Magnesium Borate Synthesis by Microwave Method Using MgCl$_2$.6H$_2$O and H$_3$BO$_3$

A. S. Kipcak, P. Gurses, K. Kunt, E. Moroydor Derun, and S. Piskin

Abstract—There are many kinds of metal borates found not only in nature but also synthesized in the laboratory such as magnesium borates. Due to its excellent properties, as remarkable ceramic materials, they have also application areas in anti-wear and friction reducing additives as well as electro-conductive treating agents. The synthesis of magnesium borate powders can be fulfilled simply with two different methods, hydrothermal and thermal synthesis. Microwave assisted method, also another way of producing magnesium borate, can be classified into thermal synthesis because of using the principles of solid state synthesis. It also contributes producing particles with small size and high purity in nano-size and also used in other areas where magnesium borates are used.

Keywords—FT-IR, magnesium borates, microwave method, XRD.

I. INTRODUCTION

BORON minerals are used in glass, cement and ceramic industry, irrigation, boron fibers, metallurgical industry, nuclear applications, aerospace and aviation due to boron’s different characteristics [1]. On the other hand among the borates, magnesium borate is used in very wide range such as anti-wear additive [2], catalyst for the conversion of the hydrocarbons [3], production of superconducting materials, composition of detergents [4], preservative, and antisepsics [5], because it has the properties of corrosion resistance, high heat resistance, light weight [6]. Because magnesium borate has such different usage areas, in the recent years it became attractive for the researchers to synthesize it at different conditions with different raw materials [7].

The synthesis of magnesium borate powders can take place in two different methods, hydrothermal and thermal synthesis [8]. Hydrothermal method includes the way of heating reactants in aqueous solutions at significant temperatures. The aqueous solution, commonly water, enables to function both as a pressure transmitting medium and as a solvent [9]. On the other hand, thermal synthesis, also called solid state synthesis, is a method in which reaction occurs in high temperature furnace. Due to drawing correspondence with solid state synthesis, another way of producing magnesium borate, microwave assisted method, can take place in thermal synthesis.

In recent years, microwave processing has been studied deeply for synthesizing magnesium borate powders, because of the disadvantages of conventional methods, such as solid-state reactions at high temperatures [10], [11]. Apart from the possibility of decomposing of the product over time in the reaction vessel, the solid state method is quiet slow. Microwave assisted synthesis; in contrast, achieves the rapid rise in temperature and uniform heating. This occurs through microwaves which interact with materials causing the energy transfer to the reactants [12], [13]. As mentioned, the microwave synthesis method offers several advantages as useful energy sources such as short period, faster reaction times, higher reaction yield and less energy consumption [14], [15].

In literature, [16] and [17] used magnesium and boron sources with different mole ratios in various times to produce magnesium borate powders through microwave assisted method. In both studies with different reaction parameters, samples were obtained in amorphous phase. In [18], magnesium borates were obtained by microwave synthesis method using the raw materials, magnesium oxide (MgO) and boric acid (H$_3$BO$_3$). The reaction parameters were selected as 270W microwave power, 1:4 (MgO:H$_3$BO$_3$) molar ratio and 6, 8, 10, 12 minutes reaction times. From all characterization results, the synthesized magnesium borate at 8 minutes had the best results.

In this study; microwave assisted magnesium borate synthesis was achieved in both media with and without water. To be able to make this synthesis without water, calcination was used. In the literature, [19] calcined MgCl$_2$.6H$_2$O in HCl atmosphere until 203°C and MgCl$_2$.H$_2$O was obtained. Reference [20] used magnesium chloride hexahydrate and...
ammonium chloride to be able to obtain MgCl\(_2\).H\(_2\)O and calcined at 700°C (973K) for 1 hour.

Taking all these literature studies into consideration, it was aimed to produce magnesium borate with microwave assisted synthesis. For this reason, magnesium chloride MgCl\(_2\).6(H\(_2\)O) and boric acid (H\(_3\)BO\(_3\)) were used as raw materials with appropriate microwave power and various reaction times. After synthesis, X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) were applied to identify the obtained products with selected mole ratio.

II. MATERIALS AND METHODS

A. Raw Material Preparation and Characterization

Boric acid (H\(_3\)BO\(_3\)) was supplied from the Eti Bank Bandırma Boron and Acid Plant in Balikesir, Turkey. Then it was crushed, grinded with agate mortar (Fig. 1 (a)) and sieved (Fig. 1 (b)) to a particle size below 75 microns.

The other raw material, magnesium chloride hexahydrate (MgCl\(_2\).6H\(_2\)O), was provided from Sigma-Aldrich with 99.9% purity.

Boric acid powders were subjected to X-Ray Diffraction (XRD) analysis; Philips PANalytical brand (Fig. 2) with Cu-K\(_\alpha\) radiation at the parameters of 45kV and 40mA was used.

Starting materials were also subjected to “Vibration Spectroscopy” in order to characterize the raw materials. Infrared spectra were recorded in the range 650-1800cm\(^{-1}\), with Perkin Elmer Spectrum One (Fig. 3) Fourier Transform Infrared Spectroscopy (FT-IR). During the analysis, universal ATR sampling accessory – Diamond/Zn was applied and scan number was determined as 4 and resolution set as 4cm\(^{-1}\).

MgCl\(_2\).6H\(_2\)O was calcined at 250°C for 4 hours with Protherm PLF 120/7 furnace which is shown in Fig. 5.

B. Microwave Synthesis Using MgCl\(_2\).6H\(_2\)O and H\(_3\)BO\(_3\)

So as to increase the reaction efficiency, the powder was pelletized with Manfredi OL 57 Pelletizing Machine showed in Fig. 4. After mixing the compounds homogenously in the ratio of 1:2 (MgCl\(_2\).6H\(_2\)O:H\(_3\)BO\(_3\)), the samples are pressed at a pressure of 100bar in a couple of minutes.

Subsequently, the pellets were put into the microwave oven with the selected 270W microwave power for 2, 4, and 6 minutes, respectively.

C. Calcination of MgCl\(_2\).6H\(_2\)O

D. Microwave Synthesis Using MgCl\(_2\) and H\(_3\)BO\(_3\)

In order to see the effect of the calcined magnesium chloride on the reaction yield, microwave assisted method was applied using MgCl\(_2\) and H\(_3\)BO\(_3\) in the ratio of 1:2 (MgCl\(_2\):H\(_3\)BO\(_3\)). The steps for the pelletization were repeated and reaction parameters were set as 270W microwave power.
and 2, 4, 6 minutes, as well.

E. Microwave Synthesis Using MgCl₂, H₃BO₃ and H₂O

H₂BO₃ and MgCl₂ were taken with the Mg:B mole ratio of 1:4. 1 mL of deionized water was added to H₂BO₃ and then MgCl₂ was added. This sample was put inside the microwave oven that’s power was adjusted to 270 Watt for 2, 4, 6, 8, 10 and 12 minutes, respectively.

After that, samples were taken from the microwave oven; these were washed with ethanol and then dried in the Ecocell oven at 40°C.

III. RESULTS AND DISCUSSION

A. Raw Material Characterization Results

XRD results and pattern of magnesium chloride hexahydrate and boric acid were shown in Fig. 6 and Table I, respectively.

According to the XRD results of the raw materials magnesium chloride hexahydrate (MgCl₂·6H₂O) was found with powder diffraction file (pdf) number of “01F077F1268”. The “01F073F2158” pdf numbered boric acid represented the standard diffraction pattern of “Sassolite”, as well.

FT-IR spectrums of the boric acid and magnesium chloride hexahydrate were shown in Fig. 7. From the FT-IR analysis, the spectrums were in good agreement with the scanned FT-IR ATR inorganic library and the results were given in Table II.

B. MgCl₂·6H₂O and H₃BO₃ Microwave Synthesis Results

XRD patterns and results of the first synthesis were shown in Fig. 8.

According to the XRD patterns, no magnesium borate powders were detected. The peaks represented contaminated Corundum powders (Al₂O₃), which came from the alumina coated ceramic crucible, were used during the synthesis. Due to the adverse effect of coated ceramic crucible on the product, the next experiments were conducted with the watch glasses.

C. MgCl₂·6H₂O Calcination Results

Four different forms can be obviously seen by examining the XRD results. As expected after the calcination process, magnesium chloride was appeared in two varied form with the powder diffraction file number of “01-074-0521” and “01-072-1517”. Apart from dehydrated magnesium chloride, crystal structured hydrated forms were observed, as well. Yet, correspondingly to the literature, it can be also seen that the total conversion of MgCl₂·6H₂O to MgCl₂ was not occurred.
Detailed identification results are shown in Fig. 9 and Table III, respectively.

**Table III**

<table>
<thead>
<tr>
<th>Reference Code</th>
<th>Mineral Name</th>
<th>Formula Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-074-0521</td>
<td>Magnesium Chloride</td>
<td>MgCl₂</td>
</tr>
<tr>
<td>01-072-1517</td>
<td>Magnesium Chloride</td>
<td>MgCl₂</td>
</tr>
<tr>
<td>00-053-0260</td>
<td>Magnesium Chloride Hydrate</td>
<td>MgCl₂·H₂O</td>
</tr>
<tr>
<td>00-011-0328</td>
<td>Magnesium Chloride Hydroxide</td>
<td>Mg(OH)Cl</td>
</tr>
</tbody>
</table>

According to the XRD results shown in Fig. 11 and Table IV, respectively, it was observed that the synthesized products were formed in amorphous-based. Although the pattern consisted of a number of peaks which belong to Mcallisterite minerals with pdf number of “01-070-1902”, exact structure of magnesium borate powders were not formed.

**Table IV**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Reference Code</th>
<th>Mineral Name</th>
<th>Mineral Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>01-070-1902</td>
<td>Mcallisterite</td>
<td>Mg₂(B₂O₄(OH)₂)·9H₂O</td>
</tr>
<tr>
<td>4</td>
<td>01-070-1902</td>
<td>Mcallisterite</td>
<td>Mg₂(B₂O₄(OH)₂)·9H₂O</td>
</tr>
<tr>
<td>6</td>
<td>01-070-1902</td>
<td>Mcallisterite</td>
<td>Mg₂(B₂O₄(OH)₂)·9H₂O</td>
</tr>
</tbody>
</table>

According to the FT-IR spectrum results in Fig. 10, it can be obviously seen that the peaks of [OH] were formed and were not completely disappeared. With this analysis, FT-IR spectrums corroborate the results of XRD patterns.

**Peak List of FT-IR Results**

<table>
<thead>
<tr>
<th>Peak</th>
<th>2 min</th>
<th>4 min</th>
<th>6 min</th>
<th>Peak Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>1636.75</td>
<td>1637.52</td>
<td>1635.02</td>
<td>δ (H-O-H)</td>
</tr>
<tr>
<td>Peak 2</td>
<td>932.24</td>
<td>940.56</td>
<td>940.42</td>
<td>ν₁(B₃O₅O₂)</td>
</tr>
</tbody>
</table>

FT-IR spectra of the synthesized samples were assigned referring to the literature [23], [24]. Peak 1, between band values 1637.52 and 1635.02 cm⁻¹ can be assumed as H-O-H bending mode. The wide band range between 940.56 and 932.24 cm⁻¹ is assigned as symmetric stretching of B₃O₅O₂.
E. MgCl₂, H₂BO₃ and H₂O Microwave Synthesis Results

XRD patterns of the third synthesized products and accurate results are given in Fig. 13 and Table VI, respectively.

Fig. 13 XRD patterns of the third synthesized magnesium borates

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Reference Code</th>
<th>Mineral Name</th>
<th>Mineral Formula</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>00-019-0754</td>
<td>MgBH</td>
<td>Mg₂B₄O₇·7H₂O</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>01-071-2409</td>
<td>Nepskoite</td>
<td>Mg₂B₂O₇·2H₂O</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>00-050-1637</td>
<td>Nepskoite</td>
<td>Mg₂Cl(OH)·6H₂O</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>01-076-0539</td>
<td>MgBH</td>
<td>MgO(B₂O₃)·6H₂O</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>01-076-0540</td>
<td>Admontite</td>
<td>MgO(B₂O₃)·7H₂O</td>
<td></td>
</tr>
</tbody>
</table>

| Table VI: RESULTS OF THE THIRD SYNTHESIZED MAGNESIUM BORATES |

As it can be seen from the patterns and results, no crystal structure has been formed at 2 minutes. Up to the reaction time of 8 minutes, Nepskoite mineral was monitored due to the existence of H₂O, which was added before the reaction. Formation of the minerals began at 8 minutes and continued significantly up to 12 minutes of reaction time. Comparing the intensities of the observed peaks, it can be monitored that the best formation occurred at 10 minutes.

FT-IR spectrums and peak list of the third synthesized magnesium borates are given in Table VII and Fig. 14, respectively.

From the FT-IR analysis results of the synthesized magnesium borates in this experiment compromise with the ones in literature and shows the characteristic magnesium borate hydrate peaks [24], [25], [26].

IV. CONCLUSIONS

With the aim of synthesizing magnesium borate powders, microwave assisted method was applied in this study. For this purpose, the experiments were conducted step by step, basically changing the raw material, mole ratio of the starting materials and reaction time. Microwave power was always set to 270W, though.

The results of the experiments were analyzed and found that no formation occurred with the raw materials of MgCl₂·6H₂O and H₂BO₃. After that, calcination process was carried out in order to analyze the effect of itself on the yield of magnesium borate production. Nevertheless, accurate results were also not monitored by using the calcined magnesium borate. In the third step, H₂O was added to the calcined magnesium borate and H₂BO₃ mixture. The given results of this experiment showed that the crystal structure was formed after 4 minutes of reaction time. The optimum experimental result was monitored at 10 minutes, though.

It could be seen that, microwave method is an effective and optional way to obtain magnesium borate powders. Needless to say, it will be enhanced with further experiments.

REFERENCES
