A novel approach for the production of zinc borate (4ZnO \cdot B_2O_3 \cdot H_2O) using a single-step hydrothermal method

Abstract: Zinc borate having the formula of 4ZnO \cdot B_2O_3 \cdot H_2O has been used as a fire retardant for polymers requiring high processing temperatures since it has a high dehydration temperature (around 415°C). The effects of reaction time, reaction temperature were investigated on the heterogeneous reaction between solid zinc oxide and boric acid solution. A stoichiometric amount of zinc oxide and 5.0% excess boric acid were used in experiments and the other parameters, mixing speed (1700 rpm), the solid-liquid ratio of 20%, and the amount of seed crystal (3.9% wt) were kept constant for all experiments. A 91.1% conversion was obtained at 120°C for 5 h of reaction time. Precipitated product was filtered and washed by hot water to remove the excess boric acid. Finally it was dried until reaching to a constant mass in an air circulating oven at 105°C. Powder products were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). FTIR spectrum and XRD pattern of powders are consistent with data of the zinc borate given in the literature. According to SEM analysis, whiskers are less than 1 µm in diameter and their lengths are in the range of 1-10 µm.

Keywords: zinc borate, fire retardant, whisker, hydrothermal method, heterogeneous reaction

1 Introduction

Zinc borates are in the top ten in terms of global production and use of boron-based industrial chemicals (Schubert, 2011). Every year, a substantial amount of zinc borates is produced and used for various applications in industry due to their specific properties e.g. a flame retardant, corrosion inhibitors, smoke suppressant, synergistic effect, anti-bacterial property, good mechanical properties, and high surface area (Schubert, 2019). The utilization of zinc borates in the formulation of polymer-based composites ensures that the composite has a good flame retardant and thermal stability (Feng et al., 2015).

There are various hydrated zinc borates having different formulas as following: 2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O, 2ZnO \cdot 3B_2O_3 \cdot 3H_2O, 2ZnO \cdot 3B_2O_3 \cdot 7H_2O, 4ZnO \cdot B_2O_3 \cdot H_2O, 2ZnO \cdot 3B_2O_3 \cdot 9H_2O, 3ZnO \cdot 5B_2O_3 \cdot 14H_2O, ZnO \cdot B_2O_3 \cdot 2H_2O, 6ZnO \cdot 5B_2O_3 \cdot 3H_2O, and ZnO \cdot B_2O_3 \cdot 2H_2O (Schubert, 1995). The molar ratio of B_2O_3/ZnO and the number of hydrates in zinc borate structures could be arranged by varying the several parameters such as reaction stoichiometry, temperature, time, mixing rate and solid-liquid ratio. Zinc borate with the formula of 4ZnO \cdot B_2O_3 \cdot H_2O is preferred in the polymer and rubber industries since it has a high dehydration temperature (approx. 415°C). The use of those inorganic flame retardants has been increasing as they replace the organic chlorine/bromine based additives which have been used in polymers for several decades. 4ZnO \cdot B_2O_3 \cdot H_2O is suitable for extrusion requiring high processing temperatures (Gao and Zhang, 2015). It is also utilized in paint, electrical/electronic, transportation and building material applications (Shen et al., 2008). Recently, luminescence property of zinc borate with 4ZnO \cdot B_2O_3 \cdot H_2O structure has been investigated by doping different lanthanides (Eu³⁺, Eu²⁺, and Tb³⁺) (Cao et al., 2018). Morphology and particle size of zinc borates, which are used as an additive in polymers, are extremely important. Zinc borate whiskers have improved mechanical properties of polymers since they behave like a fiber and have a high...
surface area due to low dimensions. In addition, they not only enhance the flame retardant property of polymer but also increase the strength of polymer matrices (Gao and Zhang, 2015).

Production of zinc borate \((4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O})\) has been investigated in literature by using several techniques, such as two-step method (Schubert, 1995), surface active agent supported hydrothermal method (Shi et al., 2008), wet chemical method (Mergen et al., 2012) and one-step precipitation reaction (Gao and Zhang, 2015) where stoichiometric ratio of reactants, stirring rate, reaction temperature and time were investigated. While ZnO and zinc salts are used as a zinc source; boric acid and/or borate salts like borax are used in the production of zinc borates. In the wet chemical method, \(2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}\) was initially produced by the reaction of zinc nitrate \((\text{Zn(NO}_3)_2\cdot 6.5\text{H}_2\text{O})\) and borax pentahydrate \((\text{Na}_2\text{B}_4\text{O}_5\cdot 5\text{H}_2\text{O})\). Then, it was converted into \(4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}\) in the second step. Morphology of product had acicular or a rod-shaped structure. The diameter of the rods was in the range of 5-50 nm, whereas lengths of rod-shaped structures were above 1 µm (Mergen et al., 2012). The synthesis of zinc borate \((2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O})\) was studied using both zinc sulfate and zinc oxide with the help of sonication. The utilization of ultrasonic energy in the reaction has increased the reaction rate inducing a lower reaction time and 90% yield was obtained at low temperatures (Ersan et al., 2016, 2020). In another study, \(\text{Na}_2\text{B}_4\text{O}_5\cdot 10\text{H}_2\text{O}\) and sodium dodecylbenzene sulfonate were mixed together and \(\text{Zn(NO}_3)_2\cdot 6.5\text{H}_2\text{O}\) solution was added into that mixture. In this method, higher reaction time was required for a complete conversion. Zinc borate particles had nanowhisker morphology with particle size of 50-100 nm (Gao and Zhang, 2015). In surface active agent supported hydrothermal method, \(\text{ZnSO}_4\cdot 7\text{H}_2\text{O}\) and surfactant (PEG 300) were mixed, the slurry reacted with \(\text{Na}_2\text{B}_4\text{O}_5\cdot 10\text{H}_2\text{O}\) for 24 h of reaction time. Nano and microstructured particles are in the form of wire, rod, and lamella-like shapes and microspheres (Shi et al., 2008). In the two-step method, production of \(4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}\) was carried out by reaction of ZnO and \(\text{H}_3\text{BO}_3\) in the presence of seed crystal of \(4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}\) at the boiling point of the mixture. After ZnO mixed with water, the slurry was heated as much as to boiling temperature of the mixture. \(\text{H}_3\text{BO}_3\) is added gradually into the reaction mixture (Schubert, 1995). As mentioned above, those methods have some disadvantages, such as long reaction time, multiple steps and impurities remained in the product due to surfactant used. These disadvantages will significantly influence the production cost of the zinc borate. The development of a feasible method for the production of zinc borate \((4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O})\) is important to eliminate those drawbacks. The overall reaction occurring between zinc oxide and boric acid is shown in Eq. 1. In this reaction, boric acid is added in several steps to maintain the solution pH above 6. Therefore, reaction conditions, such as reaction temperature, time, stoichiometric ratio of \(\text{B}_2\text{O}_3/\text{ZnO}\), pH, solid-liquid ratio, seed crystal, and mixing speed affect significantly the reaction between zinc oxide and boric acid (Schubert, 2019).

\[
2\text{ZnO}_\text{(s)} + \text{B(OH)}_3\text{(aq)} \rightarrow \text{Zn}_2\text{(BO}_3\text{)OH}_\text{(s)} + \text{H}_2\text{O}_\text{(l)}
\]  

The aim of this study is to produce zinc borate of \(4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}\) using the heterogeneous reaction of boric acid and zinc oxide by a single step hydrothermal method. The effects of reaction temperature and time were investigated keeping the other parameters constant. Powders obtained in the experiments were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

## 2 Results and discussion

As zinc oxide is insoluble in the aqueous phase, the reaction of boric acid and zinc oxide is a heterogeneous even though a portion of ZnO dissolves in the acidic medium of boric acid solution. Boric acid is a Lewis acid producing proton by dissolving in water where zinc oxide particles are attacked by those protons. Particle size of zinc oxide significantly influences its dissolution. On the other hand, the concentration of boric acid in aqueous phase dominates the borate anions formation. In the reaction medium, \(\text{Zn}^{2+}\) cations and borate anions (metaborate, triborate, pentaborate and etc.) crystallizes on the surface of seed crystal planes. The reaction mechanism between zinc oxide and boric acid was suggested as following:

- Formation of borate anions, \(\text{B(OH)}_4^-\), and proton, \(\text{H}_3\text{O}^+\), by dissolution of boric acid in an aqueous phase.
- Dissolution of zinc oxide particles in aqueous phase by proton, \(\text{H}_3\text{O}^+\).
- Mass transfer of \(\text{Zn}^{2+}\) cations to bulk phase (physical).
- Reaction takes place between borate ions and \(\text{Zn}^{2+}\) cations (chemical).
- Crystal growth of zinc borate molecules on the surface of the seed which provides a template surface.
2.1 FTIR analysis

Solid product was obtained by the reaction of zinc oxide and boric acid at different reaction temperature (90°C, 100°C, 110°C, and 120°C) and for reaction time (5 h), and the other parameters mixing speed (1700 rpm), solid-liquid ratio (20%) and the amount of seed crystal (3.9%) were kept constant. The FTIR spectra of powders obtained in the reactions are shown in Figure 1.

The broad band at 3356 cm\(^{-1}\) and at 3406 cm\(^{-1}\) in Figure 1 (Spectrum c) is due to O–H groups in the structure of zinc borate (Zhang et al., 2011). The shoulder peak at 1338 cm\(^{-1}\) and the peak 1244 cm\(^{-1}\) belong to the asymmetric stretching of B\(_{\text{B}}\)–O and in-plane bending of B–O–H, respectively. The medium peak at 1024 cm\(^{-1}\) and weak peak at 744 cm\(^{-1}\) are for asymmetric and symmetric stretching vibrations of B\(_{\text{A}}\)–O, respectively (Jun et al., 1995). The peaks at 714 cm\(^{-1}\) and 534 cm\(^{-1}\) are attributed to the out-of-plane bending of B\(_{\text{A}}\)–O and the in-plane bending of B\(_{\text{A}}\)–O, respectively. The small peak at 470 cm\(^{-1}\) is due to the in-plane bending of B\(_{\text{A}}\)–O.

When FTIR spectra of powder products synthesized at 110°C and 120°C in Figure 1 (Spectra c and d) are compared with the peaks of 4ZnO⋅B\(_2\)O\(_3\)⋅H\(_2\)O in the literature (Zhang et al., 2011), it is seen that they are compatible with the major peaks of 4ZnO⋅B\(_2\)O\(_3\)⋅H\(_2\)O. The presence of zinc oxide was determined from the vibration band between 400 cm\(^{-1}\) to 500 cm\(^{-1}\) in Figure 1 (Spectra a and b) (Nagaraju et al., 2017). It was concluded that reaction time less than 5 h is not enough to reach to a complete conversion as seen from the comparison of the spectra in Figure 2.

Zinc borate samples were obtained by the reaction of zinc oxide and boric acid for different reaction times (3, 4, 5, and 6 h) and at reaction temperature of 110°C, at the mixing rate of 1700 rpm. The FTIR spectra of those powders are shown in Figure 1. The major peaks of FTIR spectra of the products obtained for 5 and 6 h of reaction time given in Figure 2 (Spectra c and d) are consistent with the spectrum of the zinc borate (Zhang et al., 2011). However, spectra of the samples produced for the reaction time of 3 and 4 h in Figure 2 (Spectra a and b) are not consistent with the spectrum of zinc borate (4ZnO⋅B\(_2\)O\(_3\)⋅H\(_2\)O). The presence of zinc oxide was determined from the vibration band between 400 cm\(^{-1}\) to 500 cm\(^{-1}\) in Figure 2 (Spectra a and b) (Nagaraju et al., 2017). It was concluded that reaction time less than 5 h is not enough to reach to a complete conversion as seen from the comparison of the spectra in Figure 2.

2.2 XRD analysis

XRD patterns of the powders synthesized at 110°C and 120°C and for the reaction time of 5 h keeping the all
other parameters constant are shown in Figure 3 (Patterns a and b). $2\theta$ values for the main peaks of zinc borate ($4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$) were reported as 18.9°, 23.0°, 29.0°, and 37.0° (Gönen et al., 2018; Shi et al., 2007). $2\theta$ values of the XRD patterns of solid products are determined as 18.83°, 22.25°, 28.51°, and 36.45° which are completely consistent with the XRD pattern given in the literature (Gönen et al., 2018).

XRD pattern of solid product synthesized at 110°C and for 4 h shown in Figure 3 (Pattern c) is not consistent with the pattern given in the literature and $2\theta$ values of the main peaks are 31.79°, 34.43°, and 36.27° as depicted in Figure 3 (Pattern c). These main peaks belong to zinc oxide, and they indicated that unreacted zinc oxide is present in the powder (Nagaraju et al., 2017). The reaction time of 4 h is not enough to complete the reaction. Thus unreacted zinc oxide was determined in the XRD analysis that result supports the finding in FTIR analysis.

2.3 SEM analysis

Particle size, surface morphology and the degree of agglomeration of the powders produced at different reaction conditions were examined using SEM. Figures 4a-c represent the SEM microphotographs of solid products obtained at 110°C for 4, 5, and 6 h. Figures 4d shows the product obtained at 120°C for 5 h.

According to SEM microphotographs of the samples in Figures 4b-d it can be said that they have whisker...
structures. Those whisker structures exhibited almost homogeneous distribution as shown in Figures 4c,d. The diameter of whiskers is less than 1 µm, and their length is in the range of 1-10 µm. In Figure 4a, the particles are in the form of layers which are agglomerated. By increasing the reaction time from 4 h to higher values, agglomerated structures were transformed into thin and long rods. It can be said that low reaction time (4 h) is not enough to produce the desired zinc borate morphology. According to SEM images, reaction time has significantly affected the morphology of zinc borate whiskers which are likely controlled by changes in rates of crystallization and growth mechanisms. The formation of whisker structures for zinc borate in this study would provide good mechanical properties in polymer composite as given in literature (Gao and Zhang, 2015).

2.3.1 EDS (energy dispersive X-ray spectroscopy) analysis

EDS analysis of solid product obtained at 110°C for 5 h is shown in Figure 5. The theoretical composition of zinc borate (4ZnO·B₂O₃·H₂O) is 63.31% zinc, 30.97% oxygen, and 5.23% boron. The chemical composition of the zinc borate sample was determined as Zn: 52.6%, O: 24.4%, and B: 23.0% using the data in the EDS analysis. While the experimental and theoretical composition value of Zn and O are close to each other, the value of B is completely different as boron element has low atomic mass (Zhao et al., 2014).

2.4 TGA analysis

TG thermogram of the solid product obtained at 110°C for 5 h reaction time is shown in Figure 6. Zinc borate sample decomposed thermally in one step which began at around 410°C and ended at around 600°C. The mass loss occurred in this temperature range is 4.1% which approximately corresponds to the theoretical amount of water (4.35%) in zinc borate. The removal of water from the zinc borate structure is shown by Eq. 2 (Gönen et al., 2018).

\[ 4\text{ZnO}\cdot\text{B}_2\text{O}_3\cdot\text{H}_2\text{O} \rightarrow 4\text{ZnO}\cdot\text{B}_2\text{O}_3 + \text{H}_2\text{O} \]
2.5 Volumetric analysis

After each experiment, the slurry was filtered and the filter cake was washed with hot distilled water to remove the unreacted boric acid. The amount of boric acid in the mother liquor and wash water was determined by volumetric analysis. Conversion value for reaction was calculated by using the amount of boric acid remained in the solution after reaction and shown Table 1.

The conversion values of 15.9% and 19.7% were determined for run 1 and run 4, which were carried out at the temperature of 90°C and 100°C. When the temperature is raised to 110°C for 5 and 6 h reaction time, 84.1% and 90.5% conversion values were obtained. It was inferred that the temperature is the most significant parameter in the production of zinc borate. The maximum conversion value (91.1%) was obtained at 120°C and for 5 h in the zinc borate synthesis.

Table 1: The variation of conversion by reaction conditions

| Run | Temperature (°C) | Reaction time (h) | Conversion |
|-----|------------------|-------------------|------------|
| 1   | 90               | 5                 | 15.9       |
| 2   | 120              | 5                 | 91.1       |
| 3   | 110              | 5                 | 84.1       |
| 4   | 100              | 5                 | 19.7       |
| 5   | 110              | 4                 | 77.0       |
| 6   | 110              | 3                 | 70.4       |
| 7   | 110              | 6                 | 90.5       |

3 Conclusions

The synthesis of zinc borate (4ZnO·B₂O₃·H₂O) was carried out by reaction of boric acid and zinc oxide using a single step hydrothermal method in presence of seed crystal. FTIR spectrum and XRD pattern of zinc borate are consistent with those determined in literature. According to SEM images, zinc borate has whisker structure. Whiskers are less than 1 µm in diameter and their length are in the range of 1-10 µm. The maximum conversion was calculated as 91.1% at the reaction conditions of 120°C for 5 h. The reaction parameters could be further optimized by using the Design of Experiment. The formation of whisker structures in zinc borate would provide good mechanical strengths beside its fire retardant properties.
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Experimental

Materials

Zinc oxide (purity > 99.0% wt) and boric acid (99.9% wt) were obtained from Merck and EtiMaden Inc., respectively. Zinc borate (Firebrake 415) as a seed crystal was obtained from US Borax. Sodium hydroxide (purity > 99.0% wt), phenolphthalein \( \text{C}_{20}\text{H}_{14}\text{O}_{4} \), and glycerol (99.5% wt) used in volumetric analysis were purchased from Merck, Dalan Chemical Industry, respectively. Distilled water was used for all experiments. Physical and chemical properties of zinc borate (Firebrake 415) used as a reference material are shown Table 2 (Emre, 2011).

| Chemical formula | 4ZnO·B₂O₃·H₂O |
|------------------|----------------|
| Molecular weight | 413.15         |
| Chemical composition | ZnO% B₂O₃% H₂O% |
|                   | 78.79 16.85 4.36 |
| Its appearance    | White, odorless, powder |
| Average particle size | 5 μm |
| Solubility        | 7.1 mg/L water |
| Density           | 3.7 g/cm³ |
| Stability         | > 415°C |
| Melting point     | 1150-1200°C |

Methods

A stoichiometric amount of zinc oxide powder was mixed with a 50 mL of distilled water then the slurry was transferred to the reactor (Parr 5500). Four flat blade turbine was utilized in the reactor. When the temperature of the slurry reached to the boiling point temperature, excess boric acid (5% wt), and seed crystal were added to the slurry. In all experiments, the reaction started as soon as the temperature of reactor reached the desired reaction temperature. The effect of reaction temperature (90°C, 100°C, 110°C, and 120°C) and reaction time (3, 4, 5, and 6 h) on the heterogeneous reaction between boric acid and zinc oxide was investigated in the presence of seed crystal as shown in Table 3. The stirring rate of 1700 rpm, stoichiometric amounts of reactants and solid/liquid ratio of 20% and the amount of seed (3.9% wt) were kept constant for all experiments.

| Run | Temperature (°C) | Time (h) |
|-----|-----------------|----------|
| 1   | 90              | 5        |
| 2   | 120             | 5        |
| 3   | 110             | 5        |
| 4   | 100             | 5        |
| 5   | 110             | 4        |
| 6   | 110             | 3        |
| 7   | 110             | 6        |

Stirring speed and reaction temperature were regulated by the temperature control unit of the Parr reactor. Solid product formed at the end of the reaction was separated using filtration unit under the vacuum of 700 mmHg. Filter cake was washed by hot distilled water to remove unreacted materials twice. The amount of boric acid remained in the aqueous phase and filtrate was determined by volumetric analysis. Wet filter cake was dried in an air circulating oven at 105°C until reaching the constant mass.

Characterization of solid products

Dried powder products were characterized by X-ray powder diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), thermal gravimetric analysis (TGA), and energy dispersive X-ray spectroscopy (EDS). The crystal structure of solid product was determined by X-ray diffractometer (Philips Xpert-Pro) in which registration was recorded in the 20 range of 10-70° with CuKa radiation (45 kV and 40 mA). Fourier transform infrared spectrometer (Shimadzu IR Prestige-21) was used to determine the vibrational modes and functional groups of solid product. A 2.5 mg of powder product was mixed with 100 mg of KBr in an agate mortar and it was pressed up to 8 tons to form pellets which are used in the analyses conducted between the wavenumbers 400 and 4000 cm⁻¹. Thermal gravimetric analyses (TGA) were carried out using SETARAM Labsys TG. 10-15 mg of solid product were placed into an alumina pan and it was heated from 30°C to 600°C in nitrogen atmosphere with the flow rate (40 mL·min⁻¹), at the heating rate of 10°C·min⁻¹. Scanning electron microscope (Philips XL30 SFEG) with energy dispersive X-ray spectroscopy (EDS) utility was used to identify the morphology, particle size and composition of powders.
Volumetric analysis

The amount of boric acid in the mother liquor and filtrate was determined by volumetric analysis. Phenolphthalein as an indicator and glycerin which catalysts the formation of proton were added into 10 mL sample taken from the mother liquor and filtrate. Then the solution was titrated with 1 M NaOH. The amount of boric acid in the total solution was determined by the amount of NaOH used at the end of titration (Budak and Gönen, 2014). The reaction conversion is calculated by using the following Eq. 3:

\[
\text{Conversion} (\%) = \frac{M_0 - M}{M_0} \times 100 \tag{3}
\]

where: \(M_0\) is the amount of boric acid at the beginning of reaction; \(M\) is the amount of boric acid that remained in the solution at the end of reaction.

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References

Budak A., Gönen M., Extraction of boric acid from colemanite mineral by supercritical carbon dioxide. J. Supercrit. Fluid., 2014, 92, 183-189.

Cao S., Jiao Y., Han W., Ge C., Song B., Wang J., et al., Hydrothermal synthesis of 4ZnO·B\(_2\)O\(_3\)·H\(_2\)O·Ln\(^{(3+)}\) (Ln=Eu, Tb) phosphors: Morphology-tunable and luminescence properties. Spectrochim. Acta A, 2018, 190, 231-238.

Emre Ö., Çeşitli Bor Minerallerinden Hidrofobik ve Nanoyapılı Çinko Borat Üretim Yöntemlerinin Geliştirilmesi. Postgraduate thesis, Yıldız Technical University, Istanbul, Tukey, 2011.

Ersan A.C., Kipcak A.S., Ozen Y.M., Tugrul N., An accelerated and effective synthesis of zinc borate from zinc sulfate using sonochemistry. Main Group Met. Chem., 2020, 43, 7-14.

Ersan A.C., Yıldırım M., Kipcak A.S., Tugrul N., A Novel Synthesis of Zinc Borates from a Zinc Oxide Precursor via Ultrasonic Irradiation. Acta Chim. Slov., 2016, 63(4), 881-890.

Feng C., Zhang Y., Liang D., Liu S., Chi Z., Xu J., Influence of zinc borate on the flame retardancy and thermal stability of intumescent flame retardant polypropylene composites. J. Anal. Appl. Pyrol., 2015, 115, 224-232.

Gao P., Zhang Y., Synthesis and Characterization of Zinc Borate Nanowhiskers and Their Inflaming Retarding Effect in Polystyrene. J. Nanomater., 2015, 1-6.

Gönen M., Balköse D., Ülkü S., Dehydration Kinetics of Zinc Borates (2ZnO·3B\(_2\)O\(_3\)·3H\(_2\)O and 4ZnO·B\(_2\)O\(_3\)·H\(_2\)O) by Thermal Analysis. In: Vakhрушев A.V., Haghi R., de Julián-Ortiz J.V. (Eds.), Physical Chemistry for Chemists and Chemical Engineers: Multidisciplinary Research Perspectives. CRC Press, 2018.

Jun L., Shuping X., Shiyang G., FT-IR and Raman spectroscopic study of hydrated borates. Spectrochim. Acta A, 1995, 51(4), 519-532.

Mergen A., İpek Y., Bölek H., Öksüz M., Production of nano zinc borate (4ZnO·B\(_2\)O\(_3\)·H\(_2\)O) and its effect on PVC. J. Eur. Ceram. Soc., 2012, 32(9), 2001-2005.

Nagaraju G., Udayabhanu, Shivaraj, Prashanth S.A., Shastri M., Yathish K.V., et al., Electrochemical heavy metal detection, photocatalytic, photoluminescence, biodiesel production and antibacterial activities of Ag-ZnO nanomaterial. Mater. Res. Bull., 2017, 94, 54-63.

Schubert D.M., Boron oxides, boric acid, and borates. In: Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, New Jersey, USA, 2011.

Schubert D.M., Hydrated Zinc Borates and Their Industrial Use. Molecules, 2019, 24(13), 2419.

Schubert D.M., Zinc Borate, U.S. patent 5,472,644, December 1995.

Shen K.K., Kochesfahani S., Jouffret F., Zinc borates as multifunctional polymer additives. Polym. Adv. Technol., 2008, 19(6), 469-474.

Shi X., Li M., Yang H., Chen S., Yuan L., Zhang K., et al., PEG-300 assisted hydrothermal synthesis of 4ZnO·B\(_2\)O\(_3\)·H\(_2\)O nanorods. Mater. Res. Bull., 2007, 42(9), 1649-1656.

Shi X., Yuan L., Sun X., Chang C., Sun J., Controllable Synthesis of 4ZnO·B\(_2\)O\(_3\)·H\(_2\)O Nano-/Microstructures with Different Morphologies: Influence of Hydrothermal Reaction Parameters and Formation Mechanism. J. Phys. Chem. C, 2008, 112(10), 3558-3567.

Zhang Y.Y., Li P., Liu Z.H., Controllable synthesis and flame retardant properties of bunch-, chrysanthemum-, and plumy-like 4ZnO·B\(_2\)O\(_3\)·H\(_2\)O nanostructures. Powder Technol., 2011, 210(3), 208-211.

Zhao C., Jiao Y., Chen Y.K., Ren G., The Tribological Properties of Zinc Borate Ultrafine Powder as a Lubricant Additive in Sunflower Oil. Tribol T., 2014, 57(3), 425-434.