International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:9, No:12, 2015

Determination of the Zinc Oxide and Boric Acid Optimum Molar Ratio on the Ultrasonic Synthesis of Zinc Borates

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***Abstract*—**Zinc borates are used as a multi-functional flame retardant additive for its high dehydration temperature. In this study, the method of ultrasonic mixing was used in the synthesis of zinc borates. The reactants of zinc oxide (ZnO) and boric acid (H_3BO_3) were used at the constant reaction parameters of 90°C reaction temperature and 55 min of reaction time. Several molar ratios of ZnO:H_3BO_3 (1:1, 1:2, 1:3, 1:4 and 1:5) were conducted for the determination of the optimum reaction ratio. Prior to synthesis the characterization of the synthesized zinc borates were made by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). From the results Zinc Oxide Borate Hydrate [$Zn_3B_6O_{12}.3.5H_2O$], were synthesized optimum at the molar ratio of 1:3, with a reaction efficiency of 95.2%.

***Keywords*—**Zinc borates, ultrasonic mixing, XRD, FT-IR, reaction efficiency.

I. Introduction

BORON is not found in nature as an element form, it interacts with carbon and other similar elements and form compounds of boron minerals. Industrial production of high-purity boron is carried out in an expensive and difficult process. Depending on the main elements, they contain boron minerals, calcium borate, magnesium borate, sodium borate, sodium-calcium borate and other borate compounds are divided into five main groups. Zinc borate can be synthesized in a laboratory, although not found naturally.

Zinc borate has many application areas ranging from polymers to paints. Different types of zinc borates that are important inorganic hydrated borates can be used as flame and fire retardant and corrosion inhibitor [1], [2]. Depending the contents of zinc and boric oxides, its properties varies and used widely in plastic, rubber, ceramics, paint, wire, electrical insulation, wood applications, cement and pharmaceutical industries [3], [4]. In addition, zinc borates can be grouped in the synthetic hydrate metal borates [5].

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Zinc borate is produced by reaction between aqueous boric acid and zinc oxide 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 has the unusual property of retaining its water of hydration at temperatures up to 290°C. This thermal stability makes it attractive as a fire retardant additive for plastics and rubbers that require high processing temperatures. It is also used as an anticorrosive pigment in coatings.

The different types of zinc borate are important for reducing the use of inorganic hydrated borate as flame retardant and corrosion. Zinc and boron oxide content to vary depending on their properties and plastic, rubber, ceramics, paint, cable, electrical insulation, wood applications, cement is commonly used in pharmaceutical industry. In addition, synthetic hydrated zinc borate can be classified as metal borates.

In ultrasonic irradiation, the chemical effects of ultrasound do not come from a direct interaction of the ultrasonic sound wave with the molecules in the solution. The simplest explanation for this is that sound waves propagating through a liquid at ultrasonic frequencies do so with a wavelength that is significantly longer than that of the bond length between atoms in the molecule. Therefore, the sound wave cannot affect that vibrational energy of the bond, and can therefore not directly increase the internal energy of a molecule.

In this study, using zinc oxide and boric acid a new method of ultrasonic irridation is used for the synthesis of zinc borates and their effects on the production of the reaction temperature and is investigated. The materials and products are analyzed with X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR).

II. Materials and Methods

A. Raw Materials

Zinc borates were produced by using zinc oxide and boric acid. Boric acid (H_3BO_3) retrieved from Kirka Boron Management Plant in Bandirma; Zinc Oxide was provided by Tekkim Kimya Sanayi. Characterizations of ZnO and H_3BO_3 were conducted by XRD (Fig. 1) and FT-IR spectroscopy with Universal ATR sampling accessory – Diamond / ZnSe Crystal.

B. Ultrasonic Synthesis and Characterizations

Initial experiments were carried out using different ways for producing zinc borate with zinc oxide and boric acid. In this experiment, varied molar ratios of the ZnO(Zn) and H_3BO_3 (H) were tested. Experiment temperature was chosen at 90 ^oC,

and reaction time is set to 40-60 minutes. These parameters were estimated from [6]. For the experiments, between 0.1 and 0.2 mol H_3BO_3 were dissolved in 20-30 ml pure water in reaction temperature, then different molar ratios of ZnO was added to reactor. After the addition of the raw materials, commercial zinc borate ($Zn_3B_6O_{12}\cdot 3.5H_2O$) received from local market in Turkey (in terms of H_3BO_3, 1% w/w) as added for the better crystallization.

Fig. 1 Philips PANalytical XRD

Fig. 2 Perkin Elmer Spectrum One FT-IR Spectrometer

The raw materials were reacted by ultrasonic irradiation method in a closed temperature-controlled system. At the end of the reaction, each solution was filtered through Whatman blue ribbon filter paper and the crystallized products on the filter paper were washed with the 1-2 L pure water at 60°C to eliminate unreacted boric acid. Then, filtered products dried in the incubator (Ecocell 111, Germany) at 105°C for 1-2 h. Obtained products were characterized by XRD and FT-IR.

III. Results and Discussion

A. Raw Material Characterization

XRD patterns and results of ZnO, H_3BO_3 and commercial $Zn_3B_6O_{12}.3.5H_2O$ were given in Figs. 3-5 and Table I.

From the XRD analysis of ZnO, it is seen that compound was consist of "01-089-7102" compound that their structural formula is ZnO. H_3BO_3 and commercial $Zn_3B_6O_{12}.3.5H_2O$ were found as, "01-073-2158" coded sassolite (H_3BO_3) and "00-035-0433" coded zinc oxide borate hydrate, respectively.

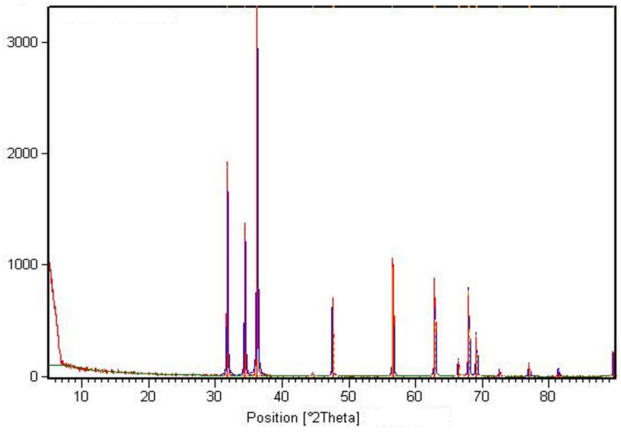

Fig. 3 XRD pattern of ZnO

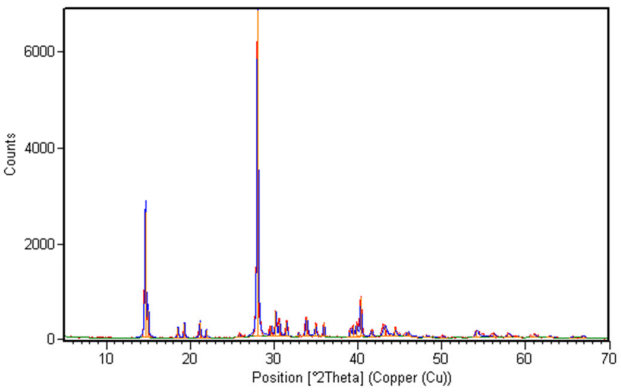

Fig. 4 XRD pattern of H_3BO_3

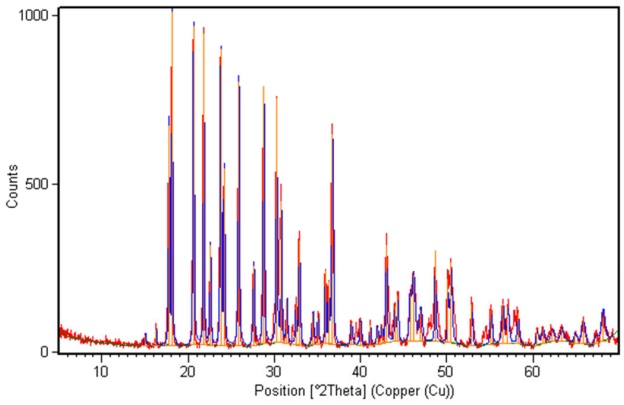

Fig. 5 XRD pattern of commercial $Zn_3B_6O_{12}.3.5H_2O$

TABLE I
XRD Results of Raw Materials

Reference Code	Compound Name	Chemical Formula
01-089-7102	ZnO	ZnO
01-073-2158	Sassolite	H_3BO_3
00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}\cdot 3.5H_2O$

FT-IR spectrum of ZnO, H_3BO_3 and commercial $Zn_3B_6O_{12}\cdot 3.5H_2O$ were given in Figs. 6, 7 and 8, respectively.

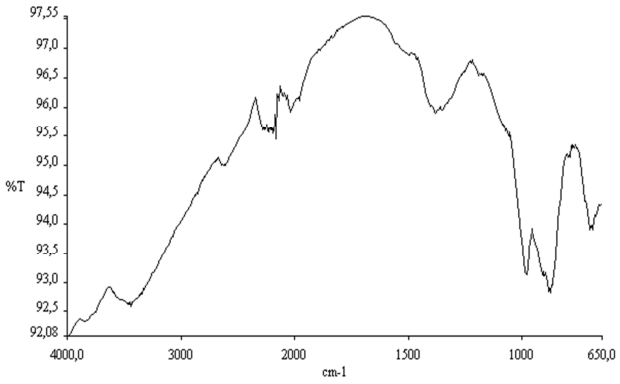

Fig. 6 FT-IR spectrum of ZnO

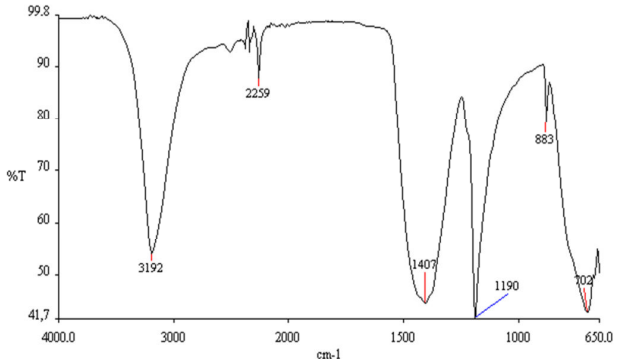

Fig. 7 FT-IR spectrum of H_3BO_3

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.

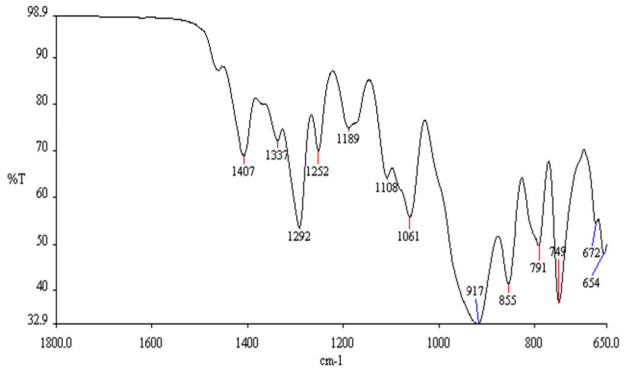

Fig. 8 FT-IR spectrum of commercial $Zn_3B_6O_{12}.3.5H_2O$

Commercial $Zn_3B_6O_{12}.3.5H_2O$ 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 (Z:N:H)	Reference code	Mineral Name	Mineral Formula	Score
1:1	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	6
1:2	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	40
1:3	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	65
1:4	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	63
1:5	00-035-0433	Zinc Oxide Borate Hydrate	$Zn_3B_6O_{12}.3.5H_2O$	58

XRD scores of the zinc borates synthesized from zinc oxide and boric acid in same temperature and same reaction time (90°C and 55 minutes) is shown in Table II. Synthesized zinc borate from zinc oxide and boric acid was found as ' zinc oxide borate hydrate ($Zn_3B_6O_{12}.3.5H_2O$)' with powder diffraction file number (pdf number) of '00-035-0433'. From the XRD scores of synthesized zinc borates the best molar ratio is seen as 1/3. Obtained zinc borates coded as ' set code – mole ratio - reaction temperature – reaction time ' which the sets codes are ' Z-H 1:1 90-55'. XRD patterns of the selected zinc borates were given in Fig. 9.

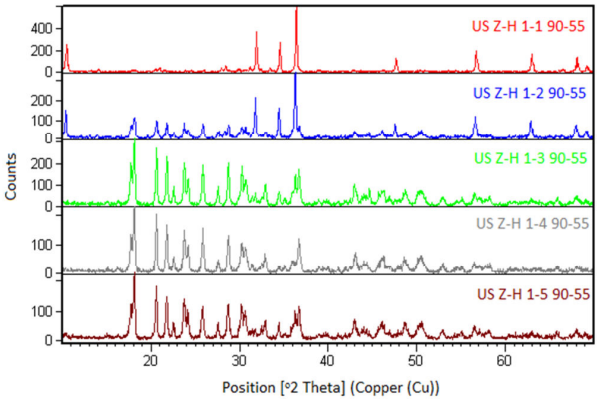

Fig. 9 XRD patterns of the products

FTIR spectra of the products are given in Fig. 10. Bending vibrations of the H-O-H band are a little bit observed between 1500 and 1420 cm^{-1}. The existence of the band between 1420-1339 cm^{-1} is showed to the asymmetric stretching vibrations of trihedral (BO_3) borate groups. The peaks in the range between 1175-1058 cm^{-1} is observed to the asymmetric stretching vibrations of tetrahedral (BO_4) borate groups. Bending of symmetric stretching vibrations of trihedral (BO_3) borate groups are showed between 1058 and 924 cm^{-1}.The peaks in the range between 876-859 is showed to the symmetric stretching vibrations of tetrahedral borate groups. The peak observed between 859-659 cm^{-1} indicates the plane bending vibrations of trihedral borate groups.

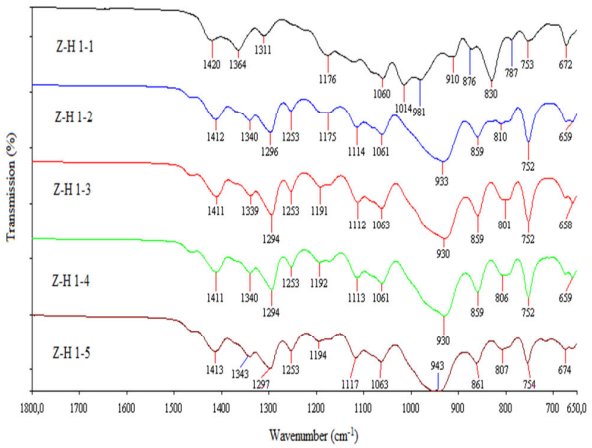

Fig. 10 FT-IR patterns of the products that were obtained

TABLE III
FT-IR PEAK INTERPRETATIONS

Peaks (cm^{-1})	Peak Interpretation	Symbol
1500-1420	Bending of H-O-H	δ(H-O-H)
1420-1339	B_3-O asymmetrical stretching	$\nu_{as}(B_3\text{-}O)$
1240-1099	Bending of B-O-H	δ(B-O-H)
1175-1058	B_4-O asymmetrical stretching	$\nu_{as}(B_4\text{-}O)$
1058-924	B_3-O symmetrical stretching	$\nu_s(B_3\text{-}O)$
872-864	Boric acid characteristic peak	$\nu_p(H_3BO_3)$
876-859	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)

IV. CONCLUSION

In this study, zinc borates were synthesized optimum at the molar ratio of 1:3, with a maximum reaction efficiency of 95.2%.

At the future studies, reaction time and the reaction temperature changes will be investigated in the synthesis of zinc borates and may be produced with different zinc and boron materials.

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Ali Can Ersan was born in İstanbul in 1990. Ersan was graduated from Department of Chemistry in Yildiz Technical University in 2008. After the graduation he started to second university Department of Business Administration in Anadolu University in 2011 and he started his M.Sc. studies about Chemical Engineering Yildiz Technical University in 2012. He studied about zinc borate production by using ultrasonic method with different materials.

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Meral Yildirim was graduated from B.Sc. in 2011, M.Sc. in 2013 from Chemical Engineering Department in Yildiz Technical University, Istanbul. She is currently continuing her Ph. D. education at the same university. She is interested in synthesis and characterization of borate minerals, waste management and cement-concrete production.

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