

Crystal Structure and Thermal Decomposition Studies of Barium Borophosphate, BaBPO₅

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The crystal structure and thermal decomposition process of barium borophosphate BaBPO₅ have been studied by a combination of X-ray powder diffraction (XRD) and vibration spectroscopic techniques. The structure of BaBPO₅ is refined by Rietveld technique, which indicates that the structure units of this compound are PO₄ and BO₄ tetrahedra as well as irregular rare earth polyhedra. The thermal decomposition process of BaBPO₅ have been observed by the XRD patterns of decomposition samples under a series of heat treatments. The Raman and infrared spectra of the initial compound BaBPO₅ and its decomposed products Ba₃BP₃O₁₂ and Ba₂P₂O₇ showed the variations of the anion groups of boron and phosphorus. Assignments have been deduced from the systematic investigation of natural compounds and isotopic species with the help of isotopic shift data of ¹⁰B–¹¹B. © 1998 Academic Press

1. INTRODUCTION

The structural complexity of borophosphate compounds is influenced by localized bonding arrangements of the principal components, B₂O₃ and P₂O₅. In the structure of borate, boron atoms can form planar or pyramidal BO₃ group with 3-oxygen atoms by trigonal *sp*² bonds, or tetrahedral BO₄ group with 4-oxygen atoms by tetrahedral *sp*³ bonds (1). Besides, borate can contain not only the above two simple groups, but also many complex groups, such as the more elaborate symmetrical B₃O₆ boroxol ring (2), unsymmetrical B₃O₇ ring which containing interconnected BO₃ and BO₄ (3), and infinite chain (BO₂)_n containing only threefold coordinated borons (4). In the structure of

phosphate there are mainly two kinds of groups: the relatively simple PO₄ tetrahedral group, and the complex P₂O₇ group consisting of two distorted tetrahedra PO₄ with nonlinear P–O–P bond (5). For the borophosphate Levesseur *et al.* (6) reported the existence of “BPO₇ group” which is the basic constituent of a silica-like network where B and P are four-fold coordinated and all oxygens are bridging ones. In addition, the introduction of alkaline earth oxide may create new structural units. Therefore, the considerable variety in crystal structure of borophosphate compounds provides a great deal object for the study aiming at exploring new functional materials, especially for the nonlinear optical materials.

BaBPO₅ compound was first prepared by Bauer (7), who defined their chemical formula as 2BaO·B₂O₃·P₂O₅. Melting point and X-ray powder diffraction data of this compound was given. X-ray powder diffraction patterns show that this compound is isostructural with stillwellite-LnBSiO₅ (*Ln* refers to lanthanides). Although B₂O₃, P₂O₅ and BaO are technologically important, no other report on the study of ternary compounds BaBPO₅ has been published except that of Bauer (7). In this paper, the crystal structure and thermal decomposition of stillwellite-type compounds BaBPO₅ have been investigated.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of the Compounds

The samples with nominal composition of BaBPO₅ including isotopic compound were synthesized by standard solid state reactions as described in (8). The prereacted

material was calcined at $950 \pm 10^\circ\text{C}$ for about 48 h, which was called as-synthesized samples. The sintering temperature of the heat treatments for the as-synthesized sample BaBPO_5 was from 1100°C to 1150°C .

Boron was available either as natural B (containing ^{10}B 18.83 mol%) or ^{10}B -rich one (^{10}B occupying 89.99 mol%). In order to assign and separate the internal vibrational spectra modes of boron and phosphorus polyhedra, and to propose the right structure information of anion polyhedra, the borate isotopic ^{10}B species of BaBPO_5 and its thermal decomposed product $\text{Ba}_3\text{BP}_3\text{O}_{12}$ were synthesized.

2.2. X-Ray Powder Diffraction Analysis

XRD structure analysis of the compounds was performed using a M18AHF X-ray diffractometer with $\text{CuK}\alpha$ radiation ($50\text{ kV} \times 200\text{ mA}$) by a graphite monochromator. The XRD data for phase identification and structure refinement were collected at ambient temperature. The scattering slit is 0.50° , the divergence slit 0.50° , and the receiving slit 0.15 mm . The scanning step width is 0.02° in 2θ . The sampling time of the XRD data for structure refinement is 2s per step, and the 2θ range is from 10° to 120° .

2.3. Vibration Spectra

The room temperature Raman scattering (RS) spectra of the compounds were obtained with a Spectra Physics Ar ion laser excitation. The Raman system includes a SPEX-1403 double monochromator with 1800 lines/mm holographic grating, a cooled R31034-02 photomultiplier, and photon counting electronics. All RS spectra were obtained at 200 mW of 5145 and 4880 Å laser lines, in order to eliminate misidentification of our Raman data due to possible fluorescence from trace impurities. The spectral band pass was 2 cm^{-1} .

Infrared transmittance spectra were measured at room temperature in KBr discs using a PE-983 G IR spectrophotometers in the frequency range $200\text{--}1500\text{ cm}^{-1}$. Wavenumber accuracy is within $\pm 2\text{ cm}^{-1}$ for narrow bands.

3. CRYSTAL STRUCTURE OF BaBPO_5

3.1. X-Ray Diffraction Data

The trial and error indexing program TREOR (9) was used in determining the unit cell parameters, and the PIRUM program (10) was used to refine the unit cell parameters from the observed 2θ values. This compound belongs to the hexagonal system, with lattice constants $a = 7.109(1)\text{ \AA}$, $c = 6.990(2)\text{ \AA}$, $V = 305.93(3)\text{ \AA}^3$, and $Z = 3$. Table 1 gives the indexing results of the XRD patterns of the BaBPO_5 compound.

TABLE 1
List of d -Value, Diffraction Intensities and the Indexes of BaBPO_5 Compound

h	k	l	$d_{\text{obs}} (\text{\AA})$	$d_{\text{cal}} (\text{\AA})$	I_{obs}	I_{cal}
1	0	1	4.62	4.62	39	43
1	1	0	3.56	3.55	100	100
1	1	1	3.17	3.17	9	8
2	0	0	3.08	3.08	39	35
1	0	2	3.04	3.04	75	80
2	0	1	2.817	2.817	14	14
1	1	2	2.493	2.492	12	12
0	0	3	2.328	2.330	23	11
2	1	0		2.327		14
2	0	2	2.310	2.310	26	27
2	1	1	2.208	2.208	48	44
1	0	3	2.179	2.179	3	3
3	0	0	2.053	2.052	11	9
3	0	1	1.9690	1.9692	7	6
1	1	3	1.9490	1.9486	17	17
2	1	2	1.9372	1.9370	51	53
2	2	0	1.7775	1.7773	6	5
3	0	2	1.7698	1.7697	6	6
2	2	1	1.7227	1.7225	6	5
3	1	0	1.7078	1.7076	15	14
0	1	4	1.6812	1.6810	8	9
3	1	1	1.6587	1.6588	5	4
2	1	3	1.6467	1.6465	5	5
2	2	2	1.5843	1.5842	9	9
3	1	2	1.5341	1.5343	8	8
0	2	4	1.5199	1.5196	8	8
2	2	3	1.4128	1.4131	8	2
3	2	0		1.4125		4
0	4	2	1.4086	1.4087	9	9
1	2	4	1.3974	1.3973	14	15
3	1	3	1.3775	1.3773	6	6
3	2	2	1.3095	1.3096	8	8

The diffraction patterns show only one systematic absence of reflections: that is, planes $(00l)$ are absent unless $l = 3n$. This criterion fails to distinguish the possible space groups, $P6_222$ ($P6_422$), $P6_2$ ($P6_4$), $P3_121$ ($P3_221$), $P3_112$ ($P3_212$) and $P3_1$ ($P3_2$), any one of which provides possible sets of threefold positions for the barium, boron, and phosphorus ions.

3.2. Initial Atomic Positions

A preliminary report on the crystal structure of BaBPO_5 's isostructural compound $Ln\text{BSiO}_5$ has been published by Voronkov et al. (11). They considered that the structural units of stillwellite are SiO_4 and BO_4 tetrahedra as well as irregular lanthanide polyhedra, and predicted the way of arranging the structural units by comparison the crystal structure of stillwellite with that of rhabdophanite ($\text{CePO}_4 \cdot n\text{H}_2\text{O}$). The space group of rhabdophanite used by

Mooney (12) is *P*6₂22, and the space group of stillwellite suggested by Voronkov *et al.* (11) is *P*3₁21.

Although the symmetry of BaBPO₅ is lower than that of CePO₄·*n*H₂O, its departure from the CePO₄·*n*H₂O structure arrangement must be small, otherwise unreasonable interatomic distances would result. Therefore, the atomic positions of CePO₄·*n*H₂O can be used as a reference in deducing the atomic positions of BaBPO₅. The initial atomic parameters can be obtained by the coordinate transformation from space group *P*6₂22 to *P*3₁21. The whole transformation process could be accomplished by modifying any arbitrary atomic coordinate (*x*, *y*, *z*) in space group *P*6₂22 to the corresponding coordinate (*y*, *x*, *z* − 1/3) in space group *P*3₁21.

3.3 Rietveld Refinement of XRD Data

According to the initial structure model described above, we refined the structure parameters of stillwellite-type compound BaBPO₅ with the powder X-ray diffraction data by the Rietveld method (13) using the computer program DBWS3.2S-PC-9005. The thermal parameters (*B*) were assumed to be isotropic, and the thermal parameters of alkaline earth and lighter atoms including boron, phosphate, and oxygen atoms were arbitrarily fixed at 0.5 and 1 Å², respectively. In the early stage of atomic position refinement, they were not refined in order to avoid divergence.

According to the assumed structural model, the positions of Ba, P, O(1), and O(2) can be determined roughly. For the positions of the leaving three oxygen atoms (O(3)), there are two possibilities: one is on the 3(b) site, the other is on the 6(c) site with half occupancy. The attempts to refine the structure with O(3) on the ideal 3(b) site were successful.

Taking O(3) atoms in the general 3(b) positions, the convergence of this structure refinement was obtained with good *R*-values. Table 2 lists the final *R* factors, the refined lattice constants, atomic and thermal parameters and their estimated standard deviations in parentheses for the stillwellite-type compound BaBPO₅. Table 3 lists the selected

TABLE 2
Refined Structure Parameters from Powder X-Ray Rietveld Analysis for BaBPO₅ in Space Group *P*3₁21, *Z* = 3

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Ba	3(a)	0.3949(32)	0	0.3333	0.31(4)
P	3(b)	0.3922(32)	0	0.8333	1.40(5)
B	3(a)	−0.0816(32)	0	0.3333	0.51(5)
O(1)	6(c)	0.3274(32)	0.1414(32)	−0.0392(32)	1.04(6)
O(2)	6(c)	0.4279(32)	0.8606(32)	−0.0323(32)	1.28(7)
O(3)	3(b)	−0.0355(32)	0	0.8333	1.11(2)

Note. *R*_p = 8.42%, *R*_{wp} = 12.34%, *s* = 1.87, *a* = 7.1094(1) (Å), *c* = 6.9895(1) (Å).

TABLE 3
Selected Bond Distances (Å) and Bond Angles(°) in BaBPO₅

Bonds or angles	<i>N</i> ^a	Bonds or angles	<i>N</i> ^a		
Ba–O(1)	2.916(7)	2	P–O(1)	1.575(9)	2
Ba–O(1)	2.887(7)	2	P–O(2)	1.476(9)	2
Ba–O(2)	2.688(7)	2	mean	1.526	
Ba–O(2)	2.792(7)	2	B–O(1)	1.604(9)	2
Ba–O(3)	2.765(7)	1	B–O(3)	1.338(9)	1
mean	2.815		B–O(3)	1.444(9)	1
			mean	1.497	
O(1)–O(2)	2.434(6)		O(1)–O(3)	2.442(10)	
O(1)–O(2)	2.507(6)		O(1)–O(3)	2.436(10)	
O(1)–P–O(2)	105.8(4)		O(1)–B–O(3)	106.4(8)	
O(1)–P–O(2)	110.5(4)		O(1)–B–O(3)	111.5(8)	

^a *N* is the number of equivalent bonds.

bond distances and bond angles for this compound, the mean interatomic distances and bond angles are in good agreement with the reported results on the structure of borate and phosphate compounds (14, 15). Figure 1 shows the Rietveld refinement results for the BaBPO₅. The plus symbols represent the observed diffraction patterns, the solid lines represent the calculated patterns, and the curves at the bottom of this figure represent the difference between the observed and calculated patterns. The short vertical lines mark the positions of possible Bragg reflections for the stillwellite compound BaBPO₅. The remarkably good fit between the observed and calculated patterns supports the structure parameters listed in Table 2.

Figure 2 shows a projection of the barium borophosphate structure in unit cell on the basal plane. The whole structure is composed of columns built of alternate barium and phosphorus polyhedra extending along the *C* axis, where barium and phosphorus were not collinear along the *C* axis. Figure 3 emphasizes this columns arrangement of ABPO₅

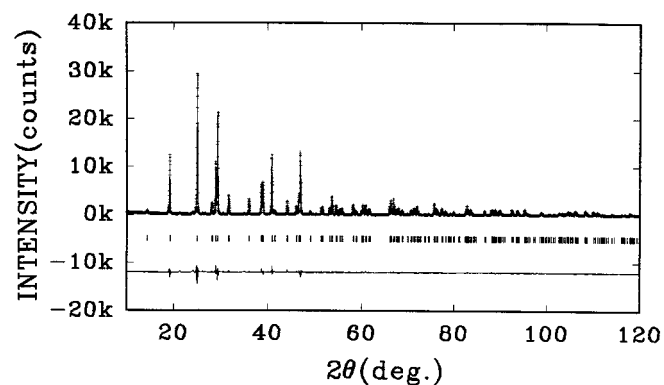


FIG. 1. Observed, calculated, and difference X-ray powder diffraction profiles for stillwellite type compound BaBPO₅.

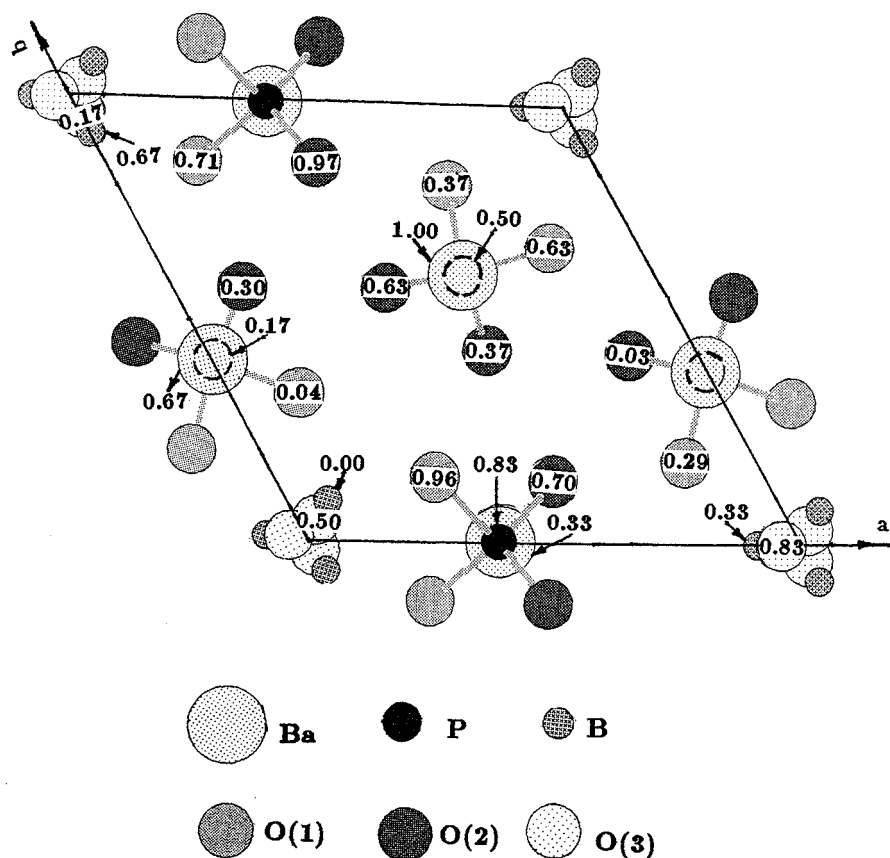


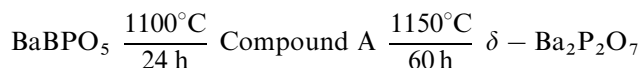
FIG. 2. Projection of BaBPO₅ structure in unit cell on basal plane. The numbers give the z coordinates of the atoms.

structure. Each barium–phosphorus columns is linked to four neighboring columns, so the open channels running through the structure along the hexagonal axis can accommodate the BO₄ tetrahedra. All the polyhedra share corners through oxygen atoms.

4. THERMAL DECOMPOSITION OF BaBPO₅

4.1. Thermal Decomposition Process

When the as-synthesized sample BaBPO₅ was sintered at 1100°C for more than 12 h, a new phase (denoted as compound A) appeared with the loss of weight. In order to investigate the thermal decomposition systematically, a series of heat treatments were carried out on the as-synthesized sample BaBPO₅. As the XRD patterns of sintering products shown in Fig. 4, the thermal decomposition process of BaBPO₅ can be summarized as follows:



4.2. Decomposition Products Analysis

In order to obtain the accurate composition of compound A, a series of samples with different nominal composition along the BaBPO₅–Ba₂P₂O₇ pseudo-binary system were synthesized by solid state reaction and the final sintering condition is at 1100°C for 24 h. The XRD patterns of the sample with chemical formula Ba₃BP₃O₁₂ were consistent with those of the compound A, and the chemical analysis of this sample showed the molar ratio with Ba : B : P ≈ 3 : 1 : 3.

The crystal structure of Ba₃BP₃O₁₂ has been determined by single crystal XRD method (16), the results are as follows: orthorhombic system, space group *Ibca*, with lattice constants $a = 7.0859(13) \text{ \AA}$, $b = 14.2903(22) \text{ \AA}$, $c = 22.1868(32) \text{ \AA}$, $V = 2246.6(3) \text{ \AA}^3$, and $Z = 8$. In this crystal, boron and phosphorus are tetrahedral coordinated by oxygen. The polyhedra form one-dimensional infinite helices that contain two additional PO₄ groups connected to the BO₄ unit.

The final decomposition product (sample D in Fig. 4) is the high temperature form of Ba₂P₂O₇ (denoted as δ -Ba₂P₂O₇) (18), it belongs to the hexagonal structure, space

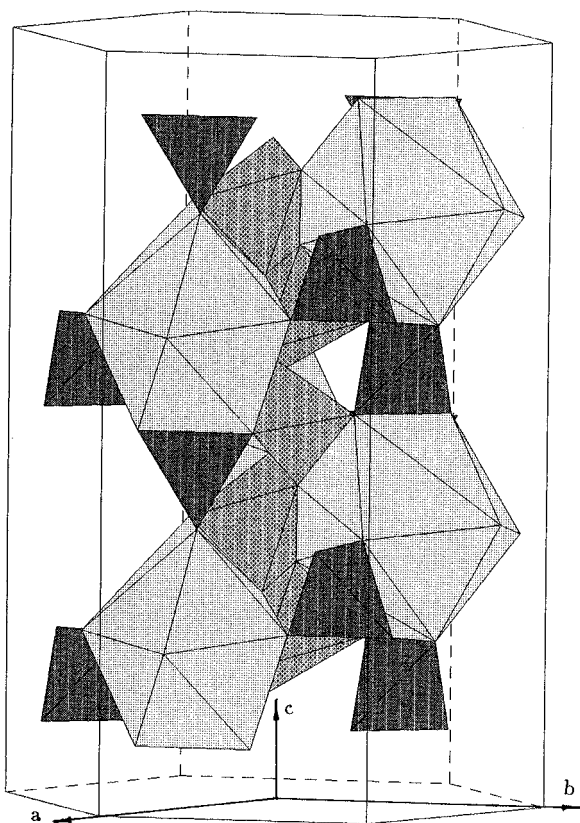


FIG. 3. A view of the structure to emphasize the columns arrangement of the BaBPO₅ structure.

group $P6_3$, with lattice constants $a = 9.4175 \text{ \AA}$, $c = 7.081 \text{ \AA}$, and $Z = 3$.

4.3. Vibrational Spectra Analysis

4.3.1. General considerations. Spectroscopy is an important technique for the characterization of inorganic anion groups and may be used in conjunction with X-ray diffraction for determination of crystal structure. Although several collections of IR and Raman spectra of borate and phosphate compounds have been published (19–26), no vibrational spectra investigation of borophosphate compounds has been carried out. The Raman and infrared spectra of BaBPO₅ and its decomposition products Ba₃BP₃O₁₂ and Ba₂P₂O₇ including their boron isotopic species are shown in Fig. 5 and 6. All the experimental results, including isotopic shifts, are collected in Tables 4–6, respectively.

As mentioned above, both BaBPO₅ and Ba₃BP₃O₁₂ compounds contain BO₄⁵⁻ and PO₄³⁻ tetrahedra sharing one oxygen atom, so there are two possible group theoretical treatments for the interpretation of the intramolecular modes, one is to interpretate the spectra by the vibrations of

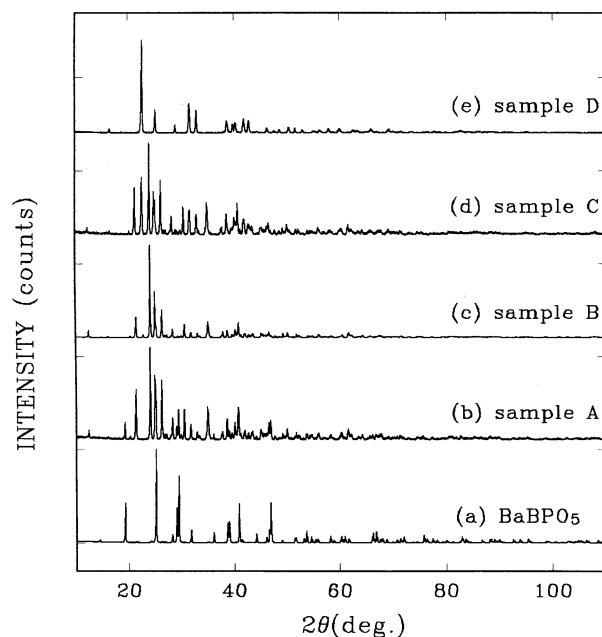


FIG. 4. X-ray powder diffraction patterns of the sintering products of BaBPO₅ in different heat treatment conditions: (a) the as-synthesized sample BaBPO₅; (b) sample A annealed at 1100°C for 12 h, phase is identified as BaBPO₅ + compound A; (c) sample B annealed at 1100°C for 24 h, phase is identified as pure compound A; (d) sample C annealed at 1100°C for 48 h, phase is identified as pure compound A + Ba₂P₂O₇; (e) sample D annealed at 1150°C for 60 h, phase is identified as pure compound Ba₂P₂O₇.

the tetrahedral BO₄⁵⁻ and PO₄³⁻ units separately; the other is by the treatment of the whole BPO₇⁶⁻ units with some supplement of BO₄⁵⁻ and PO₄³⁻ units. The choice of interpretation treatments could be determined by the comparison with the vibrational spectra of BPO₄. The compound BPO₄ synthesized under the general conditions has tetragonal structure, space group $I4$, with lattice constants $a = 4.3425 \text{ \AA}$, $c = 6.6415 \text{ \AA}$, and $Z = 2$. The crystal structure belongs to HO₇-type (27), and is formed by infinite chains of BPO₇ units, so its vibrational spectra could be used as a reference. For the sake of convenience, the vibrational spectra of BPO₄ are also shown in Figs. 5 and 6. By careful analysis of the spectra of these compounds, it was found that most of the surplus bands of Ba₃BP₃O₁₂, which did not appear in the spectra of BaBPO₅, are consistent with the characteristic bands of BPO₄. From another point of view, it was also verified that the vibration spectra of BaBPO₅ could only be interpreted in terms of BO₄ and PO₄ units, not of BPO₇ units; and conversely, the vibrational spectra of Ba₃BP₃O₁₂ could only be interpreted in terms of the whole BPO₇⁶⁻ units with some supplementation by BO₄⁵⁻ and PO₄³⁻ units.

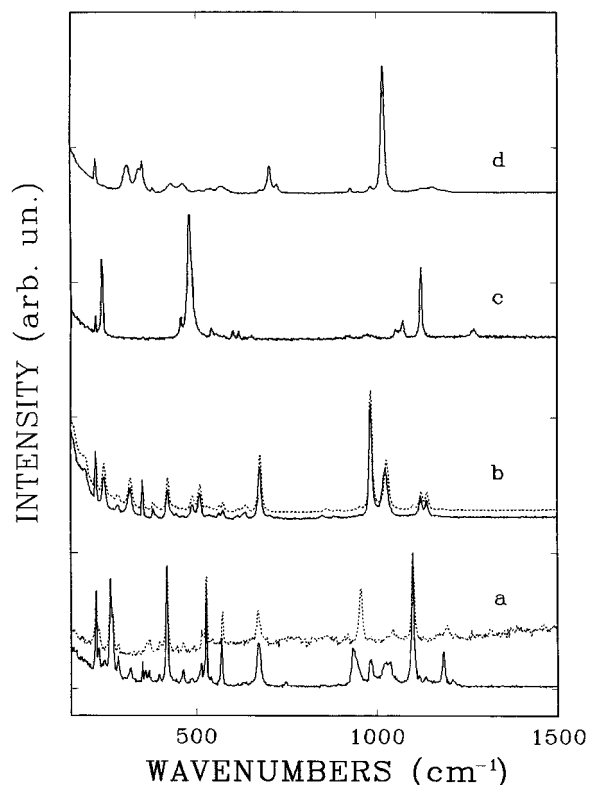


FIG. 5. Raman spectra of (a) BaBPO₅, (b) Ba₃BP₃O₁₂, (c) BPO₄, and (d) Ba₂P₂O₇ showing the ¹⁰B–¹¹B isotopic shifts. The dotted lines represent the spectra of ¹⁰B isotopic species.

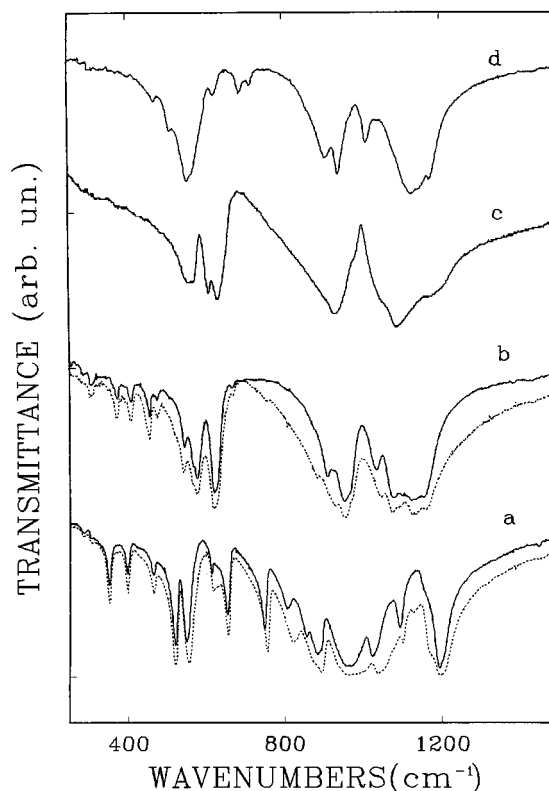


FIG. 6. Infrared spectra of (a) BaBPO₅, (b) Ba₃BP₃O₁₂, (c) BPO₄, and (d) Ba₂P₂O₇ showing the ¹⁰B–¹¹B isotopic shifts. The dotted lines represent the spectra of ¹⁰B isotopic species.

4.3.2. *Vibrational spectra assignments of BaBPO₅.* These spectra may be divided into three regions approximately:

- (1) A series of high-frequency bands which are observed in 1200–650 cm⁻¹ region: these are related to the stretching vibrations of the tetrahedral BO₄ and PO₄ ions;
- (2) A pattern of bands in the 650–360 cm⁻¹ region, these bands are expected to be due to the bending vibrations of the tetrahedral groups;
- (3) The bands below 360 cm⁻¹ is corresponded to the external modes.

The internal modes of BO₄ and PO₄ ions can be assigned on the basis of results obtained from vibrational spectra measurements of other borate and phosphate groups, and from the expectation that the internal modes of the “free” tetrahedral complex will be close in frequency to that of the parent mode. The fundamental vibrational frequencies for BO₄ and PO₄ ions are listed in Table 7, two sets of values are given for each ion in comparison, one is for the “free” complex (in solution) and the other for the solid compounds. As discussed above, in such crystals BO₄ and PO₄ tetrahedra co-shared one oxygen atom, so the vibrational modes relating the motion of this atom may interact. On the other hand, their corresponding vibrational frequencies of the fundamental are so close, especially for the asymmetrical

stretching mode ν_3 . Therefore, it is worthwhile to investigate the vibrational spectra by the study of isotopic species.

According to the expected isotopic shifts evaluation for purely ν_3 and ν_4 of BO₄⁵⁻ (28), the isotopic shifts related to the BO₄⁵⁻ asymmetrical stretching mode ν_3 should be about 25 cm⁻¹, that of ν_4 should be about 3 cm⁻¹. As shown in Table 4, there is substantial discrepancy of the isotopic shifts in the ν_3 (BO₄) region: the values are from 4 to 22 cm⁻¹. If the shift is too large for a totally symmetric vibration, and too small for an asymmetric vibration, it is clear that this bands must be assigned to complex vibrations with simultaneous asymmetric character ν_3 (BO₄) and other modes.

The 1200–360 cm⁻¹ region is essentially related to internal (stretching and bending) modes of the BO₄⁵⁻ and PO₄³⁻ tetrahedra whereas most of the lower frequency bands must be assigned to external modes. The tentative assignments proposed in Table 4 have been deduced, which will not be discussed in details. The stretching frequencies of the BO₄⁵⁻ and PO₄³⁻ groups have been assigned with the help of isotopic data of ¹⁰B–¹¹B, some of the observed stretching frequencies can not be assigned to a vibration which could be specifically symmetric (ν_1) or asymmetric (ν_3) with respect to the special boron or silicon atoms. This result is not unexpected, since under the influence of the site group (C_2)

TABLE 4
Raman and Infrared Band Wavenumbers (cm⁻¹), Isotopic Shifts, and Assignments^a for BaBPO₅

Raman			Infrared			Assignments
BaB ¹⁰ PO ₅	BaB ¹¹ PO ₅	Δν	BaB ¹⁰ PO ₅	BaB ¹¹ PO ₅	Δν	
1194 m	1214 w 1190 s	4	1197 s 1103 m	1196 s 1095 s	8	v ₃ (PO ₄) v ₃ (PO ₄) + v ₃ (BO ₄)
1098 s	1098 s					v ₃ (PO ₄)
1044 w	1028 s	16	1038 s 969 br.	1022 s 965 s	16 4	v ₃ (BO ₄) v ₃ (PO ₄) + v ₃ (BO ₄) v ₃ (BO ₄)
956 s	934 s	22	895 s	885 s 856 sh.	10	v ₃ (BO ₄) + v ₁ (PO ₄) v ₃ (BO ₄)
			824 m	805 m	19	
			756 s	748 s	8	v ₁ (BO ₄) + v ₃ (BO ₄)
670 s	672 s	2	656 s	654 s	2	v ₁ (BO ₄)
			618 w	614 w	4	v ₄ (BO ₄)
574 m	570 m	4	555 s	549 s	6	
528 s	528 s		520 s	520 s		v ₄ (PO ₄)
514 w	514 w					
462 m	462 m		465 m	466 m	1	v ₂ (BO ₄) + v ₂ (PO ₄)
418 s	418 s					
396 w	396 w		398 m	397 m	1	
368 m	368 w					
360 w	358 w 316 m		351 m	350 m 316 m		
282 w	280 m					External modes
260 s	260 s					
224 m	226 m					

^a Relative intensities: s, strong; m, medium; w, weak; sh., shoulder; br., broad.

and factor group (D_3), both ν_1 and ν_3 of the free tetrahedra are split into several components, some of which belong to the same representation and thus are able to interact. But here again, the study of isotopic species is the only way to prove experimentally that such interactions do really occur.

4.3.3. Vibrational spectra assignments of Ba₃BP₃O₁₂. As discussed above, the intramolecular modes of Ba₃BP₃O₁₂ can be interpreted by mainly BPO₇⁶⁻ units with some supplement of BO₄⁵⁻ and PO₄³⁻ units. Therefore, in the spectra of Ba₃BP₃O₁₂ except the bands which are assigned as the vibrational modes of BPO₇ chains, the remaining bands are in agreement with the general vibrational modes of BO₄⁵⁻ and PO₄³⁻ tetrahedral groups. The tentative assignments have been deduced in Table 5.

4.3.4. Vibrational spectra assignments of Ba₂P₂O₇. Many investigators have measured and analyzed the infrared spectra of pyrophosphates for structural information (28, 29), but published Raman spectroscopic data on pyrophosphates are extremely rare, except for the vibrational spectra of α -alkaline earth pyrophosphates (30) and Na₄P₂O₇ in melt (31).

The Raman spectrum of δ -Ba₂P₂O₇ is illustrated in Fig. 5 while its infrared spectrum is illustrated in Fig. 6. Its empirical band assignments are listed in Table 6. The assignments are made empirically with respect to those reported earlier for the α -Ba₂P₂O₇ (30). Even though δ -Ba₂P₂O₇ and α -Ba₂P₂O₇ possess different factor groups, i.e., δ -Ba₂P₂O₇ possess hexagonal structure, but α -Ba₂P₂O₇ has orthorhombic structure, their observed structure such as band shapes and relative intensities of bands are somewhat similar. Apparently, these similarities for the two different structure crystals can be related to the same anion groups P₂O₇⁴⁻.

The band assignments made in this investigation for δ -Ba₂P₂O₇ are consistent with those made earlier for α -Ba₂P₂O₇ (see Table 6). For instance, the intense band in the Raman spectrum at 1018 cm⁻¹ can be assigned to the symmetric terminal P–O stretching mode. This mode was observed at 1049 cm⁻¹ for α -Ba₂P₂O₇. Also, this Raman band is more intense than the band belonging to the symmetric bridge P–O stretching mode. The strong infrared band of δ -Ba₂P₂O₇ at 1126 and 1172 cm⁻¹ can be assigned as an antisymmetric terminal P–O stretch mode, where

TABLE 5
Raman and Infrared Band Wavenumbers (cm^{-1}), Isotopic Shifts, and Assignments^a for $\text{Ba}_3\text{BP}_3\text{O}_{12}$

Raman		Infrared		Assignments
$\text{Ba}_3\text{BP}_3\text{O}_{12}$	BPO_4	$\text{Ba}_3\text{BP}_3\text{O}_{12}$	BPO_4	
1140 m		1126 s, br.		$\nu_3(\text{PO}_4)$
1122 m	1124 m			$\nu(\text{BPO}_7)$
	1074 w	1079 s, br.	1091 s, br.	
		1037 (13 ^b) sh.		$\nu_3(\text{BO}_4)$
1024 m				$\nu_3(\text{PO}_4)$
984 s		957 s		$\nu_1(\text{PO}_4)$
		918 (22) sh.		$\nu_3(\text{BO}_4)$
676 m				$\nu_1(\text{BO}_4)$
636 w				$\nu_4(\text{BO}_4)$
		623 s	630 m	
			608 m	$\nu(\text{BPO}_7)$
		577 s	560 m	
574 w				$\nu_4(\text{BO}_4)$
510 m		543 w		$\nu_4(\text{PO}_4)$
488 w	482 s			$\nu(\text{BPO}_7)$
		453 m		
420 m		406 w		$\nu_2(\text{BO}_4) + \nu_2(\text{PO}_4)$
378 w		370 (10) w		
316 m		305 w		External modes
224 m	236 m			$\nu(\text{BPO}_7)$

^a Relative intensities: s, strong; m, medium; w, weak; sh., shoulder; br. broad.

^b The figures in parentheses denote the isotopic shifts of $\text{Ba}_3^{10}\text{BP}_3\text{O}_{12}$.

$\alpha\text{-Ba}_2\text{P}_2\text{O}_7$ show this mode at 1109, 1126, and 1156 cm^{-1} , respectively. The intense infrared band of $\delta\text{-Ba}_2\text{P}_2\text{O}_7$ at 553 cm^{-1} is likely to be the antisymmetric deformation modes, where this mode is observed in the infrared spectrum of $\alpha\text{-Ba}_2\text{P}_2\text{O}_7$ near 556 cm^{-1} . Similar relationships observed between the other infrared and Raman bands of $\delta\text{-Ba}_2\text{P}_2\text{O}_7$ and $\alpha\text{-Ba}_2\text{P}_2\text{O}_7$ can be used in the assignment of the remaining internal vibrational modes for the $\text{P}_2\text{O}_7^{4-}$ anion of $\delta\text{-Ba}_2\text{P}_2\text{O}_7$.

5. CONCLUSIONS

The crystal structure and thermal decomposition process of barium borophosphate BaBPO_5 have been studied by a combination of X-ray powder diffraction (XRD) and vibration spectroscopic techniques. The structure of BaBPO_5 is refined by Rietveld technique, which indicates that the structure units of this compound are PO_4 and BO_4 tetrahedra as well as irregular rare earth polyhedra. The thermal decomposition process of BaBPO_5 have been observed by the XRD patterns of decomposition samples under a series of heat treatments.

The Raman and infrared spectra of the initial compound BaBPO_5 and its decomposed products $\text{Ba}_3\text{BP}_3\text{O}_{12}$ and

TABLE 6
Raman and Infrared Band Wavenumbers (cm^{-1}) and Assignments^a for $\delta\text{-Ba}_2\text{P}_2\text{O}_7$

Raman		Infrared		Assignments
$\delta\text{-Ba}_2\text{P}_2\text{O}_7$	$\alpha\text{-Ba}_2\text{P}_2\text{O}_7$	$\delta\text{-Ba}_2\text{P}_2\text{O}_7$	$\alpha\text{-Ba}_2\text{P}_2\text{O}_7$	
	1167 w	1172 sh.	1156 sh.	
1154 w	1164 w			
	1128 m	1126 s, br.	1126 s, br.	$\nu_{\text{as}}(\text{PO}_3)$
	1102 w		1109 s, br.	
	1090 w			
1018 s	1049 s	1013 m	1034 m	$\nu_{\text{s}}(\text{PO}_3)$
984 w	1004 w		1003 s	$\nu_{\text{as}}(\text{PO}_3)$
928 w	953 m	939 s	969 sh.	$\nu_{\text{as}}(\text{POP})$
		910 m	958 s	
724 w	753 s	715 w	736 m	$\nu_{\text{s}}(\text{POP})$
704 m		686 m		
	617 w	621 w	609 w	
	605 w		603 w	
570 w	570 m		564 sh.	
	552 w	553 s	556 s	
540 w	534 w	509 sh.	539 m	$\delta(\text{PO}_2)$
460 w	485 m		487 w	
428 w	443 w	470 w	472 w	
378 w	350 sh.		431 w	
340 m	336 m		337 w	

^a Relative intensities: s, strong; m, medium; w, weak; sh., shoulder; br. broad.

$\text{Ba}_2\text{P}_2\text{O}_7$ showed the variations of the anion groups of boron and phosphorus. The preceding vibrational spectra analysis may be considered as a good example of the possibilities offered by the isotopic substitution and reported data comparison in the case of crystals of moderate to fair complexity. Although such considerations about the mixing or nonmixing of vibrations remain qualitative in nature, they correspond to realistic, and not simply reasonable, assignments. Maybe more detailed assignments could be deduced from the investigation of single crystals. But even in this case, this type of investigation is unable to give information about the mixing of normal modes which belong to the

TABLE 7
Vibrational Frequencies of the Fundamental (in cm^{-1}) for BO_4 and PO_4 Ions

Ref.	System	$\nu_1(A_1)$	$\nu_2(E)$	$\nu_3(F_2)$	$\nu_4(F_2)$
BO_4 (24)	$\text{B}(\text{OH})_4^-$ in aqueous solution	754	379	945	533
(19)	Rare-earth borates	854	481	1050	702
PO_4 (25)	Na_3PO_4 in aqueous solution	938	420	1017	567
(26)	General compounds	980	363	1082	515

same representation. Thus, it appears practically impossible to arrive at a detailed, unequivocal correlation between the observed frequencies and the various vibrational modes.

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