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Hydrothermal synthesis and crystal structures of Li,Ba-nanoborate, $LiBaB_9O_{15}$, and Ba-borophosphate, $BaBPO_5$

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Abstract

Two compounds Li,Ba-nanoborate $LiBaB_9O_{15}$ (**I**) and Ba-borophosphate $BaBPO_5$ (**II**) were synthesized in the hydrothermal systems $BaCl_2–Li_2CO_3–B_2O_3–H_2O$ and $BaO–B_2O_3–P_2O_5–H_2O$ (T=280 °C, P=100 bar, 20 days). The crystal structures of **I** and **II** were established from X-ray single crystal diffraction: (**I**) space group $R\bar{3}c$, $a=10.982(2)$, $c=17.067(3)$ Å, $V=1782.6(5)$ Å^3, $R_{hkl}=0.033$ for 347 $|F_o|>4\sigma(F_o)$; (**II**) space group $P3_22$, $a=7.114(1)$, $c=6.993(1)$ Å, $V=306.49(8)$ Å^3, $R_{hkl}=0.0252$ for 576 $|F_o|\geq 4\sigma(F_o)$. While (**II**) is isotypic to the stillwellite, $LiBaB_9O_{15}$ represents a completely novel type of crystal structure. It comprises a borate framework with tunnels filled by Ba atoms in 12-fold coordination and by Li atoms in unusual 3-fold coordination.

Keywords: Optical materials; Chemical synthesis; Crystal structure; X-ray diffraction

1. Introduction

The study of synthetic Li,Ba-nanoborate $LiBaB_9O_{15}$ is part of a program on the crystal chemistry of lithium and barium borates that includes structure determination of phases obtained under hydrothermal conditions. The reason of search for new borates is the relationship between crystal structure and optical properties of non-linear optical materials—alkaline and alkaline-earth borates. Five Li,Ba-borates, namely $Li_6Ba_2B_4O_{11}$ [1], $LiBa_2B_5O_{10}$ [1,2], $LiBaB_9O_{15}$, synthesized by solid state reaction [3], $LiBaBO_3$ [4] and $LiBa_2[B_{10}O_{16}(OH)_3]$ [5] have been reported sofar. The crystal structures of $LiBa_2B_5O_{10}$ [2], $LiBaBO_3$ [4] and $LiBa_2[B_{10}O_{16}(OH)_3]$ [5] are already known whereas the crystal structure of $LiBaB_9O_{15}$ is described herein.

Ba-borophosphate $BaBPO_5$ belongs to the stillwellite, $CeBSiO_5$, structural type, which comprises a large group of compounds with general formula $M^{2+}BX^{5+}O_5$, where M^{2+}=Ca, Sr, Ba and X^{5+}=P, As. Some other borophosphates are also known, namely Zn_3BPO_7, Mg_3BPO_7 [6], $Ba_3[(PO_4)_2BPO_4]$ [7] and $Pb_3[(PO_4)_2BPO_4]$ [8]. The interest in their synthesis and characterization is mainly due to the perspectives of exploring new functional materials which exhibit non-linearity in optical properties.

The crystal structure and the results of thermal decomposition studies of $BaBPO_5$ were recently reported in Ref. [9]. Similarly to $CaBPO_5$ and $SrBPO_5$ [7], the structure of $BaBPO_5$ was refined by the Rietveld method in the space group $P3_12$ in contrast to the structure of the chemically related $PbBAsO_5$ which was determined on a single crystal to belong to space group $P3_1$ [10]. It is worthy to note that the c parameter of $BaBPO_5$ according to data in Ref. [9] should be two times smaller as compared with that reported in Ref. [11]: 6.990 vs. 13.977 Å. Apart from that, the relatively high values of $R_p=0.084$ and $R_{wp}=0.123$, of the thermal displacement parameter for the P atom and the unusual set of interatomic distances B–O (1.338–1.604 Å) in the BO_4 tetrahedra [9], prompted us to reinvestigate the crystal structure of $BaBPO_5$. The results of this work are reported below.

2. Experimental

Colourless transparent single crystals of Li,Ba-nanoborate $LiBaB_9O_{15}$ and Ba-borophosphate $BaBPO_5$ were synthesised in the hydrothermal (T=280 °C, P=100 bar) systems $BaCl_2–Li_2CO_3–B_2O_3–H_2O$ ($BaCl_2/Li_2CO_3/$

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$B_2O_3=2:1:2$) and $BaO–B_2O_3–P_2O_5–H_2O$ ($BaO/B_2O_3/P_2O_5=1:1:1$), respectively. In the experiments which resulted in the synthesis of the Ba-borophosphate $BaBPO_5$, the starting materials were put into autoclaves which contained a small amount of HCl (0.5 M) as a solvent. The duration of the syntheses was 20 days. The crystals of Li,Ba-nanoborate have isometric habits and those of Ba-borophosphate can be described as elongated plates with a maximal size of 1 mm. The identification of both phases was carried on through a X-ray powder diffraction study. The experimental data were collected on an ADP-2 diffractometer (Cu Kα radiation, $\lambda=1.54056$, Ni-filter; $5.00° < 2\theta < 80.00°$; 2θ scan with steps of 0.02°; the exposure time per step, 5 s). The comparison of the powder diffraction patterns with the ICDD data base [12] revealed similarity of the synthesised phases with Li,Ba-nanoborate $LiBaB_9O_{15}$ and with Ba-borophosphate $BaBPO_5$. The qualitative electron probe microanalysis using a SEM Philips PW 6800/70 with EDS electron probe, proved the presence of Ba as the main element in both phases.

Two sets of intensity data were obtained on a Siemens P4 four circle diffractometer using graphite monochromatized Mo Kα radiation ($\lambda=0.71073$ Å). The intensity of three standard reflections measured every 97 observations did not show fluctuations larger than 3%. The experimental details of the data collection are given in Table 1. All intensities were corrected for absorption by an ψ-scan system according to the ellipsoid approximation and reduced to $|F|^2$. The software package SHELX-97 [13] was used in the structure determination. The figures were obtained with the use of the program ATOMS [14].

2.1. $LiBaB_9O_{15}$

The unit cell parameters were derived through a least squares fit using 24 medium θ reflections $10.5 < 2\theta < 24.4°$. The crystal structure determination by direct methods and refinement were performed in space group $R\bar{3}c$, using 347 reflections with $I > 2\sigma(I)$. The E synthesis presented a peak which was assumed as due to the Ba atom. Its position was refined in an isotropic approach and a subsequent synthesis allowed to locate the O atoms and part of the B atoms. The structure determination has been completed with a $\Delta\rho$ synthesis. Thus the formula of the compound, $LiBaB_9O_{15}$, has been established as a result of its structural investigation. The refinement of the structure with anisotropic displacement parameters for all atoms decreased the R factor to 0.033 for 347 $|F_o| > 4\sigma(F_o)$ and to 0.0478 for all 458 data; wR $(F^2)=0.0787$. Refined atomic coordinates and interatomic distances are given in Tables 2 and 3. The final electron density map was featureless: maximum $\Delta\rho=1.44$ e Å^{-3}, minimum $\Delta\rho=-1.12$ e Å^{-3}. The bond-strength values, calculated according to Ref. [15], are presented in Table 4.

Table 1
Experimental details of the structure determinations of $LiBaB_9O_{15}$ and $BaBPO_5$

Formula	$LiBaB_9O_{15}$	$BaBPO_5$
Cell weight	2889.31	777.32
Crystal system	Trigonal	Trigonal
Space group; Z	$R\bar{3}c$; 6	$P3_22$; 2
Unit cell dimensions (Å)	$a=10.982(2)$, $c=17.067(3)$	$a=7.114(1)$, $c=6.993(1)$
Unit cell volume (Å^3)	1782.6(5)	306.49(8)
F (000)	1344	348
Density (calc.) (g cm^{-3})	2.69	4.21
Linear absorption coefficient (mm^{-1})	3.43	10.01
Radiation; λ (Å)	Mo Kα; 0.71073	Mo Kα; 0.71073
Crystal size (mm)	0.12×0.10×0.12	0.10×0.10×0.16
Diffractometer	Siemens P4	Siemens P4
Scan type	θ–2θ	θ–2θ
2θ range (°)	6.42–55	6.62–59.95
Indices range	$-1\leq h\leq 13$, $-14\leq k\leq 1$, $-22\leq l\leq 1$	$-9\leq h\leq 9$, $-10\leq k\leq 10$, $-9\leq l\leq 9$
Collected reflections	1224	1289
Unique reflections	458	586
R(int) from merging equivalents	0.0572	0.0519
Criterion for significance	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Absorption correction	ψ-scan	ψ-scan
Structure refinement	Full-matrix least squares	Full-matrix least squares
Number of refined parameters	42	40
$R1$ (conventional R factor)	0.0480 for all 458 data; 0.0330 for 347 $F_o > 4\sigma(F_o)$	0.0257 for all 586 data; 0.0252 for 576 $F_o > 4\sigma(F_o)$
$wR2$ (weighted R on on F^2)	0.0862	0.0773
S (goodness of fit)	1.050	0.572
Program	SHELX-97 [13]	SHELX-97 [13]

Table 2
Fractional atomic coordinates and equivalent displacement parameters U_{eq} (in Å^2) for $LiBaB_9O_{15}$

Atom	x/a	y/b	z/c	U_{eq}
Ba	0	0	0	0.0162(3)
B1	0.2681(5)	0.8699(5)	0.9784(3)	0.014(1)
B2	1/3	0.0974(6)	11/12	0.011(1)
Li	1/3	2/3	11/12	0.09(2)
O1	0.2263(3)	0.1148(3)	0.8732(2)	0.0138(6)
O2	0.2521(4)	0.9837(3)	0.9726(2)	0.0148(7)
O3	0	0.1719(4)	1/4	0.0167(10)

Table 4
Bond–valence parameters for $LiBaB_9O_{15}$ [15]

Atom	O1	O2	O3	$\Sigma_{cations}$
Ba	$0.128^{[\times 6]}$	$0.192^{[\times 6]}$	–	1.920
B1	1.070	1.058	$^{[\times 2]}0.902$	3.030
B2	$0.745^{[\times 2]}$	$0.771^{[\times 2]}$	–	3.032
Li	–	–	$0.320^{[\times 3]}$	0.960
Σ_{anions}	1.943	2.021	2.124	–

Left and right superscripts indicate the number of equivalent bonds for anions and cations, respectively.

Table 5
Fractional atomic coordinates and equivalent displacement parameters U_{eq} (in Å^2) for $BaBPO_5$

Atom	x/a	y/b	z/c	U_{eq}
Ba	0	0.39502(6)	1/3	0.0092(2)
P	0.3896(3)	0	1/6	0.0077(4)
B	0	−0.093(2)	1/3	0.010(2)
O1	0.1395(7)	0.3230(7)	−0.0379(7)	0.0104(9)
O2	0.8562(8)	0.4274(8)	−0.0350(7)	0.0156(10)
O3	0	−0.0411(9)	5/6	0.0109(11)

2.2. $BaBPO_5$

The unit cell parameters were derived by a least-squares fit using 32 medium θ reflections $13<2\theta<22°$. The crystal structure determination and refinement were performed in space group $P3_22$. After merging, $R=0.0252$ for 576 $|F_o|\geq 4\sigma(F_o)$ and $R=0.0257$ for all 586 independent reflections. Refined atomic coordinates and interatomic distances are given in Tables 5 and 6. The final electron density map was featureless: maximum $\Delta\rho = 1.82$ e Å^{-3}, minimum $\Delta\rho = -1.50$ e Å^{-3}. A bond–valence analysis is presented in Table 7.

Considering that the structures of natural stillwellites have the general formulas $REE[BSiO_5]$ (REE = Ce, La (dominant), Pr, Nd, Th) [16,17] and that some of their synthetic analogues, namely $PbBAsO_5$ [8], $LaBGeO_5$ [18], were described in the polar axial space group $P3_1$, the structure of $BaBPO_5$ was also refined in $P3_2$ up to $R=0.0398$ for 1048 $|F_o|\geq 4\sigma(F_o)$ and 0.0407 for all 1069 independent reflections. The assumption of twinning did

Table 3
Interatomic distances (Å) for $LiBaB_9O_{15}$

Barium polyhedron		Boron polyhedra		Lithium polyhedron	
Ba–O2^{a}	2.900(3)	B1–O1^{m}	1.346(5)	Li–O3^{n}	1.888(5)
–O2^{b}	2.900(3)	–O2	1.350(6)	–O3^{r}	1.888(5)
–O2^{c}	2.900(3)	–O3^{n}	1.409(5)	–O3^{s}	1.888(5)
–O2^{d}	2.900(3)				
–O2^{e}	2.900(3)	⟨B1–O⟩	1.368	⟨Li–O⟩	1.888
–O2^{f}	2.900(3)				
–O1^{g}	3.052(3)	B2–O2^{o}	1.467(5)		
–O1^{h}	3.052(3)	–O2^{p}	1.467(5)		
–O1^{i}	3.052(3)	–O1	1.480(5)		
–O1^{j}	3.052(3)	–O1^{q}	1.480(5)		
–O1^{k}	3.052(3)				
–O1^{l}	3.052(3)	⟨B2–O⟩	1.473		
⟨Ba–O⟩	2.976				

Symmetry code

a: $x-y+1,\ x,\ -z+1$
b: $-x+y-1,\ -x,\ z-1$
c: $y-1,\ -x+y-1,\ -z+1$
d: $-y+1,\ x-y+1,\ z-1$
e: $x,\ y-1,\ z-1$
f: $-x,\ -y+1,\ -z+1$
g: $-x+y,\ -x,\ z-1$
h: $x-y,\ x,\ -z+1$
i: $-y,\ x-y,\ z-1$
j: $y,\ -x+y,\ -z+1$
k: $x,\ y,\ z-1$
l: $-x,\ -y,\ -z+1$
m: $-x+y+1/3,\ y+2/3,\ z+1/6$
n: $x+1/3,\ y+2/3,\ z+2/3$
o: $x,\ y-1,\ z$
p: $-x+2/3,\ -x+y-2/3,\ -z+11/6$
q: $-x+2/3,\ -x+y+1/3,\ -z+11/6$
r: $-y+1/3,\ x-y+2/3,\ z+2/3$
s: $-x+y+1/3,\ -x+2/3,\ z+2/3$

Table 6
Interatomic distances (Å) for $BaBPO_5$

Barium polyhedron		Phosphorus polyhedron		Boron polyhedron	
Ba–O2^a	2.666(5)	P–O2^h	1.497(5)	B–O3^g	1.439(6)
–O2^b	2.666(5)	–O2^i	1.497(5)	–O3^f	1.439(6)
–O2^c	2.823(3)	–O1^j	1.578(4)	–O1^l	1.523(9)
–O2^d	2.823(5)	–O1^k	1.578(4)	–O1^j	1.523(9)
–O1^a	2.901(4)				
–O1^b	2.901(4)	⟨P–O⟩	1.537	⟨B–O⟩	1.481
–O1	2.915(5)				
–O1^e	2.915(5)	O2^h–O2^i	2.556(10)	O3^g–O3^f	2.385(6)
–O3^f	2.919(5)	O2^h–O1^j	2.472(6)	O3^g–O1^l	2.436(7)
–O3^g	2.919(5)	O2^h–O1^k	2.527(6)	O3^g–O1^j	2.454(4)
		O2^i–O1^j	2.472(6)	O3^f–O1^l	2.436(7)
⟨Ba–O⟩	2.845	O2^i–O1^k	2.527(6)	O3^f–O1^j	2.454(4)
		O1^j–O1^k	2.490(9)	O1^l–O1^j	2.322(8)
		⟨O–O⟩	2.507	⟨O–O⟩	2.415

Symmetry code

a: $-x+y,\ -x+1,\ z+1/3$	e: $-x,\ -x+y,\ -z+2/3$	i: $y,\ x-1,\ -z$
b: $x-y,\ -y+1,\ -z+1/3$	f: $-x+y,\ -x,\ z-2/3$	j: $-x+y,\ -x,\ z+1/3$
c: $x-1,\ y,\ z$	g: $-y,\ x-y,\ z-1/3$	k: $y,\ x,\ -z$
d: $-x+1,\ -x+y+1,\ -z+2/3$	h: $-x+y+1,\ -x+1,\ z+1/3$	l: $x-y,\ -y,\ -z+1/3$

not improve the *R* factor and indicated that the volume of the second individual is close to 0. Thus the space group $P3_22$ reported previously for the structures of alkaline earth stillwellites, $M^{2+}BPO_5$ (M^{2+} = Ca, Sr) [7] and for HT form of $LaBGeO_5$ [18] was confirmed.

3. Discussion

3.1. $LiBaB_9O_{15}$

The structure contains a three-dimensional borate framework, formed by $B(1)O_3$ triangles and $B(2)O_4$ tetrahedra (Figs. 1 and 2). Three-membered polyhedral rings (2△1□) composed of two BO_3 triangles and one BO_4 tetrahedron can be considered as a fundamental building block (FBB) [19] within the framework. This kind of FBB form the finite clusters in the structures of ameghinite, sborgite, and ammonioborite. Infinite chains based on similar type of FBB were revealed in the larderellite.

As a matter of fact the FBB unit appears as finite cluster only in the structure of ameghinite, because sborgite and ammonioborite are based on the FBB 4△1□ (two 3-membered rings 2△1□ share the same BO_4 tetrahedron) and larderellite presents the same FBB 4△1□ connected to build an infinite chain. So ameghinite is the only natural borate presenting FBB 2△1□. The scheme given below reproduces the structure of the FBB 2△1□, with three oxygen atoms (O_{br}) linked to two B atoms and four oxygen atoms (O_{nbr}) linked to only one B atom (‘free’ vertices of the FBB unit) (Fig. 3). In the crystal structure

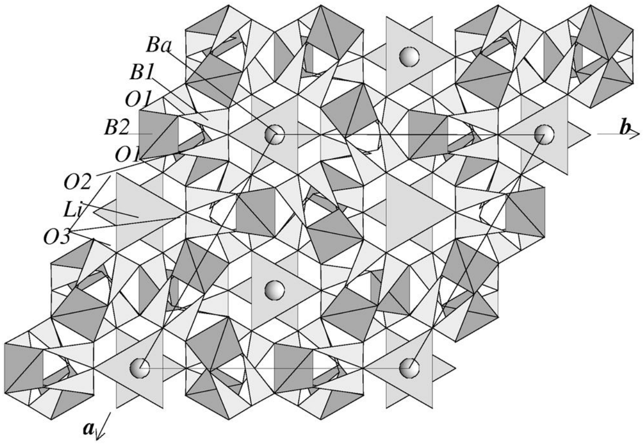

Fig. 1. Projection of $LiBaB_9O_{15}$ on (001).

Table 7
Bond–valence parameters for $BaBPO_5$ [15]

Atom	O1	O2	O3	$\Sigma_{cations}$
Ba	$0.192^{[\times2]}+0.185^{[\times2]}$	$0.362^{[\times2]}+0.237^{[\times2]}$	$^{[\times2]}0.183^{[\times2]}$	2.318
P	$1.073^{[\times2]}$	$1.335^{[\times2]}$	–	4.816
B	$0.663^{[\times2]}$	–	$^{[\times2]}0.832^{[\times2]}$	2.990
Σ_{anions}	2.113	1.934	2.030	–

Left and right superscripts indicate the number of equivalent bonds for anions and cations, respectively.

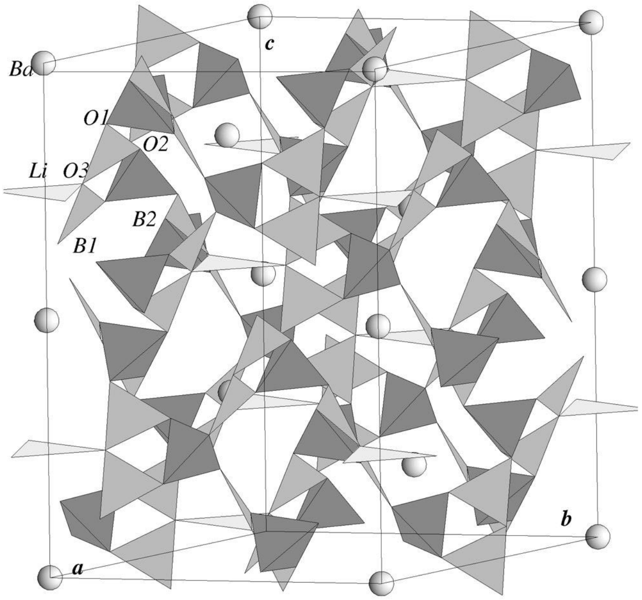

Fig. 2. The crystal structure of $LiBaB_9O_{15}$, perspective view.

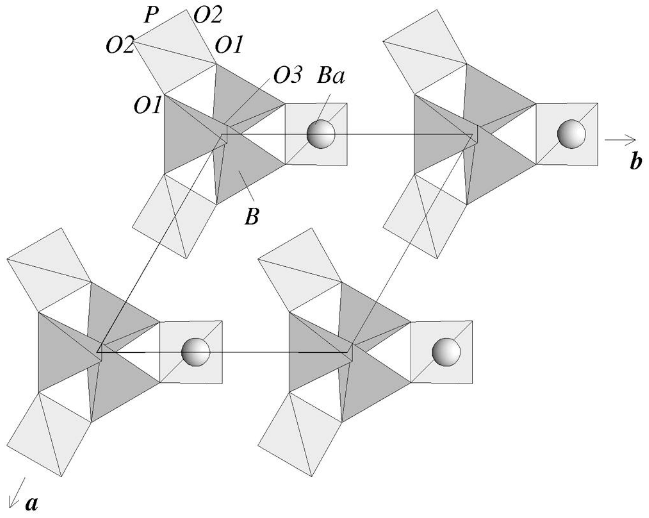

Fig. 4. Crystal structure of $BaBPO_5$ as seen along [001].

of Li,Ba-nanoborate each free vertex is linked to another FBB; in particular the two free vertices of the tetrahedron are linked to triangular B of adjacent FBBs, whereas the two free vertices of the triangles are linked to tetrahedral B of adjacent FBBs. In summary, each FBB has the formula $B_3O_{[br]3}O_{[nbr]4}$ with the four non-bridging oxygens being common to two adjacent FBB and therefore counting for half. As a consequence, the stoichiometry of the framework is $B_3O_3O_2$, namely B_3O_5 as it appears in the formula of the compound $LiBaB_9O_{15}$.

The borate framework in $LiBaB_9O_{15}$ contains large tunnels parallel to $[0\underline{0}1]$, filled by Ba and Li cations which alternate along the $\bar{3}$ inversional axes. The Ba atoms are located in typical 12-fold polyhedra whereas the Li atoms are within unusual triangles formed by O(3) atoms with interatomic distances Li–O(3) of 1.888 Å. The LiO_3 triangles with similar Li–O distances were already revealed in a series of metalloorganic compounds, namely in bicyclic structures of lithium ester enolates [20], in homoleptic titanium (III) thiolate complexes [21], and in lithium borylamide salts [22]. This kind of co-ordination is also anticipated for Li in the structure of bikitaite heated at temperatures higher than 480 °C [23].

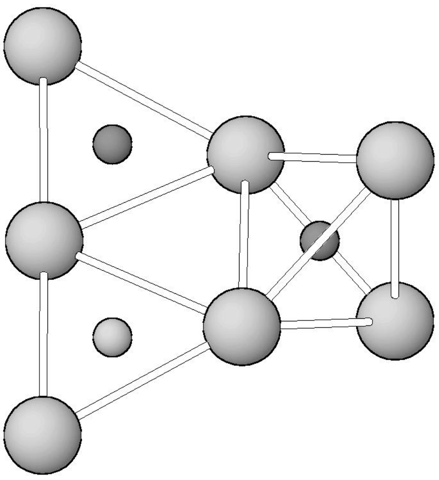

Fig. 3. The FBB composed of two BO_3 triangles and one BO_4 tetrahedron in the crystal structure of $LiBaB_9O_{15}$.

3.2. $BaBPO_5$

Similar to all stillwellite-like compounds, the main structural elements of $BaBPO_5$ are spiral tetrahedral chains [001] (Figs. 4 and 5) built of three-membered rings. The contacts between the BO_4 tetrahedra that form the central part of these chains are reinforced by PO_4 tetrahedra and thus $[BPO_5]$ heterotetrahedral chain complexes are produced. Like many other structures which contain complex chains formed by chemically different tetrahedra (for example, euclase, väryrynenite, hellandite etc.) the tetrahedra of cations with higher valence can be considered as the 'branches'. Spiral chains formed by BO_4 tetrahedra, screwing along the 3_2 axis, provide the linkage between the columns along [001] composed of Ba 10-fold polyhedra alternated with PO_4 tetrahedra. This kind of columns formed by alternating large cation polyhedra and tetrahedra

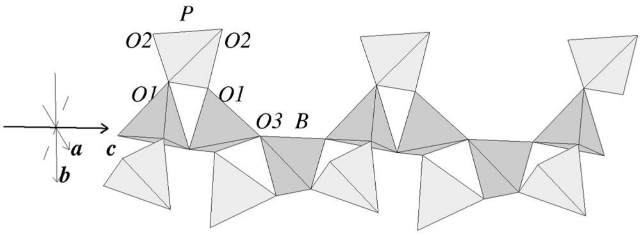

Fig. 5. The heterotetrahedral chain $[BPO_5]^{2-}$, running parallel to [001], in $BaBPO_5$.

were revealed in the structures of rhabdophane, xenotime, zircon, anhydrite and garnet.

The possible phase transformation at high temperature in the stillwellite structure type which is accompanied by the replacement of the polar space group $P3_1(3_2)$ by $P3_12$ was reported in Ref. [17]. Later on it was confirmed by the results of high-resolution neutron powder diffraction of $LaBGeO_5$ [18] which adopts at 530 °C the space group $P3_12$. During the heating of this phase the expansion of the La-polyhedron is higher compared to BO_4 and GeO_4 tetrahedra and the 9-fold coordination of La is replaced by a 10-fold coordination in the HT form. In this connection, the crystallization of $BaBPO_5$ with even bigger BaO_{10} polyhedra in space group $P3_22$ does not look completely unusual.

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