

# Hydrothermal and Microwave Synthesis of Boron Phosphate, $BPO_4$

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$BPO_4$  was previously synthesized by the solid state reactions of  $(NH_4)_2HPO_4$  and  $B_2O_3$  at  $1000^\circ C$  and was characterized by X-ray powder diffraction and IR methods. We have now succeeded in preparing  $BPO_4$  from  $H_3BO_3$  and  $P_2O_5$  using hydrothermal synthesis by heating at  $160^\circ C$  for 2 days and obtained a single phase product. We observed that a microwave-assisted synthesis takes only 3 to 5 minutes to transform a solid mixture of  $(NH_4)_2B_4O_7 \cdot 4H_2O$ , and solid  $H_3PO_4$  or  $B_2O_3 + P_2O_5$  into the crystalline title compound. Its X-ray powder diffraction data and IR spectra were in good agreement with the literature values.

**Key Words:** Boron Phosphate,  $BPO_4$ , Microwave Synthesis, Hydrothermal synthesis.

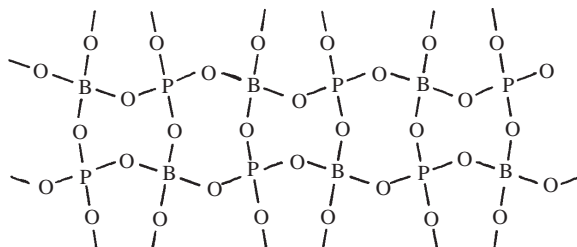
## Introduction

$BPO_4$ , which is a very well known compound, is an important catalyst, especially for organic reactions<sup>1</sup>. The other importance of  $BPO_4$  is its usage as a phosphating agent. Vasovic et al.<sup>2</sup> investigated the phosphating feature of  $BPO_4$  to obtain Mg, Ca, Zn and Pb phosphates through solid state reactions of  $BPO_4$  with the corresponding oxides. The strength of porcelain can be considerably improved by the addition of  $BPO_4$ <sup>3</sup>. It is also used as an insulator<sup>4</sup>. Glasses capable of absorbing a substantial portion of electromagnetic radiation contain  $BPO_4$ <sup>5</sup>. Furthermore, in electronic packaging substrate technology, borophosphosilicate glass ceramics have been used in recent years<sup>6-9</sup>.

$BPO_4$  was first prepared from the mixtures of  $B_2O_3$  and  $(NH_4)_2HPO_4$  or  $B_2O_3$  and  $P_2O_5$  by solid state synthesis at high temperatures ( $T_{max} = 1000^\circ C$ ) by our group and others<sup>10-15</sup>. The crystal structure contains  $BO_4$  and  $PO_4$  tetrahedra.  $BPO_4$  is a copolymer of two water soluble and low melting oxides: boric

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oxide and phosphorous oxide. It is insoluble, chemically inert and has a high softening point. It is a four connective crystalline polymer whose structure (Fig. 1) is similar to that of silica<sup>16</sup>.



**Figure 1.** Structure of BPO<sub>4</sub>

In recent years, much progress has been made in the synthesis of materials by hydrothermal and microwave methods. Conventional techniques such as solid state reactions at high temperatures or photochemical, catalytic, ultrasonic and high pressure reactions are used to stimulate chemical reactions which proceed slowly under ambient conditions<sup>17</sup>. On the other hand, the use of controlled microwave energy for ceramic processing and drying and for melting silica, alumina and aluminosilicate gels have been reported<sup>18</sup>.

Microwave heating techniques have stimulated interest in recent years because of their potential advantages, including significant reductions in manufacturing costs<sup>19</sup>. Microwave energy is widely used to process a variety of ceramic materials. For example, the use of microwave plasma produces highly excited electronic states by the decomposition of gaseous species that recombine to give metastable phases. Kamo et al.<sup>20</sup> synthesized diamond depending on this principle. There are many advantages of microwave processing over conventional processing methods<sup>18,19,21</sup>: 1. Significant reductions in manufacturing costs due to energy savings and shorter processing times, 2. Improved product uniformity, 3. Improved or unique microstructure and properties. 4. Improved product quality, 5. Very rapid processing (2 to 50 times faster than conventional methods), 6. Capability of high energy concentration in short times and in selected regions, 7. Acceleration of sintering and diffusion and thus densification at lower temperatures.

Microwave heating is fundamentally different from conventional processes. In the microwave process, heat is generated internally within the material instead of originating heat. The materials, that can be processed by microwave energy are dielectrics (electrically insulating) such as Al<sub>2</sub>O<sub>3</sub>, MgO and SiO<sub>2</sub> and most glasses. They are transparent to microwaves at ambient temperatures<sup>19</sup>. Recently, microwave energy was used for the synthesis of inorganic borophosphate materials such as Na<sub>5</sub>[B<sub>2</sub>P<sub>3</sub>O<sub>13</sub>] prepared by our group. The synthesis of Na<sub>5</sub>[B<sub>2</sub>P<sub>3</sub>O<sub>13</sub>] took only two minutes to transform a solid mixture of borate and phosphate hydrates into crystalline title compound<sup>22</sup>.

The basic idea for a microwave-assisted preparation of borophosphates is consistent with the observation of the high microwave susceptibilities of those phosphate and borate hydrates<sup>23</sup>. A novel microwave-assisted preparation of crystalline and glassy materials using NaH<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O, which has high absorbing microwave ability, was proposed by Vaidhyanathan and Rao<sup>23</sup>, in which microwave radiation is expected to activate the rotational degrees of freedom in H<sub>2</sub>O molecules present in the sample NaH<sub>2</sub>PO<sub>4</sub>.2H<sub>2</sub>O. The sample first melts as a consequence, forming a highly concentrated solution of NaH<sub>2</sub>PO<sub>4</sub> in H<sub>2</sub>O. In the second stage, the H<sub>2</sub>O molecules escape from the solution leaving behind "hot" NaH<sub>2</sub>PO<sub>4</sub>, which is suspected as it is itself sufficiently microwave absorbing either due to increased dielectric loss or due to the nearness of a dielectric anomaly. This material then continues to be heated even further where upon in the

third stage the chemically bound water (-H and -OH groups) in the structure of  $\text{NaH}_2\text{PO}_4$  is eliminated by condensation. Anhydrous  $\text{NaPO}_3$  melt is formed at the end. Vaidhyanathan *et al.* also tested some phosphate and borate compounds for their microwave-absorbing abilities<sup>23,24</sup>. According to this study, with  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , when exposed to microwave radiation for 7 minutes, weight loss was observed. It was found to be dehydrated and a porous product was obtained. For  $\text{Na}_3\text{BO}_3 \cdot 4\text{H}_2\text{O}$  (7-minute exposure), the same results were observed except the product had a rubbery appearance. Recent reports of the syntheses of several inorganic solids have been reviewed by Rao *et al.*<sup>24</sup>.

In this work, we developed a previously unreported simple and fast microwave-assisted reaction for the synthesis of  $\text{BPO}_4$ .

On the other hand, to synthesize single crystal and polycrystalline compounds, hydrothermal synthesis is an excellent method. A lot of chromate, phosphate, borate, and borophosphate compounds are produced with hydrothermal synthesis<sup>25</sup>. The most common arrangement required for such crystallization is the temperature gradient that helps to transport the material from the zone of high solubility to the zone of low solubility. This method has some significant advantages over other chemical synthesis techniques. Many materials can be produced directly in the desired crystalline phase at relatively low temperatures (around 350°C), thus eliminating any need for the calcination treatment prior to sintering. Most of the borophosphates are preferably prepared by hydrothermal methods at temperatures below 200°C, like  $\text{Na}_5[\text{B}_2\text{P}_3\text{O}_{13}]$ <sup>22</sup>,  $(\text{NH}_4)_2[\text{B}_3\text{PO}_7(\text{OH})_2]$ <sup>2</sup>,  $\text{Li}[\text{B}_3\text{PO}_6(\text{OH})_3]$ <sup>27</sup>,  $\text{K}_3[\text{B}_5\text{PO}_{10}(\text{OH})_3]$ <sup>28</sup>,  $\text{NH}_4\text{Mg}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot \text{H}_2\text{O}$ <sup>[29,30]</sup>,  $\text{NaMg}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot \text{H}_2\text{O}$ <sup>30,31</sup> and  $\text{Fe}(\text{H}_2\text{O})_2[\text{BP}_2\text{O}_8] \cdot \text{H}_2\text{O}$ <sup>32</sup>. The preparation of  $\text{BPO}_4$  by a hydrothermal method was also presented for the first time in this paper.

In addition to the two above methods, the sol-gel method was also proved to be good method for synthesis of  $\text{BPO}_4$ <sup>33</sup>. Starting from the ethanol-derived precursor, Af *et al.* synthesized  $\text{BPO}_4$  directly by a sol-gel route<sup>34</sup>.

## Experimental

### Substances

$(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{BO}_3$ ,  $\text{B}_2\text{O}_3$ ,  $(\text{NH}_4)_2\text{HPO}_4$  and  $\text{P}_2\text{O}_5$  (from Merck and Aldridge)

### Instruments

X-ray powder diffraction patterns (XRD) were taken by using a Philips diffractometer with PW 1050/25 goniometer and Co  $K\alpha$  radiation (30-40 kV, 10-20 mA,  $\lambda = 1.79021 \text{ \AA}$ ) and Huber Diffractometer with Cu  $K\alpha$  radiation (30-40 kV, 10-20 mA,  $\lambda = 1.54059 \text{ \AA}$ ).

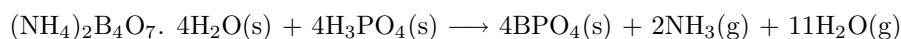
A Nicolet 510 FTIR Infrared Spectrometer was used in the region 400-4000  $\text{cm}^{-1}$ . Spectra of solid samples were obtained from KBr pellets with a 100:10 (wt/wt) KBr to product ratio.

The solid state reactions were carried out in air with the aid of Heraeus, SFL West-6100, and Ney 2-525 furnaces. The heating range was 550-1500°C using Cr-Ni-Cr and Rh-Pt-Rh thermocouples and controller. Microwave reactions were carried out in an Arçelik MD58 I, kitchen-type microwave oven (2.450GHz, 1000 W).

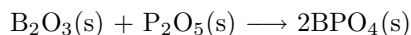
## Procedure

Three different (two new and one conventional) routes were employed for the synthesis of BPO<sub>4</sub>.

For microwave-assisted synthesis of BPO<sub>4</sub>, a dry and ground solid mixture (2.5g) of (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·4H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> (molar ratio of 1:4) was placed in a Teflon beaker and was treated in a conventional kitchen microwave system (2.450 GHz; max 1000 W) for a short period (3 minutes). The mixture melted partially after exposure to microwave radiation and copious bubbling of the materials was seen. After 3 minutes, the irradiation was terminated and the sample was allowed to cool inside the oven. The proposed reaction for the microwave-assisted synthesis of BPO<sub>4</sub> is as follows:

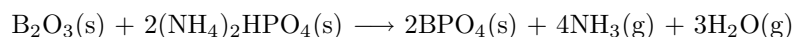


This experiment was also performed for the mixture of B<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>, according to the chemical reaction given below. The time required for this reaction is about 5 minutes. The following reaction is expected:



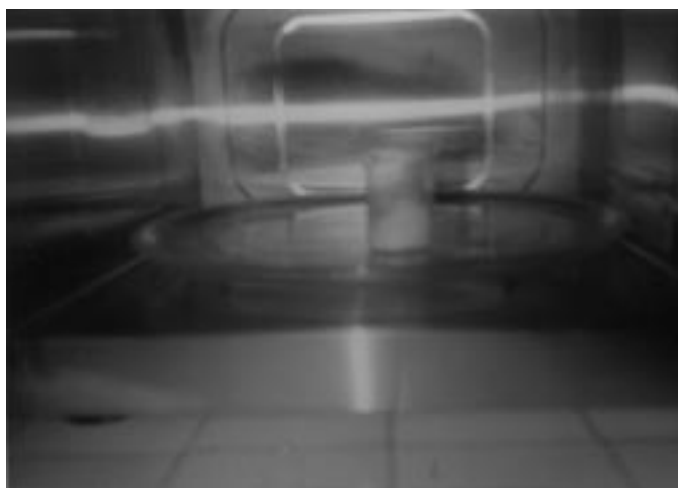
On the other hand, the synthesis of BPO<sub>4</sub> was carried out by a hydrothermal method starting from mixtures H<sub>3</sub>BO<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> in a 6:1 molar ratio. The reactants were mixed in 10 ml distilled water and treated under stirring with 25 ml concentrated HNO<sub>3</sub> until the components dissolved completely. The clear solution was heated without boiling and concentrated to 15 ml and then transferred to a Teflon-coated steel autoclave (65% filling) and heated at 160°C for 2 days. The crystalline products were filtered off in vacuo, washed with distilled water and dried at 60°C.

For the solid state synthesis of BPO<sub>4</sub>, for comparison purposes, the reaction was performed at 1000°C in a porcelain crucible. In order to prevent melting of the reactants, the heating rate was kept slow during the first heating. For this purpose, the mixture was heated to 300°C at a rate of 2°C/min. Then the temperature was gradually increased to 1000°C and the sample was kept at this temperature for 7 h. The proposed chemical reaction is as follows:

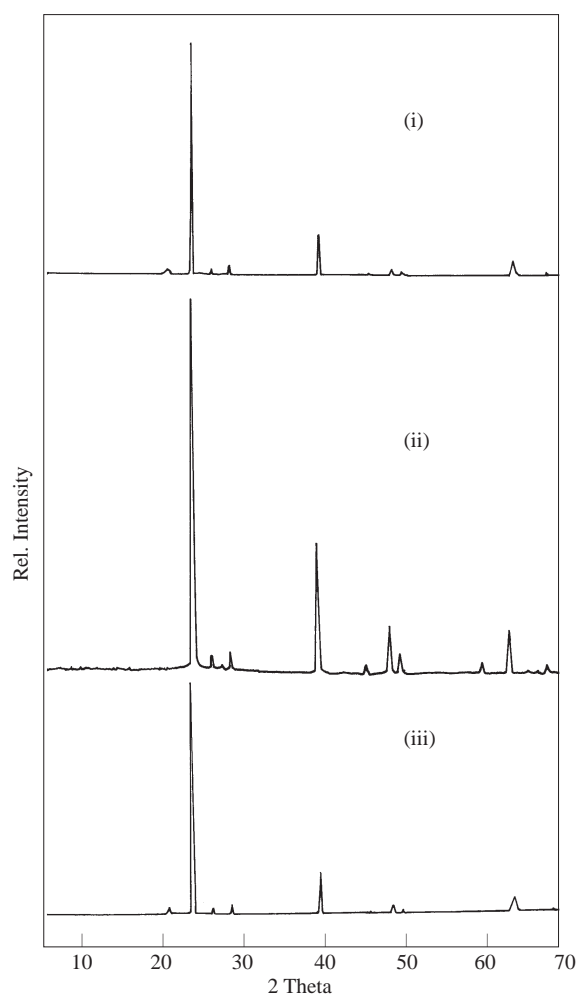


## Results and Discussion

The first step of the microwave-assisted reaction (~1 minute) is the loss of water molecules from the components. Then flashes are seen in the center of the mixture. The reaction mixture continues to glow during the duration of the reaction (Fig. 2) as stated by Vaidhyanathan and Rao<sup>21</sup> for other reactions. Due to this glowing, the temperature of the solid mixture increases suddenly. However, it is not obvious which materials (starting materials or products) caused an increase in temperature. We were able to take a photograph of the reaction vessel only when the door of the microwave oven was closed. Unfortunately it was impossible to measure the temperature during glowing. However, to estimate approximately the lower bound of the reaction temperatures, control experiments were performed in open atmosphere for nitrides. It was found that the approximate temperature after 5 minutes exposure in air was around 870-1100 K<sup>21</sup>.

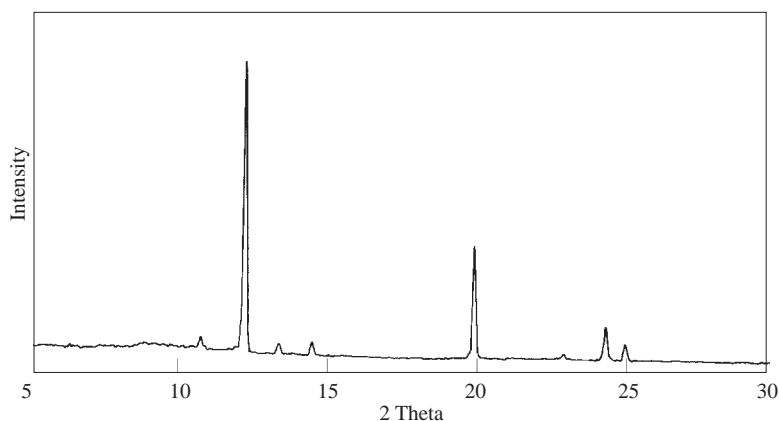


**Figure 2.** Photograph Taken During the Reaction of  $(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 2\text{H}_2\text{O} + \text{H}_3\text{PO}_4$  by Microwave Method



**Figure 3.** The X-ray Powder Diffraction Pattern of the Products Obtained by i) Solid State Reaction, ii) Hydrothermal Reaction and iii) Microwave-Assisted Method

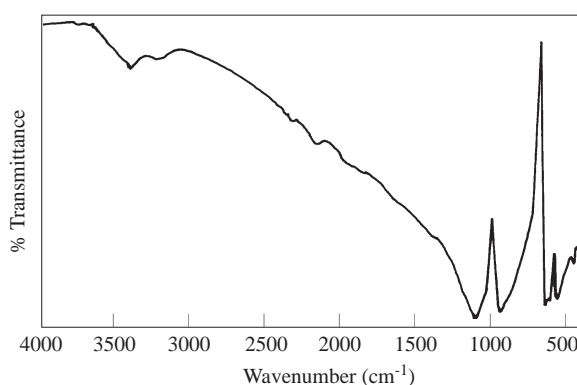
The X-ray powder patterns of the products obtained by solid state (i), hydrothermal (ii) and microwave methods (iii) using  $(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O} + 4\text{H}_3\text{PO}_4$  were the same but their intensities were different (Fig. 3). All the peaks in the X-ray powder pattern belong to tetragonal  $\text{BPO}_4$ . The X-ray powder pattern of the product obtained by the reaction of  $\text{B}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$  with microwave method is presented in Fig. 4. The extra weak peaks in the patterns are due to vaseline, which was used in the sample preparation.



**Figure 4.** The X-Ray Powder Diffraction Pattern of the Product for  $\text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$  Reactions Using Microwave Method

The crystal structure of  $\text{BPO}_4$  obtained in all reactions is tetragonal. The reported unit cell parameters (JCPDS card No: 34-132) are  $a = 4.342$ ,  $c = 6.645 \text{ \AA}$ , which are in good agreement with our unit cell parameters and the ones reported with others<sup>10,11,35</sup>.

There was a good agreement between the IR spectrum of  $\text{BPO}_4$  and tetragonal  $\text{BPO}_4$  given in the literature<sup>16,36</sup>. The IR spectrum of boron phosphate contains four strong, rather broad bands at 550, 615, 925, and  $1085 \text{ cm}^{-1}$ , which can be seen in Fig. 5. As stated by Kniep *et al.*<sup>37</sup>, P-O-P linking was not present in borophosphates, which was confirmed in this study<sup>38</sup>.



**Figure 5.** IR Spectrum of  $\text{BPO}_4$

## Conclusion

Phosphates have traditionally been synthesized by means of a solid state reactions at high temperatures. In this study, boron phosphate,  $\text{BPO}_4$ , was successfully synthesized through solid state, hydrothermal

and microwave-assisted reactions. Microwave-assisted methods have many benefits over the conventional methods, such as shorter reaction time, lower energy requirements and pure phase composition. The IR and powder diffraction pattern is in good agreement with the reported data.

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