

Research Article

Effect of Magnesium Borates on the Fire-Retarding Properties of Zinc Borates

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Magnesium borate (MB) is a technical ceramic exhibiting high heat resistance, corrosion resistance, great mechanical strength, great insulation properties, lightweightness, high strength, and a high coefficient of elasticity. Zinc borate (ZB) can be used as a multifunctional synergistic additive in addition to flame retardant additives in polymers. In this study, the raw materials of zinc oxide (ZnO), magnesium oxide (MgO), and boric acid (H_3BO_3) were used in the mole ratio of 1:1:9, which was obtained from preexperiments. Using the starting materials, hydrothermal synthesis was applied, and characterisation of the products was performed using X-Ray diffraction (XRD) and Fourier transform infrared (FT-IR) and Raman spectroscopies. The forms of $Zn_3B_6O_{12} \cdot 3.5H_2O$, $MgO(B_2O_3)_3 \cdot 7(H_2O)$, and $Mg_2(B_6O_7(OH)_6)_2 \cdot 9(H_2O)$ were synthesised successfully. Moreover, the surface morphology was investigated using scanning electron microscopy (SEM), and the B_2O_3 content was determined. In addition, the reaction yields were calculated. The results of the B_2O_3 content analysis were in compliance with the literature values. Examination of the SEM images indicated that the obtained nanoscale minerals had a reaction efficiency ranging between 63–74% for MB and 87–98% for ZB. Finally, the fire-retarding properties of the synthesised pure MBs, pure ZBs, and mixtures of MB and ZB were determined using differential thermal analysis and thermal gravimetry (DTA-TG) and differential scanning calorimetry (DSC).

1. Introduction

Magnesium borates can be used in the ceramic industry, in detergent formulations, in the production of superconducting materials, and as catalysts for the conversion of hydrocarbons due to the content of boron in the friction-reducing additives in the oils and the insulating coating compositions [1–3].

Single-crystalline magnesium borate $Mg_2B_2O_5$ nanorods have been synthesised via a simple route based on the calcinations of mixed powders containing $Mg(OH)_2$ and H_3BO_3 at $900^\circ C$ in 3 h. The nanorods have typical diameters in the range of 70–120 nm and lengths up to a few micrometres [4]. Single-phase $Mg_3B_2O_6$ and $Mg_2B_2O_5$ ceramics have been synthesised from MgO and B_2O_3 using solid-state reaction techniques. At the end of the experiments, $Mg_2B_2O_5$ forms in the 1250 – $1280^\circ C$ temperature range and $Mg_3B_2O_6$ forms in the 1200 – $1300^\circ C$ temperature range [5]. B and MgO (with

a mole ratio of 1:1) have been thoroughly mixed to prepare $Mg_3B_2O_6$ nanobelts. Under flowing mixed Ar/ H_2O gases, the mixture of B and MgO was heated to $1100^\circ C$, held at this temperature for 90 min, and then subsequently cooled to room temperature [6]. Using $MgCl_2 \cdot 6H_2O$ and $NaBH_4$ powders as the starting materials for the production of monoclinic $Mg_2B_2O_5$, the mixture was first milled for 120 h and then sintered at $800^\circ C$ for 2 h. It was observed that mechanical processes were needed to form Mg-B-H [7].

A new magnesium borate, β - $2MgO \cdot 3B_2O_3 \cdot 17H_2O$, has been synthesised using the method of phase transformation of a double salt and characterised using XRD, IR, and Raman spectroscopy as well as TG. The results indicated that β - $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ is less stable than β - $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ [8]. Another magnesium borate, $MgO \cdot 3B_2O_3 \cdot 3.5H_2O$, has been synthesised using the method of phase transformation of a double salt. The structural formula of this compound was $Mg[B_6O_9(OH)_2] \cdot 2.5H_2O$. No

impurity lines were observed, and the synthetic sample was suitable for the calorimetric experiments [9]. Magnesium borates can be used in various applications with different compounds [10, 11]. A study reports a facile route using the precipitation reaction and sequential calcination to synthesise three-dimensional (3D) flower-like magnesium borate ($\text{Mg}_3\text{B}_2\text{O}_6$) nanoarchitectures with poly(vinyl pyrrolidone) (PVP) as the template. The uniform flower-like magnesium borate sphere structures assembled by nanosheets have been successfully synthesised via a facile precipitation reaction assisted by PVP and sequential calcination [12].

A hydrocalcite-like compound prepared through chemical deposition using calcined dolomite as the magnesium source (D-LDH) was applied to remove borate. LDH for environmental applications was prepared using calcined dolomite as the raw magnesium source. The sorption results suggest that D-LDH can be used to remove borate from aqueous solution at ambient temperature and pressure. The analyses results of the solid residues indicate that borate was removed by D-LDH-700 in two ways: the coprecipitation of borate with $\text{Mg}(\text{OH})_2$ to form a complex and the intercalation of borate anions during the formation of LDHs [13].

Zinc borate is an important inorganic hydrated borate that finds applications ranging from polymers to paints for various purposes, such as a flame retardant or corrosion inhibitor, depending on the type of zinc borate [14]. Zinc borate is a multifunctional fire retardant containing different proportions of zinc and boric oxides [15]. Zinc borate is widely used in plastic, rubber, ceramics, paint, wire, electrical insulation, wood, cement, and pharmaceutical industries due to its properties [16, 17]. The production of $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ from zinc oxide and boric acid via a rheological phase reaction was studied by Shi et al. [18]. Zinc borate is produced via the reaction between aqueous boric acid and zinc oxide. This compound has the unusual property of retaining its water of hydration at temperatures up to 290°C . This thermal stability makes zinc borate attractive as a fire-retardant additive for plastics and rubbers that require high processing temperatures [19]. Shi et al. [20] investigated $4\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot \text{H}_2\text{O}$ nanorods synthesised via a hydrothermal route with the surfactant PEG-300 as the template. The pH value and synthetic temperature greatly affected the composite, while the temperature and time affected the morphology of the products. A study on the flame-retardant property of $4\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot \text{H}_2\text{O}$ nanorods is currently underway. Igarashi et al. [21] synthesised zinc borates using a two-step reaction. In the first step, zinc oxide and boric acid were combined and stirred at 60°C for 1.5 h to achieve crystal formation. In the second step, the mixture was stirred continuously at 90°C for 4 h, and seed crystals were added to the reaction mixture to enhance crystal growth. The characterisation of the products was performed using XRD, TG, DTA, and SEM. In addition, the effects of the experimental conditions and particle size distribution on the characteristics of the products were investigated. This synthetic method is green, and without pollution, it provides a yield of approximately 100%.

A previous study has demonstrated that the pure fire retardants undergo structural changes with temperature.

The interactions between magnesium oxide and the two forms of zinc borate were observed to differ. Zinc borate ($2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$) was observed to react with MgO to form of a different crystalline phase, magnesium orthoborate, with crystalline ZnO as a by-product of the reaction. The observed change in morphology also supported the structural observations. The other form of zinc borate ($4\text{ZnO}\cdot \text{B}_2\text{O}_3\cdot \text{H}_2\text{O}$) did not appear to react with MgO and formed ZnO , with possible dehydrated zinc borate still present. MgO was detected in the mixture when heated to 700°C [22]. Novel one-pot homologation reactions of isoquinoline with lithium dialkyl-TMP-zincate- 2MgBrCl /trimethyl borate are described in a previous study [23]. The one-pot homologation reactions of isoquinoline were efficiently achieved in the presence of the trimethyl borate/ MgBrCl complex via directed orthometalation and a 1,2-migratory addition reaction.

The main purpose of this study is to synthesise two different borate compounds of magnesium borates and zinc borates in the same hydrothermal reactor with high efficiency using the same reaction time and reaction temperature. The magnesium borate compounds have been studied in the literature; however, the reaction times (>48 h) and reaction temperatures ($>100^\circ\text{C}$) used were not simple.

Similar to magnesium borates, zinc borates have also been studied in the literature, and the formation temperature and time are given as 90°C and 4 h, respectively. For the green chemistry approach, lower reaction times and reaction temperatures were used for the synthesis of magnesium borates and zinc borates. The molar ratio of the ZnO , MgO , and H_3BO_3 components was determined by Tugrul et al. [24]. Tugrul et al. [24] studied only the formation of zinc and magnesium borates at 100°C using the aforementioned molar ratio.

Zinc borates are also known for their flame-retarding properties. Starting with this property, the effect of magnesium borates on the flame-retarding properties of zinc borates is studied, which has never been studied in the literature. The results of the magnesium borate addition to the fire-retarding properties of zinc borate will contribute to the literature.

After the hydrothermal production, the synthesised products were characterised using a Philips PANalytical Xpert-Pro XRD, a Perkin Elmer Spectrum One FT-IR, a Perkin Elmer Raman Station 400F Raman Spectrometer, and a CamScan Apollo 300 SEM. Additionally, the B_2O_3 contents of the synthesised compounds were determined using titration, and their reaction yields were calculated. Finally, fire-retarding experiments were conducted using a Perkin Elmer Diamond DTA-TG and DSC.

2. Materials and Methods

2.1. Materials Preparation. The materials used in the syntheses were zinc oxide (ZnO), magnesium oxide (MgO), boric acid (H_3BO_3), and commercial zinc borate. ZnO , MgO , and H_3BO_3 were supplied from Colakoglu Chemistry Limited Company, Merck Chemicals, and EtiMine Works in the Kirka region of Eskisehir/Turkey. H_3BO_3 was crushed, ground with agate mortar, and sieved using 200 meshes, whereas ZnO ,

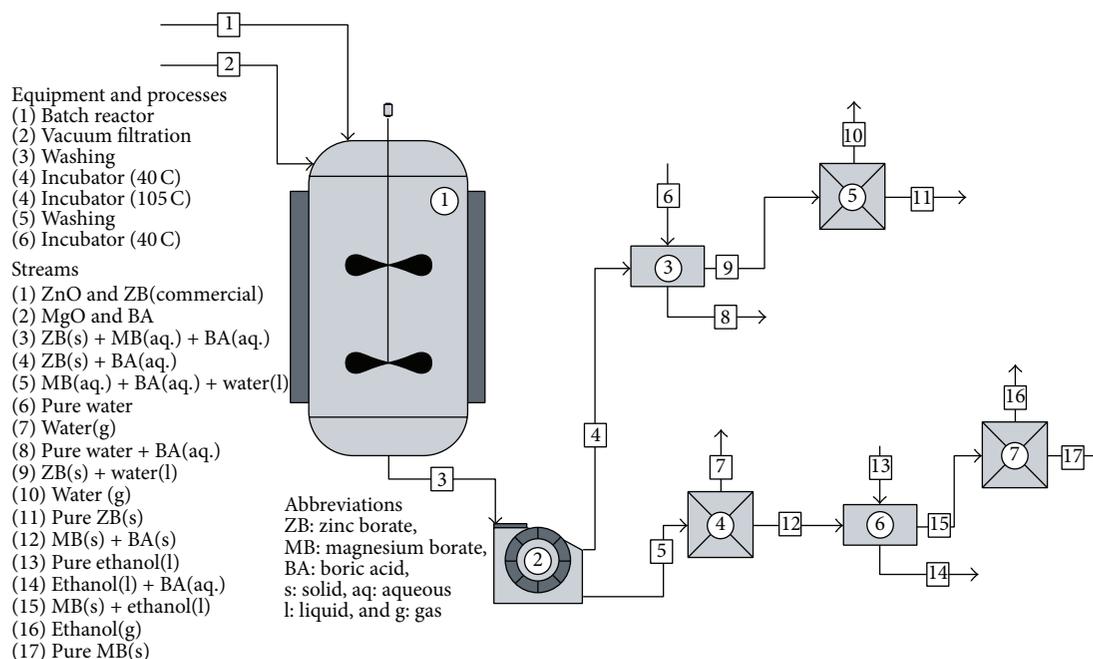


FIGURE 1: Reaction scheme of magnesium and zinc borates.

MgO, and commercial zinc borate were used as supplied. All the raw material identification was performed using a Philips PANalytical XRD. In the XRD analysis, a Cu-K α tube at 45 kV and 40 mA was used with a 0.030° step, 0.50-s step time, 0.060°C/s scan speed, and 0–90° range. The ICSD patterns were scanned using the inorganic library provided in the instrument's programme.

2.2. Hydrothermal Syntheses. For the synthesis, the mole ratio of ZnO, MgO, and H₃BO₃ was determined experimentally and observed to be 1:1:9 after preliminary experiments [24]. The liquid phase in the experiments was demineralised water (18.3 m Ω ·cm) obtained from a Human Power I+ Water Purification System. The reaction temperature range was selected to be between 60 and 100°C, and four different reaction times were used to investigate the phase transition between different types of zinc borates and magnesium borates based on the reaction time changes. The reaction intervals were set to 30, 60, 90, and 120 min. In the synthesis procedure, first, H₃BO₃ was dissolved in water at the desired temperature; then, ZnO and zinc borate (in terms of H₃BO₃, 0.5% w/w) were added, and after the determined interval, MgO was added to the mixture. Therefore, the reaction times were 60, 120, 180, and 240 min for the zinc borates and 30, 60, 90, and 120 min for the magnesium borates. The detailed reaction scheme is presented in Figure 1.

2.3. Characterisation of the Products. The products were processed through XRD, FT-IR, and Raman spectral analyses, SEM morphologies, B₂O₃ determinations, and reaction yields in the given order. The XRD analyses were performed using the parameters indicated in Section 2.1; the ranges used for the zinc borates and magnesium borates were

between 0–70° and 0–60°, respectively. The spectrum range was selected as 1600–650 cm⁻¹ in the FT-IR analyses and as 1400–250 cm⁻¹ in the Raman spectral analyses. Any peaks above these ranges were not observed in either of the spectral analyses, and the characteristic peaks of the borate compounds were reported to be observed in the range of 500–1500 cm⁻¹ [25].

In the FT-IR analyses, a Perkin Elmer Spectrum One Fourier Transform Infrared Spectrometer with a universal ATR sampling accessory-Diamond/Zn was used; the scan number was set to 4, and the resolution was set to 4 cm⁻¹. Raman analyses were performed using a Perkin Elmer Raman Station 400F Raman spectrometer, with the exposure time (seconds) and number of exposures set to 4. The data interval was set as 2 cm⁻¹; full (100%) laser power and the “auto baseline” option were also used.

The surface morphologies of the synthesised magnesium borate minerals and their particle size analyses were performed using a CamScan Apollo 300 Field-Emission SEM at 20 kV. A back-scattering electron (BEI) detector was used, and the scale of magnification was in the range of 5000–20000x.

The boron oxide content of the boron minerals needed to be determined to evaluate the commercial value of the boron minerals. This analysis was performed using the method reported by Derun et al. [26] and Kipcak et al. [27].

Yield analysis was also performed using the method reported by Derun et al. [26] and Kipcak et al. [27]. ZnO and MgO were identified as the key components; the experimental runs were performed in triplicate, and the minimum yields were calculated. The number of moles of product at the final stage, N_D , was divided by the number of consumed moles of the key reactant A to calculate the overall yield, Y_D (1).

TABLE 1: XRD results and crystallographic data of the raw materials.

Raw material	ZnO	MgO	H ₃ BO ₃	Zinc borate (commercial)
Pdf number	01-079-2205	01-077-2179	01-073-2158	00-035-0433
Name	Zinc oxide	Periclase	Sassolite	Zinc oxide borate hydrate
Formula	ZnO	MgO	H ₃ BO ₃	Zn ₃ B ₆ O ₁₂ ·3.5(H ₂ O)
Score	91	78	62	79
Crystal system	Hexagonal	Cubic	Anorthic	Monoclinic
<i>a</i> (Å)	3.2501	4.2114	7.039	7.6950
<i>b</i> (Å)	3.2501	4.2114	7.053	9.8028
<i>c</i> (Å)	5.2071	4.2114	6.578	6.8378
α (°)	90.00	90.00	92.58	90.00
β (°)	90.00	90.00	101.17	107.03
γ (°)	120.00	90.00	119.83	90.00
<i>z</i>	2.00	4.00	4.00	2.00

The number of moles of *A* that was consumed was calculated using the initial (N_{A0}) and final (N_A) moles of the reactant. For a batch system, the equation then becomes [26–28]

$$Y_D = \frac{N_D}{N_{A0} - N_A}. \quad (1)$$

2.4. Thermal Analyses. In the DTA-TG experiments, the aim was to determine the energy and weight differences caused by the temperature change present in the produced zinc and magnesium borates. The instrument used was a Perkin Elmer Diamond DTA-TG. The analyses were conducted under oxygen atmosphere, the temperature change was set to 10°C per min, and the temperature range was between 30–700°C for TG and 30–600°C for DSC (Differential Scanning Calorimeter). Pure zinc borate obtained at 100°C and 120 min of reaction time and magnesium borate obtained at 100°C and 60 min of reaction time were selected for the thermal analyses. The following ratios of zinc and magnesium borate were evaluated: 1-0, 2-1, 1-1, 1-2, and 0-1.

3. Results and Discussion

3.1. Raw Materials XRD Results. The XRD results for the raw materials used in the experiments are shown in Table 1. According to the XRD results, ZnO, MgO, H₃BO₃, and zinc borate (commercial) were characterised as “01-079-2205” coded zinc oxide, “01-077-2179” coded periclase, “01-073-2158” coded sassolite, and “00-035-0433” coded zinc oxide borate hydrate, respectively.

3.2. Syntheses XRD Results. The XRD results for the synthesised magnesium and zinc borates are presented in Tables 2 and 3, respectively. In addition, the crystallographic data for the synthesised magnesium and zinc borates are provided in Table 4.

According to the results in Table 2, the major phase obtained is “01-070-1902” coded Mcallisterite (Mg₂(B₆O₇·(OH)₆)₂·9(H₂O)). Another type of magnesium borate, which is “01-076-0540” coded admontite (MgO(B₂O₃)₃·7(H₂O)), is also observed. In addition, at the reaction temperature of

70°C and 30 min of reaction time, “01-075-0539” coded magnesium borate hydrate, (MgO(B₂O₃)₃·6(H₂O)), is observed. At all the reaction temperatures and reaction times, Mcallisterite is observed to be the major phase, whereas admontite is major only at 70°C and 90 min. These results are also consistent with the results reported in Derun et al. [26] and Lehmann and Rietz [29], where the authors synthesised different types of magnesium borates (MgB₆O₁₀·*x*H₂O (*x* = 5, 6, 7, and 7.5)).

In the XRD results of the zinc borates, six different types of zinc borates were obtained. Among these phases, the expected type of zinc borate, which is zinc oxide borate hydrate with a XRD code of “00-035-0433”, is observed at 80°C and 90°C, for the 180 and 240 min reaction times, and at 100°C for the 120, 180, and 240 min reaction times. For these parameters, the obtained zinc borate (Zn₃B₆O₁₂·3.5(H₂O)) is consistent with that obtained in the study of Ren et al. [30].

To better understand the relationship between the reaction temperature, reaction time, and the XRD scores, Figure 2 was prepared using Statsoft Statistica.

Among these syntheses, according to the XRD scores, 90°C and 100°C are the optimum temperatures for magnesium borate, and 100°C is the optimal temperature for the zinc borates. Because 100°C is common for both syntheses, 100°C is optimum for the combined synthesis. Because at 100°C, the expected type of zinc borate, zinc oxide borate hydrate, is obtained at 120 min of reaction time, 120 min is optimum for zinc borate; thus, 60 min is also optimum for magnesium borates. These determined optimum phase XRD patterns are presented in Figure 3.

3.3. FT-IR and Raman Results of Products. The FT-IR and Raman spectra for the optimum phases are presented in Figures 4 and 5, respectively.

According to the FT-IR spectra, the asymmetric stretching of three-coordinate boron [$\nu_{as}(B_{(3)}-O)$] was observed in the range of 1411–1251 cm⁻¹. The peaks between 1236 and 1112 cm⁻¹ correspond to the bending of B-O-H [$\delta(B-O-H)$]. Asymmetric stretching of the four-coordinate boron [$\nu_{as}(B_{(4)}-O)$] was observed between 1059 and 964 cm⁻¹.

TABLE 2: XRD results of the synthesised magnesium borate minerals.

Reaction temperature (°C)	Reaction time (minutes)	XRD scores of		
		01-076-540	01-070-1902	01-075-0539
60	30	67	71	—
	60	71	29	—
	90	43	68	—
	120	32	70	—
70	30	58	75	18
	60	—	88	—
	90	74	—	—
	120	—	87	—
80	30	17	84	—
	60	47	83	—
	90	8	74	—
	120	54	76	—
90	30	—	90	—
	60	25	87	—
	90	32	86	—
	120	31	89	—
100	30	9	84	—
	60	15	89	—
	90	49	85	—
	120	64	83	—

Pdf number = 01-076-0540, Admontite, $\text{MgO}(\text{B}_2\text{O}_3)_3 \cdot 7(\text{H}_2\text{O})$

Pdf number = 01-070-1902, Mcallisterite, $\text{Mg}_2(\text{B}_6\text{O}_7(\text{OH})_6)_2 \cdot 9(\text{H}_2\text{O})$

Pdf number = 01-075-0539, magnesium borate hydrate, $\text{MgO}(\text{B}_2\text{O}_3)_3 \cdot 6(\text{H}_2\text{O})$.

Symmetric stretching of the three-coordinate boron [$\nu_s(\text{B}_{(3)}\text{-O})$] was observed at the zinc borate peak of 920 cm^{-1} . Symmetric stretching of the four-coordinate boron [$\nu_s(\text{B}_{(4)}\text{-O})$] was observed between 857 and 791 cm^{-1} . The zinc borate peak at 749 cm^{-1} corresponds to $\nu_p(\text{B}(\text{OH})_4)^-$, and the magnesium borate peak at 670 cm^{-1} corresponds to bending of three-coordinate boron [$\delta(\text{B}_{(3)}\text{-O})$]. The FT-IR results are consistent with previous studies [15, 26, 27].

In the Raman spectra, the ZB peaks observed between 1295 and 1187 cm^{-1} correspond to $\nu_{as}(\text{B}_{(3)}\text{-O})$. $\nu_{as}(\text{B}_{(4)}\text{-O})$ was observed at the zinc borate peaks of 1087 cm^{-1} and 1047 cm^{-1} . $\nu_s(\text{B}_{(3)}\text{-O})$ was obtained at the magnesium borate peaks between 951 and 880 cm^{-1} . $\nu_s(\text{B}_{(4)}\text{-O})$ was observed at the zinc borate peak of 847 cm^{-1} . $\nu_p(\text{B}(\text{OH})_4)^-$ was observed between the peaks of 755 and 641 cm^{-1} . The $528\text{--}499\text{ cm}^{-1}$ peaks correspond to $\delta(\text{B}_{(3)}\text{-O})/\delta(\text{B}_{(4)}\text{-O})$ and $\nu_p(\text{B}_5\text{O}_6(\text{OH})_4)^-$. The other peaks at $437\text{--}295\text{ cm}^{-1}$ were $\delta(\text{B}_{(4)}\text{-O})$. These Raman bands are consistent with previous studies [26, 27].

3.4. SEM Morphologies of Products. SEM images of the products are presented in Figure 6. According to the obtained magnesium borate images, the magnesium borates are crystallised into planar rectangular shapes. Due to the agglomeration, the crystal sizes were observed as micrometres at 5000x magnification; however, at x magnification, the

agglomeration is brighter, and the crystals sizes are between $1.04\text{ }\mu\text{m}$ and 253.30 nm . The zinc borates are crystallised into thorn-like shapes, and particle sizes were between 549.38 nm and 243.39 nm , as observed in a previous study [18].

3.5. Contents and Reaction Yields of B_2O_3 Products. The B_2O_3 contents of the synthesised magnesium and zinc borates are shown in Table 5. Because the theoretical B_2O_3 content of magnesium [26, 27, 31] and zinc borates [32] is between 50 and 55%, the obtained data are consistent with the literature values. The B_2O_3 contents are between 54.34–40.46% and 54.79–39.42% in the magnesium and zinc borates, respectively.

The reaction yields are shown in Table 6. According to the data, the reaction yields increased with increasing reaction temperature and time. The maximum reaction yields are 74.4% and 98.6% for the magnesium and zinc borates, respectively.

3.6. Thermal Analysis Results. From TG/DTG and DSC analyses, several results were obtained and are presented in Figures 7, 8, and 9 and Table 7. The moisture contents are calculated in the region of $30\text{--}105^\circ\text{C}$.

3.6.1. Zinc Borate. Two endothermic peaks are observed at 394.74°C and 420.10°C in zinc borate. The initial and final temperatures of the first peak are 105°C and 413.56°C ,

TABLE 3: XRD results of the synthesised zinc borates.

Reaction temperature (°C)	Reaction time (minutes)	XRD scores of					
		00-035-0433	00-011-0279	00-032-1461	01-075-0766	00-021-1474	00-032-1462
60	60	—	—	35	21	13	—
	120	12	—	38	19	—	7
	180	—	10	45	29	—	20
	240	13	9	37	27	—	9
70	60	17	18	45	37	—	—
	120	22	23	51	38	10	—
	180	33	20	48	39	—	11
	240	22	12	46	32	—	—
80	60	18	—	47	32	7	—
	120	20	11	43	25	—	—
	180	70	—	—	—	—	—
	240	66	—	—	—	—	—
90	60	17	45	—	28	33	—
	120	20	—	39	20	—	—
	180	68	—	—	—	—	—
	240	71	—	—	—	—	—
100	60	22	17	41	32	9	—
	120	75	—	—	—	—	—
	180	78	—	—	—	—	—
	240	76	—	—	—	—	—

Pdf number = 00-035-0433, zinc oxide borate hydrate, $Zn_3B_6O_{12} \cdot 3.5(H_2O)$

Pdf number = 00-011-0279, zinc borate hydrate, $Zn_2B_6O_{11} \cdot 7(H_2O)$

Pdf number = 00-032-1461, zinc borate hydrate, $Zn_3B_{10}O_{18} \cdot 14(H_2O)$

Pdf number = 01-075-0766, zinc borate hydroxide hydrate, $Zn(B_3O_3(OH)_5) \cdot H_2O$

Pdf number = 00-021-1474, zinc borate hydrate, $Zn_6B_{10}O_{11} \cdot 3(H_2O)$

Pdf number = 00-032-1462, zinc borate hydrate, $ZnB_{10}O_{16} \cdot 4.5(H_2O)$.

TABLE 4: Crystallographic data of the synthesised magnesium and zinc borates.

Mineral name	Admontite	Mcallisterite	Zinc oxide borate hydrate
Pdf number	01-076-0540	01-070-1902	00-035-0433
Chemical formula	$MgO(B_2O_3)_3 \cdot 7(H_2O)$	$Mg_2(B_6O_7(OH)_6)_2 \cdot 9(H_2O)$	$Zn_3B_6O_{12} \cdot 3.5(H_2O)$
Molecular weight (g/mole)	375.27	768.56	596.04
Crystal system	Monoclinic	Rhombohedral	Monoclinic
Space group	P21/c (No. 14)	Pr3c (No. 167)	P21/n (No. 14)
a (Å)	12.6610	11.5490	7.6950
b (Å)	10.0910	11.5490	9.8028
c (Å)	11.3220	35.5670	6.8378
α (°)	90.00	90.00	90.00
β (°)	109.60	90.00	107.03
γ (°)	90.00	120.00	90.00
z	4.00	6.00	2.00
Density (calculated) ($g \cdot cm^{-3}$)	1.83	1.86	2.93
Characteristic peaks I (%) / 2θ (°)	100.0/7.404	100.0/10.139	100.0/23.743
	56.9/16.848	35.7/15.332	96.0/21.770
	38.6/12.064	32.9/31.875	96.0/25.847

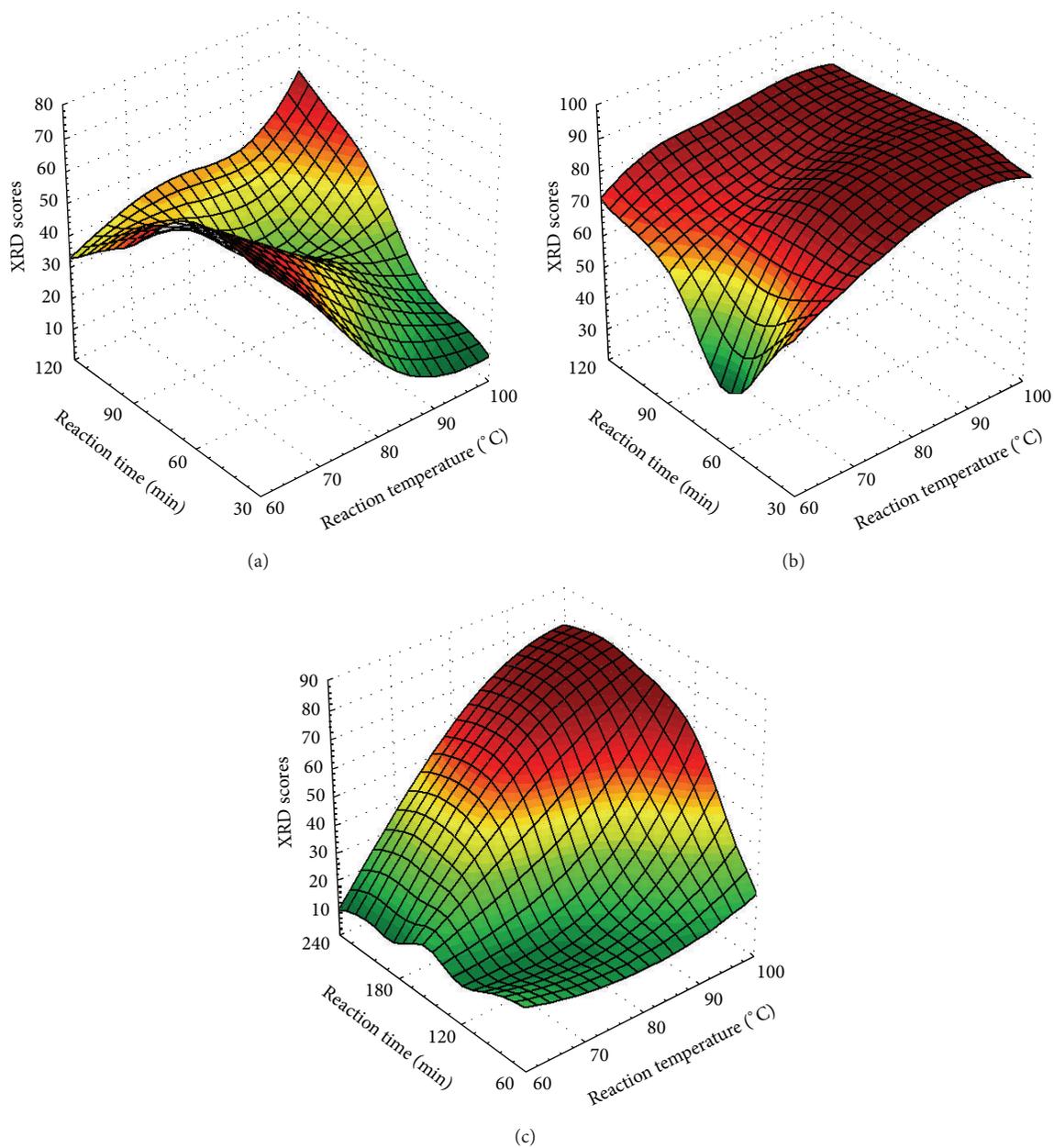


FIGURE 2: Formation of (a) admontite, (b) Mcallisterite, and (c) zinc oxide borate hydrate using the XRD scores.

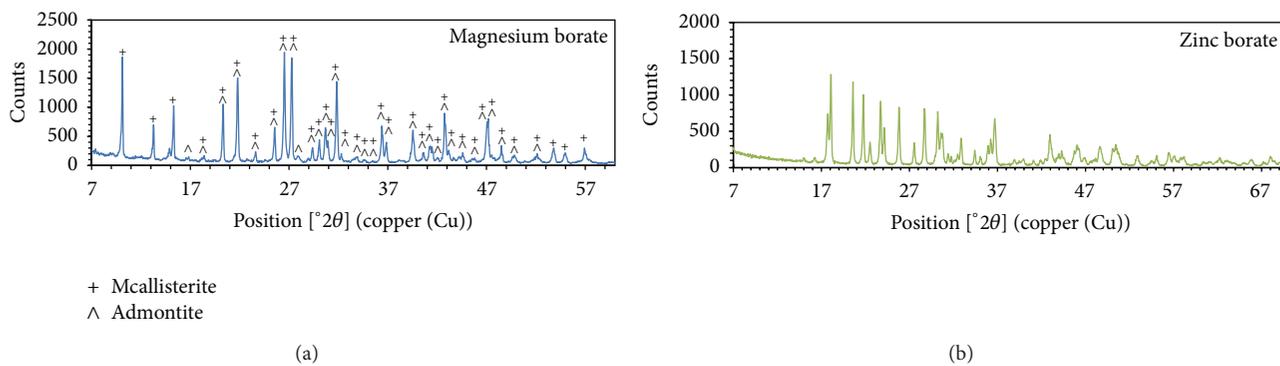


FIGURE 3: XRD patterns of the optimum phases of the magnesium and zinc borates.

TABLE 5: B₂O₃ contents (%) of the synthesised magnesium borate minerals and zinc borate compounds.

Reaction temperature (°C)	Reaction time (minutes) for		B ₂ O ₃ contents (%) of	
	Magnesium borate	Zinc borate	Magnesium borate	Zinc borate
60	30	60	45.34 ± 0.26	43.64 ± 1.93
	60	120	54.34 ± 1.61	40.29 ± 1.79
	90	180	51.39 ± 1.61	48.77 ± 0.51
	120	240	50.34 ± 1.78	44.08 ± 1.53
70	30	60	40.46 ± 1.02	39.42 ± 1.38
	60	120	42.99 ± 0.53	39.51 ± 0.77
	90	180	47.33 ± 1.53	46.80 ± 0.81
	120	240	45.82 ± 1.78	41.80 ± 1.66
80	30	60	48.34 ± 0.41	41.60 ± 0.73
	60	120	42.09 ± 0.77	47.15 ± 0.97
	90	180	40.73 ± 1.92	40.26 ± 0.36
	120	240	41.48 ± 1.63	40.33 ± 1.88
90	30	60	41.91 ± 1.99	46.88 ± 1.92
	60	120	42.41 ± 1.43	45.85 ± 1.25
	90	180	48.74 ± 1.69	50.18 ± 0.16
	120	240	46.06 ± 0.66	52.55 ± 1.98
100	30	60	46.41 ± 0.36	44.26 ± 1.01
	60	120	48.97 ± 0.34	47.41 ± 0.93
	90	180	48.12 ± 0.76	52.87 ± 1.78
	120	240	48.51 ± 0.81	54.79 ± 0.36

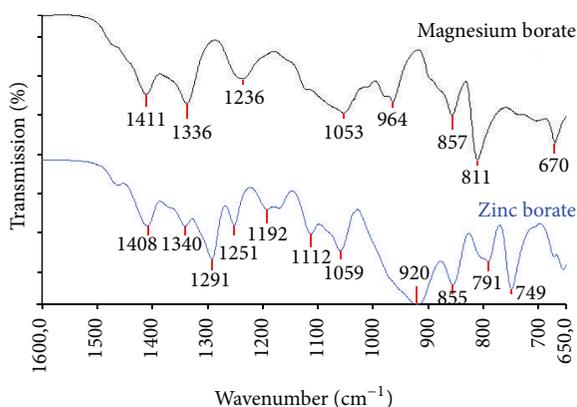


FIGURE 4: FT-IR patterns of the optimum phases of the magnesium and zinc borates.

respectively. In this region, the weight difference of the zinc borates is 9.713%, which is equal to 2.5 moles of crystal water. The initial and final temperatures of the second peak are 413.56°C and 683.52°C, respectively. In this region, the weight difference of the zinc borates is 3.913%, which is equal to 1.0 mol of crystal water. The results indicate that the product is more resistant in terms of thermal decomposition when the results are compared with previous studies [18]. As in the DSC results, the first endothermic region started at 308.68°C and ended at 412.64°C, and the enthalpy in this region was observed to be 73.30 J/g. In the second region, the enthalpy between 412.64°C and 446.31°C was 7.87 J/g. The total zinc borate enthalpy was 81.17 J/g.

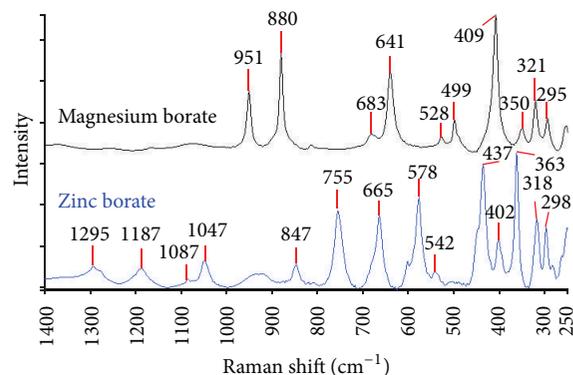


FIGURE 5: Raman patterns of the optimum phases of the magnesium and zinc borates.

3.6.2. Magnesium Borate. In magnesium borate, one endothermic peak was observed at 183.60°C. The initial weight loss began at 105°C and finished at 684.54°C. In this region, the Mcallisterite type of magnesium borate lost all of its crystal water, 35.854% (9H₂O and 6H₂O originating from 12 moles of OH⁻). The magnesium borate endothermic region was observed between 124.17°C and 356.42°C, where the enthalpy change was 830.55 J/g.

3.6.3. Zinc Borate and Magnesium Borate Mixtures. In the mixtures, one endothermic peak is observed for magnesium borate, and two endothermic peaks are observed for the zinc borates.

TABLE 6: Minimum obtained reaction yields (%) of the synthesised magnesium borate and zinc borate minerals.

Reaction temperature (°C)	Reaction time (minutes) for		Minimum reaction yields (%) of	
	Magnesium borate	Zinc borate	Magnesium borate	Zinc borate
80	90	180	63.5	87.1
	120	240	65.3	88.4
90	90	180	68.1	91.8
	120	240	70.8	93.1
100	60	120	69.9	95.7
	90	180	72.3	98.1
	120	240	74.4	98.6

TABLE 7: TG/DTG and DSC results of the synthesised magnesium borate minerals and zinc borate.

	PC Peaks	Z		ZM 2-1			ZM 1-1			ZM 1-2			M
		1	2	1	2	3	1	2	3	1	2	3	1
TG/DTG	Mo. (%)	1.023		0.972			1.094			1.113			1.074
	T_i (°C)	105.00	413.56	105.00	323.57	410.71	105.00	319.26	412.15	105.00	321.65	410.48	105.00
	T_p (°C)	394.74	420.10	177.52	393.28	419.00	177.40	393.57	420.59	181.44	393.06	420.93	183.60
	T_f (°C)	413.56	683.52	323.57	410.71	682.06	319.26	412.15	682.36	321.65	410.48	683.93	684.54
	Δm (%)	9.713	3.913	15.395	4.846	2.511	19.334	4.405	2.254	22.658	3.316	2.215	35.854
	$\sum \Delta m$ (%)	13.626		22.752			25.993			28.189			35.854
DSC	T_i (°C)	308.68	412.64	110.18	335.70	410.88	121.04	352.21	409.82	120.02	351.16	408.18	124.17
	T_p (°C)	391.03	423.55	179.34	390.74	423.07	179.99	390.69	422.41	183.16	389.13	421.71	185.28
	T_f (°C)	412.64	446.31	293.27	410.88	439.98	318.98	409.82	440.11	316.83	408.18	435.77	356.42
	ΔH (J/g)	73.30	7.87	418.66	54.08	8.29	490.06	44.84	6.18	584.80	28.15	4.55	830.55
	$\sum \Delta H$ (J/g)	81.17		481.03			541.08			617.50			830.55

PC: product code, Mo.: moisture, i: initial, p: peak, f: final, Z: zinc borate, and M: magnesium borate.

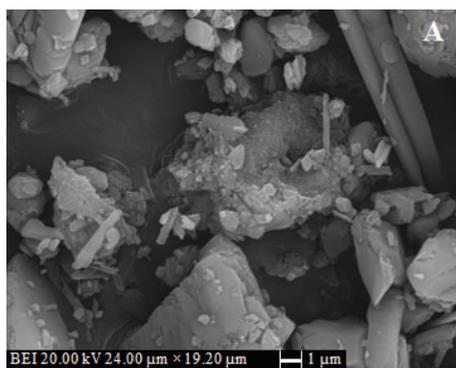
TABLE 8: The weight losses, both percentages and moles, of the pure zinc and magnesium borates at the endothermic peaks.

	MB, Δm (%)	MB, Δn (moles)	ZB, Δm (%)	ZB, Δn (moles)
ZM 2-1 region (°C)				
105.00–323.57	31.738	13.279	1.768	0.454
323.57–410.71	1.763	0.738	7.614	1.956
410.71–682.06	2.349	0.983	4.243	1.090
\sum	35.850	15.000	13.625	3.500
ZM 1-1 region (°C)				
105.00–319.26	31.619	13.229	1.714	0.440
319.26–412.15	1.901	0.795	7.834	2.012
412.15–682.36	2.331	0.975	4.077	1.047
\sum	35.851	15.000	13.625	3.500
ZM 1-2 region (°C)				
105.00–321.65	31.685	13.256	1.736	0.446
321.65–410.48	1.812	0.758	7.613	1.956
410.48–683.93	2.356	0.986	4.273	1.098
\sum	35.853	15.000	13.622	3.500

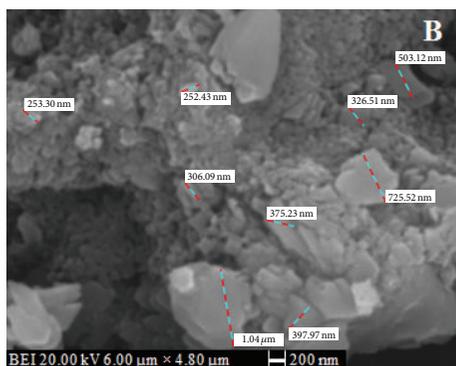
MB: pure magnesium borate, ZB: pure zinc borate.

At the mole ratio of zinc to magnesium borates of 2 : 1, the endothermic peak values are 177.52°C, 393.28°C, and 419.00°C. The initial and final temperatures of the first peak are 105°C and 323.57°C, respectively. In this region, the mixture lost 15.395% of its weight. In the same region, the pure zinc and magnesium borates lost 1.768% (0.454 mol H₂O)

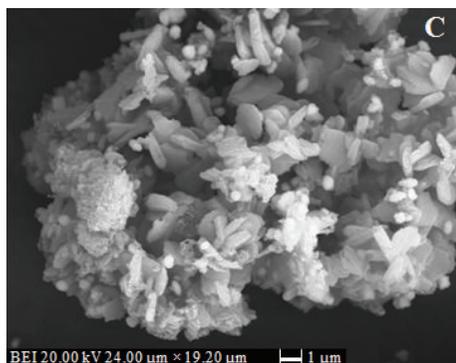
and 31.738% (13.279 moles H₂O) of their weights, respectively. In the second region, the initial and final temperatures were 323.57°C and 410.71°C, respectively. In this region, the mixture lost 4.846% of its weight. In the same region, the pure zinc and magnesium borates lost 7.614% (1.956 moles H₂O) and 1.763% (0.738 mol H₂O) of their weights, respectively.



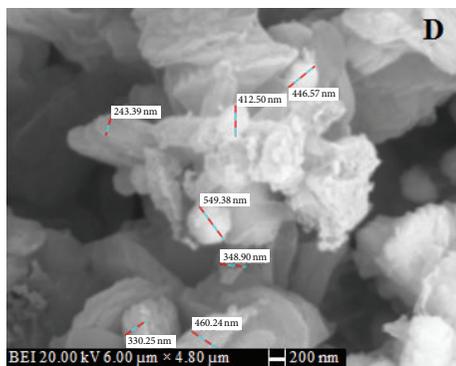
(a)



(b)



(c)



(d)

FIGURE 6: SEM images of the optimum phases of (a) magnesium borates (5000x magnification), (b) magnesium borates (20000x magnification), (c) zinc borate (5000x magnification), and (d) zinc borate (20000x magnification).

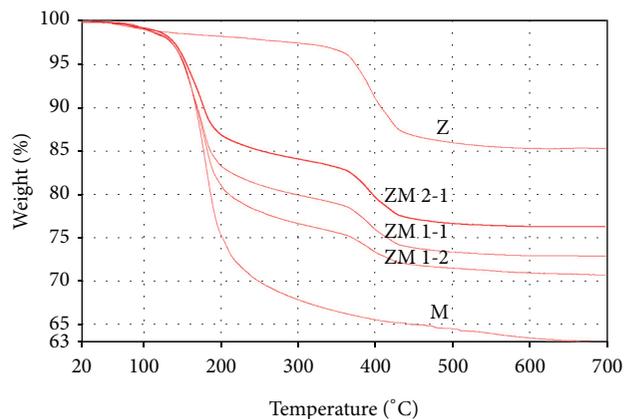


FIGURE 7: TG of the synthesised optimum phases of the magnesium and zinc borates and mixtures of the magnesium and zinc borates.

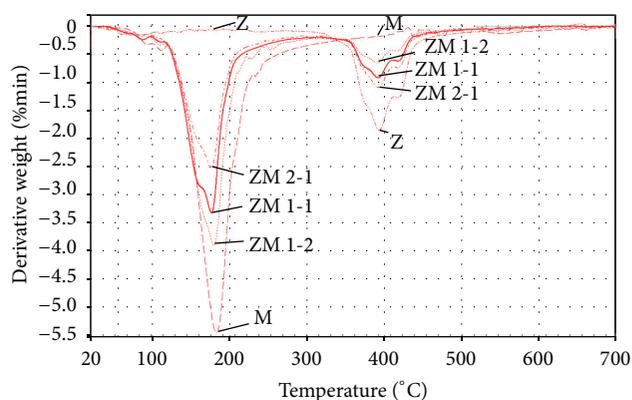


FIGURE 8: DTG of the synthesised optimum phases of the magnesium and zinc borates and mixtures of the magnesium and zinc borates.

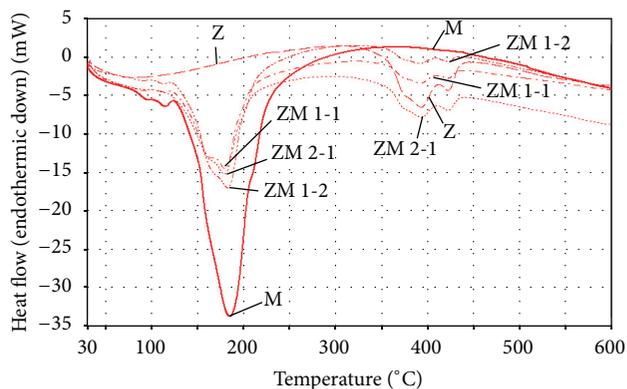


FIGURE 9: DSC of the synthesised optimum phases of the magnesium and zinc borates and mixtures of the magnesium and zinc borates.

In the last region, the initial and final temperatures were 410.71°C and 682.06°C, respectively. The mixture lost 2.511% of its weight. The pure zinc and magnesium borates lost 4.243% (1.090 moles H₂O) and 2.349% (0.983 mol H₂O) of their weights, respectively, in the last region. The mixtures of

both 1-1 and 1-2 were calculated, and the values are given in Table 8.

In the DSC results of the mixture of 2-1, three endothermic peak enthalpies are observed, 418.66 J/g, 54.08 J/g, and 8.29 J/g, with a total enthalpy of 481.03 J/g. The values for the other mixtures are calculated and given in Table 7.

4. Conclusions

In conclusion, 100°C was observed to be optimum for the synthesis. In addition, 120 min is optimum for zinc borate; thus, 60 min is also optimum for magnesium borates. The particle size of the magnesium borates was observed to be between 1.04 μm and 253.30 nm, and the particle size of the zinc borates was observed to be between 549.38 nm and 243.39 nm. The B₂O₃ content of the products was between 54.34–40.46% and 54.79–39.42% for the magnesium and zinc borates, respectively, and the maximum reaction yields were 74.4% and 98.6%, respectively. Furthermore, the XRD, FT-IR, and TG/DTA analyses indicated that combined hydrothermal synthesis was successfully achieved under the optimised reaction conditions, and the product that was synthesised exhibited high thermal stability, which makes it very suitable to use for various applications. Because MB contains 15 moles of structural water inside the mineral, it is very suitable as a fire-resistant material. In addition, when losing its structural water, it takes 830.55 J/g from the environment, while ZB only takes 81.17 J/g when losing its 3.5 moles of water. However, as observed in the DSC results, MB starts to lose its water at 124.17°C, while ZB starts to lose its water at 308.68°C. Therefore, the mixture of ZB and MB will be more suitable as a fire-resistant material. Compared with mixtures of ZB and MB, ZM 1-1 is the best among the other combinations because this mixture starts to lose its structural water at 121.04–352.21–409.82°C in the three regions, while the mixtures of ZM 2-1 and ZM 1-2 start to lose their structural waters at 110.18–335.70–410.88°C and 120.02–351.16–408.18°C, respectively.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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