Effects of Span 60 template and freeze drying on zinc borate produced from zinc nitrate hexahydrate and borax decahydrate

Burcu Alp, Mehmet Gönen, Sevdiye Atakul Savrık & Devrim Balköse

Published online: 30 Aug 2021.

Submit your article to this journal

Article views: 90

View related articles

View Crossmark data

Taylor & Francis
Taylor & Francis Group

Check for updates

Effects of Span 60 template and freeze drying on zinc borate produced from zinc nitrate hexahydrate and borax decahydrate

Burcu Alp[a], Mehmet Gönen[a], Sevdiye Atakul Savrık[b], and Devrim Balköse[c]

[a]Department of Chemical Engineering, Süleyman Demirel University, Isparta, Turkey; [b]Akzo Nobel Inc. Gaziemir, İzmir, Turkey; [c]Department of Chemical Engineering, Izmir Institute of Technology, Urla İzmir, Turkey

ABSTRACT

Zinc borate is an important additive to polymers and lubricants. The process variables such as reactant concentration, presence of template in precipitating medium and drying method determine the composition and particle size of zinc borates. In the present study, zinc borate precipitate obtained by mixing aqueous zinc nitrate and borax decahydrate solutions was dried either by conventional method or by freeze drying. The products were well characterized by advanced methods. Zinc borate from $1\,mol\,dm^{-3}$ reactants had $(2.1\pm0.5)\times(2.5\pm0.5)\times(1.3\pm0.2)\,\mu m$ and $(0.5\pm0.1)\times(1.3\pm0.1)\times(0.028\pm0.01)\,\mu m$ dimensions by conventional and freeze drying respectively. Individual particles smaller in size is obtained since the particles are not agglomerated due to absence of surface tension of liquid water for case of freeze drying. Planar particles agglomerated into 20 to $60\,\mu m$ crystals in the presence of template Span 60 in $1\,mol\,dm^{-3}$ reactants for conventional drying. Nano zinc borate particles with primary particle size of $(46\pm9)\,nm$ were obtained by decreasing the reactant concentration to $0.1\,mol\,dm^{-3}$. The primary particle size was decreased to $(40\pm3)\,nm$ by addition of Span 60 to dilute solutions. However zinc borate nanoparticles obtained from dilute solutions adhered to each other forming agglomerates during conventional drying. Their freeze drying would allow formation of a freely flowing nano powder.

Introduction

Zinc borates are industrially important chemicals which are used as flame retardant additives in polymers, and additives in lubricants. Zinc borates can be produced either by the heterogeneous reaction of zinc oxide and boric acid or from the homogeneous reaction of borax and water soluble zinc salts. Eltepe et al.[1] investigated the effect of reaction time and temperature for zinc borate synthesis from boric acid and zinc oxide. Gönen et al.[2,3] applied both supercritical carbon dioxide drying and supercritical ethanol drying techniques for the production of nano zinc borates. Carbonates form during supercritical carbon dioxide drying and zinc borate decomposed to zinc oxide and boric acid in supercritical ethanol drying. Acarali et al.[4,5] and Akgül et al.[6] investigated the synthesis of zinc borates from zinc oxide and boric acid. Acarali et al.[4] used palm oil to make hydrophobic zinc borates. Acarali et al.[4,5] and Schubert[7] reviewed industrially important zinc borate hydrates.

The use of borax as a boron source for the nano-sized metal borate synthesis has increased recently.[8,9] The transfer of the structure from a variety of organic templates (e.g., PEG, PVP, CTAB, etc.) to the inorganic product allowed to the formation of otherwise unattainable inorganic structures. 2D and 3D nano/microstructures of $4ZnO\cdot B_2O_3\cdot H_2O$ with different morphologies have been successfully synthesized by a hydrothermal route in the presence of surfactant polyethylene glycol-300 (PEG-300) from $Na_2B_4O_7\cdot10H_2O$ and $ZnSO_4$.[10] Savrik et al.[11] synthesized zinc borate from borax and zinc nitrate by inverse emulsion technique for lubrication. Nano-sized zinc borate particles were obtained by homogeneous precipitation technique developed by Ting et al.[12] Ammonia was added to the mixture of dilute zinc nitrate and borate solution in this method. The precipitation reaction of metal ions and precipitator can reach molecular level, which ensures the sedimentation of desired nanomaterials yielding and separating out homogeneously from the solution. The precipitation mechanism is based on

CONTACT Devrim Balköse ✉ devrimbalkose@iyte.edu.tr, devrimbalkose@gmail.com 🖃 Department of Chemical Engineering, Izmir Institute of Technology, Urla İzmir, Turkey.

the formation of $Zn(NH_3)_4{}^{2+}{}_{(aq)}$ complex, therefore a few Zn^{2+} ions present in the solution which inhibits the enlargement of the zinc borate crystals and provides formation of nano-sized particles. Nano zinc borate as a lubricant additive was produced from 0.1 mol dm^{-3} borax and zinc nitrate by Savrik et al.[13] The gelatinous zinc borate precipitates were dried under vacuum at 10 kPa for 18 hours at 25 °C to obtain nanoparticles. The average particle sizes of zinc borates were determined as 35.3 nm and 234 nm for without any template and with Span 60, respectively. When the zinc borate nanoparticles were added to light neutral oil, the wear scar diameter and friction coefficient was lowered by 50% and 20% respectively.[13]

The dispersibility of the zinc borate particles in polymers and lubricating oils is required in industrial applications of zinc borates. Since drying of zinc borates by conventional methods causes agglomeration, an alternative method such as freeze drying could be used to obtain a freely flowing powder. Freeze drying or lyophilization is a technique in which water is sublimated from the frozen material under vacuum. In recent years, ultrafine nano particles were obtained by the freeze drying method. There are two fundamental necessities in the freeze drying: the first one is to prevention of the particles' agglomeration or keeping of the three dimensional network e.g., silica aerogel. The latter one is the removal of water from the materials which are temperature sensitive such as proteins. Abdelwahed et al.,[14] Chen and Wang[15] and Mi et al.[16] reviewed freeze drying of nanoparticles. There are many examples for the application of freeze drying to produce nano particles. Silver nanopowders with regular shape and uniform diameter were prepared in four steps: preparing the precursor solution, freezing the solution, drying the congealed sample, and calcining the drying product. The starting raw materials were silver nitrate and caustic soda, whereas the precursor was silver diammine solution. The products of freeze drying are pure amorphous silver nanopowders without hard agglomerations. Silver cubic nanocrystals are subsequently obtained by calcination.[17] Nano copper particles were obtained by washing with distilled water, collecting centrifugally, adding to the mixed solution of distilled water and ethanol (25% by vol.), as well as completing by freeze drying.[18] Tachiwaki et al.[19] produced the fine powders for the YBCO superconductor by freeze-drying of the suspensions synthesized by co-precipitation of carbonates. Zeng et al. used $AlCl_3 \cdot 6H_2O$ and ammonia as precursor materials to precipitate boehmite

(γ-AlO(OH)) in aqueous solution, peptized boehmite to a transparent sol with nitric acid and then freeze dried the sol. Al_2O_3 particles with an average diameter of 42 nm were obtained by calcining the freeze dried bohemite at 1100 °C.[20] Tallon et al. synthesized of γ-Al_2O_3 nanopowders by a freeze-drying method.[21] Aqueous solutions of $Al_2(SO_4)_3 \cdot 18H_2O$ were freeze dried to get homogeneous spherical granules of amorphous aluminum sulfate with diameters ranging from 1 to 100 μm. These porous granules formed by soft agglomerates of nanoparticles with primary particle size lower than 20 nm. Freeze dried amorphous aluminum sulfate powder heated to decompose at 825 °C to form γ-Al_2O_3. Bovone et al. investigated the large scale production of doped Nano sized boron powder. Dissolved precursor (B_2O_3) and doping agent (Si) was cryogenically frozen in liquid nitrogen and finally lyophilized. The nano structured boron precursor obtained in freeze drying was further processed by magnesiothermic reaction in which it was reduced by magnesium metal.[22] Freeze drying is usually utilized to get a well distributed precursor which is further processed by calcination or other techniques e.g., reduction to get nano particles. Polycaprolactone (PCL) nanoparticles prepared by the emulsification-diffusion method and then freeze dried at different rates.[23] The freezing process can break the nanoparticles and cause the leakage of their contents during the freeze-drying step.

The particle size of zinc borates is an important property in its applications. While micron sized particles are sufficiently used in flame retarding applications, nano sized particles are essential as lubricant additives. Present study aims at the synthesis of micron sized and nano sized zinc borate particles by controlling the process variables. Thus the effects of concentration, use of template Span 60 (sorbitan mono stearate), conventional and freeze drying methods on zinc borate produced from zinc nitrate and borax were investigated. The wet zinc borate cakes were dried by conventional and freeze drying methods and the products were characterized by Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction, Scanning Electron Microscopy (SEM), thermal gravimetric (TG) analysis and particle size analysis.

Materials and methods

Materials

Borax decahydrate (99.9%) obtained from Eti Maden Inc. and zinc nitrate hexahydrate (99.9%) from Fluka,

Table 1. Experimental conditions of reaction between 50 cm^3 borax decahydrate solution and 50 cm^3 zinc nitrate hexahydrate solution and the sample codes of the products.

| Sample code | Drying method | Temperature (°C) | | Mixing time (hr) | Mixing rate (rpm) | Concentration (mol dm^{-3}) | | |
		Preparation	Drying			Zinc nitrate	Borax	Span 60 (g)
Zinc borate	Conventional	70	110	4	900	1	1	0
Zinc borate with Span 60	Conventional	70	110	2	900	1	1	1
Freeze dried zinc borate	Freeze drying	70	−51	4	900	1	1	0
Nano zinc borate	Conventional	25	25	2	600	0.1	0.1	0
Nano zinc borate with Span 60	Conventional	25	25	2	600	0.1	0.1	0.0086

Span 60 from Sigma Aldrich, ethanol (99.8%) from Riedel were used in the experiments. De-ionized water was used in all experiments.

Production of zinc borate and zinc borate with Span 60 from borax decahydrate and zinc nitrate hexahydrate by conventional drying

Zinc borate was produced by mixing 50 cm^3 of 1.0 mol dm^{-3} borax decahydrate and 50 cm^3 of 1.0 mol dm^{-3} zinc nitrate hexahydrate at 70 °C for 4 hours in Haake temperature controlled stainless steel reactor by mixing at 900 rpm rate. Zinc borate with Span 60 was obtained by adding 1 g Span 60 to the mixture of 50 cm^3, 1.0 mol dm^{-3} borax decahydrate and 50 cm^3, 1.0 mol dm^{-3} zinc nitrate hexahydrate at 70 °C for 2 hours in a glass reactor by mixing at 900 rpm rate. In order to remove the unreacted zinc nitrate and sodium borate decahydrate, the prepared precipitates were washed using de-ionized water. Subsequently, zinc borates were washed three times by ethanol to replace water. Conventional drying was achieved in an air circulating oven at 110 °C till constant weight was obtained.

Production of nano zinc borate and nano zinc borate with Span 60 by conventional drying

50 cm^3 of 0.1 mol dm^{-3} sodium borate solution was added instantly to 50 cm^3 of 0.1 mol dm^{-3} zinc nitrate solution to obtain a hydrosol and mixed at 600 rpm for 2 hours at ambient temperature of 25 °C. The experiments were repeated by adding 1 cm^3 of 0.002 mol dm^{-3} (corresponding to 0.0086 g) Span 60 to the mixture. Since the particles formed passed through the filter paper due to their small size, they were separated from the aqueous phase by centrifugation using Rotofix 32 centrifuge (Andreas Hettich GmbH, Tutlingen Germany) at 2000 rpm for 10 minutes, washed with ethanol and centrifuged again at 2000 rpm for 10 minutes. The obtained gelatinous precipitates were dried conventionally under vacuum at 10 kPa for 18 hours at 25 °C to get nanoparticles. Because the nanoparticles were in an agglomerated state they were ground in a porcelain mortar and pestle before the characterization.

Freeze drying of zinc borate

Zinc borate from 1 mol dm^3 solutions were freeze dried using Labconco Free Zone-4.5 freeze drier (Labconco Corparation, Kansas City, USA). Before freeze drying, 15 g of wet zinc borate sample was mixed with 50 ml of ethanol and then filtered. Partially dried zinc borate sample by ethanol placed in a vial of the equipment and it was frozen at −18 °C in a deep freeze. The frozen sample was placed in freeze drier and it was dried at −51 °C under vacuum at 0.020 mbar pressure for 14 hours. The codes and preparation conditions of the zinc borates are as shown in Table 1.

Characterization of the samples

Diborontrioxide (B$_2$O$_3$) and zinc oxide (ZnO) contents of zinc borate samples were determined by analytical titration using 0.1 N NaOH and 0.1 mol dm^{-3} EDTA, respectively. Erichrome Black T indicator for Zn titration by EDTA, methyl red for HCl titration and phenolphthalein for B(OH)$_3$ by NaOH were used as indicators.[24] Elemental analysis of zinc borate with Span 60 was performed by CHNS elemental analysis (Leco Corporation, St. Joseph MI, USA).

SEM images were taken with Philips XL30 SFEG (Philips XL30 SFEG, FEI Company, Oregon, USA) to examine the morphology of zinc borate particles. Conductive double sided tape was used to fix the particles to the specimen holder before sputtering them with a thin layer of gold. EDX analysis with the same instrument was made for nano zinc borate particles with and without Span 60.

X-Ray diffraction pattern was obtained using Philips Xpert-Pro X-ray diffractometer (Panalytical, Almelo, Netherlands). The incident CuK$_\alpha$ radiation at 45 kV and 40 mA with 0.154 nm wavelength was used in the analysis. The dried powders were examined using a 0.5-mm thick glass sample holder.

Table 2. ZnO, B_2O_3, and H_2O contents of conventional and freeze dried zinc borates.

Sample code	ZnO (%)	B_2O_3 (%)	B_2O_3/ZnO molar ratio	H_2O (%) From chemical analysis	From TGA
Zinc Borate	40.14	42.93	1.25	18.7	18.0
Zinc borate with Span 60	30.14	46.6	1.92	23.2	22.8
Freeze dried Zinc borate	38.8	41.5	1.25	19.7	17.7
Nano zinc borate	56.7	26.3	0.54	–	17.7
Nano zinc borate with Span 60	60.6	22.4	0.43	–	16.7

Fourier Transform Infrared Spectrometer Shimadzu 8601(Shimadzu, Kyoto, Japan) was used to determine functional groups of the products. Zinc borate-KBr pellets were prepared by mixing 4.0 mg of zinc borate and 196 mg of KBr in an agate mortar and pressing the mixture under 8 tons.

Thermal gravimetric (TG) analyses were carried out by using Shimadzu TGA-51 (Shimadzu Co. Kyoto Japan). Zinc borate samples (10–15 mg) were loaded into an alumina pan and heated from room temperature to 600 °C at 10 °C min^{-1} under N_2 flow of 40 cm^3 min^{-1}.
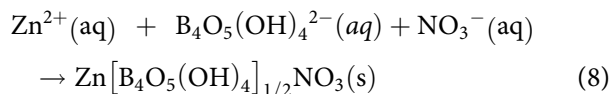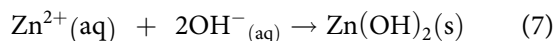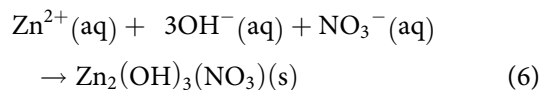
Particle size distribution of particles dispersed in water was determined either by Malvern Zetasizer 3000 (Malvern Panalytical, Malvern, UK) or Malvern Mastersizer 2000 (Malvern Pananalytical, Malvern, UK).

Results and discussion

The following reactions occur during zinc borate synthesis. Borax dissolves in aqueous phase according to Eq. (1) to form tetra borate anion $[B_4O_5(OH)_4]^{2-}$ and sodium cation 70 °C. In Eq. (2), zinc nitrate dissolves to produce zinc cations and nitrate anions. These are expected reactions based on literature data of borate and polyborate anions.[25,26] The formed polyborate anions and zinc cations precipitate when mixed together as shown in Eq. (3). There are various types of zinc borate species which can be produced by changing reaction parameters or molar ratio of reactants. After the precipitation, formed building blocks, $(Zn[B_4O_5(OH)_4])$, rearrange and produce the $Zn[B_3O_3(OH)_5]\cdot H_2O$ or $Zn[B_3O_3(OH)_5]$ as depicted in Eqs. (4) and (5), respectively. Further polymerization of these units results in sheets and networks of three dimensional structures.

$$Na_2B_4O_5(OH)_4 \cdot 8H_2O(s) \rightleftharpoons 2Na^+(aq) + B_4O_5(OH)_4^{2-}(aq) + 8H_2O \quad (1)$$

$$Zn(NO_3)_2 \cdot 6H_2O(s) \rightleftharpoons Zn^{2+}(aq) + 2NO_3^-(aq) + 6H_2O(l) \quad (2)$$

$$B_4O_5(OH)_4^{2-}(aq) + Zn^{2+}(aq) + H_2O(l) \rightarrow Zn[B_4O_5(OH)_4] \cdot H_2O(s) \quad (3)$$

$$Zn[B_4O_5(OH)_4] \cdot H_2O(s) + 2H_2O(l) \rightarrow Zn[B_3O_3(OH)_5] H_2O(s) + B(OH)_3(s) \quad (4)$$

$$Zn[B_3O_3(OH)_5] H_2O(s) \rightarrow Zn[B_3O_3(OH)_5](s) + H_2O(l) \quad (5)$$
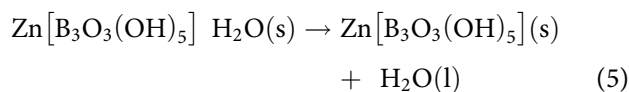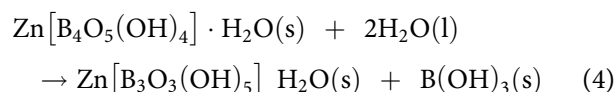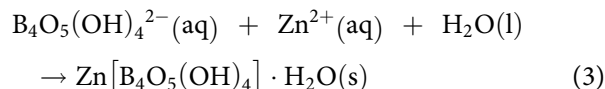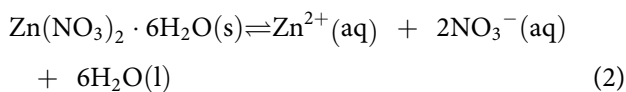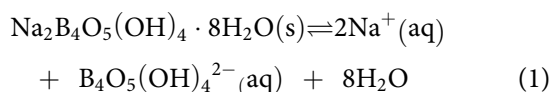
Other possible parallel reactions taking place in the reaction medium are shown in Eqs. (6)–(8).

$$Zn^{2+}(aq) + 3OH^-(aq) + NO_3^-(aq) \rightarrow Zn_2(OH)_3(NO_3)(s) \quad (6)$$

$$Zn^{2+}(aq) + 2OH^-_{(aq)} \rightarrow Zn(OH)_2(s) \quad (7)$$

$$Zn^{2+}(aq) + B_4O_5(OH)_4^{2-}(aq) + NO_3^-(aq) \rightarrow Zn[B_4O_5(OH)_4]_{1/2}NO_3(s) \quad (8)$$

As soon as borax and zinc nitrate solutions were mixed, a white precipitate was formed from borate anion and zinc cation in the mixture. Since zinc borate species is sparingly soluble in aqueous phase, supersaturation is exceeded immediately after mixing. In this reactive crystallization, nucleation, crystal growth on formed nuclei, and interaction of those formed crystals take place. Borax-zinc nitrate system includes also other dissolved ions, such as Na^+ and NO_3^- ions. The presence of those ions in equilibrium with crystals formed in the medium affects crystallization process. The crystals dissolve, reform, and transform to the different zinc borate species during long reaction periods.

The properties of zinc borates

The samples were analyzed by titration method and their compositions are shown in Table 2. The conventional and freeze dried zinc borate samples had B_2O_3/ZnO ratio of 1.25 and the sample with Span 60 had this ratio as 1.99. On the other hand, EDX analysis showed that nano zinc borate and nano zinc borate with Span 60 had B_2O_3/ZnO ratio as 0.54 and 0.43 respectively.
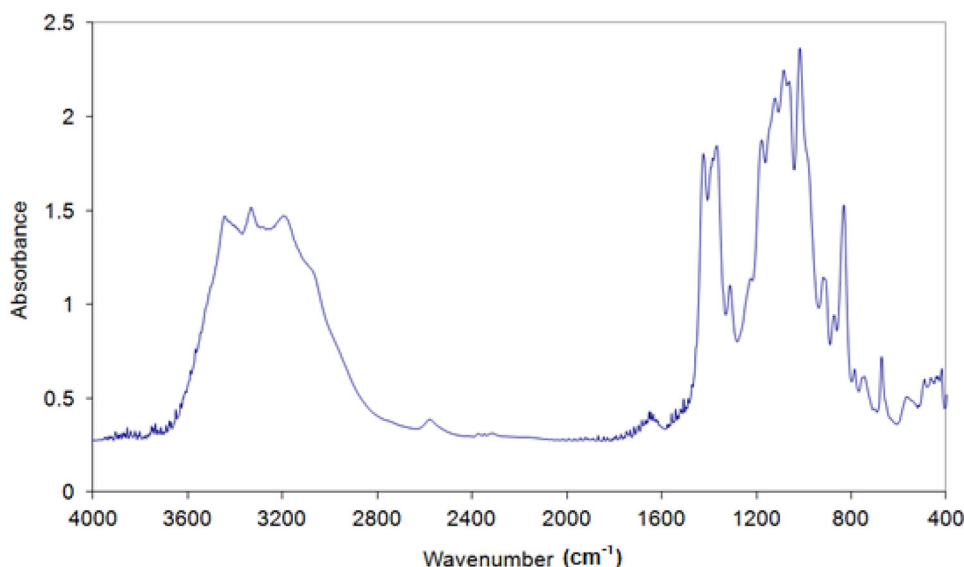
Figure 1. FTIR spectrum of zinc borate produced in 4 h reaction time at 70 °C.

The conventional dried zinc borate had 18.08% water as indicated by the material balance of chemical analysis. The elemental analysis (CHNS) of conventional dried zinc borate with Span 60 showed that both carbon (1.91%) and hydrogen (2.89%) elements were present in the product. Neither N nor S element existed in the sample. The presence of carbon element for the sample arises from the Span 60 and the 1.91% C demonstrates that this sample contains 2.85% Span 60 since 1 gram of this surfactant includes 66.9% C, 10.6% H and 22% O elements by weight.[27] H element introduced by Span 60 should be 0.31% and 2.58% H should be present in zinc borate as water. This corresponds 23.2% H_2O in zinc borate fraction.

While TG analysis is a dynamic method, elemental analysis is based on the analysis of combustion products of the sample that was burned at 900 °C. For this reason TG analysis indicated lower water content than elemental analysis for all samples.

Characterization of zinc borates

FTIR
The FTIR spectrum of conventionally dried zinc borate is shown in Figure 1. The peaks observed between 1450–1300 cm^{-1} and 1200–1000 cm^{-1} are related to asymmetric stretching vibrations of trihedral borate ($B_{(3)}$-O), and tetrahedral borate ($B_{(4)}$-O) groups, respectively. The other peaks between 960–740 cm^{-1} belong to symmetric stretching vibrations of ($B_{(3)}$-O) and($B_{(4)}$-O) groups.[28] Moreover, the peaks between 3200–3600 cm^{-1} and the at 2590 cm^{-1} belong to stretching vibrations of OH groups and stretching vibrations due to hydrogen bonding in the structure

of zinc borate. This product includes interstitial water in its structure since there is H-O-H bending vibration at 1650 cm^{-1} wavenumber.

The FTIR spectrum of zinc borate prepared via precipitation technique in the presence of Span 60 is shown in Figure 2 and it exhibits both the specific peaks of the surfactant and the zinc borate having seven moles of crystal water ($2ZnO \cdot 3B_2O_3 \cdot 7H_2O$). The characteristic peaks of zinc borate are assigned referring the literature.[29] The band at 1047 cm^{-1} is the stretching of $B_{(4)}$-O, and the peaks between 745–658 cm^{-1} are belonging to out of plane bending mode of $B_{(3)}$-O. The presence of CH_2 stretching peaks of Span 60 at 2850, 2920 cm^{-1} reveals that small amount of Span 60 was present in the sample.

Zinc borate, which was produced from borax and zinc nitrate in stainless steel reactor using 900 rpm stirring rate, was dried by freeze drying to observe the drying effects. Figure 3 shows the FTIR spectrum of freeze dried zinc borate produced from borax and zinc nitrate. The characteristic peaks defined previously in Figure 1 were aligned with FTIR spectrum of freeze dried sample. Those characteristic peaks reveal the presence of zinc borate type of $ZnO \cdot B_2O_3 \cdot 2H_2O$.

The FTIR spectra of the nano zinc borate and nano zinc borate with Span 60 are very similar to each other as seen in Figure 4. There is a broad peak at 3358 cm^{-1} due to hydrogen-bonded O-H group vibrations. Asymmetric $B_{(3)}$-O vibrations were observed at 1383 cm^{-1} and at 1350 cm^{-1}. H-O-H bending vibration was detected at 1624 cm^{-1}. At 1014 cm^{-1} a peak for symmetric $B_{(3)}$-O vibration was present. Besides it, out of plane bending vibration of $B_{(3)}$-O gave a small peak at 694 cm^{-1} .
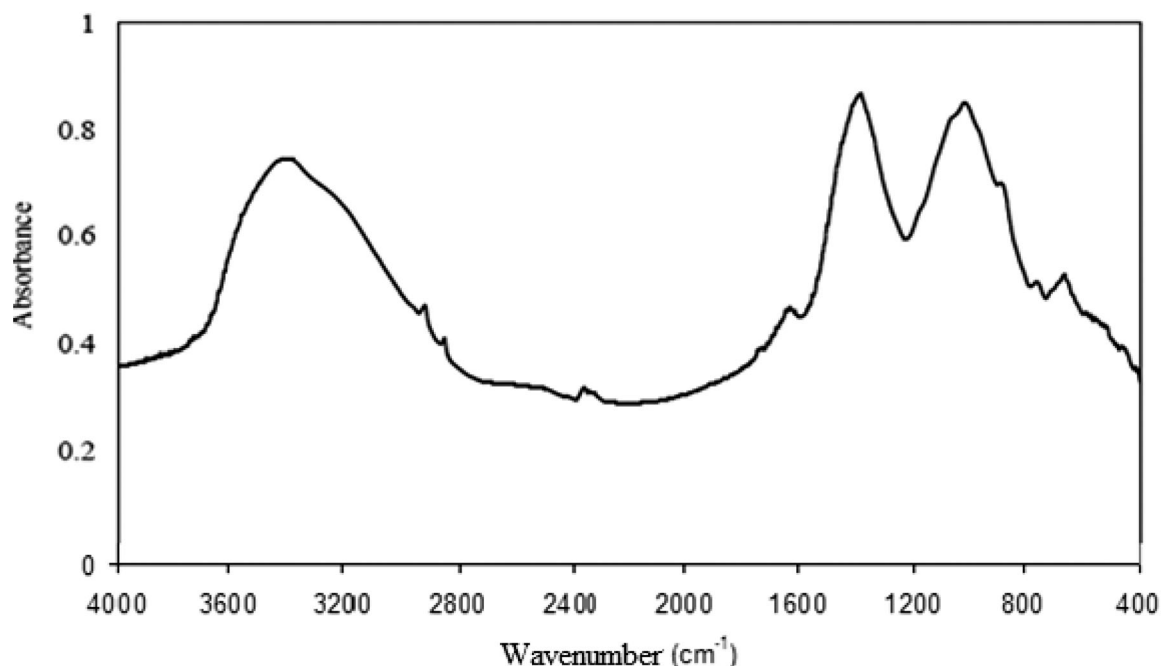
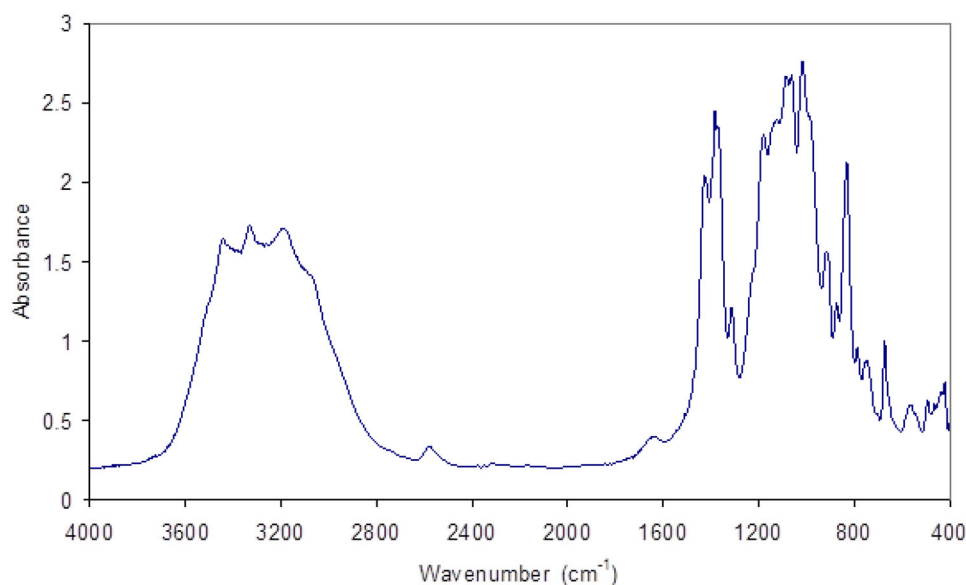**Figure 2.** FTIR spectrum of zinc borate with Span 60.

Figure 3. FTIR spectrum of freeze dried zinc borate.

X-ray diffraction. The presence of peaks with high intensity in x-ray diffraction diagram of conventional dried zinc borate in Figure 5 shows that the product has a crystalline structure. The major peaks in XRD patterns of zinc borate at 10.22°, 20.75°, 28.20°, and 33.18° 2θ values are different than the well-known zinc borates, such as $2ZnO·3B_2O_3·7H_2O$, $2ZnO·3B_2O_3·3H_2O$[30] and $4ZnO·B_2O_3·H_2O$.[31] These peaks coincided with the x-ray diffraction diagram of $ZnO·B_2O_3·2H_2O$ which was reported first time by Gönen.[24]

Figure 6 shows the XRD pattern of the zinc borate produced via precipitation technique with Span 60 in aqueous medium. The presence of peaks with high intensity shows that product has a crystalline structure. The major peaks in XRD pattern of zinc borate are observed at 13.07°, 17.58°, 19.66°, 25.54°, 26.38°, 27.04°, 29.42° and 36.97° 2θ values. When these values were compared to those in the JPDS database, it was implied that the specific peaks were consistent with those of $Zn(B_3O_3(OH)_5)·H_2O$. In literature this type of zinc borate was also defined as $2ZnO·3B_2O_3·7H_2O$.[1] Moreover, no other crystalline phases can be detected, which is indicative of pure $2ZnO·3B_2O_3·7H_2O$ obtained under the current
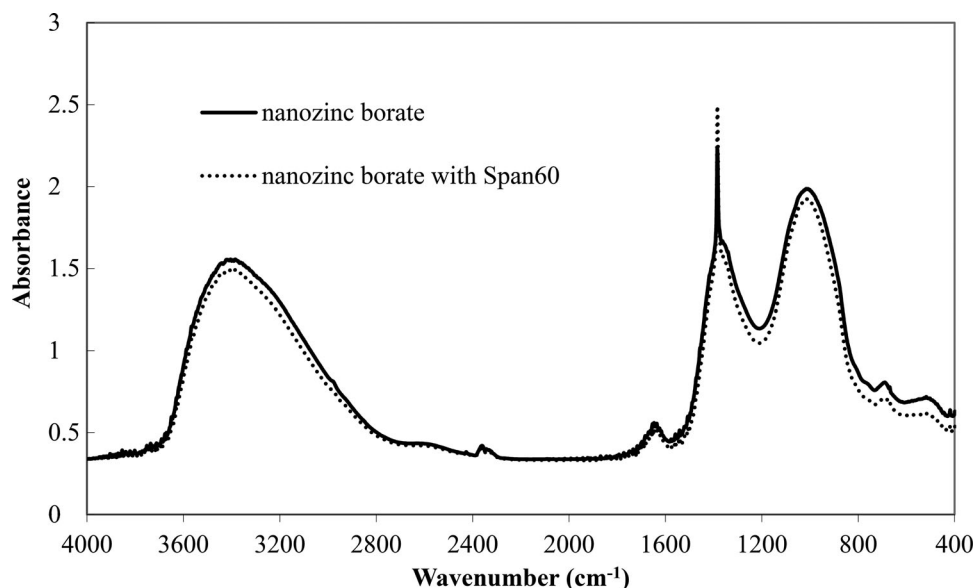
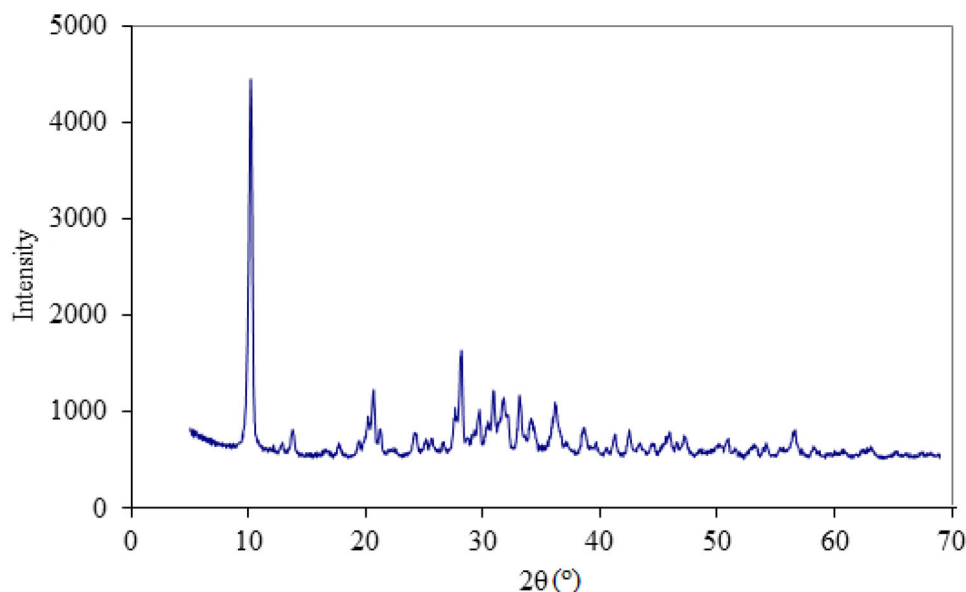**Figure 4.** FTIR spectra of nano zinc borate and nano zinc borate with Span 60.

Figure 5. XRD pattern of conventionally dried zinc borate.

synthetic conditions. All the diffraction peaks can be perfectly indexed to $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$ with JPDS PDF File Number 721789.

Only a broad peak is observed at 2θ value of $28°$ in X-ray diffraction diagram of the nano zinc borate and nano zinc borate with Span 60 samples in Figure 7. The small size of the crystals formed caused broadening of the diffraction lines.

Thermal gravimetric analysis. TG curves of conventionally dried zinc borate, zinc borate with Span 60 and freeze dried zinc borate are shown in n Figure 8. Conventionally dried zinc borate decomposed in one step between 160–400 °C temperature ranges. The

total mass loss occurred as 18.0% due to removal of water. It corresponds to the H_2O content of $ZnO \cdot B_2O_3 \cdot 2H_2O$ and could be compared to the calculated water content value of 19.25%. It can be inferred the zinc borate sample has the structure of $ZnO \cdot B_2O_3 \cdot 2H_2O$ based on H_2O content.

TG curve of zinc borate with Span 60 in Figure 8 indicates that mass loss of the sample is 22.08% due to the removal of water of crystallization.

Figure 8 also represents TG curve of the zinc borate produced by freeze drying. The total mass loss occurred as 17.7% % when the sample was heated from ambient temperature to 600 °C. Zinc borate sample started to lose mass at around 180 °C and very
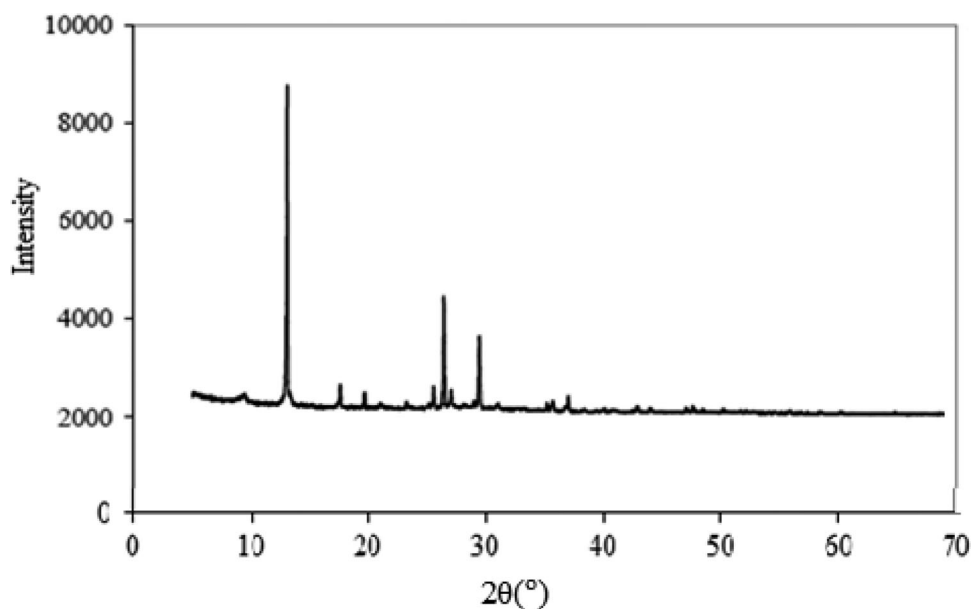
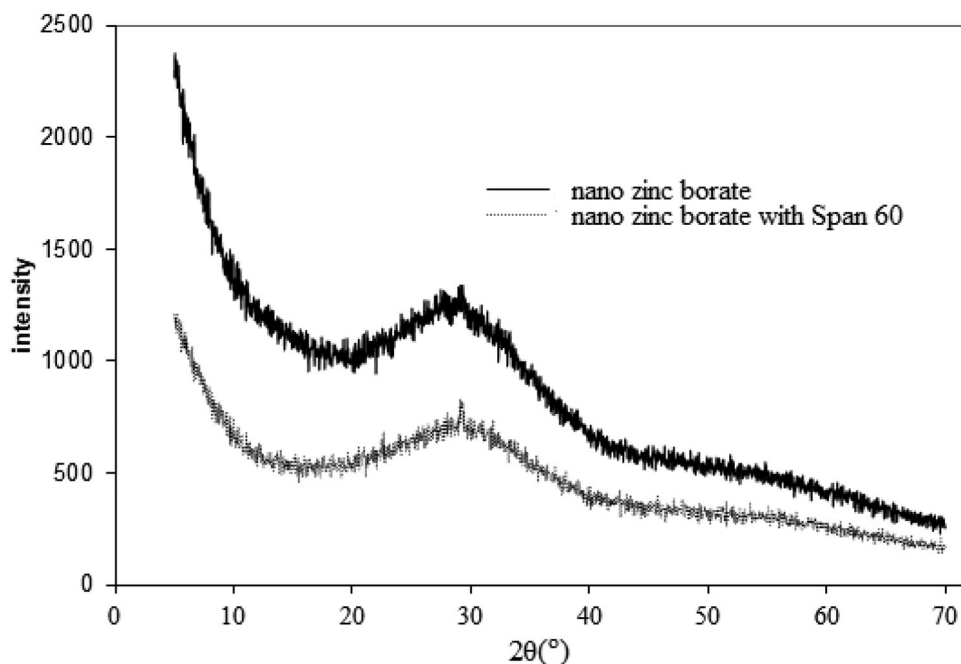**Figure 6.** X-ray diffraction diagram of zinc borate with Span 60.

Figure 7. X-ray diffraction diagrams of nano zinc borate and nano zinc borate with Span 60.

little mass loss was observed between 400 °C and 600 °C. The mass loss of 17.7% is due to the condensation of hydroxyl groups in that temperature range corresponds to water content of $ZnO \cdot B_2O_3 \cdot 2H_2O$ and can be compared to the calculated water content value of 19.25%. B_2O_3/ZnO molar ratio for zinc borate was calculated as 1.2 from analytical titration results as given in Table 2. This result supported the zinc borate structure of $ZnO \cdot B_2O_3 \cdot 2H_2O$.

The water content of the samples in this study is reported in Table 2. Conventional and freeze dried zinc borates had nearly the same water content (18.7%, and 19.7% respectively) as indicated by TG analysis. However, zinc borate with Span 60 had higher water content (22.8%).

The important points in the TG curves of the samples are shown in Table 3. The dehydration onset temperature (100 °C) of zinc borate with Span 60 was lower than that (180 °C and 200 °C) of the conventionally and freeze dried zinc borates respectively.

TG curves of nano zinc borate and nano zinc borate with Span 60 are almost identical as shown in
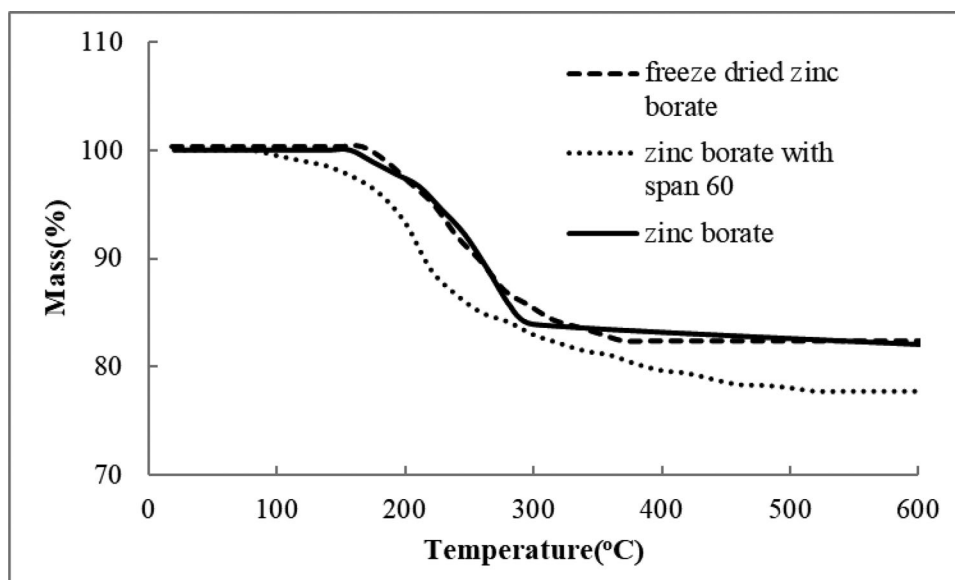
Figure 8. TGA curve of conventionally dried zinc borate, zinc borate with Span 60 and freeze dried zinc borate.

Table 3. The important points from TG curves of the samples.

Sample code	Dehydration onset (98% mass) temperature(°C)	Temperature (°C) at 90% mass	Mass (%) at 600 °C
Zinc borate	180	265	82.3
Zinc borate with Span 60	100	230	77.7
Freeze dried zinc borate	200	260	82.3
Nano zinc borate	90	158	82.3
Nano zinc borate with Span 60	100	172	83.3

Figure 9. The temperature of onset of mass loss was 90 °C and 100 °C since they were conventionally dried at 25 °C. The presence of gel water in wet nano zinc borates required higher temperatures than 25 °C that was used in conventional drying. The total mass loss up to 600 °C was 17.7% and 16.7% for nano zinc borate and nano zinc borate with Span 60 which corresponded to the water content of the samples.

Alp et al.[32] showed that $Zn[B_3O_3(OH)_5]\cdot H_2O$ and $Zn[B_3O_4(OH)_3]$ dehydrated with 24% and 12% mass losses due to evaporation of the water initially present and formed by the condensation of B-OH groups mainly at around 129 °C and 320 °C, respectively. Parallel to dehydration, a negligible amount of boric acid was sublimed from both zinc borates on heating up to 250 °C. In the present study, the onset temperature of the mass loss and the total mass loss % were different than either of the $Zn[B_3O_3(OH)_5]\cdot H_2O$ and $Zn[B_3O_4(OH)_3]$ as shown in Table 3. That set out the formation of different zinc borates other than $Zn[B_3O_3(OH)_5]\cdot H_2O$ and $Zn[B_3O_4(OH)_3]$. The mass loss around 19.0% of the zinc borate, freeze dried zinc borate, nano zinc borate and nano zinc borate due to the removal of water corresponds to the H_2O content of $ZnO\cdot B_2O_3\cdot 2H_2O$ and could be compared to its calculated water content value of 19.25%. It can be

inferred that the four zinc borate samples have the structure of $ZnO\cdot B_2O_3\cdot 2H_2O$ based on their H_2O content.[24]

Zinc borate, zinc borate with Span 60 and freeze dried were thermally more stable than nano zinc borate and nano zinc borate with Span 60 since they had 10% mass loss at 230–260 °C and 158–172 °C respectively.

Particle morphology. The particles are in the form flakes having average dimensions of $(2.1\pm 0.5)\times (2.5\pm 0.5)\times (1.3\pm 0.2)$ μm as seen in SEM micrograph of conventionally dried zinc borate in Figure 10.

SEM micrographs of the crystals obtained by using Span 60 are shown in Figure 11. Micron sized prismatic crystals as well as lamellar-like crystals are observed in the microphotographs. Closer inspection reveals that the lamellar-like crystals in 20–60 μm size are the conglomeration of planar particles with $(11\pm 1)\times (3.5\pm 0.1)\times (0.5\pm 0.1)$ μm dimensions.

SEM images of freeze dried zinc borate at different magnifications are shown in Figure 12. Particles have a plate-like morphology with $(0.5\pm 0.1)\times (1.3\pm 0.1)\times (0.028\pm 0.01)$ μm dimensions. Since the water is frozen in the bulk of product, particles are enforced to orient in certain place (layer by layer). After the removal of water
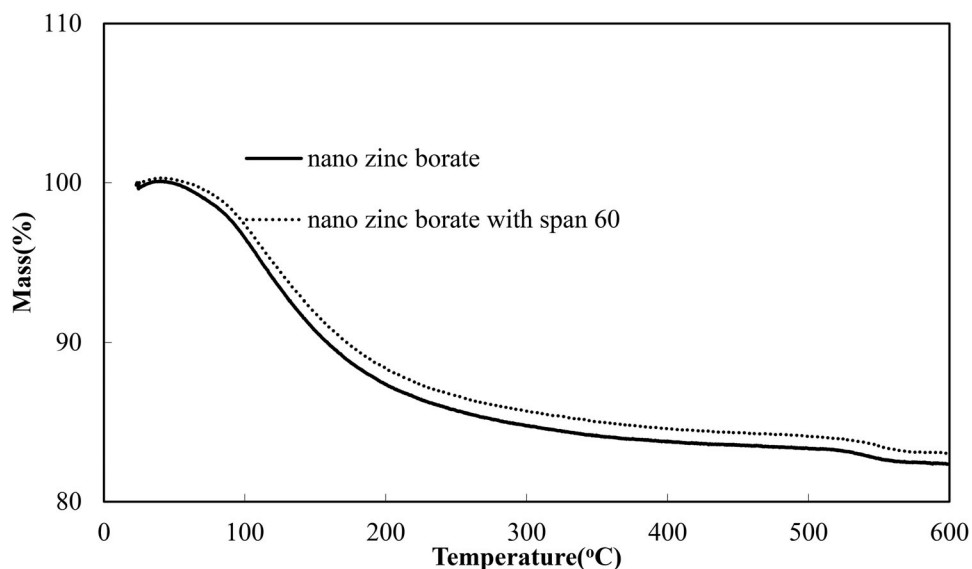
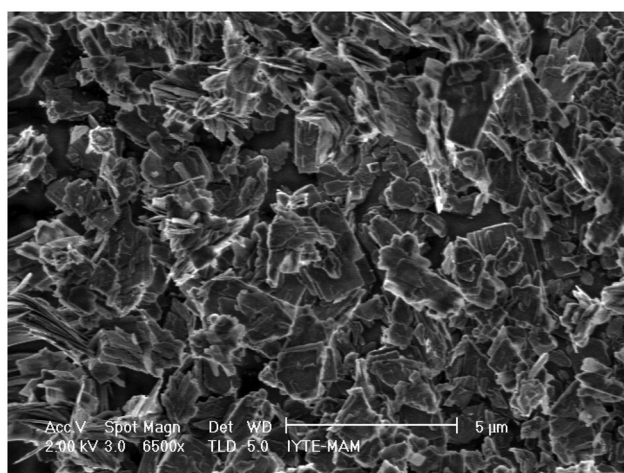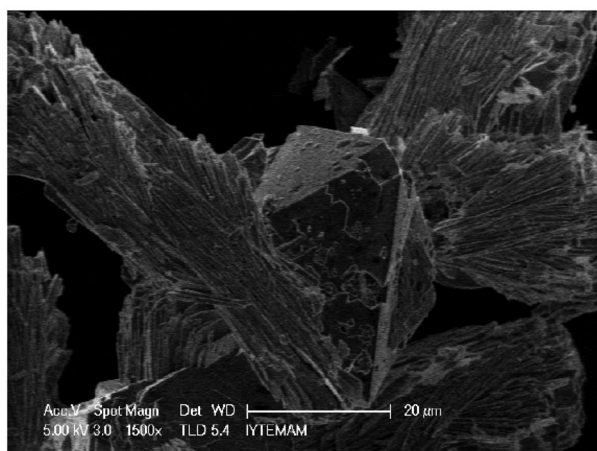Figure 9. TG curves of nano zinc borate and nano zinc borate with Span 60.

Figure 10. SEM microphotograph of conventionally dried zinc borate at 6500× magnification.

from solid to gas phase by sublimation, particles are obtained as single flakes with (28 ± 10) nm thickness.

The SEM micrographs of the dried nano zinc borate samples are shown in Figure 13. The dried powders consisted of agglomerates of primary particles of (46 ± 9) nm and (40 ± 3) nm for nano zinc borate and nano zinc borate with Span 60. The particles were attracted to each other due to capillary forces during drying. Water in the wet samples was replaced with ethanol which had a lower surface tension to decrease the attractive forces between the particles due to capillarity. However they were also agglomerated even by the drying of the ethanol washed hydrogel.[13]
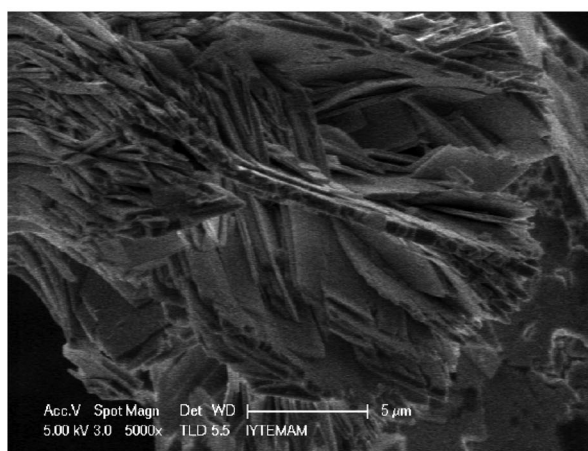
(a)   (b)

Figure 11. SEM images of zinc borate produced in the presence of Span 60 (a) 1500×, (b) 5000× magnifications.
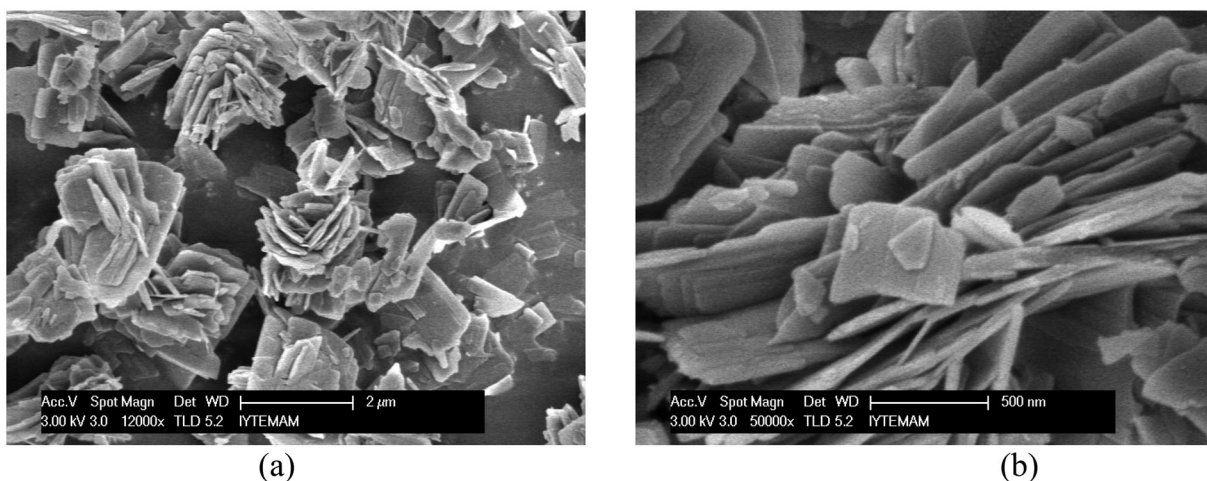
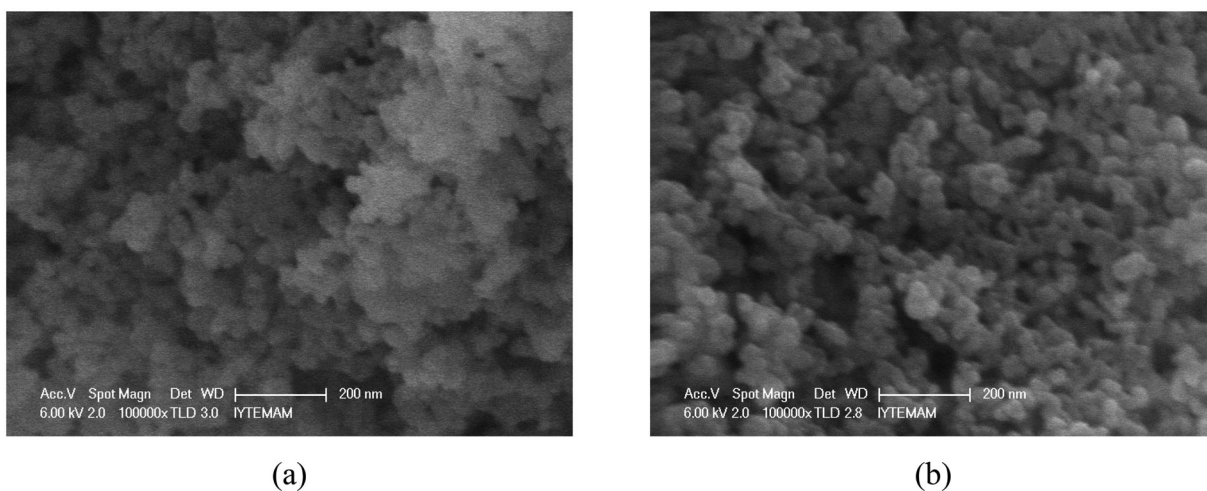**Figure 12.** SEM microphotograph of freeze dried zinc borate (a) 12,000×, (b) 50,000× magnification.

Figure 13. SEM micrographs of nano zinc borate and nano zinc borate with Span 60.

Particle size distribution. Particle size distribution of zinc borate sample has a bimodal distribution as shown in Figure 14. Zinc borate produced at the end of 4 h reaction time has particles in two ranges; the first group has an average particle size of 460 nm whereas second group has mean particle size of 1.9 μm.

Particle size distribution of zinc borate produced in the presence of Span 60 determined by Mastersizer 2000 is indicated in Figure 15. The distribution had two small intensity peak being maximum 0.5 μm and 3 μm and one high intensity peak at 27 μm. The mastersizer assumes particles are spherical and report the results accordingly. The three peaks could be due to three different dimensions of the particles. Each dimension is assumed as spheres by the instrument.

Nano zinc borates particle size distribution is shown in Figure 16. 6.6% of the particles had size of (33 ± 5) nm, 11% of the particles had mean size of (31 ± 15) nm and 82% of the particles had size of (336 ± 132) nm. Nano zinc borate with Span 60 was mono disperse. 100% of the particles had size of (236 ± 20) nm.
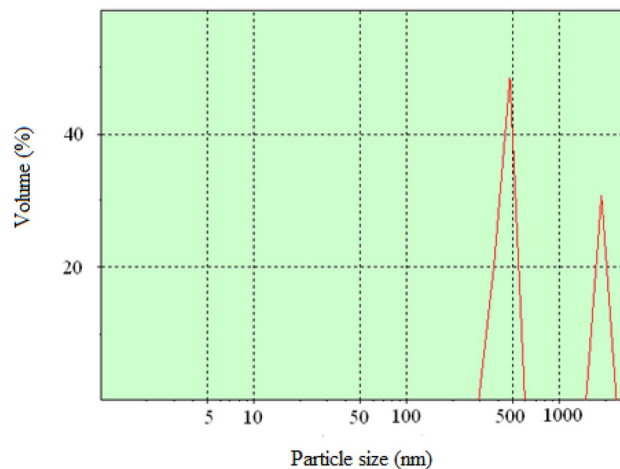

Figure 14. Particle size distribution of conventional dried zinc borate (Malvern Zetasizer 3000 HSA).
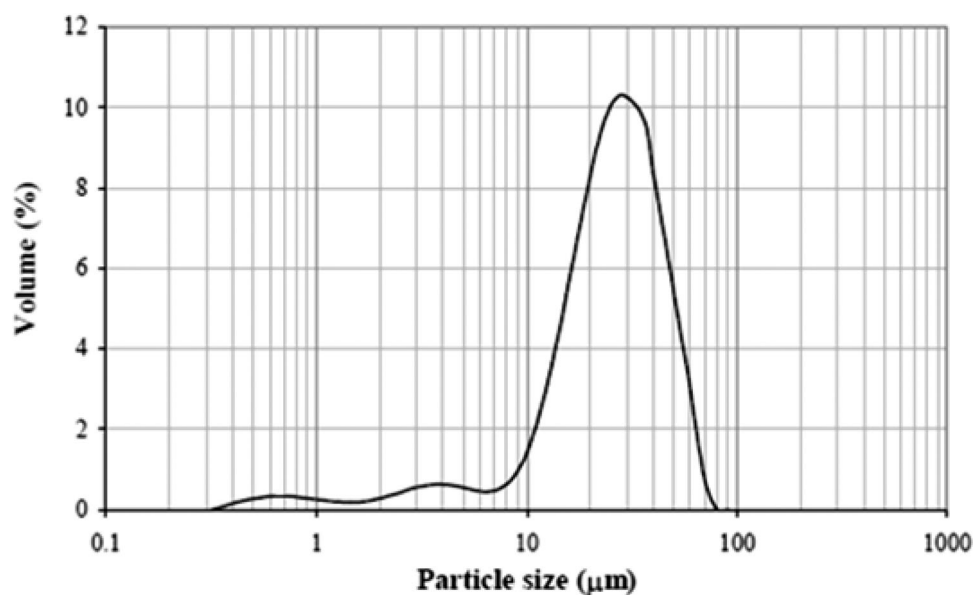
Figure 15. Particle size distribution of zinc borate with Span 60 (Malvern Mastersizer 2000).
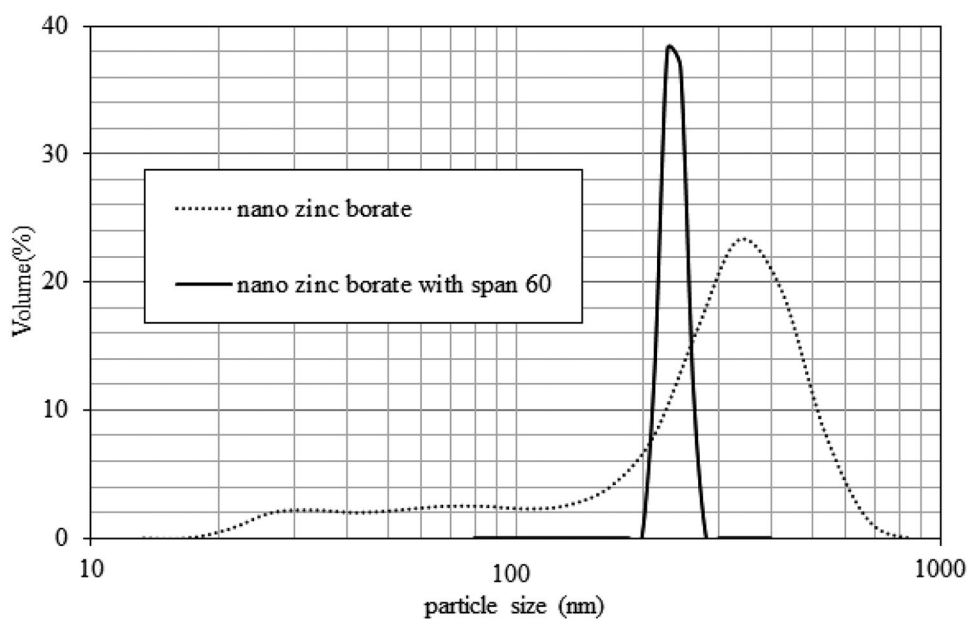

Figure 16. Particle size distribution of nano zinc borate and zinc borate with Span 60 (Malvern Mastersizer 2000).

The size of the particles obtained from SEM micrographs and zetasizer is tabulated in Table 4 to show that the particles were present as agglomerates in the aqueous phase. Both nano zinc borate particles and nano zinc borate particles with Span 60 were agglomerated when they were dispersed in aqueous solutions with a broad size distribution. While SEM micrographs showed that they had primary particles of (46 ± 9) nm and (40 ± 3) for nano zinc borate and Nano zinc borate with Span 60, their particle size in water was higher and had a broad range of distribution.

Zinc borates were obtained by precipitation method in the present study. Nucleation and growth are two consecutive processes in obtaining crystals by precipitation. Nano particles form by nucleation and they grow by subsequent addition of reactants from solution to their surfaces. In concentrated solutions the reactants are abundant to make the particles grow to large sizes. However in dilute solutions the growth stops due to scarcity of the reactants.

The shape of the crystals obtained by precipitation can be controlled by adding templates. In the case of zinc borate prepared in the presence of Span 60, selected surfaces of the particles were covered by Span 60 allowing them to grow in the surfaces not covered with Span 60. Thus the morphology of the particles,

Table 4. Particle size of the zinc borates.

Sample	SEM			Zetasizer		
	Width (μm)	Length (μm)	Thickness (μm)	1st peak (μm)	2nd peak (μm)	3rd peak (μm)
Zinc borate	2.1 ± 0.5	2.5 ± 0.5	1.3 ± 0.2	0.460	1.9	–
Zinc borate with Span 60	11 ± 1	3.5 ± 0.1	0.5 ± 0.1	0.5	3	27
	Planar particles were agglomerated into lamellar like crystals in 20 to 60 μm size					
Freeze dried zinc borate	0.5 ± 0.1	1.3 ± 0.1	0.028 ± 0.01	–	–	–
Nano zinc borate	0.046 ± 0.009	–	–	0.033 ± 0.005	0.031 ± 15	0.336 ± 0.132
Nano zinc borate with Span 60	0.040 ± 0.003	–	–	0.236 ± 0.020		

the boric acid to zinc oxide ratio and the crystal structure of the zinc borate were different compared to the case without Span 60. The particle size of the sample was larger for zinc borate with Span 60 indicating the sticking of primary particles during conventional drying.

The crystals obtained are not very stable in size after precipitation. They undergo changes in particle size during drying Particles were attracted and adhere to each other when water was removed by conventional drying due to surface tension of water (72 mN m^{-1} at 25 °C). Water was attempted to be replaced by ethanol which had a lower surface tension (22 mN m^{-1} at 25 °C) in the present study. However the total removal of water was only possible by conventional drying at 110 °C. Thus the adhesion of the particles to each other causing agglomeration was observed in conventional drying since liquid water with high surface tension pulled the particles together during evaporation process. The zinc borate was freeze dried to avoid the sticking of the particles. During evacuation process the ethanol phase was completely removed by evaporation of the liquid phase since the temperature of the freeze drying (−51 °C) was much higher than the freezing point of ethanol (−113 °C). On the other hand, water was in ice form and it sublimed directly to vapor phase avoiding the pulling of the particles due to surface tension. Thus single particles were obtained since they did not stick to each other. Lamellar crystals having thickness (28 ± 10) nm and which did not stick to each other were obtained by freeze drying of zinc borates obtained from 1 mol dm^3 solutions. TG analysis of conventionally dried and freeze dried samples indicated nearly the same amount of water at the end of the drying.

Zinc borate from zinc nitrate and borate decahydrate were obtained by mixing 1 mol dm^{-3} solutions had different composition, crystal structure and particle geometry when Span 60 was added as template. The high concentration of the solutions led to the growth of the particles and thus micron sized agglomerated particles were obtained.

Nano particles of zinc borate formed when dilute solutions with 0.1 mol dm^{-3} concentration were used. The nano particles that were obtained in aqueous phase were attracted to each other due to capillary forces during drying. Water in the wet samples was attempted to be replaced with ethanol which has a lower surface tension to decrease the attractive forces between the particles due to capillarity. However nano particles also agglomerated even drying of the ethanol washed hydrogel. Since silver,[17] copper,[18] alumina,[21] B$_2$O$_3$ precursor[22] and polycaprolactone[23] nanoparticles were obtained successfully by freeze drying, freeze drying of the zinc borate nano particles would allow drying without agglomeration of nano zinc borate particles.

Even if the same equilibrium state is obtained in conventional and freeze drying, the rate of drying is very slow in freeze drying since the vapor pressure of ice is very low compared to liquid water. Thus, even if the slow drying is a disadvantage of freeze drying, it's worth to use it in drying zinc borate crystals. The formation of independent particles is only possible by this method.

Conclusion

Composition, crystal structure and particle morphology of zinc borate produced from zinc nitrate and borax decahydrate could be controlled by solution concentration, template addition and drying by conventional and freeze drying. The B$_2$O$_3$/ZnO ratio was 1.25 for conventional and freeze dried zinc borate and they had nearly the same water content (18.7%, and 19.7% respectively) as indicated by TG analysis. While dehydration onset temperature was 180 °C for conventionally dried sample, it was 200 °C for freeze dried sample.

Zinc borate with Span 60 had a different B$_2$O$_3$/ZnO ratio 1.92 and its water content was 23.2 and 22.8% by chemical analysis and TG analysis respectively. Its dehydration onset temperature (100 °C) was also lower. Nano zinc borate and nano zinc borate

with Span 60 from dilute solutions had lower B_2O_3/ZnO ratio 0.54 and 0.43 than that of zinc borate from concentrated solutions. They contained 17.7% and 16.7% water, respectively, and their dehydration onset temperature were 90 °C and 100 °C since they were dried at 25 °C under vacuum.

$ZnO \cdot B_2O_3 \cdot 2H_2O$ and $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$ were present respectively in conventionally dried zinc borate and in conventionally dried zinc borate with Span 60. Nano zinc borate and nano zinc borate with Span 60 samples were not crystalline as indicated by their x-ray diffraction diagrams.

The use of higher solution concentration (1 mol dm^{-3}) leads to the growth of the particles and thus micron sized agglomerated particles were obtained if conventional drying was applied. Lamellar crystals having thickness (28 ± 10) nm which did not stick to each other were obtained by freeze drying of zinc borates form 1 mol dm^3 concentrated solutions. The synthesis of Nano sized primary particles with (46 ± 9) nm and (40 ± 3) nm for cases with and without Span 60 was achieved using the dilute initial solution of 0.1 mol dm^{-3}. However, the nanoparticles of zinc borate adhered to each other during conventional drying process. When they were dispersed in water they were present as agglomerates with broad size distribution. A freely flowing nano powder could only be obtained by freeze drying of zinc borates from dilute solutions.

The equilibrium and kinetics of freeze drying of the micro and nano particles of zinc borates will be studied in future work.

Disclosure of interest statement

There is no conflict of interest with anyone about this paper.

Funding

References

[1] 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*, 2367–2371. DOI: 10.1021/ie0610243.

[2] Gönen, M.; Balköse, D.; Ülkü, S. Supercritical Ethanol Drying of Zinc Borates of $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$ and $ZnO \cdot B_2O_3 \cdot 2H_2O$. *The Journal of Supercritical Fluids* **2011**, *59*, 43–52. DOI: 10.1016/j.supflu.2011.08.004.

[3] Gönen, M.; Balköse, D.; Gupta, R. B.; Ülkü, S. Supercritical Carbon Dioxide Drying of Methanol − Zinc Borate Mixtures. *Ind. Eng. Chem. Res.* **2009**, *48*, 6869–6876. DOI: 10.1021/ie9003046.

[4] Acarali, N.-B.; Tugrul, N.; Derun, E.-M.; Piskin, S. Production and Characterization of Hydrophobic Zinc Borate by Using Palm Oil. *Int. J. Miner. Metall. Mater.* **2013**, *20*, 1081–1088. DOI: 10.1007/s12613-013-0837-x.

[5] Acarali, N. B.; Ozturk, E.; Bardakci, M.; Piskin, M. B.; Tugrul, N. Nurcan Tugrul N. Zinc Borate Production with Boron Mineral Source: Effect of Process Parameters on Yield and Hydrophobicity. *Gospodarka Surowcami Mineralnymi/Mineral Resources Management* **2015**, *31*, 95–110. DOI: 10.1515/gospo-2015-0040.

[6] Akgul, O.; Acarali, N.-B.; Tugrul, N.; Derun, E.-M.; Piskin, S. X-Ray, Thermal, FT-IR and Morphological Studies of Zinc Borate in Presence of Boric Acid Synthesized by Ulexite. *Period. Mineral.* **2014**, *83*, 77–88. DOI: 10.2451/2014PM0005.

[7] Schubert, D. M. Hydrated Zinc Borates and Their Industrial Use. *Molecules (Basel, Switzerland).* **2019**, *24*, 2419. DOI: 10.3390/molecules24132419.

[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 Nanoplatelets. *Colloids Surf, A.* **2008**, *312*, 99–103. DOI: 10.1016/j.colsurfa.2007.06.029.

[9] Zheng, Y.; Tian, Y.; Ma, H.; Qu, Y.; Wang, Z.; An, D.; Guan, S.; Gao, X. Synthesis and Performance Study of Zinc Borate Nanowhiskers. *Colloids Surf, A.* **2009**, *339*, 178–184. DOI: 10.1016/j.colsurfa.2009.02.018.

[10] Shi, X.; Xiao, Y.; Yuan, L.; Sun, J. Hydrothermal Synthesis and Characterizations of 2D and 3D $4ZnO \cdot B_2O_3 \cdot H_2O$ Nano/Microstructures with Different Morphologies. *Powder Technol.* **2009**, *189*, 462–465. DOI: 10.1016/j.powtec.2008.07.007.

[11] Savrik, S.-A.; Balkose, D.; Ülkü, S. Synthesis of Zinc Borate by Inverse Emulsion Technique for Lubrication. *J. Therm. Anal. Calorim.* **2011**, *104*, 605–612. DOI: 10.1007/s10973-010-1159-0.

[12] Ting, C.; Cheng, D. J.; Shuo, W. L.; Gang, F. Preparation and Characterization of Nano-Zinc Borate by a New Method. *J. Mater. Process. Technol.* **2009**, *209*, 4076–4079. DOI: 10.1016/j.jmatprotec.2008.09.029.

[13] Savrik, S. A.; Alp, B.; Ustun, F.; Balköse, D. Nano Zinc Borate as a Lubricant Additive. *J. Turkish Chem. Soc. A Chem.* **2017**, *5*, 45–52. DOI: 10.18596/jotcsa.370763.

[14] Abdelwahed, W.; Degobert, G.; Stainmesse, S.; Fessi, H. Freeze-Drying of Nanoparticles: Formulation, Process and Storage Considerations. *Adv. Drug Deliv. Rev.* **2006**, *58*, 1688–1713. DOI: 10.1016/j.addr.2006.09.017.

[15] Chen, G.; Wang, W. Role of Freeze Drying in Nanotechnology. *Dry. Technol.* **2007**, *25*, 29–35. DOI: 10.1080/07373930601161179.

[16] Mi, S.; Liu, Z. Q.; Luo, C.; Cai, L.; Zhang, Z. Z.; Li, L. Q. A Review on Preparing New Energy Ultrafine Powder Materials by Freeze-Drying. *Dry. Technol.* **2020**, *38*, 1544–1564. DOI: 10.1080/07373937.2019.1651733.

[17] Wei, Z. S.; Jun, L.; Hai, X. C. Preparation of Silver Nanopowder by Freeze-Drying Procedure. *Dry. Technol.* **2009**, *27*, 529–533. DOI: 10.1080/07373930802715278.

[18] Peng, R.; Guo, J.; Han, S.; Zeng, Q.; Cao, W.; Du, H. Tribological Performance of Freeze-Drying Nano-Copper Particle as Additive of Paroline Oil. *Mater. Res. Express.* **2020**, *7*, 025028. https://iopscience.iop.org/article/10.1088/2053-1591/ab726c. DOI: 10.1088/2053-1591/ab726c.

[19] Tachiwaki, T.; Sugimoto, J.; Ito, T.; Hiraki, A. Characterization of Freeze-Dried Powders Prepared by Alkoxide Route for YBCO Superconductors. *Appl. Surf. Sci.* **1996**, *100–101*, 272–276. DOI: 10.1088/0953-2048/4/11/009.

[20] Zeng, W.; Rabelo, A. A.; Tomasi, R. Synthesis of Al_2O_3 Nanopowder by Sol-Freeze Drying Method. *Key Eng. Mater.* **2001**, *189*, 16–20.

[21] Tallón, C.; Moreno, R.; Nieto, M. I. Synthesis of γ-Al_2O_3 Nanopowders by Freeze-Drying. *Mater. Res. Bull.* **2006**, *41*, 1520–1529. DOI: 10.1016/j.materresbull.2006.01.021.

[22] Bovone, G.; Kawale, S.; Bernini, C.; Siri, A. S.; Vignolo, M. Freeze Drying Technique to Prepare Doped Nanosized B Powder. *Dry. Technol.* **2016**, *34*, 923–929. DOI: 10.1080/07373937.2015.1086783.

[23] Choi, M. J.; Briançon, S.; Andrieu, J.; Min, S.-G.; Fessi, H. Effect of Freeze-Drying Process Conditions on the Stability of Nanoparticles. *Dry. Technol.* **2004**, *22*, 335–346. DOI: 10.1081/DRT-120028238.

[24] Gönen, M. Nanosized Zinc Borate Production, Ph.D. Dissertation in Chemical Engineering. İzmir Institute of Technology: İzmir, **2009**.

[25] Briggs, M. Boron Oxides, Boric Acid, and Borates. In *Kirk-Othmer Encyclopedia of Chemical Technology* [online]; Wiley, **2001**. https://org/10.1002/0471238. DOI: 10.1002/0471238961.0215181519130920.a01.pub2. (accessed September 1, 2020).

[26] Schubert, D. M. Borates in Industrial Use. In *Group 13 Chemistry III. Structure and Bonding*; Roesky, H. W., Atwood, D. A., Eds.; Springer: Berlin, Heidelberg, **2003**. DOI: 10.1007/3-540-46110-8_1.

[27] Savrık, S. A. Enhancement of Tribological Properties of Mineral Oil by Addition of Span 60 and Zinc Borate. Ph.D. Dissertation in Chemical Engineering, İzmir Instiute of Technology, İzmir, **2010**.

[28] Jun, L.; Shuping, X.; Shiyang, G. FT-IR and Raman Spectroscopic Study of Hydrated Borates. *Spectrochim. Acta, A.* **1995**, *51*, 519–532. DOI: 10.1016/0584-8539(94)00183-C.

[29] Gao, Y.-H.; Liu, Z.-H.; Wang, X.-L. Hydrothermal Synthesis and Thermodynamic Properties of $2ZnO·3B_2O_3·3H_2O$. *J. Chem. Thermodyn.* **2009**, *41*, 775–778. DOI: 10.1016/j.jct.2008.12.012.

[30] Sawada, H.; Igarashi, H.; Sakao, K. Zinc Borate, and Production Method and Use Thereof, U. S. Patent No: 6780913, **2004**, B2.

[31] Yalçı n, A.; Gönen, M. A Novel Approach for the Production of Zinc Borate ($4ZnO·B_2O_3·H_2O$) Using a Single-Step Hydrothermal Method. *Main Group Met. Chem.* **2021**, *44*, 1–8. DOI: 10.1515/mgmc-2021-0001.

[32] Alp, B.; Gönen, M.; Savrık, S. A.; Balköse, D.; Ülkü, S. Dehydration, Water Vapor Adsorption and Desorption Behavior of $Zn[B_3O_3(OH)_5] \cdot H_2O$ and $Zn[B_3O4(OH)_3]$. *Dry. Technol.* **2012**, *30*, 1610–1620. DOI: 10.1080/07373937.2012.701258.