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SOLID STATE SYNTHESIS OF CHLORINE CONTAINING DEHYDRATED MAGNESIUM BORATES

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ABSTRACT

The 72% of the World boron reserves are in Turkey. The biggest portion of boron reserves leads the boron studies. Due to its important properties boron usage areas are extending. In this study the chlorine containing magnesium borate synthesis by solid-state method is investigated. The reaction temperatures were set between 500°C - 700°C. Magnesium chloride hexahydrate ($MgCl_2.6H_2O$) used as chlorine and magnesium source, magnesium oxide (MgO) used as magnesium source and boric acid (H_3BO_3) used as boron source. The effect on the synthesis by the molar ratio change of the raw materials was investigated. Synthesized minerals characterization analyses were done by the techniques of X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). From the results of this study the chlorine containing magnesium borate of boracite ($Mg_3B_7O_{13}Cl$) was obtained. The side products of dehydrated magnesium borates namely magnesium borate (MgB_4O_7) and suanite ($Mg_2B_2O_5$) were also formed. The formation of boracite was started at the reaction temperature of 500°C and the temperature increase effected the $Mg_3B_7O_{13}Cl$ formation positively.
Keywords: Chlorine containing magnesium borate, boracite, dehydrated magnesium borate, solid-state synthesis.

KLOR İÇERİKLİ SUSUZ MAGNEZYUM BORATLARIN KATI-HAL YÖNTEMİ İLE SENTEZLENMESİ

ÖZET

Dünya bor yataklarının yaklaşık %72'si Türkiye'de bulunmaktadır. Stratejik öneme sahip borun Türkiye'de fazla miktarda bulunması, bor üzerine yapılan çalışmaların önemini daha da arttırmaktadır. Borun özellikleri nedeniyle kullanım alanları gün geçtikçe genişlemektedir. Bu çalışmada katı-hal yöntemi ile klor içerikli magnezyum borat sentezi hedeflenmiştir. Katı-hal sentezleri 500°C ile 700°C'de arasında gerçekleştirilmiştir. Klor ve magnezyum kaynağı olarak magnezyum klorür hekzahidrat ($MgCl_2.6H_2O$), magnezyum kaynağı olarak magnezyum oksit (MgO) ve bor kaynağı olarak borik asit (H_3BO_3) kullanılmıştır. Kullanılan hammaddelerin mol oranı değişiminin sentez üzerindeki etkisi araştırılmıştır. Sentezlenen ürünlerin karakterizasyon çalışmaları X-Işını Kırınımı (XRD) ve Fourier Dönüşümlü Kızılötesi Spektroskopisi (FT-IR) ile gerçekleştirilmiş ve yorumlanmıştır. Yapılan analizler sonunda klor içerikli magnezyum borat minerali olarak borasit ($Mg_3B_7O_{13}Cl$) elde edilmiştir. Yan ürün olarak ise susuz magnezyum bileşiklerinden, magnezyum borat (MgB_4O_7) ve suanit ($Mg_2B_2O_5$) elde edilmiştir. 500°C'de $Mg_3B_7O_{13}Cl$ oluşumu başlarken sıcaklık artışı klor içerikli magnezyum boratın sentezini olumlu yönde etkilemiştir.
Anahtar Sözcükler: Klor içerikli magnezyum borat, borasit, susuz magnezyum borat, katı-hal sentezi.

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1. INTRODUCTION

Boron, an element, which only exists in nature in the form of a compound with other elements but not in its pure form, is one of the key elements naturally existing on Earth owing to its present properties. Approximately 72% of the total boron reserves on Earth are located within the Turkish borders. The most significant boron deposits in Turkey are Bigadiç, Sultançayırı and Kırka deposits situated in Balıkesir, Kütahya and Eskişehir. A subgroup of boron minerals; magnesium borates play a significant role in industrial applications owing to their high corrosion resistance and high thermal resistance. Magnesium borates exist in the nature and they may be readily synthesized. Naturally occurring magnesium borate beds are encountered in salty lakes. The boron deposits in Turkey are known to be poor in terms of their magnesium borate content. The synthesis of magnesium borates therefore need to be thoroughly studied. Chlorine containing magnesium borates may also be used as cleaning agents in detergent manufacture in addition to possessing all characteristics inherent to magnesium borates [1-6].

A number of studies about on solid-state synthesis are available in the literature. These studies focused on synthesis in a high temperature furnace using MgO, $MgCl_2.6H_2O$, $Mg(NO_3)_2.6H_2O$, $Mg(OH)_2$ together with B_2O_3 and H_3BO_3. The common ground in this type of syntheses is the formation of dehydrated magnesium borate compounds [7-15]. Dosler *et al*. determined that $Mg_2B_2O_5$ was the major structure at 1000^oC whereas it was $Mg_3B_2O_6$ at 1300^oC [7]. Guler *et al*. obtained pure $Mg_2B_2O_5$ at 900^oC [8]. Qasrawi *et al*. characterized the $Mg_2B_2O_5$ crystals formed through combustion at 1250^oC for 3 hours and they conducted the thermal analysis of the samples [9]. Elssfah *et al*. synthesized nano-scale $Mg_2B_2O_5$ crystals with a particle size ranging between 70-120 nm [10]. Li *et al*. obtained nano-sized $Mg_2B_2O_5$ product in a two stage process from $MgCl_2.6H_2O$ and $NaBH_4$ as the raw materials [11]. Erdogan investigated the effect of B/Mg ratio and reaction time in magnesium borate production via combustion at solid state and in solution using $Mg(NO_3)_2$ as the magnesium source and H_3BO_3 as the boron source [12]. Ay reported satisfactory results at 900^oC [13]. Zhang *et al*. synthesized $Mg_3B_2O_6$ of varying lengths and width ranging between 100-300nm [14]. Zeng *et al*. achieved nano-sized $Mg_2B_2O_5$ particles [15].

The solid state studies were limited to the magnesium borate family as discussed above. Boracite, a chlorine-containing borate compound, has many different forms. Boracite is generally represented by the formula $M_3B_7O_{13}X$. M is the two valence cation of Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn or Cd and X is the one valence anion of F, Cl, Br, I, OH or NO_3 [16]. In some cases, X may be S, Se or Te and M may be single valence Li [17]. Only 4 natural types of boracite exist. These are "ericaite" ($(Fe,Mg)_3B_7O_{13}Cl$); named after its purple colour, "chambersite" ($Mn_3B_7O_{13}Cl$); named after a town in Texas, "congolite" ($Fe_3B_7O_{13}Cl$); named after its location of discovery and "trembathite" ($(Mg, Fe)_3B_7O_{13}Cl$); named after a Canadian mineralogist [18, 19]. Boracite is typically found in evaporite sequences associated with gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$), halite (NaCl), sylvite (KCl), carnallite ($KMgCl_3.6(H_2O)$, kainite ($MgSO_4.KCl.3H_2O$) and hilgardite ($Ca_2B_5O_9Cl.H_2O$) [20]. Synthetic boracites were prepared using 4 techniques including sintering flow method, vapour transfer method, pressurized mechanical method and hydrothermal method. The most successful method used in the synthesis of halogen boracites was reported as the vapour transfer method of Schimid [19]. This process was recently developed for the preparation of Fe-Cl boracites produced during solution mixing, heating, grinding and the H_2 reduction. However, the product was reported to be in a mixture with α-Fe formed during H_2 reduction [19]. The study by Z. H. Wang *et al*. for the synthesis and characterization of Fe-Cl boracite also used this method for synthesis [21]. On the other hand, Jing Ju *et al*. studied the utilization of the flow method in boracite synthesis [22].

An investigation of the boracite synthesis studies indicated the lack of studies regarding the synthesis of magnesium containing boracites. The present study aims to synthesize chlorine containing magnesium borate minerals using the solid-state method. The reaction temperature

was determined to vary between 500-700°C, the reaction time was selected as 240 minutes and the raw material concentration ratios were determined as $MgCl_2.6H_2O$ (1 mol) : MgO (4-6 mol) : H_3BO_3 (13-15 mol) as a result of the pre-analysis.

2. EXPERIMENTAL

2.1. Raw Material Characterization

$MgCl_2.6H_2O$ to be used as the source of magnesium and chlorine, MgO to be used as the source of magnesium were purchased from Merck Chemicals and H_3BO_3 used as the boron source was provided from EtiBank Bandirma Boron and Acid Plant. $MgCl_2.6H_2O$ and MgO were used directly without any pre-treatment whereas H_3BO_3 was ground in an agate mortar (Retsch RM 200) and sieved through 75μm and the undersize grains were used. The identification of the raw materials was carried out in Philips PANanalytical X-Pert Pro XRD prior to synthesis. The parameters for the XRD analysis were 45kV and 40mA using Cu-Kα rays (λ=1.53 cm^{-1}). Additionally, the characteristic bands of the raw materials were determined in a Perkin Elmer Spectrum One FT-IR Spectrometer with Universal Attenuation Total Reflectance (ATR) sampling accessory with a diamond / ZnSe Crystal; in a measurement range of 4000-650cm^{-1} (scan number was 4 and resolution 4 cm^{-1}).

2.2. Solid-State Synthesis and Product Characterization

The reaction temperature range and the duration of the reaction were determined in pre-analyses. Homogeneous mixtures were formed into a pellet using a Manfredi OL 57 pellet preparation device under 100 bar pressure. A more efficient synthesis reaction was targeted via a reduction in the surface area of the raw material mixtures. The theoretical synthesis equation (1) that does not produce any side products is also given. However, considering that HCl gas will be produced in the system, the chlorine to be used in synthesis will be stoichiometrically less in proportion thus the formation of dehydrated magnesium borate minerals would be expected in addition to the synthesis of boracite. The reactions were carried out in different mole ratios given in Table 1 to investigate the effect of different stoichiometric ratios and reaction temperatures on boracite formation.

$$MgCl_2.6H_2O + 5MgO + 14H_3BO_3 \rightarrow 2(Mg_3B_7O_{13}Cl) + 27H_2O \quad (1)$$

Table 1. Reaction parameters of the chlorine containing magnesium borates

Molar Ratios			Reaction Temperature Range (°C)	Reaction Time (min)
$MgCl_2.6H_2O$	MgO	H_3BO_3		
1	4	13	500-700	240
1	4	14	500-700	240
1	4	15	500-700	240
1	5	13	500-700	240
1	5	14	500-700	240
1	5	15	500-700	240
1	6	13	500-700	240
1	6	14	500-700	240
1	6	15	500-700	240

The homogeneous mixture pellets were allowed to react in a high temperature furnace (Protherm MOS 180/4) in alumina dust covered ceramic crucibles. The minerals obtained during

synthesis were ground in a ceramic mortar and the identification tests were carried out using XRD and the characteristic bands were determined using FT-IR spectrometry with the parameters given in "2.1 Preparation of the Samples" section.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Identification of the Raw Materials

The XRD patterns and the FT-IR spectra of the raw materials were given in Figures 1 and 2 and the results were given in Table 2. The XRD scores were out of 100 and the FT-IR scores were out of 1.

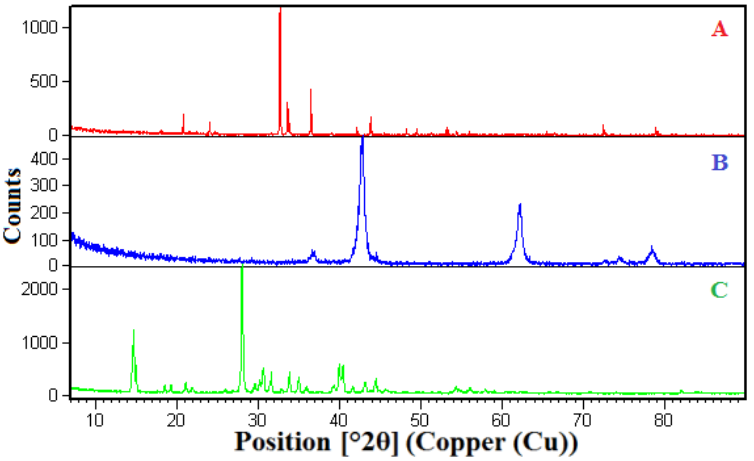


Figure 1. Raw materials XRD patterns; A. $MgCl_2.6H_2O$, B. MgO, C. H_3BO_3

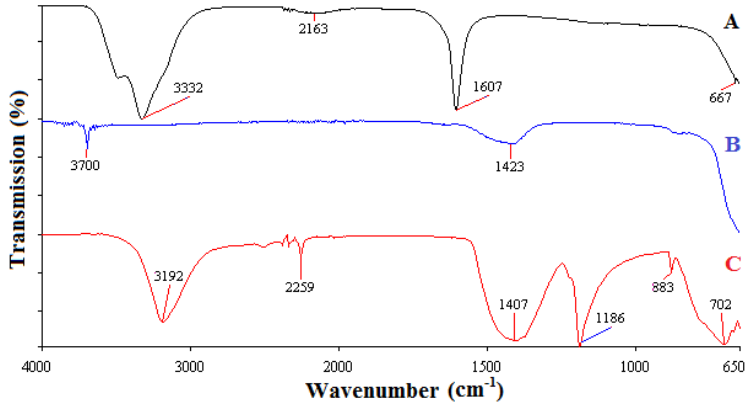


Figure 2. Raw materials FT-IR spectra; A. $MgCl_2.6H_2O$, B. MgO, C. H_3BO_3

The characteristic peaks of the raw materials were determined using the XRD patterns and the FT-IR spectra. $MgCl_2.6H_2O$ was determined as "Bischofite" with pdf code "01-077-1268" (powder diffraction file), MgO as "Periclase" with pdf code "01-087-0651" and H_3BO_3 as "sassolite" with pdf code "01-073-2158".

Table 2. XRD and FT-IR ATR inorganic library results

XRD Results			FT-IR Results			Common Results
Pdf code #	**Mineral Name**	**Score**	**Code**	**Mineral Name**	**Score**	**Mineral Formula**
01-077-1268	Bischofite	16	AI0084	Magnesium chloride	0.864	$MgCl_2.6H_2O$
01-087-0651	Periclase	78	AI0086	Magnesium oxide	0.941	MgO
01-073-2158	Sassolite	62	AI0031	Boric acid	0.704	H_3BO_3

3.2. Identification of the Synthesized Minerals

3.2.1. XRD Results

The XRD results of the synthesized minerals are given in Table 3.

Table 3. Chlorine containing magnesium borates XRD results

Reaction Temperature (°C)	Molar ratios	XRD Scores		
		Boracite*	Magnesium borate*	Suanite*
500	1:4:13	19	-	-
	1:4:14	15	-	-
	1:4:15	19	-	-
	1:5:13	11	-	-
	1:5:14	15	-	-
	1:5:15	15	-	-
	1:6:13	7	-	-
	1:6:14	1	-	-
	1:6:15	9	-	-
600	1:4:13	62	74	23
	1:4:14	52	79	22
	1:4:15	48	74	17
	1:5:13	62	71	19
	1:5:14	60	75	22
	1:5:15	51	78	27
	1:6:13	62	74	31
	1:6:14	62	72	29
	1:6:15	59	74	28
700	1:4:13	67	75	28
	1:4:14	61	80	29
	1:4:15	61	80	27
	1:5:13	64	76	30
	1:5:14	54	73	26
	1:5:15	55	76	25
	1:6:13	71	75	36
	1:6:14	59	70	29
	1:6:15	56	74	27

* Boracite, pdf # = 01-071-0750, $Mg_3B_7O_{13}Cl$
* Magnesium borate, pdf # = 00-031-0787, MgB_4O_7
* Suanite, pdf # = 01-073-2107, $Mg_2B_2O_5$

XRD results indicated the formation of boracite ($Mg_3B_7O_{13}Cl$) with code "01-071-0750" started at 500°C. The stoichiometric ratio of the reactant raw materials was determined as 1-5-14 ($MgCl_2.6H_2O$:MgO:H_3BO_3) according to the synthesis equation given in (1). However, the $Mg_3B_7O_{13}Cl$ formation scores with ratios of 1-4-13 and 1-4-15 were higher. The $Mg_3B_7O_{13}Cl$ scores were considerably higher at 600°C and a score of 62 was achieved at ratios of 1-4-13, 1-5-13, 1-6-13 and 1-6-14. In addition to $Mg_3B_7O_{13}Cl$, MgB_4O_7 (code "00-031-0787") was obtained as the major phase and $Mg_2B_2O_5$ ("01-073-2107") was obtained as the minor phase at 600°C. The scores for MgB_4O_7 were 79 at 1-5-14, 78 at 1-5-15 and 74 at 1-4-13, 1-4-15, 1-6-13 and 1-6-15. The highest score of 31 was achieved at a ratio of 1-6-13 for the minor phase; $Mg_2B_2O_5$.

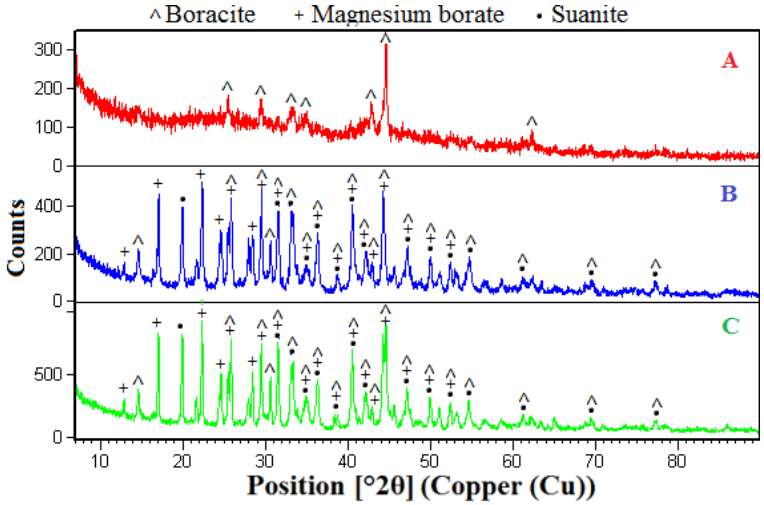
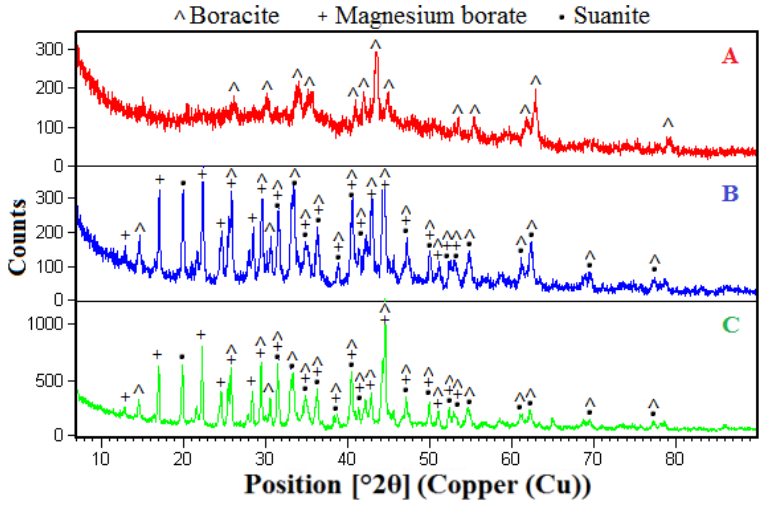


Figure 3. 1-4-13 ratio raw materials XRD patterns obtained at;
A. 500°C, B. 600°C, C. 700°C

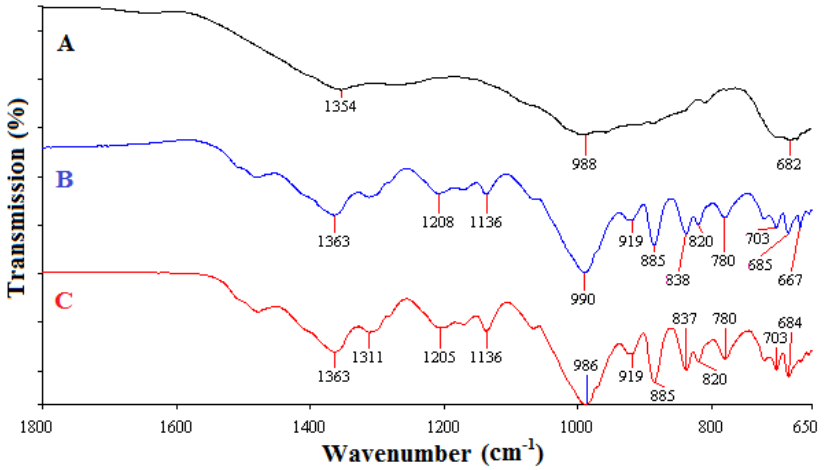


Şekil 4. 1-6-13 ratio raw materials XRD patterns obtained at;
A. 500°C, B. 600°C, C. 700°C

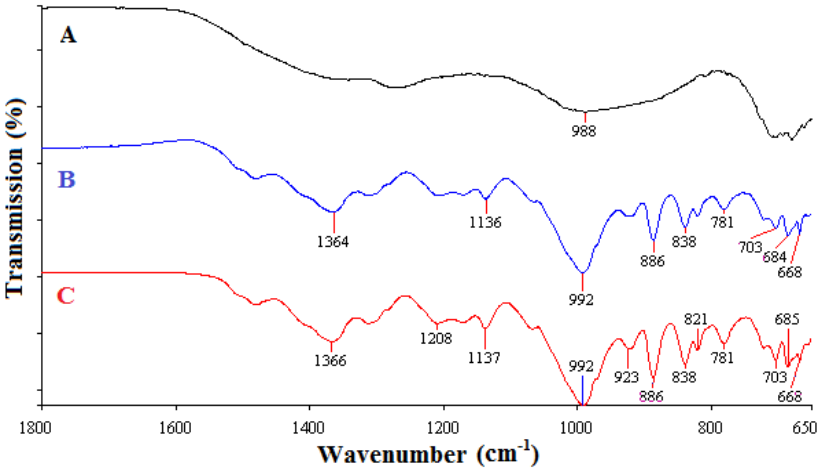
Increasing the reaction temperature to 700°C caused an increase in the score of 62 at 1-4-13 and 1-6-13, to 67 at 1-4-13 and to 71 at 1-6-13. The scores of the major and minor phase dehydrated magnesium borate minerals were also higher at 700°C. The XRD patterns of the minerals obtained at the 1-4-13 and 1-6-13 mixing ratios corresponding to the highest $Mg_3B_7O_{13}Cl$ scores were displayed in Figures 3 and 4. As shown in the figures, the boracite peak formation was detected at 500°C, the scores were higher at 600°C and the peaks were more distinct. The counts were even higher at 700°C and better crystallized products were obtained.

3.2.2. FT-IR Results

The FT-IR spectra of the synthesized minerals are given in Figures 5 and 6.



Şekil 5. 1-4-13 ratio raw materials FT-IR spectra obtained at;
A. 500°C, B. 600°C, C. 700°C



Şekil 6. 1-6-13 ratio raw materials FT-IR spectra obtained at;
A. 500°C, B. 600°C, C. 700°C

The spectral range was determined as 1600-650 cm^{-1} since no peak higher than 1600 cm^{-1} was observed in the obtained spectra. The characteristic peaks for magnesium borate were not distinct at 500°C and they were observed to become more distinguishable with increasing temperature. The peaks in the range of 1366-1311 cm^{-1} were the asymmetrical stretching of the 3-coordinate boron [$\nu_{as}(B_{(3)}\text{-}O)$]. The peaks in the rage of 1208-1136 cm^{-1} and 992-986 cm^{-1} belong to the boron oxygen hydrogen stretching [δ(B-O-H)] and the asymmetrical stretching of the 4-coordinate boron [$\nu_{as}(B_{(4)}\text{-}O)$], respectively. The symmetrical stretching of the 3-coordinate boron [$\nu_{as}(B_{(3)}\text{-}O)$] and the symmetrical stretching of the 4-coordinate boron [$\nu_{as}(B_{(4)}\text{-}O)$] were identified at 923-885 cm^{-1} and 838-780 cm^{-1}, respectively. The peaks at 703-667 cm^{-1} were the stretching of the 3-coordinate boron [$\delta(B_{(3)}\text{-}O$].

4. CONCLUSIONS

Chlorine containing magnesium borate was synthesized in the present study. $MgCl_2.6H_2O$, MgO and H_3BO_3 were used as the raw materials at different mole ratios. The effect of varying mole ratios on synthesis was investigated and the optimal mole ratios were determined as 1-4-13 and 1-6-13 at 600°C and as 1-6-13 at 700°C. The XRD analysis indicated the presence of MgB_4O_7 with a higher score than boracite and the $Mg_2B_2O_5$ mineral with lower score in addition to the theoretically expected product of $Mg_3B_7O_{13}Cl$. Thus, the following reaction actually took place:

$$MgCl_2.6H_2O + 6MgO + 13H_3BO_3 \rightarrow a(Mg_3B_7O_{13}Cl) + b(HCl) + c(H_2O) + d(MgB_4O_7) + e(Mg_2B_2O_5) \quad (2)$$

Kipcak *et al*. investigated the solid-state synthesis of dehydrated magnesium borate from MgO and H_3BO_3 at a temperature range of 600°C-1000°C. They reported low XRD scores (6-14) for the $Mg_2B_2O_5$ type magnesium borate synthesized at molar ratios of 3:2 and 1:1 at 600°C and 700°C, respectively, whereas the magnesium borate product obtained at 800°C was $Mg_3B_2O_6$ with a high score (64-86) [24].

The Cl^- ions within the structure of $MgCl_2.6H_2O$ raw material acted as a catalyst for the formation of dehydrated magnesium borate synthesis positively affecting the production temperature. The high scores achieved by Kipcak *et al*. at 800°C were achieved at 700°C in the present work. The MgB_4O_7 synthesis score was determined as 80 with mole ratios of 1-4-14 and 1-4-15. Characteristic peaks for magnesium borates were identified in the FT-IR spectra and the results were determined to be in conjunction with previous studies [24-26].

In conclusion, chlorine containing dehydrated magnesium borates were successfully synthesized at relatively not very high temperatures (600°C and 700°C).

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