

A Niobium Phosphate with a Tunnel Structure: $\text{Ca}_{0.5+x}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$

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A new niobium phosphate, $\text{Ca}_{0.5+x}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$ has been isolated. It crystallizes in the $R32$ space group, with the following parameters of the hexagonal cell: $a_H = 13.379 \text{ \AA}$, $c_H = 10.371 \text{ \AA}$. The determination of the structure by a single crystal X-ray diffraction study shows that its host lattice $[\text{Nb}_6\text{P}_3\text{O}_{24}]_x$ can be described as the assemblage of mixed chains $[\text{Nb}_2\text{PO}_{13}]_x$ running along c_H in which one PO_4 tetrahedron alternates with two NbO_6 octahedra. This framework delimits huge tunnels where the cesium cations are located and cages formed by $[\text{Nb}_6\text{P}_3\text{O}_{36}]$ units occupied by calcium. The most striking feature of this framework deals with its similarity with the hexagonal tungsten bronze of Magnéli (HTB). The latter is discussed here by considering the stacking along c of $[\text{Nb}_2\text{PO}_8]_x$ layers whose geometry is closely related to that of the HTBs. The possibility of nonstoichiometry leading to a mixed valency of niobium is considered. © 1991 Academic Press, Inc.

Introduction

Inorganic phosphates involving transition metals in octahedral coordination represent a wide field of investigation which appears promising for various applications, owing to the possibility of modifying the physical properties of those materials by introduction either of magnetic cations or of mixed valent elements. The phosphate tungsten bronzes well known for their anisotropic semimetallic or metallic properties illustrate this possibility [see for review Ref (1)]. Recently, several niobium phosphate bronzes were discovered (2–6), showing the great ability of NbO_6 octahedra and PO_4 tetrahedra to form original mixed frameworks characterized by a tunnel or a cage structure. The most striking feature of those phos-

phates deals with their close relationships with pure octahedral structures and especially with the oxygen tungsten bronzes. For instance the bronze $\text{KNb}_3\text{P}_3\text{O}_{15}$ (2) is closely related to the tetragonal tungsten bronze (TTB) described by Magnéli (7), whereas the bronzes $\text{K}_3\text{Nb}_6\text{P}_4\text{O}_{26}$ (3), $\text{K}_4\text{Nb}_8\text{P}_5\text{O}_{34}$ (4) and $\text{K}_7\text{Nb}_{14}\text{P}_9\text{O}_{60}$ (5) exhibit a great similarity with the Magnéli hexagonal tungsten bronze (HTB) (8) and the intergrowth tungsten bronzes (ITB) described by Hussain and Kihlborgh (9). In the same way the sodium phosphate bronze $\text{Na}_4\text{Nb}_6\text{P}_6\text{O}_{35}$ (6) was found to be closely related to the diphosphate tungsten bronzes with pentagonal tunnels (10) and consequently related to the perovskite structure. This suggests that the crystal chemistry study of oxide systems involving niobium and phosphorus is at its

TABLE I
Ca_{0.5}Cs₂Nb₆P₃O₂₄ INTERETICULAR DISTANCES

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>dI</i> / <i>I</i> ₀
1	0	1	7.705	7.720	8
0	1	2	4.722	4.728	16.4
2	1	1	4.023	4.031	3
0	0	3	3.450	3.453	30
1	2	2	3.342	3.343	100
1	1	3	3.069	3.068	60
4	0	1	2.789	2.788	6
3	1	2	2.731	2.729	13
3	0	3	2.572	2.573	14
1	0	4	2.527	2.527	4
1	4	1	2.461	2.455	1
2	2	3	2.401	2.402	7.5
-2	0	4	2.364	2.364	4.5
2	1	4	2.231	2.229	1.5
2	4	1	2.141	2.141	1.2
0	1	5	2.040	2.040	18
1	3	4	2.016	2.016	6
6	0	0	1.932	1.930	18.5
3	3	3	1.872	1.872	10
5	2	0	1.851	1.854	4

very beginning and should lead to numerous phases more or less related to the pure octahedral oxides. We report here on a new niobium phosphate, Ca_{0.5+x}Cs₂Nb₆P₃O₂₄, whose structure is again closely related to that of the HTB series.

Synthesis

The compound Ca_{0.5}Cs₂Nb₆P₃O₂₄ was synthesized from an homogeneous and pulverized mixture of CaCO₃, Cs₂CO₃, Nb₂O₅, and H(NH₄)₂PO₄ in appropriate ratios, first heated up to 593 K in air for 3 hr to eliminate H₂O, CO₂, and NH₃ and then heated up to 1300 K in air for 2 days. The X-ray diffraction pattern of the phase was indexed (Table I) in an hexagonal cell in agreement with the parameters from the single crystal study (Table II) which showed a rhombohedral symmetry *R*32. Single crystals of the phase Ca_{0.5+x}Cs₂Nb₆P₃O₂₄ were obtained using impure Cs₂CO₃ containing calcium from a mix-

ture corresponding to the nominal composition "CsNb₄PO₁₂" in the following way: a mixture of Cs₂CO₃, Nb₂O₅, and H(NH₄)₂PO₄ was first heated in air to eliminate H₂O, CO₂, and NH₃; then, in a second step, appropriate amounts of niobium were added, and the intimate mixture was heated up to 1120 K in an evacuated silica ampoule for 4 days. The Ca_{0.5+x}Cs₂Nb₆P₃O₂₄ composition of the crystals was determined by microprobe analysis.

Structure Determination

A black crystal with dimensions 0.26 × 0.17 × 0.10 mm was selected for the structure determination. The cell parameters reported in Table II were determined and refined by diffractometric techniques at 294 K with a least square refinement method based upon 25 reflections with 18° < θ < 22°. The intensity data were collected with a CAD-4

TABLE II
SUMMARY OF CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR Ca_{0.5}Cs₂Nb₆P₃O₂₄

1. Crystal data	
Space group	<i>R</i> 32
Cell dimensions	<i>a</i> = 13.3799 (9) Å <i>c</i> = 10.3713 (10) Å
Volume	<i>V</i> = 1607.(5) Å ³
<i>Z</i>	3
2. Intensity measurement	
λ (Mok α)	0.71073 Å
Scan Mode	ω - θ
Scan width (°)	1.10 + 0.35 tan θ
Slit aperture (mm)	1 + tan θ
Max θ (°)	45°
Standard reflections, three measured every 3000 sec (no decay)	
Reflections with <i>I</i> > 3 σ	1414
3. Structure solution and refinement	
Parameters refined	63
Agreement factors	<i>R</i> = 0.034, <i>R</i> _w = 0.037
<i>d</i> ρ _{max}	0.78 e Å ⁻³

TABLE III
POSITIONAL PARAMETERS AND THEIR ESTIMATED
STANDARD DEVIATIONS

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Cs	0.3587(1)	0.3353(1)	0.2211(2)	4.70(3)
Nb	0.52097(2)	0.16219(2)	0.01378(3)	0.642(3)
P	0.22882(9)	0.000	0.000	0.41(2)
O(1)	0.1486(2)	0.9776(3)	0.1159(2)	0.86(3)
O(2)	0.5133(3)	0.180	-0.167	0.80(3)
O(3)	0.3459(2)	0.1075(2)	0.0254(3)	0.87(4)
O(4)	0.4746(3)	0.000	0.000	0.78(5)
O(5)	0.6770(2)	0.2174(2)	0.0300(3)	0.76(3)
Ca	0.000	0.000	0.000	1.27(5)

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

Enraf-Nonius diffractometer. The data collection parameters are reported in Table II. The reflections were corrected for Lorentz and polarization effects, no absorption corrections were performed.

Atomic coordinates of the heaviest atoms were deduced from the Patterson function and the other atoms were located by subsequent Fourier series. Refinement of the multipliers of Cs and Ca led to the respective values of 0.333 and 0.084, corresponding to the formulation $\text{Ca}_{0.504}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$. These values were fixed in the further calculations. Refinement of the atomic coordinates and their anisotropic thermal parameters led to $R = 0.034$, $R_w = 0.037$, and to the atomic parameters of Table III.

Description of the Structure and Discussion

The $[\text{Nb}_6\text{P}_3\text{O}_{24}]_\infty$ host lattice is built up from corner-sharing NbO_6 octahedra and PO_4 tetrahedra as shown from the view of the structure along $[001]_H$ (Fig. 1). Each PO_4 tetrahedron is linked to four NbO_6 octahedra and consequently is characterized by a classical geometry with four almost identical P–O distances ranging from 1.52 to 1.53 Å and with O–P–O angles ranging from 106

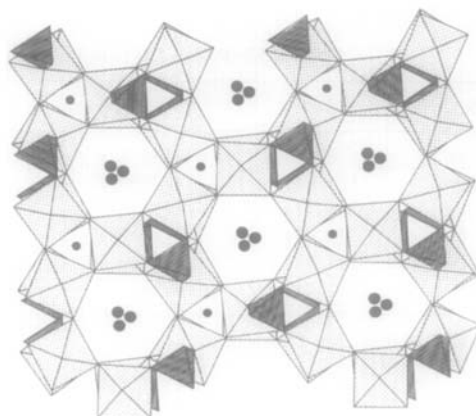


FIG. 1. Projection along *c* of $\text{Ca}_{0.5}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$.

to 112° (Table IV). Each NbO_6 octahedron shares four vertices with other NbO_6 octahedra, and two vertices with PO_4 tetrahedra. In the same way the NbO_6 octahedron is almost regular, with four shorter Nb–O dis-

TABLE IV
 $\text{Ca}_{0.5}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$: DISTANCES (Å) AND ANGLES (°) IN
THE PO_4 TETRAHEDRON

P	O(I ⁱⁱⁱ)	O(I ^{iv})	O(3)	O(3 ^y)
O(I ⁱⁱⁱ)	1.538(3)	2.459(3)	2.506(3)	2.500(4)
O(I ^{iv})	106.2(2)	1.538(3)	2.500(4)	2.506(3)
O(3)	109.6(1)	109.2(2)	1.529(2)	2.546(4)
O(3 ^y)	109.2(2)	109.6(1)	112.7(2)	1.529(2)

Note. Symmetry code. The following are the special positions of the atoms i–xiv as indicated in Tables IV–VI.

i	$-x + \frac{2}{3}$	$-x + y - \frac{2}{3}$	$-z + \frac{1}{3}$
ii	$1 - x + y$	$1 - x$	z
iii	x	$-1 + y$	z
iv	$1 + x - y$	$1 - y$	$-z$
v	$x - y$	$-y$	$-z$
vi	$x - \frac{1}{3}$	$y + \frac{1}{3}$	$z + \frac{1}{3}$
vii	$-x + \frac{2}{3}$	$-x + y + \frac{1}{3}$	$-z + \frac{1}{3}$
viii	$x - y - \frac{1}{3}$	$-y + \frac{1}{3}$	$-z + \frac{1}{3}$
ix	$-y + \frac{2}{3}$	$x - y + \frac{1}{3}$	$z + \frac{1}{3}$
x	$y - \frac{1}{3}$	$x + \frac{1}{3}$	$-z + \frac{1}{3}$
xi	$-1 - x + y$	$-x$	z
xii	$-1 + y$	x	$-z$
xiii	$-x$	$-1 - x + y$	$-z$
xiv	$1 - y$	$1 + x - y$	z

TABLE V
 $\text{Ca}_{0.5}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$: DISTANCES (Å) AND ANGLES (°) IN THE NbO_6 OCTAHEDRON

Nb	O(1 ⁱ)	O(2)	O(3)	O(4)	O(5)	O(5 ⁱⁱ)
O(1 ⁱ)	2.113(2)	3.993(2)	2.850(4)	2.980(3)	2.697(4)	2.801(4)
O(2)	170.0(1)	1.895(1)	2.784(4)	2.794(1)	2.848(4)	2.695(3)
O(3)	85.7(1)	88.8(1)	2.079(3)	2.754(5)	3.908(4)	2.754(4)
O(4)	94.5(1)	93.47(4)	86.4(1)	1.941(1)	2.831(3)	3.968(2)
O(5)	85.7(1)	99.3(1)	171.0(1)	96.9(1)	1.841(3)	2.814(4)
O(5 ⁱⁱ)	84.8(1)	86.3(1)	83.9(1)	170.3(1)	92.8(1)	2.041(2)

Note. Please see footnote to Table IV.

tances corresponding to the Nb–O–Nb bonds (1.84 to 2.04 Å), and two longer Nb–O distances (2.07–2.11 Å) corresponding to the Nb–O–P bonds (Table V).

The view of the structure along the $[100]_{\text{H}}$ direction of the hexagonal cell (Fig. 2), shows that it can be described as the assemblage of identical $[\text{Nb}_2\text{PO}_{13}]_{\infty}$ chains running along c_{H} , showing the corners of their polyhedra. Those chains (Fig. 3a) result from the alternative stacking of two NbO_6 octahedra with one PO_4 tetrahedron. Each of them is linked laterally in the $(001)_{\text{H}}$ plane to identical chains in two different ways. Each chain is linked to two chains by sharing only the corners of its NbO_6 octahedra, forming six-sided brownmillerite windows (Fig. 3b), and

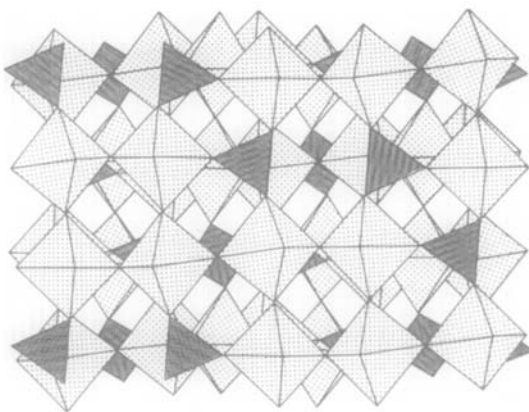


FIG. 2. Projection of the structure along a .

to two other chains in such a way that the corners of its PO_4 tetrahedra are shared with the NbO_6 octahedra of the next chain (Fig. 3c).

This arrangement of the $[\text{Nb}_2\text{PO}_{13}]_{\infty}$ chains leads to the formation octahedral $[\text{Nb}_6\text{O}_{27}]$ units built up from six corner-sharing NbO_6 octahedra (Fig. 3b), which were previously observed in $\text{Ba}_3\text{Nb}_6\text{Si}_4\text{O}_{26}$ (11) and $\text{Na}_6\text{Nb}_8\text{P}_5\text{O}_{35}$ (12).

These structural units delimit empty tri-capped trigonal prisms (Fig. 3b). The $[\text{Nb}_6\text{O}_{27}]$ units are stacked with PO_4 tetrahedra alternately forming $[\text{Nb}_6\text{P}_3\text{O}_{33}]_{\infty}$ columns (Fig. 3b) running along c_{H} . Laterally in the $(001)_{\text{H}}$ plane, these columns share the corners of polyhedra, forming very large eight-sided tunnels running along c_{H} (Fig. 1) where the cesium ions are located. Those tunnels are connected through brownmillerite windows in such a way that three windows form also an elongated cage (Fig. 3b) where the calcium ions are strongly bonded to six oxygen atoms forming a trigonal prism with Ca–O distances of 2.46 Å.

In the tunnels the Cs^+ cations, which exhibit a ninefold coordination, are not located on the axis but are off-centered, i.e., distributed over three split sites which are $\frac{1}{3}$ occupied owing to the too short distances of two split sites (Fig. 1). The rather large Cs–O distances, ranging from 3.12 to 3.59 Å (Table VI), explain that cesium exhibits a high thermal B factor ($B \approx 4.70$).

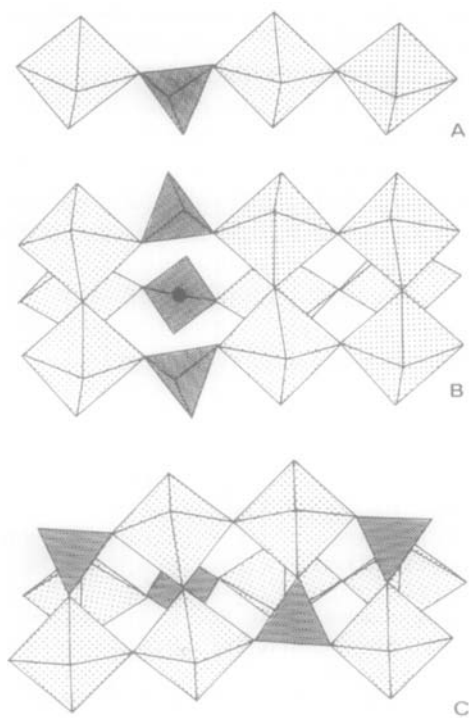


FIG. 3. (A) The $[\text{Nb}_2\text{PO}_{13}]_\infty$ chains. (B) Assemblage of three $[\text{Nb}_2\text{PO}_{13}]_\infty$ chains through the corner of their NbO_6 octahedra forming brownmillerite windows [BM]. (C) Assemblage of three $[\text{Nb}_2\text{PO}_{13}]_\infty$ chains through the corners of their NbO_6 octahedra and PO_4 tetrahedra.

Another way of describing this structure consists in the consideration of $[\text{Nb}_2\text{PO}_{13}]_\infty$ units (Fig. 4) built up from one PO_4 tetrahedron and two NbO_6 octahedra. These units share their corners along c forming $[\text{Nb}_2\text{PO}_{10}]_\infty$ columns (Fig. 3c), in which two successive $[\text{Nb}_2\text{PO}_{13}]_\infty$ units are deduced from the other by a 3_1 symmetry operation. Laterally these columns share the corners of their polyhedra, forming the $[\text{Nb}_6\text{P}_3\text{O}_{24}]_\infty$ framework characterized by wide tunnels (Fig. 1).

The consideration of the projection of the structure along c (Fig. 1) shows a striking similarity with the hexagonal tungsten bronze of Magnéli (8). One indeed observes

TABLE VI
BOND DISTANCES IN $\text{Ca}_{0.5}\text{Cs}_2\text{Nb}_6\text{P}_3\text{O}_{24}$

Oxygen atoms surroundings Cs^+	
Cs–O(4 ^{vi})	3.120(4) Å
Cs–O(3 ^{vii})	3.127(4) Å
Cs–O(5 ^{viii})	3.144(3) Å
Cs–O(5 ⁱⁱ)	3.204(4) Å
Cs–O(3 ^{ix})	3.279(4) Å
Cs–O(1 ^x)	3.310(3) Å
Cs–O(4 ⁱⁱ)	3.321(3) Å
Cs–O(5 ^{vi})	3.332(4) Å
Cs–O(3)	3.594(4) Å
Oxygen atoms surrounding Ca^{2+}	
Ca–O(1 ⁱⁱⁱ)	2.466(3) Å
Ca–O(1 ^{iv})	2.466(3) Å
Ca–O(1 ^{xi})	2.466(3) Å
Ca–O(1 ^{xii})	2.466(3) Å
Ca–O(1 ^{xiii})	2.466(3) Å
Ca–O(1 ^{xiv})	2.466(3) Å

Note. Please see footnote to Table IV.

that the $[\text{Nb}_6\text{P}_3\text{O}_{24}]_\infty$ framework is built up from identical $[\text{Nb}_2\text{PO}_{13}]_\infty$ layers parallel to $(001)_\text{H}$ (Fig. 5) in which one recognizes the $[\text{Nb}_3\text{O}_{15}]$ structural units characteristic of the TTB (7) and HTB (8) structures. In those layers the $[\text{Nb}_6\text{O}_{15}]$ units share the corner of their octahedra forming intersecting ribbons zigzaging along the $\langle 100 \rangle$ directions and whose geometry is absolutely similar to that observed for HTBs. The main difference with respect to HTBs deals with the ordered replacement of NbO_6 octahedra (see Fig. 5 dashed lines) by PO_4 tetrahedra, leading to

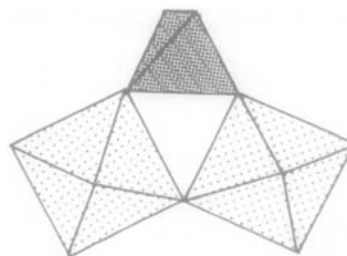


FIG. 4. $[\text{Nb}_2\text{PO}_{13}]_\infty$ units.

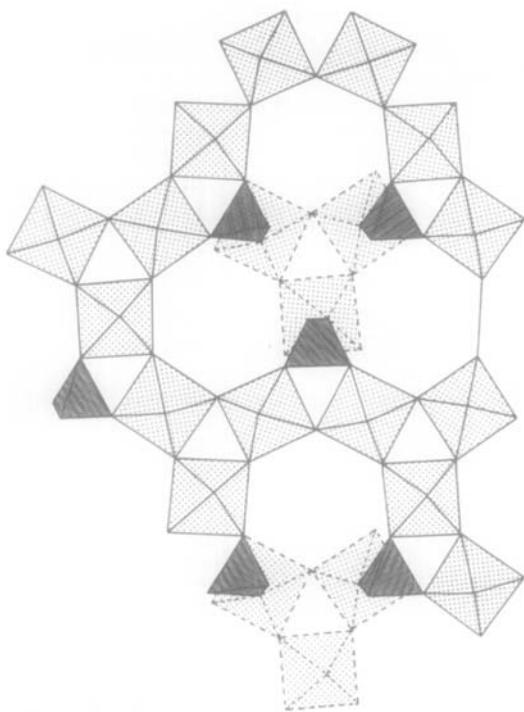


FIG. 5. $[\text{Nb}_2\text{PO}_8]$ layers.

the formation of $[\text{Nb}_2\text{PO}_{13}]$ units instead of $[\text{Nb}_3\text{O}_{15}]$ units.

It is worth pointing out that two successive $[\text{Nb}_2\text{PO}_8]_\infty$ layers (continued and dashed line, respectively, on Fig. 5) are disposed along c in such a way that if they were at the same level they would reconstruct the host lattice of the hexagonal tungsten bronze.

As a concluding remark it is worth pointing out that the crystal which was investigated here is dark, indicating a mixed va-

lency Nb(IV)/Nb(V), whereas the powder was synthesized in air, and consequently is white in agreement with the presence of only Nb(V). This is due to a possibility of non-stoichiometry on the calcium sites which are half occupied ($x = 0$), in the case of the Nb(V) phosphate, and exhibit an occupancy factor greater than 0.50 in the case of the mixed valent Nb(V)/Nb(IV) black crystal. The investigation of this phenomenon in connection with the electron transport properties of these oxides is in progress.

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