Low Temperature Solid-State Zinc Borate Synthesis from ZnO and H$_3$BO$_3$

A. S. Kipcak, N. Baran Acarali, E. Moroydor Derun, N. Tugrul, and S. Piskin

**Abstract**—Zinc borate can be used as multi-functional synergistic additives with flame retardant additives in polymers. Zinc borate is white, non-hygroscopic and powder type product. The most important properties are low solubility in water and high dehydration temperature. Zinc borates dehydrate above 290°C and anhydrous zinc borate has thermal resistance about 400°C. Zinc borates can be synthesized using several methods such as hydrothermal and solid-state processes. In this study, the solid-state method was applied at low temperatures of 600°C and 700°C using the starting materials of ZnO and H$_3$BO$_3$ with several mole ratios. The reaction time was determined as 4 hours after some preliminary experiments. After the synthesis, the crystal structure and the morphology of the products were examined by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). As a result the forms of ZnB$_2$O$_4$·3H$_2$O, Zn$_3$(BO$_3$)$_2$·ZnB$_2$O$_4$ were synthesized and obtained along with the unreacted ZnO.

**Keywords**—FT-IR, solid-state method, zinc borate, XRD.

I. INTRODUCTION

Zinc borate is an important inorganic hydrated borate that finds applications ranging from polymers to paints for various purposes, such as; flame retardant, corrosion inhibitor, etc. depending on the type of zinc borate [1]. Zinc borate is a multifunctional fire retardant containing different proportion of zinc and boric oxides [2]. Zinc borate are widely used in plastic, rubber, ceramics, paint, wire, electrical insulation, wood applications, cement and pharmaceutical industries due to its properties [3], [4]. Zinc borate which has different crystal structures is a synthetic hydrate metal borate [5].

Zinc borate is produced by reaction between aqueous boric acid and zinc oxide above 70°C. Zinc borate is (2ZnO·3B$_2$O$_3$·3.5H$_2$O) one of the several types of zinc borates. This compound has the unusual property of retaining its water of hydration at temperatures up to 290°C. This thermal stability makes it attractive as a fire retardant additive for plastics and rubbers that require high processing temperatures. It is also used as an anticorrosive pigment in coatings [6].

Shi et al. [7] studied the preparation of 2ZnO·3B$_2$O$_3$·3H$_2$O from zinc oxide and boric acid via a rheological phase reaction. The products were characterized by XRD, TG, DTA, and SEM. Moreover, the effects of experimental conditions and particle size distribution on the characteristics of the products were investigated. The aforementioned synthetic method is facile, creates no pollution and provides a yield of approximately 100%. Thus, zinc borate is an important green material that can be used to remove various toxic gases and organic compounds and can be synthesized in an environmentally friendly manner.

Igarashi et al. [8] synthesized zinc borates in a two-step reaction. In the first step, zinc oxide and boric acid were combined and stirred at 60°C for 1.5 hours to achieve crystal formation. In the second step, the mixture was stirred continuously at 90°C for 4 hours, and seed crystals were added to the reaction mixture to enhance crystal growth.

In this study, the solid-state synthesis of dehydrated zinc borates at 600 and 700°C were aimed. Synthesized products are characterized by X-Ray Diffraction (XRD) (Philips PANalytical, Xpert-Pro) and Fourier Transform Infrared Spectroscopy (FT-IR) (Perkin Elmer, Spectrum One).

II. MATERIALS AND METHODS

A. Raw Material Preparation

Zinc oxide was supplied from Colakoglu Chemistry Limited Company and boric acid was retrieved from Kirka Boron Management Plant in Eskisehir. Zinc oxide was used without pretreatment and boric acid was crushed, grinded with agate mortar and sieved to 200 meshes (Fig. 1). Identification analysis of both zinc oxide and boric acid were made by Philips PANalytical X-Ray Diffraction that can be seen in Fig. 2.
After the identification analysis with XRD, Perkin Elmer Brand Fourier Transform Infrared Spectroscopy (FT-IR) technique with Universal ATR sampling accessory – Diamond / ZnSe Crystal was used. Measurement range was selected as 4000–650 cm\(^{-1}\), scan number was 4 and resolution set as 4 cm\(^{-1}\) (Fig. 3).

In the pelletization process, the samples were pressed at a pressure of 100 bars for the duration of two minutes. The ratios of raw materials were selected as 1:2, 1:3, 1:4, 1:5 and 1:6, where first component was zinc oxide and second component was boric acid.

C. Solid-State Synthesis

After the pelletization processes, the pellets were subjected to high temperature furnace with the ceramic crucibles. The temperature increment was selected as 10°C/min and reaction time as 240 minutes. 600 and 700°C were studied.

D. Characterization of the Products

All products were characterized by XRD (Philips PANalytical, Xpert-Pro). Furthermore, FT-IR (Perkin Elmer, Spectrum One) was used to identify the functional groups present in the products.

III. RESULTS AND DISCUSSION

A. Raw Material Characterization Results

XRD analysis results of raw materials were given in Figs. 5-8 and Table I.
TABLE I
XRD RESULTS OF REACTIVES

<table>
<thead>
<tr>
<th>Reference Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-079-2205</td>
<td>Zinc oxide</td>
<td>ZnO</td>
<td>91</td>
</tr>
<tr>
<td>01-073-2158</td>
<td>Sassolite</td>
<td>$\text{H}_3\text{BO}_3$</td>
<td>62</td>
</tr>
</tbody>
</table>

From the results of the XRD analysis “01-079-2205” coded zinc oxide and “01-073-2158” coded sassolite was found.

TABLE II
XRD RESULTS OF PRODUCTS SYNTHESIZED 600°C

<table>
<thead>
<tr>
<th>$\text{ZnO}_x\text{H}_3\text{BO}_y$ Ratio</th>
<th>Pdf no</th>
<th>Name</th>
<th>Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>01-071-0634</td>
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<td>ZnB$_3$O$_7$</td>
<td>16</td>
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<tr>
<td></td>
<td>00-016-0283</td>
<td>Zinc Borate</td>
<td>ZnB$_3$O$_7$</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>01-071-2063</td>
<td>Zinc Borate</td>
<td>Zn$_3$(BO$_3$)$_2$</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>01-079-2205</td>
<td>Zinc Oxide</td>
<td>ZnO</td>
<td>53</td>
</tr>
<tr>
<td>1:3</td>
<td>01-071-0634</td>
<td>Zinc Borate</td>
<td>ZnB$_3$O$_7$</td>
<td>14</td>
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<tr>
<td></td>
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<tr>
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<td>Zn$_3$(BO$_3$)$_2$</td>
<td>9</td>
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<td></td>
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<td>ZnO</td>
<td>53</td>
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<td>ZnB$_3$O$_7$</td>
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<td>Zinc Oxide</td>
<td>ZnO</td>
<td>75</td>
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<tr>
<td></td>
<td>01-079-2205</td>
<td>Zinc Oxide</td>
<td>ZnO</td>
<td>81</td>
</tr>
</tbody>
</table>

At 600°C reaction time five different types of dehydrated zinc borates were formed. Also in the XRD results unreacted
ZnO was seen at all the ratios means that the formations of zinc borates were not completed at this temperature. The major zinc borate phase seen at all ratios, except 1:3, was “01-071-0634” coded zinc borate (ZnB₂O₄). At 1:3 ratio the major phase was seen as “00-0004-0631” coded zinc borate (ZnB₂O₃). The highest crystal scores of zinc oxides were at the ratio from 1:2 to 1:5 and no peaks of zinc oxide was seen at 1:6. The highest crystal scores of zinc oxides were at the ratio from 1:2 to 1:5 and no peaks of zinc oxide was seen at that temperature, but its crystal score was decreasing with the ratio of 1:4 and at all the ratios the major phase was seen as “01-071-0634” coded zinc borate (ZnB₂O₄).

C. FT-IR Results

FT-IR spectrums of the synthesized minerals both at 600 and 700°C temperature were shown in Fig. 11 and Fig. 12. The peak interpretations were given in Table IV.

From the 700°C XRD results it was seen that two types of zinc borates were formed. Unreacted zinc oxide was also seen at that temperature, but its crystal score was decreasing with the ratio from 1:2 to 1:5 and no peaks of zinc oxide was seen at 1:6. The highest crystal scores of zinc oxides were seen at the ratio of 1:4 and at all the ratios the major phase was seen as “01-071-0634” coded zinc borate (ZnB₂O₄).

IV. CONCLUSION

Zinc borate (ZB) is a multifunctional fire retardant containing different proportion of zinc, magnesium and boric oxides, respectively. The analysis results (XRD, FT-IR and Raman) showed that low temperature solid-state zinc borate synthesis from ZnO and H₃BO₃ was achieved. At 600 and 700°C temperature the formation of “01-071-0634” coded zinc borate (ZnB₂O₄) was the major phases and at the ratio of 1:4, crystal scores were the highest. As seen from (1), the formation of ZnB₄O₇ zinc borate at 1:4 ratio was produced as expected.
ZnO(s) + 4H$_3$BO$_3$(s) $\xrightarrow{\text{heat}}$ ZnB$_4$O$_7$(s) + 6H$_2$O(g) (1)

The FT-IR results of the products showed the characteristic peaks of the dehydrated zinc borates.

REFERENCES


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Nil Baran Acarali was graduated from B.Sc. in Food Eng. Department at Trakya Univ., Edirne in 2000, both M.Sc. and Ph.D. in Chemical Eng. Department at Yildiz Tech. Univ., Istanbul in 2003 and 2008 respectively. She has published nine articles in science citation index, over twenty nine studies in international conference proceedings and national proceedings. Her articles have forty two cited references. The research interests are supercritical fluids technology, polymer technology, boron technology, fly ash characterization and heavy metal adsorption. The research field in boron technology is zinc borate production. Dr. Baran Acarali is an online member of boron research.

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