Crystal structure of barium oxonitridophosphate, $Ba_3P_6O_6N_8$

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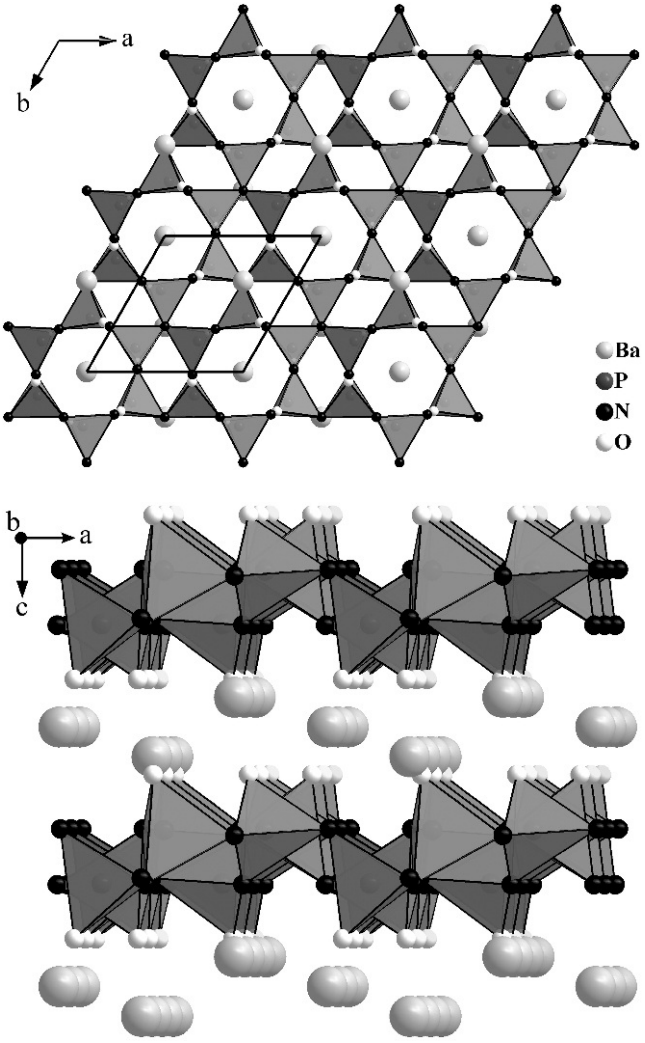

Abstract

$Ba_3N_8O_6P_6$, trigonal, $P\bar{3}$ (no. 147), a = 7.40227(9) Å, c = 6.3144(1) Å, V = 299.6 Å^3, Z = 1, *R(I)* = 0.008, *R(P)* = 0.041, T = 297(2) K.

Source of material

$Ba_3P_6O_6N_8$ was synthesized by a high-pressure, high-temperature reaction from $Ba(N_3)_2$ and amorphous PON in a Walker-type multi-anvil assembly. A finely ground mixture (ratio $Ba(N_3)_2$: PON = 1 : 2; approx. 50 mg) was placed into a capsule made of hexagonal boron nitride and compressed in a MgO octahedron with an edge length of 18 mm. At 6 GPa the sample was heated over 15 min to about 920 °C. This temperature was maintained for 15 min, and finally the sample was cooled down to room temperature over 30 min. Further details concerning the assembly are described in [1]. $Ba_3P_6O_6N_8$ was obtained as a light gray, air- and water stable, microcrystalline solid.

Experimental details

A Rietveld refinement was performed starting from the atomic parameters of isotypic $Sr_3P_6O_6N_8$. Preferred orientation of the crystallites was described with a spherical harmonics function of 4th order. Displacement parameters of atoms N/O have been constrained to one common value.

Discussion

A few years ago, the $Ba_3Si_6O_{12}N_2$:Eu^{2+} and its solid solution series $Ba_{3-x}Sr_xSi_6O_{12}N_2$ have been discovered as efficient green phosphors for phosphor-converted light-emitting diodes [2,3]. Just shortly before, the structure type of this silicate compound, however, was elucidated for the oxonitridophosphate $Sr_3P_6O_6N_8$ [4]. It exhibits a highly condensed layered structure. $Sr_3P_6O_6N_8$ was successfully synthesized by transfering the so-called azide high-pressure synthesis route to the P/O/N system. This synthesis route was originally applied for the preparation of nitridophosphates in combination with P_3N_5 [5,6]. The benefits of reacting a metal azide with P_3N_5 in the closed system at high pressure are that the respective metal nitride is generated in-situ while simultaneously the decomposition of P_3N_5 is suppressed by the high nitrogen partial pressure. By employing this method using amorphous PON as starting material, we were able to synthesize $Sr_3P_6O_6N_8$ and by now also $Ba_3P_6O_6N_8$. According to the pressure-homologue rule, the higher homologue $Ba_3P_6O_6N_8$ can also be generated at lower pressures such as 4 GPa. As for Si/O/N, however, evidence for a calcium homologue ($Ca_3P_6O_6N_8$) is not existent, not even at higher pressures.

The crystal structure of $Ba_3P_6O_6N_8$ consists of two-dimensional layer anions $[P_6O_6N_8]^{6-}$ parallel (001) and Ba^{2+} ions in-between. The anions are composed of vertex-sharing Q^3-type P(ON$_3$) tetrahedra, which form condensed 4- and 6-rings with twofold and threefold N atoms involved within the layer. The O atoms are bound terminally. The bond lengths P—N were determined to 159.1 and 166.4 pm (to N2) and 172.5 pm (to N3). As expected, the bond length d(P—O1) = 144.9 pm is significantly shorter. The Ba^{2+} ions are 10-fold coordinated by four N (d(Ba—N) = 295.4 pm and 297.3 pm) and six O atoms (283.0, 293.1 pm), and 12-fold by 6 N (272.2 pm) and 6 O atoms (345.0 pm), respectively.

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Table 1. Data collection and handling.

Powder:	light gray
Wavelength:	Mo $K_{\alpha 1}$ radiation (0.70930 Å)
μ:	10.6 cm^{-1}
Diffractometer:	STOE STADI P
$2\theta_{max}$, stepwidth:	60.0, 0.01°
$N(points)_{measured}$:	5800
$N(hkl)_{measured}$:	604
$N(param)_{refined}$:	68
Programs:	TOPAS [7], DIAMOND [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
Ba1	2*d*	⅔	⅓	0.3853(2)	0.0101(5)
Ba2	1*b*	0	0	½	0.0129(6)
P	6*g*	0.7747(5)	0.1747(6)	0.8967(5)	0.0053(8)
N1	2*d*	⅔	⅓	0.918(2)	0.006(1)
N2	6*g*	0.686(2)	0.019(1)	0.107(2)	0.006
O	6*g*	0.709(1)	0.072(1)	0.684(1)	0.006

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