

**EFFECTS OF MOLE RATIO TO CHLORINE ADDED MAGNESIUM BORATE SYNTHESIS
AT 1000°C USING THE RAW MATERIALS OF MAGNESIUM CHLORIDE, MAGNESIUM
OXIDE AND BORIC ACID**

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Abstract

In today's world, there are many application areas of boron and the studies about boron still continue. Boron is found in minerals with other elements in nature. Magnesium borates, which are a class of boron minerals, are the most important technical ceramics for their properties of; high heat-resisting, corrosion-resisting, super mechanical strength, superinsulation, light weight, high strength, and high coefficient of elasticity. In this study the solid-state method is applied to different stoichiometric mole ratios of $MgCl_2 \cdot 6H_2O$, MgO and H_3BO_3 . The characterization techniques of XRD, FT-IR and Raman are applied to the produced magnesium borates. From the XRD results three types of magnesium borates; boracite ($Mg_3B_7O_{13}Cl$), magnesium borate (MgB_4O_7) and suanite ($Mg_2(B_2O_5)$), were formed. The highest crystalline minerals were obtained at the mole ratio of 1-6-14. Vibration analysis of FT-IR and Raman spectrums showed that the produced magnesium borates characteristic peaks were in good agreement with the literature.

Keywords: Boric Acid, Magnesium Borates, Magnesium Chloride, Magnesium Oxide, Solid-State Synthesis

1. INTRODUCTION

Production of pure boron is a hard and expensive process. On the other hand magnesium borate minerals are common additives of industry with the properties of strong thermal, mechanic and chemical such as; high heat resistance, corrosion resistance and high coefficient of elasticity. Because of the high boron content, magnesium borate minerals are meeting the needs of raw materials in world market. Magnesium borates can be used as both magnesium and boron sources in industries such as in ceramic industry, in the production of superconducting materials, in the composition of detergents, due to the content of boron in the friction-reducing additives in oils and insulating coating compositions (Derun 2012, TR Prime Ministry SPO 2006, Li 2010, Zeng 2008).

Boracite ($Mg_3B_7O_{13}Cl$), which is called magnesium borate chloride mineral, can be used as the source for obtaining synthetic boracite with ferro-electric and ferromagnetic properties. In addition, very high percentage of boron oxide with a value of 62.2 increases the importance of boracite mineral. Boracite which has reserves in Central Europa, Russia, Bolivia and China, consist of natural sea water and gypsum precipitation. Formed boracite mineral hardness is about 7 to 7.5 mohs. It is usually found in crystalline form (Gurel, 2012).

Three basic methods are available for artificial obtained in magnesium borate. These are hydrothermal, thermal and microwave methods. Except boracite, there is hydrate magnesium chloride mineral which is called shabinit ($Mg_5(BO_3)Cl_2(OH)_5 \cdot 4(H_2O)$). However, it is not preferred because of its crystal water in its structure. Magnesium borate synthesis can be classified as solid-state and liquid-state synthesis method. In solid-state synthesis method, which is used in this study, commonly can be

described as the calcination of powder mixtures at high temperatures (Senberber 2012, Guler 2009, Zhihong 2004).

There are some examples of synthesis procedure in literature. Elssfah et al. (2007), produced $\text{Mg}_2\text{B}_2\text{O}_5$ via simple route based on calcinations of mixed powders containing $\text{Mg}(\text{OH})_2$ and H_3BO_3 in 900°C . Zeng et al., in 2008 synthesized $\text{Mg}_2\text{B}_2\text{O}_5$ with heating the mixture of $\text{Mg}(\text{BO}_2)_2$ and graphite directly in vacuum at 1200°C for 1 hour. Obut in 2008, searched different sources of boron effects on synthesis in solid – state thermal methods.

In literature, the main point of the studies generally is the effect of temperature changing on produced magnesium borate structure. In this study, it is aimed to investigate the effect of raw materials mole ratios to the structure of synthesized mineral obtained in solid-state conditions. Another novelty of this study is the synthesis of chlorine added magnesium borate, which isn't studied before.

2. EXPERIMENTAL PROCEDURE

Magnesium oxide (MgO) is selected as main magnesium source whereas magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) is selected for the chloride addition to magnesium borate structure. Boron source is selected as boric acid (H_3BO_3). Magnesium sources are used without any pretreatment. H_3BO_3 was crushed, grinded in Retsch agate mortar and sieved in Fritsch sieve (Figure 1).



Figure 8. a. Retsch agate mortar, b. Fritsch sieve

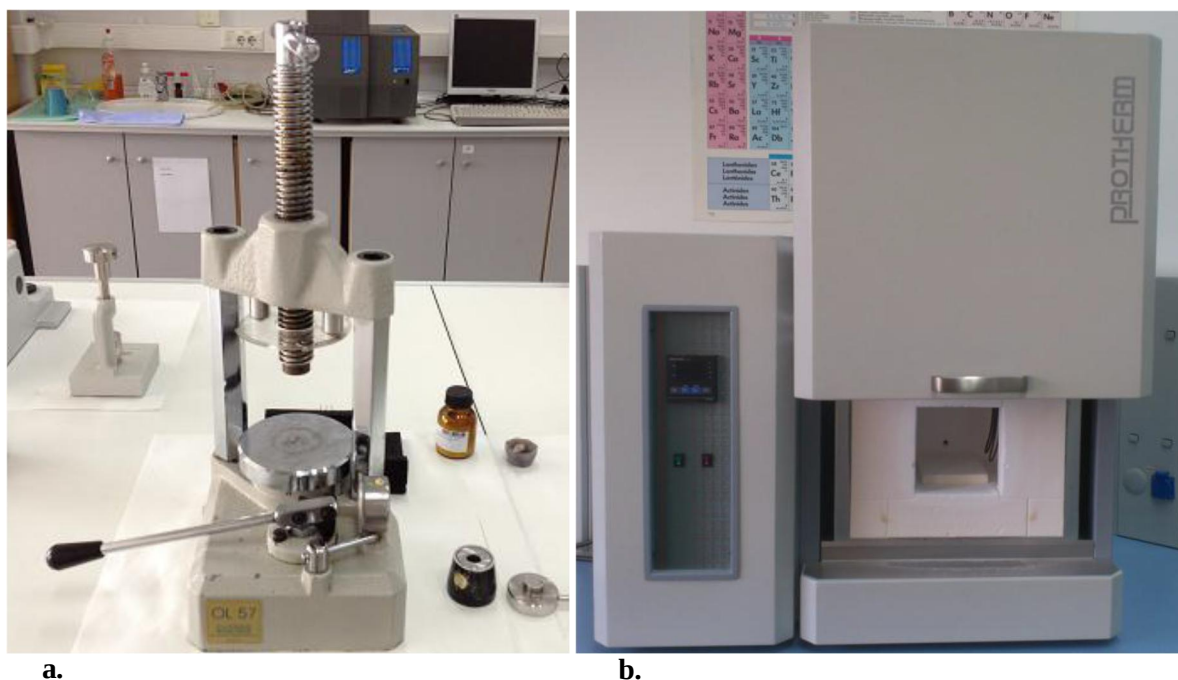


Figure 9. a. Pellet press of Manfredi OL 57, b. high temperature furnace of Protherm MOS 180/4

After preparation, raw materials were mixed at stoichiometric ratios which can be seen Table 1. The mixtures were pelleted with 200 bars of pressure by Pellet press of Manfredi OL 57 and the pellets were reacted with a high temperature furnace at reaction temperature of 1000°C and reaction time of 4 hours.

Table 3. Mole ratios of pelleted raw material mixtures

MgCl ₂ (MC)	MgO (MO)	H ₃ BO ₃ (H)	Mole ratio of MC:MO:H	Reaction Code
1	4	13	1-4-13	MC-MO-H-1-4-13
1	4	14	1-4-14	MC-MO-H-1-4-14
1	4	15	1-4-15	MC-MO-H-1-4-15
1	5	13	1-5-13	MC-MO-H-1-5-13
1	5	14	1-5-14	MC-MO-H-1-5-14
1	5	15	1-5-15	MC-MO-H-1-5-15
1	6	13	1-6-13	MC-MO-H-1-6-13
1	6	14	1-6-14	MC-MO-H-1-6-14
1	6	15	1-6-15	MC-MO-H-1-6-15

Raw materials and synthesized products were identified by Philips PANalytical X-Ray Diffraction (XRD), as shown in Figure 3.



Figure 10. Philips PANalytical X-Ray Diffractometer

Raw materials and synthesized chlorine added magnesium borates were also characterized by Perkin Elmer Brand Fourier Transform Infrared Spectroscopy (FT-IR) technique with Universal ATR sampling accessory – Diamond / ZnSe Crystal. Measurement range was selected as $4000 - 650 \text{ cm}^{-1}$ for the raw materials and $1800 - 650 \text{ cm}^{-1}$ for the products, scan number was 4 and resolution was set to 4 cm^{-1} (Figure 4).

Perkin Elmer Brand Raman Spectroscopy was used for further analysis. For Raman Spectroscopy, the exposure time was set to 4 seconds and number of exposures was set to 4. Measurement range was selected as $3280 - 250 \text{ cm}^{-1}$ for the raw materials and $1800 - 250 \text{ cm}^{-1}$ for the products and data interval was selected as 2 cm^{-1} . During the experiments full (100%) laser power was used and auto baseline was selected (Figure 4).

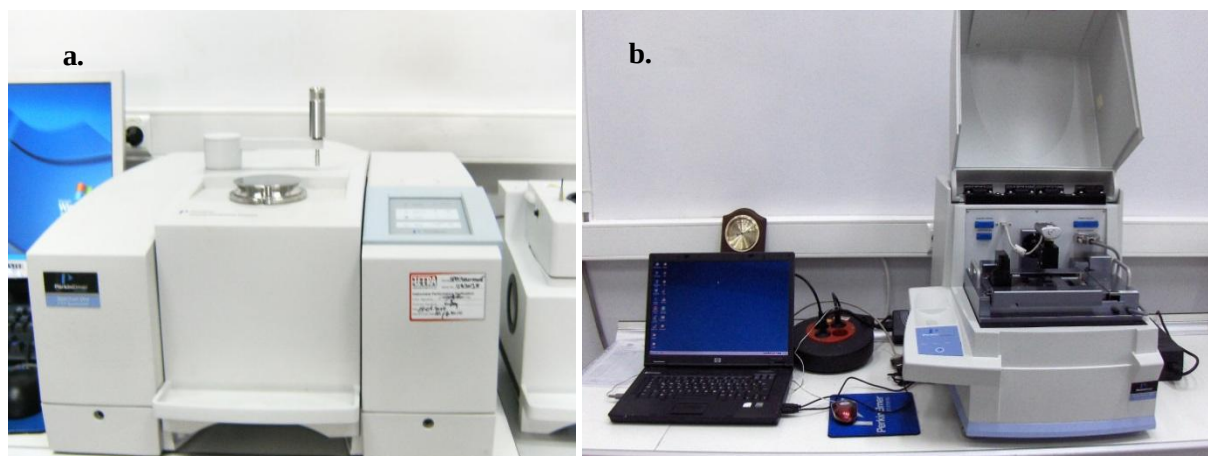


Figure 11. a. Perkin Elmer Spectrum One FT-IR Spectrometer, b. Perkin Elmer Raman Station 400F, Raman Spectrometer

3. RESULTS & DISCUSSION

3.1 Raw Materials Characterization Results

Raw materials XRD patterns and results were given in Fig. 5., Fig. 6. and Table 2, respectively.

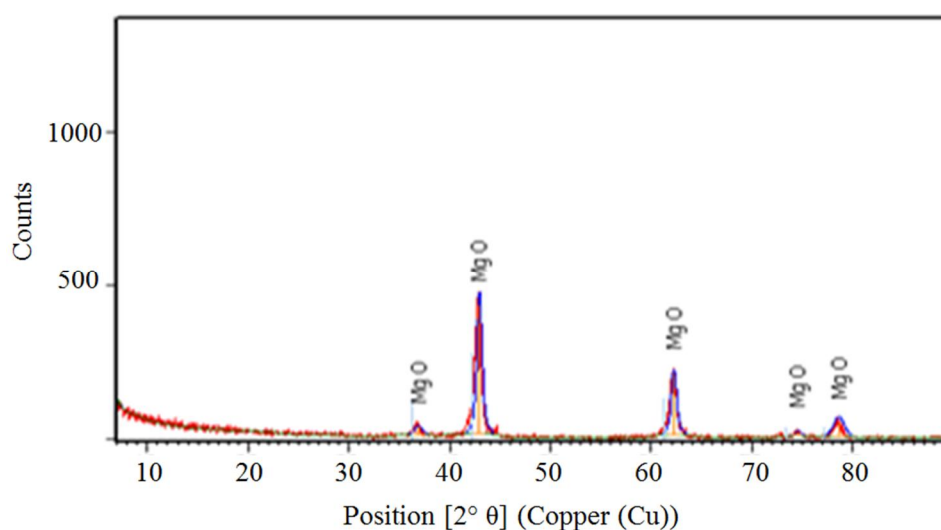


Figure 12. Magnesium oxide XRD pattern

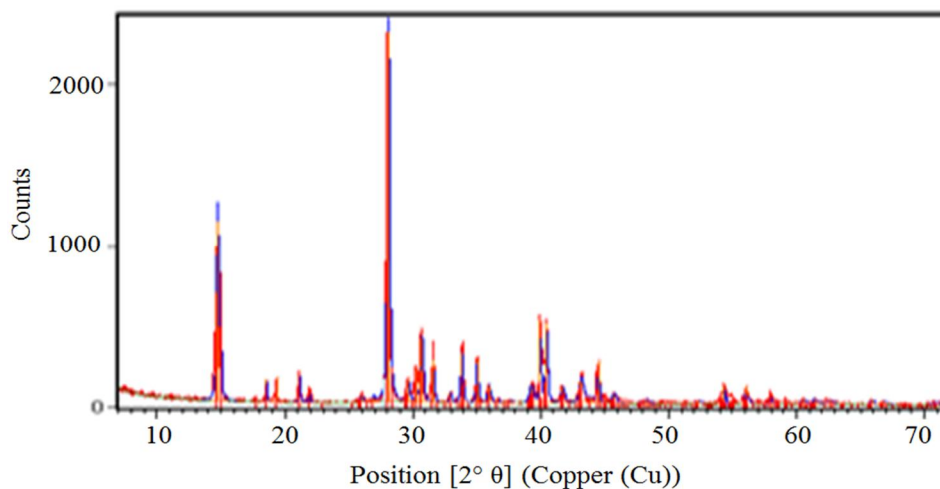


Figure 13. Boric acid XRD pattern

According to the XRD results magnesium oxide was found as “Periclase (MgO)” and boric acid was found as “Sassolite (H_3BO_3)”.

Table 4. XRD results of the raw materials

Raw material	Reference code	Mineral name	Mineral formula	Score
MgO	01-077-2179	Periclase	MgO	88
H_3BO_3	01-073-2158	Sassolite	H_3BO_3	62

FT-IR spectra and FT-IR ATR inorganic library results of the raw materials were given in Fig. 7., and Table 3, respectively.

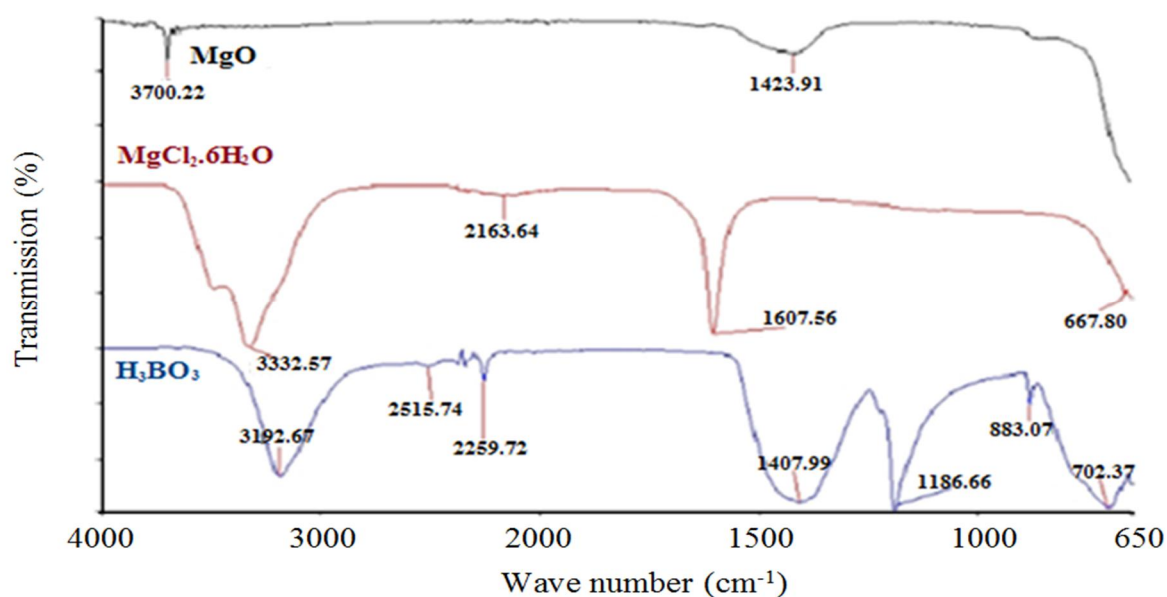


Figure 14. FT-IR spectra of the raw materials

According to the FT-IR ATR Inorganic library results magnesium oxide was found as “MgO”, boric acid was found as “H₃BO₃” and Magnesium chloride was found as “MgCl₂.6H₂O”.

Table 5. FT-IR ATR Inorganic library results of the raw materials

Score	Library code	Mineral name	Mineral formula
0.941	AI0086	Magnesium oxide	MgO
0.704	AI0031	Boric acid	H ₃ BO ₃
0.864	AI0084	Magnesium chloride	MgCl ₂ .6H ₂ O

3.2 Products XRD Results

XRD results and patterns of the products were given in Table 4 and Fig. 8., respectively. According to the XRD analysis, three types of magnesium borate minerals, which were boracite (Mg₃B₇O₁₃Cl), magnesium borate (MgB₄O₇) and suanite (Mg₂(B₂O₅)), were formed. Among the formations the major part was seen as suanite and the minor part was boracite. The highest suanite, magnesium borate and boracite scores were obtained from the mole ratio of 1-6-14 with the scores of “71”, “60” and “24”, respectively.

Table 6. XRD results of the products

Mole ratio	XRD scores of the synthesized minerals		
	Boracite	Magnesium borate	Suanite
			
1-4-15	19	27	61
1-4-14	20	37	61
1-4-13	22	39	66
1-5-15	21	36	63
1-5-14	18	52	68
1-5-13	20	44	69
1-6-15	20	51	70
1-6-14	24	60	71
1-6-13	13	20	66

* Boracite = pdf #: 01-071-0750, formula: Mg₃B₇O₁₃Cl

* Magnesium borate = pdf #: 00-031-0787, formula: MgB₄O₇

* Boracite = pdf #: 01-073-2107, formula: Mg₂(B₂O₅)

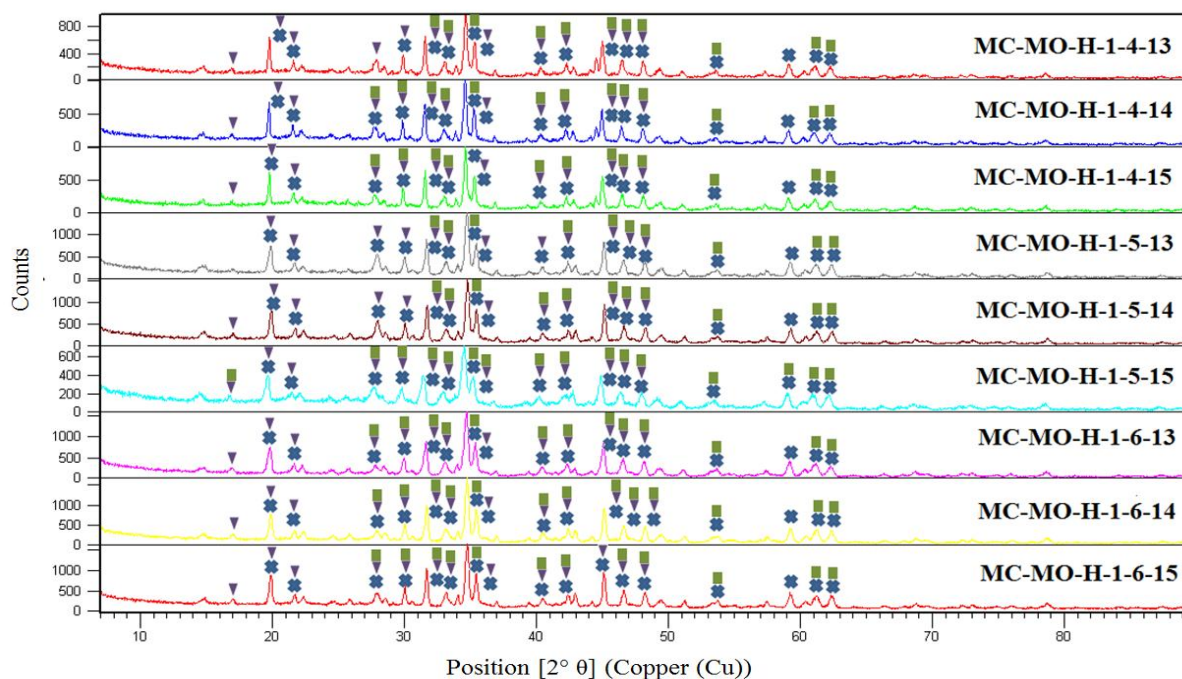


Figure 15. XRD patterns of the products

3.3 Products FT-IR Results

FT-IR spectra of the synthesized products were given in Fig. 9.

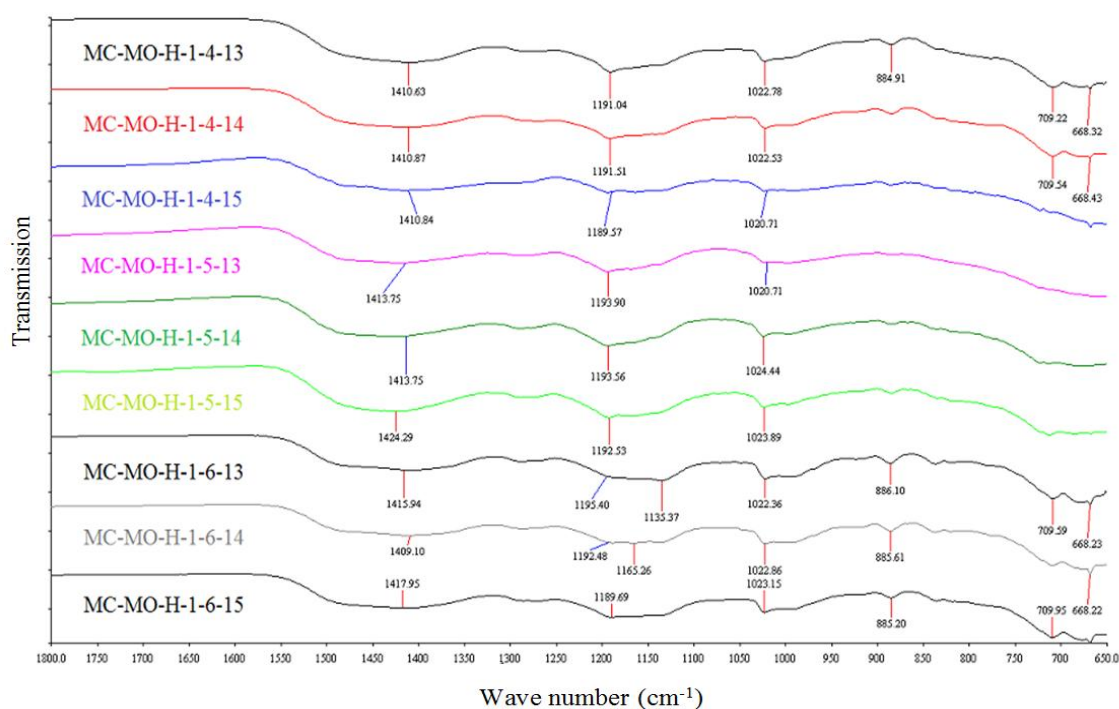


Figure 16. FT-IR spectra of the products

According to the FT-IR spectrums, $\square_{as}(B_{(3)}-O)$ were seen at the peak values around 1410 cm^{-1} . $\square_{op}(OH)^-$ was seen at the peak values around 1190 cm^{-1} , due to the moisture content of the products obtained. $\square_{as}(B_{(4)}-O)$ and $\square_s(B_{(3)}-O)$ were seen at the peaks at about 1020 cm^{-1} and 885 cm^{-1} , respectively. Final peak values at about 700 cm^{-1} and 680 cm^{-1} were $\square_s(B_{(3)}-O)$. The peak explanations of the products were given in Table 5.

Table 7. FT-IR peak explanations of the products

Peaks	Explanation	Symbols
$1600\text{-}1400\text{ cm}^{-1}$	Tri coordinate B-O asymmetrical stretching	$\square_{as}(B_{(3)}-O)$
$1200\text{-}950\text{ cm}^{-1}$	Four coordinate B-O asymmetrical stretching	$\square_{as}(B_{(4)}-O)$
$950\text{-}850\text{ cm}^{-1}$	Tri coordinate B-O symmetrical stretching	$\square_s(B_{(3)}-O)$
$750\text{-}650\text{ cm}^{-1}$	Tri coordinate B-O stretching	$\square(B_{(3)}-O)$

3.4 Products Raman Results

Raman spectrums and the peak explanations of the synthesized products were given in Fig. 10. and Table 6, respectively.

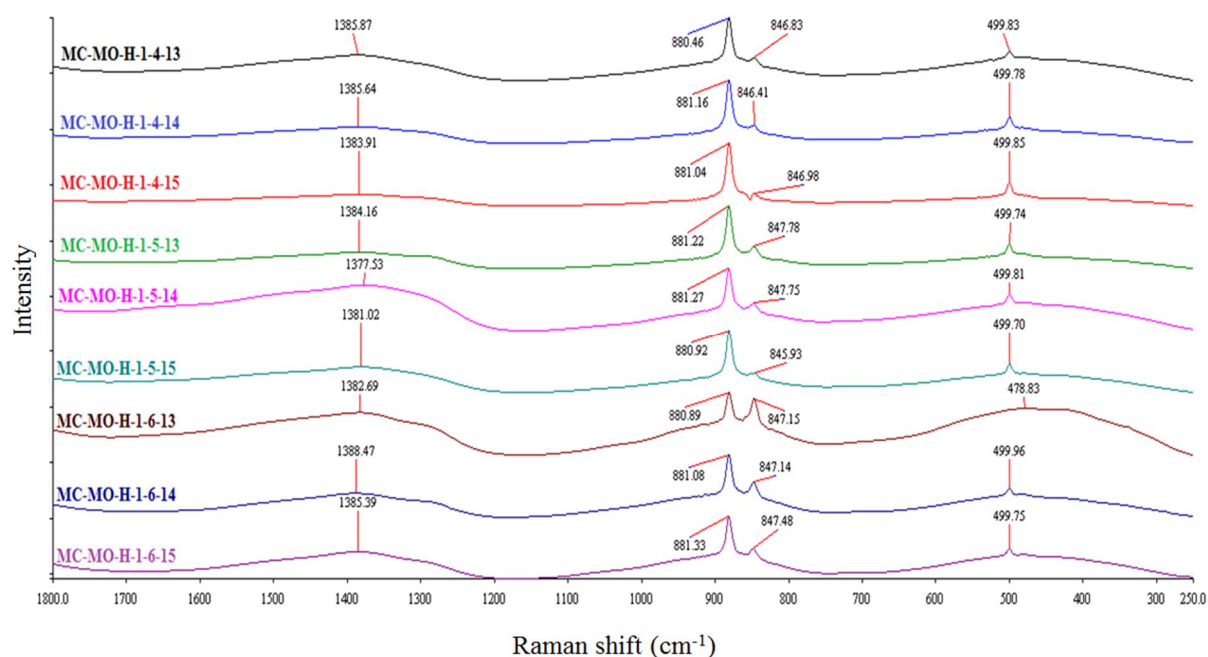


Figure 17. Raman spectrums of the products

According to the Raman spectrums, $\square_{as}(B_{(3)}-O)$ were seen at the peak values around 1380 cm^{-1} . $\square_s(B_{(3)}-O)$ was seen at the peak values around 881 cm^{-1} . $\square_s(B_{(4)}-O)$ was seen at the peaks at about 845 cm^{-1} . Final peak value at about 499 cm^{-1} was $[B_5O_6(OH)_4]^-$ and $\square(B_{(3)}-O)$.

Table 8. Raman peak explanations of the products

Peaks	Explanation	Symbols
1600-1200 cm^{-1}	Tri coordinate B-O asymmetrical stretching	$\square_{\text{as}}(\text{B}_{(3)}\text{-O})$
964-872 cm^{-1}	Tri coordinate B-O symmetrical stretching	$\square_{\text{s}}(\text{B}_{(3)}\text{-O})$
872-755 cm^{-1}	Four coordinate B-O symmetrical stretching	$\square_{\text{s}}(\text{B}_{(4)}\text{-O})$
516-300 cm^{-1}	$[\text{B}_5\text{O}_6(\text{OH})_4]^-$ ion and four coordinate B-O stretching	$[\text{B}_5\text{O}_6(\text{OH})_4]^-$ and $\square(\text{B}_{(3)}\text{-O})$

4. CONCLUSION

In this study the effect of raw material mole ratio ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}:\text{MgO}:\text{H}_3\text{BO}_3$) on the production of dehydrated magnesium borate synthesis was studied at the conditions of 1000°C and 4 hours of reaction time. Three types of dehydrated magnesium borates were obtained at the synthesis. Among them the major component was determined as “suanite” with the analysis technique of XRD. Also the FT-IR and Raman analyses were made in order to strengthen the formation of the magnesium borate formation. From these two spectroscopic analyses (FT-IR and Raman) the characteristic peaks of magnesium borates were obtained.

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