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Zinc Borate Synthesis Using Hydrozincite and Boric Acid with Ultrasonic Method

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***Abstract*—**Zinc borate is an important inorganic hydrate borate material, which can be used as a flame retardant agent and corrosion resistance material. This compound can loss its structural water content at higher than 290°C. Due to thermal stability; Zinc Borate can be used as flame retardant at high temperature process of plastic and gum. In this study, the ultrasonic reaction of zinc borates were studied using hydrozincite ($Zn_5(CO_3)_2\cdot(OH)_6$) and boric acid (H_3BO_3) raw materials. Before the synthesis raw materials were characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). Ultrasonic method is a new application on the zinc borate synthesis. The synthesis parameters were set to 90°C reaction temperature and 55 minutes of reaction time, with 1:1, 1:2, 1:3, 1:4 and 1:5 molar ratio of starting materials ($Zn_5(CO_3)_2\cdot(OH)_6$: H_3BO_3). After the zinc borate synthesis, the products were analyzed by XRD and FT-IR. As a result, optimum molar ratio of 1:5 is determined for the synthesis of zinc borates with ultrasonic method.

***Keywords*—**Borate, ultrasonic method, zinc borate, zinc borate synthesis.

I. Introduction

ZINC borate is important inorganic hydrated borate that is used in many industrial areas [1]. There are various types of zinc borates that can be used as flame retardant and corrosion inhibitor [2], [3]. Their properties vary depending on the contents of zinc and boric oxides. Zinc borates with different properties are used commonly in plastic, rubber, ceramics, paint, wire, electrical insulation, wood applications, cement and pharmaceutical industries [4], [5]. Zinc borates known as inorganic hydrated borate can also be classified in the synthetic hydrate metal borates [6].

In classical method, zinc borate is synthesized by reaction between aqueous boric acid and zinc oxide in temperature above 70°C. Zinc borate is ($2ZnO\cdot3B_2O_3\cdot3.5H_2O$) one of the several types of zinc borates. This compound can protect its structural water up to 290°C. This thermal stability provides it to be used as a fire retardant additive for plastics and gum that require high processing temperatures [7].

In literature, zinc borate compounds have been synthesized by using solid-state reactions and hydrothermal method [8]. These studies have been resulted in time consuming process and high operating temperatures.

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In this study, the ultrasonic reaction of zinc borates were studied using hydrozincite ($Zn_5(CO_3)_2\cdot(OH)_6$) and boric acid (H_3BO_3) raw materials. The synthesis parameters were set to 90°C reaction temperature and 55 minutes of reaction time, with 1:1, 1:2, 1:3, 1:4 and 1:5 molar ratio of starting materials ($Zn_5(CO_3)_2\cdot(OH)_6$: H_3BO_3). After the zinc borate synthesis, the products are analyzed by XRD and FT-IR. As a result, this synthesis is aimed to be realized in lower temperature and shorter time.

II. Materials and Methods

A. Raw Materials

$Zn_5(CO_3)_2\cdot(OH)_6$ was supplied from Alfa Aesar® (≥99.0%purity) and H_3BO_3 was retrieved from Kirka Boron Management Plant in Bandirma. $Zn_5(CO_3)_2\cdot(OH)_6$ were used without pretreatment and H_3BO_3 was treated using agate mortar (Fig. 1 (a)) and sieved to 200 meshes (Fig. 1 (b)).

Characterizations of $Zn_5(CO_3)_2\cdot(OH)_6$ and H_3BO_3 were conducted by PANalytical X-ray Diffraction Instrument (Fig. 2) and Perkin Elmer Spectrum One FT-IR Spectrometer spectroscopy with Universal ATR sampling accessory – Diamond / ZnSe Crystal (Fig. 3). The XRD measurement range was 45kV, 40mA, 7-70°C. The FT-IR measurement range was 1800–650 cm^{-1}, scannumber was 4, and resolution was 4 cm^{-1}.

Fig. 1 Agate mortar (a), Sieve (b)

Fig. 2 Philips PANalytical XRD

Fig. 3 Perkin Elmer Spectrum One FT-IR Spectrometer

B. Ultrasonic Synthesis and Characterizations

In the synthesis, several molar ratios of the $Zn_5(CO_3)_2{\cdot}(OH)_6$ (ZCO) and H_3BO_3 (B) were tested. The molar ratios are Zn/B ratios. Demineralized water (18.3 mΩ.cm) that produced from the equipment of Human Power I+ Water Purification System was used at the liquid phase.

Experiment temperature was selected as 90°C, and reaction time were set to 55 minutes. These parameters were determined from several pre-experiments.

H_3BO_3 was dissolved in demineralized water at the 90°C temperature then $Zn_5(CO_3)_2{\cdot}(OH)_6$ was added. After the addition of $Zn_5(CO_3)_2{\cdot}(OH)_6$, commercial zinc borate ($Zn_3B_6O_{12}{\cdot}3.5H_2O$) retrieved from local market in Turkey (in terms of H_3BO_3, 1.0% w/w) was added. At reaction, the components were mixed with using ultrasonic method. At the end of the 55 minutes, formed zinc borate crystals were washed with distilled water and dried in the oven at 105°C for 24 hours. Obtained products were characterized by XRD and FT-IR.

III. Results and Discussion

A. Raw Material Characterization

XRD patterns and results of $Zn_5(CO_3)_2{\cdot}(OH)_6$, H_3BO_3 and commercial $Zn_3B_6O_{12}{\cdot}3.5H_2O$ were given in Figs. 4-6 and Table I.

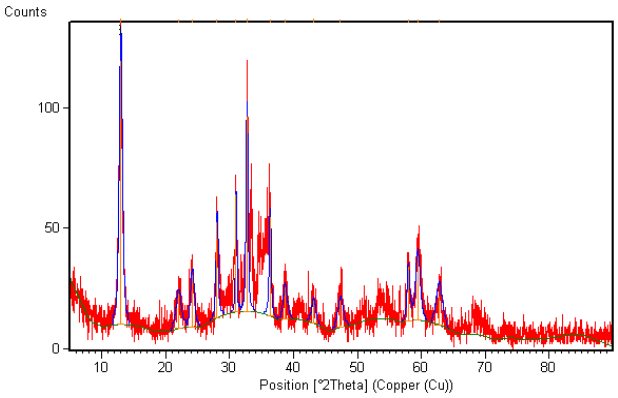

Fig. 4 XRD pattern of $Zn_5(CO_3)_2{\cdot}(OH)_6$

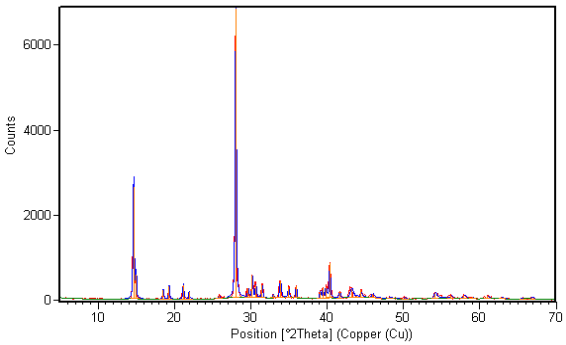

Fig. 5 XRD pattern of H_3BO_3

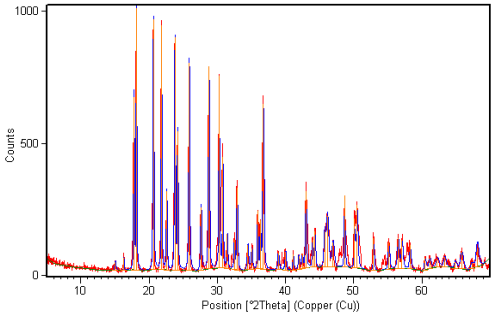

Fig. 6 XRD pattern of commercial $Zn_3B_6O_{12}.3.5H_2O$

TABLE I
XRD Results of Raw Materials

Reference Code	Compound Name	Chemical Formula	Score
00-019-1458	Hydrozincite	$Zn_5(CO_3)_2{\cdot}(OH)_6$	32
01-073-2158	Sassolite	H_3BO_3	62
00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}{\cdot}3.5H_2O$	80

From the XRD analysis of $Zn_5(CO_3)_2{\cdot}(OH)_6$ was found as "00-019-1458" coded hydrozincite. H_3BO_3 and commercial $Zn_3B_6O_{12}{\cdot}3.5H_2O$ were found as, "01-073-2158" coded sassolite (H_3BO_3) and "00-035-0433" coded zinc oxide borate hydrate, respectively.

FT-IR spectrum of H_3BO_3 and commercial $Zn_3B_6O_{12}{\cdot}3.5H_2O$ were given in Figs. 7 and 8, respectively.

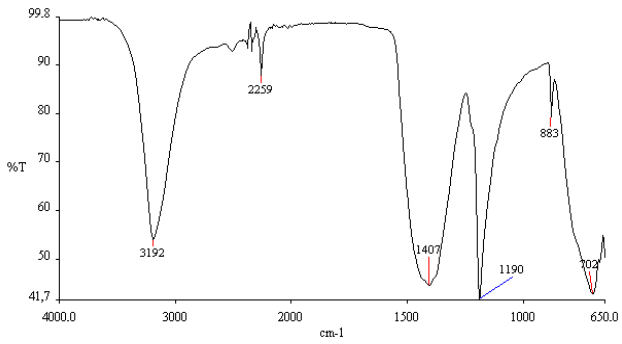

Fig. 7 FT-IR spectrum of H_3BO_3

According to the FT-IR inorganic library search, H_3BO_3 was found as: "Boric acid (H_3BO_3)" with 0.704 score (out of 1) and "AI0031" code.

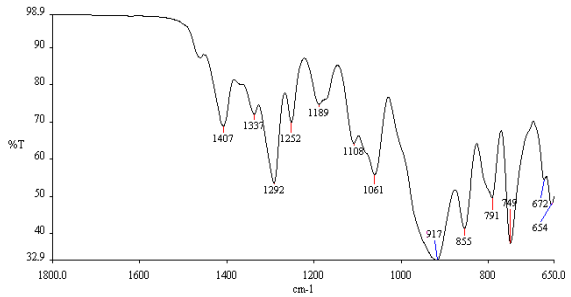

Fig. 8 FT-IR spectrum of commercial $Zn_3B_6O_{12}.3.5H_2O$

Also commercial $Zn_3B_6O_{12}\cdot 3.5H_2O$ was not found in the FT-IR inorganic library search, but the boron-oxygen characteristic peaks were observed in the spectrum. The detailed examination will be done at the results section.

B. Synthesized Products

The XRD results of the synthesized zinc borates were given in Table II.

TABLE II
XRD RESULTS OF SYNTHESIZED ZINC BORATES

Molar Ratio (Zn:B)	Reference code	Mineral Name	Mineral Formula	Score
1:1	-	-	-	-
1:2	-	-	-	-
1:3	-	-	-	-
1:4	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}\cdot 3.5H_2O$	62
1:5	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}\cdot 3.5H_2O$	71

Between the molar ratios of 1:1 and 1:5 the expected formation occurs at 1:4 and 1:5, with XRD score of 62 and 71, respectively.

The reaction scheme of 1:5 was given in (1):

$$Zn_5(CO_3)_2\cdot(OH)_6(s) + 25\,H_3BO_3(s) + xH_2O(l) \rightarrow \frac{5}{3}\left[Zn_3B_6O_{12}\cdot 3.5(H_2O)(s)\right] + 15\,H_3BO_3(aq) + yH_2O(l) \quad (1)$$

Also the reaction yields were calculated between 73-97% at the molar ratios of 1:4 - 1:5. The XRD patterns of the zinc borates were given in Fig. 9.

The molar ratios of 1:1, 1:2 and 1:3 were not observed product occurrence. The molar ratios of 1:4 and 1:5, with the increase of boric acid rate, were sighted zinc borate formation. At these molar ratios, the analyzed XRD results were 62 and 71, and the reaction yields were calculated 73% and 97%, respectively. According to other methods of zinc borate synthesis, ultrasonic method was accomplished higher XRD scores and yields.

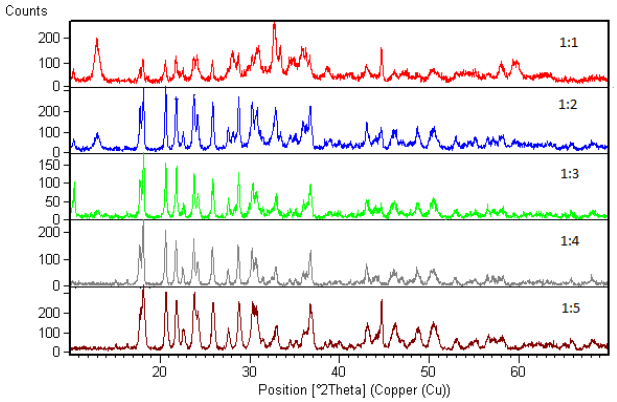

Fig. 9 XRD patterns of synthesized zinc borates

The FT-IR spectra and peak interpretations of the synthesized zinc borates were given in Fig. 10 and Table III, respectively.

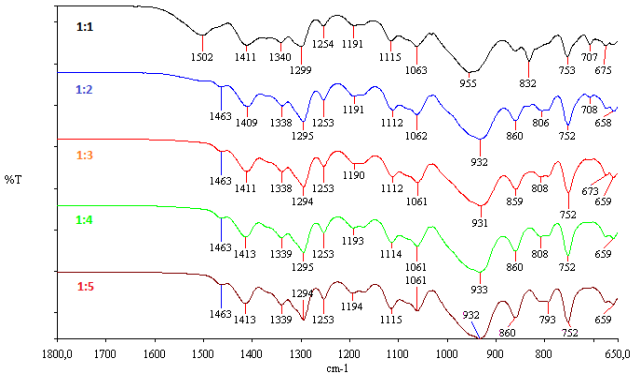

Fig. 10 FT-IR spectra of the synthesized zinc borates

TABLE III
FT-IR PEAK INTERPRETATIONS

Peaks (cm^{-1})	Peak Interpretation	Symbol
1778-1424	Bending of H-O-H	δ(H-O-H)
1423-1241	B_3-O asymmetrical stretching	$\nu_{as}(B_3\text{-}O)$
1240-1099	Bending of B-O-H	δ(B-O-H)
1098-958	B_4-O asymmetrical stretching	$\nu_{as}(B_4\text{-}O)$
957-873	B_3-O symmetrical stretching	$\nu_s(B_3\text{-}O)$
872-864	Boric acid characteristic peak	$\nu_p(H_3BO_3)$
863-756	B_4-O symmetrical stretching	$\nu_s(B_4\text{-}O)$
755-677	Characteristic peak of $[B(OH)_4]^-$	$\nu_p[B(OH)_4]^-$
676-642	B_3-O bending	δ(B_3-O)

The characteristic peaks of zinc borates can be seen in Fig. 10. In the FT-IR spectra given in Fig, 10 and commercial $Zn_3B_6O_{12}\cdot 3.5H_2O$; the peaks between 1502-1424 cm^{-1} represent the Bending of (H-O-H). The peaks between 1413-1253 cm^{-1} represents the three coordinate boron asymmetrical stretching. Bending of (B-O-H) is seen between the peaks of 1193-1112 cm^{-1}. Four coordinate boron asymmetrical and three coordinate boron symmetrical stretching are observed between the peaks of 1063-977 cm^{-1} and 955-873 cm^{-1}, respectively. Between the peaks of 860-793 cm^{-1}, four coordinate boron symmetrical stretching are formed. Last two

regions where $\nu_p[B(OH)_4]^-$ and bending of three coordinate boron were seen at the peaks between 753-707 cm^{-1} and 675-658 cm^{-1}, respectively.

IV. Conclusion

In this study the optimum molar ratio of the Zn:B were determined as 1:5 for the zinc borate synthesis. The reaction steps were given in (1) before, washing and drying steps are given in (2) and (3), respectively.

Step of washing

$$5/3\left(Zn_3B_6O_{12}.3.5H_2O\right)+15\,H_3BO_3+bH_2O \rightarrow 5/3\left(Zn_3B_6O_{12}.3.5H_2O\right)+cH_2O \quad (2)$$

Step of drying

$$5/3\left(Zn_3B_6O_{12}.3.5H_2O\right)+cH_2O \xrightarrow{105^oC} 5/3\left(Zn_3B_6O_{12}.3.5H_2O\right) \quad (3)$$

At the future studies, reaction time and the reaction temperature changes will be investigated in the ultrasonic synthesis of zinc borates.

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