

# Zinc Borate Synthesis Using Hydrozincite and Boric Acid with Ultrasonic Method

D. S. Vardar, A. S. Kipcak, F. T. Senberber, E. M. Derun, N. Tugrul, S. Piskin

**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 lose 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 ( $Zn_5(CO_3)_2(OH)_6$ ) 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 ( $Zn_5(CO_3)_2(OH)_6 : H_3BO_3$ ). 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 ( $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ ) 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.

D. S. Vardar, A. S. Kipcak, F. T. Senberber, E. M. Derun, S. Piskin and N. Tugrul are with the Yildiz Technical University, Department of Chemical Engineering, Davutpasa Campus, 34210 Esenler, Istanbul, Turkey (e-mail: duyugusenaa@windowslive.com, skipcak@yildiz.edu.tr, tsenberber@gmail.com, moroydor@yildiz.edu.tr, piskin@yildiz.edu.tr, ntugrul@yildiz.edu.tr).

In this study, the ultrasonic reaction of zinc borates were studied using hydrozincite ( $Zn_5(CO_3)_2(OH)_6$ ) 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 ( $Zn_5(CO_3)_2(OH)_6 : H_3BO_3$ ). 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

$Zn_5(CO_3)_2(OH)_6$  was supplied from Alfa Aesar® ( $\geq 99.0\%$  purity) and  $H_3BO_3$  was retrieved from Kirka Boron Management Plant in Bandirma.  $Zn_5(CO_3)_2(OH)_6$  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  $Zn_5(CO_3)_2(OH)_6$  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  $1800-650\text{ cm}^{-1}$ , scannumber was 4, and resolution was  $4\text{ cm}^{-1}$ .



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 m $\Omega$ .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.

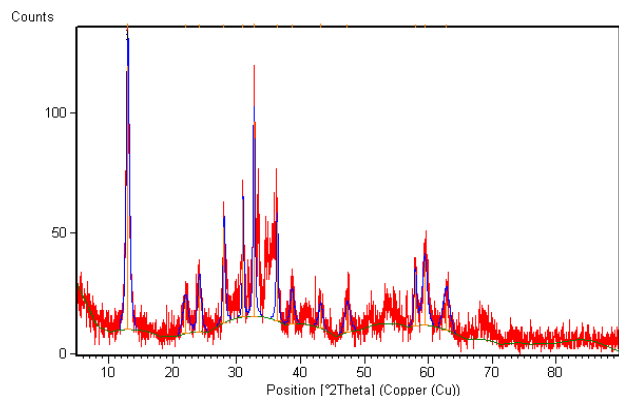
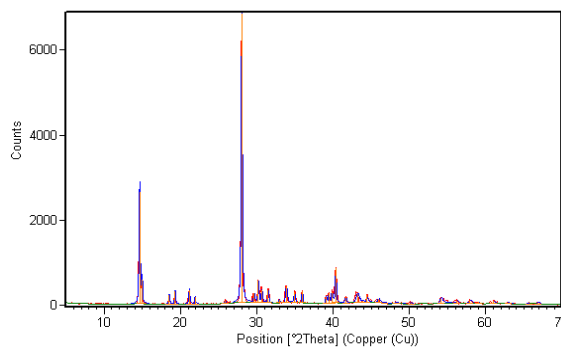
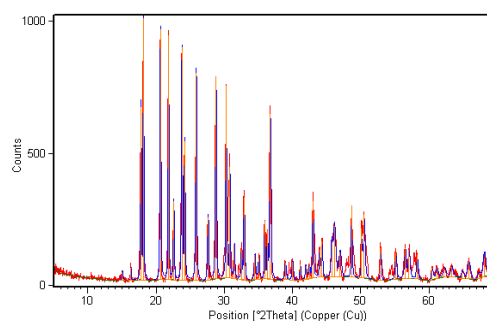
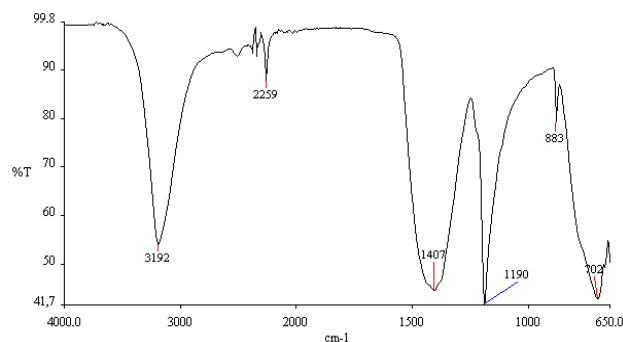
Fig. 4 XRD pattern of  $Zn_5(CO_3)_2 \cdot (OH)_6$ Fig. 5 XRD pattern of  $H_3BO_3$ Fig. 6 XRD pattern of commercial  $Zn_3B_6O_{12} \cdot 3.5H_2O$ 

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.

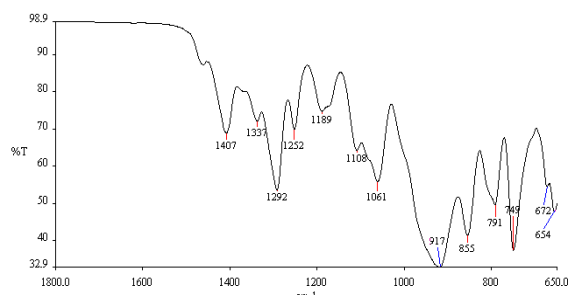


Fig. 8 FT-IR spectrum of commercial  $Zn_3B_6O_{12} \cdot 3.5H_2O$

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

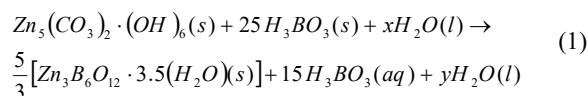
The XRD results of the synthesized zinc borates were given in Table II.

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):



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.

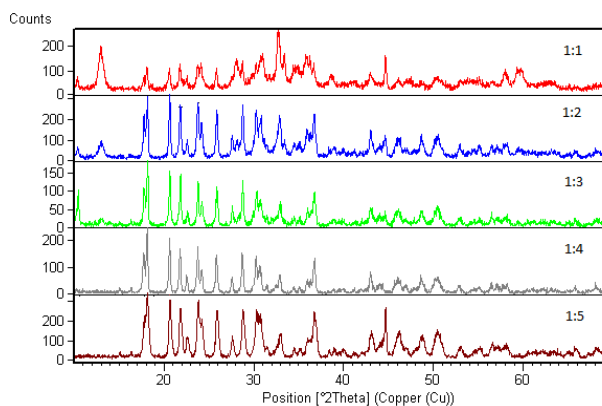


Fig. 9 XRD patterns of synthesized zinc borates

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

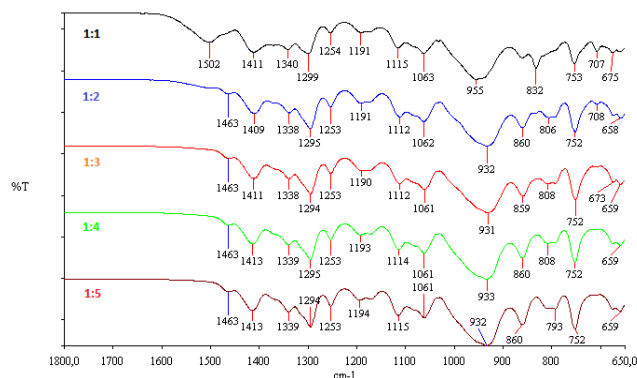


Fig. 10 FT-IR spectra of the synthesized zinc borates

TABLE III  
FT-IR PEAK INTERPRETATIONS

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

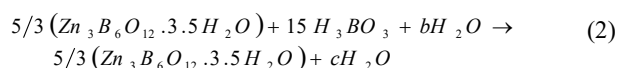
The characteristic peaks of zinc borates can be seen in Fig. 10. In the FT-IR spectra given in Fig. 10 and commercial  $Zn_3B_6O_{12} \cdot 3.5H_2O$ ; the peaks between 1502-1424  $cm^{-1}$  represent the Bending of (H-O-H). The peaks between 1413-1253  $cm^{-1}$  represents the three coordinate boron 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  $\nu_p[\text{B}(\text{OH})_4]$  and bending of three coordinate boron were seen at the peaks between  $753\text{-}707\text{ cm}^{-1}$  and  $675\text{-}658\text{ cm}^{-1}$ , respectively.

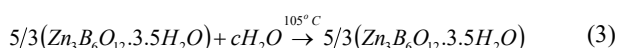
#### IV. CONCLUSION

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*



*Step of drying*



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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**Duygu Sena Vardar** was born in Yalova in 1991. Vardar Duygu Sena was graduated from Department of Chemical Engineering in Yildiz Technical University in 2013. Vardar is still a Student of Master degree in Yildiz Technical University.



**Azmi Seyhun Kipcak** was graduated from Department of Chemical Engineering in Ege University in 2002. After completing the university studies he graduated from Bilgi University from the department of Master of Business Administration in 2004. He worked in Kultur University from 2003 to 2007 as a research assistant then he transferred to Yildiz Technical University at 2008, where he started his M.Sc. studies about Chemical Engineering in 2006. He completed his M.Sc. and Ph.D. studies at Yildiz Technical University in 2009 and 2013, respectively. He studied on neutron shielding with boron minerals and the characterization of boron minerals by using XRD, XRF, FT-IR, Raman, DTA/TG, DSC and ICP-OES at the M.Sc. studies and studied on the synthesis of magnesium borates from different raw materials and wastes at the Ph.D. Also he is improving the neutron shielding studies with the synthesized materials and working on the element analysis of Turkish Teas and Coffees. Another research field about the studies he is working is the zinc borate synthesis.



**Fatma Tugce Senberber** was graduated from B.Sc. at Yildiz Technical University in 2010. After she completed her M.Sc. studies at Yildiz Technical University in 2012, she started to Ph.D. studies at the same year and same department of university. She is interested in boron technologies such as alternative synthesis methods of boron minerals and evaluation of industrial wastes in synthesis process. She also studied the characterization methods by instrumental analysis, kinetic studies of minerals and alternative application areas of synthesized minerals.



**Emek Moroydor Derun** was born in Istanbul in 1976. Moroydor Derun was graduated from B.Sc. in 1998, M.Sc. in 2000 and Ph. D. in 2005 from Chemical Engineering Department at Yildiz Technical University, Istanbul. Her research interest is in the area of waste management, lightweight concrete, semiconductive materials and boron technology. She has many articles and studies in international and national conference proceedings and articles.



**Nurcan Tugrul** was born in Gaziantep in 1973. Tugrul was graduated from B.Sc., M.Sc. and Ph.D. in Chemical Eng. Department at Yildiz Technical University, Istanbul. Her research interest is in the area of chemical technologies, evaluation of industrial wastes, food drying. She has many articles and studies in international and national conference proceedings and articles.



**Sabriye Piskin** graduated from Istanbul Technical University on Chemical Engineering with M.Sc. degree in 1974. She completed a Ph.D. degree at the same department in 1983. Her research interests include boron minerals and compounds, hydrogen storage technologies, fuel cell applications, materials characterization, coal, waste management, corrosion, implants and synthetic materials production.