

**BORON PHOSPHATE: ITS SYNTHESIS, GRADUAL CRYSTALLISATION
AND CHARACTERISATION OF BULK PROPERTIES**

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ABSTRACT

Boron phosphate, BPO_4 , was synthesised from the equimolar mixture of H_3PO_4 and H_3BO_3 at temperatures from 25 to 1200 °C. IR spectra, X-ray diffraction pattern, thermal analysis and chemical analysis of boron and phosphorus show that the synthesis occurs already at the room temperature and that the crystallisation is a gradual process. The molar ratio of boron and phosphorous remains at 1:1 independently of the temperature of synthesis.

INTRODUCTION

Boron phosphate, BPO_4 , finds its use as a dehydration catalyst and its surface properties and catalysis mechanisms have been widely investigated [1,2,3]. However, studies of its preparation and characterisation of bulk properties are scant. As far as 1904, Mylius and Meusser [4] reported of the two modifications of the compound: one soluble in water and one not. The former was a white amorphous powder which formed as a result of the evaporation of the water solution of H_3BO_3 and H_3PO_4 on the water bath. After heating the water soluble form for 2 hours at 1000 °C they obtained the latter form in which small crystals were visible with bare eye. Gruner [5] performed identical experiment and X-ray diffraction patterns were identical for both forms.

Gruner also evaporated the solution of the water soluble form at room temperature and obtained crystals which looked similar to boric acid. He assumed that the outcome of both preparations were complex mixed boric phosphoric acids.

Boron phosphate can be prepared in various other ways e.g. from phosphoric acid and triethyl borate [6] or triethyl phosphate and boron trichloride [7]. Only the preparation from the acids is dealt with in our paper.

Kubasov and Kitaev [8] studied the infra-red spectra in KBr matrix of samples obtained by heating the equimolar amounts of acids. The temperatures studied were from 300 °C to 800 °C. They also prepared samples from dehydrated acids and managed to assign some parts of the spectra with the analysis of the effect of washing the samples with water. Ashboren [9] performed a similar study with the temperature range from 130 °C to 800 °C and data obtained from various analyses (chemical, specific weight, specific surface area, TGA+DTA, X-ray diffraction).

The structure of boron phosphate is isomorphous with β -cristoballite. High pressure form isomorphous with α -quartz can also be obtained [10].

The aim of our work was to clarify the somewhat ambiguous data on the properties of boron phosphate and the preparation from the boric and phosphoric acids. We wanted to find out if the material obtained at different temperatures was indeed BPO_4 and how this effected its cristallinity. Also, we wanted to prove or disprove the existence of any possible crystallohydrates and any possible changes in structure with the elevated temperature of synthesis. Therefore we used even wider range of temperatures i.e. 25-1200 °C in our experiments.

EXPERIMENTAL METHODS

Preparation

The acids used were analytical grade 14,5 M H_3PO_4 (Kemika Zagreb) and 99,8 % min. H_3BO_3 (Merck).

Conditions of preparation are shown in Table 1. Apart from those reactions we also tried to react the equimolar water solution of H_3BO_3 (0,5M) and H_3PO_4 (0,5M) at

room temperature with slow evaporation. Since the outcome was not the boron phosphate, the reaction is not included in the table.

TABLE 1. Conditions of preparation and weight loss during the synthesis of boron phosphate (BPO_4) from equimolar mixture of boric (H_3BO_3) and phosphoric acid (H_3PO_4).

<i>Sample No.</i>	<i>Heating Time</i>	<i>Temp. (°C)</i>	<i>Heating Apparatus</i>	<i>Weight Loss (%)</i>
1	72 hours	25	vacuum dried over P_4O_{10}	27,7
2	until dry plus 30 minutes	100	water bath	27,3
3	10 minutes	130	electric oven	40,6
4	10 minutes	400	electric oven	41,1
5a	10 minutes	800	electric oven	42,9
5b	48 hours	800	electric oven	43,5
6	48 hours	1200	electric oven	44,2

The mixture of H_3PO_4 and H_3BO_3 was homogenised in a ceramic mortar until clearly homogenous gel was obtained (app. 1 hour). The mixture was heated in a platinum crucible and the thermocouple sensor was placed next to the crucible.

We also exposed the samples to atmospheric water and found out by means of the weight change that they were only slightly hygroscopic. Samples 1-3 were fairly soluble in boiling water but samples 4-6 were insoluble.

Chemical analysis

High temperature form of boron orthophosphate is not soluble even in concentrated acids and bases. All the samples (even the water soluble ones, for the sake of comparison) were finally dissolved in the melt of sodium hydroxide. Since the solubility can be a problem as mentioned in the literature [9], we are giving the full details of the procedure in Appendix A.

Phosphate was determined spectrophotometrically as heteropoly acid in water as described elsewhere [11]. Boron was determined spectrophotometrically as kinalizarine

complex in concentrated sulphuric acid [12]. Perkin Elmer UV/VIS/NIR Lambda 19 spectrophotometer was used. Details of analyses are also given in Appendix A.

Instrumental analysis

Infrared spectra were taken on a Perkin Elmer FT-IR 1720 X spectrometer in either paraffin oil or polyoil matrix in CsI monocrystal windows. X-ray diffraction patterns were taken on a Seifert Enraf Nonius Guinier camera (Cu K_{α}). The patterns were compared with standard patterns in μ PDSM computer database [13]. Thermal analyses were done on Netzch STA-409, Mettler TG M3 and Mettler DSC 20 instruments.

RESULTS

The slow evaporation of equimolar water solution of H_3BO_3 (0,5M) and H_3PO_4 (0,5M) at room temperature gave soft, greasy, transparent platelets which crystallised out of solution. Both X-ray diffraction pattern and IR spectra showed they were identical with boric acid H_3BO_3 . In the samples prepared as noted in the Table 1, we obtained white powder which was clearly crystalline in the high temperature samples. The results of chemical analysis are shown in Table 2. The results approximately correspond to the calculated values (29,28 % P and 10,22% B in BPO_4) except for the samples 1 and 2. Molar ratio is approximately 1:1 for all samples. If the rest of the weight is ascribed to water, samples 1 and 2 have 19 %, sample 3 has 3 % and sample 4 has 5 %. The percent of water in sample 1 corresponds to the formula $BPO_4 \cdot 1,4H_2O$.

TABLE 2. The results of the chemical analysis.

sample no.	weight (mg)	weight percent P	weight percent B	mol. ratio P:B = 1:x	sum of w. percent $P_2O_5+B_2O_3$
1	258,5	23,4	8,4	1,028	80,7
2	215,5	23,3	8,5	1,045	80,9
3	203,8	28,1	10,2	1,042	97,2
4	197,7	28,2	9,5	0,963	95,0
5a	264,4	28,9	10,3	1,019	99,4
5b	225,5	29,1	10,6	1,047	101,0
6	213,3	29,0	10,5	1,041	100,5

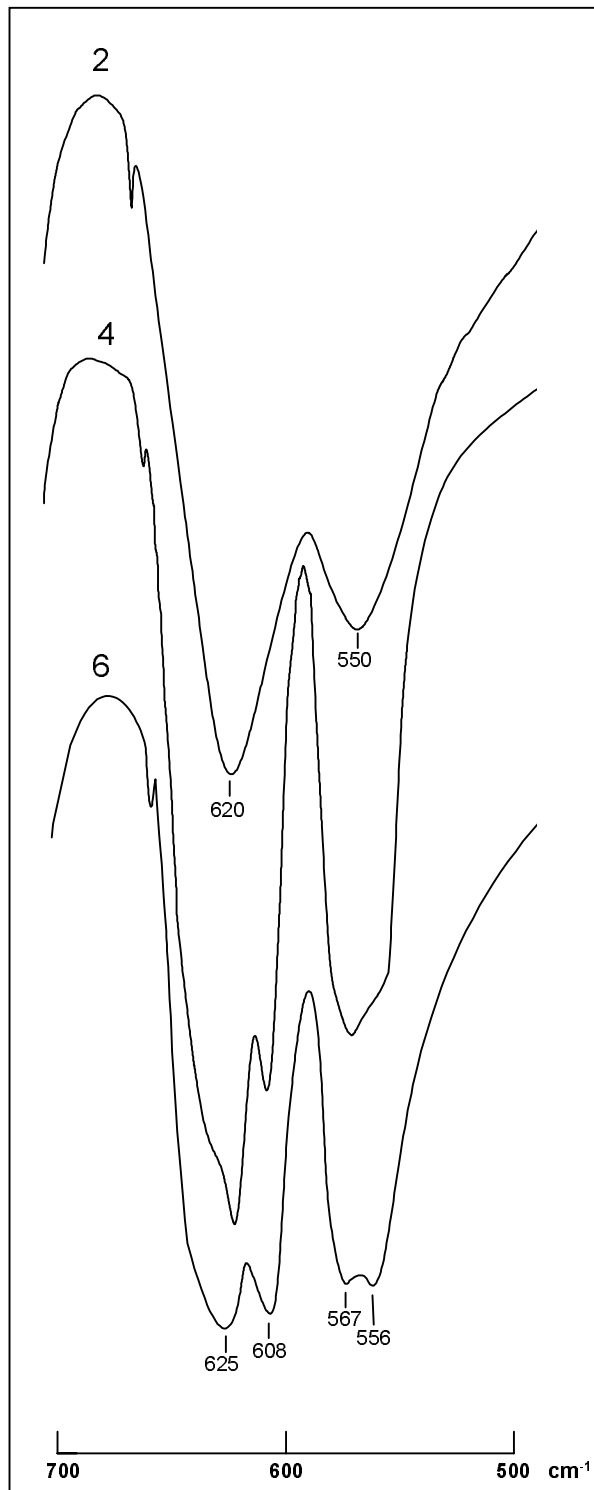


FIGURE 1. IR spectra of the samples 2,4 and 6 in the range from 500 to 700 cm⁻¹

X-ray diffraction data are shown in Table 3. Increase in resolution with the temperature of synthesis can be seen. More diffraction lines appear progressively. Except for the strongest band, an increase in interplanar distances also occurs. In the last product these distances are again slightly diminished. Diffraction lines at 1,5679 Å ($I_{rel} = 20$) and 1,5693 Å ($I_{rel} = 25$) can both only be seen in products 3 and 4, and diffraction line at 3,1856 Å ($I_{rel} = 10$) can only be seen in sample 1.

Infrared spectra have the following characteristics:

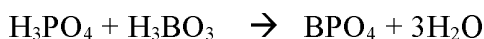
1. Broad shoulder-like absorption band in the area of 3700 -2500 cm^{-1} . It is present in the spectra of the low temperature samples (1, 2, 3).
2. Absorption bands at 3210 and 1640 cm^{-1} which appear in the spectra of all products however with different relative intensities.
3. Weak bands at 2262 and 2154 cm^{-1} (3), 2162 cm^{-1} (4), 2157 cm^{-1} (5a), 2154 cm^{-1} (5b), 2152 cm^{-1} (6). The shift toward lower frequencies with increasing temperature of synthesis can be seen.
4. Strong, broad band with peaks at 1085 cm^{-1} and 1190 cm^{-1} (the latter less clear).
5. Strong band at 930 cm^{-1} .
6. Bands at 620 and 550 cm^{-1} (1, 2, 3). The former splits into two bands at 625 and 608 cm^{-1} (4, 5a, 5b, 6). The latter splits on the spectra of product 6 into bands at 567 and 556 cm^{-1} (Figure 1).

We deal with the assignation of IR spectra in the discussion section.

DSC curve of sample 1 has two endothermic peaks. The first one is sharp and appears at 155 °C if sealed crucible is used. With one hole in crucible lid the peak temperature moves to 107 °C and with six holes it drops to 93 °C. The second DSC effect is much less intense and remains constant at all experimental conditions at 210 °C. TG analysis of sample 1 shows two vague steps at temperatures approximately corresponding the above effect. Also slow mass loss is present up to 900°C. The mass loss decreases with increasing temperature of synthesis. DTA analysis of sample 6 shows considerable change in heat capacity in the whole temperature area (40-700°C).

DISCUSSION

The reaction of phosphoric and boric acids can be described by equation:



The reaction rate seems to be determined by the diffusion of water [14]. We found out that the reaction occurs already at room temperature (sample 1).

The IR spectra can be assigned as follows. Broad shoulder-like absorption band in the area of 3700 -2500 cm^{-1} of low temperature samples (1,2,3) can be ascribed to stretching modes of O-H groups bound geminally to P or B atom with hydrogen atom bound with hydrogen bond to oxygen atom of geminal or neighbouring O-H group [3]. Absorption bands at 3210 and 1640 cm^{-1} which appear in the spectra of all products (with different intensities) can be ascribed to stretching and deformation modes of strongly adsorbed water. We didn't try to assign the weak bands at 2262 and 2154 cm^{-1} (3), 2162 cm^{-1} (4), 2157 cm^{-1} (5a), 2154 cm^{-1} (5b), 2152 cm^{-1} (6) but they usually belong to the combination bands. The shift toward lower frequencies with increasing temperature of synthesis can be seen. These bands are also described in literature [2] but also not assigned. Strong, broad band with peaks at 1085 cm^{-1} and 1190 cm^{-1} (the latter less clear) belongs to $\nu_3(\text{BO}_4)$ stretching and strong band at 930 cm^{-1} belongs to $\nu_3(\text{PO}_4)$ stretching modes respectively[8]. Deformation absorption bands of groups O-B-O and O-P-O (ν_4) appear at 620 and 550 cm^{-1} (1, 2, 3). The former splits with the rise in synthesis temperature into two bands at 625 and 608 cm^{-1} (4, 5a, 5b, 6). The latter splits on the spectra of product 6 into bands at 567 and 556 cm^{-1} . Splitting of the two bands can be ascribed to crystallisation of amorphous boron phosphate which occurs through binding of free O-B-O and O-P-O groups to the three-dimensional network similar to SiO_2 . In this process chemically bound water is also released and the corresponding broad band can only be seen in the spectra of products 1, 2 and 3. There are no bands at 1470 and 790 cm^{-1} which would belong to stretching and bending modes of boric acid which indicates that there is no free acid in the samples.

Conclusions from the IR spectra are confirmed with other analyses. X-ray powder patterns (Table 3) yield sharper and more diffraction lines progressively with the temperature of synthesis. This shows the gradual increase in crystallinity. Diffraction lines at 1,5679 Å ($I_{\text{rel}} = 20$) and 1,5693 Å ($I_{\text{rel}} = 25$) can both only be seen in products 3 and 4, and diffraction line at 3,1856 Å ($I_{\text{rel}} = 10$) can only be seen in sample 1. They are probably due to the hydration which only occurs to a smaller degree.

The DSC endothermic effects can be ascribed to the desorption of water. The first peak (noticed at 155, 107 and 93°C, depending on the number of holes in the lid) belongs to the surface bound water and the second one at 210°C most probably to the release of chemically bound water. This process does not depend on the partial pressure of water as the reaction occurs inside the material. It is known that specific surface of BPO₄ is the greatest at about 200°C. The slight mass loss at higher temperatures shown by TG is due to the loss of P₂O₅ and B₂O₃ from the not wholly crystalline material. Interestingly enough, Volkovich et al. describe the endothermic peak at 82°C and exothermic at 195°C (synthesis of BPO₄ from the acids). The authors ascribe these peaks to the dehydration and crystallisation respectively [15]. According to our results the crystallisation is not a one-step process but rather a gradual one, proceeding with the elevation of temperature. This is further confirmed with the solubility of samples which is also described in literature [15] and the change of heat capacity with temperature as determined by DTA.

The chemical analysis (Table 2) confirms this since the molar ratio remains approximately 1:1 which indicates together with the results of TG that no substantial loss of oxides is present. This is not in accordance with literature [9] and is probably dependent on the way of preparation.

APPENDIX A: Details of chemical analyses

Solubilization of samples

Weigh the excess (10-15 x) of NaOH into nickel pot and carefully heat with gas burner. When the melting is completed stop the heating and allow the melt to solidify on the walls of the pot by slowly turning it. Let it cool down and then weigh a well

powdered sample to the bottom. Cover the sample with a platelet of NaOH and then carefully heat the pot again until the sample is dissolved. The reaction can be quite vigorous so the pot should preferably be covered with a nickel lid. Let it cool again on the walls, wipe the outer side and dissolve in hydrochloric acid (HCl conc.:water = 2:3). The final solution should be acidic.

Quantitative analysis of phosphorous

The sample should not have more than 2,0 mg of phosphorous per 25 ml solution and should be slightly acidic. Transfer 25 ml of sample solution into 50 ml flask, add 5 ml 1 : 2 solution of HNO₃ conc. and 5 ml of vanadate solution. Add 5 ml of molybdate solution, dilute to mark and thoroughly mix. After five minutes measure absorbance at 460 nm in 1 cm cell. Use no-sample solution as a reference.

Vanadate solution: Dissolve 2,5 g NH₄VO₃ in 500 ml of boiling water. Let it cool and add 20 ml HNO₃ conc. Dilute to 1 litre and store in a PE bottle.

Molybdate solution: Dissolve 50 g of (NH₄)₆Mo₇O₂₄ · 4H₂O in 1 litre of warm (50 °C) water. Store in a PE bottle.

Quantitative analysis of boron

Transfer 1 ml sample (1-8 µg of boron) of sample solution into the test vessel (boron free glass) and add 10,00 ml of kinalizarine solution. Shut, mix and cool in water. When cooled, leave at room temperature for 20 min. Measure adsorbance at 620 nm and use no-sample solution as a reference.

Kinalizarine solution: Dissolve 45 mg of kinalizarine in 1 litre of H₂SO₄ (96%). Let it stand for one day and mix occasionally.

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POVZETEK

Borov fosfat, BPO_4 , smo sintetizirali iz ekvimolarne zmesi H_3PO_4 in H_3BO_3 pri temperaturah od 25 do 1200 °C. IR spektri, rentgenski praškovni posnetki, termična analiza in kemična analiza bora ter fosforja so pokazali, da reakcija poteka že pri sobni temperaturi, kristalizacija pa je postopen proces. Molsko razmerje bora in fosforja je 1:1 ne glede na temperaturo sinteze.