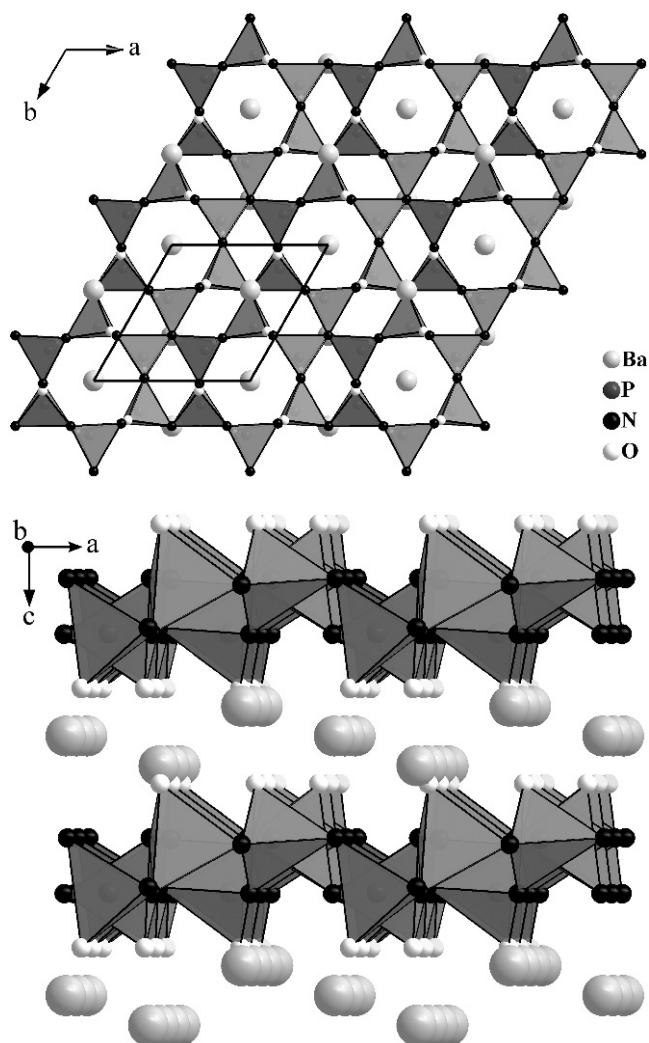


Crystal structure of barium oxonitridophosphate, $\text{Ba}_3\text{P}_6\text{O}_6\text{N}_8$

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Abstract

$\text{Ba}_3\text{N}_8\text{O}_6\text{P}_6$, trigonal, $P\bar{3}$ (no. 147), $a = 7.40227(9)$ Å, $c = 6.3144(1)$ Å, $V = 299.6$ Å³, $Z = 1$, $R(I) = 0.008$, $R(P) = 0.041$, $T = 297(2)$ K.

Source of material

$\text{Ba}_3\text{P}_6\text{O}_6\text{N}_8$ was synthesized by a high-pressure, high-temperature reaction from $\text{Ba}(\text{N}_3)_2$ and amorphous PON in a Walker-type multi-anvil assembly. A finely ground mixture (ratio $\text{Ba}(\text{N}_3)_2$: 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 tempera-

ture over 30 min. Further details concerning the assembly are described in [1]. $\text{Ba}_3\text{P}_6\text{O}_6\text{N}_8$ 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 $\text{Sr}_3\text{P}_6\text{O}_6\text{N}_8$. 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 $\text{Ba}_3\text{Si}_6\text{O}_{12}\text{N}_2\text{:Eu}^{2+}$ and its solid solution series $\text{Ba}_{3-x}\text{Sr}_x\text{Si}_6\text{O}_{12}\text{N}_2$ 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 $\text{Sr}_3\text{P}_6\text{O}_6\text{N}_8$ [4]. It exhibits a highly condensed layered structure. $\text{Sr}_3\text{P}_6\text{O}_6\text{N}_8$ was successfully synthesized by transferring 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 $\text{Sr}_3\text{P}_6\text{O}_6\text{N}_8$ and by now also $\text{Ba}_3\text{P}_6\text{O}_6\text{N}_8$. According to the pressure-homologue rule, the higher homologue $\text{Ba}_3\text{P}_6\text{O}_6\text{N}_8$ can also be generated at lower pressures such as 4 GPa. As for Si/O/N, however, evidence for a calcium homologue ($\text{Ca}_3\text{P}_6\text{O}_6\text{N}_8$) is not existent, not even at higher pressures.

The crystal structure of $\text{Ba}_3\text{P}_6\text{O}_6\text{N}_8$ consists of two-dimensional layer anions $[\text{P}_6\text{O}_6\text{N}_8]^{6-}$ parallel (001) and Ba^{2+} ions in-between. The anions are composed of vertex-sharing Q^3 -type $\text{P}(\text{ON})_3$ 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 $d(\text{P—O1}) = 144.9$ pm is significantly shorter. The Ba^{2+} ions are 10-fold coordinated by four N ($d(\text{Ba—N}) = 295.4$ 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°
$N(\text{points})_{\text{measured}}$:	5800
$N(hkl)_{\text{measured}}$:	604
$N(\text{param})_{\text{refined}}$:	68
Programs:	TOPAS [7], DIAMOND [8]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
Ba1	2d	$\frac{2}{3}$	$\frac{1}{3}$	0.3853(2)	0.0101(5)
Ba2	1b	0	0	$\frac{1}{2}$	0.0129(6)
P	6g	0.7747(5)	0.1747(6)	0.8967(5)	0.0053(8)
N1	2d	$\frac{2}{3}$	$\frac{1}{3}$	0.918(2)	0.006(1)
N2	6g	0.686(2)	0.019(1)	0.107(2)	0.006
O	6g	0.709(1)	0.072(1)	0.684(1)	0.006