

# Controlled synthesis, characterization and thermal properties of $Mg_2B_2O_5$

## Research Article

Ayşe Üçyıldız, İsmail Girgin\*

Mining Engineering Department, Hacettepe University,  
06800 Beytepe, Ankara, Turkey

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**Abstract:** Optimum conditions for synthesizing monoclinic and triclinic  $Mg_2B_2O_5$  compounds by high-temperature solid-state reactions were investigated. Mixtures composed of boric acid and magnesium oxide at  $MgO:B_2O_3$  mole ratios of 1:0.25, 1:0.5 and 1:1.5 were heated for 1 hour at temperatures between 600–1050°C and the formed phases were identified by XRD analysis. Monoclinic  $Mg_2B_2O_5$  was formed by heating at 850°C for 4 hours together with minimum amounts of triclinic  $Mg_2B_2O_5$ , while triclinic  $Mg_2B_2O_5$  was formed as a single phase at 1050°C for the same reaction time. The products obtained at optimum conditions were subjected to a series of tests to determine their chemical compositions, particle size distributions, surface area values, IR spectra and TG/DTA patterns.

**Keywords:** Inorganic materials • Oxide materials • Solid state reactions • Thermal analysis • X-ray diffraction

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## 1. Introduction

Magnesium borates with compositions of  $xMgO \cdot yB_2O_3 \cdot zH_2O$  and  $xMgO \cdot yB_2O_3$  may be found in nature and can also be prepared synthetically in the laboratory.  $2MgO \cdot B_2O_3 \cdot xH_2O$  compounds are synthesized by the phase transformation of chloropinnoite [1], by precipitation from solution and by sol-gel methods using different magnesium and boron compounds [2,3]. The disadvantages of synthesis in aqueous media include low recoveries due to product solubility and difficulty with obtaining crystalline products and reproducible results [4,5].

Anhydrous triclinic and monoclinic (suanite)  $Mg_2B_2O_5$  compounds were synthesized by conventional heating [6–13], partial precipitation [14], chemical vapor deposition [15], microwave heating [16], high-energy milling [17,18], methods using different magnesium- and boron-containing precursors.  $Mg_2B_2O_5$  compounds may be used as a ferroelastic material [19], a catalyst for conversion of hydrocarbons [20], a nanorod or nanowire for use in nanomaterials [21,22] and an allochromatic pigment after doping by solution combustion synthesis [23].

In this report, we describe the generation of formed phases at  $MgO:B_2O_3$  mole ratios of 1:0.25, 1:0.5 and 1:1.5 and define the formation conditions of monoclinic (m-) and triclinic (t-)  $Mg_2B_2O_5$  compounds using  $H_3BO_3$  and MgO. The compounds were extensively characterized to determine their chemical and physical properties. Our findings contribute to a larger study that is aimed at synthesizing magnesium borate compounds by high temperature solid-state reactions [24].

## 2. Experimental Procedure

Homogeneous mixtures were prepared at  $MgO:B_2O_3$  mole ratios of 1:0.25, 1:0.5 and 1:1.5. MgO and  $H_3BO_3$  were Merck grade and were ground together in a mortar. The prepared mixtures were subjected to TG/DTA analyses between 25–1200°C under static air atmosphere by a Setaram Labsys thermal analyser to determine the probable formation temperatures. After determination of the reaction temperatures by TG/DTA analyses, freshly prepared mixtures at known  $MgO:B_2O_3$  mole ratios were heated for 1 hour in a muffle furnace at the pre-determined temperatures between 600–1050°C.

\* E-mail: girgin@hacettepe.edu.tr

Formed magnesium borate phases were identified by XRD analyses using a Rigaku x-ray diffractometer. The optimum MgO:B<sub>2</sub>O<sub>3</sub> mole ratio and the temperature at which the highest amount of m- and t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> phases formed were determined. Subsequently, the effect of the heating time (1-8 hours) on the reaction was determined and optimized.

The solids prepared at optimum conditions were analyzed on the basis of their chemical compositions, particle size distributions (Sympatek laser sizer), B.E.T. surface area values (Quantachrome Monosorb), TG/DTA patterns and IR spectra (Perkin-Elmer).

### 3. Results and Discussion

TG/DTA patterns of each starting compound and the mixtures prepared at MgO:B<sub>2</sub>O<sub>3</sub> mole ratios of 1:0.25, 1:0.5 and 1:1.5 are given in Fig. 1. The weight loss observed in the TG pattern of H<sub>3</sub>BO<sub>3</sub> and the corresponding endothermic peaks between 80-320°C in the DTA pattern were related to the removal of crystal water. The weight loss in the TG pattern of MgO was due to the moisture and carbon dioxide sorbed from the air [25] and accordingly, magnesium oxide was pre-calcined before use in the preparation of initial mixtures. The weight loss values of the initial mixtures depending on MgO:B<sub>2</sub>O<sub>3</sub> mole ratios increased as the amount of B<sub>2</sub>O<sub>3</sub> increased. It can be clearly seen that magnesium oxide and borate components of the initial mixtures react between 640-705°C as indicated by an exothermic peak in the DTA patterns. A very small endothermic peak observed around 1000°C in the DTA pattern of the mixture at MgO:B<sub>2</sub>O<sub>3</sub> mole ratio of 1:1.5 indicates a

transformation in the reaction medium.

Considering the peak temperatures obtained from DTA results, mixtures prepared at MgO:B<sub>2</sub>O<sub>3</sub> mole ratios of 1:0.25, 1:0.5 and 1:1.5 were heated at 600°C, 750°C, 850°C, 950°C and 1050°C for 1 hour in a muffle furnace and the obtained solids were identified by XRD analyses (Fig. 2).

It is seen from Fig. 2 that no crystalline peaks in the XRD patterns of the samples were observed at 600°C in agreement with the DTA results given in Fig. 1. At 750°C, the amount of unreacted B<sub>2</sub>O<sub>3</sub> (PDF No: 6-297) increases as the B<sub>2</sub>O<sub>3</sub> contents of the mixtures increase. For mixtures prepared at MgO:B<sub>2</sub>O<sub>3</sub> mole ratio of 1:0.25, increasing the temperature up to 1050°C is observed to cause a decrease in the amount of unreacted MgO (PDF No: 4-829) contents of the samples. m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> (PDF No: 16-168) formed at 750°C begins to be transformed into t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> (PDF No: 15-537) at 850°C and this transformation is completed at 1050°C. Experimental results show that at a MgO:B<sub>2</sub>O<sub>3</sub> mole ratio of 1:0.25, the major phase formed between 850°C to 1050°C is Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub> (PDF No: 5-648).

When the B<sub>2</sub>O<sub>3</sub> content of the mixture is increased (MgO:B<sub>2</sub>O<sub>3</sub> mole ratio 1:0.5), the interaction between starting compounds increases above 850°C and the corresponding peaks of unreacted MgO and B<sub>2</sub>O<sub>3</sub> begin to disappear. m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> formed at 750°C is transformed into t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> by temperature increase with significant formation at 950°C until finally t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> is the only phase present at 1050°C. On the other hand, MgB<sub>4</sub>O<sub>7</sub> (PDF No: 31-787), whose optimum formation conditions were investigated in our previous study [26], begins to form at 850°C. It is seen from the XRD patterns of the heated mixtures prepared at 1:1.5 MgO:B<sub>2</sub>O<sub>3</sub> mole ratio

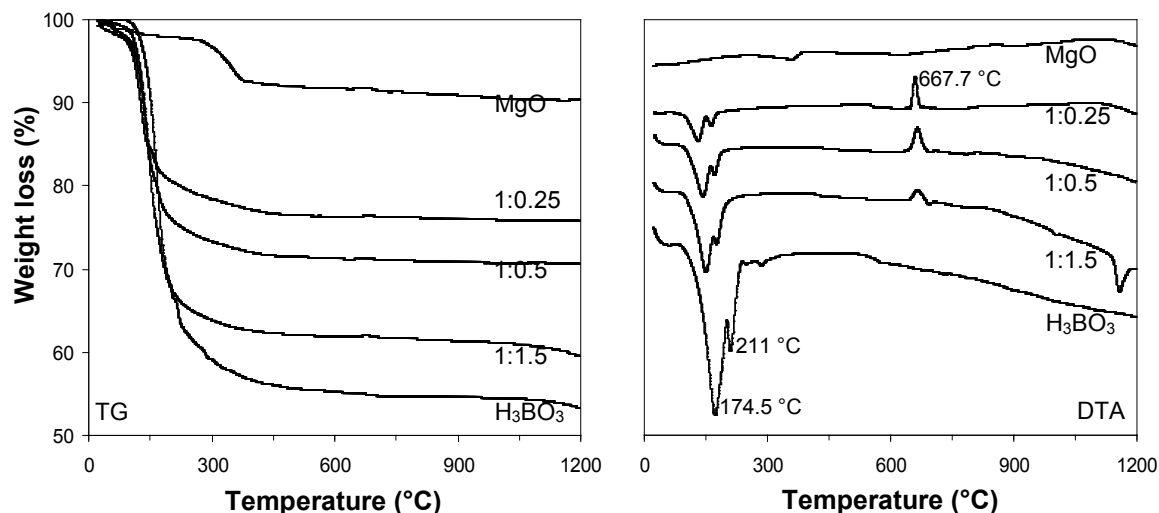
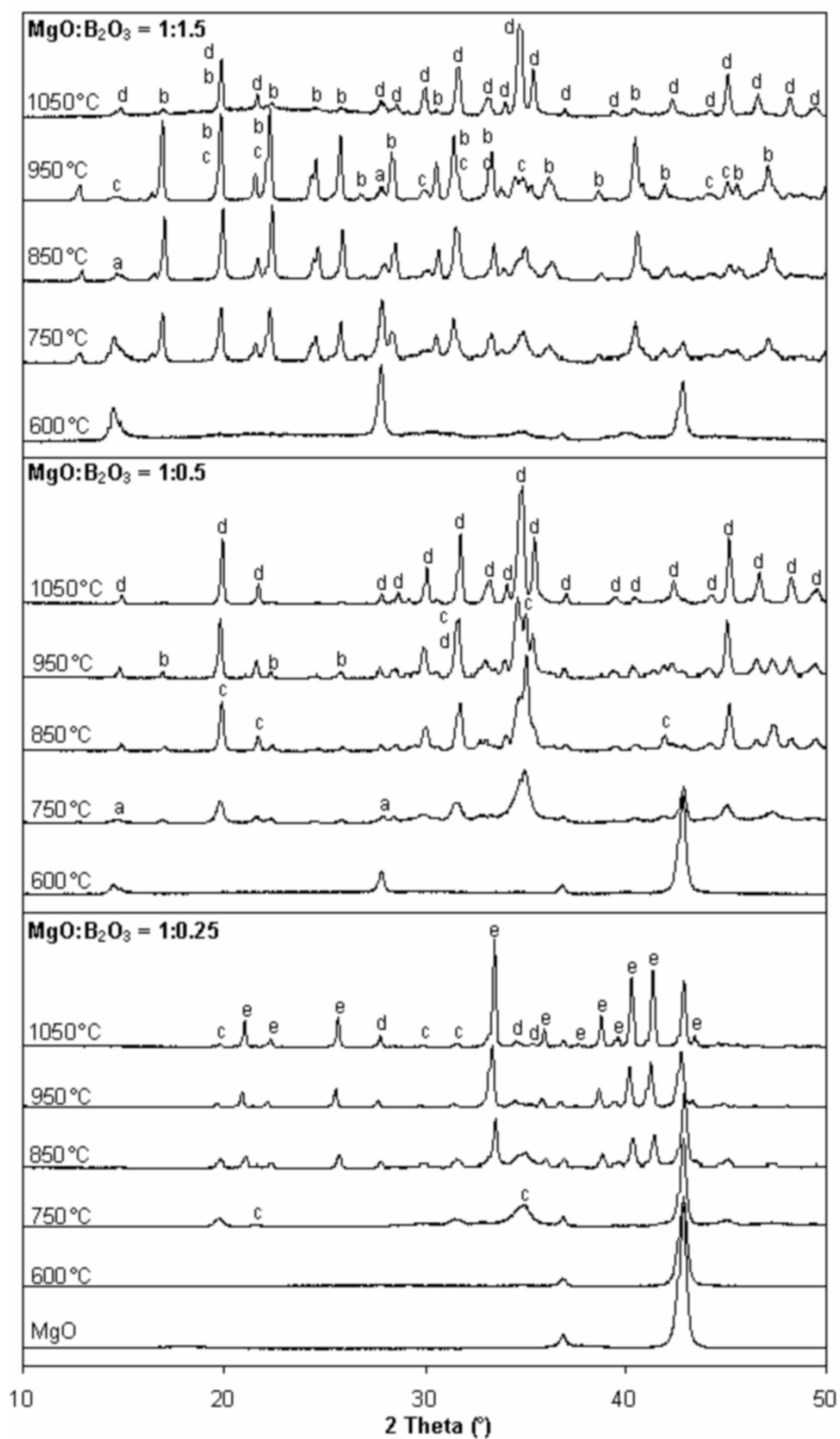
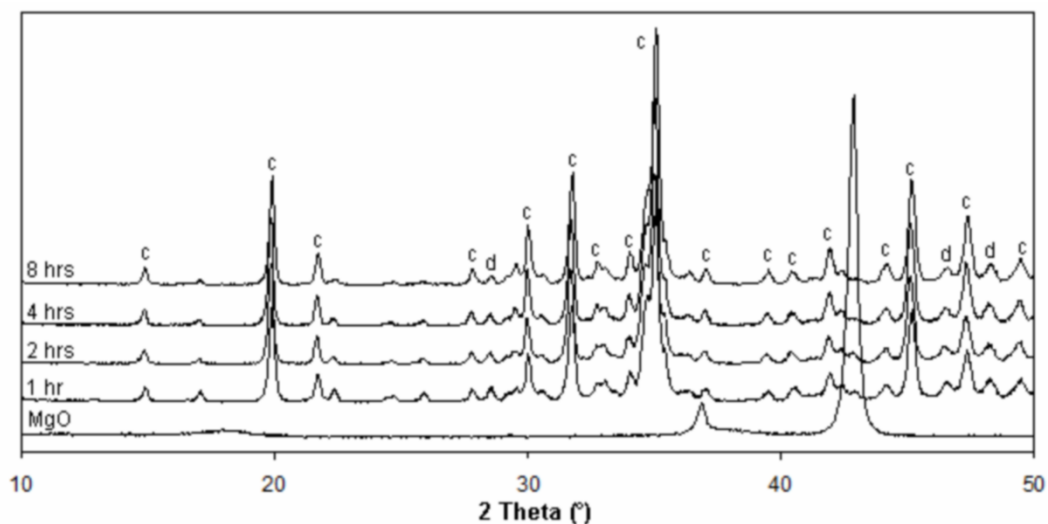


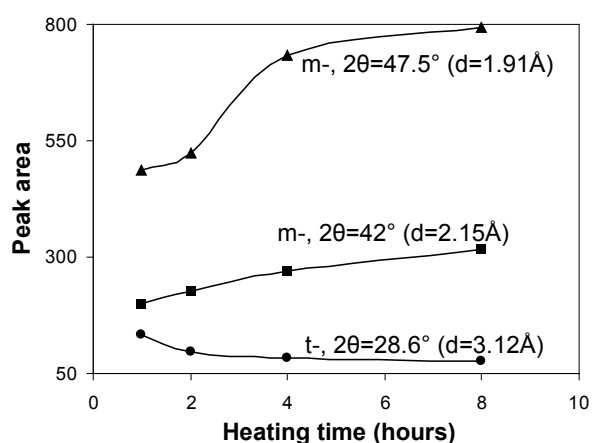
Figure 1. TG/DTA patterns of H<sub>3</sub>BO<sub>3</sub>, MgO and the mixtures prepared at various MgO:B<sub>2</sub>O<sub>3</sub> mole ratios.



**Figure 2.** XRD patterns of the solids synthesized at different temperatures and MgO:B<sub>2</sub>O<sub>3</sub> mole ratios (a: B<sub>2</sub>O<sub>3</sub>, b: MgB<sub>4</sub>O<sub>7</sub>, c: m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, d: t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, e: Mg<sub>3</sub>B<sub>2</sub>O<sub>6</sub>).



**Figure 3.** Effect of heating time on the formation of  $m\text{-Mg}_2\text{B}_2\text{O}_5$  at  $850^\circ\text{C}$  and  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratio of 1:0.5 (c: $m\text{-Mg}_2\text{B}_2\text{O}_5$ , d: $t\text{-Mg}_2\text{B}_2\text{O}_5$ ).

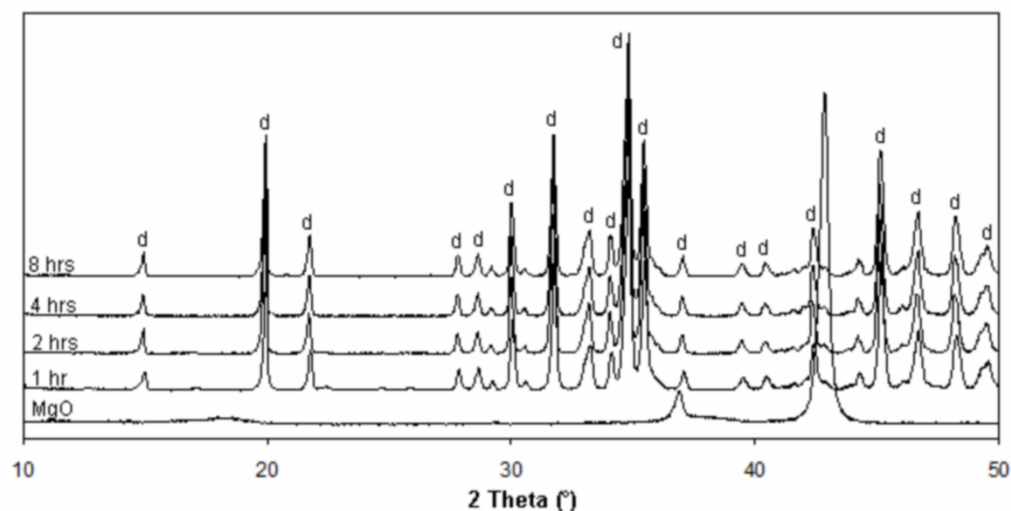


**Figure 4.** Change of peak areas for  $m\text{-Mg}_2\text{B}_2\text{O}_5$  and  $t\text{-Mg}_2\text{B}_2\text{O}_5$  by reaction time.

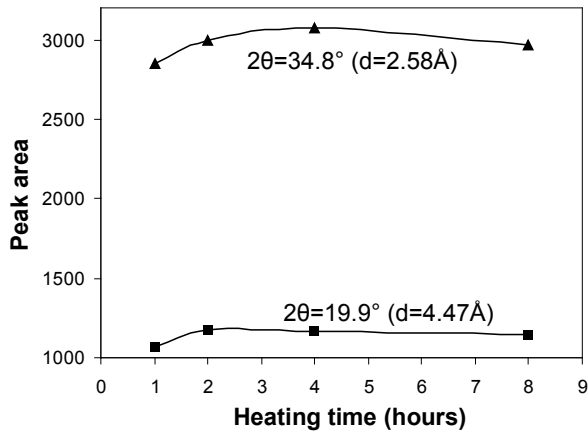
(Fig. 2) that the major phase formed at  $750^\circ\text{C}$ ,  $850^\circ\text{C}$  and  $950^\circ\text{C}$  is  $\text{MgB}_4\text{O}_7$  with  $m\text{-Mg}_2\text{B}_2\text{O}_5$  and/or  $t\text{-Mg}_2\text{B}_2\text{O}_5$  as a minor product. When the temperature is increased to  $1050^\circ\text{C}$ , the amount of  $\text{MgB}_4\text{O}_7$  decreases while the amount of  $t\text{-Mg}_2\text{B}_2\text{O}_5$  increases.

As  $m\text{-Mg}_2\text{B}_2\text{O}_5$  and  $t\text{-Mg}_2\text{B}_2\text{O}_5$  exhibited their more intense peaks at  $850^\circ\text{C}$  and  $1050^\circ\text{C}$  respectively, mixtures at  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratio of 1:0.5 were heated for 2, 4 and 8 hours at these temperatures to find out the effect of the heating time on the reactions. XRD patterns of the obtained solids at  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratio of 1:0.5 and  $850^\circ\text{C}$  for heating times of 1, 2, 4 and 8 hours are given in Fig. 3.

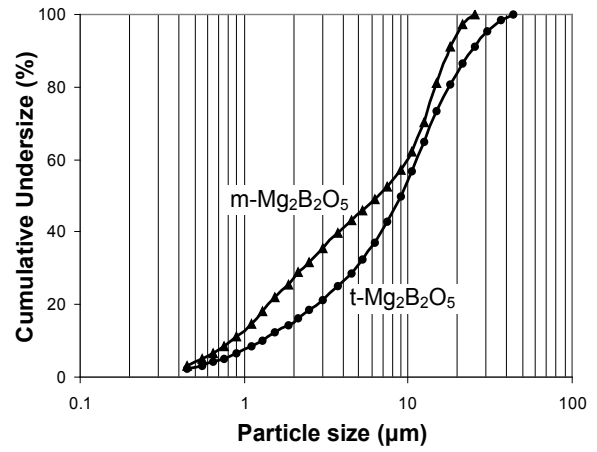
The effect of heating time on the purity of the synthesized  $m\text{-Mg}_2\text{B}_2\text{O}_5$  was observed by determining the change in the areas of the more intense peaks of



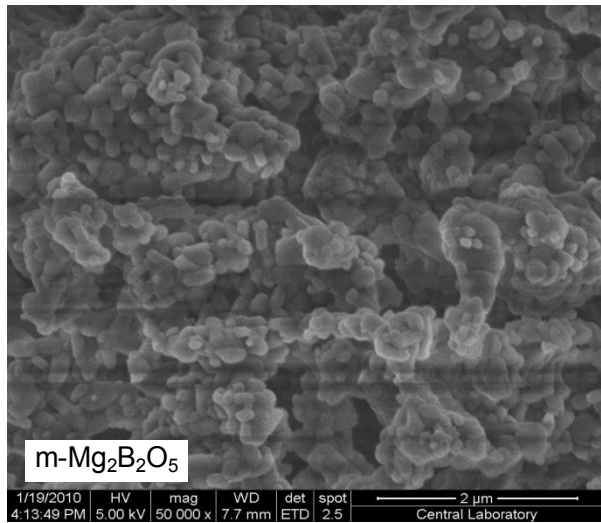
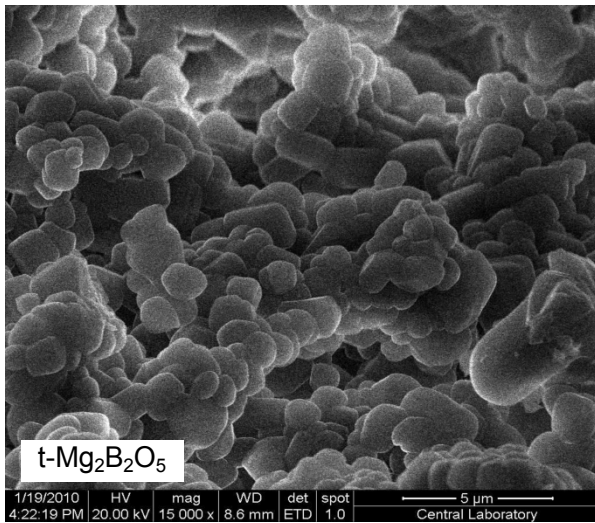
**Figure 5.** Effect of heating time on the formation of  $t\text{-Mg}_2\text{B}_2\text{O}_5$  at  $1050^\circ\text{C}$  and  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratio of 1:0.5 (d: $t\text{-Mg}_2\text{B}_2\text{O}_5$ ).



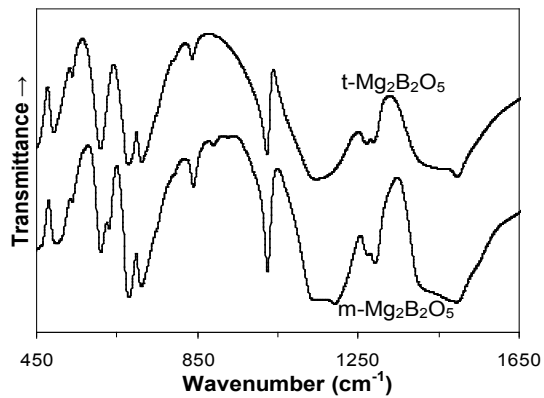
**Figure 6.** Change of peak areas for  $t-Mg_2B_2O_5$  by reaction time.



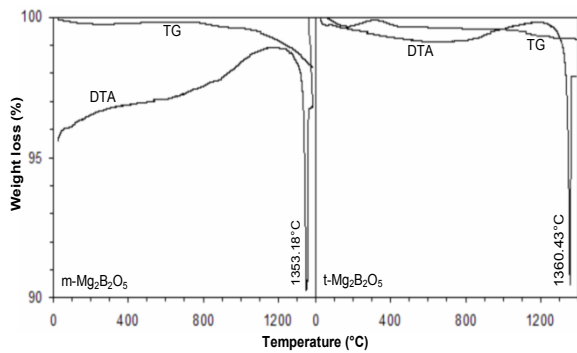
**Figure 7.** Particle size distribution of the samples prepared at optimum conditions.



**Figure 8.** SEM photographs of the samples prepared at optimum conditions.



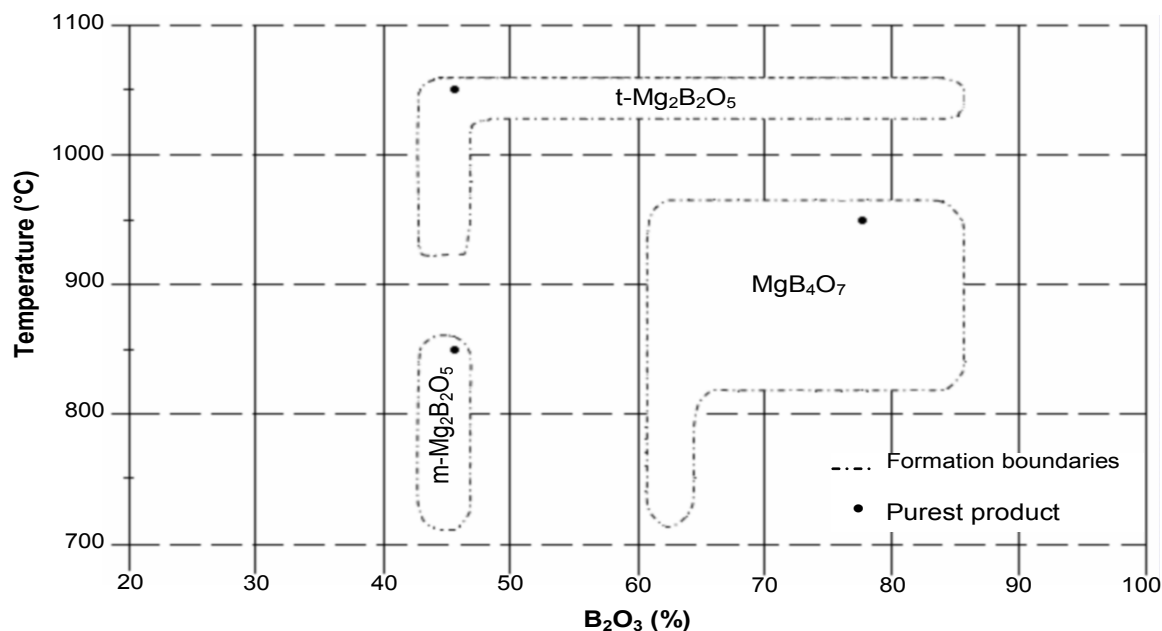
**Figure 9.** IR spectra of the solids prepared at optimum conditions.



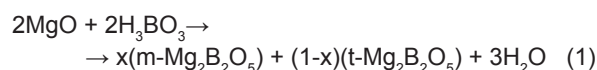
**Figure 10.** TG/DTA patterns of the solids prepared at optimum conditions.

**Table 1.** Chemical analyses results of the synthesized compounds.

Compound	Theoretical (%)		Experimental (%)		Loss on ignition (%)	Total
	MgO	B <sub>2</sub> O <sub>3</sub>	MgO	B <sub>2</sub> O <sub>3</sub>		
m-Mg <sub>2</sub> B <sub>2</sub> O <sub>5</sub>	53.66	46.34	53.06	47.93	0.24	101.23
t-Mg <sub>2</sub> B <sub>2</sub> O <sub>5</sub>	53.66	46.34	53.11	46.37	0.16	99.64

**Figure 11.** Formation zones of t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and MgB<sub>4</sub>O<sub>7</sub>.

m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> as major and minor products, respectively (Fig. 4). By increasing the heating time, increases in the peak areas of m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> at  $2\theta=42^\circ$  and  $47.5^\circ$  were observed while the peak area of t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> at  $2\theta=28.6^\circ$  was decreased. Accordingly, for MgO:B<sub>2</sub>O<sub>3</sub> mole ratio of 1:0.5, a heating temperature of 850°C and a heating time of 4 hours were selected as optimum conditions for the formation of m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> with minimum amounts of t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> (Eq. 1).



XRD patterns of the solids obtained at MgO:B<sub>2</sub>O<sub>3</sub> mole ratio of 1:0.5 (T=1050°C) for heating times of 1, 2, 4 and 8 hours are given in Fig. 5. It was seen that the formation of t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> was supported by a temperature increase and that it was possible to obtain it as a single phase at 1050°C. The heating time at which the maximum amount of t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> formed was determined by comparing the changes in the areas of the two intense peaks at  $2\theta=19.9^\circ$  and  $34.8^\circ$  (Fig. 6). The peak area reaches a maximum at a heating time of 4 hours, after which there is no significant increase in the peak areas.

The optimum conditions for the formation of t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> were determined to be MgO:B<sub>2</sub>O<sub>3</sub> mole ratio of 1:0.5, a heating temperature of 1050°C, and a reaction time of 4 hours (Eq. 2). m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> were synthesized at optimum conditions and were subjected to a series of tests to determine their properties. The results of the chemical analysis of the synthesized compounds are given in Table 1, which shows that the theoretical and experimental values are in good agreement with each other.



Fig. 7 shows that the maximum particle sizes of m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> and t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> compounds are 25.5 μm and 43.5 μm, respectively with  $d_{80}$  values of ~14.7 μm and ~17.7 μm and Fig. 8 gives the SEM photographs. Reasonably, t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> has a smaller B.E.T. surface area (0.5 m<sup>2</sup> g<sup>-1</sup>) than that of m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub> (2.7 m<sup>2</sup> g<sup>-1</sup>). Also, the solubilities and the pH values of the synthesized compounds in 100 mL water were determined as 0.031 g and 9.12 for m-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, and 0.038 g and 8.89 for t-Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, respectively.

The infrared spectra of the synthesized samples (Fig. 9) are in agreement with the IR pattern of magnesium pyroborate ( $2\text{MgO}\cdot\text{B}_2\text{O}_3$ ) compound as given by Kamitsos *et al.* [27]. Fig. 9 shows that boron in the samples is found in both trigonally (absorption bands near 676, 710 and between 1390-1495  $\text{cm}^{-1}$ ) and tetrahedrally (absorption bands near 1026 and 1138  $\text{cm}^{-1}$  in the pattern of  $\text{m-Mg}_2\text{B}_2\text{O}_5$ , 1022  $\text{cm}^{-1}$  in the pattern of  $\text{t-Mg}_2\text{B}_2\text{O}_5$ ) coordinated states [28].

The endothermic peaks at 1353.18°C and 1360.43°C in the DTA patterns (Fig. 10) of  $\text{m-Mg}_2\text{B}_2\text{O}_5$  and  $\text{t-Mg}_2\text{B}_2\text{O}_5$ , respectively, indicate the melting temperatures of the corresponding compounds. These temperature values are within the range of 1312-1381°C, which is in agreement with the values given by other researchers [6,11].

After evaluation of the experimental data, the locations of the purest products and the formation zones of  $\text{t-Mg}_2\text{B}_2\text{O}_5$  and  $\text{m-Mg}_2\text{B}_2\text{O}_5$  together with  $\text{MgB}_4\text{O}_7$  [26] are given in Fig. 11.

## 4. Conclusions

Experimental results show that for all the  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratios tested,  $\text{m-Mg}_2\text{B}_2\text{O}_5$  begins to form at 750°C and is present until 1050°C. By increasing the temperature, notably at 950°C, the monoclinic form starts to be

transformed into the triclinic form. A  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratio of 1:0.5 and a heating time of 4 hours at 850°C were found to be the optimum conditions for the formation of  $\text{m-Mg}_2\text{B}_2\text{O}_5$  with minimum amounts of  $\text{t-Mg}_2\text{B}_2\text{O}_5$ .

$\text{t-Mg}_2\text{B}_2\text{O}_5$  was observed to form for all  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratios tested between 850-1050°C and the reaction was improved by increasing the temperature. This compound was formed as a single phase at  $\text{MgO}:\text{B}_2\text{O}_3$  mole ratio of 1:0.5 for a reaction time of 4 hours at 1050°C.

The melting points, solubilities and pH values of both compounds are similar to each other and  $\text{m-Mg}_2\text{B}_2\text{O}_5$  has a finer particle size distribution than  $\text{t-Mg}_2\text{B}_2\text{O}_5$  when ground under the same conditions. Although the surface area values are small,  $\text{m-Mg}_2\text{B}_2\text{O}_5$  has a slightly larger surface area than that of  $\text{t-Mg}_2\text{B}_2\text{O}_5$  as expected from the particle size distributions.

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