

Supercritical Carbon Dioxide Drying of Methanol–Zinc Borate Mixtures

Mehmet Gönen,^{*,†} Devrim Balköse,[†] Ram B. Gupta,[‡] and Semra Ülkü[†]

Department of Chemical Engineering, Izmir Institute of Technology, Gülbahçe Köyü, Urla, Izmir 35430, Turkey, and Department of Chemical Engineering, Auburn University, Auburn, Alabama 36849-5127

Supercritical carbon dioxide (CO₂) drying of zinc borate species was investigated to evaluate possible chemical alterations in the product during the drying. Methanol-wetted zinc borates produced either from borax decahydrate and zinc nitrate hexahydrate (2ZnO·3B₂O₃·7H₂O) or from zinc oxide and boric acid (2ZnO·3B₂O₃·3H₂O) were dried by both conventional and supercritical carbon dioxide drying methods. Zinc borate samples dried by both techniques were characterized using analytical titration, X-ray powder diffraction (XRD), thermo gravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, elemental analysis, and scanning electron microscopy (SEM). It was found that while zinc borate obtained from zinc oxide and boric acid did not have any chemical interaction with CO₂, carbonates were formed on the surface of zinc borate obtained from borax decahydrate and zinc nitrate hexahydrate. The main factor for the carbonate formation during supercritical CO₂ drying is anticipated as the structural differences of zinc borate species. CO₂ is a nonpolar solvent, and it does not usually react with polar substances unless water is present in the medium. While 2ZnO·3B₂O₃·3H₂O had three bound OH groups, 2ZnO·3B₂O₃·7H₂O had five bound OH groups and one mole of water of crystallization. It is proposed that the water of crystallization reacts with CO₂ forming carbonic acid. Then, carbonic acid, which is stronger than boric acid, substitutes borate ions from their zinc salts.

1. Introduction

Zinc borate is an important inorganic hydrated borate that finds applications ranging from polymers to paints for various purposes, such as flame retardant, corrosion inhibitor, etc.¹ depending on the type of zinc borate. Zinc borates function not only as flame retardant but also as smoke suppressant, afterglow suppressant, and antitracking agent for both halogen-containing and halogen-free polymers. The recent developments in this area were reviewed by Shen and co-workers.² Zinc borates are also used as heat stabilizer for polyvinyl chloride (PVC). Mixtures of zinc borate and zinc phosphate showed a synergistic effect on retarding dehydrochlorination of PVC.³ They neutralize the hydrogen chloride eliminated by dehydrochlorination and prevent autocatalytic effect of hydrogen chloride on thermal degradation.

Since boron atoms can coordinate to three (BO₃) and four (BO₄) oxygen atoms, it enables the formation of a substantial number of chemical structures. In addition to the monomeric structures in the units, borates occur in polymeric configurations, as well. Polymerization takes place by the elimination of water molecule from two hydroxyl (OH) groups of borate units. Further polymerization of borates forms sheet or network line structures. The most of the natural borates contain water of crystallization; but the synthetically produced borates can be formulated to contain hydroxyl groups instead of bound water or vice versa. For example,¹ zinc borate with a formula of 2ZnO·3B₂O₃·3H₂O has (OH) groups in its structure (Zn[B₃O₄(OH)₃]), on the other hand, zinc borate with an oxide formula of 2ZnO·3B₂O₃·7H₂O has both (OH) groups and water of crystallization as Zn[B₃O₃(OH)₅]·H₂O in its structure according to the IR analysis.

There are several types of zinc borates (4ZnO·B₂O₃·H₂O, ZnO·B₂O₃·~1.12H₂O, ZnO·B₂O₃·~2H₂O, 6ZnO·5B₂O₃·3H₂O, 2ZnO·3B₂O₃·7H₂O, 2ZnO·3B₂O₃·3H₂O, 3ZnO·5B₂O₃·14H₂O, ZnO·5B₂O₃·4.5H₂O) that have been developed since 1940s. Only 4ZnO·B₂O₃·H₂O and 2ZnO·3B₂O₃·3H₂O are preferred in polymers that require high processing temperature, as they have high dehydration temperatures of 410 and 290 °C, respectively.⁴ On the other hand, 2ZnO·3B₂O₃·7H₂O releases its water at about 200 °C and it is used as a lubricating additive or flame retardant where low processing temperature is needed. For instance, 2ZnO·3B₂O₃·7H₂O and 2ZnO·3B₂O₃·3H₂O are used to provide flame retardancy for polyethylene and polypropylene, respectively, since they are stable at the processing temperatures of polyethylene (120–150 °C) and polypropylene (160–200 °C). In case of fire, both of them will function as flame retardant by releasing H₂O and forming a glass film. While 2ZnO·3B₂O₃·7H₂O is produced from borax decahydrate and zinc salt at below about 70 °C, 2ZnO·3B₂O₃·3H₂O is produced commercially by the reaction of zinc oxide with boric acid at 90 °C.⁵ 2ZnO·3B₂O₃·7H₂O consumes less energy during its production than 2ZnO·3B₂O₃·3H₂O since it is produced at a lower temperature. If processing conditions allow, it is more economical to use 2ZnO·3B₂O₃·7H₂O.

There have been a number of recent studies for zinc borate production. For example, Shi et al. produced 2ZnO·3B₂O₃·3H₂O by a rheological phase reaction method using zinc oxide and boric acid.⁶ As this technique utilized a small amount of water in the reaction, it did not produce an aqueous waste stream that needs to be treated.⁶ But the large particles (about 19 μm in diameter) obtained were unsuitable for many applications. The synthesis of 4ZnO·B₂O₃·H₂O with different morphologies was studied using borax decahydrate and zinc sulfate hexahydrate in a surfactant assisted hydrothermal reaction method.⁷ The influence of hydrothermal reaction parameters, such as initial pH, temperature, time, and raw materials' concentrations were investigated. The optimal initial pH range was pointed

* To whom correspondence should be addressed. E-mail: gonem19@gmail.com.

[†] Izmir Institute of Technology.

[‡] Auburn University.

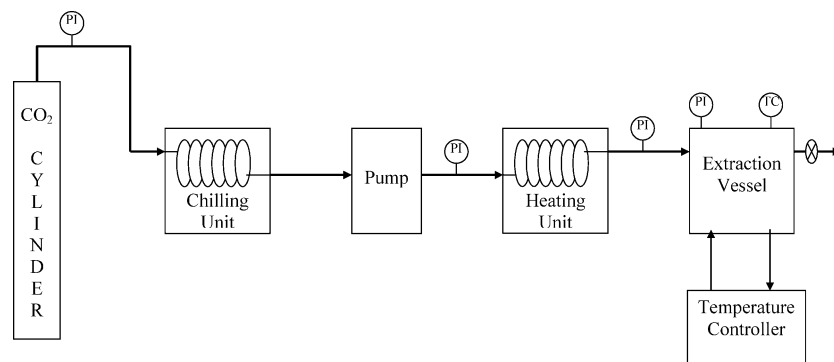


Figure 1. Schematic representation of supercritical CO₂ drying system.

out as 8–9 and at pH values of 3, 6, and 10 no product formation was reported. The reaction temperature between 90 and 180 °C was stated as adequate for the synthesis of 4ZnO·B₂O₃·H₂O crystals. The reaction time was also examined based on the morphological changes of product and increasing reaction time caused random orientation of produced nanorods.⁷ However, thermal behavior of produced zinc borate samples was not investigated.

The number of studies in nanosized zinc borate production has increased substantially due to many potential applications.^{8,9} For instance, Tian and co-workers produced zinc borate nanodiscs from borax and zinc sulfate in the presence of oleic acid as a modifying agent.⁹ The produced nanodiscs were used as lubricating oil additive and they decreased friction coefficient value from 0.12 to 0.02. Nanoparticles agglomerate owing to the influence of interfacial tension during conventional drying.¹⁰ Supercritical fluid drying where the solvent is removed above its critical temperature (T_c) and critical pressure (P_c) is suggested to overcome the agglomeration and sticking of nanoparticles. In other words, since the liquid–vapor interface and capillary pressure are eliminated in supercritical fluid drying, particles do not tend to gather. Supercritical fluids have been used in areas ranging from natural products extraction, materials cleaning, chemical reactions, nanoparticle preparation and drying.^{11,12} The production of nanosized metal borates was studied using supercritical ethanol drying and supercritical CO₂ drying.^{13,14} Supercritical CO₂ drying has been utilized in many applications owing to the fact that carbon dioxide is inexpensive, environmentally benign, not flammable, nontoxic and can be regenerated easily by a cycle system. The preparation of nanometer copper borate with supercritical carbon dioxide drying was studied by Hu and co-workers.¹⁵ In those studies, supercritical CO₂ drying was preferred to prevent the agglomeration of metal borate particles. However, there are some ambiguities, such as the interaction between copper borate and supercritical CO₂ not being taken into account and the thermal behavior of copper borate not being examined considering the above phenomenon.

To prevent agglomeration of wet zinc borate particles filtered from aqueous medium during drying, water was replaced with methanol by washing and filtering the particles with methanol. Methanol is a solvent having a lower surface tension (22.1 mN/m) than that of water (72.0 mN/m) and it is miscible in all proportions with supercritical carbon dioxide. During supercritical carbon dioxide drying, methanol was extracted from zinc borate particles by supercritical carbon dioxide in a flowing system. It was expected that the particles would not stick to each other since there is no liquid surface tension attracting them. Even if no interaction of carbon dioxide with zinc borate was expected based on previous publications,¹⁵ interactions were observed in this study. This paper aims to elucidate the

interactions between zinc borate species and supercritical carbon dioxide. For this purpose, zinc borates produced from “borax decahydrate and zinc nitrate hexahydrate” and “boric acid and zinc oxide” pairs were dried both by conventional and supercritical CO₂ techniques, and the samples were characterized before and after drying by using X-ray diffraction, FTIR spectroscopy, TGA, elemental analysis and scanning electron microscopy.

2. Experimental Details

2.1. Materials. Sodium borate decahydrate (99.5–105.0%), zinc oxide (99.9%), and boric acid (99.99%) from Sigma-Aldrich, and zinc nitrate hexahydrate (99.9%) from Fluka were used in the production of zinc borate species. D-Mannitol and EDTA from Sigma-Aldrich were used in the determination of B₂O₃ and zinc contents in zinc borates. Deionized water from Milli-Q purification system and methanol (99.9%) from Sigma-Aldrich were used in experiments. CO₂ (99.9%) was obtained from Air Gas Company.

2.2. Synthesis of Zinc Borates. Zinc borate species were produced by using two different raw material pairs. In the first, zinc borate (ZnB-1) was produced by using 50 cm³ 1 mol·dm⁻³ borax decahydrate and 50 cm³ 1 mol·dm⁻³ zinc nitrate hexahydrate at 70 °C for 5 h reaction time.^{9,13} In the latter, zinc borate (ZnB-2) was produced from 4.7 mol·dm⁻³ boric acid and stoichiometric amount of zinc oxide to adjust B₂O₃/ZnO molar ratio 2.0¹⁶ at 90 °C for 5 h reaction time. Both reactions were carried out in a 250 cm³ glass bottle equipped with a magnetic stirrer and a temperature controller.

To remove the unreacted zinc nitrate hexahydrate and sodium borate decahydrate in the first method and unreacted boric acid in the second method, the prepared precipitates were washed using deionized water. Subsequently, zinc borates were washed three times with methanol to replace water. Zinc borate samples contained approximately 70% in mass methanol.

2.3. Drying of Zinc Borates Wetted with Methanol. Different portions of the samples were either conventionally dried in air circulating oven at 110 °C until reaching a constant weight or by supercritical CO₂ drying for different periods. The supercritical CO₂ drying of zinc borate was performed in a supercritical CO₂ extraction system as shown in Figure 1.

In supercritical CO₂ drying, 4.0 g zinc borate sample (ZnB-1 or ZnB-2, wetted with methanol) was first packaged in a filter paper pouch and then put into the 100 cm³ extraction autoclave. The autoclave was pressurized with CO₂ up to 10 MPa at 40 °C using a pump (Thar P-50). The temperature of extraction vessel was maintained at 40 °C by a temperature controller and a heating tape. Dynamic drying was performed at 10 MPa with a CO₂ flow rate of 2.5–3.0 g·min⁻¹ for different drying times.

Table 1. Composition of the Samples

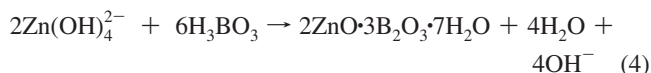
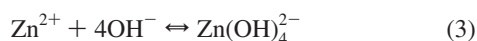
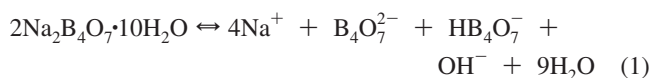
sample	N%	C%	CO ₂ %		H%	H ₂ O%		B ₂ O ₃ /ZnO	ZnCO ₃ %
			from C%	from TGA		from H%	from TGA		
ZnB-1	0.23	0.153	0.56		2.52	22.68	23.01	1.35	
ZnB-1SC-1		1.26	4.62	4.78	2.26	20.3	16.88		13.87
ZnB-1SC-2		1.43	5.24	5.50	2.22	19.98	15.35		15.67
ZnB-1SC-3		1.47	5.39	5.76	2.24	20.10	15.27		16.41
ZnB-2							13.31	1.5	
ZnB-2SC		0.26	0.95		1.43	12.87	13.16	1.5	

While ZnB-1 was dried for 2, 3, and 4 h periods; ZnB-2 was dried for 2 h only. These samples were called as ZnB-1SC-1, ZnB-1SC-2, ZnB-1SC-3, and ZnB-2SC, respectively. Afterward, the autoclave was slowly depressurized to atmosphere at 40 °C. Finally, supercritical CO₂ dried zinc borate samples were obtained.

2.4. Characterization of Zinc Borates. Zinc borate samples were characterized using the following techniques before and after supercritical drying process. The crystalline structure and purity of the zinc borate samples were determined using X-ray powder diffractometer (Philips Xpert-Pro) with Cu K α radiation at 45 kV and 40 mA. The scattering data were collected in the 5–70° 2 θ range. Scanning electron microscopes, (SEM), (Philips XL30 SFEG and Zeiss DSM 940), were used for identification of particle size and morphology. The transmission spectra of KBr pellets prepared by mixing 4.0 mg of zinc borate and 196 mg of KBr in an agate mortar and pressing the mixture under 10 tons were obtained using Nicolet 360 and Shimadzu 8601 Fourier transform infrared (FTIR) spectrophotometers. Thermal gravimetric analyses (TGA) were performed using Shimadzu TGA-51. Zinc borate samples (10–15 mg) were loaded into an alumina pan and heated from room temperature to 600 at 10 °C/min under N₂ flow of 40 mL/min. H, C, and N content of samples were measured by using Leco CHNS-932 elemental analyzer.

3. Results and Discussion

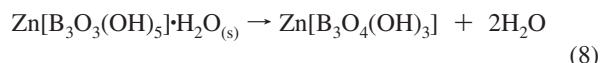
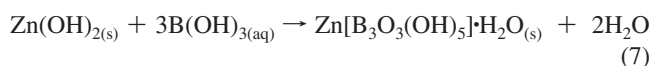
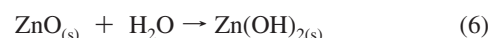
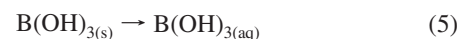
The possible reactions in the production of zinc borate from borax decahydrate and zinc nitrate hexahydrate are as follows:



In the production of zinc borate from borax and water-soluble zinc salt, the initial pH of the mixture has a significant role. While a formed product decomposes in acidic solutions, zinc oxide forms in basic mixtures.⁷ When borax was dissolved in water (eq 1), pH of mixture was around 9.0. The tetraborate anions produce boric acid according to eq 2. Zn²⁺ cations in the aqueous solution of zinc nitrate hexahydrate forms zinc tetrahydroxide anions by reacting with OH⁻ anions (eq 3). Finally, boric acid reacts with zinc tetrahydroxide anions to produce zinc borate according to eq 4. The pH of mixture at the end of reaction after filtration was measured as 6.4.

Boric acid dissolves in water as shown in eq 5. Since the boric acid is a Lewis acid, zinc oxide forms zinc hydroxide in that media according to eq 6. Then, zinc hydroxide and boric

acid reacts to zinc borate building block as shown in eq 7. Boric acid may also form other borate anions regarding the pH and concentration of boric acid and they may also involve in the zinc borate synthesis. Formed zinc borate specie in eq 7 turned into ultimate product releasing water as shown in eq 8. As the reaction was carried out in the excess of boric acid, the medium was acidic at the pH value of 5.



To determine the elemental composition of zinc borate samples and the effect of supercritical CO₂ drying, C, H, N contents of samples that were produced from “borax decahydrate and zinc nitrate hexahydrate, ZnB-1” and “boric acid and zinc oxide, ZnB-2” and supercritical CO₂ dried samples were determined as shown in Table 1. Hydrogen content of zinc borate produced from borax and zinc nitrate hexahydrate (ZnB-1) was found as 2.52% which is very close to the theoretical value of 2.84%. Carbon and nitrogen contents of zinc borate (ZnB-1) are negligible and indicating that it was washed efficiently formed nitrate ions present in the reaction mixture. The presence of carbon in ZnB-1 was not expected any way. However, it can be seen that during supercritical carbon dioxide drying due to the reaction of carbon dioxide with ZnB-1, the carbon content of sample increased to 1.26% for 2 h dried sample. With the increase of drying time to 3 and 4 h, the carbon content increased from 1.26% to values of 1.43% and 1.47%, respectively. Another considerable change occurred in the H content of zinc borate during supercritical drying: it decreased from 2.52% to 2.22% as carbon dioxide flow caused the removal of some OH groups, as well. On the other hand, the hydrogen content of supercritical dried zinc borate (ZnB-2SC) obtained from boric acid and zinc oxide was found as 1.43% which corresponds to the theoretical value of 1.42%. Nitrogen was not present and carbon content was not significant as expected for this sample. Conventional dried zinc borate produced from boric acid and zinc oxide was not examined in the elemental analysis.

3.1. Characterization of Supercritical CO₂ Dried Zinc Borate Produced from Borax Decahydrate and Zinc Nitrate Hexahydrate. Using analytical titration method, the mole ratio of B₂O₃/ZnO was found as 1.35 (Table 1), which is very close to the value in theoretical formula of 2ZnO · 3B₂O₃ · 7H₂O. FTIR spectra of zinc borates produced from borax decahydrate and zinc nitrate hexahydrate conventionally and supercritical CO₂ dried for 2, 3, and 4 h are shown in Figure 2. The spectrum in Figure 2a indicates that zinc borate species has an identical spectrum with the spectrum given for

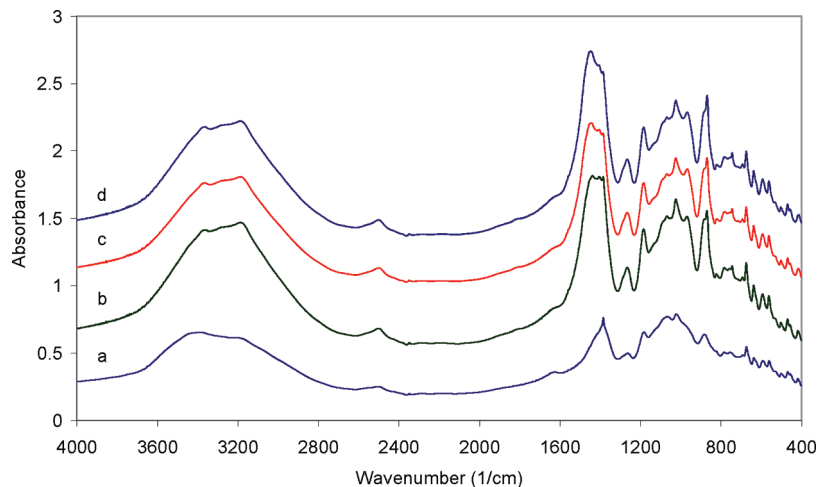


Figure 2. FTIR spectra of zinc borates dried (a) conventionally at 110 °C (ZnB-1) and by SC CO₂ at different drying times: (b) 2 h (ZnB-1SC-1), (c) 3 h (ZnB-1SC-2), (d) 4 h (ZnB-1SC-3).

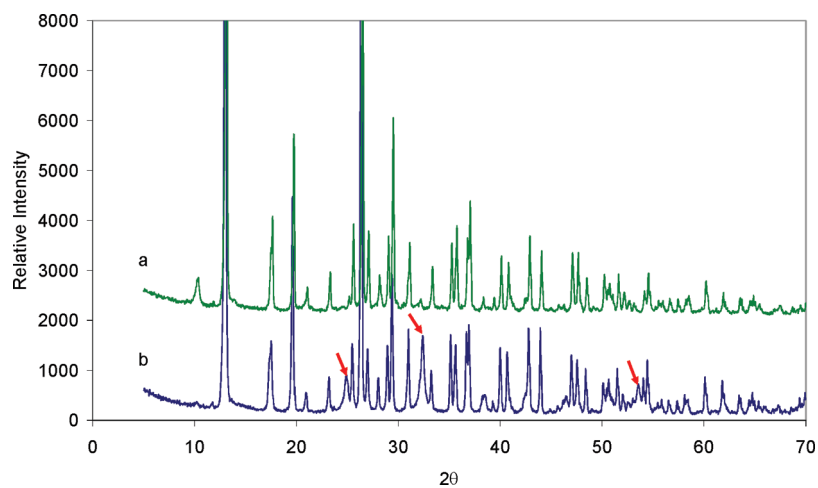


Figure 3. XRD patterns of zinc borates dried (a) conventionally at 110 °C (ZnB-1) and (b) by supercritical CO₂ for 4 h (ZnB-1SC-3).

$2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$.¹⁷ The band at 1641 cm^{-1} is assigned to the H—O—H bending mode, which shows the compound containing the crystalline water. (Figure 2a). The other major peaks in the spectrum of zinc borate (ZnB-1) before and after supercritical drying are given in Table 3.

The peaks at about 1450 cm^{-1} (shoulder peak) and 835 cm^{-1} in FTIR spectra of supercritical CO₂ dried zinc borate samples in Figure 2b–d belong to carbonate ions.¹⁸ It was inferred from the comparison of Figure 2a and Figure 2b–d that zinc borate species ZnB-1 interacted chemically with carbon dioxide during the supercritical drying. No methanol was present in the samples since peaks related to C—H vibrations of methanol at 2900 cm^{-1} were not observed in the FTIR spectra.

Figure 3a shows the XRD pattern of zinc borate that was produced from borax decahydrate and zinc nitrate hexahydrate (ZnB-1) and dried at 110 °C. As the major peaks at about 13.0° , 18.0° , 20.0° , 27.0° , and 30.0° 2θ values are identical to the peaks of $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$, it is concluded that the product is $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 7\text{H}_2\text{O}$. Figure 3b represents the XRD pattern of zinc borate that was dried by supercritical CO₂. This pattern was redrawn while the intensity value was constrained to 8000 so that the small peaks can be seen easily. From the comparison of Figure 3a and Figure 3b, it can be deduced that there are extra peaks in the XRD pattern of supercritical CO₂ dried zinc borate. The peaks at 2θ values of 24.96° , 32.45° , and 53.67° , indicated by arrows, belong to zinc carbonate crystal structure.¹⁸

During the supercritical CO₂ drying under 10 MPa and 40 °C, zinc borate reacted with CO₂ to produce zinc carbonate. The formation of zinc carbonate during drying was also supported by FTIR analysis.

SEM photographs of zinc borate and supercritical CO₂-dried zinc borate samples are shown in Figure 4a–d. Figure 4a clearly shows that there are two types of particles; the first type is micrometer-sized prismatic rods and the second kind is nanosized flakes. By comparison of the SEM image of Figure 4a with that of Figure 4d, it can be seen that reaction started on the surface of the micrometer-sized particles and the amount of zinc borate reacted with CO₂ on the surface has increased with increasing drying time. The particle size of spherical particles on the surface of zinc borate varies between 200 and 500 nm.

TGA curves of zinc borate samples produced from borax decahydrate and zinc nitrate hexahydrate and supercritical CO₂ dried samples are given in Figure 5. In these thermograms, the first step starts at around 180 °C, (T_1), and it represents the removal of water from the structure by evaporation of crystallization water and water formed by condensation of OH groups. The second step which occurs at around 370 °C, (T_2), is due to the removal of CO₂ from zinc carbonate structure. Conventionally dried zinc borate at 110 °C begins to lose its hydration water at 180 °C with a mass loss of 23.0% (Figure 5a) which is close to the theoretical value 25.32% calculated from the

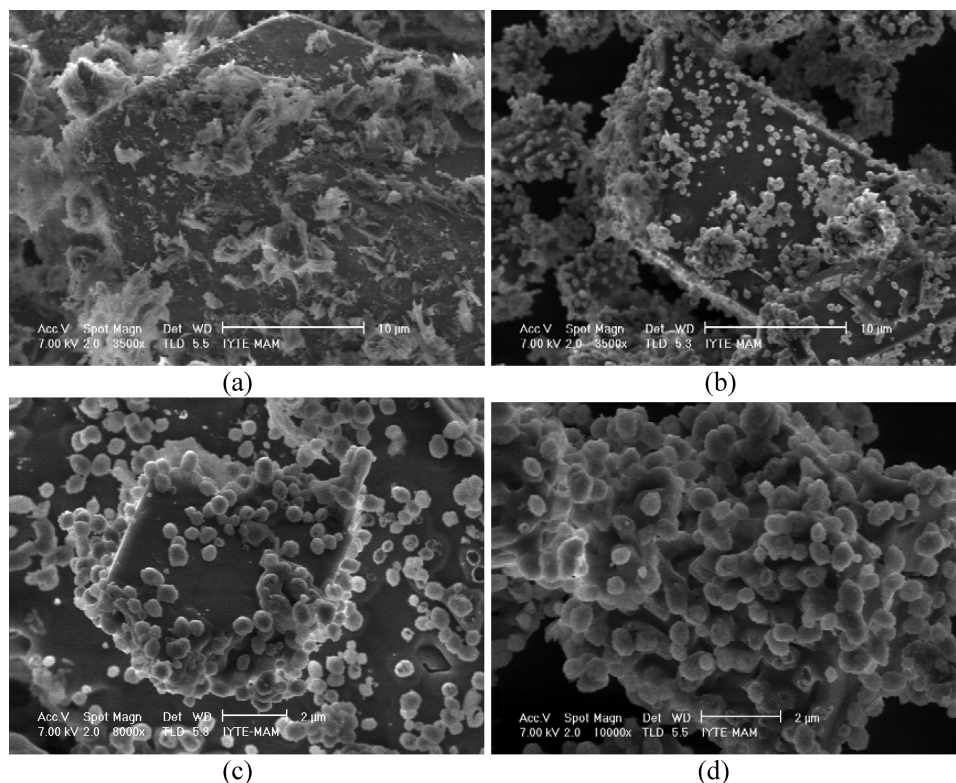


Figure 4. SEM microphotographs of zinc borates dried (a) conventionally at 110 °C (ZnB-1) and by SC CO₂ at different drying times: (b) 2 h (ZnB-1SC-1), (c) 3 h (ZnB-1SC-2), (d) 4 h (ZnB-1SC-3).

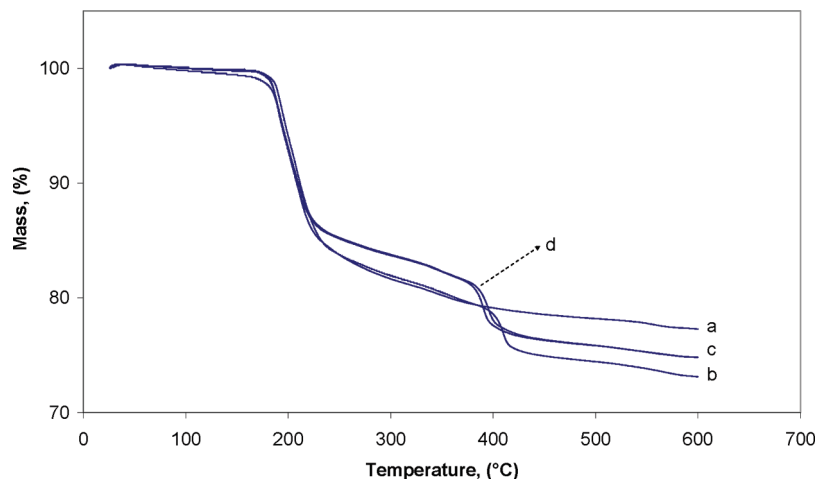


Figure 5. TGA curves of zinc borates dried (a) conventionally at 110 °C (ZnB-1) and by SC CO₂ at different drying times: (b) 2 h (ZnB-1SC-1), (c) 3 h (ZnB-1SC-2), (d) 4 h (ZnB-1SC-3).

formula of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$. On the other hand, zinc borates dried by supercritical CO₂ under 10 MPa and 40 °C for drying time of 2–4 h show two steps in the TGA curves (Figure 5b–d). The first step that started at 180 °C with a mass loss of 16.88% belongs to the water loss of zinc borate, and the second step that occurred at 370 °C with a mass loss of 4.78% (ZnB-1SC-1) pertains to the decomposition of zinc carbonate.¹⁹ After supercritical CO₂ drying, the approximate composition of the ultimate product is zinc borate (85%) and zinc carbonate (15%) as calculated from the CO₂ weight loss. CO₂ % found from C content and TGA and H₂O % from H content and TGA were very close to each other as reported in Table 1. The thermal stability properties of zinc borates and samples that were dried by supercritical CO₂ are summarized in Table 2. The CO₂ content of ZnB-1SC1, ZnB-1SC2, and ZnB-1SC-3 samples was

Table 2. Thermal Behavior of Zinc Borate Samples

sample	T1 (°C)	H ₂ O loss %	T2 (°C)	CO ₂ loss %
ZnB-1	180	23.01		
ZnB-1SC-1	180	16.88	386	4.78
ZnB-1SC-2	180	15.35	370	5.50
ZnB-1SC-3	180	15.27	370	5.76
ZnB-2	291	13.31		
ZnB-2SC	303	13.16		

determined by TGA as 4.78%, 5.50%, and 5.76%, respectively (Table 2). They contained 13.87–16.41% (wt) ZnCO₃ as listed in Table 1.

3.2. Characterization of Supercritical CO₂ Dried Zinc Borate Produced from Boric Acid and Zinc Oxide. The zinc borate (ZnB-2) prepared from boric acid and zinc oxide at 90 °C for 5 h reaction time is a zinc borate species with the oxide

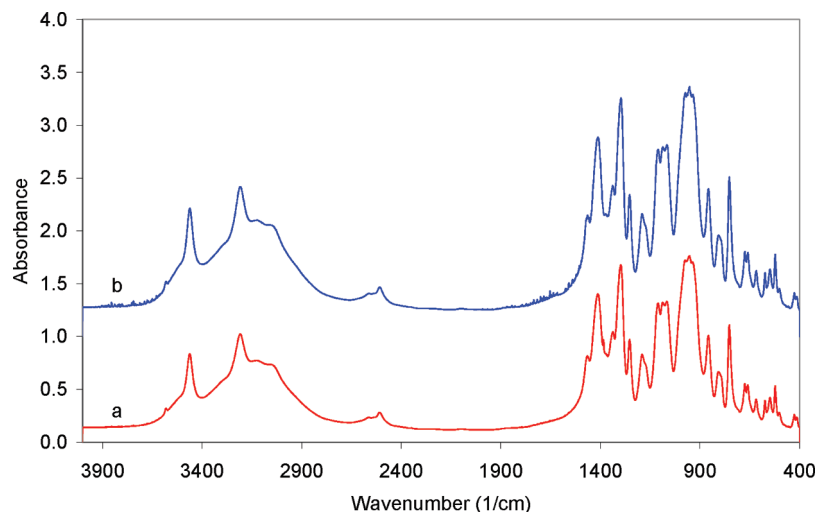


Figure 6. FTIR spectra of zinc borates dried (a) by SC CO₂ for 2 h (ZnB-2SC) and (b) by conventional means at 110 °C (ZnB-2).

Table 3. Observed Wavenumbers (cm⁻¹) in FTIR Spectra for Zinc Borate Samples

from borax decahydrate and zinc nitrate hexahydrate (ZnB-1)		from zinc oxide and boric acid; before and after supercritical extraction (ZnB-2)	assignment
before supercritical CO ₂ extraction	after supercritical CO ₂ extraction		
3417	3417	3471	$\nu(\text{O}-\text{H})$
3186	3186	3227	
2515	2515	2520	
1641	1641		$\delta(\text{H}-\text{O}-\text{H})$
	1450		CO_3^{-2}
1384	1384	1425	$\nu_{\text{as}}(\text{B}_3-\text{O})$
		1346	
		1305	
1274	1274	1257	$\delta(\text{B}-\text{O}-\text{H})$
1188	1188	1200	$\nu_{\text{as}}(\text{B}_4-\text{O})$
1078	1078	1118	
1028	1028		
-	970		CO_3^{-2}
889	889	960	$\nu_s(\text{B}_3-\text{O})$
		864	
790	790	816	$\nu_s(\text{B}_4-\text{O})$
759	759	756	
675	675		$\gamma(\text{B}_3-\text{O})$
640	640	624	$\nu_p(\text{B}_3\text{O}_4(\text{OH})_3)^{-2}$
596	596	553	$\delta(\text{B}_3-\text{O}), \delta(\text{B}_4-\text{O})$
563	563	526	
472	472	432	$\delta(\text{B}_4-\text{O})$
420	420		

formula of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The mole ratio of $\text{B}_2\text{O}_3/\text{ZnO}$ was determined as 1.50 from analytical titration, and water content was determined by thermal gravimetric analysis as 13.31% (Table 2) that corresponds to its theoretical value of 12.69%. The FTIR spectrum of the conventionally dried compound (Figure 6b) shows some important properties of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. All hydrated borate salts have a broad peak at $2200\text{--}3600\text{ cm}^{-1}$ ²⁰ resulting from stretching vibrations of OH groups in their structure; $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ has two major sharp peaks at 3210 and 3470 cm^{-1} in this region which is accepted as characteristics of this type.²¹ Another important feature of this product is that it does not have crystallization water in its structure since it does not have a peak at 1635 cm^{-1} belonging to bending vibrations of H_2O molecules in its IR spectrum. The chemical structure of zinc borate of this type has been recently updated by Schubert and his co-workers as $(\text{Zn}[\text{B}_3\text{O}_4(\text{OH})_3])$ which has a polymeric network structure.¹ Figure 6a shows the FTIR spectrum of zinc borate that was dried by supercritical CO₂ for 2 h. It can be inferred that there is no change in the chemical structure of zinc borate during supercritical drying. Conventionally dried and supercritical CO₂

dried zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) samples had identical spectra in which major peaks were summarized in Table 3.

X-ray diffraction patterns of zinc borate samples dried by supercritical CO₂ and conventionally at 110 °C are given in Figure 7a and Figure 7b, respectively. This zinc borate species has a crystal structure that is identical to that of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.¹⁶ The most important characteristic of this zinc borate species is that the major peaks begin to occur at 18.0° 2θ value, and other important peaks in the XRD pattern are observed at about 20.0° , 22.0° , 24° , 26° , 29° , 30° and 36° 2θ values. It can be concluded from the comparison of Figure 7a and Figure 7b that there is no change in the crystal structure of zinc borate after supercritical CO₂ drying.

From SEM micrographs of conventionally dried particles (Figure 8a), particle size was determined about $2\text{ }\mu\text{m}$. Particles stick to each other and supercritical CO₂ has no influence on separation of these particles (Figure 8b). Particles in both Figure 8a and Figure 8b have smooth surfaces and random shapes.

To determine the water content of zinc borate and the supercritical CO₂ drying effect, samples were analyzed by TGA. Figure 9 shows the TGA plots of zinc borates dried convention-

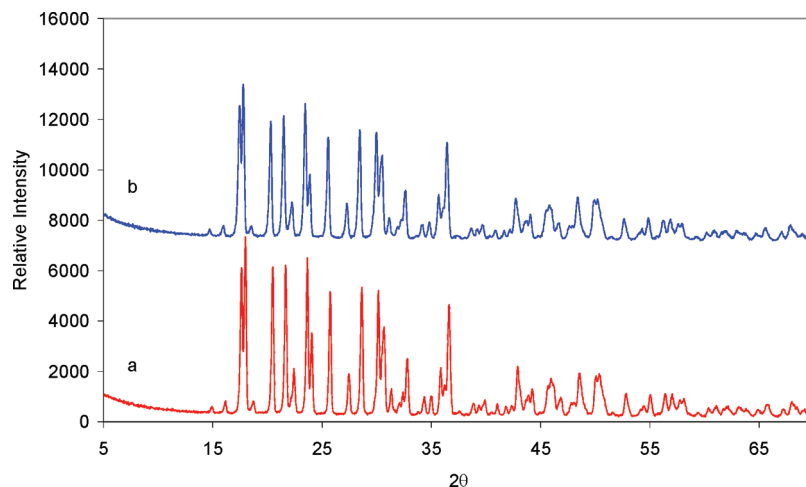


Figure 7. XRD diagrams of zinc borates dried (a) by SC CO₂ for 2 h (ZnB-2SC) and (b) by conventional means at 110 °C (ZnB-2).

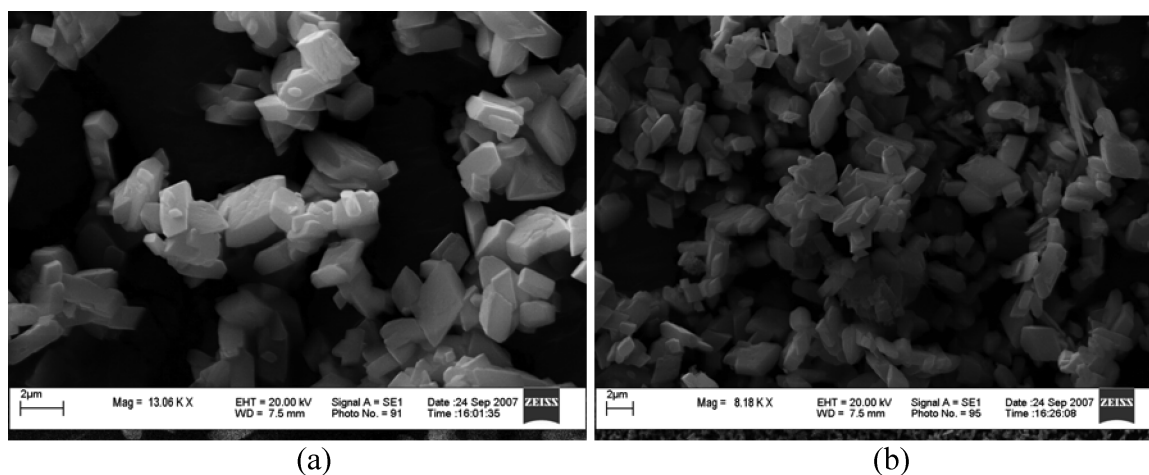


Figure 8. SEM microphotographs of zinc borates dried (a) conventionally at 110 °C (ZnB-2) and (b) by SC CO₂ (ZnB-2SC).

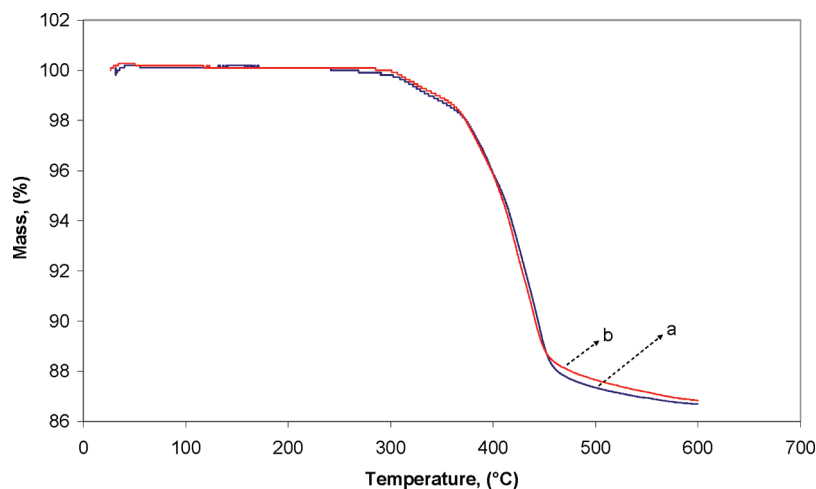
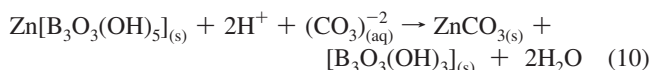
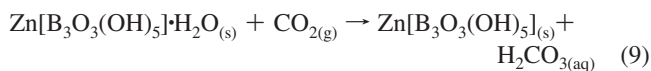


Figure 9. TGA curves of zinc borates dried (a) conventionally at 110 °C (ZnB-2) and (b) by SC CO₂ for 2 h (ZnB-2SC).

ally at 110 °C and by supercritical CO₂. Conventional dried zinc borate (ZnB-2) started to lose weight at 290 °C; supercritical CO₂ dried zinc borate began to lose weight at 303 °C as shown in Table 2. The total weight loss of both samples was about 13.0% which is very close to theoretical value of 12.69% for 2ZnO·3B₂O₃·3H₂O until 600 °C. The water content was also determined as 12.81% from elemental H content of a supercritically dried sample.

It can be concluded that ZnB-2 was not affected chemically by supercritical carbon dioxide drying.

Carbon Dioxide and Zinc Borate Interaction. It was anticipated that carbonic acid was formed from the dissolution of carbon dioxide in water that was released from the zinc borate structure under supercritical conditions as shown in eq 9. Then, zinc borate–methanol mixture reacted with carbonic acid as shown in eq 10.



Since the structure of $\text{Zn}[\text{B}_3\text{O}_4(\text{OH})_3]$ is quite stable and has no water of crystallization, no carbonate formation was observed in the drying of that zinc borate. The larger particle size of that product might be another reason for not observing any reaction, since the reaction between zinc borate and carbon dioxide takes places on the surface of the solid particles. In this study, the particle size of $\text{Zn}[\text{B}_3\text{O}_4(\text{OH})_3]$ and $\text{Zn}[\text{B}_3\text{O}_3(\text{OH})_5] \cdot \text{H}_2\text{O}$ that reacted were 2 μm and 200–500 nm, respectively.

4. Conclusion

Zinc borate species having different properties had different application fields depending on economics and final end use. $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ obtained from borax decahydrate and zinc nitrate hexahydrate has structure of $\text{Zn}[\text{B}_3\text{O}_3(\text{OH})_5] \cdot \text{H}_2\text{O}$ that comprises both water of crystallization and bound water as OH groups attached to main unit. However, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ obtained from boric acid and zinc oxide has the structure of $(\text{Zn}[\text{B}_3\text{O}_4(\text{OH})_3])$, which has no water of crystallization. Water of crystallization is more labile and reactive than bound OH groups. While zinc borate having water of crystallization in its structure reacted partially with CO_2 to produce zinc carbonate, zinc borate without water of crystallization did not react with CO_2 under supercritical drying conditions. The presence of nanosized spherical particles on the zinc borate surface made the surface reaction detectable in the time period of drying for $\text{Zn}[\text{B}_3\text{O}_3(\text{OH})_5] \cdot \text{H}_2\text{O}$. The final product contained about 15% zinc carbonate. Even if no interaction of carbon dioxide with zinc borate was expected based on previous publications on magnesium borate and copper borate, interactions were observed in this study for $\text{Zn}[\text{B}_3\text{O}_3(\text{OH})_5] \cdot \text{H}_2\text{O}$. Since no interaction was observed for 2 μm sized $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ particles in the present study, further studies are being made on synthesis of nanoparticles of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and their drying with supercritical carbon dioxide.

Acknowledgment

The authors acknowledge the financial support from The Scientific and Technical Research Council of Turkey (TÜBİTAK) (project number: 105M358) and TÜBİTAK scholarship for study in Prof. Ram B. Gupta's laboratory.

Literature Cited

(1) Schubert, D. M.; Alam, F.; Visi, M. Z.; Knobler, C. B. Structural characterization and chemistry of industrially important zinc borate $\text{Zn}[\text{B}_3\text{O}_4(\text{OH})_3]$. *Chem. Mater.* **2003**, *15*, 866–871.

(2) Shen, K. K.; Kochesfahani, S.; Jouffret, F. Review article: Zinc borates as multifunctional polymer additives. *Polym. Adv. Technol.* **2008**, *19*, 469–474.

(3) Erdoğan, C. A.; Atakul, S.; Balköse, D.; Ülkü, S. Development of synergistic heat stabilizers for pvc from zinc borate-zinc phosphate. *Chem. Eng. Commun.* **2009**, *196*, 148–160.

(4) Schubert, D. M. Zinc Borate. U.S. Patent 5,472,644, December 5, 1995.

(5) *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; John, Wiley and Sons: New York, 1994; Vols 10, 4.

(6) Shi, X.; Xiao, Y.; Li, M.; Yuang, L.; Sun, J. Synthesis of an industrially important zinc borate, $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, by a rheological phase reaction method. *Powder Technol.* **2008**, *186*, 263–266.

(7) Shi, X.; Yuan, L.; Sun, X.; Chang, C.; Sun, J. Controllable synthesis of $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ nano-/microstructures with different morphologies: Influence of hydrothermal reaction parameters and formation mechanism. *J. Phys. Chem. C* **2008**, *112*, 3558–3567.

(8) Tian, Y.; He, Y.; Yu, L.; Deng, Y.; Zheng, Y.; Sun, F.; Liu, Z.; Wang, Z. In situ and one-step synthesis of hydrophobic zinc borate nanoplalets. *Colloids Surf., A* **2008**, *312*, 99–103.

(9) Tian, Y.; Guo, Y.; Jiang, M.; Sheng, Y.; Hari, B.; Zhang, G.; Jiang, Y.; Zhou, B.; Zhu, Y.; Wang, Z. Synthesis of hydrophobic zinc borate nanodiscs for lubrication. *Mater. Lett.* **2006**, *60*, 2511–2515.

(10) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press Inc: San Diego, 1990; pp 501–509.

(11) Perrut, M. Supercritical fluid applications: industrial developments and economic issues. *Ind. Eng. Chem. Res.* **2000**, *39*, 4531–4535.

(12) O'Neil, A.; Watkins, J. J. Fabrication of device nanostructures using supercritical fluids. *MRS Bull.* **2005**, *30*, 967–975.

(13) Dong, J. X.; Hu, Z. S. A study of the anti-wear and friction-reducing properties of the lubricant additive, nanometer zinc borate. *Tribol. Int.* **1998**, *31*, 219–222.

(14) Hu, Z. S.; Lai, R.; Lou, F.; Wang, L. G.; Chen, Z. L.; Chen, G. X.; Dong, J. X. Preparation and tribological properties of nanometer magnesium borate as lubricating oil additive. *Wear* **2002**, *252*, 370–374.

(15) Hu, Z. S.; Dong, J. X.; Chen, G. X.; Lou, F. Preparation of nanometer copper borate with supercritical carbon dioxide drying. *Powder Technol.* **1999**, *102*, 171–176.

(16) Sawada, H.; Igarashi, H.; Sakao, K. Zinc Borate and Production Method and Use Thereof. U. S. Patent. 6,780,913 B2, August 24, 2004.

(17) Gao, Y. H.; Liu, Z. H. Synthesis and thermochemistry of two zinc borates, $\text{Zn}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$ and $\text{Zn}_3\text{B}_{10}\text{O}_{18} \cdot 14\text{H}_2\text{O}$. *Thermochim. Acta* **2009**, *484*, 27–31.

(18) Kanari, N.; Mishra, D.; Gaballah, I.; Dupré, B. Thermal decomposition of zinc carbonate hydroxide. *Thermochim. Acta* **2004**, *410*, 93–100.

(19) Wu, W.; Jiang, Q. Preparation of nanocrystalline zinc carbonate and zinc oxide via solid-state reaction at room temperature. *Mater. Lett.* **2006**, *60*, 2791–2794.

(20) Jun, L.; Shuping, X.; Shiyang, G. FT-IR and Raman Spectroscopic Study of Hydrated Borates. *Spectrochim. Acta* **1995**, *51A-4*, 519–532.

(21) Eltepe, H. E.; Balköse, D.; Ülkü, S. Effect of Temperature and Time on Zinc Borate Species Formed from Zinc Oxide and Boric Acid in Aqueous Medium. *Ind. Eng. Chem. Res.* **2007**, *46-8*, 2367–2371.

Received for review February 23, 2009
Revised manuscript received April 24, 2009
Accepted May 8, 2009

IE9003046