X-Ray, Thermal, FT-IR and morphological studies of zinc borate in presence of boric acid synthesized by ulexite

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Abstract

Zinc borate (ZB) is an industrially important flame retardant material and ulexite is a plenty mineral in Turkey. In this study, ZB was prepared via an aqueous reaction method using zinc oxide, reference ZB as seed and synthesized boric acid by ulexite as initial materials. This route was facile and acceptable for an economic and a new way to produce ZB. The products were characterized by X-ray Powder Diffraction (XRPD), Thermo gravimetric/Differential Thermal Analysis (TG/DTA) and Fourier Transform Infrared Spectroscopy (FT-IR). Scanning electron microscope (SEM) was used to determine the morphological structure. The effects of experimental conditions on the product yield were investigated. Namely, the main factors that affect the formation of ZB were H_3BO_3/ZnO (boric acid/zinc oxide) ratio, water volume, amount of seed (in terms of boric acid, w/w) and reaction time. In conclusion, it was observed that boric acid by using ulexite and ZB was synthesized successfully.

Key Words: zinc borate; zinc oxide; ulexite; boric acid.

Introduction

Boron is an element that has the ability to form a large number of complex chemical compounds. Boron compounds are important raw materials in many branches of industry (Kucuk and Kocakerim, 2005).

Turkey has the 72% of world borate reserves which are able to use as important raw materials in many branches of industry, and used increasingly and expanding continuously in the production of medicines, disinfectants, cosmetics, detergent materials and in the glass, polymer, dye and plating, steel, refractory

materials industries. Ulexite, which is a sodium–calcium borate with a chemical formula of $NaCaB_5O_9 \cdot 8H_2O$, is available in huge quantities in nature and is commercially important. It is used in the production of boron compounds, especially boric acid and boron materials, such as boron glass and wool. Turkey has the largest boron resources in the world, and ulexite is available together with other borates around the regions of Balıkesir-Bigadic, and Kutahya-Emet. Boric acid (H_3BO_3) is produced industrially from borate minerals and brines. Alkali and alkaline earth metal borates (such as borax, colemanite, ulexite or kernite) react with strong acids to form boric acid (Mergen et al., 2003).

Boric acid is used by many industries, with the largest use in the glass and ceramic industry where it is mainly used in textile grade glass fibers, borosilicate glasses, enamels, frits and glazes. In these applications, boron accelerates melting and refining, enhances color, increases resistance to mechanical and thermal shock, decreases the thermal expansion coefficient, reduces glaze viscosity and surface tension and enhances the glaze strength and durability. Boric acid also has many other application areas, such as fire retardant material, in nuclear applications, in medical and pharmaceutical sector, in photography, and in the electronic sector. In addition, boric acid is a starting material for the manufacture of many borates, per borates, fluoborates, boron carbide, boron oxide, boron esters, borides and other boron alloys (Sevim et al., 2006).

Zinc borates have been used in industry since the 1940s, and with the discoveries of hydrated zinc borates with different compositions. ZB has been the subject of significant research for applications including the polymer additive which serves as the char promoter, the flame retardant synergist, the preservative in wood composites, the smoke and afterglow suppressant due to its ability to undergo endothermic dehydration in fire conditions, and optical properties, and the additive for lubrication (Tian et al., 2008).

There are major advantages in using $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$ as flame retardant because of its high thermal stability, no toxicity, low cost, and good performance in particular in halogen-free systems (Shi et al., 2007). ZB ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) (Shete et al., 2004; Ting et al., 2009; Shi et al., 2009; Schubert et al., 2003; Samyn et al., 2007; Bobkova and Khot'ko, 2005; Ting et al., 2008) in general is produced with the reaction between zinc oxide and boric acid. Boric acid is dissolved in water between the temperatures 95 and 98 °C, and zinc oxide and seed crystals of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ is added to this solution at a certain stoichiometric ratio (Eltepe et al., 2007).

In this study, it was investigated that a method which is production ZB (Shi et al., 2008; Chang et al., 2006; Gurhan et al., 2009; Genovese and Shanks, 2007) by ulexite that is boric acid source. Up to now, many approaches have been undertaken for the preparation of ZB. The zinc source materials included zinc oxide, zinc salts, and zinc hydroxide, and the boron source materials employed could be boric acid by ulexite. A characteristic feature of these routes at present was that the reactions were carried out in aqueous

solution. As a result, FT-IR, XRPD, TG/DTA and SEM which indicated that the synthesis of boric acid by using ulexite and ZB were successful under the determined reaction conditions.

Experimental

Materials

Ulexite ($NaCaB_5O_9 \cdot 8H_2O$) was supplied by Eti Mine Works in Balikesir-Bigadic with a molecular weight 405.12 g/mole and employed without any further treatments. Reference ZB (molecular formula: $2.1ZnO \cdot 3B_2O_3 \cdot 3.2H_2O$ with 37% ZnO and 47% B_2O_3 and a maximum of 16% water of crystallization were used in the experiments as reference materials) was obtained from Eti Mine Works. Zinc oxide (97% pure) was acquired from Colakoglu Chemicals Ltd. Distilled water was applied for all synthesis and treatment processes.

Synthesis of boric acid and ZB

Synthesis of ZB from ulexite was occurred by 2 steps reaction method. Firstly, boric acid was produced by ulexite. Ulexite was mixed with required amount of water in a glass beaker at 98 °C for half an hour, added sulfuric acid to the mixture at stoichiometric ratio. The experiments were dried at 50 °C. Boric acid, calcium sulphate and sodium sulphate were obtained by differential precipitation from a main liquid. Boric acid crystals formed in the solution when the concentration of boric acid ions exceeded the saturation limits of boric acid. Boric acid synthesized by ulexite was characterized by XRPD and B_2O_3% assay method.

The ZB reaction was conducted in a closed glass beaker at 95 °C on a magnetic stir plate. The experiments were carried out by dissolving of boric acid in a glass beaker in distilled water. Temperature was controlled using a digital temperature sensor and magnetic stirrer provided constantly stirring during the reaction.

The products were dried at 105 °C for 20 h. Dry, fine powdered ZB particles were produced. The analysis results showed that ZB was synthesized successfully. The yield values were calculated per gram of zinc oxide consumed (1):

$$2ZnO + 6H_3BO_3 \longrightarrow 2ZnO \cdot 3B_2O_3 \cdot 3H_2O + 6H_2O \quad (1)$$
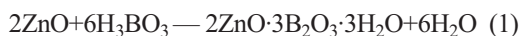
Results and discussion

The effect of the reaction time on the ZB reaction yield was showed in Figure 1a. The optimum reaction time was 3 hours of reaction time. When reaction time was 3h, the reaction yield was the peak value (Optimum reaction parameters: H_3BO_3:ZnO = 3.5:1, 25 ml of water, 1% of seed, 3 hours, 95 °C).

Supersaturation, nucleation and crystal formation are necessary for crystal growth. Moreover, supersaturation is the driving force for crystallization. The results of previous studies indicated that a decrease in the volume of water caused an increase in yield. At a 3.5:1 ratio of H_3BO_3/ZnO, the volume of water providing the greatest yield of ZB was 25 ml (0.5% seed content) (Figure 1b).

Reference ZB has been used as a seed 0.5-2% of the amount of H_3BO_3 in the reaction to obtain the effect of the seed on the ZB reaction yield.
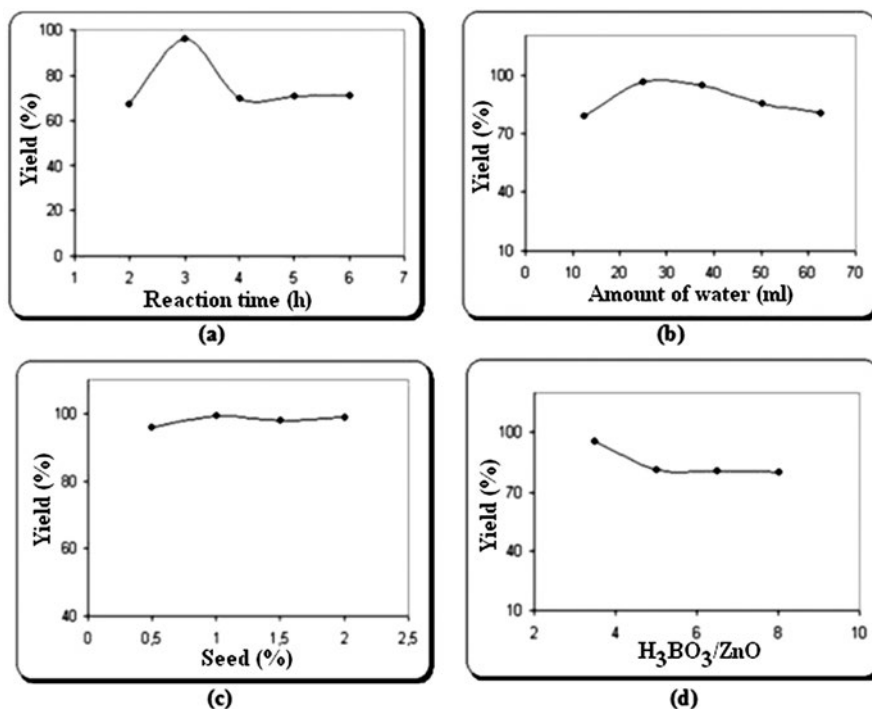
Figure 1. The effects of process parameters on ZB yield: (a) Reaction time, (b) Water volume, (c) Amount of seed, (d) H_3BO_3/ZnO ratio.

Standard ZB was used as a seed crystal to reduce the reaction time and to improve the quality of the product. As discussed in the previous study (Kılınc et al., 2010), the reaction of boric acid and zinc oxide did not yield ZB product if ZB crystals were not added to the solution as seed. In this study, as seen in Figure 1c, the optimum seed amount was 1% of the amount of H_3BO_3 in the reaction.

The effect of the reactant ratio on the ZB reaction yield was investigated in range of 3.5:1-8:1. As seen in Figure 1d when H_3BO_3/ZnO ratio was 3.5:1, the reaction yield was in maximum. According to previous studies, firstly H_3BO_3/ZnO

ratio was used as 3:1, but XRPD pattern of ZB showed that there was still ZnO reactant in ZB production. Thus, 3.5:1 of reactant ratio was assumed optimum reactant ratio.

The results of the temperature studies indicated that the yield of the reaction increased dramatically with an increase in temperature until a maximum yield was obtained at 95 °C. The temperature value was selected as 95 °C similar to the previous study (Shete et al., 2004). After reaction, the system (95 °C) was cooled down to a variety of temperatures in a range of 80-10 °C and five different experiments were carried out to examine the differential of cooling

temperature. Cooling the reaction mixture to temperatures greater than 50 °C caused a significant decrease in yield.

Characterizations

All products were characterized by XRPD (Philips Panalytical, Xpert-Pro) to identify phases. FT-IR (Perkin Elmer, Spectrum One) (Resolution: 0.5 cm^{-1} - 64 cm^{-1}) was used to identify functional groups present in the products. Thermal analyses of samples were carried out by using TG/DTA (Perkin Elmer-Pyris Diamond) and SEM analysis (Cam Scan-Apollo 300) was used to obtain the physical morphology. In addition, reference ZB was identified as $ZnO/B_2O_3/H_2O$ = 39.21/47.46/13.33 (%) with $2.1ZnO·3B_2O_3·3.2H_2O$ formula.

XRPD

All of the samples were characterized by XRPD to identify phases of the ZB with Cu Kα radiation at 45 kV and 40 mA. The registrations were mainly performed in the 0°-80° 2θ range. The characteristic peaks of ZB were observed in range of 15-70° 2θ from XRPD analysis as expected. Figure 2 shows the XRPD pattern of ulexite, which was recorded in a range of diffraction angle from 0 to 60 °C. In the sample, the representative of (010) diffraction peak, corresponding to 12.35719Å peak at 7.1538°, had the maximum (100%) intensity. This identified the $NaCaB_5O_9.8H_2O$ in the anorthic crystal system with P-1 space group and, space group number of 2. $NaCaB_5O_9·8H_2O$ had a unit cell structure of a, b, c = 8.8160Å, 12.8700Å, 6.6780Å. The other peaks of pure ulexite were at 21.4370 A°, 29.8102 A° and 44.7602 Å (PDF number: 00-009-0448).
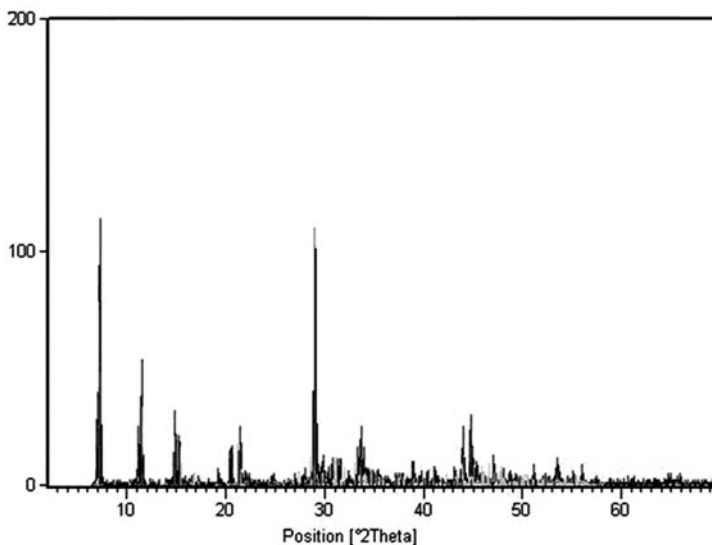

Figure 2. XRPD analysis of the ulexite.

The structure of reference boric acid was compared with boric acid synthesized by ulexite. The specific peaks of boric acid were determined at 15.0760 Å, 28.305 Å, 40.395 Å and 58.174 Å. The XRPD analysis results showed that the structure of synthesized boric acid was similar with peaks as reference boric acid (Figure 3). The specific peaks of boric acid were determined at 18.365 Å, 20.576 Å, 21.384 Å, 25.578 Å, 36.231 Å, 42.715 Å and 58.960 Å. Thus, ZB

produced at optimum conditions was similar to reference ZB with peaks (Figure 4).

TG/DTA

ZB samples, ulexite (10-15 mg) were loaded into a silisium pan and heated from 30 to 700 °C at 10 °C/min under N_2 flow. TG/DTA instrument was calibrated by means of the melting points of indium ($T_m = 156.6$ °C) and tin ($T_m = 231.9$ °C) under the same conditions with the sample.
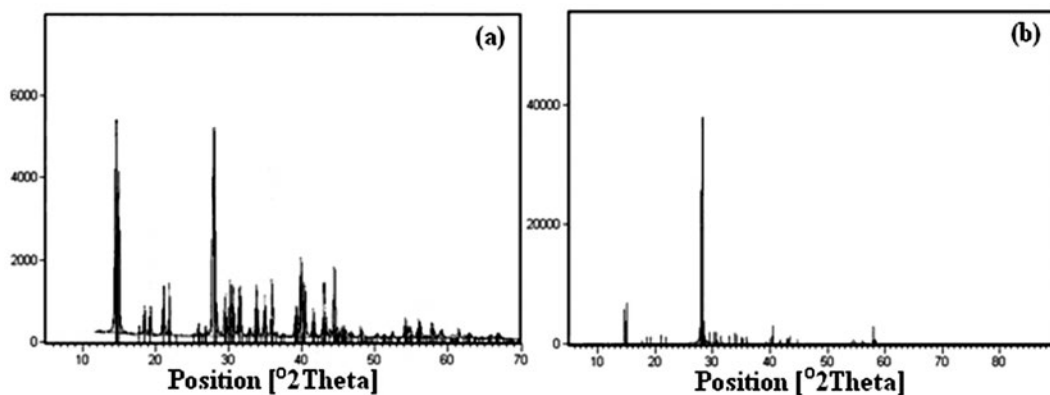

Figure 3. XRPD analysis: (a) Reference boric acid, (b) Produced boric acid.
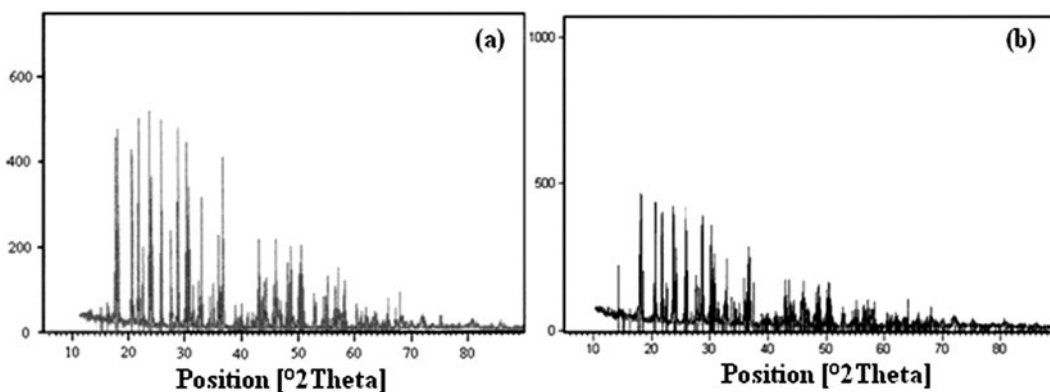

Figure 4. XRPD analysis: (a) Reference ZB, (b) Produced ZB.

Samples were ground in agate mortar and stored under inert atmosphere before the analysis.

The TG and DTG analyses showed that thermal decomposition of ulexite began at about 70 °C and proceeded up to 240 °C. Two partly overlapping DTG peaks were observed at around 150 and 180 °C, corresponding weight looses of 8 and 17%, respectively. The reaction stopped at 290 °C. The change in weight continued up to about 550 °C by which time 35% of the weight had been lost. The results of DTA analysis showed that there were three distinct reactions. The first occurred within the temperature range 70-240 °C and the others were accompanied by two partly overlapping endotherms. This was consistent with the DTG analysis. An exothermic reaction was observed in the range 600-640 °C with a maximum at 636 °C. After further heating, one exothermic peak occurred at 636 °C corresponding to the recrystallization of amorphous $NaCaB_5O_9$ to CaB_2O_4 (Figure 5).

On the TG curve, a sharp weight loss (13.99%) began to happen when the temperature was around 232 °C as expected from the results of various authors (Eltepe et al., 2007; Shi et al., 2008). This process was corresponding to loss of water of crystallization through condensation of B–OH groups (Figure 6).

FT-IR

The KBr disc method was used by mixing 4.0 mg of ZB and 196 mg of KBr to determine which functional groups were present in the samples. A pellet was obtained by pressing the powder mixture under 8 tons of pressure.

The FT-IR spectra of the ulexite showed the following infrared absorption bands (Figure 7). The bands at 3416 cm^{-1} represented the stretching mode of O–H. The band at 1626 cm^{-1} was assigned to free H_2O band. The band at 1409 cm^{-1} was assigned to the asymmetric stretching mode of B–O in BO_3. The bands at 1353, 1316, and 1209 cm^{-1} were assigned to the in-plane bending band of $(OH)^{-1}$. The bands at 1051, 976, and 856 cm^{-1} were determined with the asymmetric stretching of B–O in BO_4. The bands at 746 and 712 cm^{-1} were assigned to the out-of-plane bending of $(OH)^{-1}$ and symmetric stretching band of B–O in BO_4. When boric acid by ulexite was compared with reference boric acid by FT-IR spectrum as seen in Figure 7 and Figure 8, it was determined that boric acid by ulexite had same bands with reference boric acid (Table 1).

The band which indicates stretching vibrations of O-H was obvious at 3459 cm^{-1}. Bending vibrations of H-O-H band which were due to crystal water included in compound was slightly seen at 1647 cm^{-1}. The presence of the band at 1341 cm^{-1} assigned to asymmetric stretching vibrations of trihedral (BO_3) borate groups. The peaks at around 1060 and 928 cm^{-1} were assigned to asymmetric and symmetric stretching vibrations of tetrahedral (BO_4) borate groups. The peak observed at 675 cm^{-1} wavelength indicated in plane bending vibrations of trihedral (BO_3) groups. The FT-IR spectrums of the products showed the formation of reference ZB (Figure 8).

SEM

SEM was used to determine morphological structure of products. The particle size of boric
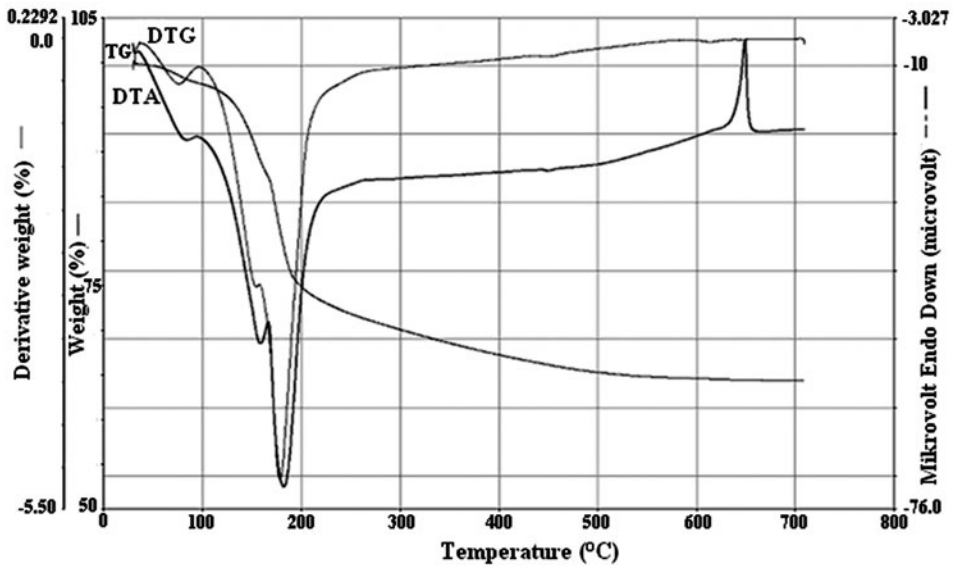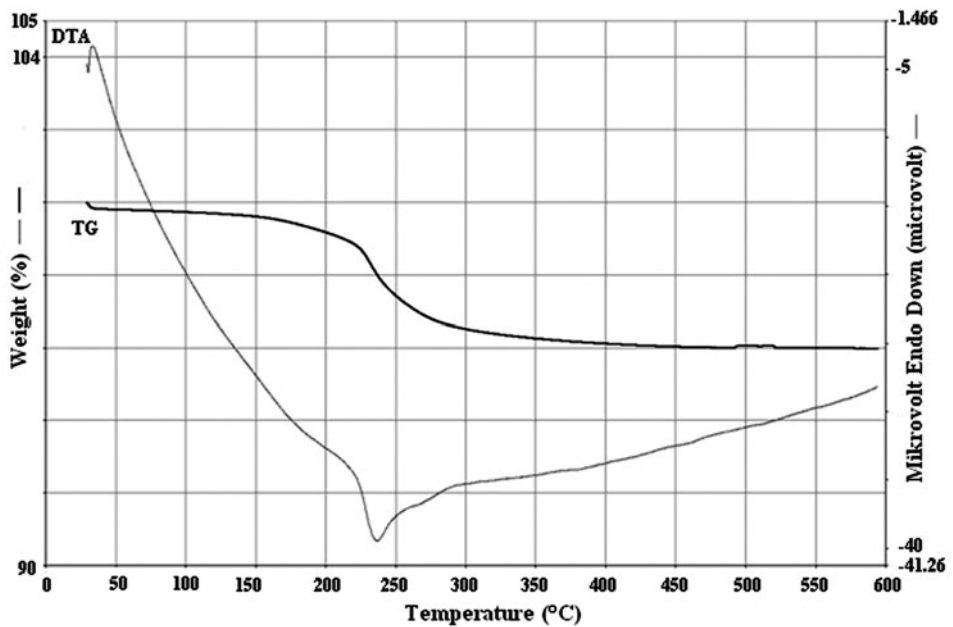
Figure 5. TG/DTA curve of ulexite.

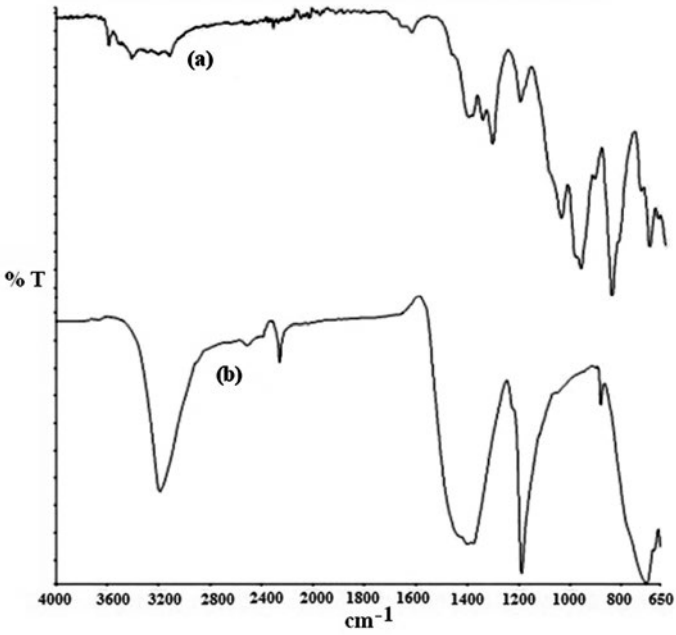Figure 6. TG/DTA curve of ZB synthesized by ulexite.

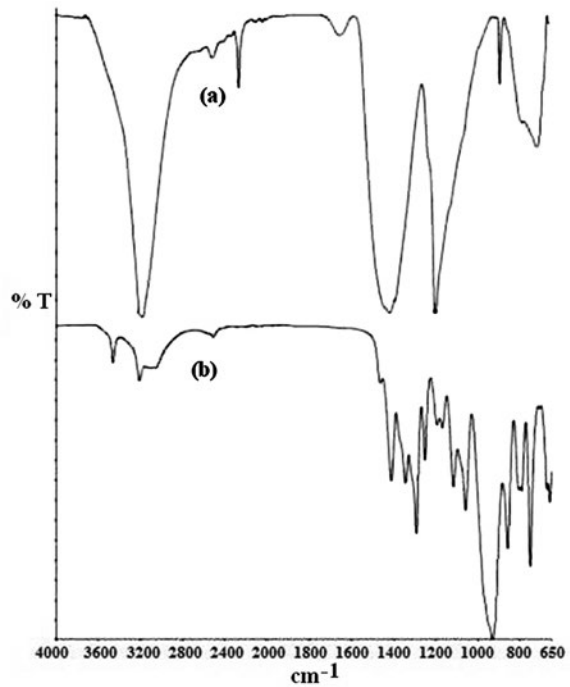Figure 7. FT-IR spectra: (a) Ulexite, (b) Reference boric acid.

Figure 8. FT-IR spectra: (a) Boric acid synthesized by ulexite, (b) Produced ZB.

Table 1. FT-IR bands of reference boric acid and synthesized by ulexite.

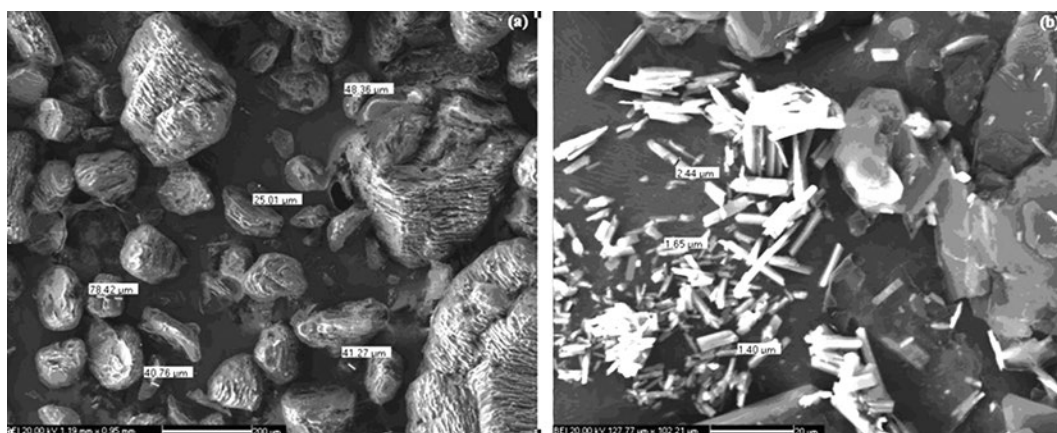| Reference boric acid	Boric acid synthesized by ulexite
O-H tension bands: 3188.91 cm^{-1}	O-H tension bands: 3192.19 cm^{-1}
Asymmetric B-O bands in BO_2: 2259.75, 2516.04 cm^{-1}	Asymmetric B-O bands in BO_2 2259.82, 2515.36 cm^{-1}
Asymmetric B-O bands in BO_3: 1405.55 cm^{-1}	Asymmetric B-O bands in BO_3: 1408.54 cm^{-1}
OH bands: 1190.06 cm^{-1}	OH bands: 1191.16 cm^{-1}
Asymmetric B-O bands in BO_4: 882.99 cm^{-1}	Asymmetric B-O bands in BO_4: 882.88 cm^{-1}
Symmetric B-O bands in BO_4: 712.27 cm^{-1}	Symmetric B-O bands in BO_4: 705.12 cm^{-1}

Figure 9. SEM images: (a) Reference boric acid x 500, (b) Produced boric acid x 940.

acid by ulexite was 1.65 mm at minimum. Therefore, the particle size of produced boric acid was more undersize than reference boric acid (Figure 9). The particle diameters of produced ZB were in range of 1-5 mm (Figure 10).

Conclusion

In conclusion, ZB was produced under the optimised reaction conditions. The usage of reference ZB as seed increased the yield of the product by reducing the reaction time and improving the quality of the product. Accordingly, it was found that optimum points of ZB reaction were 0.5% of seed, 25 ml of water, 3.5:1 of H_3BO_3/ZnO reactant ratio. Furthermore, the results of the XRPD, FT-IR, TG/DTA and SEM analyses indicated that ZB
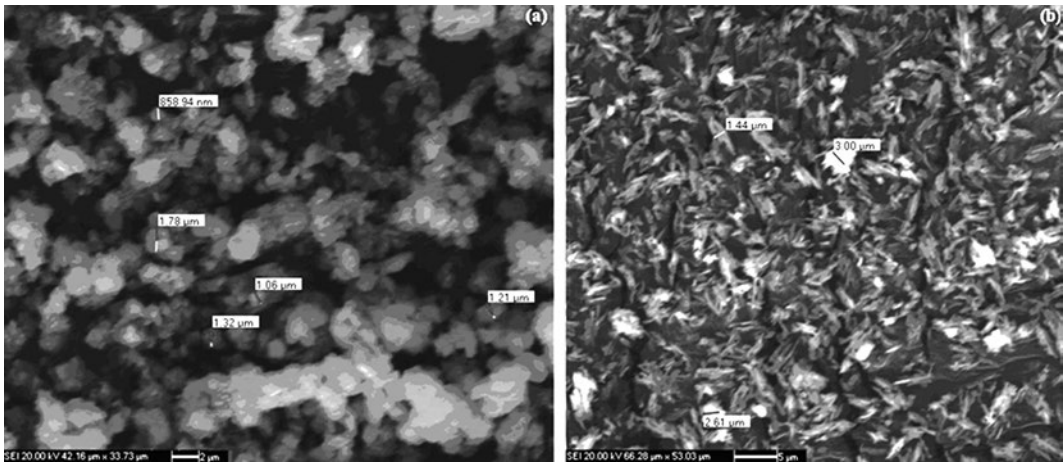
Figure 10. SEM images: (a) Reference ZB x 2845, (b) Produced ZB x 1800.

was successfully synthesized under the optimised reaction conditions and the product synthesized had high thermal stability to use for various applications. Consequently, it was achieved that ZB could be produced via obtaining boric acid synthesized by ulexite. Turkey is an abundant country in terms of ulexite. By this means, ulexite may be evaluate for various applications with consist of this study.

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