

# Ab initio structure determination of new compound $\text{Ba}_3(\text{BO}_3)(\text{PO}_4)$

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## Abstract

The crystal structure of new compound  $\text{Ba}_3\text{BPO}_7$  was determined by ab initio method from high-resolution conventional X-ray powder diffraction data. The Rietveld refinement converged to  $R_p = 5.92\%$ ,  $R_{wp} = 8.87\%$ ,  $R_{exp} = 5.00\%$  with the following details: Hexagonal, space group  $P6_3mc$ ,  $a = 5.4898(1) \text{ \AA}$ ,  $c = 14.7551(1) \text{ \AA}$ ,  $Z = 2$ . The basic unit of the structure is the  $[\text{BaO}_{10}]$ – $[\text{BO}_3]$ – $[\text{PO}_4]$  polar polyhedra-chain composed of  $\text{Ba1}$ – $\text{B}$ – $\text{P}$ – $\text{O}$  cluster. These chains, running along  $c$ -axis, stack in a HCP mode to build the whole structure with triangular prism channels. The channels are parallel to  $c$ -axis too, in which  $\text{Ba2}$  and  $\text{Ba3}$  are located.

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**Keywords:**  $\text{Ba}_3\text{BPO}_7$ ; Borophosphate; Structure determination; X-ray powder diffraction

## 1. Introduction

Alkaline or alkaline earth borates and phosphates such as  $\beta$ - $\text{Ba}_2\text{B}_2\text{O}_4$ ,  $\text{LiB}_3\text{O}_5$  [1,2] and  $\text{KTiOPO}_4$  [3] have been in research focus for decades for their wide applications in laser and nonlinear optic technologies. Recently, in the search for new functional materials, attention has been partly switched to borophosphates, which contain both the borate group and the phosphate group as basic structural units. Borophosphates, such as  $\text{MBPO}_5$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ ) [4,5],  $\text{Zn}_3\text{BPO}_7$ ,  $\text{Mg}_3\text{BPO}_7$  [6],  $\text{Na}_5\text{B}_2\text{P}_3\text{O}_{13}$  [7],  $\text{Co}_5\text{BP}_3\text{O}_{14}$  [8],  $\text{Ba}_3[(\text{PO}_4)_2\text{BPO}_4]$  [9], and  $\text{Pb}_3[(\text{PO}_4)_2\text{BPO}_4]$  [10] have been synthesized and characterized. The phase relations, crystal structures and vibrational spectroscopy of some alkaline earth borophosphates have been systematically investigated [11–13]. A new series of borophosphates  $A_3\text{BPO}_7$  ( $A = \text{Ca}, \text{Sr}, \text{Ba}$ ) have been obtained and characterized [14]. Here we report the structure determination of  $\text{Ba}_3\text{BPO}_7$  by conventional high-resolution powder X-ray diffraction.

## 2. Experimental

Polycrystalline  $\text{Ba}_3\text{BPO}_7$  was prepared by high-temperature solid state reactions. Analytically pure  $\text{BaCO}_3$ ,  $\text{H}_3\text{BO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  were mixed in a molar ratio of 3:1:1 and grounded, heated at  $1200^\circ\text{C}$  in a Pt crucible for 48 h and then cooled to room temperature.

X-ray powder diffraction data of  $\text{Ba}_3\text{BPO}_7$  were measured on an automated Philips PW3040/60 high-resolution diffractometer equipped with  $\text{Ge}(111)$  monochromator. Only  $\text{CuK}\alpha_1$  was used for diffraction. Experimental details are listed in Table 1. The data were collected in a continuous mode and then transferred into a stepscan-like format of stepsize  $2\theta = 0.008^\circ$ .

Powder second-harmonic generation measurement was performed with laser powder frequency doubler.

## 3. Results and discussion

### 3.1. Indexing

The powder diffraction pattern was indexed using the program TREOR [15], on the basis of a hexagonal cell:  $a = 5.4888(1) \text{ \AA}$ ,  $b = 5.4888(1) \text{ \AA}$ ,  $c = 14.7513(1) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$  (with figure of merit  $M_{33} = 153$ ,

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Table 1  
Experimental details of X-ray powder diffraction and Rietveld refinement for Ba<sub>3</sub>BPO<sub>7</sub>

Diffractometer	Philips PW3040/60
Radiation type	CuK $\alpha$ <sub>1</sub>
Wavelength (Å)	1.54060
Source to sample distance (mm)	240
Detector to sample distance (mm)	240
Scan mode	Continuous
Scan time (min)	570.86
Profile range (2 $\theta$ °)	9.00–120.00
Number of observations ( <i>N</i> )	13750
Number of contributing reflections	140
Number of structure parameters ( <i>P</i> <sub>1</sub> )	14
Number of profile parameters ( <i>P</i> <sub>2</sub> )	12
<i>R</i> <sub>B</sub> (%)	4.99
<i>R</i> <sub>p</sub> (%)	5.92
<i>R</i> <sub>wp</sub> (%)	8.87
<i>R</i> <sub>exp</sub> (%)	5.00
<i>S</i>	1.78

Note:  $R_B = \sum |I_o - I_c| / \sum I_o$ ,  $R_p = \sum |Y_{io} - Y_{ic}| / \sum Y_{io}$ ,  $R_{wp} = [\sum w_i (Y_{io} - Y_{ic})^2 / \sum (w_i Y_{io})^2]^{1/2}$ ,  $R_{exp} = [(N - P_1 - P_2) / \sum (w_i Y_{io})^2]^{1/2}$ ,  $S = \sum [w_i (Y_{io} - Y_{ic})^2 / (N - P_1 - P_2)]^{1/2}$ .

$F_{33} = 144$  (0.002953, 78)). The crystal system was assigned as hexagonal or trigonal with systematic absences:  $00l\ l = 2n + 1$ ;  $hhl\ l = 2n + 1$ .

### 3.2. Cell contents determination

The chemical formula, Ba<sub>3</sub>BPO<sub>7</sub>, was derived from the molar ratio and reaction properties of the starting materials. The unit cell should contain 2 formula, i.e., 6 barium, 2 phosphorus, 2 boron, and 14 oxygen atoms since the calculated density (4.883 g/cm<sup>3</sup>) is comparable with the measured density of known Ba-borophosphates [6]. Room temperature Raman scattering spectra and infrared transmission spectra measurements show that the phosphorous atoms are tetrahedrally coordinated while the boron atoms are triply coordinated [14] by oxygen atoms.

### 3.3. Space group determination

According to the cell dimensions and systematic absences, the possible space groups are  $P3_1c$ ,  $P\bar{3}_1c$ ,  $P6_3mc$ ,  $P\bar{6}2c$  and  $P6_3/mmc$ . Of these five space groups, two are centrosymmetric and the other three are noncentrosymmetric. The SHG measurement shows minor second harmonic effects, which indicates Ba<sub>3</sub>BPO<sub>7</sub> is either intrinsically noncentrosymmetric or centrosymmetric but with a little deviation. The noncentrosymmetric space groups are preferred because the center of symmetry can be easily added to the structure if it is centrosymmetric. Of the three noncentrosymmetric space groups,  $P6_3mc$  was first chosen for its higher symmetry. In fact,  $P3_1c$  is a subgroup of  $P6_3mc$ . All the symmetry elements of  $P3_1c$  are included in

$P6_3mc$ . The noncentrosymmetric space group  $P\bar{6}2c$  was also tried, but the structure could not be solved. After the structure was solved, symmetries among the unique atoms were carefully checked. The results show that there is no additional symmetry element(s).

### 3.4. Pattern decomposition

Integrated intensities for solving the structure through the techniques for single crystal analysis were extracted from the powder diffractogram in the range  $9^\circ < 2\theta < 120^\circ$  using the program Fullprof [16] on the basis of Le Bail profile-fitting procedure. Pattern decomposition with the space group  $P6_3mc$  converged to  $R_p = 3.98\%$ ,  $R_{wp} = 3.88\%$ . A set of 140 reflections was extracted from the powder diffraction pattern. For this space group, the intensities of exact overlapping reflections are equi-partitionable among the exact overlapping reflections [17]. The intensities of these reflections are thus accurate enough for the following work.

### 3.5. Structure determination

The direct methods program SHELX97 [18] was used to build the structure model from the extracted intensities. Although no identifiable molecular fragments showed in the E-map, the 3 independent Ba atoms are very obvious. The highest peak in the sequential differential Fourier electron density map was located at (0, 0, 0), which was assigned as phosphorus. Several more cycles of differential Fourier synthesis revealed the position of the rest independent atoms in the unit cell (Table 3).

### 3.6. Rietveld refinement

The trial structure built through direct methods and differential Fourier synthesis was then used as the starting model for the sequential Rietveld refinement. At the beginning, all the refinable atomic coordinates were attempted to be refined, but the refinement would not converge. So, the atomic coordinate *x* and *y* of O1 were adjusted to an ideal position, i.e., the [BO<sub>3</sub>] cluster was restrained to be an equilateral triangle with B at the center and O1 (including two symmetry equivalent atoms) on the vertexes of the triangle. The B–O bond length was determined in such a way that the bond valence summation of B should be 3<sup>+</sup>, the formal oxidation state of boron, in accordance with Brown's bond valence theory [19]. Similarly, the positions of O2 and O3 were also fixed to restrain the [PO<sub>4</sub>] cluster to be a regular tetrahedra. Then, the *z* coordinates of Ba1, Ba2, Ba3, O1, B and the profile parameters were refined. In the following cycles, the thermal parameters of Ba1, Ba2, Ba3 and O1, O2, O3 were set to the same values, respectively. And then, all the atoms were refined

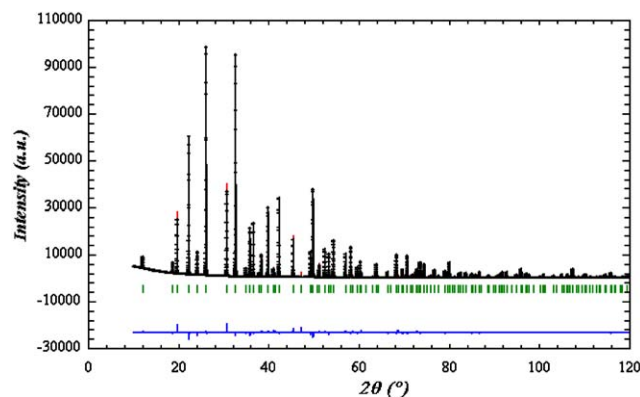


Fig. 1. The final Rietveld refinement plot for  $\text{Ba}_3\text{BPO}_7$ . Continuous line corresponds to observed pattern, the small crosses (+) the calculated values; vertical bars (|) indicate the Bragg positions. The bottom traces depicts the differential plot of experimental and calculated intensities.

Table 2  
Crystallographic data for  $\text{Ba}_3\text{BPO}_7$

Identification code	$\text{Ba}_3\text{BPO}_7$
Empirical formula	$\text{Ba}_3(\text{BO}_3)(\text{PO}_4)$
Formula weight	565.80
Temperature	293(2) K
Wavelength	1.54060 Å
Crystal system, space group	Hexagonal, $P6_3mc$
Unit cell dimensions	$a = 5.4898(1)$ Å, $\alpha = 90^\circ$ $b = 5.4898(1)$ Å, $\beta = 90^\circ$ $c = 14.7551(1)$ Å, $\gamma = 120^\circ$
Volume	$385.141(1)$ Å <sup>3</sup>
Z, Calculated density	2, 4.883 g/cm <sup>3</sup>
Absorption coefficient	120.079 mm <sup>-1</sup>
$F(000)$	488

Note: Cell parameters listed here are the final refined results, which are slightly different from the results of indexing procedure.

isotropically. The refinement procedure was very stable and converged to  $R_p = 5.92\%$ ,  $R_{wp} = 8.87\%$ ,  $R_{exp} = 5.00\%$ . The experimental pattern, the calculated pattern and the corresponding differential profile are shown in Fig. 1. The crystallographic details, final refined fractional coordinates and isotropic atomic thermal parameters for  $\text{Ba}_3\text{BPO}_7$  are listed in Tables 2 and 3, respectively. The observed and calculated intensities are given in Table 4.

### 3.7. Structure description and evaluation

Selected bond lengths and angles are given in Table 5. Fig. 2 shows the distribution of  $[\text{PO}_4]$  tetrahedron,  $[\text{BO}_3]$  triangles, and the barium atoms in the unit cell. As shown in Fig. 3(a), Ba1 is coordinated by 10 oxygen atoms, of which 6 from 3  $[\text{BO}_3]$  triangles and 4 from 2  $[\text{PO}_4]$  tetrahedron, to form the  $[\text{BaO}_{10}]$  polyhedron. The clusters are then linked together by oxygen atom O3

Table 3  
Atomic coordinates and equivalent isotropic thermal parameters (Å<sup>2</sup>) for  $\text{Ba}_3\text{BPO}_7$

Atom		x	y	z	$B_{eq}$
Ba1	2(a)	0.0000	0.0000	0.2186(7)	/
		0.0000	0.0000	0.2165(1)	1.030(17)
Ba2	2(b)	0.3333	0.6667	0.0321(6)	/
		0.3333	0.6667	0.0338(2)	1.030(17)
Ba3	2(b)	0.3333	0.6667	0.3877(5)	/
		0.3333	0.6667	0.3875(2)	1.030(17)
P	2(a)	0.0000	0.0000	0.0000	/
		0.0000	0.0000	0.0000	0.971(67)
B	2(b)	0.3333	0.6667	0.749(9)	/
		0.3333	0.6667	0.7540(3)	1.405(300)
O1	6(c)	0.524(10)	0.476(10)	0.259(6)	/
		0.5230(0)	0.4770(0)	0.2540(3)	1.570(64)
O2	6(c)	0.849(7)	0.151(7)	0.045(4)	/
		0.8478(0)	0.1522(0)	0.0345(0)	1.570(64)
O3	2(a)	0.0000	0.0000	0.407(18)	/
		0.0000	0.0000	0.3960(0)	1.570(64)

Note: 1st line, coordinates from SHELXL97; 2nd line, coordinates from Rietveld refinement  $B_{eq}$  is defined as one-third of the trace of the orthogonalized  $B_{ij}$  tensor.  $B$  for all atoms during the structure solution are set to be the default value by the program SHELX97 and not given here.

Table 4  
List of calculated and observed intensities and d-spacing of selected reflections for  $\text{Ba}_3\text{BPO}_7$

hkl	$I_{calc}$	$I_{obs}$	$d_{calc}$	$d_{obs}$	hkl	$I_{calc}$	$I_{obs}$	$d_{calc}$	$d_{obs}$
1 0 3	100.00	100.00	3.418	3.417	2 0 5	12.32	11.60	1.851	1.851
1 1 0	97.51	96.93	2.745	2.744	1 0 8	12.05	11.22	1.719	1.719
1 0 2	60.10	57.22	3.996	3.994	2 2 6	10.95	10.88	1.198	1.198
1 0 4	37.01	40.20	2.914	2.913	2 0 1	9.70	10.10	2.347	2.346
1 1 6	42.60	40.00	1.832	1.831	4 1 6	10.14	10.10	0.956	0.956
2 0 3	36.60	35.99	2.140	2.140	2 1 8	9.31	8.82	1.287	1.287
2 0 2	30.89	31.52	2.263	2.262	2 1 5	8.58	8.60	1.535	1.535
1 0 1	23.78	27.37	4.525	4.523	3 1 3	8.50	8.60	1.274	1.273
0 0 6	24.17	23.98	2.459	2.458	0 0 4	9.90	8.50	3.689	3.687
1 0 5	21.69	20.40	2.507	2.506	4 1 0	7.87	8.21	1.037	1.037
2 0 4	17.83	19.54	1.998	1.998	2 0 8	7.28	7.34	1.457	1.457
2 1 3	19.01	19.00	1.688	1.688	2 1 1	6.08	6.69	1.784	1.783
3 0 0	16.01	15.86	1.585	1.585	0 0 2	5.06	5.66	7.377	7.370
2 1 2	13.98	14.33	1.746	1.746	2 1 14	6.02	5.61	0.909	0.909
2 2 0	13.71	14.17	1.372	1.372	3 1 2	5.02	5.46	1.298	1.298
2 1 4	12.27	12.92	1.615	1.615	3 2 3	5.20	5.43	1.065	1.065
3 0 6	13.45	12.80	1.332	1.332					

Note: Only reflections with relative intensity greater than 5 are listed.

to form a  $[\text{BaO}_{10}]$ – $[\text{BO}_3]$ – $[\text{PO}_4]$  polar polyhedra-chain running along the  $c$ -axis, which is the basic unit of the crystal structure. These parallel chains, connected to each other by sharing oxygen atom O1, stack in the hexagonal close packing (HCP) mode to build a structure with triangular prism channels in which Ba2, Ba3 and their symmetry equivalents are located (Fig. 3(b)). The coordination geometries of Ba2 and Ba3 are shown in Figs. 4(a) and (b), respectively.

Table 5  
Selected Bond lengths [Å] and angles [°] for Ba<sub>3</sub>BPO<sub>7</sub>

Ba1–O1	2.820(1)	Ba3–O2#15	2.769(2)
Ba1–O1#1	2.820(1)	Ba3–O2#16	2.769(2)
Ba1–O1#2	2.820(1)	Ba3–O2#17	2.769(2)
Ba1–O1#3	2.820(1)	Ba3–O3#11	3.172(1)
Ba1–O1#4	2.820(1)	Ba3–O3#12	3.172(1)
Ba1–O1#5	2.820(1)	Ba3–O3	3.172(1)
Ba1–O2#6	2.998(2)		
Ba1–O2#7	2.998(2)	P–O2#8	1.534(0)
Ba1–O2#8	2.998(2)	P–O2#6	1.534(0)
Ba1–O3	2.706(2)	P–O2#7	1.534(0)
		P–O3#18	1.534(0)
Ba2–O1	3.716(4)		
Ba2–O1#14	3.716(4)	B–O1#17	1.366(0)
Ba2–O1#3	3.716(4)	B–O1#15	1.366(0)
Ba2–O2#5	2.748(0)	B–O1#16	1.366(0)
Ba2–O2#10	2.748(0)		
Ba2–O2#7	2.748(0)	O2#8–P–O2#6	109.537(0)
Ba2–O2#11	2.748(0)	O2#8–P–O2#7	109.537(0)
Ba2–O2#8	2.748(0)	O2#6–P–O2#7	109.537(0)
Ba2–O2#2	2.748(0)	O2#8–P–O3#18	109.405(0)
Ba2–O3#18	3.765(1)	O2#6–P–O3#18	109.405(0)
Ba2–O3#9	3.765(1)	O2#7–P–O3#18	109.405(0)
Ba2–O3#13	3.765(1)		
		O1#17–B–O1#17	120.000(0)
Ba3–O1#3	2.670(3)	O1#17–B–O1#15	120.000(0)
Ba3–O1#14	2.670(3)	O1#18–B–O1#15	120.000(0)
Ba3–O1	2.670(3)		

Note: [PO<sub>4</sub>] and [BO<sub>3</sub>] are restrained to be regular tetrahedron and triangles respectively Symmetry transformations used to generate equivalent atoms: #1  $x-1, y-1, z$ ; #2  $-y+1, x-y, z$ ; #3  $-x+y, -x+1, z$ ; #4  $-x+y, -x, z$ ; #5  $-y, x-y, z$ ; #6  $-y, x-y-1, z$ ; #7  $x-1, y, z$ ; #8  $-x+y+1, -x+1, z$ ; #9  $-x, -y+1, z-1/2$ ; #10  $-x+y+1, -x+2, z$ ; #11  $x, y+1, z$ ; #12  $x+1, y+1, z$ ; #13  $-x+1, -y+1, z-1/2$ ; #14  $-y+1, x-y+1, z$ ; #15  $-x+1, -y+1, z+1/2$ ; #16  $x-y, x, z+1/2$ ; #17  $y, -x+y+1, z+1/2$ ; #18  $-x, -y, z-1/2$ .

Bond valence calculations according to Brown's rules are listed in Table 6. It is obvious that the bond valence sums are reasonable.

#### 4. Discussion

To our knowledge, the other two borophosphates of the same formula type with Ba<sub>3</sub>BPO<sub>7</sub> are Zn<sub>3</sub>BPO<sub>7</sub> and Mg<sub>3</sub>BPO<sub>7</sub> [6]. But the structure type of these two compounds is different from that of Ba<sub>3</sub>BPO<sub>7</sub>. On the contrary, the atomic distribution of BaPBO<sub>3</sub> [20] and SrPBO<sub>3</sub> [21] are very similar to that of Ba<sub>3</sub>BPO<sub>7</sub> although they have different formula type (Table 7 and Fig. 5). For Zn<sub>3</sub>BPO<sub>7</sub>, if the phosphorus atom P is taken as the origin, and axis *a* is halved, the structure is still different from the Ba<sub>3</sub>BPO<sub>7</sub> structure. These differences perhaps stem from the different coordination environment of Zn and Ba. Compared with Ba, Zn has a smaller coordination number and the Zn–O polyhedron is relatively rigid. To form a new structure, these

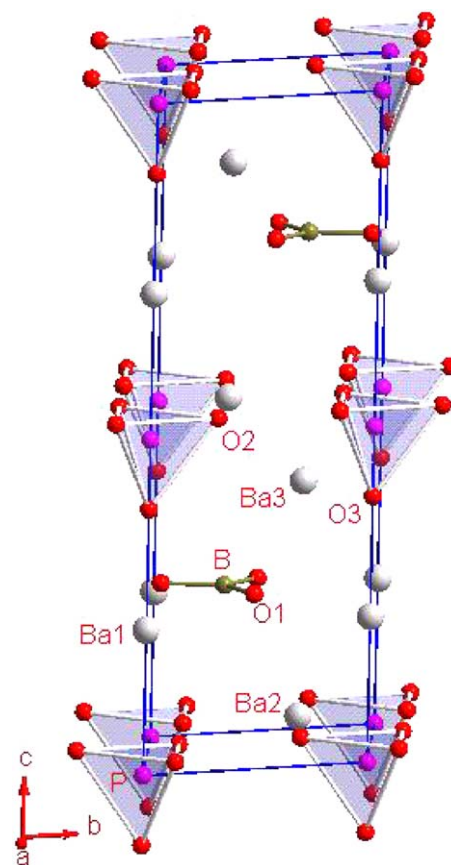


Fig. 2. Crystal structure of Ba<sub>3</sub>BPO<sub>7</sub>.

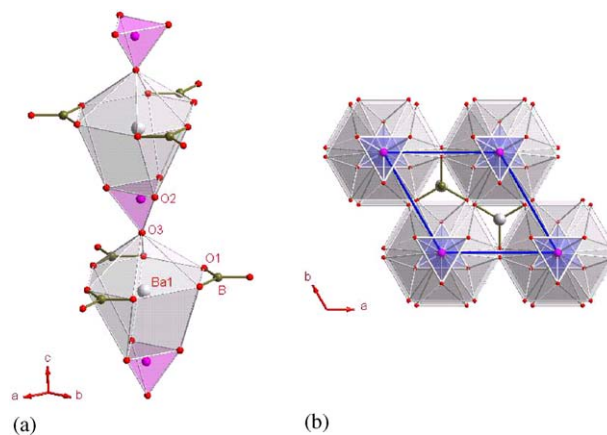


Fig. 3. (a) [BaO<sub>10</sub>]-[BO<sub>3</sub>]-[PO<sub>4</sub>] polar polyhedra-chain running along the *c*-axis and (b) stacking of [BaO<sub>10</sub>]-[BO<sub>3</sub>]-[PO<sub>4</sub>] polar polyhedra-chain in the unit cell.

requirements must be met. As a result, the Zn, [PO<sub>4</sub>] and [BO<sub>3</sub>] have to be adjusted to a suitable position.

In this work, compound Ba<sub>3</sub>BPO<sub>7</sub> was synthesized and the structure was investigated by conventional high-resolution X-ray powder diffraction. All the independent atoms in the unit cell were located through *ab initio* procedure and the structure was refined by Rietveld method. To solve the crystal structure from X-ray

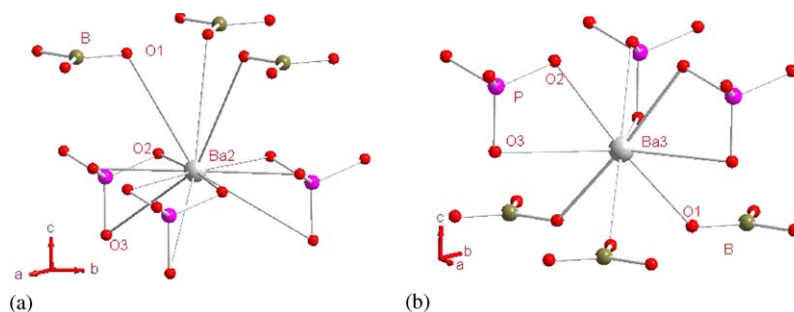


Fig. 4. (a) Coordination geometry of Ba<sub>2</sub> and (b) coordination geometry of Ba<sub>3</sub>.

Table 6  
Bond valence calculations for Ba<sub>3</sub>BPO<sub>7</sub>

	O1	O2	O3	$\sum v_{ij}$
Ba1	0.235	0.145	0.321	2.165
Ba2	0.021	0.286	0.018	1.834
Ba3	0.352	0.270	0.091	2.141
P	0	1.252	1.252	5.006
B	1.014	0	0	3.041
$\sum v_{ij}$	1.857	2.240	1.900	

Table 7  
Crystallographic data for Zn<sub>3</sub>BPO<sub>7</sub> and Ba<sub>3</sub>PBO<sub>3</sub>

Identification code	Ba <sub>3</sub> BPO <sub>7</sub>	Ba <sub>3</sub> PBO <sub>3</sub>	Zn <sub>3</sub> BPO <sub>7</sub>
Crystal system,	Hexagonal	Hexagonal	Monoclinic
space group	<i>P6<sub>3</sub>mc</i>	<i>P6<sub>3</sub>/mmc</i>	<i>Cm</i>
Unit cell dimensions	$a = 5.4898 \text{ \AA}$ $c = 14.7551 \text{ \AA}$	$a = 5.502 \text{ \AA}$ $c = 13.506 \text{ \AA}$	$a = 9.72 \text{ \AA}$ $b = 12.72 \text{ \AA}$ $c = 4.87 \text{ \AA}$ $\beta = 119.8^\circ$
Volume	$385.14 \text{ \AA}^3$	$354.10 \text{ \AA}^3$	$523.20 \text{ \AA}^3$
Z	2	2	4

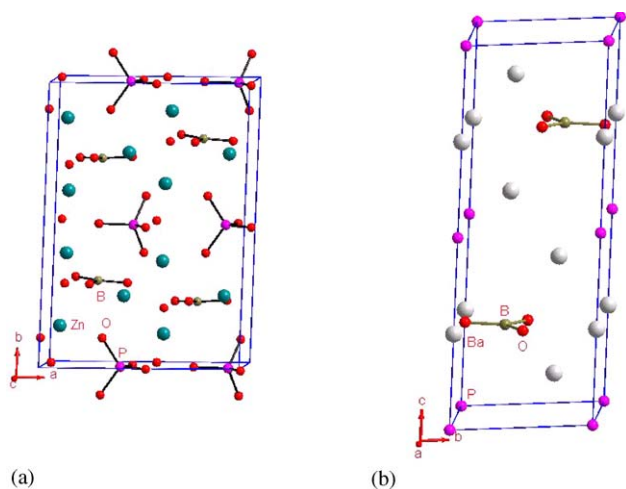


Fig. 5. (a) Crystal structure of Zn<sub>3</sub>BPO<sub>7</sub> and (b) crystal structure of Ba<sub>3</sub>PBO<sub>3</sub>.

powder diffraction data, building the model from known structure is a simple and powerful method. But this method is not infallible. As mentioned above, Zn<sub>3</sub>BPO<sub>7</sub> or Mg<sub>3</sub>BPO<sub>7</sub> seems to be a very good candidate model for Ba<sub>3</sub>BPO<sub>7</sub>. But the fact is that Ba<sub>3</sub>PBO<sub>3</sub> or Sr<sub>3</sub>PBO<sub>3</sub>, although has some difference with Ba<sub>3</sub>BPO<sub>7</sub>, can provide much more hints than Zn<sub>3</sub>BPO<sub>7</sub> or Mg<sub>3</sub>BPO<sub>7</sub>. The ab initio method is a good approach to solve the structure when no trial structures are available.

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