

# The Determination of the Zinc Sulfate, Sodium Hydroxide and Boric Acid Molar Ratio on the Production of Zinc Borates

N. Tugrul, A. S. Kipcak, E. Moroydor Derun, S. Piskin

**Abstract**—Zinc borate is an important boron compound that can be used as multi-functional flame retardant additive due to its high dehydration temperature property. In this study, the raw materials of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaOH}$  and  $\text{H}_3\text{BO}_3$  were characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) and used in the synthesis of zinc borates. The synthesis parameters were set to 100°C reaction temperature and 120 minutes of reaction time, with different molar ratio of starting materials ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}:\text{NaOH}:\text{H}_3\text{BO}_3$ ). After the zinc borate synthesis, the identifications of the products were conducted by XRD and FT-IR. As a result, Zinc Oxide Borate Hydrate [ $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ ], were synthesized at the molar ratios of 1:1:3, 1:1:4, 1:2:5 and 1:2:6. Among these ratios 1:2:6 had the best results.

**Keywords**—Zinc borate,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{H}_3\text{BO}_3$ , XRD, FT-IR.

## I. INTRODUCTION

ZINC borate have 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]. Also zinc borates can be grouped in the synthetic hydrate metal borates [5].

Zinc borate is produced by reaction between aqueous boric acid and zinc oxide above 70°C. Zinc borate is ( $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$ ) 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].

The preparation of  $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  from zinc oxide and boric acid by a rheological phase reaction is studied by Shi et al. [7]. XRD, TG, DTA and SEM used for the characterization

analyses. In addition, the effects of experimental conditions and particle size distribution on the characteristics of the products were studied. The synthetic method for the production of zinc borates is easy, pollution friendly and have high reaction yield between 95-99%. Additionally, zinc borate it can be used to remove various toxic gases and organic compounds.

Igarashi et al. [8] studied the synthesis of zinc borates in a two-step reaction. 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 determination of the optimum molar ratio of zinc sulfateheptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium hydroxide ( $\text{NaOH}$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ) is aimed in the hydrothermal synthesis of zinc borates. Synthesized products are characterized by Philips Panalytical, Xpert-ProX-Ray Diffraction (XRD) and Perkin Elmer, Spectrum One Fourier Transform Infrared Spectroscopy (FT-IR).

## II. MATERIALS AND METHODS

### A. Raw Materials

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was supplied from Sigma Aldrich Reagent Plus® ( $\geq 99.0\%$  purity),  $\text{NaOH}$  was supplied from Merck Chemicals (Product number: 1.06462.5000,  $\geq 97.0\%$  purity) and  $\text{H}_3\text{BO}_3$  was retrieved from Kirka Boron Management Plant in Bandirma.  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NaOH}$  were used without pretreatment and  $\text{H}_3\text{BO}_3$  was treated using agate mortar and sieved to 200 meshes (Fig. 1). Characterizations of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3$  were conducted by XRD (Fig. 2) and FT-IR spectroscopy with Universal ATR sampling accessory – Diamond / ZnSe Crystal (Fig. 3).



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

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Fig. 2 Philips PANalytical XRD



Fig. 3 Perkin Elmer Spectrum One FT-IR Spectrometer

#### B. Hydrothermal Syntheses and Characterizations

In the synthesis, several molar ratios of the  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (Z) NaOH (N) and  $\text{H}_3\text{BO}_3$  (H) were tested. 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 100°C, and reaction time were set to 120 minutes. These parameters were selected from the study of Tugrul et al. [9].

$\text{H}_3\text{BO}_3$  was dissolved in demineralized water at the 100°C temperature then  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and NaOH were added. After the addition of NaOH, commercial zinc borate ( $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ ) retrieved from local market in Turkey (in terms of  $\text{H}_3\text{BO}_3$ , 0.5% w/w) was added. At the end of the 120 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  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_3\text{BO}_3$  and commercial  $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$  were given in Figs. 4-6 and Table I.

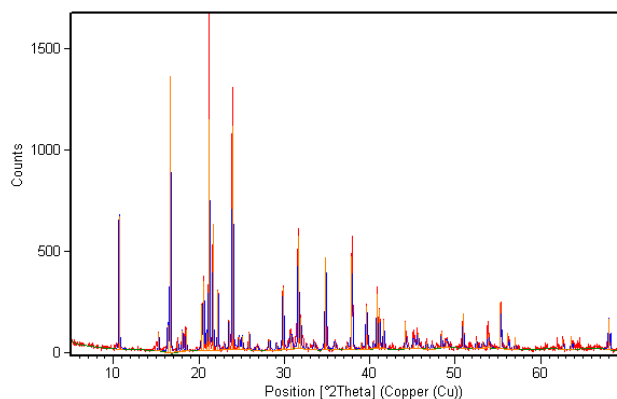
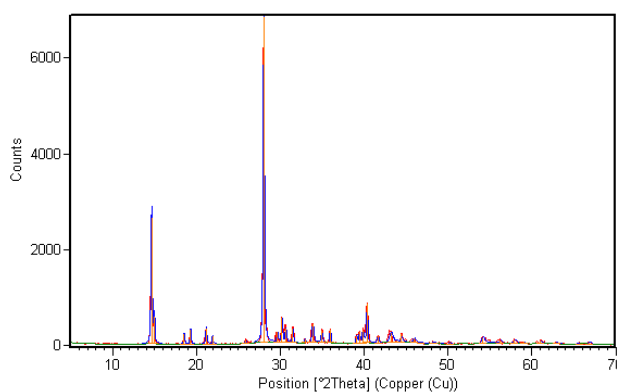
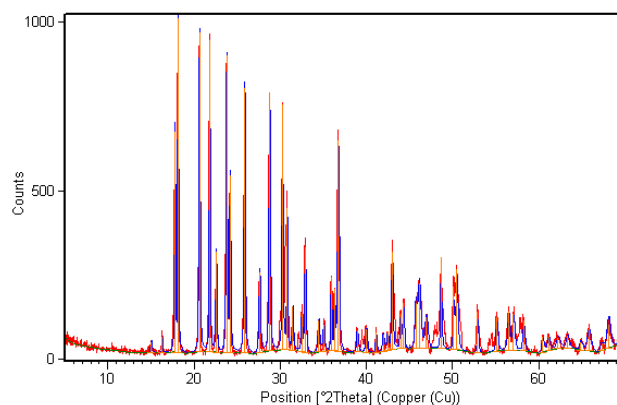
Fig. 4 XRD pattern of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ Fig. 5 XRD pattern of  $\text{H}_3\text{BO}_3$ Fig. 6 XRD pattern of commercial  $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ 

TABLE I  
XRD RESULTS OF RAW MATERIALS

| Reference Code | Compound Name             | Chemical Formula                                                 | Score |
|----------------|---------------------------|------------------------------------------------------------------|-------|
| 01-075-0949    | Bianchite                 | $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$                        | 55    |
| 00-009-0395    | Goslarite                 | $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$                        | 24    |
| 01-073-2158    | Sassolite                 | $\text{H}_3\text{BO}_3$                                          | 62    |
| 00-035-0433    | Zinc Oxide Borate Hydrate | $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ | 80    |

From the XRD analysis of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , it is seen that compound was consist of “01-075-0949” coded bianchite and

“00-009-0395” coded goslarite, that their structural formulas are  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , respectively.  $\text{H}_3\text{BO}_3$  and commercial  $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$  were found as, “01-073-2158” coded sassolite ( $\text{H}_3\text{BO}_3$ ) and “00-035-0433” coded zinc oxide borate hydrate, respectively.

FT-IR spectrum of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaOH}$ ,  $\text{H}_3\text{BO}_3$  and commercial  $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$  were given in Figs. 7, 8, 9 and 10, respectively.

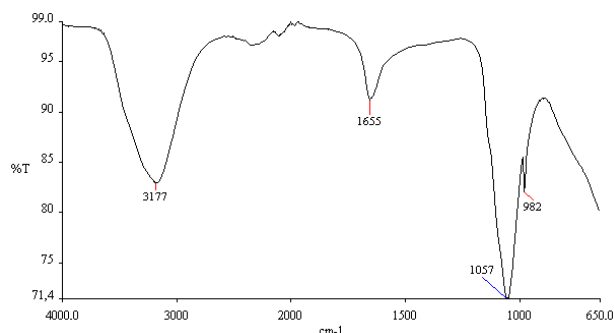


Fig. 7 FT-IR spectrum of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

According to the FT-IR inorganic library search,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was found as: “Zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ )” with 0.588 score (out of 1) and “AI0167” code.

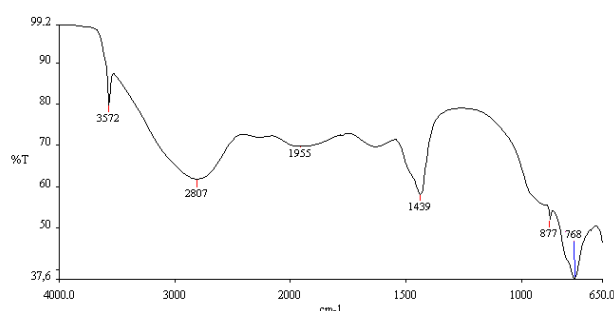


Fig. 8 FT-IR spectrum of  $\text{NaOH}$

$\text{NaOH}$  was not found in the FT-IR inorganic library search.

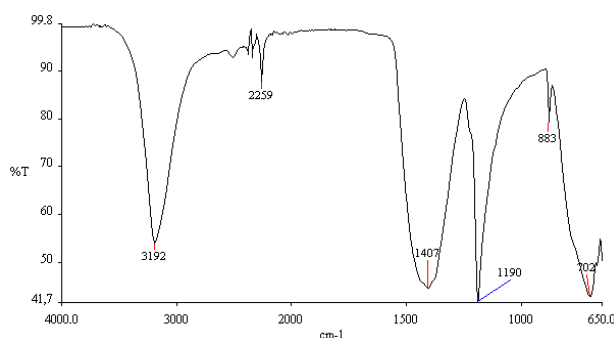


Fig. 9 FT-IR spectrum of  $\text{H}_3\text{BO}_3$

According to the FT-IR inorganic library search,  $\text{H}_3\text{BO}_3$  was found as: “Boric acid ( $\text{H}_3\text{BO}_3$ )” with 0.704 score (out of

1) and “AI0031” code.

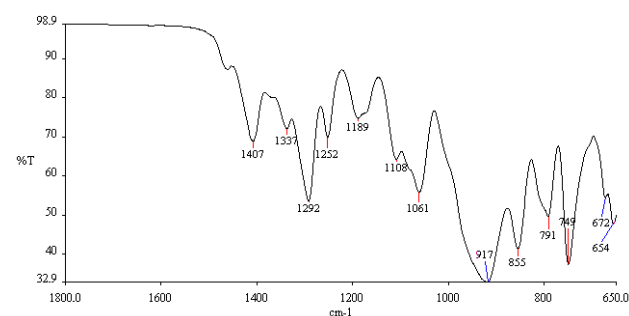


Fig. 10 FT-IR spectrum of commercial  $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$

Also commercial  $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$  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.

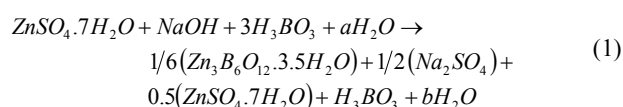
### B. Synthesized Products

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

TABLE II  
XRD RESULTS OF SYNTHESIZED ZINC BORATES

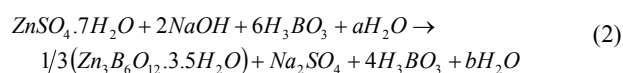
| Molar Ratio (Z:N:H) | Reference code | Mineral Name              | Mineral Formula                                                  | Score |
|---------------------|----------------|---------------------------|------------------------------------------------------------------|-------|
| 1:1:1               | -              | -                         | -                                                                | -     |
| 1:1:2               | -              | -                         | -                                                                | -     |
| 1:1:3               | 00-035-0433    | Zinc Oxide Borate Hydrate | $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ | 72    |
| 1:1:4               | 00-035-0433    | Zinc Oxide Borate Hydrate | $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ | 68    |
| 1:2:4               | -              | -                         | -                                                                | -     |
| 1:2:5               | 00-035-0433    | Zinc Oxide Borate Hydrate | $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ | 72    |
| 1:2:6               | 00-035-0433    | Zinc Oxide Borate Hydrate | $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ | 75    |

Between the molar ratios of 1:1:1 and 1:1:4 the expected formation occurs at 1:1:3 and 1:1:4, with XRD score of 72 and 68, respectively. The reaction scheme was given in (1):



From the reaction it is seen that both raw materials used were excess that led to lower reaction yields (<50%).

At the second step of the reactions it is decided to increase to molar ratio of  $\text{NaOH}$  in order to decrease the  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  from the products. From the XRD results of the second part synthesis, it is seen that in the molar ratio of 1:2:5 and 1:2:6, the formation of zinc borates was accomplished with very high XRD scores of 72 and 75, respectively. The new reaction scheme was given in (2):



Also the reaction yields were calculated between 95-98% at the molar ratios of 1:2:5 and 1:2:6. The XRD patterns of the zinc borates were given in Figs. 11 and 12, respectively.

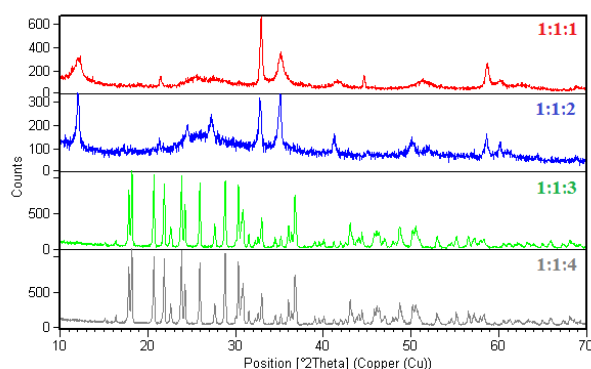


Fig. 11 XRD patterns of first step synthesized zinc borates

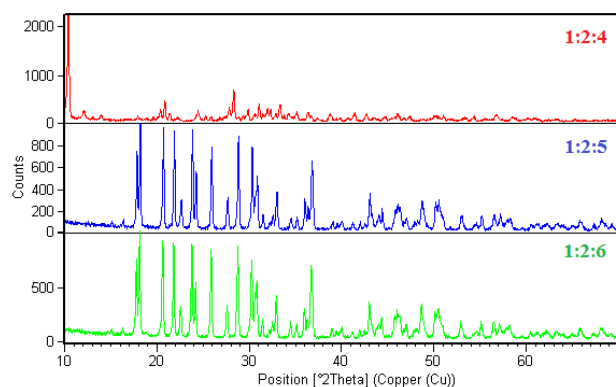


Fig. 12 XRD patterns of second step synthesized zinc borates

The FT-IR spectrums and peak interpretations of the synthesized zinc borates were given in Figs. 13, 14 and Table III, respectively.

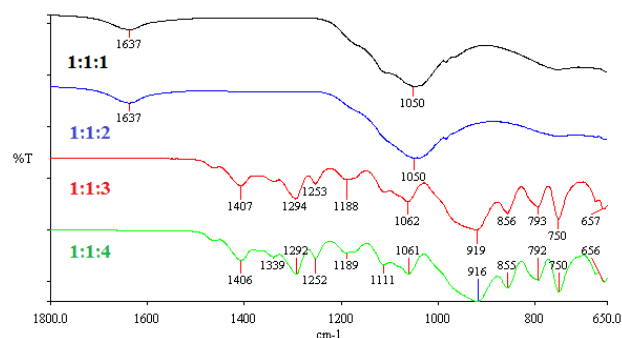


Fig. 13 FT-IR spectra of the first step synthesized zinc borates

It is seen that at the molar ratios of 1:1:1 and 1:1:2 the characteristic peaks of zinc borates were not seen.

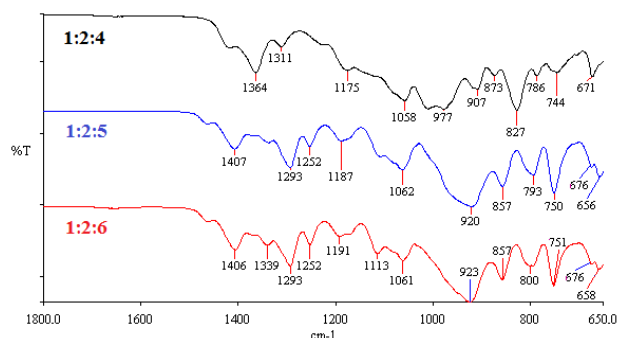


Fig. 14 FT-IR spectra of the first step synthesized zinc borates

Some characteristic peaks were seen of the molar ratio of 1:2:4 but at the ratio of 1:2:5 and 1:2:6 all of the characteristic peaks of zinc borates were matched. At the FT-IR spectral 1:1:3, 1:1:4, 1:2:5, 1:2:6 and commercial  $\text{Zn}_3\text{B}_6\text{O}_{12} \cdot 3.5\text{H}_2\text{O}$ ; the peaks between  $1407\text{--}1252\text{ cm}^{-1}$  represents the three coordinate boron asymmetrical stretching. Bending of (B-O-H) is seen between the peaks of  $1191\text{--}1111\text{ cm}^{-1}$ . Four coordinate boron asymmetrical and three coordinate boron symmetrical stretching are observed between the peaks of  $1062\text{--}977\text{ cm}^{-1}$  and  $923\text{--}873\text{ cm}^{-1}$ , respectively. Between the peaks of  $857\text{--}786\text{ cm}^{-1}$ , 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  $751\text{--}744\text{ cm}^{-1}$  and  $676\text{--}654\text{ cm}^{-1}$ , respectively.

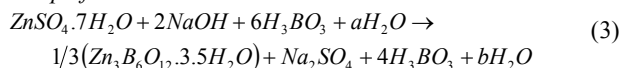
TABLE III  
FT-IR PEAK INTERPRETATIONS

| Peaks ( $\text{cm}^{-1}$ ) | Peak Interpretation                                | Symbol                           |
|----------------------------|----------------------------------------------------|----------------------------------|
| 1778-1424                  | Bending of H-O-H                                   | $\delta(\text{H-O-H})$           |
| 1423-1241                  | $\text{B}_3\text{-O}$ asymmetrical stretching      | $\nu_{as}(\text{B}_3\text{-O})$  |
| 1240-1099                  | Bending of B-O-H                                   | $\delta(\text{B-O-H})$           |
| 1098-958                   | $\text{B}_4\text{-O}$ asymmetrical stretching      | $\nu_{as}(\text{B}_4\text{-O})$  |
| 957-873                    | $\text{B}_3\text{-O}$ symmetrical stretching       | $\nu_s(\text{B}_3\text{-O})$     |
| 872-864                    | Boric acid characteristic peak                     | $\nu_p(\text{H}_3\text{BO}_3)$   |
| 863-756                    | $\text{B}_4\text{-O}$ symmetrical stretching       | $\nu_s(\text{B}_4\text{-O})$     |
| 755-677                    | Characteristic peak of $[\text{B}(\text{OH})_4]^-$ | $\nu_p[\text{B}(\text{OH})_4]^-$ |
| 676-642                    | $\text{B}_3\text{-O}$ bending                      | $\delta(\text{B}_3\text{-O})$    |

#### IV. CONCLUSION

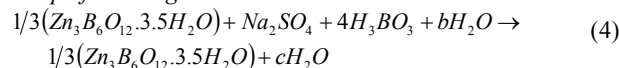
In this study the optimum molar ratio of the Z:N:H were determined as 1:2:6 for the zinc borate synthesis. The reaction, washing and drying steps are given in 3), (4) and (5), respectively.

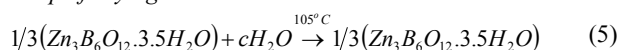
##### Step of reaction



where zinc borate was obtained at crystal phase

##### Step of washing



*Step of drying*

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

## ACKNOWLEDGMENT

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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.



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