Low Temperature Solid-State Zinc Borate Synthesis from ZnO and H₃BO₃

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

Abstract—Zinc borates 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 around 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 H₃BO₃, 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 ZnB₂O₄·3H₂O, ZnB₂O₃·3H₂O, ZnB₂O₄·5H₂O and ZnB₂O₃ 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·3B₂O₃·3.5H₂O) 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·3B₂O₃·3H₂O 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 (FTRIR) 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\(^\circ\)C/min and reaction time as 240 minutes. 600 and 700\(^\circ\)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

<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>H₃BO₃</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

<table>
<thead>
<tr>
<th>ZnO:H₃BO₃ 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>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>00-016-0283</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>01-071-2063</td>
<td>Zinc Borate</td>
<td>Zn₃(BO₃)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>00-004-0631</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>00-004-1777</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>00-004-2063</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>01-079-2205</td>
<td>Zinc Oxide</td>
<td>ZnO</td>
<td>33</td>
</tr>
<tr>
<td>1:4</td>
<td>01-071-0634</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>01-079-2205</td>
<td>Zinc Oxide</td>
<td>ZnO</td>
<td>75</td>
</tr>
<tr>
<td>1:5</td>
<td>01-071-0634</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>00-004-2063</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>01-079-2205</td>
<td>Zinc Oxide</td>
<td>ZnO</td>
<td>74</td>
</tr>
<tr>
<td>1:6</td>
<td>01-071-0634</td>
<td>Zinc Borate</td>
<td>ZnB₃O₇</td>
<td>11</td>
</tr>
<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 (ZnB₂O₄). The highest crystal score was obtained at the ratio of 1:5.

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).

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.

At the peaks around 1400cm⁻¹ and 1190cm⁻¹, the asymmetrical stretching of three coordinate boron and asymmetrical stretching of four coordinate boron were appeared. Other peaks at around 1050cm⁻¹, between 910 - 880cm⁻¹ and one peak observed at 987.73cm⁻¹ were also the asymmetrical stretching of four coordinate boron. And the last peaks seen at about 710cm⁻¹ might be the stretching of three coordinate boron.

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 ZnB₂O₄ zinc borate at 1:4 ratio was produced as expected.
heat
\[
\text{ZnO(s) + 4H}_2\text{BO}_3(s) \rightarrow \text{ZnB}_4\text{O}_7(s) + 6\text{H}_2\text{O(g)} \quad (1)
\]

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

REFERENCES

Azmi Seyhun Kipcak was graduated from Department of Chemical Engineering in Ege University in 2002. After completing the university studies he graduated from Bilgi University from the department of Master of Business Administration in 2004. He worked in Kultur University from 2003 to 2007 as a research assistant then he transferred to Yildiz Technical University at 2008, where he started his M.Sc. studies about Chemical Engineering in 2006. He completed his M.Sc. and Ph.D. studies at Yildiz Technical University in 2009 and 2013, respectively. He studied on neutron shielding with boron minerals and the characterization of boron minerals by using XRD, XRF, FT-IR, Raman, DTA/TG, DSC and ICP-OES at the M.Sc. studies and studied on the synthesis of magnesium borates from different raw materials and wastes at the Ph.D. Also he is improving the neutron shielding studies with the synthesized materials and working on the element analysis of Turkish Teas and Coffees. Another research field about the studies he is working is the zinc borate synthesis.

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.

Emek Moroydor Derun was born in Istanbul in 1976. Moroydor Derun was graduated from B.Sc. in 1998, M.Sc. in 2000 and Ph. D. in 2005 from Chemical Engineering Department at Yildiz Technical University, Istanbul. Her research interest is in the area of waste management, lightweight concrete, semiconductive materials and boron technology. She has many articles and studies in international and national conference proceedings and articles.

Nurcan Tugrul was born in Gaziantep in 1973. Tugrul was graduated from B.Sc., M.Sc. and Ph.D. in Chemical Eng. Department at Yildiz Technical University, Istanbul. Her research interest is in the area of chemical technologies, evaluation of industrial wastes, food drying. She has many articles and studies in international and national conference proceedings and articles.

Sabriye Piskin graduated from Istanbul Technical University on Chemical Engineering with M.Sc. degree in 1974. She completed a Ph.D. degree at the same department in 1983. Her research interests include boron minerals and compounds, hydrogen storage technologies, fuel cell applications, materials characterization, coal, waste management, corrosion, implants and synthetic materials production.