

# X-RAY Powder Diffraction and IR Study of Calcium Borophosphate, $\text{CaBPO}_5$

**A. BAYKAL, G. GÖZEL, M. KIZILYALLI\***

*Department of Chemistry Middle East Technical University,  
Ankara-TURKEY*

**M. TOPRAK**

*Royal Institute of Technology, Department of Material Science and Engineering,  
Materials Chemistry Division, Stockholm-SWEDEN*

**R. KNIEP**

*Max-Planck-Institut Für Chemische Physik Fester Stoffe  
im VEM-Sachsenwerk Pirnaer Landstr. 176 D-01257 Dresden-GERMANY*

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In this study,  $\text{CaBPO}_5$  was synthesized by different solid state reactions than reported before and its X-ray powder diffraction and IR data were reported. In one of these solid state reactions  $\text{BPO}_4$  was used as a phosphating agent.

The examination of the X-ray powder diffraction data showed that this compound crystallized in a hexagonal system and the refined unit cell parameters were  $a = 6.684$ ,  $c = 6.616(2)$  Å, with  $Z=3$  as reported before. From the observed reflections, the space group was determined as  $P3_121$ , and its density was found to be 3.15 g/cc. The X-ray powder diffraction and IR data, which were in agreement with the reported crystal structure, are given the first time in this work.

**Key Words:** Ca, Phosphate, Borophosphate,  $\text{CaBPO}_5$ , X-ray Powder Diffraction, and Crystal structure

## Introduction

Alkaline-earth borophosphates are interesting solid-state materials which have an isoelectronic relationship with silicates. These materials are biocompatible with the living body, so they are called bioceramics. The crystal structure of these alkaline earth borophosphates has been solved and reported by Gözel<sup>1</sup> and Kniep et al.<sup>2</sup> for the first time in the literature. The infrared studies of these materials have not been reported before. The lack of vibrational spectra can lead to a misinterpretation of their X-ray powder diffraction data.

Most of the best-known materials with optical and electro-optical applications are either borates or phosphates<sup>3</sup>. Names such as BBO ( $\beta\text{-BaB}_2\text{O}_4$ )<sup>4</sup>, LBO ( $\text{LiB}_3\text{O}_5$ )<sup>5</sup>, KTP ( $\text{KTiOPO}_4$ ) and KDP ( $\text{KH}_2\text{PO}_4$ )<sup>6</sup> are well-known commercially and are heavily used industrially for making a range of different optical

\*To whom correspondence should be addressed

elements. In the last couple of years, the first few compounds combining both borate and phosphate groups were synthesized and structurally characterized. High temperature syntheses have produced a handful of metal borophosphates, all of main group metals.

Rulmont and Tarte<sup>7</sup> were able to synthesize LnBSiO<sub>5</sub> and LnBGeO<sub>5</sub>, which have stillwellite (CeBSiO<sub>5</sub>) structure. These compounds received some attention in connection with the hydrothermal crystallization of a radioactive waste storage glass.

As has been stated before<sup>2</sup> in the field of microporous solids, the intermediate phases of M<sub>2</sub><sup>I</sup>O M<sup>II</sup>O-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> (-H<sub>2</sub>O) systems (M<sup>I</sup> = alkali metal, M<sup>II</sup> = alkaline earth metal) have been "forgotten". Bauer<sup>8,9</sup> reported the synthesis and X-ray diffraction patterns of the isostructural (hexagonal) phases M<sup>II</sup>[BPO<sub>5</sub>] (M<sup>II</sup> = Ca, Sr, Ba). PbBPO<sub>5</sub> has been synthesized and characterized by Rulmont and Tarte<sup>10</sup>.

Ca[BPO<sub>5</sub>] was obtained as a single-phase microcrystalline powder using solid state reactions at 900°C by Gözel<sup>1</sup> and Kniep *et al.*<sup>2</sup>, but Sr[BPO<sub>5</sub>] was not successfully obtained as a single phase. <sup>11</sup>B and <sup>31</sup>P Mass-NMR spectroscopy showed that Ca[BPO<sub>5</sub>] was nearly pure but Sr[BPO<sub>5</sub>] contains β-Sr<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and BPO<sub>4</sub> as impurities<sup>11</sup>.

Ramamoorthy and Rockett<sup>12</sup> confirmed the existence of Ca[BPO<sub>5</sub>] from phase equilibria studies on the system CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> at 900°C. Sedmale *et al.*<sup>13</sup>, using the BaO.B<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub> system, prepared a glassy compound. After Gözel's study<sup>1</sup> on the crystal structure solution of MBPO<sub>5</sub>, Shi Y. *et al.*<sup>14</sup> studied the crystal structure and thermal decomposition of BaBPO<sub>5</sub> by X-ray diffraction and vibration spectroscopy and found that the decomposed products are Ba<sub>3</sub>BP<sub>3</sub>O<sub>12</sub> and Ba<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. The structure of BaBPO<sub>5</sub> is refined by the Rietveld technique, which indicates that the structure units of this compound are PO<sub>4</sub> and BO<sub>4</sub> tetrahedra as well as irregular rare earth polyhedra.

The aim of this work is to synthesize Ca[BPO<sub>5</sub>] by different solid state reactions and confirm the reported structure by indexing X-ray powder diffraction data and interpreting the IR data.

## Experimental

### Substances

CaHPO<sub>4</sub>.2H<sub>2</sub>O, H<sub>3</sub>BO<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub> (From Aldridge), and BPO<sub>4</sub> (prepared in our laboratory).

### Instrumentation

X-ray powder diffraction patterns (XRD) were taken by Philips diffractometer with PW 1050/25 goniometer and Co (Kα 30-40 kV, 10-20 mA, λ = 1.79021 Å) radiation, and by Huber Diffractometer with Cu (Kα<sub>1</sub> 30-40 kV, 10-20 mA, λ = 1.54059 Å).

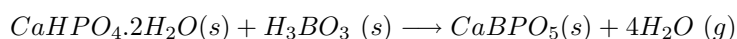
A Nicolet 510 FTIR Infrared Spectrometer was used in the region 400-4000 cm<sup>-1</sup>. Spectra of solid samples were obtained from KBr pellets with 100:30 (wt/wt) KBr to product ratio.

The solid state reactions were carried out in air with the aid of Heraeus, SFL West-6100, and Ney 2-525 furnaces. Heating range was 550-1500°C using Cr-Ni-Cr and Rh-Pt-Rh thermocouples and controller.

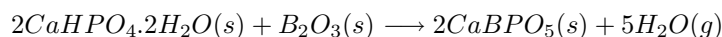
## Procedure

The synthesis of CaBPO<sub>5</sub> was attempted with three different sets of starting materials. The reactants were weighed separately and ground together in an agate mortar. Then the mixture was transferred into a porcelain crucible, weighed again and put into a furnace for heating.

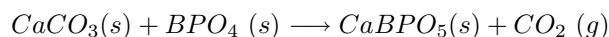
*i.* In the first method, for comparison purposes, the compound was synthesized by heating CaHPO<sub>4</sub>·2H<sub>2</sub>O with H<sub>3</sub>BO<sub>3</sub> at 600°C for 6 h and then at 900°C for three days using the procedure of Bauer *et al.*<sup>8,9</sup> and Gözel<sup>1</sup>. The reaction was as follows:



*ii.* The reaction reported above was repeated by using B<sub>2</sub>O<sub>3</sub> instead of H<sub>3</sub>BO<sub>3</sub>. The reactants were heated at 900°C for 3 days. The reaction is given by the following equation:



*iii.* The third method is reported for the first time in this work. BPO<sub>4</sub> was previously synthesized and used in the following reaction. The mixture of reactants was heated at 900°C for 4 days. The predicted reaction is as follows:



## Results and Discussion

In the first and second method, CaBPO<sub>5</sub> was obtained successfully. Theoretical and experimental weight losses were in agreement, which were 31% and 30.7% for the first reaction, and 21.75 and 22.4% for the second, respectively.

In the X-ray powder pattern of the product obtained by the third method, together with CaBPO<sub>5</sub>, weak lines of BPO<sub>4</sub> were also observed. The theoretical and experimental losses were in agreement, which were 21.3% and 21.7% respectively. The X-ray powder indexing data and the X-ray powder diffraction patterns of the samples obtained in experiments *i*, *ii* and *iii* are given in Table 1 and Figure 1 respectively.

There was good agreement between the X-ray powder patterns obtained by different solid state reactions. CaBPO<sub>5</sub> obtained using the reaction in the first experiment was indexed in the hexagonal system with the unit cell parameters  $a = 6.684(2)$  and  $c = 6.616(2)$  Å, and space group P3<sub>1</sub>21, which were in good agreement with the reported data<sup>1,2</sup>.

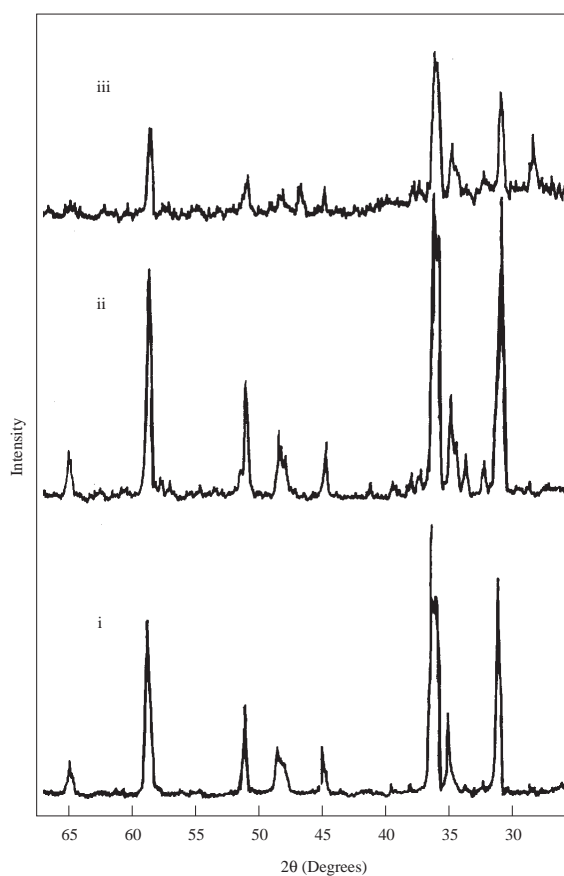


Figure 1. The X-ray Powder Diffraction Patterns of Experiments i, ii, and iii

Table 1. X-ray Powder Diffraction Data of CaBPO<sub>5</sub>

Exp.i		Exp. ii		Exp. iii		hkl
I/I <sub>o</sub>	d(Å)	I/I <sub>o</sub>	d(Å)	I/I <sub>o</sub>	d(Å)	
13	4.3355	14	4.3410	12	4.3589	1 0 1
				39	3.6301	BPO <sub>4</sub>
80	3.3337	94	3.3254	72	3.3337	1 1 0
4	3.2132	8	3.2113	7	3.2110	BPO <sub>4</sub>
30	2.9767	8	2.9768	36	2.9849	1 1 1
75	2.8904	80	2.8889	96	2.8811	2 0 0
100	2.8674	100	2.8736	100	2.8735	1 0 2
5	2.6490	5	2.6489			2 0 1
17	2.3490	17	2.3490	19	2.348	1 1 2
		12	2.1986			0 0 3
				19	2.253	BPO <sub>4</sub>
15	2.1878		2.1980			2 1 0
17	2.1789	20	2.1773			2 0 2
35	2.0765	36	2.0792	24	2.08	2 1 1
4	1.9304	4	1.9483			3 0 0
		4	1.8521			3 0 1
69	1.8248	70	1.8234	60	1.8248	2 1 2
8	1.6671	14	1.6660	6	1.6665	3 0 2
8	1.6060	14	1.6049	9	1.6049	3 1 0
3	1.5904	4	1.5904	7	1.5904	1 0 4
		2	1.5606	7	1.5606	3 1 1

Gözel<sup>1</sup> and Kniep et al.<sup>2</sup> solved the crystal structure of CaBPO<sub>5</sub> by Rietveld Refinement (Fig 2). The unit cell parameters are given in the Table 2. After the refinement, the “c” parameter was obtained as half of the Bauers parameter<sup>8,9</sup>. The unit cell parameters obtained in this work are in close agreement with the parameters obtained by Gözel<sup>1</sup> and Kniep et al.<sup>2</sup> as given in Table 2. In Table 3, the comparison of the hexagonal cell parameters of CaBPO<sub>5</sub>, PbBPO<sub>5</sub>, PbBaAsO<sub>5</sub>, LaBGeO<sub>5</sub> and PrBGeO<sub>5</sub>, which have stillwellite structures, are given. All of them confirmed the unit cell parameters given by Gözel<sup>1</sup> and Kniep et al.<sup>2</sup> and those reported in this work.

**Table 2.** The unit Cell Parameters of M<sup>II</sup>BPO<sub>5</sub> Compounds.

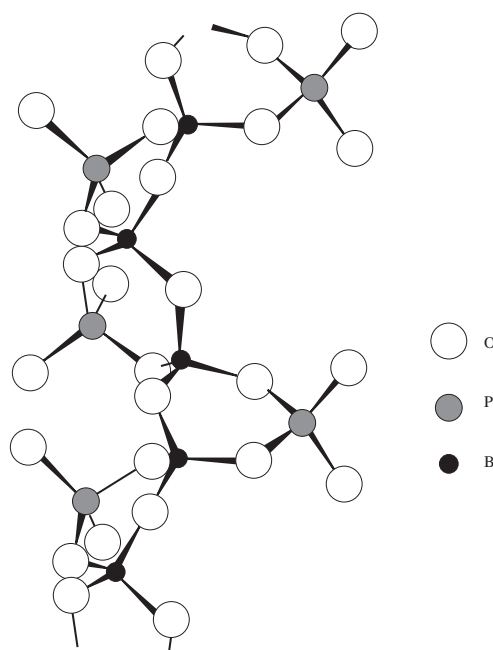
Compound	Bauer <sup>8,9</sup>		Gözel <sup>1</sup>		This work	
	a (Å)	c (Å)	a (Å)	c (Å)	a (Å)	c (Å)
CaBPO <sub>5</sub>	6.688	13.234	6.6799	6.6121	6.684	6.616

**Table 3.** Comparison of the Cell Parameters of XBPO<sub>5</sub> (X:Ca, Pb, La, and Pr; Y:P, As and Ge)

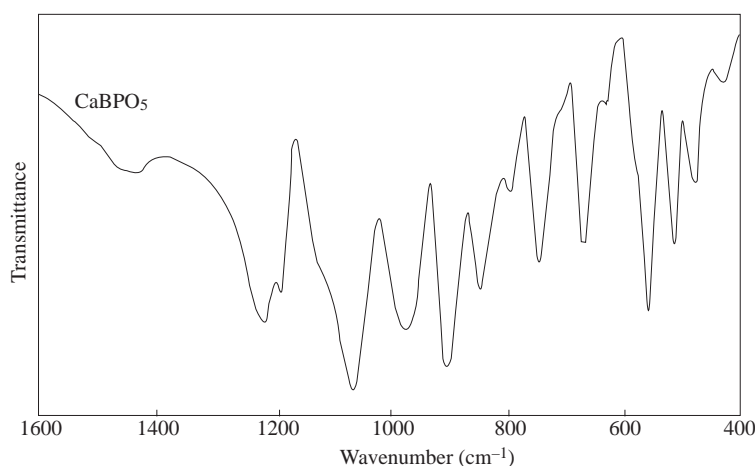
Compound	a (Å)	c (Å)
CaBPO <sub>5</sub>	6.684	6.616
PbBPO <sub>5</sub> <sup>9</sup>	6.91	6.871
PbBaAsO <sub>5</sub> <sup>9</sup>	7.113	6.942
LaBGeO <sub>5</sub> <sup>7</sup>	6.992	6.863
PrBGeO <sub>5</sub> <sup>7</sup>	6.935	6.808

## IR Study of CaBPO<sub>5</sub>

The IR spectra of the products obtained in experiments i, ii and iii are given in Fig 3. and the observed bands together with the assignments are listed in Table 4.



**Figure 2.** The Crystal Structure of CaBPO<sub>5</sub> Projected Along the c-axis Showing the Infinite Loop-Branched Chain of BO<sub>4</sub> and PO<sub>4</sub> Tetrahedra.



**Figure 3.** The IR Spectra of CaBPO<sub>5</sub>

**Table 4.** IR Assignments of CaBPO<sub>5</sub>

Assignment	Frequency (cm <sup>-1</sup> )
$\nu$ P=O	1230, 1213
$\nu_3$ (BO <sub>4</sub> )	1185, 1120, 1100
$\nu_3$ (PO <sub>4</sub> )	1068
$\nu_{as}$ (POP)	971
$\nu_1$ (PO <sub>4</sub> )	
$\nu_1$ (BO <sub>4</sub> )	899
$\nu_{as}$ (BOP)	841, 796
$\nu_s$ (BOP)	750, 700
$\nu_s$ (POP)	
$\delta$ (BOP)	673
$\delta$ (OPO)	588
$\nu_4$ (BO <sub>4</sub> )	627, 517, 439
$\nu_4$ (PO <sub>4</sub> )	485, 439, 426

The IR spectra of CaBPO<sub>5</sub> contains bands in the 1185-900 cm<sup>-1</sup> region which are characteristic of tetrahedral BO<sub>4</sub> groups, but in this region of the spectra, there are also broad bands centered around 1100-970 cm<sup>-1</sup> due to the phosphate anion<sup>14-16</sup>. Strong absorption band at 1230 cm<sup>-1</sup> and a weaker band at 1213 cm<sup>-1</sup> may be assigned to P=O nonbridging and stretching vibrations<sup>17</sup>. Bands between 850 and 750 cm<sup>-1</sup> were assigned as  $\nu_{as}$  B-O-P and  $\nu_s$  B-O-P stretching vibrations. B-O-B and B-O-P bending motions<sup>18,19</sup> were reported between 700 and 670 cm<sup>-1</sup> and  $\delta$  O-P-O in borophosphates appeared at around 588-547 cm<sup>-1</sup>. The low frequency side of the spectrum can be attributed to the  $\nu_4$  and  $\nu_2$  regions of the PO<sub>4</sub> and BO<sub>4</sub> tetrahedra<sup>19</sup>. Due to instrumental limitations it was not possible to observe the  $\nu_2$  region.

### Structure Description for CaBPO<sub>5</sub>

The crystal structure of CaBPO<sub>5</sub><sup>2</sup> projected along c-axis showing the infinite loop-branched chain of BO<sub>4</sub> and PO<sub>4</sub> tetrahedra in the hexagonal cell is given in Fig. 2. It can be described as an infinite chain of B tetrahedra each of which is connected by its free vertices two P tetrahedra, as reported by Gözel<sup>1</sup>.

## Conclusion

In this work, CaBPO<sub>5</sub> was prepared by three different solid-state reactions. The powder data of the products were found to be the same. The X-ray powder diffraction pattern and indexing of the powder data of CaBPO<sub>5</sub> was presented for the first time in this work. The method given in experiment iii, using BPO<sub>4</sub> as a phosphating agent for CaCO<sub>3</sub>, resulted in CaBPO<sub>5</sub>, which was pure enough for comparison purposes. The IR spectra of CaBPO<sub>5</sub> was also discussed and assignments were made which are in agreement with the structure.

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