranging from 104 to 114° (Table II). The three independent niobium atoms exhibit rather similar NbO_6 octahedra (Table III) in agreement with the delocalization of the electrons all over the niobium–oxygen ribbons. Each octahedron presents two short Nb–O distances (smaller than 1.98 Å) which correspond to the oxygen atoms shared by two octahedra, whereas the four other Nb–O distances which correspond to oxygen atoms shared by a PO_4 and a NbO_6 octahedron are greater than 1.99 Å.

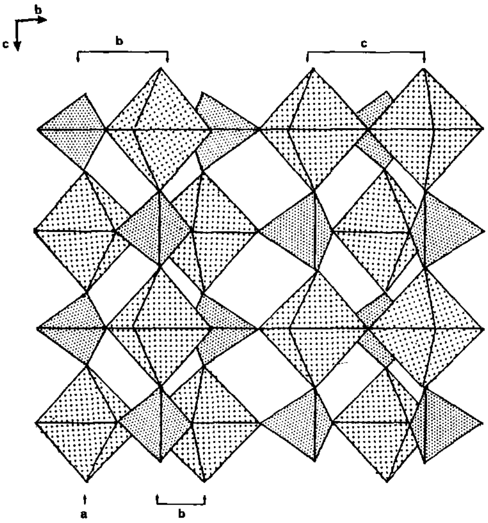

FIG. 2. Projection along *a* of the $KNb_3P_3O_{15}$ structure showing: (a) the $[PNbO_8]_\infty$ chains, (b) two chains where one octahedron and one tetrahedron share one oxygen, (c) two chains where two octahedra share one oxygen forming six-membered rings.

One interesting feature concerns the arrangement of the polyhedra along *c*. One indeed observes that the structure is formed of infinite chains $[PNbO_8]_\infty$ in which one PO_4 tetrahedron alternates with one NbO_6 octahedron (Fig. 2). Such chains are often encountered in molybdenum phosphorus and in tungsten phosphorus oxides (see, for instance, $MoPO_5$ (*4*, *5*)) and Nb PO_5 (*6*), $P_2W_2O_{11}$ (*7*), $Mo_2P_2O_{11}$ (*8*), and $NaPWO_6$ (*9*) are linked to each other in two ways alternately: two octahedra share one oxygen forming six-membered rings (Fig.

TABLE III

Distances (Å) and Angles (°) in the NbO_6 Octahedra

Nb(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(5^{i})
O(1)	1.858(1)	2.786(3)	3.905(3)	2.717(3)	2.714(2)	2.714(2)
O(2)	91.8(1)	2.017(3)	2.759(4)	3.950(4)	2.874(3)	2.874(3)
O(3)	177.30(9)	85.5(1)	2.047(3)	2.847(4)	2.872(3)	2.872(3)
O(4)	91.46(8)	176.7(1)	91.2(1)	1.935(2)	2.740(2)	2.740(2)
O(5)	89.51(5)	91.56(5)	90.56(5)	88.47(5)	1.993(2)	3.985(3)
O(5^{i})	89.51(5)	91.56(5)	90.56(5)	88.47(5)	176.8(1)	1.993(2)
Nb(2)	O(4)	O(6)	O(7)	O(8)	O(9)	O(9^{i})
O(4)	1.834(2)	2.922(4)	2.691(3)	3.882(3)	2.808(2)	2.808(2)
O(6)	97.6(1)	2.045(3)	4.010(3)	2.770(4)	2.787(3)	2.787(3)
O(7)	89.9(1)	172.5(1)	1.973(2)	2.779(3)	2.887(2)	2.887(2)
O(8)	177.2(1)	85.2(1)	87.4(1)	2.049(2)	2.783(2)	2.783(2)
O(9)	93.64(5)	86.75(5)	92.80(5)	86.50(5)	2.013(2)	4.013(3)
O(9^{i})	93.64(5)	86.75(5)	92.80(5)	86.50(5)	170.8(1)	2.013(2)
Nb(3)	O(7^{ii})	O(10^{iii})	O(11)	O(12^{iv})	O(12^{iii})	O(13)
O(7^{ii})	1.878(2)	2.662(3)	3.890(3)	2.810(2)	2.810(2)	2.892(2)
O(10^{iii})	84.5(1)	2.077(2)	2.674(4)	2.913(2)	2.913(2)	3.996(2)
O(11)	165.3(1)	80.8(1)	2.044(2)	2.821(2)	2.821(2)	2.937(3)
O(12^{iv})	92.23(5)	90.63(5)	87.95(5)	2.019(2)	4.034(4)	2.768(2)
O(12^{iii})	92.23(5)	90.63(5)	87.95(5)	175.5(1)	2.019(2)	2.768(2)
O(13)	99.15(7)	176.40(7)	95.56(8)	89.23(5)	89.23(5)	1.921(1)

Note. For symmetry code, see note to Table IV.

2) or one octahedron and one tetrahedron share one oxygen (Fig. 2) as in $MoPO_5$.

The most striking aspect of this structure is its close relationship with the tetragonal tungsten bronze structure. Considering one layer of polyhedra parallel to (001), one observes that the double chain of NbO_6 octahedra running along *b* has exactly the same arrangement as in the TTB structure. This double chain is bordered with PO_4 tetrahedra which take the place of one octahedron in the TTB structure. It results in $[Nb_3P_3O_{15}]_\infty$ ribbons (Fig. 3), in which one recognizes the different rings observed in the TTB structure (Fig. 4): five-membered rings formed of four octahedra and one tetrahedron instead of six octahedra, almost square windows formed of three octahedra and one tetrahedron which are similar to those of the perovskite tunnels, and triangular windows formed of two octahedra and one tetrahedron instead of three octahedra. The $[Nb_3P_3O_{15}]$ ribbons are shifted *a*/2 from one layer located at $z = 0$ to the next one located at $z = \frac{1}{2}$, sharing the corners of their polyhedra in such a way that the tetrahedron of one ribbon is connected to one octahedron of the ribbon belonging to the upper or the lower level. Despite this shifting of the ribbons, the structure keeps five-sided and four-sided tunnels running along *c*, as in the TTB structure. However, the nature of the cages located in these tunnels is of course different from that of the bronze: they are elongated along *c* and are consequently larger. The four-sided tunnels which are empty form cages of 18 oxygen atoms (4 + 4 + 2 + 4 + 4) as shown in Fig. 5A. In the five-sided tunnels the cages are also much more spacious than in the TTB structure; they are bounded by 22 oxygen atoms: 2 × 5 oxygens form the five-membered rings at $z = 0$ and 0.3, whereas 2 are

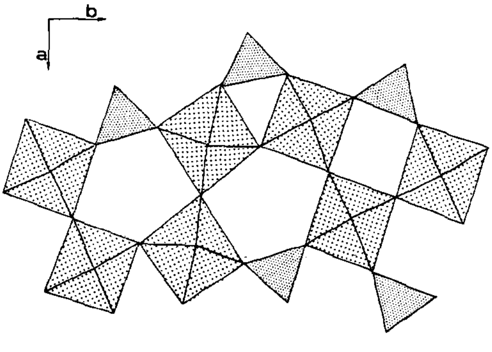

FIG. 3. The $[Nb_3P_3O_{15}]_\infty$ ribbons with the five-membered, four-membered, and triangular windows.

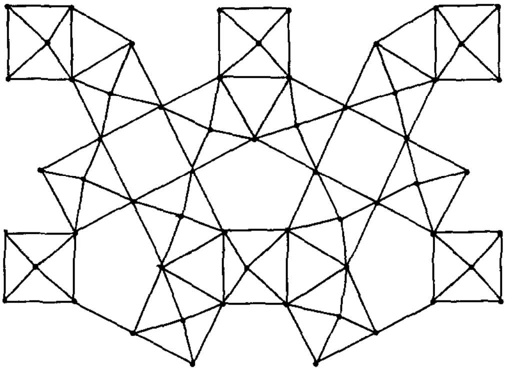

FIG. 4. The tetragonal tungsten bronze.

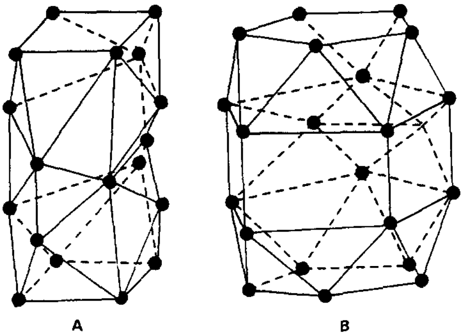

FIG. 5. Perspective views of the oxygen atoms delimiting the cages in: (A) the four-sided tunnels, (B) the five-sided tunnels.

located at $z = 0.5$ and 2×5 at $z = 0.7$ and 1 as shown in fig. 5B. The large dimensions of the cages with respect to the usual K–O distances makes the K^+ ions off centered in the cages, forming an opened polyhedron; i.e., one in which K^+ is not completely surrounded by oxygen atoms, due to the fact that it is displaced toward the walls of the cavity (Fig. 6). Consequently the K–O distances remain rather large (Table IV). One can argue that K^+ has five nearest neighbors, with distances smaller than 3.35 Å, taking this maximum value as a reference according to the procedure described by Donnay and Allmann (*10*) with Shannon's ionic radii (*11*). The two sites that are available for K^+ within the same cage, located on both sides of the mirror plane, are only half occupied owing to their short distance (1.15 Å).

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE KO_5 POLYHEDRON

K	$O(5^{v})$	$O(7^{ix})$	$O(8^{x})$	$O(9^{ix})$	O(12)
$O(5^{v})$	3.287(4)				
$O(7^{ix})$	94.3(2)	3.160(5)			
$O(8^{x})$	46.2(1)	131.2(2)	2.888(4)		
$O(9^{ix})$	73.9(1)	55.0(1)	117.6(2)	3.088(5)	
O(12)	147.9(2)	54.6(1)	161.5(2)	80.5(1)	2.955(3)

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

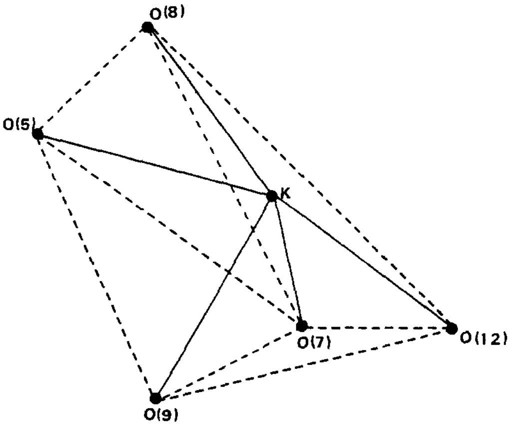

FIG. 6. The KO_5 polyhedron.

$KNb_3P_3O_{15}$ can thus be considered to have a structure related to the TTB type, which suggests various possibilities of nonstoichiometry in the different tunnels. The large size of the latter contrary to those in the TTB structure suggests the possibility of replacing potassium by larger cations such as rubidium, thallium, or cesium. Such compounds, characterized by a mixed valence of niobium and an anisotropy of the structure should present interesting electrical properties. Systematic investigations on those oxides are in progress.

References

1. B. RAVEAU, *Proc. Indian Natl. Sci. Acad. Part A* **52,** 67 (1986).
2. B. RAVEAU, *Proc. Indian Acad. Sci. (Chem Sci.)* **96,** 419 (1986).
3. A. MAGNELI, *Ark. Kemi* **1,** 269 (1949).
4. P. KIERKEGAARD AND M. WESTERLUND, *Acta Chem. Scand.* **18,** 2217 (1964).
5. P. KIERKEGAARD AND J. M. LONGO, *Acta Chem. Scand.* **24,** 427 (1970).
6. J. M. LONGO AND P. KIERKEGAARD, *Acta Chem. Scand.* **20,** 72 (1966).
7. P. KIERKEGAARD, *Acta Chem. Scand.* **14,** 657 (1960).
8. P. KIERKEGAARD, *Ark. Kemi* **19,** 1 (1962).
9. P. KIERKEGAARD, *Ark. Kemi* **18,** 552 (1962).
10. G. DONNAY AND R. ALLMAN, *Amer. Miner.* **55,** 1003 (1970).
11. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32,** 751 (1976).