Combined Hydrothermal Synthesis of Zinc and Magnesium Borates at 100°C Using ZnO, MgO and H$_3$BO$_3$

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

Abstract—Magnesium borate (MB) is a technical ceramic for high heat-resisting, corrosion-resisting, super mechanical strength, superinsulation, light weight, high strength, and high coefficient of elasticity. Zinc borate (ZB) can be used as a multi-functional synergistic additive with flame retardant additives in polymers. The most important properties are low solubility in water and high dehydration temperature. ZB dehydrates above 290°C and anhydrous ZB has thermal resistance about 400°C. In this study, the raw materials of ZnO, MgO and H$_2$BO$_3$ were used with mole ratio of 1:1:9. With the starting materials hydrothermal method was applied at a temperature of 100°C. The reaction time was determined as 30, 60, 90 and 120 minutes 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 Zinc Oxide Borate Hydrate $[\text{Zn}_2\text{B}_2\text{O}_5\cdot3\text{H}_2\text{O}]$ and Mcallisterite $[\text{Mg}_6\text{B}_6\text{O}_{12}(\text{OH})_3\cdot9\text{H}_2\text{O}]$ were synthesized.

Keywords—Magnesium borate, zinc borate, XRD, FT-IR.

I. INTRODUCTION

SINGLE-CRYSTALLINE magnesium borate $\text{Mg}_3\text{B}_2\text{O}_5$ nanorods have been synthesized via a simple route based on the calcinations of mixed powders containing $\text{Mg(OH)}_2$ and $\text{H}_2\text{BO}_3$ at 900°C in 3h. The nanorods have the typical diameters in the range of 70–120nm and the lengths up to a few micrometers [1]. Single-phase $\text{Mg}_3\text{B}_2\text{O}_5$ and $\text{Mg}_5\text{B}_2\text{O}_6$ ceramics have been synthesized from MgO and B$_2$O$_3$ by solid-state reaction techniques. At the end of the experiments $\text{Mg}_3\text{B}_2\text{O}_5$ forms 1250–1280°C temperature range and $\text{Mg}_5\text{B}_2\text{O}_6$ forms 1200–1300°C temperature range [2]. B and MgO (with a molar ratio of 1:1) have thoroughly mixed to prepare $\text{Mg}_3\text{B}_2\text{O}_5$ nanobelts. Under flowing mixed Ar/H$_2$O gases, the mixture of B and MgO was heated to 1100°C and held at this temperature for 90min, and then subsequently cooled to room temperature [3]. Using MgCl$_2$, H$_2$O and NaBH$_4$ powders as the starting materials for the production of monoclinc $\text{Mg}_3\text{B}_2\text{O}_5$, the mixture was firstly milled for 120 h, and then sintered at 800°C for 2h. It was seen that mechanic process needed to formation of Mg-B-H [4]. 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 [5]. Zinc borate is a multifunctional fire retardant containing different proportion of zinc and boric oxides [6]. Zinc borate are widely used in plastic, rubber, ceramics, paint, wire, electrical insulation, wood applications, cement and pharmaceutical industries due to its properties [7], [8]. The production of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ from zinc oxide and boric acid via a rheological phase reaction was studied by Shi et al. [9]. The characterizations of the products were done by XRD, TG, DTA and SEM. Addition: the effects of experimental conditions and particle size distribution on the characteristics of the products were investigated. This synthetic method is green, and without pollution it provides a yield of approximately 100%.

In this study, combined hydrothermal synthesis of zinc and magnesium borates at 100°C using ZnO, MgO and H$_2$BO$_3$ is 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, magnesium oxide was supplied from merck chemicals and boric acid was retrieved from Kirka Boron Management Plant in Eskisehir. Zinc oxide and magnesium oxide were used without pretreatment and boric acid was crushed, grinded with agate mortar and sieved to 200 meshes (Fig. 1). Identification analysis of zinc oxide, magnesium oxide and boric acid were made by Philips PANalytical X-Ray Diffraction that can be seen in Fig. 2.

Addition to the XRD analysis, 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 4000–6500 cm⁻¹, scan number was 4 and resolution set as 4 cm⁻¹ (Fig. 3).

The reaction intervals were set to 30, 60, 90 and 120 minutes. In synthesis procedure, firstly boric acid was dissolved in water at the desired temperature, then zinc oxide and zinc borate retrieved from local market in Turkey (in terms of boric acid, 0.5% w/w) was added, after the determined interval magnesium oxide was added to the mixture. So, reaction times were come up as 60, 120, 180 and 240 minutes for zinc borates and reaction times were come up as 30, 60, 90 and 120 minutes for magnesium borates.

C. 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.

RESULTS AND DISCUSSION

A. Raw Material Characterization

XRD analysis results of raw materials were given in Figs. 4-6 and Table I.

For synthesis, mole ratio of zinc oxide, magnesium oxide and boric acid was determined experimentally and found as 1:1:9. The liquid phase was used as demineralized water (18.3 mΩ·cm) that produced from the equipment of Human Power I+ Water Purification System.

Experiment temperature was selected as 100°C, and four different reaction times were conducted to investigate the phase transition between different types of zinc borates and magnesium borates according to the reaction time changes.
The XRD results of the synthesized zinc borates and magnesium borates at 100°C were given in Tables II and III, respectively.

**TABLE I**

<table>
<thead>
<tr>
<th>Reference Code</th>
<th>Compound Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-079-2205</td>
<td>Zinc oxide</td>
<td>ZnO</td>
</tr>
<tr>
<td>01-073-2158</td>
<td>Sassolite</td>
<td>H₂BO₃</td>
</tr>
<tr>
<td>01-087-0651</td>
<td>Periclase</td>
<td>MgO</td>
</tr>
</tbody>
</table>

From the results of the XRD analysis “01-079-2205” coded zinc oxide (ZnO), “01-073-2158” coded sassolite (H₂BO₃) and “01-087-0651” coded periclase (MgO) were found.

FT-IR spectrums of zinc oxide, magnesium oxide and boric acid were given in Figs. 7 and 8.

**B. XRD Results**

The XRD results of the synthesized zinc borates and magnesium borates at 100°C were given in Tables II and III, respectively.

**TABLE II**

<table>
<thead>
<tr>
<th>Reaction Time (mins)</th>
<th>pdfno</th>
<th>Name</th>
<th>Formula</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>00-011-0279</td>
<td></td>
<td>Zinc Borate</td>
<td>Zn₂B₂O₇₃·7H₂O</td>
<td>17</td>
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<tr>
<td>00-032-1461</td>
<td></td>
<td>Zinc Borate Hydrate</td>
<td>Zn₂B₂O₇₃·14H₂O</td>
<td>41</td>
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<tr>
<td>60</td>
<td>01-075-0766</td>
<td>Zinc Borate Hydroxide Hydrate</td>
<td>Zn(B₂O₆(OH)₂)·H₂O</td>
<td>32</td>
</tr>
<tr>
<td>00-021-1474</td>
<td></td>
<td>Zinc Oxide</td>
<td>ZnB₂O₃·3H₂O</td>
<td>9</td>
</tr>
<tr>
<td>00-035-0433</td>
<td></td>
<td>Zinc Oxide</td>
<td>ZnB₂O₃·3.5H₂O</td>
<td>22</td>
</tr>
<tr>
<td>120</td>
<td>00-035-0433</td>
<td>Zinc Oxide Borate Hydrate</td>
<td>Zn₂B₂O₇₃·5H₂O</td>
<td>75</td>
</tr>
<tr>
<td>180</td>
<td>00-035-0433</td>
<td>Zinc Oxide Borate Hydrate</td>
<td>Zn₂B₂O₇₃·3.5H₂O</td>
<td>78</td>
</tr>
<tr>
<td>240</td>
<td>00-035-0433</td>
<td>Zinc Oxide Borate Hydrate</td>
<td>Zn₂B₂O₇₃·3.5H₂O</td>
<td>76</td>
</tr>
</tbody>
</table>

Five different zinc borates were formed at the reaction time of 60 minutes. After the reaction time of 60 minutes, the expected formation of zinc borate of “00-035-0433” zinc oxide borate hydrate (Zn₂B₂O₇₃·3.5H₂O) was formed. The highest zinc borate XRD crystal score was obtained at the reaction time of 180 minutes. The XRD patterns of the zinc borates were shown in Fig. 9.
From the XRD results it was seen that two types of magnesium borates were formed namely callisterite and admontite. These two formations were seen at all the reaction times. The highest callisterite and admontite formations were seen on 60 and 180 minutes of reaction times, respectively. The XRD patterns of the magnesium borates synthesized at 100°C were shown in Fig. 10.

C. FT-IR Results

The FT-IR spectrums and peak interpretations of the synthesized zinc borates and magnesium borates at 100°C were given in Figs. 11, 12 and Table IV, respectively.

At the FT-IR spectrums of zinc borates the peaks at 1400 cm\(^{-1}\) represents the three coordinate boron asymmetrical stretching, the peaks between 1323 and 1217 cm\(^{-1}\), represents the OH\(^{-1}\) in plane stretching due to the crystal waters inside the zinc borates. Four coordinate boron asymmetrical stretching was observed between the peaks of 1119 and 983 cm\(^{-1}\). Three coordinate boron symmetrical stretching was obtained at the peaks between 920 and 837 cm\(^{-1}\). The last peaks between the 790 and 657 cm\(^{-1}\), were the stretching of three coordinate boron.

Fig. 12 FT-IR spectrum of magnesium borates synthesized at 100°C

In magnesium borates FT-IR spectrums similar to zinc borate spectrums at around 1400 cm\(^{-1}\) represents the three coordinate boron asymmetrical stretching. Other two peaks at around 1337 and 1235 cm\(^{-1}\), was OH\(^{-1}\) in plane stretching due to the crystal waters inside the magnesium borates. The peaks between 1040 and 857 cm\(^{-1}\) represents four coordinate boron asymmetrical stretching. Also in magnesium borates OH\(^{-1}\) out of plane stretching was seen addition to zinc borates which it was due to the crystal waters inside the magnesium borates also like OH\(^{-1}\) in plane stretching. The last peak represents the stretching of three coordinate boron with the peaks values at around 670 cm\(^{-1}\).

### TABLE IV

<table>
<thead>
<tr>
<th>Peaks (cm(^{-1}))</th>
<th>Peak Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600-1400</td>
<td>B-O asymmetrical stretching</td>
</tr>
<tr>
<td>1400-1200</td>
<td>OH(^{-1}) in plane stretching</td>
</tr>
<tr>
<td>1200-950</td>
<td>B-O asymmetrical stretching</td>
</tr>
<tr>
<td>950-850</td>
<td>B-O symmetrical stretching</td>
</tr>
<tr>
<td>850-750</td>
<td>OH(^{-1}) out of plane stretching</td>
</tr>
<tr>
<td>750-650</td>
<td>B-O stretching</td>
</tr>
</tbody>
</table>

### III. CONCLUSION

Zinc borates (ZB) and Magnesium borates (MB) are multifunctional fire retardants containing different proportion of zinc, magnesium and boric oxides, respectively. The analysis results (XRD and FT-IR) showed that combined hydrothermal synthesis of zinc and magnesium borates at 100°C using ZnO, MgO and H\(_3\)BO\(_3\) was achieved.

The best XRD crystal results were obtained 180 and 120 minutes reaction time for zinc borates and magnesium borates respectively. For the combined hydrothermal synthesis of both zinc and magnesium borates either 120 or 180 minutes of reaction time was seen optimum values. The selected ratio of
raw materials ZnO:MgO:H₂BO₃ (1:1:9 or 3:3:27) was also perfectly fit with the expected two step reaction and one step washing process given in (1) between (3).

**Step 1**

\[ 2\text{ZnO} + 27\text{H}_2\text{BO}_3 + 9\text{H}_2\text{O} \rightarrow \text{Zn}_3\text{B}_2\text{O}_5 \cdot 3\text{H}_2\text{O} + 21\text{H}_2\text{BO}_3 + 9\text{H}_2\text{O} \]  

(1)

where zinc borate was obtained at crystal phase

**Step 2**

\[ 3\text{MgO} + 21\text{H}_2\text{BO}_3 + 9\text{H}_2\text{O} \rightarrow \text{Mg}_3\text{B}_2\text{O}_5 \cdot 9(\text{OH})_2 \cdot 3\text{H}_2\text{O} + 3\text{H}_2\text{BO}_3 + 9\text{H}_2\text{O} \]  

(2)

where magnesium borates were obtained at the solution phase and crystallized at 40°C.

**Step 3 (Washing process)**

\[ \text{dMgO(B}_2\text{O}_4\text{)}_3, 7(\text{H}_2\text{O}) + 3(3-d)\text{Mg}_3\text{B}_2\text{O}_5(\text{OH})_2 \cdot 9(\text{H}_2\text{O}) + 3\text{H}_2\text{BO}_3 \rightarrow \text{dMgO(B}_2\text{O}_4\text{)}_3, 7(\text{H}_2\text{O}) + 3(3-d)\text{Mg}_3\text{B}_2\text{O}_5(\text{OH})_2 \cdot 9(\text{H}_2\text{O}) \]  

(3)

where in this step, excess boric acid was removed from the crystal phase.

From the FT-IR spectrums of the zinc and magnesium borates synthesized by combined hydrothermal method, it was seen that at all the reaction times the zinc and magnesium borates were obtained. At the formation of zinc borates the different formation was seen on the 60 minutes of reaction time in XRD results, also this different formation was also seen in the FT-IR results, since some peaks were differ from the other spectrums.

**REFERENCES**


