

Production of Zinc Borate for Pilot-Scale Equipment and Effects of Reaction Conditions on Yield

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In this study, zinc borate (ZB) was synthesized by reacting zinc oxide and boric acid in the presence of standard ZB (w/w, in terms of boric acid) in order to promote crystallization. The effects of seed, H_3BO_3/ZnO (boric acid/zinc oxide) ratio, reaction time, water volume, reaction temperature and cooling temperature on yield were investigated for pilot-scale equipment. The results indicated that the addition of seed (w/w) to a saturated solution of reactants increased the yield of the reaction. The results of reaction yields obtained from either magnetically or mechanically stirred systems were compared. At various reaction times, the optimal yield was 86.78 % in a saturated aqueous solution. The products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and Thermogravimetric/Differential Thermal Analysis (TG/DTA). The results displayed that ZB was successfully produced under the optimized reaction conditions and the product synthesized had high thermal stability.

Keywords: boric acid, seed, yield, zinc borate, zinc oxide.

1. INTRODUCTION

Zinc borates are commonly used in rubber, plastic, ceramic, paint, glass, electric insulation, wood applications, cement, medicine and flame retardants. Furthermore, zinc borates are used as a preservative in wood composites, as anticorrosive pigments in coatings and as polymer additives to promote char formation in order to suppress smoke and to retard combustion [1–9]. Many methods were developed for the synthesis of zinc borates (ZnB_4O_7 , $Zn_8[(BO_3)_3O_2(OH)_3]$, $Zn_2B_6O_{11} \cdot 7H_2O$, $4ZnO \cdot B_2O_3 \cdot H_2O$, $Zn_3B_{10}O_{18} \cdot 14H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ and $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$) [10–17]. In several methods, the production of ZB is achieved in an aqueous solution of zinc oxides, zinc salts or zinc hydroxides. Boric acid and borate salts such as borax and tincalconite are used as sources of boron. For instance, Shete et al. [18] produced ZB by combining aqueous boric acid and zinc oxide at 70 °C in a kinetically controlled process. Schubert et al. [3] characterized the structure of the industrially significant ZB, $Zn[B_3O_4(OH)_3]$, and prepared single crystals for X-ray structure determination, revealing a composition of $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$. Chen et al. [19] studied the production of ZB nano-flakes ($2ZnO \cdot 2.2B_2O_3 \cdot 3H_2O$) via coordination and homogeneous precipitation of ammonia, zinc nitrate and borax. XRD, TEM, DSC, TGA/DTA and FT-IR were used to characterize the products. A pilot study revealed that ZB nano-flakes were a superior flame retardant for the combustion of polypropylene (PP). The carbon residue ratio of PP increased up to 75 % specifically with a ZB concentration of 12 % wt. Shi et al. [4] studied the

preparation of $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$ from zinc oxide and boric acid via a rheological phase reaction. The products were characterized by XRD, TG, DTA and SEM. Moreover, the effects of experimental conditions and particle size distribution on the characteristics of the products were investigated. ZB is an important green material that can be used to remove various toxic gases and organic compounds and can be synthesized in an environmentally friendly manner. Igarashi et al. [20] synthesized zinc borates in a two-step reaction. In the first step, zinc oxide and boric acid were combined and stirred at 60 °C for 1.5 hours to achieve crystal formation. In the second step, the mixture was stirred continuously at 90 °C for 4 hours, and seed crystals were added to the reaction mixture to enhance crystal growth. The results of many studies indicated that the addition of seed crystals [21] can be made use of in order to improve the yield and the purity of the desired product.

The purpose of this study was to increase the efficiency of ZB production and to investigate the effects of reaction conditions on yield. In this study, various ZB species (as $3ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$; $3ZnO \cdot 3B_2O_3 \cdot 12H_2O$) were synthesized under optimized conditions. Different from the studies available in the literature, the effect of reaction time, H_3BO_3/ZnO ratio, the amount of seed, water volume, reaction temperature and the cooling temperature on yield were investigated. Unlike other studies, the results obtained from either the magnetically or the mechanically stirred systems regarding this reaction were compared for pilot-scale equipment. In particular, effects of reaction conditions on yield were investigated. Seed crystals were added to the reaction medium to reduce reaction time and to produce ZB which had desired crystal water. The products were characterized by analytical techniques and

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FT-IR, XRD, TG/DTA, which all indicated that the synthesis of ZB was successful under the optimized reaction conditions.

2. EXPERIMENTAL

2.1. Materials

Boric acid (molecular formula: $B(OH)_3$, 99.9 % pure) and standard ZB (seed) were obtained from Eti Mine Works. Zinc oxide (97 % pure) was acquired from Colakoglu Chemicals Ltd.

2.2. Synthesis of ZB

Reaction mixtures were stirred magnetically and mechanically in different systems using boric acid and zinc oxide. In the magnetically stirred system, the reaction was conducted in a closed glass beaker at 95 °C on a magnetic stirrer plate. A digital sensor was used for temperature control. Parameters such as reaction time, H_3BO_3/ZnO ratio, water volume, reaction temperature and cooling temperature were varied. Experiments were given in Table 1. In the mechanically stirred system, the synthesis was carried out in a 1.5 L glass reactor under the determined conditions. Fig. 1 displays the experimental set up used in the study.

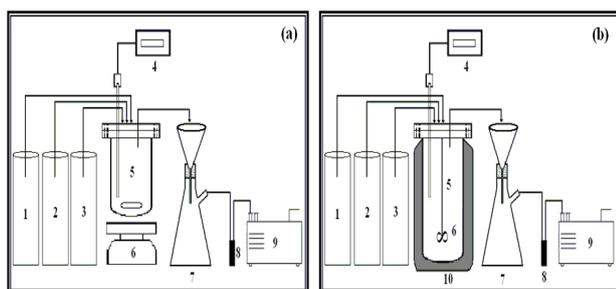


Fig. 1. Experimental set up: a – magnetically stirred system; b – mechanically stirred system. [1 – boric acid; 2 – zinc oxide; 3 – standard ZB; 4 – digital temperature controller; 5 a – glass beaker; 5 b – reactor; 6 a – magnetic stirrer plate; 6 b – mechanic stirrer; 7 – solid-liquid phase separator; 8 – trap; 9 – vacuum pump; 10 b – heating jacket]

Reactions were conducted by dissolving the required amount of boric acid into distilled water. In the next step, zinc oxide and seed (w/w, in terms of boric acid) were added into the initial boric acid solution and the reaction mixture was stirred rigorously. After 10 min, a clear liquid and solid white precipitate formed and separated into two phases. The precipitate was filtered, rinsed with distilled

Table 1. The experiments for ZB production*

| H_3BO_3/ZnO | Reaction time (h) | Water volume (ml) | Standard ZB (%) | H_3BO_3/ZnO | Reaction time (h) | Reaction temperature (°C) | Cooling temperature (°C) |
|---------------|-------------------|-------------------|-----------------|--------------------|-------------------|---------------------------|--------------------------|
| 5:1 | 4 | 15 | 0 | 3:1 (saturated) | 1 | 50 | 10 |
| | 5 | 25 → | 0.5 → | | 2 → | 75 | 20 |
| | 6 → | 50 | 1.0 | | 3 | 95 → | 50 → |
| | 7 | 75 | 1.5 | | 4 | 120 | 65 |
| | | 100 | | 5 | | 80 | |

* the optimum parameters were determined in magnetically stirred system. Then, the optimum points were iterated for mechanically stirred system.

water and dried at 105 °C for 20 h. The yield values were calculated per gram of zinc oxide consumed (1):



Reactions were carried out between 3:1–6.5:1 of H_3BO_3/ZnO ratio and 4–7 hours of reaction time. As a beginning, the optimum reactant ratio 5:1 and the optimum reaction time was 6 hours. The optimum reaction conditions were determined gradually for each parameter (Table 1).

2.3. Analytical methods

2.3.1. Analysis of ZnO

The amount of zinc oxide present in the solid samples was determined by the following EDTA titration. The sample (0.2 g–0.3 g) was dissolved in 37 % hydrochloric acid (1 ml), and a solution of ammonia buffer (15–20 ml) was added into the dissolved sample solution to achieve a pH of 9.5. The final solution was titrated with EDTA by adding a few drops of erichrome black-t indicator. The percentage of zinc oxide in the solid phase was calculated according to Eq. (2):

$$M = 0.408 \times S \times E / n, \quad (2)$$

where M, S, E and n are the percentage of ZnO in the sample (%), the volume of EDTA added (ml), the molecular weight of ZnO (g/mol) and the amount of sample (g), respectively.

2.3.2. Analysis of B_2O_3

The sample (1 g) was dissolved in 37 % hydrochloric acid. 1 ml of this solution was added into 1 ml of EDTA together with the methyl orange indicator. This solution was titrated with 0.1 N NaOH. The titration proceeded using mannitol and phenolphthalein. The percentage of B_2O_3 was calculated according to Eq. (3):

$$B_2O_3 (\%) = 56.36 \times A / B; \quad (3)$$

A and B are the consumption of NaOH (ml) for the sample and the standard boric acid, respectively.

2.4. Characterization

All products were characterized by X-ray diffraction (Philips Xpert-Pro). Furthermore, Fourier transform infrared spectroscopy (a Perkin Elmer FT-IR Spectrum One) was used to identify the functional groups present in the products. Weight loss and dehydration temperature values for the products were determined with TG/DTA.

3. RESULTS AND DISCUSSION

3.1. The effect of reaction time on yield

In this study, the optimal production parameters were determined, and the yield of ZB was investigated as a function of various parameters. Thus, the effect of each parameter was investigated individually. An initial water volume of 100 ml was selected to determine the optimal parameters. The effect of reaction time on yield is illustrated in Fig. 2. Various ratios of H_3BO_3/ZnO (3 : 1–6.5 : 1) and reaction times (4–7 hours) were evaluated under otherwise identical conditions (95 °C, 100 ml of water, 500 rpm, standard ZB: 0 %). The results revealed that the yield increased with an increase in reaction time; however, an improvement in yield was not observed after 6 h. Thus, the optimal reaction time selected under the specified conditions was 6 h. The effects of the reactant ratios and reaction times on yield were given in Table 2. In addition, the range of yield (%) was changed between 82.96 %–86.78 % with reaction time (25 ml of water (saturated), 0.5 % of seed, H_3BO_3/ZnO : 3 : 1). As expected, the produced ZB was in the form of white powder.

Table 2. The effect of the reactant ratio and reaction time on yield

| Time (h) | Yield (%) (3 : 1) | Yield (%) (3.5 : 1) | Yield (%) (5 : 1) | Yield (%) (6.5 : 1) |
|----------|-------------------|---------------------|-------------------|---------------------|
| 4 | 30.80 | 31.97 | 33.84 | 37.30 |
| 5 | 32.38 | 33.15 | 37.84 | 47.30 |
| 6 | 33.13 | 35.04 | 41.73 | 52.16 |
| 7 | 33.44 | 35.78 | 44.65 | 58.34 |

3.2. The effect of H_3BO_3/ZnO ratio on yield

Initially, the reaction was conducted in 100 ml of water with a stoichiometric ratio of H_3BO_3/ZnO . An increase in the H_3BO_3/ZnO ratio led to an increase in yield. This result can be explained that the amount of borate ions per unit amount of the solid and the driving force required for the mass transfer of borate ions in solution to zinc oxide increased with increase in H_3BO_3/ZnO [16]. A ratio of 5 : 1 was considered as optimal, similar to the previous study [17]. The effect of other parameters, including the reaction time (hour), concentration of ZB (%) and water volume (ml), on the yield of the reaction was investigated using a constant H_3BO_3/ZnO ratio of 5 : 1.

The pH of the initial boric acid solution was 3.0. Following the addition of zinc oxide, the pH of the solution increased up to 4.5 and remained constant. Thus, the production of ZB increased the pH of the solution. At the end of the reaction, the pH of the solution was 5.0. As expected, the pH remained below 7 throughout the entire reaction. Due to the presence of weak boronic acids and due to dilution with distilled water, the pH of the liquid phase after filtration was 6.5. Since an excess of boric acid was used, the solution pH was obtained to be acidic as expected from the results of various authors [15].

3.3. The effect of water volume on yield

The optimize conditions comprise of 6 hours of reaction time, 0.5 % seed content and 5 : 1 as the H_3BO_3/ZnO ratio. In addition, the yield was evaluated as a

function of water volume. Supersaturation, nucleation and crystal formation are necessary for crystal growth. Moreover, supersaturation is the driving force for crystallization. The results of previous studies indicated that a decrease in the volume of water caused an increase in yield. Therefore, as expected, any volume of water less than 100 ml provided the desired product in high yields. At a 5 : 1 ratio of H_3BO_3/ZnO , the volume of water providing the greatest yield of ZB was 25 ml (0.5 % seed content). The results of the tests are presented in Fig. 2, a. In subsequent experiments, 25 ml of water and a H_3BO_3/ZnO ratio of 3 : 1 were employed so as to reduce the overall cost of the synthesis. The optimum yield was obtained as 99.98 % in 25 ml of water. Products obtained from low-yield reactions were agglomerated; however, products of high-yielding reactions were highly crystalline and non-agglomerated. When the water volume was at nearly the saturation point, the reactions were carried out in 2 h. Production in short periods are important for industrial applications in terms of cost.

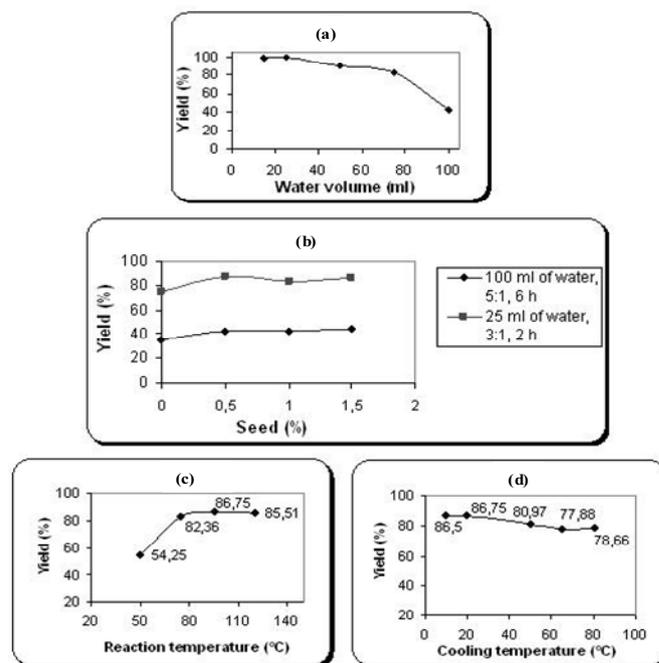


Fig. 2. The effect of process parameters on yield: a – water volume (6 h; seed: 0.5 %, H_3BO_3/ZnO : 5 : 1); b – seed contents, c – reaction temperature; d – cooling temperature

3.4. The effect of standard ZB on yield

As discussed in the previous study [17], the reaction of boric acid and zinc oxide does not yield ZB product if ZB crystals are not added to the solution as seed. On the other hand, the yield increased with an increase in ZB concentration until a maximum value was obtained at 0.5 % ZB (w/w).

As shown in Fig. 2, b, amounts of seed greater than 0.5 % (w/w) did not alter the yield; thus, 0.5 % (w/w) of seed concentration was selected for further studies. At the same time, when the seed was used for the saturated solution at the optimum point, the yield increased up to 86.74 % as shown in Fig. 2, b.

The yield values changed in range of 74.72 % and 86.01 % by increasing seed content (optimum conditions

for saturated solution). Therefore, when the results were compared, it was seen that the use of seed affected the extent that the reaction proceeded.

3.5. The effect of reaction temperature

The synthesis of ZB was conducted at temperatures between 50 °C and 120 °C. The results of the temperature studies indicated that the yield of the reaction increased dramatically with an increase in temperature until a maximum yield was obtained at 95 °C. At temperatures greater than 75 °C, only a slight increase in yield was observed. Moreover, at temperatures greater than 95 °C, the yield of the reaction remained constant. Thus, at 95 °C (yield: 86.78 %), the reaction was fully complete, and an optimal yield was obtained for saturated solution (Fig. 2, c). The temperature value selected was 95 °C similar to the previous study [18]. If the option was to carry out the reactions at low temperatures, the reaction time would be longer [17].

3.6. The effect of cooling temperature

After reaction, the system (95 °C) was cooled down to a variety of temperatures in a range of 80 °C–10 °C and five different experiments were carried out to examine the differential of cooling temperature. It was cooled from 95 °C to 80 °C (5 minutes); from 95 °C to 65 °C (10 minutes); from 95 °C to 50 °C (15 minutes); from 95 °C to 20 °C (20 minutes) and from 95 °C to 10 °C (25 minutes) as different five experiments which were carried out at 95 °C. Cooling the reaction mixture to temperatures greater than 50 °C caused a significant decrease in yield. In contrast, cooling the reaction mixture to temperatures less than 10 °C also resulted in losses in yield (Fig. 2, d).

3.7. The comparison of stirred systems

The yield values with mechanic stirred system were obtained higher than magnetically stirred system. 6 h of reaction time is going to increase incremental cost. Therefore, if the difference of about 10 % yield has been ignored, selection of 2-hour reaction will be more advantageous (Table 3).

The appearance of product was white powder. The usage of two different stirred system is considerable in terms of cost to carry out the production for pilot-scale equipment. When the yields in mechanic stirred system were scrutinized, it was seen that the yields in mechanically stirred system were higher than the yields in magnetically stirred system. The findings were compared with the small scale reactor experiments in literature and they are similar to this work [17].

Table 3. Optimum reaction conditions for produced ZB (based on 25 ml, 500 rpm)

| Time (h) | System | Seed (%) | H ₃ BO ₃ /ZnO | Yield (%) |
|----------|----------|----------|-------------------------------------|-----------|
| 6 | Magnetic | 0.5 | 5 : 1 | 99.98 |
| 6 | Mechanic | 0.5 | 5 : 1 | 99.99 |
| 2 | Magnetic | 0.5 | 3 : 1 | 86.78 |
| 2 | Mechanic | 0.5 | 3 : 1 | 92.65 |

3.8. Characterization

FT-IR spectroscopy was used to characterize the products obtained under various reaction conditions. FT-IR spectrum of ZB without seed (5 : 1, 6 h, 100 ml of water) and FT-IR spectrum of ZB in the presence of seed (5 : 1, 6 h, 0.5 % seed content, 100 ml of water) were seen in Fig. 3.

A band at 3179 cm⁻¹ was observed in the IR spectra, corresponding to stretching vibrations of O–H. The band at 1366 cm⁻¹ was assigned to the asymmetric stretching vibrations of trihedral (BO₃) borate groups, while the peaks at approximately 1063 cm⁻¹ and 1017 cm⁻¹ were assigned to the asymmetric and symmetric stretching vibrations of tetrahedral (BO₄) borate groups.

Furthermore, the peak observed at 674 cm⁻¹ indicated in-plane bending vibrations of trihedral (BO₃) groups. Thus, the FT-IR spectra of the products indicated that ZB was formed under the reaction conditions [22].

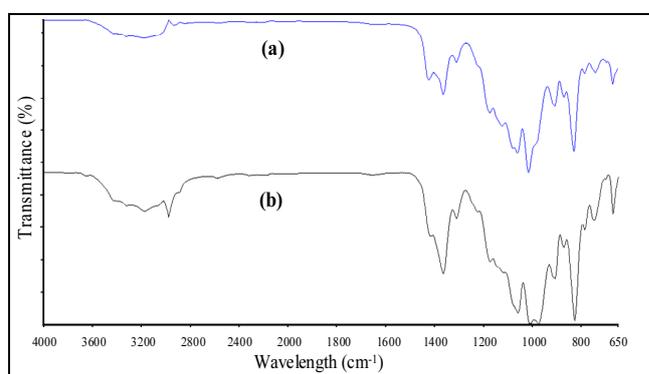


Fig. 3. FT-IR spectrum of ZB: a – without seed (5 : 1, 6 h, 100 ml of water), b – in the presence of seed (5 : 1, 6 h, 0.5 % seed content, 100 ml of water)

The use of a magnetically or mechanically stirred system did not affect the structure [19, 23].

The content of ZnO (%), and B₂O₃ (%) were determined using analytical methods, and the H₂O (%) amount was the remaining of 100 (%), respectively.

When the reaction was conducted in 100 ml of water and 0.5 % seed content (w/w) was used, ZB was produced using 3.5 moles of water under the optimized reaction conditions.

The formulas of ZB (5 : 1, 6 h, 100 ml of water) were obtained as 4ZnO·3B₂O₃·1.3H₂O when the amount of seed was 0 % (ZnO: 59.14 %, B₂O₃: 36.86 %, H₂O: 4.00 %); 3ZnO·3B₂O₃·3.5H₂O when the amount of seed was 0.5 % (ZnO: 47.32 %, B₂O₃: 40.47 %, H₂O: 12.21 %).

As a result, this particular type of ZB that was produced can be used as a flame retardant in various sectors, extensively. XRD analysis of standard ZB, ZB synthesized (magnetically stirred system) and ZB synthesized (mechanic system) [H₃BO₃/ZnO: 3 : 1, 2 h, 0.5 % seed content, 25 ml of water] were seen Fig. 4.

As expected, the XRD spectra possessed the characteristic peaks of ZB, which are located between 15°–70° 2θ. The XRD spectrum of ZB produced under optimal conditions was similar to that of the standard ZB, confirming a successful synthesis (Fig. 4). Moreover, the volume of water present in the product was higher under saturated conditions. For instance, 3ZnO·3B₂O₃·12H₂O,

$3.1\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ and $2.9\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 6.8\text{H}_2\text{O}$ were obtained in 25 ml of water. The use of different types of stirring in the systems did not affect the chemical formula significantly.

The formulas of ZB [$\text{H}_3\text{BO}_3/\text{ZnO}$: 3 : 1, 2 h, 25 ml of water (saturated solution)] were $3\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 12\text{H}_2\text{O}$ (magnetically stirred system) when the amount of seed was 0 % (ZnO: 36.75 %, B_2O_3 : 31.32 %, H_2O : 31.93 %); $3.1\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ (magnetically stirred system) when the amount of seed was 0.5 % (ZnO: 43.32 %, B_2O_3 : 35.36 %, H_2O : 21.32 %); $2.9\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 6.8\text{H}_2\text{O}$ (mechanic system) when the seed was 0.5 % (ZnO: 41.87 %, B_2O_3 : 36.62 %, H_2O : 21.51 %) and $2\text{ZnO}\cdot 2.8\text{B}_2\text{O}_3\cdot 3.1\text{H}_2\text{O}$ was the standard seed (ZnO: 47.46 %, B_2O_3 : 39.21 %, H_2O : 13.33 %).

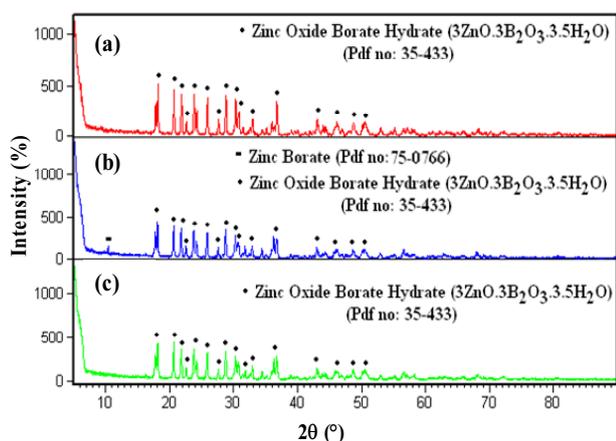


Fig. 4. XRD analysis: a – standard ZB used as seed; b – ZB synthesized (magnetically stirred system); c – ZB synthesized (mechanic system) [$\text{H}_3\text{BO}_3/\text{ZnO}$: 3 : 1, 2 h, 0.5 % seed content, 25 ml of water]

TG measurements were carried out using Perkin-Elmer Pyris Diamond TG/DTA equipment in a temperature range from 20 °C to 850 °C. TG/DTA curve recorded in nitrogen atmosphere at 10 °C/min heating rate was given for optimum reaction conditions in Fig. 5. The $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ has been reported to be thermally stable up to 290 °C by Schubert et al. [3]. On the TG curve, a sharp weight loss (13.89 %) was observed to occur when the temperature was around 243 °C for the standard ZB.

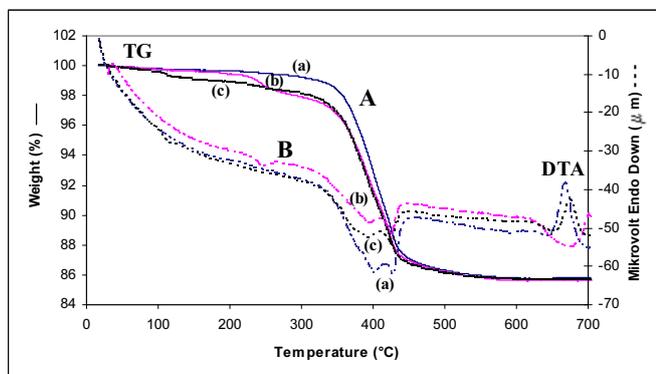


Fig. 5. TG/DTA analysis: A – all TG; B – all DTA: a – standard ZB; b – ZB synthesized (magnetically stirred system); c – ZB synthesized (mechanically stirred system) [$\text{H}_3\text{BO}_3/\text{ZnO}$: 3 : 1, 2 h, 0.5 % of seed, 25 ml of water]

This process corresponded to the loss of water during crystallization through the condensation of B–OH groups. For the magnetically stirred system and the mechanically stirred system, the total weight loss was 13.27 % and 13.18 % between 213.8 °C–500 °C and 114 °C–590 °C respectively as expected from the results of various authors [4, 18, 19, 23].

The results showed that the products, which were synthesized in both the magnetically stirred and the mechanically stirred systems, had high dehydration temperature values as that of the standard ZB (Fig. 5).

4. CONCLUSIONS

In conclusion, the crystal water present in the product was higher under saturated conditions. $3\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3.5\text{H}_2\text{O}$ was produced when the reaction was conducted in 100 ml of water and 0.5 % seed content was used. $3\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 12\text{H}_2\text{O}$, $3.1\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$ and $2.9\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 6.8\text{H}_2\text{O}$ were obtained in 25 ml of water. The use of standard ZB as the seed increased the yield of the reaction by reducing the reaction time to produce ZB which had desired crystal water. At various reaction times, the optimal yield was 86.78 % in a saturated aqueous solution. This high optimal yield was applicable for pilot-scale equipment. The addition of seed to the reaction mixture did not alter the structure of the product as obtained in FT-IR analysis in terms of similar groups. Furthermore, the results of the XRD, FT-IR and TG/DTA analyses indicated that ZB was successfully synthesized under the optimized reaction conditions and the product that was synthesized had high thermal stability, which makes it very suitable to use in coatings, thermoplastics, thermosets and textile industry.

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