

The Effect of the Reaction Time on the Microwave Synthesis of Magnesium Borates from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, MgO and H_3BO_3

E. Moroydor Derun, P. Gurses, M. Yildirim, A. S. Kipcak, T. Ibroska, S. Piskin

Abstract—Due to their strong mechanical and thermal properties magnesium borates have a wide usage area such as ceramic industry, detergent production, friction reducing additive and grease production. In this study, microwave synthesis of magnesium borates from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Magnesium chloride hexahydrate), MgO (Magnesium oxide) and H_3BO_3 (Boric acid) for different reaction times is researched. X-ray Diffraction (XRD) and Fourier Transform Infrared (FT-IR) Spectroscopy are used to find out how the reaction time sways on the products. The superficial properties are investigated with Scanning Electron Microscopy (SEM). According to XRD analysis, the synthesized compounds are 00-041-1407 pdf coded Shabinite ($\text{Mg}_5(\text{BO}_3)_4\text{Cl}_2(\text{OH})_5 \cdot 4(\text{H}_2\text{O})$) and 01-073-2158 pdf coded Karlite ($\text{Mg}_7(\text{BO}_3)_3(\text{OH},\text{Cl})_5$).

Keywords—Magnesium borate, microwave synthesis, XRD, SEM.

I. INTRODUCTION

BORATES are significant compounds because of their properties of lightweight, mechanical resistance, low thermal expansion temperature [1]. As a subgroup of borates magnesium borates are noticeable materials owing to their thermal and mechanical endurance, high coefficient of elasticity [2]-[4]. Magnesium borates are used as thermo luminescence materials, corrosion and friction reducing additive, hydrocarbon production catalysts, a matrix for ferro-elastic materials [4]-[10]. They also have an important potential to be a radiation shielding material.

The main production ways of magnesium borates are solid-state and hydrothermal method. In hydrothermal method, the synthesized the compounds are hydrated on the other hand, in thermal method the products are dehydrated.

Several methods of magnesium borate synthesis have been reported up to the present. Agaogulları et al. synthesized different compounds such as MgB_4O_7 , $\text{Mg}_2\text{B}_2\text{O}_5$ and $\text{Mg}_3\text{B}_2\text{O}_6$ by mechanical annealing [5]. Zhihong and Mancheng used hydrothermal method to produce $2\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ from MgO and H_3BO_3 [11]. Li et al. synthesized $\text{Mg}_2\text{B}_2\text{O}_5$ nanorods by mechanical treatment and sintering methods [1]. Karakassides

et al. used sol-gel route to manufacture magnesium borate compounds [12]. Li et al. used chemical vapor deposition method to produce $\text{Mg}_2\text{B}_2\text{O}_5$ compound [13].

Microwave-assisted synthesis of magnesium borates is a solid-state method in which boron and magnesium sources are mixed homogeneously and reacted in a microwave furnace [14]. In literature there are a few studies about microwave synthesis of magnesium borates. Ay et al. used MgNO_3 , B_2O_3 and H_3BO_3 as raw materials to produce magnesium borates at 750W microwave power and a reaction time of 10 minutes. However, the products were amorphous for different molar ratios of starting materials [15]. Guler et al. reacted MgO and H_3BO_3 in a microwave furnace at 700 W during 10 minutes of reaction time, but similarly with Ay [15] the products were amorphous [16]. Kipcak et al. used reactants of MgO and H_3BO_3 for microwave synthesis of magnesium borates at different microwave powers and magnesium borate hydrate minerals were produced at the reaction conditions of 270W- 8 minutes and 360W-3minutes.

In the present study, the impact of reaction time on microwave synthesis of magnesium borate compounds is investigated. The purpose of the study is to produce magnesium borates at shorter reaction times than literature. The starting materials were chosen as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, MgO and H_3BO_3 . X-ray Diffraction (XRD), Fourier Transform Infrared (FT-IR) Spectroscopy analyses were applied to the products of different reaction times (between 15 and 240 seconds). The surface structures of synthesized compounds were examined by Scanning Electron Microscopy (SEM).

II. EXPERIMENTAL

A. Preparation of Raw Materials

To synthesize magnesium borates by microwave method $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Magnesium chloride hexahydrate), MgO (Magnesium oxide) and H_3BO_3 (Boric acid) were selected as starting materials. H_3BO_3 was procured from Boron Management Plant in Bandirma, Turkey and ground with agate mortar before usage. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and MgO were supplied from Merck Chemicals and used without any pre-treatment.

B. Synthesis of Magnesium Borates via Microwave Method

In microwave synthesis of magnesium borates the molar ratio of raw materials was determined as 1:1:8 ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$: MgO : H_3BO_3). The starting materials were in the form of

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powder so they were mixed homogeneous and pelletized by Manfredi brand OL57 model press equipment under a pressure of 100 bars to get a closer connection of materials (Fig. 1).



Fig. 1 Manfredi brand OL57 model press equipment



Fig. 2 The prepared pellets

Pellets were put in the microwave furnace with the microwave power of 360W. The reaction times were adjusted as 15, 30, 45, 60, 90, 120, 180, 240 seconds. After reactions the pellets were ground and the products were obtained in powder form.



Fig. 3 Prepared pellets in microwave furnace

C. Characterization Studies of Raw Materials and Synthesized Compounds

With the object of identify the raw materials and produced magnesium borates X-Ray Diffraction (XRD), Fourier Transform Infrared (FT-IR) Spectroscopy techniques were used. Philips Panalytical XRD instrument was used with Cu-K α tube and the parameters of 45 kV and 40mA. In FT-IR analyses Attenuation Total Reflection (ATR) apparatus was used with scan number of 4, resolution of 4cm⁻¹ and scan range of 1800cm⁻¹–650 cm⁻¹. Also, the surface texture of both raw materials and products were scrutinized by CamScan

Apollo 300 Field-Emission Scanning Electron Microscopy (SEM) and the chosen detector was Back Scattering Electron (BEI).

III. RESULTS AND DISCUSSIONS

A. Characterization Results of Raw Materials

XRD patterns and results of raw materials are given in Fig. 4 and Table I respectively. The raw materials found as Bischofite (MgCl₂·6H₂O), Periclase (MgO) and Sassolite (H₃BO₃) with powder diffraction file (pdf) numbers of 01-077-1268, 01-077-2179 and 01-073-2158, respectively.

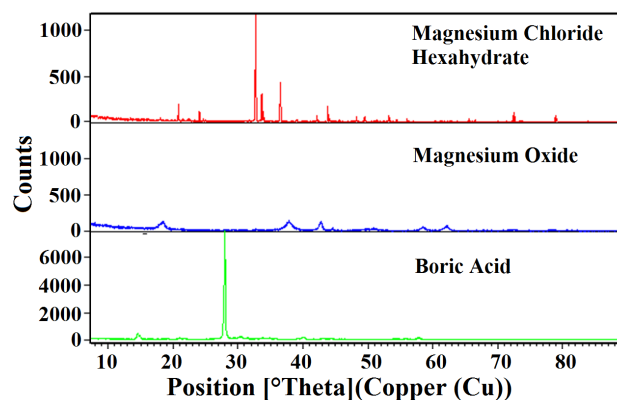


Fig. 4 XRD patterns of raw materials

FT-IR spectra of MgCl₂·6H₂O, MgO, H₃BO₃ are given in Fig. 5. The raw materials are in rapport with FT-IR ATR inorganic library.

TABLE I
XRD RESULTS OF RAW MATERIALS

Pdf code	Raw Material	Mineral Name	Mineral Formula
01-077-1268	Magnesium chloride hexahydrate	Bischofite	MgCl ₂ ·6H ₂ O
01-077-2179	Magnesium oxide	Periclase	MgO
01-073-2158	Boric acid	Sassolite	H ₃ BO ₃

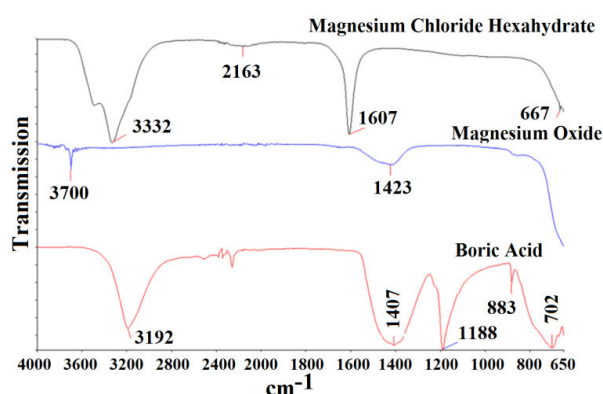


Fig. 5 FT-IR spectra of raw materials

B. Characterization Results of Raw Materials

XRD patterns and results of synthesized magnesium borates for different reaction times are shown in Fig. 6 and Table II,

respectively.

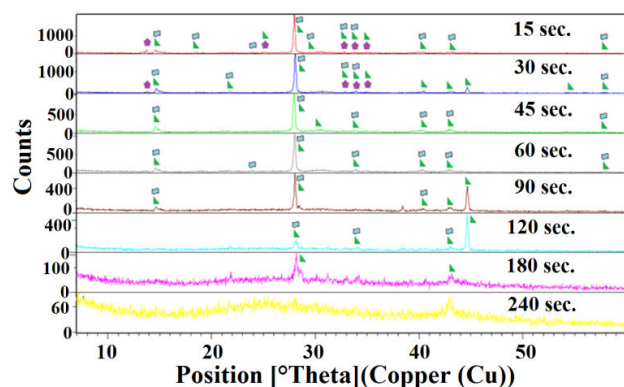


Fig. 6 XRD patterns of synthesized magnesium borate minerals

According to XRD results of products it is seen that with increasing reaction time the product structure turns to amorphous form. For a reaction time of 15 seconds, the crystal structures of synthesized magnesium borate minerals are at the highest level. Both in reactions of 15 and 30 seconds two different types of magnesium borates of Shabynite and Karlite are produced. Up to the reaction time of 120 seconds the formation of crystalline Shabynite is continued. At the reaction times of 180 and 240 seconds the products do not consist crystal phases of magnesium borates.

TABLE II
XRD RESULTS OF SYNTHESIZED MINERALS

Time (second)	Symbol	Pdf code	Mineral Name	Mineral Formula
15	■	00-041-1407	Shabynite	$Mg_5(BO)_3Cl_2(OH)_5 \cdot 4(H_2O)$
	▲	01-073-2158	Sassolite	H_3BO_3
30	■	00-036-0381	Karlite	$Mg_7(BO)_3(OH,Cl)_5$
	▲	00-041-1407	Shabynite	$Mg_5(BO)_3Cl_2(OH)_5 \cdot 4(H_2O)$
45	■	01-073-2158	Sassolite	H_3BO_3
	▲	00-036-0381	Karlite	$Mg_7(BO)_3(OH,Cl)_5$
60	■	00-041-1407	Shabynite	$Mg_5(BO)_3Cl_2(OH)_5 \cdot 4(H_2O)$
	▲	01-073-2158	Sassolite	H_3BO_3
90	■	00-041-1407	Shabynite	$Mg_5(BO)_3Cl_2(OH)_5 \cdot 4(H_2O)$
	▲	01-073-2158	Sassolite	H_3BO_3
120	■	00-041-1407	Shabynite	$Mg_5(BO)_3Cl_2(OH)_5 \cdot 4(H_2O)$
	▲	01-073-2158	Sassolite	H_3BO_3
180	■	-	-	-
240	■	-	-	-

Also, for all reactions the excess boric acid content is observed from XRD results. Therefore, the products of the reaction time of 15 seconds, which has the best results are washed with 96% ethanol to eliminate the excess boric acid. The XRD patterns and results of washed product of the reaction time of 15 seconds are shown in Fig. 7 and Table III.

According to XRD results of washed magnesium borate minerals the synthesized minerals are Shabynite ($Mg_5(BO)_3Cl_2(OH)_5 \cdot 4(H_2O)$) with pdf code of 00-041-1407 and Karlite ($Mg_7(BO)_3(OH,Cl)_5$) with pdf code of 00-036-0381. Also, it is seen from the Fig. 4, the intension of characteristic peaks of magnesium borates are increased after

the removal of boric acid.

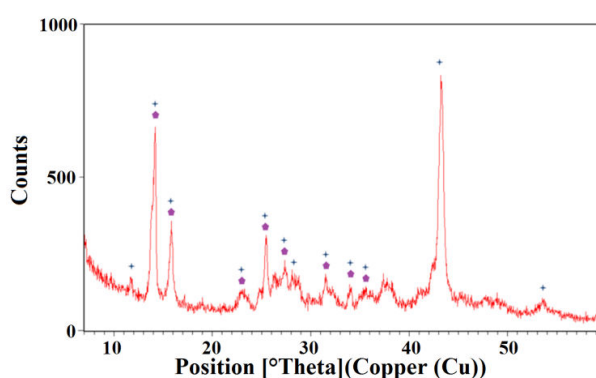


Fig. 7 XRD patterns of washed magnesium borate minerals

TABLE III
XRD RESULTS OF WASHED PRODUCTS

Time (second)	Symbol	Pdf code	Mineral Name	Mineral Formula
15	■	00-041-1407	Shabynite	$Mg_5(BO)_3Cl_2(OH)_5 \cdot 4(H_2O)$
	▲	00-036-0381	Karlite	$Mg_7(BO)_3(OH,Cl)_5$

FT-IR spectra of synthesized magnesium borate minerals are shown in Fig. 8. The differences between peaks for every reaction time were minor. According to FT-IR results, the peaks in the ranges of $1652-1613\text{ cm}^{-1}$ showed $\delta(H-O-H)$ bending. The peaks between $1373-1357\text{ cm}^{-1}$ corresponded to bending of $[v_{as}(B_{(3)}-O)]$ and asymmetric stretching of the four coordinate boron $[v_{as}(B_{(4)}-O)]$ was observed in the ranges of $1190-996\text{ cm}^{-1}$.

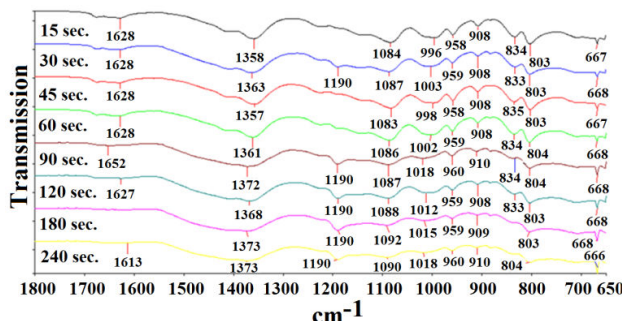


Fig. 8 FT-IR spectra of synthesized magnesium borate minerals

Between the ranges $960-908\text{ cm}^{-1}$ symmetric stretching of three coordinate boron $[v_s(B_{(3)}-O)]$ was beholden. The peaks between $835-803\text{ cm}^{-1}$ were coincided with symmetric stretching of the four coordinate boron $[v_s(B_{(4)}-O)]$. The peaks around 667 cm^{-1} indicated the bending of $[\delta(B_{(3)}-O)]$.

The FT-IR results of the synthesized magnesium borates confirm with the literature and show the specific magnesium borate peaks.

The SEM image of synthesized magnesium borate at the reaction time of 15 seconds is given in Fig. 9.

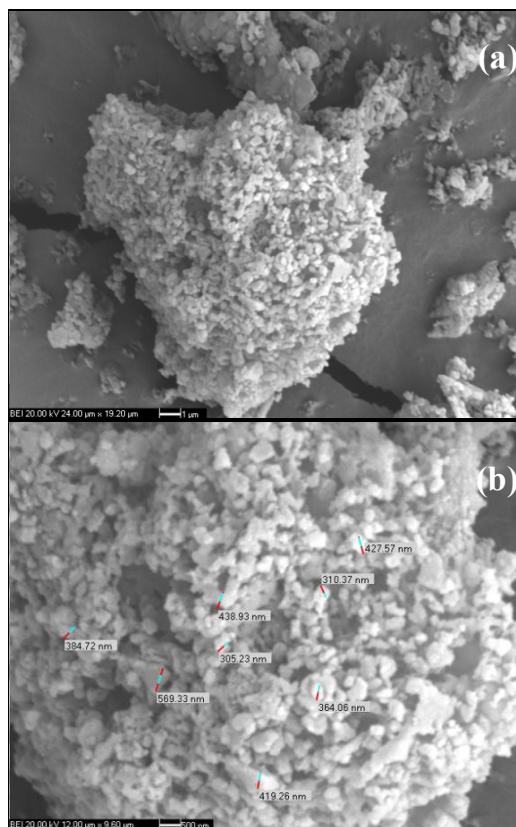


Fig. 9 SEM image of synthesized magnesium borate mineral (a) x5000, (b) x10000

According to SEM image, the obtained products are formed of sphere-like crystal aggregates. The magnified image shows that many nano scale particles come together and build up big granular structures. It is observed that the grain diameters of minerals are varied between 570 nm-310 nm.

IV. CONCLUSIONS

In this study, it was aimed to produce magnesium borates with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, MgO , H_3BO_3 as raw materials via microwave method. Starting out by the purpose of finding out reaction time effects on microwave synthesis of magnesium borates, the operation conditions were chosen as 360W microwave power and 1:1:8 raw material ratios for different reaction times of 15, 30, 45, 60, 90, 120, 180, 240 seconds.

The results of experiments showed that with increasing reaction time the crystallinity of synthesized minerals were decreasing. The best XRD scores were achieved at the reaction time of 15 seconds. For all reaction times the products of experiments were mixture of magnesium borate minerals and boric acid. After washing process of removing excess boric acid obtained products were two magnesium borate minerals of $\text{Mg}_5(\text{BO}_3)_3\text{Cl}_2(\text{OH})_5 \cdot 4(\text{H}_2\text{O})$ and $\text{Mg}_7(\text{BO}_3)_3(\text{OH},\text{Cl})_5$.

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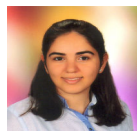
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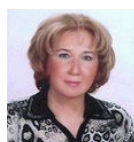
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