Structure of $Ba_{0.84}Rb_3Nb_8P_5O_{34}$

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Abstract

The niobium phosphate bronze $Ba_{0.84}Rb_3Nb_8P_5O_{34}$
is isotypic with $Na_{2-x}K_2Nb_8P_5O_{34}$, *i.e.* it corre-
sponds to the first member of the series $[K_3Nb_6P_4$-
$O_{26}]_n.KNb_2PO_8$. Its tunnel structure is closely related
to that of the hexagonal tungsten bronzes (HTB).
The three-dimensional framework $[Nb_8P_5O_{34}]_\infty$ con-
sists of $[Nb_6P_4O_{26}]_\infty$ layers derived from HTB's,
linked through $[Nb_2PO_8]_\infty$ chains. In the tunnels, the
rubidium and barium ions are distributed in an
ordered way: two sites are fully occupied by rubi-
dium whereas the third site, which exhibits 16%
vacancies, is occupied by barium.

Comment

The synthesis and the structure determination of the
title compound were undertaken because of the close
structural relationship between the niobium phos-
phate bronzes $(K_3Nb_6P_4O_{26})_n.KNb_2PO_8$ (Leclaire,
Benabbas, Borel, Grandin & Raveau, 1989; Benab-
bas, Borel, Grandin, Leclaire & Raveau, 1990*a*,*b*)
and the hexagonal tungsten bronzes (HTB) (Magnéli
& Blomberg, 1951). In order to test the possible
replacement of potassium by barium and rubidium,
crystals of this new phase were synthesized from
different nominal compositions $(Rb_2BaNb_8P_4O_{31}$,
$Rb_2BaNb_{12}P_3O_{38}$ and $Rb_2BaNb_{28}P_9O_{91})$ heated at
1273 K for six months in an evacuated silica
ampoule. The bronze $Ba_{0.84}Rb_3Nb_8P_5O_{34}$ is isotypic
with the bronze β-$Na_{2-x}K_2Nb_8P_5O_{34}$ (Benabbas,
Borel, Grandin, Leclaire & Raveau, 1991), *i.e.* its
$[Nb_8P_5O_{34}]_\infty$ framework consists of corner-sharing
NbO_6 octahedra and PO_4 tetrahedra forming mixed
$[Nb_2PO_8]_\infty$ chains linked to $[Nb_6P_4O_{26}]_\infty$ layers
derived from HTB's by replacing some octahedra by
PO_4 tetrahedra; bond lengths and angles are very
similar in both structures. In the tunnels two sorts of
site, Rb(1) and Rb(2), are fully occupied by rubidium
with eightfold and ninefold coordinations respec-
tively; such sites were fully occupied by potassium
and potassium and sodium respectively in

β-$Na_{2-x}K_2Nb_8P_5O_{34}$. In the latter bronze, the third
site is partially occupied by barium (84%) sitting
in the O_4 tetrahedron instead of sodium (73%).
This bronze, the first member of the family
$[A_3Nb_6P_4O_{26}]_n.ANb_2PO_8$, suggests that other mem-
bers should be synthesized in which A = Rb, Tl^I, Cs,
with or without barium.
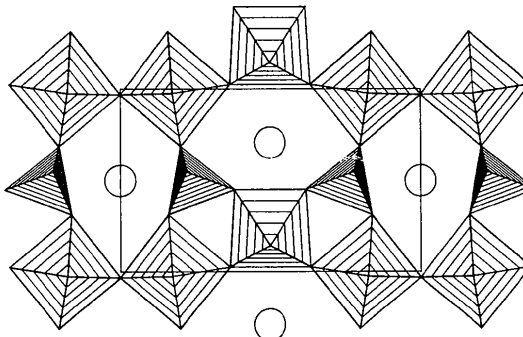
Fig. 1. View along the *a* axis of the $[Nb_6P_4O_{26}]_\infty$ layers in
$Ba_{0.84}Rb_2Nb_8P_5O_{34}$.

Table 1. *Positional parameters* ($Å^2$) *and their e.s.d.'s*

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Ba	0.5	0.5	0.5	1.88 (2)
Rb(1)	0.0	0.0	0.5	1.46 (4)
Rb(2)	0.0	0.5	0.2912 (4)	2.00 (4)
Nb(1)	0.5	0.1804 (1)	0.1991 (2)	0.52 (1)
Nb(2)	0.17662 (7)	0.17662 (7)	0.0	0.397 (7)
P(1)	0.5	0.5	0.0	0.57 (6)
P(2)	0.2423 (2)	0.2423 (2)	0.5	0.48 (2)
O(1)	0.5	0.0	0.256 (2)	1.1 (3)
O(2)	0.3658 (5)	0.1746 (7)	0.025 (1)	0.65 (9)
O(3)	0.3811 (7)	0.2211 (8)	0.451 (1)	1.0 (1)
O(4)	0.5	0.384 (1)	0.143 (2)	1.4 (2)
O(5)	0.178 (1)	0.0	0.032 (2)	0.9 (1)
O(6)	0.1611 (6)	0.2017 (6)	0.313 (1)	0.8 (1)

Calculations performed on a MicroVAX II computer with the
SDP system (B. A. Frenz & Associates, Inc., 1982). The θ-scan
width was $(0.90 + 0.35\tan\theta)°$. Drawing made with *STRUPLO*84
(Fischer, 1985).

Table 2. *Distances* (Å) *and angles* (°) *in the* NbO_6 *and*
PO_4 *polyhedra and main* Rb—O *and* Ba—O *distances*

Nb(1)	O(1)	O(2)	O(2^i)	O(3)	O(3^i)	O(4)
O(1)	1.957 (4)	2.78 (1)	2.78 (1)	2.96 (1)	2.96 (1)	4.15 (2)
O(2)	94.7 (4)	1.820 (7)	2.86 (1)	2.80 (1)	3.88 (2)	2.76 (1)
O(2^i)	94.7 (4)	103.6 (5)	1.820 (7)	3.88 (1)	2.80 (1)	2.76 (1)
O(3)	93.4 (5)	90.6 (3)	163.0 (3)	2.107 (7)	2.54 (1)	2.92 (1)
O(3^i)	93.4 (5)	163.0 (3)	90.6 (3)	74.0 (4)	2.107 (7)	2.92 (1)
O(4)	178.7 (7)	86.1 (4)	86.1 (4)	85.6 (4)	85.6 (4)	2.20 (1)

Nb(2)	O(2)	O(2^{ii})	O(5)	O(5^{ii})	O(6)	O(6^{ii})
O(2)	2.023 (6)	2.90 (1)	2.73 (1)	3.92 (1)	2.88 (1)	2.79 (1)
O(2^{ii})	91.6 (5)	2.023 (6)	3.92 (1)	2.73 (1)	2.79 (1)	2.88 (1)
O(5)	88.4 (5)	178.2 (5)	1.894 (2)	2.72 (1)	2.82 (1)	2.81 (1)
O(5^{ii})	178.3 (5)	88.4 (6)	91.6 (5)	1.894 (2)	2.81 (1)	2.82 (1)
O(6)	90.3 (3)	86.9 (3)	91.3 (3)	91.5 (3)	2.038 (8)	4.07 (2)
O(6^{ii})	86.9 (3)	90.3 (3)	91.5 (3)	91.3 (3)	175.9 (3)	2.038 (8)

P(1)	O(4)	O(4^{ii})	O(4^{iii})	O(4^{iv})
O(4)	1.545 (14)	2.55 (1)	2.48 (1)	2.55 (1)
O(4^{ii})	110.9 (6)	1.545 (14)	2.55 (1)	2.48 (1)
O(4^{iii})	106.7 (9)	110.9 (6)	1.545 (14)	2.55 (1)
O(4^{iv})	110.9 (6)	106.7 (9)	110.9 (6)	1.545 (14)

	P(2)	O(3)	O(3^{iv})	O(6)	O(6^v)
O(3)	1.529 (8)		2.49 (1)	2.53 (2)	2.52 (2)
O(3^{iv})	109.1 (7)	1.529 (8)		2.52 (2)	2.53 (2)
O(6)	109.9 (4)	110.3 (4)		1.548 (8)	2.49 (2)
O(6^v)	110.3 (4)	109.9 (4)		107.3 (6)	1.548 (8)

Rb(1)—O(6) × 8	3.005 (8)	Rb(2)—O(3^v)	3.148 (9)
Rb(2)—O(1^{vi})	2.92 (2)	Rb(2)—O(3^{vi})	3.148 (9)
Rb(2)—O(2^{ii})	3.107 (8)	Rb(2)—O(3^{ix})	3.148 (9)
Rb(2)—O(2^{iv})	3.107 (8)	Rb(2)—O(3^x)	3.148 (9)
Rb(2)—O(2^{vii})	3.107 (8)		
Rb(2)—O(2^{viii})	3.107 (8)	Ba—O(4) × 4	2.61 (2)

Symmetry code: (1) $1 - x, y, z$; (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) $-y, 1 - x, 1 - z$.

Experimental

Crystal data

$Ba_{0.84}Rb_3Nb_8P_5O_{34}$
$M_r = 1814$
Tetragonal
$P\bar{4}m2$
$a = 10.6604$ (8) Å
$c = 6.4434$ (4) Å
$V = 732.2$ (1) Å^3
$Z = 1$
$D_x = 4.11$ Mg m^{-3}
Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 18$–$25°$
$\mu = 9.2$ mm^{-1}
$T = 294$ K
Rod
$0.103 \times 0.032 \times 0.026$ mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer, graphite monochromator
Bisecting geometry, ω–$4/3\theta$ scans
Absorption correction: none
3414 measured reflections
3414 independent reflections

975 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 45°$
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 12$
3 standard reflections frequency: 50 min intensity variation: <0.1%

Refinement

Refinement on F
Final $R = 0.039$
$wR = 0.046$
$S = 1.009$
975 reflections
70 parameters
$w = F\sin(\theta/\lambda)$

$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 2.7$ e Å^{-3}
Atomic scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV)

Lists of structure factors and anisotropic thermal parameters, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55242 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1000]

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$Ba_{15}Al_{13.4}Ga_{14.5}$, a Disordered Structure Derived from Sr_5Al_9

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Abstract

The structure of the title compound may be derived from the ordered Sr_5Al_9 structure by redistribution of the Ga and Al atoms. In $Ba_{15}Al_{13.4}Ga_{14.5}$, the Al1 site is occupied by a mixture of 63% Al and 37% Ga and the Al2 site is totally filled by Ga. Only 69% of the Al3 site is occupied by Al, the remaining 31% being replaced by pairs of Ga atoms in a new partially filled position. The structure has features, characteristic of the Sr_5Al_9 and the ternary $Rb_4Au_7Sn_2$ types, which are related to the Laves phases, and can be described as an intergrowth of $MgZn_2$ and Ba_3Al_5 slabs (69%) as found in Sr_5Al_9, and $Rb_2Au_3Sn_2$ and Ba_3Al_5 slabs (31%).

Comment

By substituting one partner element for another in the binary phases formed by alkaline-earth and rare-earth metals, it is possible to make a more detailed study of the effect of a smooth variation of certain atomic properties such as atom size, electronegativity or electron concentration. Iandelli (1987) applied such an approach to $MAl_{2-x}Ga_x$ systems where M is a bivalent element (Ca, Sr, Eu or Yb) and x is in the range 0–2. The structure of the equi-atomic phase CaAlGa, a disordered variant of the $CeCu_2$-type, has also been refined (Fornasini & Pani, 1991). As no data were available for the analogous barium system, an alloy with nominal composition BaAlGa was prepared and the crystal structure determined. Weighed amounts of the three elements (Ba 99.5%, Al and Ga 99.999% pure) were placed in a tantalum crucible, arc welded under an argon atmosphere and melted in an induction furnace. As there is a close similarity between the crystal data, Sr_5Al_9 (Manyako, Zarechnyuk & Yanson, 1987) was used as starting model in the refinement.