World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:7, No:5, 2013

Low Temperature Solid-State Zinc Borate Synthesis from ZnO and H_3BO_3

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***Abstract*—**Zinc borates can be used as multi-functional synergistic additives with flame retardant additives in polymers. Zinc borate is white, non-hygroscopic and powder type product. The most important properties are low solubility in water and high dehydration temperature. Zinc borates dehydrate above 290°C and anhydrous zinc borate has thermal resistance about 400°C. Zinc borates can be synthesized using several methods such as hydrothermal and solid-state processes. In this study, the solid-state method was applied at low temperatures of 600°C and 700°C using the starting materials of ZnO and H_3BO_3 with several mole ratios. The reaction time was determined as 4 hours after some preliminary experiments. After the synthesis, the crystal structure and the morphology of the products were examined by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). As a result the forms of ZnB_4O_7, $Zn_3(BO_3)_2$, ZnB_2O_4 were synthesized and obtained along with the unreacted ZnO.

***Keywords*—**FT-IR, solid-state method, zinc borate, XRD.

I. Introduction

ZINC borate is an important inorganic hydrated borate that finds applications ranging from polymers to paints for various purposes, such as; flame retardant, corrosion inhibitor, etc. depending on the type of zinc borate [1]. Zinc borate is a multifunctional fire retardant containing different proportion of zinc and boric oxides [2]. Zinc borate are widely used in plastic, rubber, ceramics, paint, wire, electrical insulation, wood applications, cement and pharmaceutical industries due to its properties [3], [4]. Zinc borate which has different crystal structures is a synthetic hydrate metal borate [5].

Zinc borate is produced by reaction between aqueous boric acid and zinc oxide above 70°C. Zinc borate is ($2ZnO.3B_2O_3.3.5H_2O$) 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 [6].

Shi et al. [7] studied the preparation of $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$ from zinc oxide and boric acid via a rheological phase reaction. The products were characterized by XRD, TG, DTA, and SEM. Moreover, the effects of experimental conditions and particle size distribution on the characteristics of the products were investigated. The aforementioned synthetic method is facile, creates no pollution and provides a yield of approximately 100%. Thus, zinc borate is an important green material that can be used to remove various toxic gases and organic compounds and can be synthesized in an environmentally friendly manner.

Igarashi et al. [8] synthesized zinc borates in a two-step reaction. In the first step, zinc oxide and boric acid were combined and stirred at 60°C for 1.5 hours to achieve crystal formation. In the second step, the mixture was stirred continuously at 90°C for 4 hours, and seed crystals were added to the reaction mixture to enhance crystal growth.

In this study, the solid-state synthesis of dehydrated zinc borates at 600 and 700°C were aimed. Synthesized products are characterized by X-Ray Diffraction (XRD) (Philips PANalytical, Xpert-Pro) and Fourier Transform Infrared Spectroscopy (FT-IR) (Perkin Elmer, Spectrum One).

II. Materials and Methods

A. Raw Material Preparation

Zinc oxide was supplied from Colakoglu Chemistry Limited Company and boric acid was retrieved from Kirka Boron Management Plant in Eskisehir. Zinc oxide was used without pretreatment and boric acid was crushed, grinded with agate mortar and sieved to 200 meshes (Fig. 1). Identification analysis of both zinc oxide and boric acid were made by Philips PANalytical X-Ray Diffraction that can be seen in Fig. 2.

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(a) (b)

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

Fig. 2 Philips PANalytical X-Ray Diffraction

After the identification analysis with XRD, Perkin Elmer Brand Fourier Transform Infrared Spectroscopy (FT-IR) technique with Universal ATR sampling accessory – Diamond / ZnSe Crystal was used. Measurement range was selected as 4000–650cm^{-1}, scan number was 4 and resolution set as 4cm^{-1} (Fig. 3).

Fig. 3 Perkin Elmer Spectrum One FT-IR Spectrometer

B. Pelletization Process

Before the solid-state synthesis the samples were mixed homogenously and pelletized with, Manfredi OL 57, pelletizing equipment (Fig. 4).

Fig. 4 Manfredi OL 57 Pelletiser

In the pelletization process, the samples were pressed at a pressure of 100bars for the duration of two minutes. The ratios of raw materials were selected as 1:2, 1:3, 1:4, 1:5 and 1:6, where first component was zinc oxide and second component was boric acid.

C. Solid-State Synthesis

After the pelletization processes, the pellets were subjected to high temperature furnace with the ceramic crucibles. The temperature increment was selected as 10^{o}C/min and reaction time as 240 minutes. 600 and 700^{o}C were studied.

D. Characterization of the Products

All products were characterized by XRD (Philips PANalytical, Xpert-Pro). Furthermore, FT-IR (Perkin Elmer, Spectrum One) was used to identify the functional groups present in the products.

III. Results and Discussion

A. Raw Material Characterization Results

XRD analysis results of raw materials were given in Figs. 5-8 and Table I.

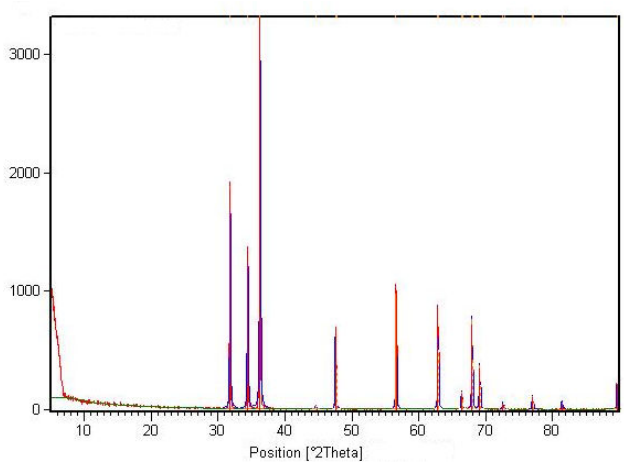

Fig. 5 XRD analysis of ZnO

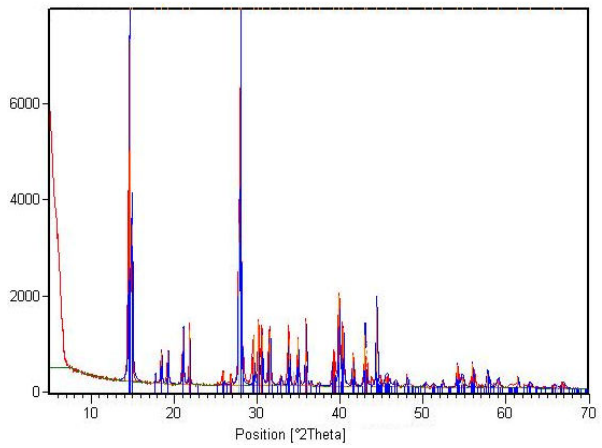

Fig. 6 XRD analysis of standard boric acid

TABLE I
XRD RESULTS OF REACTIVES

Reference Code	Compound Name	Chemical Formula	Score
01-079-2205	Zinc oxide	ZnO	91
01-073-2158	Sassolite	H_3BO_3	62

From the results of the XRD analysis "01-079-2205" coded zinc oxide and "01-073-2158" coded sassolite was found.

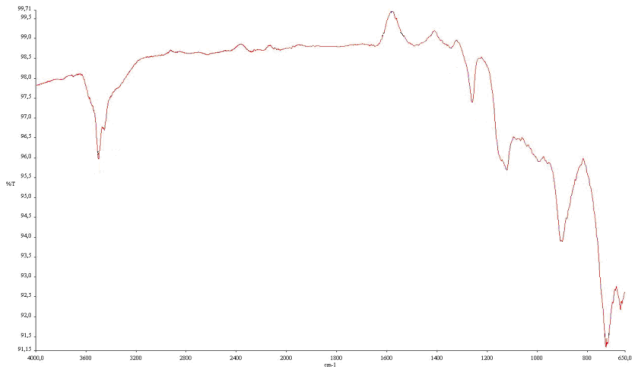

Fig. 7 FT-IR spectrum of ZnO

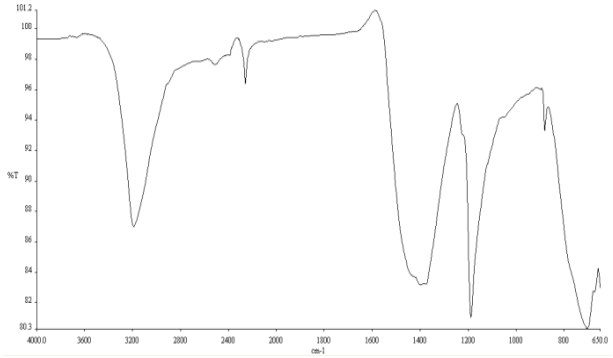

Fig. 8 FT-IR spectrum of boric acid

FT-IR spectrums were showed that the characteristic bands of the raw materials both zinc oxide and boric acid.

B. XRD Results

The XRD patterns of the products synthesized at 600°C were given in Fig. 9 and Table II. The XRD patterns of the products synthesized at 600°C were given in Fig. 10 and Table III.

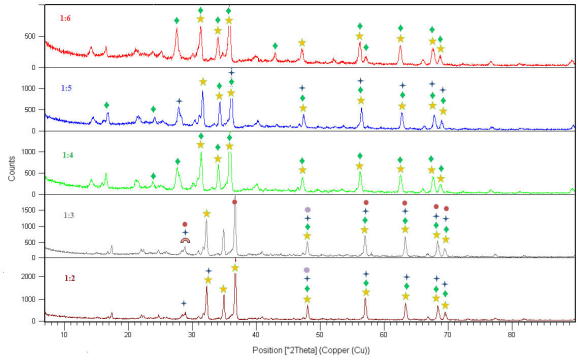

Fig. 9 XRD pattern of the products synthesized at 600°C
01-071-0634: 00-016-0283: 01-071-2063:
00-004-0631: 01-085-1778: 01-079-2205:

TABLE II
XRD RESULTS OF PRODUCTS SYNTHESIZED 600°C

$ZnO:H_3BO_3$ Ratio	Pdf no	Name	Formula	Score
1:2	01-071-0634	Zinc Borate	ZnB_4O_7	16
	00-016-0283	Zinc Borate	ZnB_4O_7	15
	01-071-2063	Zinc Borate	$Zn_3(BO_3)_2$	9
	01-079-2205	Zinc Oxide	ZnO	53
1:3	01-071-0634	Zinc Borate	ZnB_4O_7	14
	00-016-0283	Zinc Borate	ZnB_4O_7	15
	00-004-0631	Zinc Borate	ZnB_2O_4	25
	00-004-1778	Zinc Borate	ZnB_2O_4	14
	00-004-2063	Zinc Borate	ZnB_2O_4	11
	01-079-2205	Zinc Oxide	ZnO	33
1:4	01-071-0634	Zinc Borate	ZnB_4O_7	32
	01-079-2205	Zinc Oxide	ZnO	75
1:5	01-071-0634	Zinc Borate	ZnB_4O_7	37
	00-004-2063	Zinc Borate	ZnB_2O_4	16
	01-079-2205	Zinc Oxide	ZnO	74
1:6	01-071-0634	Zinc Borate	ZnB_4O_7	11
	01-079-2205	Zinc Oxide	ZnO	81

At 600°C reaction time five different types of dehydrated zinc borates were formed. Also in the XRD results unreacted

ZnO was seen at all the ratios means that the formations of zinc borates were not completed at this temperature. The major zinc borate phase seen at all ratios, except 1:3, was "01-071-0634" coded zinc borate (ZnB_4O_7). At 1:3 ratio the major phase was seen as "00-0004-0631" coded zinc borate (ZnB_2O_4). The highest crystal score was obtained at the ratio of 1:5.

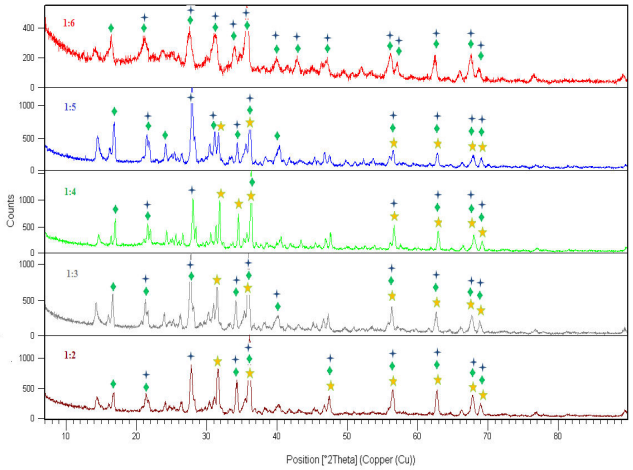

Fig. 10 XRD pattern of the products synthesized at 700°C

01-071-0634: ◆ 01-071-2063: ✦ 01-079-2205: ★

TABLE III
XRD RESULTS OF PRODUCTS SYNTHESIZED 700°C

$ZnO:H_3BO_3$ Ratio	Pdf no	Name	Formula	Score
1:2	01-071-0634	Zinc Borate	ZnB_4O_7	42
	00-004-2063	Zinc Borate	ZnB_2O_4	34
	01-079-2205	Zinc Oxide	ZnO	73
1:3	01-071-0634	Zinc Borate	ZnB_4O_7	26
	00-004-2063	Zinc Borate	ZnB_2O_4	29
	01-079-2205	Zinc Oxide	ZnO	70
1:4	01-071-0634	Zinc Borate	ZnB_4O_7	59
	00-004-2063	Zinc Borate	ZnB_2O_4	39
	01-079-2205	Zinc Oxide	ZnO	65
1:5	01-071-0634	Zinc Borate	ZnB_4O_7	59
	00-004-2063	Zinc Borate	ZnB_2O_4	31
	01-079-2205	Zinc Oxide	ZnO	66
1:6	01-071-0634	Zinc Borate	ZnB_4O_7	20
	00-004-2063	Zinc Borate	ZnB_2O_4	21

From the 700°C XRD results it was seen that two types of zinc borates were formed. Unreacted zinc oxide was also seen at that temperature, but its crystal score was decreasing with the ratio from 1:2 to 1:5 and no peaks of zinc oxide was seen at 1:6. The highest crystal scores of zinc oxides were seen at the ratio of 1:4 and at all the ratios the major phase was seen as "01-071-0634" coded zinc borate (ZnB_4O_7).

C. FT-IR Results

FT-IR spectrums of the synthesized minerals both at 600 and 700°C temperature were shown in Fig. 11 and Fig. 12. The peak interpretations were given in Table IV.

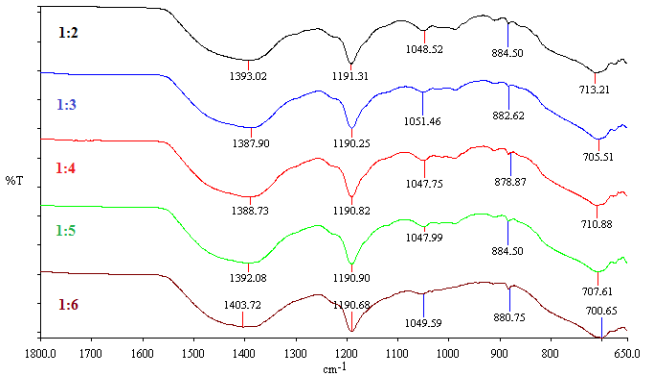

Fig. 11 FT-IR spectrums of the products synthesized at 600°C

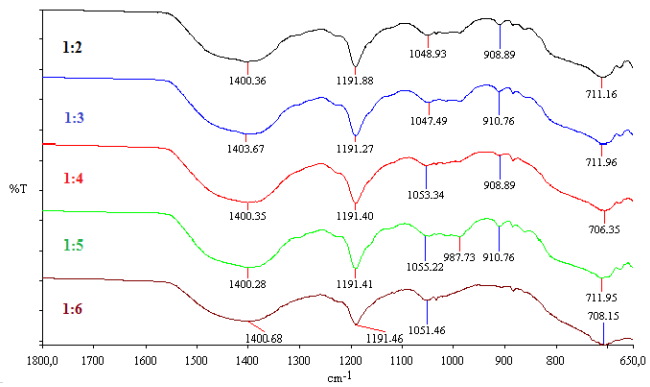

Fig. 12 FT-IR spectrums of the products synthesized at 700°C

TABLE IV
FT-IR PEAK INTERPRETATIONS

Peaks (cm^{-1})	Peak Interpretation
1600-1400	B_3-O asymmetrical stretching
1400-1200	OH^{-1} in plane stretching
1200-950	B_4-O asymmetrical stretching
950-850	B_3-O symmetrical stretching
850-750	OH^{-1} out of plane stretching
750-650	B_3-O stretching

At the peaks around 1400cm^{-1} and 1190cm^{-1}, the asymmetrical stretching of three coordinate boron and asymmetrical stretching of four coordinate boron were appeared. Other peaks at around 1050cm^{-1}, between 910 - 880cm^{-1} and one peak observed at 987.73cm^{-1} were also the asymmetrical stretching of four coordinate boron. And the last peaks seen at about 710cm^{-1} might be the stretching of three coordinate boron.

IV. CONCLUSION

Zinc borate (ZB) is a multifunctional fire retardant containing different proportion of zinc, magnesium and boric oxides, respectively. The analysis results (XRD, FT-IR and Raman) showed that low temperature solid-state zinc borate synthesis from ZnO and $H_3BO_3$was achieved. At 600 and 700°C temperature the formation of "01-071-0634" coded zinc borate (ZnB_4O_7) was the major phases and at the ratio of 1:4, crystal scores were the highest. As seen from (1), the formation of ZnB_4O_7 zinc borate at 1:4 ratio was produced as expected.

$$ZnO(s)+4H_3BO_3(s)\xrightarrow{heat}ZnB_4O_7(s)+6H_2O(g) \quad (1)$$

The FT-IR results of the products showed the characteristic peaks of the dehydrated zinc borates.

REFERENCES

[1] M. Gonen, D. Balkose, R. B. Gupta, and S. Ulku, "Super critical carbondioxide drying of methanol zinc borate mixtures", *Ind. Eng. Chem. Res*.,vol. 48, pp. 6869–6876, 2009.
[2] C. Ting, D. Jian-Cheng, W. Long-Shuo, and F. Gang, "Preparation and characterization of nano-zinc borate by a new method", *J. Mater. Process. Tech*., vol. 209, pp. 4076–4079, 2009.
[3] D. Gürhan, G. Ö. Çakal, İ. Eroğlu, and S. Özkar, Kesikli reaktörde çinko borat üretimini etkileyen parametrelerin incelenmesi, 1. National Boron Workshop Symposium Book, April 28-29, Ankara, 2005.
[4] D. Schubert, F. Alam, M. Visi and C. Knobler, "Structural characterization and chemistry of the industrially important zinc borate $Zn[B_3O_4(OH)_3]$", *Chem. Mater*., vol. 15, pp. 866-871, 2002.
[5] H. E. Eltepe, D. Balköse, and S. Ülkü, "Effect of temperature and time on zinc borate species formed from zinc oxide and boric acid in aqueous medium", *Ind. Eng. Chem. Res*., vol. 46, pp. 2367-2371, 2007.
[6] A. V. Shete, S. B. Sawant, and V. G. Pangarkar, "Kinetics of fluid–solid reaction with an insoluble product: zinc borate by the reaction of boric acid and zinc oxide", *J. Chem. Technol. Biot.*, vol. 79, pp. 526–532, 2004.
[7] X. Shi, Y. Xiao, M. Li, L. Yuan, and J. Sun, "Synthesis of an industrially important zinc borate, $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, by a rheological phase reaction method" *Powder Technol*., vol. 186,pp. 263-266, 2008.
[8] H. Igarashi, H. Sawada, A. Tatebe, and K.Sakao, Patent No: 6780913, U.S.A., 2002.

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Nil Baran Acarali was graduated from B.Scin Food Eng. Department at Trakya Univ., Edirne in 2000, both M.Sc. and Ph.D. in Chemical Eng. Department at Yildiz Tech. Univ., Istanbul in 2003 and 2008, respectively. She has published nine articles in science citation index, over twenty nine studies in international conference proceedings and national proceedings. Her articles have fourty two cited references. The research interests are supercritical fluids technology, polymer technology, boron technology, fly ash characterization and heavy metal adsorption. The research field in boron technology is zinc borate production. Dr. Baran Acarali is an online member of boron research.

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