

# Solid-State Synthesis, X-ray Powder Investigation and IR Study of $\alpha$ - $\text{Mg}_3[\text{BPO}_7]$

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## Abstract

$\alpha$ - $\text{Mg}_3[\text{BPO}_7]$  (low temperature form) which is isostructural with  $\text{Zn}_3[\text{BPO}_7]$  has been synthesized by the solid-state reactions of  $\text{MgHPO}_4 \cdot \text{H}_2\text{O}$  with  $\text{MgCO}_3$  and  $\text{H}_3\text{BO}_3$  at  $1200^\circ\text{C}$ ,  $\text{Mg}_3\text{B}_2\text{O}_6$  with  $\text{MgCO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  at  $1100^\circ\text{C}$ , and  $\text{MgO}$  with  $\text{B}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  at  $1100^\circ\text{C}$  with the molar ratios of 1:2:1, 1:3:2 and 6:1:1, respectively. The structure of  $\alpha$ - $\text{Mg}_3[\text{BPO}_7]$  was found to be orthorhombic (as already reported), with refined unit cell parameters of  $a = 8.495(3)$ ,  $b = 4.886(1)$  and  $c = 12.565(4)$  Å; the space group is *Immm* with  $Z = 4$ . The indexed X-ray powder diffraction data and the IR spectrum of  $\alpha$ - $\text{Mg}_3[\text{BPO}_7]$  are also given. The latter reveals trigonal planar coordination of boron. © 1998 Elsevier Science Limited. All rights reserved

## 1 Introduction

The structural chemistry of boron, oxygen and phosphorus compounds is very complex and considerable research should be done regarding the development of these materials. Although the  $\text{B}_2\text{O}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{MO}$  system ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ) is technologically important, the ternary phase relations of the alkaline earth metals have not been studied in detail.<sup>1–7</sup> On the other hand, different methods of borophosphate syntheses with solid state and sol gel processes have continued to advance in recent years, so it is also important to investigate them with a view to several materials applications. Moreover the unusual structural configuration of alkaline earth borophosphates lead to zeolite—like properties, with potential applications as bio-ceramics for molecular sieves.

Bauer<sup>3,4</sup> established the existence of a compound  $\text{CaBPO}_5$  with the composition  $2\text{CaO} \cdot \text{P}_2\text{O}_5 \cdot \text{B}_2\text{O}_3$ . Rulmont and Tarte<sup>5</sup> confirmed that they crystallize in the stilwellite<sup>8</sup> structure. Kniep<sup>6</sup> *et al.* and Gözel<sup>7</sup> solved the structure of  $\text{CaBPO}_5$  and  $\text{SrBPO}_5$  by Rietveld method. Recently Goetzmann *et al.*<sup>9</sup> reported that  $\text{CaBPO}_5$  paste in a polymer binder was used for corrosion protection of metal surfaces, which was found to be superior to a calcium borate and calcium diphosphate mixture. The existence of the two compounds,  $\alpha$ - $\text{Mg}_3[\text{BPO}_7]$  and  $\alpha$ - $\text{Zn}_3[\text{BPO}_7]$  has been shown previously by Liebertz and Stahr.<sup>1</sup> Gözel<sup>7</sup> reported the synthesis and the indexed powder data of  $\text{Mg}_3[\text{BPO}_7]$ ,  $\text{Sr}_3[\text{BPO}_7]$  and  $\text{Ba}_3[\text{BPO}_7]$ . According to Liebertz and Stahr<sup>1</sup> both compounds occur in two forms:  $\alpha$ - $\text{Mg}_3[\text{BPO}_7]$  (low temperature form) is orthorhombic with the probable space group *Immm* (No. 44) and  $Z = 4$ ;  $\beta$ - $\text{Mg}_3[\text{BPO}_7]$  (high temperature form) is hexagonal with the space group  $\text{P}\bar{6}\text{m}2$  or  $\text{P}\bar{6}2\text{m}$  and  $Z = 6$ . The transition from the high temperature form into low temperature form is very slow for  $\text{Zn}_3[\text{BPO}_7]$ , but fast for  $\text{Mg}_3[\text{BPO}_7]$ . The cell parameters of  $\alpha$ - $\text{Mg}_3[\text{BPO}_7]$ ,  $\alpha$ - $\text{Zn}_3[\text{BPO}_7]$  and  $\beta$ - $\text{Zn}_3[\text{BPO}_7]$  were determined by Liebertz and Stahr.<sup>1</sup> For the low temperature forms of  $\text{Mg}_3[\text{BPO}_7]$  and  $\text{Zn}_3[\text{BPO}_7]$  the data are very similar with  $a = 8.497(5)$ ,  $b = 4.880(5)$ ,  $c = 12.558(5)$  Å and  $a = 8.438(5)$ ,  $b = 4.884(5)$ ,  $c = 12.558(5)$  Å, respectively. The cell dimensions for the hexagonal  $\beta$ - $\text{Zn}_3[\text{BPO}_7]$  are  $a = 8.439(3)$ ,  $c = 13.030(3)$  Å, but the hexagonal form of  $\text{Mg}_3[\text{BPO}_7]$  was not reported. Recently Bluhm *et al.*<sup>10</sup> found a new crystal structure of  $\alpha$ - $\text{Zn}_3(\text{BO}_3)(\text{PO}_4)$ , by the reaction of  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$  and  $\text{ZnCO}_3$  as starting materials. The structure is monoclinic, space group *Cm*, with  $a = 9.725(2)$ ,  $b = 12.723(3)$ ,  $c = 4.874(3)$ ,  $\beta = 119.80^\circ(4)$  and  $Z = 4$ . The structure contains trigonally planar  $\text{BO}_3$  and tetrahedral  $\text{PO}_4$  units which are not joined together. However Gözel<sup>7</sup> also reported a monoclinic

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form for  $\text{Ca}_3[\text{BPO}_7]$  with unit cell dimensions of  $a = 8.602$ ,  $b = 4.891$ ,  $c = 12.806$  Å and  $\beta = 102.30^\circ$ , but the product was mixed with boron-containing apatite.

The aim of this work is to prepare  $\text{Mg}_3[\text{BPO}_7]$  by new solid-solid reactions and to characterize the products by XRD, IR and DTA techniques.

## 2 Experimental

### 2.1 Chemical substances

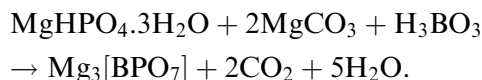
The following reagent grade chemicals were used in the synthesis of  $\alpha\text{-Mg}_3[\text{BPO}_7]$ :  $\text{MgCO}_3$ ,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{H}_3\text{BO}_3$  and  $\text{Mg}_3\text{B}_2\text{O}_6$  (Fluka and Merck).

### 2.2 Instrumentation

X-ray diffraction data of the product were collected on three separate diffractometers: a STOE powder diffractometer (STADI P model) with position-sensitive detector, silicon monochromator and  $\text{CuK}_\alpha$  radiation; a Huber Guinier diffractometer (Type 642 and  $\text{CuK}_\alpha$  radiation); and a Philips diffractometer (PW 1050/25 and  $\text{CoK}_\alpha$  radiation). The refinement procedure of the unit cell parameters was done by the Huber program. A Nicolet 510 FTIR spectrophotometer was used to obtain the spectra of the products in the region  $4000\text{--}400\text{ cm}^{-1}$ . The DTA studies of the reactions were carried out on a Netzsch-DTA 401 Model apparatus with Rh–Pt–Rh thermocouple. Magnesium and phosphorus concentrations were determined by EDX analysis with a Jeol scanning electron microscope (JSM-6400).

### 2.3 Procedures

$\text{Mg}_3[\text{BPO}_7]$  was prepared<sup>7</sup> by the solid-state reaction of the components  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgCO}_3$  and  $\text{H}_3\text{BO}_3$  in the molar ratio of 1:2:1. The following reaction was predicted:

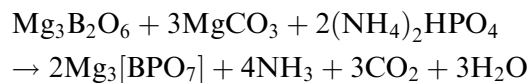


The reactants were weighed separately and ground together in an agate mortar. Then, the reaction was performed at  $1000\text{--}1200^\circ\text{C}$  in a covered platinum crucible for 15 h. After the heat treatment the furnace was turned off but left closed to allow slow cooling of the sample. The same compounds were also obtained when fast cooling was applied.

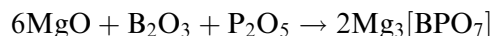
A DTA study of the process was performed in the  $25\text{--}1500^\circ\text{C}$  temperature range with a  $2^\circ\text{C min}^{-1}$  heating and cooling rate, in order to determine the melting behaviour of  $\text{Mg}_3[\text{BPO}_7]$ .

The synthesis of  $\text{Mg}_3[\text{BPO}_7]$  was also attempted by two further solid state reactions:

a.  $\text{Mg}_3\text{B}_2\text{O}_6$ ,  $\text{MgCO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$  in the molar ratio of 1:3:2 was heated at  $1100^\circ\text{C}$ . The following reaction was anticipated:



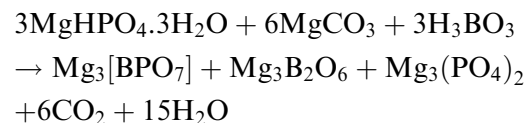
b. Solid state reactions of  $\text{MgO}$ ,  $\text{B}_2\text{O}_3$ , and  $\text{P}_2\text{O}_5$  in the molar ratio of 6:1:1. The heat treatment was performed at  $1100^\circ\text{C}$ . The following reaction was expected:



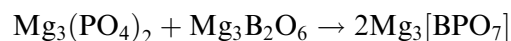
## 3 Results and Discussions

### 3.1 Solid-state reaction of $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O} + 2\text{MgCO}_3 + \text{H}_3\text{BO}_3 \rightarrow \text{Mg}_3[\text{BPO}_7] + 2\text{CO}_2 + 5\text{H}_2\text{O}$

The solid-state reaction between  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{MgCO}_3$  with  $\text{H}_3\text{BO}_3$  in a 1:2:1 molar ratio was performed at  $1000$  and  $1200^\circ\text{C}$ . In the X-ray powder diffraction pattern of the sample prepared at  $1000^\circ\text{C}$ , the side products,  $\text{Mg}_3(\text{PO}_4)_2$  (JCPDS Card No. 33-876) and  $\text{Mg}_3\text{B}_2\text{O}_6$  (JCPDS Card No. 38-1475) were observed together with  $\alpha\text{-Mg}_3[\text{BPO}_7]$ . This is consistent with the following equation for intermediate formation:



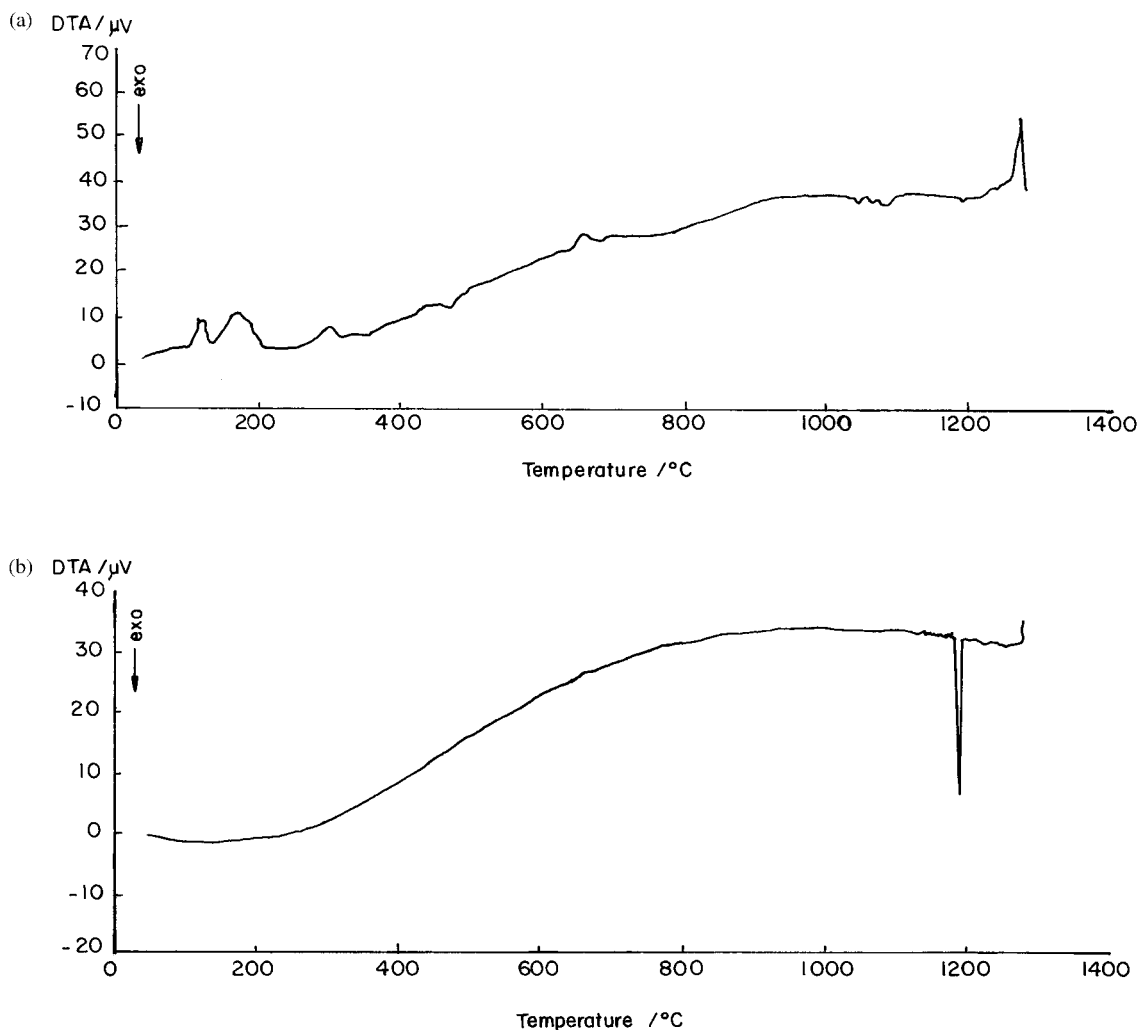
At  $1200^\circ\text{C}$   $\alpha\text{-Mg}_3[\text{BPO}_7]$  was obtained as the main product. Very weak  $\text{Mg}_3(\text{PO}_4)_2$  lines were still present in the powder pattern of the sample and  $\text{Mg}_3\text{B}_2\text{O}_6$  lines disappeared. Therefore the following reaction had taken place between  $\text{Mg}_3(\text{PO}_4)_2$  and  $\text{Mg}_3\text{B}_2\text{O}_6$ .



No considerable change has been observed when the reaction was continued at  $1500^\circ\text{C}$ , except the appearance of some weak lines which may be due to high temperature  $\beta$ -form of  $\text{Mg}_3[\text{BPO}_7]$ .

### 3.2 DTA studies

DTA study of the above reaction is given in Fig. 1(a) (heating) and Fig. 1b (cooling). In these figures, the endothermic effect above  $1200^\circ\text{C}$  in the heating process could be either ascribed to the melting point of the compound or the phase transformation of  $\alpha\text{-Mg}_3[\text{BPO}_7]$  (low temperature form)



**Fig. 1.** DTA study of  $\text{MgHPO}_4 + 2\text{MgCO}_3 + \text{H}_3\text{BO}_3$  reaction in (a) 25–1500° (heating) and (b) 1500–25°C (cooling) temperature range.

to  $\beta\text{-Mg}_3[\text{BPO}_7]$  (high temperature form). The exothermic effect below 1200°C in the cooling process could be explained by the phase transformation of  $\beta\text{-Mg}_3[\text{BPO}_7]$  to  $\alpha\text{-Mg}_3[\text{BPO}_7]$ .

According to Liebertz<sup>1</sup> the low temperature form of this compound exists at about 775 K with the high temperature form unstable at room temperature. Then this reversible effect could be regarded as a polymorphic change since we did not observe any melting during the solid state reactions even for very long heating periods. On the other hand presence of weak lines of  $\beta\text{-Mg}_3[\text{BPO}_7]$  together with  $\alpha\text{-Mg}_3[\text{BPO}_7]$  in the product heated at 1500°C showed that the transition from high to low temperature form is fast for  $\text{Mg}_3[\text{BPO}_7]$ .

### 3.3 Analysis of Mg and P

The concentration of Mg and P elements in the compound was analyzed by Energy Dispersive X-ray Analysis and Mg/P molar ratio was found to be approximately 3.

### 3.4 Solid state reactions of $\text{Mg}_3\text{B}_2\text{O}_6 + 3\text{MgCO}_3 + 2(\text{NH}_4)_2\text{HPO}_4 \rightarrow \text{Mg}_3[\text{BPO}_7] + 4\text{NH}_3 + 3\text{CO}_2 + 3\text{H}_2\text{O}$

The reaction was performed at 1100°C for 15 h. The product obtained was found to be  $\text{Mg}_3(\text{PO}_4)_2$ . Some unreacted  $\text{Mg}_3\text{B}_2\text{O}_6$  was also observed, but the experimental and theoretical weight losses were in good agreement, which showed the complete decomposition of  $\text{MgCO}_3$  and  $(\text{NH}_4)_2\text{HPO}_4$ . After prolonged heating at 1100°C for 48 h and cooling slowly,  $\alpha\text{-Mg}_3[\text{BPO}_7]$  was observed in the X-ray pattern together with the very weak lines of  $\text{Mg}_3(\text{PO}_4)_2$ . The x-ray powder diffraction pattern was the same with the pattern of the product obtained by the first method which had an orthorhombic structure.

### 3.5 Solid state reactions of $6\text{MgO} + \text{B}_2\text{O}_3 + \text{P}_2\text{O}_5 \rightarrow 2\text{Mg}_3[\text{BPO}_7]$

The solid-state reaction was performed by heating the reactants at low temperatures (200–600°C) at the beginning to avoid melting due to presence of

$P_2O_5$  in the mixture. Then the temperature was gradually increased to  $1100^\circ C$  and kept at this temperature for about 40 h. The powder pattern was again the same as the pattern of the products obtained with the first and second methods. The product was heated for another 40 h to see if there would be any transition to high temperature form.

In this case the high temperature form  $\beta-Mg_3[BPO_7]$  was obtained together with the low temperature  $\alpha$ -form.

### 3.6 Interpretation of X-ray powder diffraction data

The X-ray powder pattern of  $\alpha-Mg_3[BPO_7]$  was indexed in the orthorhombic crystal system with

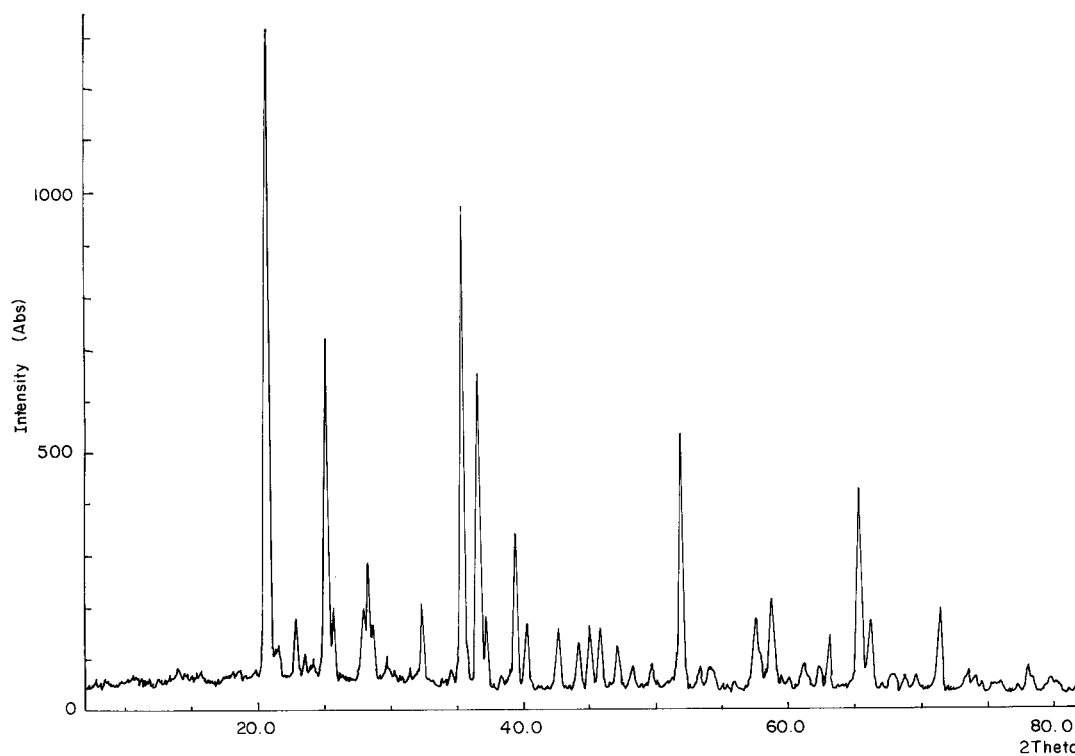


Fig. 2. X-Ray powder pattern of  $\alpha-Mg_3[BPO_7]$ .

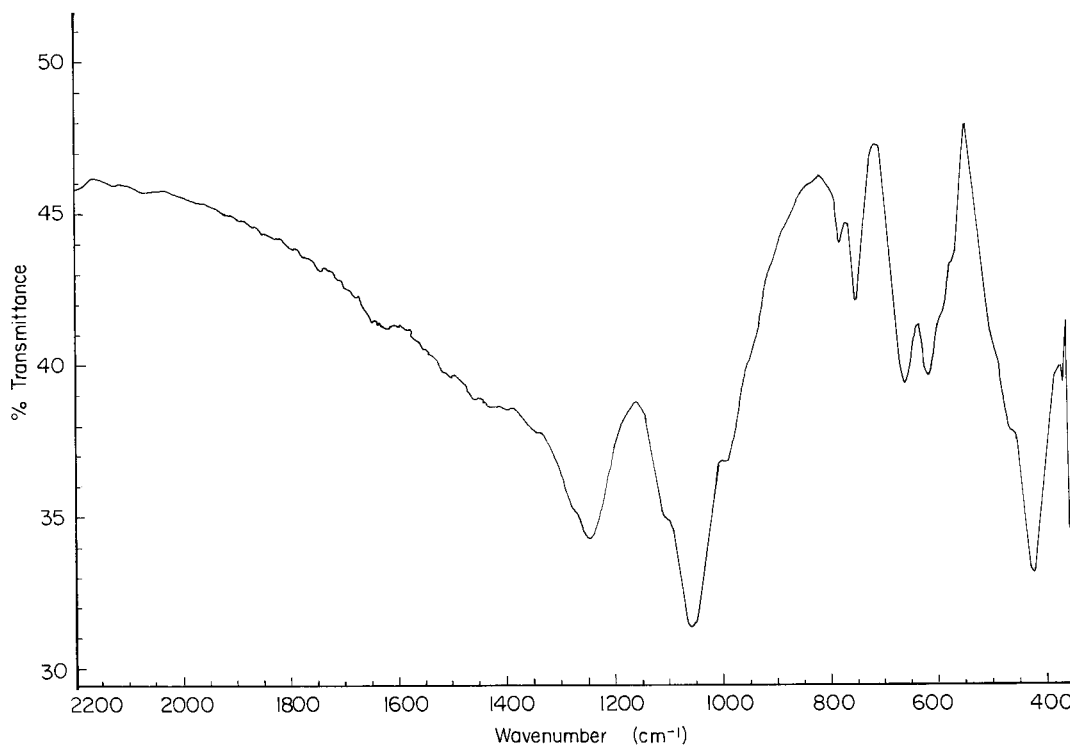


Fig. 3. IR spectrum of  $\alpha-Mg_3[BPO_7]$ .

**Table 1.** X-ray powder diffraction data for orthorhombic  $\alpha$ -Mg<sub>3</sub>[BPO<sub>7</sub>].

$I/I_0$	$d_{obs}$	$d_{calc}$	$hkl$	$I/I_0$	$d_{obs}$	$d_{calc}$	$hkl$
9 <sup>a</sup>	4.33	—	—	4	1.8287	1.8302	321
100	4.24	4.24	110	39	1.7554	1.7586	224
5 <sup>a</sup>	4.12	—	—	4	1.7147	1.7161	125
3 <sup>a</sup>	4.07	—	—	4	1.6969	1.6929	323
9 <sup>a</sup>	3.86	—	—	4 <sup>a</sup>	1.6876	—	—
3	3.78	3.75	103	12	1.5992	1.5993	130
4	3.75	3.76	103	7	1.5911	1.5905	026
3 <sup>a</sup>	3.67	—	—	3 <sup>a</sup>	1.5805	—	—
54	3.52	3.51	112	15	1.5696	1.5718	008
11 <sup>a</sup>	3.45	—	—	5 <sup>a</sup>	1.5628	—	—
5 <sup>a</sup>	3.199	—	—	3	1.5538	0.5533	422
11	3.183	3.181	013	4	1.5147	1.5170	307
19	3.142	3.144	004	4 <sup>a</sup>	1.5101	—	—
9	3.107	3.107	211	3 <sup>a</sup>	1.5059	—	—
4 <sup>a</sup>	2.995	—	—	3	1.4881	1.4896	226
13	2.760	2.763	301	8 <sup>a</sup>	1.4704	—	—
76	2.522	2.524	114	31	1.4248	0.4254	134
3 <sup>a</sup>	2.495	—	—	6 <sup>a</sup>	1.4144	—	—
8	2.4460	0.4426	020	10 <sup>a</sup>	1.4107	—	—
11 <sup>a</sup>	2.4082	—	—	3	1.3824	0.3817	602
3	2.3438	2.3469	303	3	1.3767	1.3775	332
4	2.3046	2.3077	121	3	1.3654	1.3668	035
25	2.2796	2.2768	022	3 <sup>a</sup>	1.3490	—	—
10	2.2297	2.2357	015	4	1.3244	1.3230	318
7	2.1241	2.1245	400	13 <sup>a</sup>	1.3188	—	—
10	2.1146	—	—	4	1.2872	1.2857	431
8	2.0443	2.0482	123	3 <sup>a</sup>	1.2836	—	—
10	2.0079	2.0069	222	3 <sup>a</sup>	1.2775	—	—
9	1.9786	1.9787	215	3	1.2247	1.2253	620
7	1.9274	1.9240	411	4 <sup>a</sup>	1.2221	—	—
4 <sup>a</sup>	1.9182	—	—	3 <sup>a</sup>	1.2184	—	—
4 <sup>a</sup>	1.8829	—	—	3	1.1210	1.1210	138
3	1.8749	1.8783	116	—	—	—	—

<sup>a</sup>  $\alpha$ -Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (J.C.P.D.S. Card No. 33-876).

**Table 2.** IR frequencies for  $\alpha$ -Mg<sub>3</sub>[BPO<sub>7</sub>]

Assignments	$\nu$ ( $cm^{-1}$ )
$\nu_3$ (BO <sub>3</sub> )	1200–1245
$\nu_s$ (OPO)	1104
$\nu_1$ (BO <sub>3</sub> )	1040
$\nu_2$ (BO <sub>3</sub> ) (out of plane bending)	785-750
$\nu_4$ (BO <sub>3</sub> ) (planar bending)	662–623
$\delta$ (OPO)	564 (shoulder)
$\nu_3$ (PO <sub>4</sub> )	1059
$\nu_1$ (PO <sub>4</sub> )	989
$\nu_4$ (PO <sub>4</sub> )	467,423
$\nu_2$ (PO <sub>4</sub> )	370,357

the unit cell parameters of  $a = 8.495(3)$ ,  $b = 4.886(1)$ ,  $c = 12.565(4)$  Å. The possible space group was identified as Immm with  $Z = 4$ . The powder data of this product are given in Fig. 2 and Table 1 together with the weak lines of Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. It was observed that the calculated cell parameters of  $\alpha$ -Mg<sub>3</sub>[BPO<sub>7</sub>] are almost the same with Liebertz's<sup>1</sup> cell parameters but the  $d$  spacings and indexing of the powder data has not been reported by them. The x-ray powder data of  $\beta$ -form of Mg<sub>3</sub>[BPO<sub>7</sub>] which was obtained by pro-

longed heating, could not be properly indexed since it was mixed with the  $\alpha$ -form.

### 3.7 Interpretation of IR data

Figure 3 shows the IR Spectrum of  $\alpha$ -Mg<sub>3</sub>[BPO<sub>7</sub>]. Although the band at 1245  $cm^{-1}$  could be assigned to antisymmetric vibration of OPO group in metaphosphates but the absence of a band at around 1160  $cm^{-1}$  due to symmetric OPO stretching vibration ruled out this possibility.<sup>11–13</sup> Also the absence of B–O stretching vibration at 1150  $cm^{-1}$  for BO<sub>4</sub> proved that boron is not tetrahedrally coordinated.<sup>14</sup> Bands at 1200–1245 ( $\nu_3$ ), 1040 ( $\nu_1$ ), 785–750 ( $\nu_2$ ) and 662–623  $cm^{-1}$  ( $\nu_4$ ) correspond to doubly degenerate B–O antisymmetrical stretching vibration, symmetric stretching vibration (which becomes IR active due to lowering of symmetry), out of plane bending and doubly degenerate planar bending modes respectively for an isolated BO<sub>3</sub><sup>3-</sup> unit.<sup>15–19</sup> On the other hand it was reported that the intensity of the 780  $cm^{-1}$  band increases with the increasing metal oxide content and this has been found consistent with the <sup>10</sup>B-NMR studies<sup>20</sup> showing that boron atoms are coordinated by three oxygens in MO.B<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub> systems. Recently Bluhm and Park<sup>10</sup> claimed that in  $\alpha$ -Zn<sub>3</sub>(BO<sub>3</sub>)(PO<sub>4</sub>), boron is in an isolated trigonal planar coordination. The band at 564  $cm^{-1}$  is due to bending motion of O–P–O.<sup>8,11</sup> PO<sub>4</sub><sup>3-</sup> region<sup>15</sup> is characterized by the bands at 1059 ( $\nu_3$ ), 989 ( $\nu_1$ ), 467, 423 ( $\nu_4$ ) and 370 ( $\nu_2$ )  $cm^{-1}$ . Table 2 shows the IR frequencies and assignments for the observed spectra.

## 4 Conclusion

$\alpha$ -Mg<sub>3</sub>[BPO<sub>7</sub>] has been synthesized by three different solid state reactions which have not been reported earlier in the literature.<sup>21</sup> It was found to have similar unit cell parameters and space group with orthorhombic  $\alpha$ -Mg<sub>3</sub>[BPO<sub>7</sub>],  $\alpha$ -Zn<sub>3</sub>[BPO<sub>7</sub>] as reported by Liebertz *et al.*<sup>1</sup> In this work the X-ray powder diffraction data were indexed and found to be in agreement with the space group Immm with  $Z = 4$ . The refined unit cell dimensions are  $a = 8.495$  (3),  $b = 4.886$  (1) and  $c = 12.565$  (4) Å. The monoclinic  $\alpha$ -Zn<sub>3</sub>(BO<sub>3</sub>)(PO<sub>4</sub>) structure<sup>10</sup> was not observed in this work. The IR data included the bands due to BO<sub>3</sub> units which suggested isolated trigonal coordination of boron. Attempts to prepare single crystals of Mg<sub>3</sub>[BPO<sub>7</sub>] through solid state and hydrothermal methods failed. The feasibility of carrying Rietveld refinements are currently hampered by the difficulty in finding a starting model and the presence of impurities such as Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub><sup>22</sup> in the powder pattern.

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