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Controlled synthesis, characterization and thermal properties of $Mg_2B_2O_5$

Research Article

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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*

1. Introduction

Magnesium borates with compositions of $xMgO•yB_2O_3•zH_2O$ and $xMgO•yB_2O_3$ may be found in nature and can also be prepared synthetically in the laboratory. $2MgO•B_2O_3•xH_2O$ 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.

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Formed magnesium borate phases were identified by XRD analyses using a Rigaku x-ray diffractometer. The optimum $MgO:B_2O_3$ mole ratio and the temperature at which the highest amount of m- and t-$Mg_2B_2O_5$ 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 $MgO:B_2O_3$ 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_3BO_3 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 $MgO:B_2O_3$ mole ratios increased as the amount of B_2O_3 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 $MgO:B_2O_3$ mole ratio of 1:1.5 indicates a transformation in the reaction medium.

Considering the peak temperatures obtained from DTA results, mixtures prepared at $MgO:B_2O_3$ 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_2O_3 (PDF No: 6-297) increases as the B_2O_3 contents of the mixtures increase. For mixtures prepared at $MgO:B_2O_3$ 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-$Mg_2B_2O_5$ (PDF No: 16-168) formed at 750°C begins to be transformed into t-$Mg_2B_2O_5$ (PDF No: 15-537) at 850°C and this transformation is completed at 1050°C. Experimental results show that at a $MgO:B_2O_3$ mole ratio of 1:0.25, the major phase formed between 850°C to 1050°C is $Mg_3B_2O_6$ (PDF No: 5-648).

When the B_2O_3 content of the mixture is increased ($MgO:B_2O_3$ mole ratio 1:0.5), the interaction between starting compounds increases above 850°C and the corresponding peaks of unreacted MgO and B_2O_3 begin to disappear. m-$Mg_2B_2O_5$ formed at 750°C is transformed into t-$Mg_2B_2O_5$ by temperature increase with significant formation at 950°C until finally t-$Mg_2B_2O_5$ is the only phase present at 1050°C. On the other hand, MgB_4O_7 (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 $MgO:B_2O_3$ mole ratio

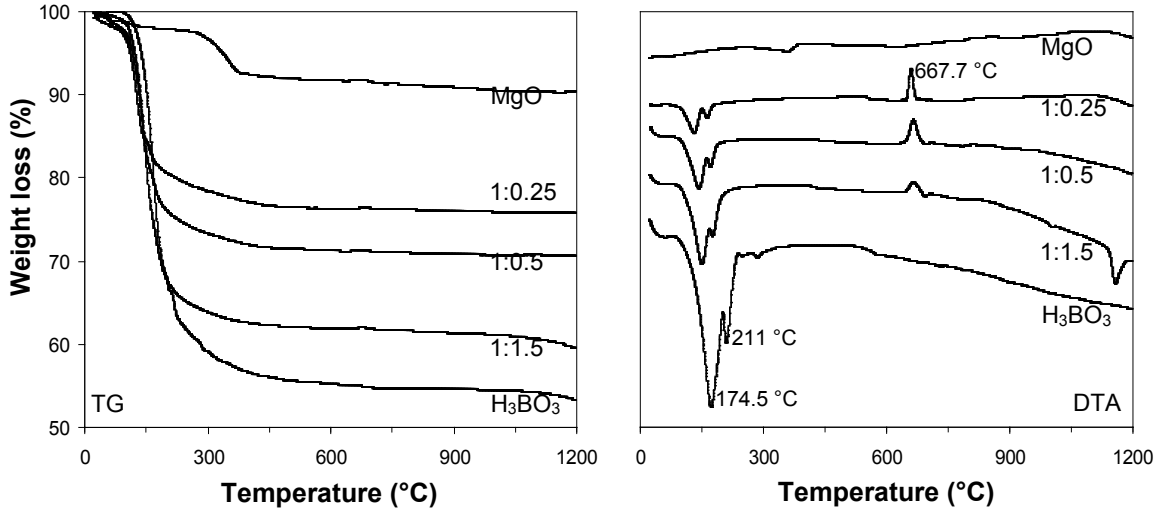

Figure 1. TG/DTA patterns of H_3BO_3, MgO and the mixtures prepared at various $MgO:B_2O_3$ mole ratios.

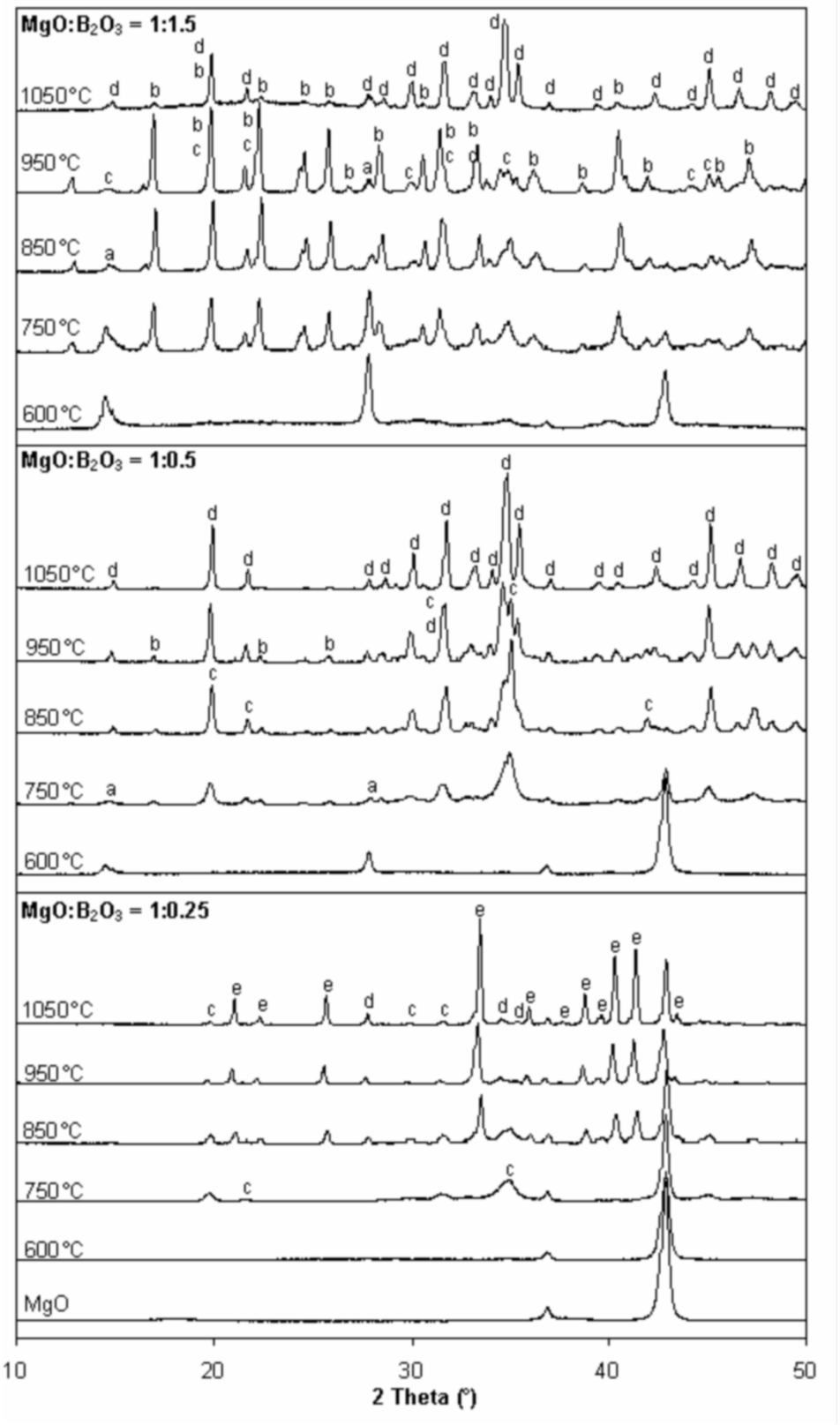

Figure 2. XRD patterns of the solids synthesized at different temperatures and $MgO:B_2O_3$ mole ratios (a: B_2O_3, b: MgB_4O_7, c: m-$Mg_2B_2O_5$, d: t-$Mg_2B_2O_5$, e: $Mg_3B_2O_6$).

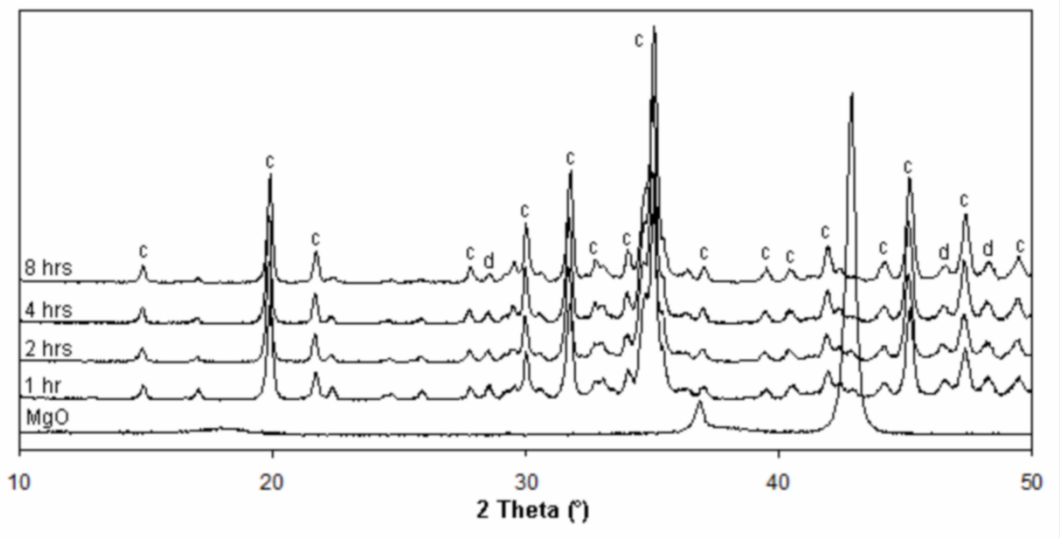

Figure 3. Effect of heating time on the formation of m-$Mg_2B_2O_5$ at 850°C and MgO:B_2O_3 mole ratio of 1:0.5 (c:m-$Mg_2B_2O_5$, d:t-$Mg_2B_2O_5$).

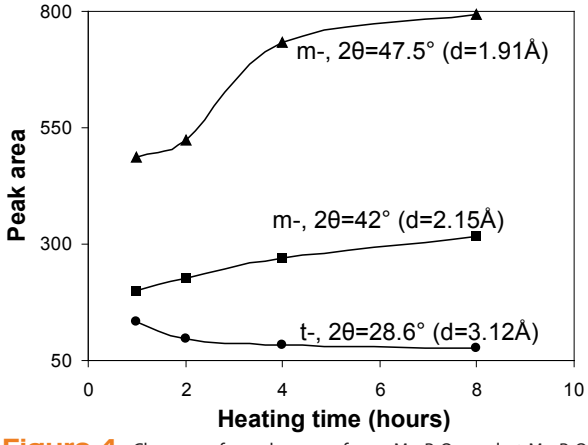

Figure 4. Change of peak areas for m-$Mg_2B_2O_5$ and t-$Mg_2B_2O_5$ by reaction time.

(Fig. 2) that the major phase formed at 750°C, 850°C and 950°C is MgB_4O_7 with m-$Mg_2B_2O_5$ and/or t-$Mg_2B_2O_5$ as a minor product. When the temperature is increased to 1050°C, the amount of MgB_4O_7 decreases while the amount of t-$Mg_2B_2O_5$ increases.

As m-$Mg_2B_2O_5$ and t-$Mg_2B_2O_5$ exhibited their more intense peaks at 850°C and 1050°C respectively, mixtures at MgO:B_2O_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 MgO:B_2O_3 mole ratio of 1:0.5 and 850°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-$Mg_2B_2O_5$ was observed by determining the change in the areas of the more intense peaks of

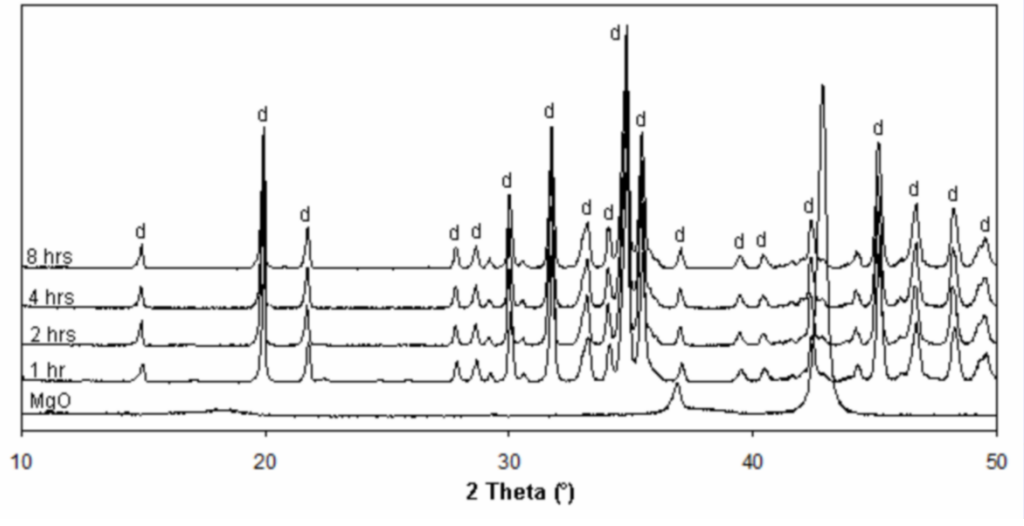

Figure 5. Effect of heating time on the formation of t-$Mg_2B_2O_5$ at 1050°C and MgO:B_2O_3 mole ratio of 1:0.5 (d:t-$Mg_2B_2O_5$).

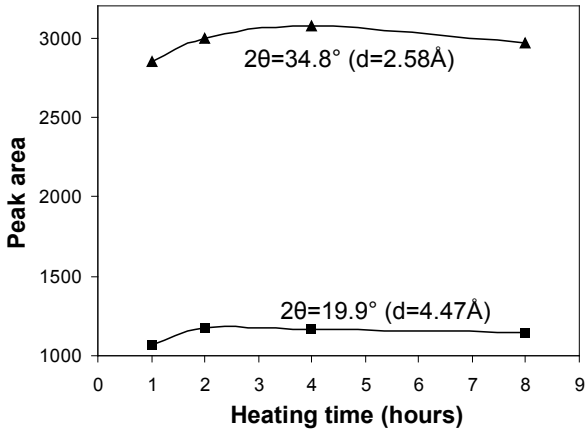

Figure 6. Change of peak areas for t-$Mg_2B_2O_5$ by reaction time.

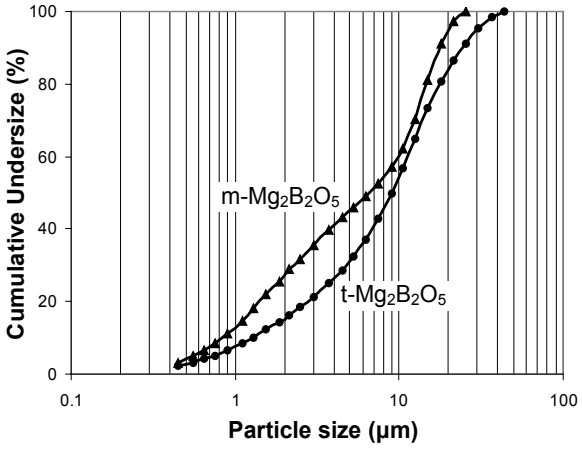

Figure 7. Particle size distribution of the samples prepared at optimum conditions.

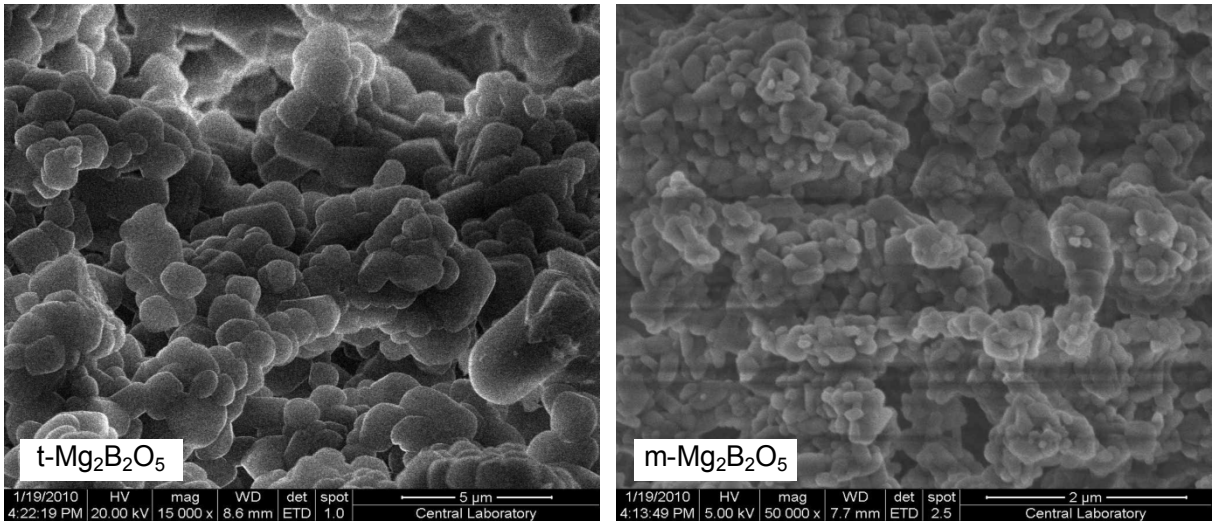

Figure 8. SEM photographs of the samples prepared at optimum conditions.

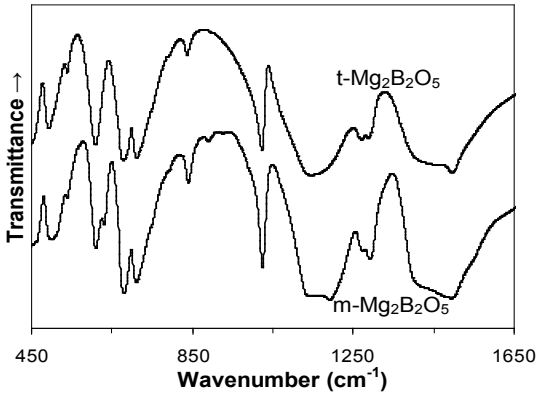

Figure 9. IR spectra of the solids prepared at optimum conditions.

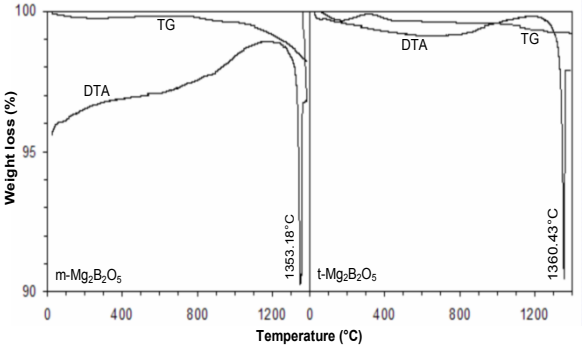

Figure 10. TG/DTA patterns of the solids prepared at optimum conditions.

Table 1. Chemical analyses results of the synthesized compounds.

	Theoretical (%)		Experimental (%)			
Compound	MgO	B_2O_3	MgO	B_2O_3	Loss on ignition (%)	Total
m-$Mg_2B_2O_5$	53.66	46.34	53.06	47.93	0.24	101.23
t-$Mg_2B_2O_5$	53.66	46.34	53.11	46.37	0.16	99.64

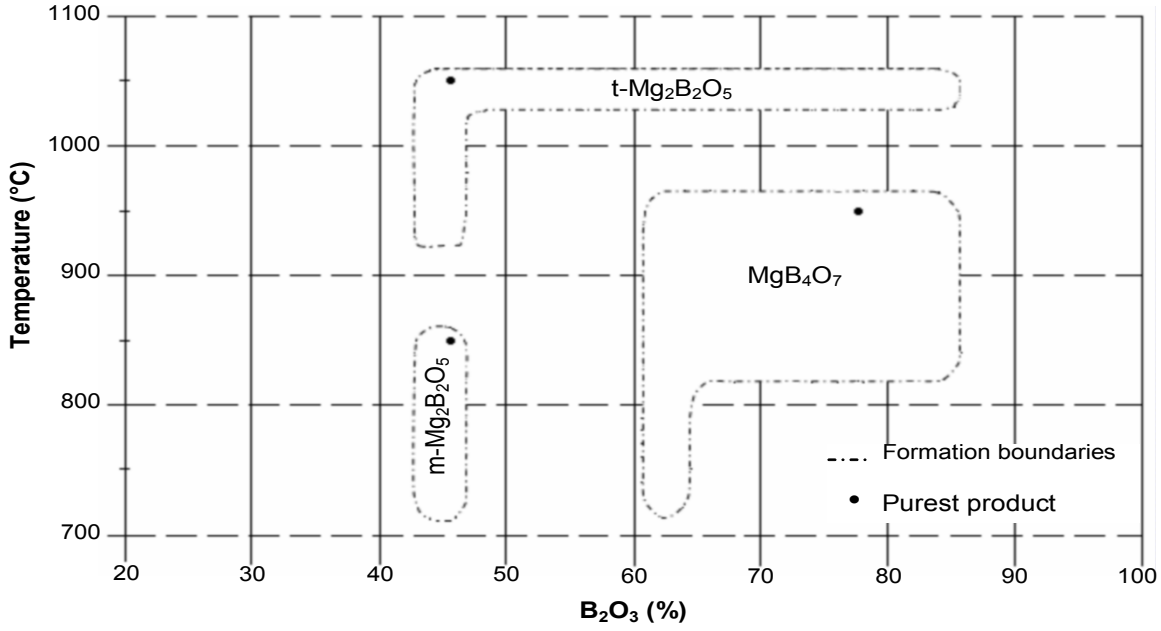

Figure 11. Formation zones of t-$Mg_2B_2O_5$, m-$Mg_2B_2O_5$ and MgB_4O_7.

m-$Mg_2B_2O_5$ and t-$Mg_2B_2O_5$ as major and minor products, respectively (Fig. 4). By increasing the heating time, increases in the peak areas of m-$Mg_2B_2O_5$ at 2θ=42° and 47.5° were observed while the peak area of t-$Mg_2B_2O_5$ at 2θ=28.6° was decreased. Accordingly, for MgO:B_2O_3 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-$Mg_2B_2O_5$ with minimum amounts of t-$Mg_2B_2O_5$ (Eq. 1).

$$2MgO + 2H_3BO_3 \rightarrow \rightarrow x(m\text{-}Mg_2B_2O_5) + (1\text{-}x)(t\text{-}Mg_2B_2O_5) + 3H_2O \quad (1)$$

XRD patterns of the solids obtained at MgO:B_2O_3 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-$Mg_2B_2O_5$ 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-$Mg_2B_2O_5$ formed was determined by comparing the changes in the areas of the two intense peaks at 2θ=19.9° and 34.8° (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-$Mg_2B_2O_5$ were determined to be MgO:B_2O_3 mole ratio of 1:0.5, a heating temperature of 1050°C, and a reaction time of 4 hours (Eq. 2). m-$Mg_2B_2O_5$ and t-$Mg_2B_2O_5$ 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.

$$2MgO + 2H_3BO_3 \rightarrow t\text{-}Mg_2B_2O_5 + 3H_2O \quad (2)$$

Fig. 7 shows that the maximum particle sizes of m-$Mg_2B_2O_5$ and t-$Mg_2B_2O_5$ 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-$Mg_2B_2O_5$ has a smaller B.E.T. surface area (0.5 $m^2\ g^{-1}$) than that of m-$Mg_2B_2O_5$ (2.7 $m^2\ g^{-1}$). 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-$Mg_2B_2O_5$, and 0.038 g and 8.89 for t-$Mg_2B_2O_5$, respectively.

The infrared spectra of the synthesized samples (Fig. 9) are in agreement with the IR pattern of magnesium pyroborate ($2MgO•B_2O_3$) 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 cm^{-1}) and tetrahedrally (absorption bands near 1026 and 1138 cm^{-1} in the pattern of m-$Mg_2B_2O_5$, 1022 cm^{-1} in the pattern of t-$Mg_2B_2O_5$) coordinated states [28].

The endothermic peaks at 1353.18°C and 1360.43°C in the DTA patterns (Fig. 10) of m-$Mg_2B_2O_5$ and t-$Mg_2B_2O_5$, 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 t-$Mg_2B_2O_5$ and m-$Mg_2B_2O_5$ together with MgB_4O_7 [26] are given in Fig. 11.

4. Conclusions

Experimental results show that for all the $MgO:B_2O_3$ mole ratios tested, m-$Mg_2B_2O_5$ 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 $MgO:B_2O_3$ 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 m-$Mg_2B_2O_5$ with minimum amounts of t-$Mg_2B_2O_5$

t-$Mg_2B_2O_5$ was observed to form for all $MgO:B_2O_3$ 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 $MgO:B_2O_3$ 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 m-$Mg_2B_2O_5$ has a finer particle size distribution than t-$Mg_2B_2O_5$ when ground under the same conditons. Although the surface area values are small, m-$Mg_2B_2O_5$ has a slightly larger surface area than that of t-$Mg_2B_2O_5$ as expected from the particle size distributions.

Acknowledgements

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