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Temperature Effect on the Solid-State Synthesis of Dehydrated Zinc Borates

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***Abstract*—**Turkey has 72 % of total world boron reserves on the basis of B_2O_3.Borates that is a refined form of boron minerals have a wide range of applications**.** Zinc borates can be used as multi-functional synergistic additives. 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 between 500 and 800°C using the starting materials of ZnO and H_3BO_3 with 1:4 mole ratio. 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), Fourier Transform Infrared Spectroscopy (FT-IR) and Raman Spectrometer. As a result the form of ZnB_4O_7 was synthesized with the highest crystal score at 800°C.

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

I. Introduction

ZINC borates are commonly used in rubber, plastic, ceramic, paint, glass, electric insulation, wood applications, cement, and medicine as the flame retardant, smoke suppressant, afterglow suppressant, and anti-tracking agent in both halogen-containing and halogen-free polymers. Furthermore, zinc borates have been used as the preservative in wood composites, as the anticorrosive pigments in coatings, and as the polymers additives to promote char formation, suppress smoke, and retard combustion [1, 2].

Zinc borate is produced by reaction between aqueous boric acid and zinc oxide above 70°C. 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 [3].

Shi et al.[4] 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.

Shi et al.[5] investigated $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ nanorods synthesized by a hydrothermal route with the surfactant of PEG-300 as template. The pH value and synthetic temperature had the important influence on the composite, while the temperature and time had the effect on the morphology of products. The study on the flame-retardant property of $4ZnO{\cdot}B_2O_3{\cdot}H_2O$ nanorodsis underway. Igarashi et al.[6] 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 between 500°C and 800°C were aimed. Synthesized products are characterized by X-Ray Diffraction (XRD) (Philips PANanalytical, Xpert-Pro), Fourier Transform Infrared Spectroscopy (FT-IR) (Perkin Elmer, Spectrum One) and 400FRaman Spectrometer (Perkin Elmer Raman Station).

II. Materials and Methods

A. RawMaterials and Characterization

Zinc oxide was supplied from Colakoglu Chemistry Limited Company and boric acid was retrieved from Kirka Boron Management Plant in Eskisehir.

All products were characterized by XRD, FT-IR and Raman to identify the structure and the functional groups present in the products.

The X-Ray analysis was carried out at an ambient temperature by using a Philips Panalytical X'Pert-Pro Diffraction with CuKa radiation (k = 0.15418 nm) at operating parameters of 40 mA and 45 kV with step size 0.02° and speed of 1°/min. Phase identification of solids was performed by inorganic crystal structure database (ICSD) (Fig. 1).

The FT-IR spectrum was achieved after force was applied to the sample, pushing it onto the diamond surface. The IR spectrum was recorded in the spectral range of 4000 to 650 cm^{-1} at ambient temperature and the resolution used was 4 cm^{-1} (Fig. 2).

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For Raman Spectrometer, the parameters of exposure time (seconds) and number of exposures was set to 4. Measurement range is selected as 3280–250 cm^{-1} and data interval was selected as 2 cm^{-1} (Fig. 3).

Fig. 1 Philips PANalytical X-Ray Diffraction

Fig. 2 Perkin Elmer Spectrum One FT-IR Spectrometer

Fig. 3 Perkin Elmer Raman Station 400FRaman 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 100 bars for the duration of two minutes. The ratios of raw materials were selected as 1:4, 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 4 hours for 500-800°C.

III. Results and Discussion

A. RawMaterial Characterization Results

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

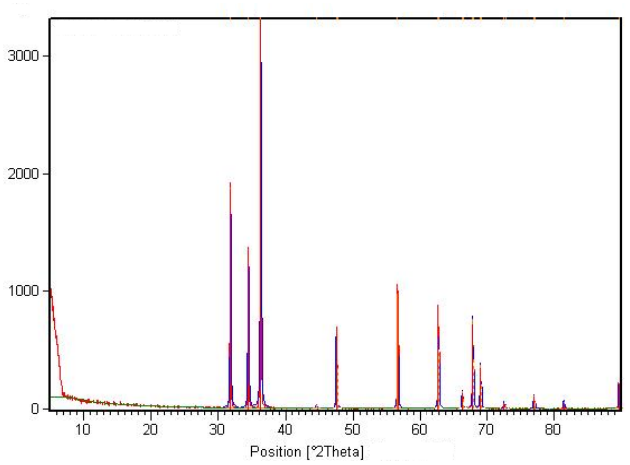

Fig. 5 XRD analysis of ZnO

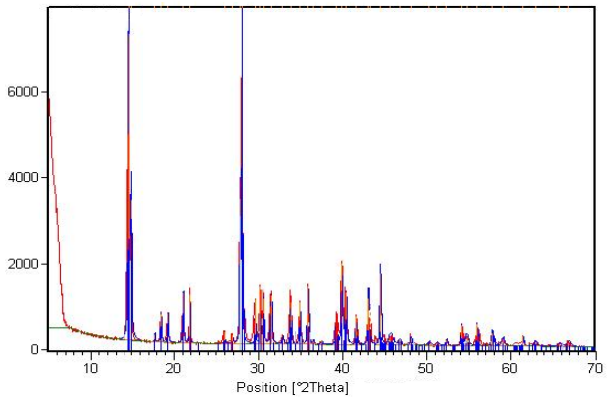

Fig. 6 XRD analysis of standard boric acid

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.

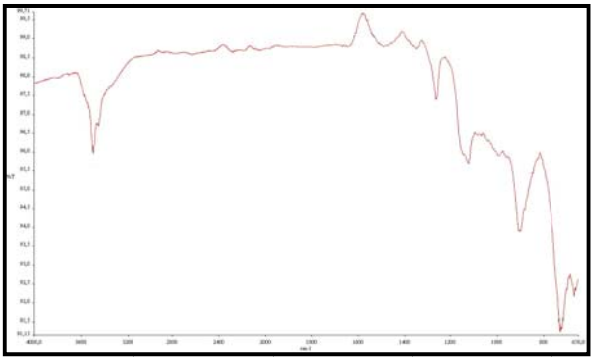

Fig. 7 FT-IR spectrum of ZnO

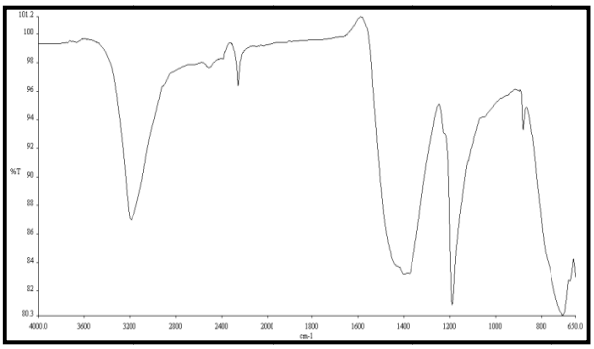

Fig. 8 FT-IR spectrum of boric acid

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 between 500°C and 800°C were given in Fig. 9 and Table II.

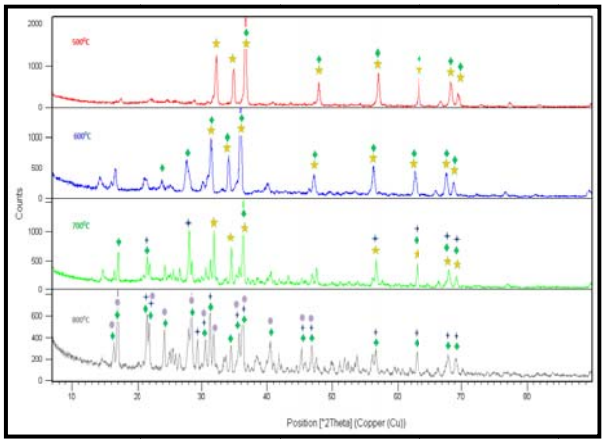

Fig. 9 XRD pattern of the synthesized zinc borates
01-071-0634: 00-016-0283:
01-071-2063: 01-079-2205:

TABLE II
XRD Results of Synthesized Products

Reaction Temperature	pdf no	Name	Formula	Score
500	01-071-0634	Zinc Borate	ZnB_4O_7	15

	01-079-2205	Zinc Oxide	ZnO	73
600	01-071-0634	Zinc Borate	ZnB_4O_7	32
	01-079-2205	Zinc Oxide	ZnO	75
700	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
800	01-071-0634	Zinc Borate	ZnB_4O_7	69
	00-004-2063	Zinc Borate	ZnB_2O_4	38
	00-016-0283	Zinc Borate	ZnB_4O_7	64

From the results of the XRD analysis, it is seen that unreacted ZnO were seen between the temperatures of 500°C and 700°C. In the temperature of 800°C, complete formation of zinc borates were occurred. At all the temperatures the zinc borate that had a formula of ZnB_4O_7 and "01-071-0634" powder diffraction file (pdf) were formed as major phase. The minor phase of another zinc borate formulated ZnB_2O_4 and "00-004-2063" powder diffraction file (pdf) were formed as minor phase at the temperatures of 700°C and 800°C. The highest crystal score was seen at the temperature set 800°C with a value of 69.

C. FT-IR and Raman Results

FT-IR and Raman spectrums of the synthesized minerals were shown in Fig. 10 and Fig. 11, the peak explanations were given in Table III and Table IV.

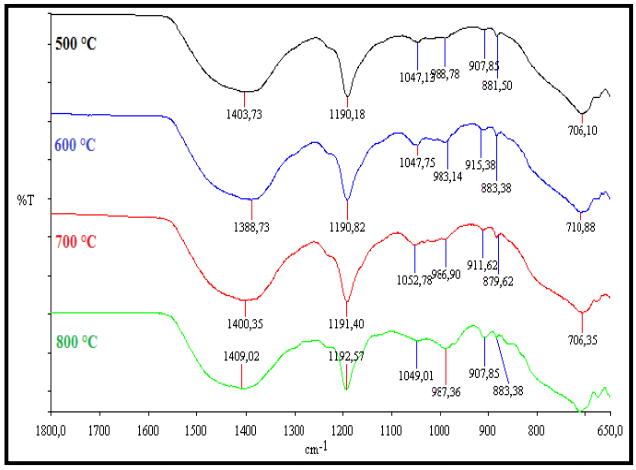

Fig. 10 FT-IR spectrums of the synthesized products

TABLE III
FT-IR PEAK EXPLANATIONS

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 greater than 1400 cm^{-1} were the asymmetrical stretching of three coordinate boron. Peaks at between 1192.57 and 983.14 cm^{-1} were the asymmetrical stretching of four coordinate boron. Symmetrical stretching of three coordinate boron peaks were observed between the band values of 915.38 and 879.62 cm^{-1}. The final peaks that were formed at about 706 cm^{-1} were the stretching of three coordinate boron.

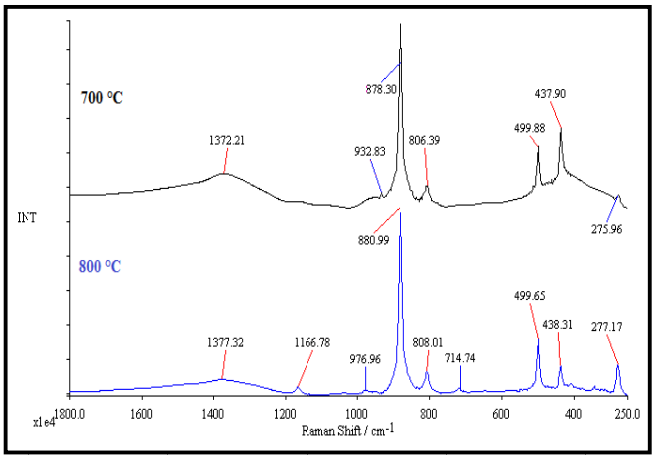

Fig. 11 Raman spectrums of the synthesized products

TABLE IV
RAMAN PEAK EXPLANATIONS

Peaks (cm^{-1})	Peak Interpretation
1600-1200	B_3-O asymmetrical stretching
1100-1060	B_4-O asymmetrical stretching
964-872	B_3-O symmetrical stretching
872-755	B_4-O symmetrical stretching
755-627	$[B(OH)_4]^-$ and B_3-O stretching
627-516	$[B_6O_7(OH)_6]^{2-}$ / $[B_3O_3(OH)_4]^-$ and $[B_4O_5(OH)_4]^{2-}$anions, B_3-O and B_4-O stretching
516-300	$[B_5O_6(OH)_4]^-$ and B_4-O stretching

The Raman spectrums of the zinc borates which were synthesized at 500°C and 600 °C, were not obtained due to their florescence effect. The florescence effect is occurred when the samples reflects the laser. These samples Raman spectrums cannot be obtained. But the zinc borates that synthesized at 700°C and 800°C were not reflected the laser so their Raman spectrums were obtained.

The peaks at around 1370 cm^{-1} were the asymmetrical stretching of three coordinate boron. The peaks were observed at 932cm^{-1}, 880 cm^{-1} and 878 cm^{-1}were the three coordinate boron symmetrical stretching.Four coordinate boron symmetrical stretching were seen at the peaks values at about 806 cm^{-1}. $[B(OH)_4]^-$ and three coordinate boron stretching were seen at 800°C reaction temperature synthesized zinc borates with a peak value of 714.74 cm^{-1}. Final peaks were due to the $[B_5O_6(OH)_4]^-$ and four coordinate boron stretching.

IV. CONCLUSION

Zinc borate (ZB) is a multifunctional fire retardant

containing different proportion of zinc/boric oxides and having high dehydration temperature. The characterization results of XRD, FT-IR and Raman showed that at the temperatures of 500°C through 700°C, solid-state zinc borate syntheses were not completed. But at the temperature of 800°C, the formations of zinc borates were completed. At all the temperatures the formation of "01-071-0634" coded zinc borate (ZnB_4O_7) was the major phase among the zinc borates. The crystal score of ZnB_4O_7 were the highest at the 800°C.

From The FT-IR and Raman results of the products showed the characteristic peaks of the dehydrated zinc borates were obtained.

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