



Research Article

LITHIUM TETRABORATE PRODUCTION FROM THE REACTION OF BORIC ACID AND LITHIUM CARBONATE USING CARBON DIOXIDEAli YALÇIN¹, Mehmet GÖNEN*²¹Süleyman Demirel University, Dept. of Chemical Engineering, ISPARTA; ORCID: 0000-0002-8722-4159²Süleyman Demirel University, Dept. of Chemical Engineering, ISPARTA; ORCID: 0000-0001-5780-4622

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ABSTRACT

In this study, the synthesis of lithium tetraborate in the presence of carbon dioxide (CO₂) in an aqueous phase was investigated. A two-step process has been developed in the present study. The first step includes an aqueous phase reaction of lithium carbonate and boric acid in the presence of CO₂ at different pressures. The second step involves the crystallization and thermal treating of the product obtained from step one at the temperatures between 300 and 400°C for 1 hour. Characterizations of the samples were performed by Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM). It was characterized that amorphous lithium tetraborate of Li₂B₄O₇·3H₂O was synthesized in the first step and then it was converted into Li₂B₄O₇ in the second step. The use of CO₂ as a modifying agent in lithium tetraborate synthesis has enhanced the dissolution rate of reactants that induced a fast-aqueous phase reaction.

Keywords: Lithium tetraborate, boric acid, CO₂, lithium carbonate, two-step process.

1. INTRODUCTION

Lithium borates are important compounds that are used as specialty chemicals in the industry. There are several types of lithium borates namely lithium metaborate (LiBO₂·8H₂O), lithium triborate (LiB₃O₅), lithium tetraborate (Li₂B₄O₇·3H₂O), and lithium pentaborate (LiB₅O₈·5H₂O) [1]. Each of the above-mentioned compounds can be synthesized using various reactants, at different stoichiometric ratios and appropriate reaction conditions of temperature and pressure (T, P). Solid-state reaction and aqueous-reaction followed by calcination are two important techniques used in lithium borate production. Anhydrous lithium tetraborate (Li₂B₄O₇), is a commercially important compound which can be produced by using reactants, such as boric acid (H₃BO₃), diboron trioxide (B₂O₃) and suitable lithium source, e.g. lithium hydroxide (LiOH) and lithium carbonate (Li₂CO₃). The Li₂B₄O₇·3H₂O was synthesized in an aqueous phase and used as a precursor in the formation of glassy and crystalline Li₂B₄O₇. The structure of Li₂B₄O₇·3H₂O was determined from its XRD data as Li(H₂O)B₂O₃(OH) [2], which is stable up to 180°C and becomes anhydrous at 320°C [1]. A number of studies have reported different methods concerning the synthesis of lithium tetraborate in the literature. Lithium tetraborate production

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with solid-state reaction was studied using lithium hydroxide monohydrate, boric acid and lithium tetraborate as a seed crystal at a temperature greater than 650 °C [3]. The solid-state reaction is mostly preferred when pure raw materials are used in exactly stoichiometric amounts. However, imperfect mixing of reactants in the solid-state reaction may result in partial product formation and raw materials remain in the product. As boric acid sublimes at higher temperatures, the initial ratio of reactants varies and causing undesired product formation [4, 5]. The synthesis of $\text{Li}_2\text{B}_4\text{O}_7$ crystals from boric acid and lithium nitrate was investigated by using proteic sol-gel and Pechini methods in which gelatin and citric acid were used as a chelating agent, respectively. In the Pechini method, ethylene glycol was also used as a co-solvent [6]. The removal of organic materials from the reaction mixture requires high-temperature treatment and any carbon residue in the product has to be eliminated by H_2O_2 washing. Since 1960, lithium tetraborate has been investigated intensively due to its thermoluminescent (TL) properties and used in versatile radiation detectors and radiation dosimeters. It has been widely used in various applications such as sensor sector, laser technology and optoelectronic material utilized in surface acoustic wave apparatuses and fluxing agent in XRF analysis of cement [7, 8, 9]. Thermoluminescent dosimeter (TLD) should have properties like simple glow curve structure, high gamma-ray sensitivity, low fading of TL signal, chemical stability, inertness, being reusable after thermal treatment, not affected by daylight and suitable effective atomic number (Z_{eff}) which is close to the value (7.42) of the soft tissue [10]. The dosimetric behavior of $\text{Li}_2\text{B}_4\text{O}_7$: Mn, TLD-800 was studied by Furetta and Pellegrini in 1981 [11]. To modify the thermoluminescence properties of lithium tetraborate, different activators, such as Cu, Ag, Mg were investigated, as well [10, 12]. Nano-sized lithium tetraborate was produced from the reaction of Li_2CO_3 and H_3BO_3 using an innovative single-step thermal treatment method in which polyvinyl propyl (PVP) was used as a capping agent to control the agglomeration and particle size. Pure nano-crystalline lithium tetraborate was obtained at temperatures between 460 and 750 °C and its average particle size was about 3.3 nm at the calcination temperature of 750 °C and in the presence of 0.027 mol of PVP [9]. In another study, lithium tetraborate was prepared from (Li_2CO_3 and H_3BO_3) in powder form using two different routes: a high-temperature solid-state synthesis and a water/solution assisted synthesis. Cu, Ag and In were doped to lithium tetraborate to investigate the thermoluminescence property of the final product during the synthesis. XRD pattern of the product is compatible with JCPDS card no: 79-0963 data of lithium tetraborate. Doping material affects the thermoluminescence properties of the lithium tetraborate. Doping of lithium tetraborate samples with only Cu (0.1 % wt.) produced the best results in terms of thermoluminescence [13]. The growth of lithium tetraborate crystals and the effects of parameters on the growth mechanisms were investigated by Robertson and Young. A high-quality lithium tetraborate single crystal with the highest purity was obtained from the melt and a model was developed to explain the non-uniform impurity distribution observed from defects in these crystals [14]. Production of lithium tetraborate tetrahydrate was studied by the reaction of H_3BO_3 and LiOH in an aqueous solution using a spray drying method. The parameters of the drying were investigated. They reported that increasing the air inlet temperature to 230°C resulted in a lithium tetraborate trihydrate as determined by TG and $\text{B}_2\text{O}_3\%$ analyses [15].

The temperature in the solid-state synthesis of lithium tetraborate varies between 400-750°C depending on the desired product [13]. The requirement for the high temperature is related to the properties of raw materials. For instance, as lithium carbonate (Li_2CO_3) decomposes over 700°C, the solid-state reaction must be carried out above this temperature when it is used as a lithium source [16]. When boric acid is heated, it dehydrates to form metaboric acid (HBO_2). As the temperature is increased over 160°C, it turns into diboron trioxide (B_2O_3) [1]. Sublimation of boric acid at elevated temperature is another issue that may change the reactants initial ratio in solid-state reaction [5]. The exact reaction between lithium oxide and diboron trioxide at 750°C is shown in Equation 1. Mass transfer limitations are major problems in solid-state reactions, thus during the reaction, reactants should be mixed and grounded.



The thermal behavior of lithium tetraborate during glass formation was investigated using the spectroscopic technique. It was reported that if the fusion temperature for lithium borate fluxes exceeds 1050 °C, flux loss will occur because of volatilization [7]. The high reaction temperature and long reaction time are some of the disadvantages encountered in the synthesis of lithium tetraborate using a solid-state reaction. The low water solubility of boric acid and lithium carbonate is another disadvantage for lithium tetraborate synthesis. The solubility of the reactants in an aqueous media can be increased by using CO₂ in the reaction. CO₂ dissolves in the aqueous phase to form carbonic acid that increases the solubility of the reactants depending on its pressure. The use of CO₂ in the production of lithium tetraborate may increase the reaction rates by decreasing the solubility limitations of both reactants. Since lithium carbonate dissolves in an aqueous medium due to the low pH, it will react with borate anion to form lithium tetraborate. In the solid-state reaction of lithium carbonate and boric acid, the temperature should be above the temperature at which lithium carbonate starts to decompose i.e., 700°C. That is why such high temperature is required in solid-state reaction [16].

The purpose of this study is to develop a novel method for producing lithium tetraborate using an aqueous phase reaction of lithium carbonate and boric acid in a CO₂-pressurized autoclave. The technique has two steps: the aqueous phase reaction takes place in the presence of CO₂ in the former step and the thermal treatment of the precursor in a furnace at higher temperatures to obtain anhydrous crystalline lithium tetraborate in the latter. Characterization of both precursor and the final product was performed using XRD, FTIR, TGA, and SEM. To the best of our knowledge, no previous reports are present in the literature for lithium tetraborate synthesis at low temperature.

2. EXPERIMENTAL

2.1. Materials

Lithium carbonate (Li₂CO₃) and boric acid (H₃BO₃) used in this study were supplied from Sigma-Aldrich (99.0% in mass) and Merck (99.5% in mass), respectively. Lithium tetraborate obtained from Merck (98.0%, in mass) was utilized as a reference to compare with the powdered product obtained after thermal treatment. Carbon dioxide (99.9% by vol., HABAŞ) was used to control the pH of the aqueous medium in the autoclave. Potassium bromide (KBr) obtained from Merck (99.99%, in mass) was used for preparing sample pellet in IR analyses. Distilled water was used in all experiments.

2.2. Methods

Lithium tetraborate synthesis consists of two main steps: an aqueous phase reaction in the presence of CO₂ and thermal treatment of the precursor at elevated temperatures. In order to produce 5.0 g of lithium tetraborate, stoichiometric amounts of Li₂CO₃ and H₃BO₃ were mixed in 90 ml of distilled water. This mixture was placed in a high-pressure autoclave and dry ice (solid CO₂) was added into the autoclave. The amount of dry ice was calculated by using the Peng-Robinson equation of state so that desired pressure can be attained in the reactor [17]. The lid of the autoclave is closed as quickly as possible to prevent CO₂ leakage, and then it is placed in a water bath, which is on a magnetic stirrer, to control the temperature and stirring rate. The experimental set-up used for all runs is shown in Fig. 1.

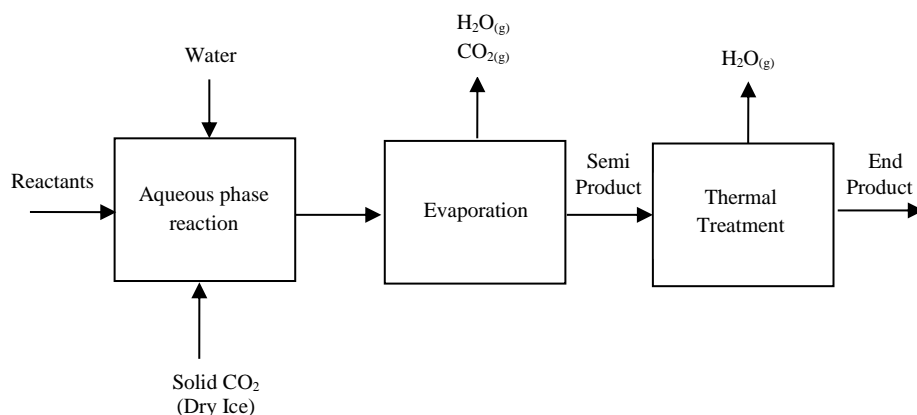


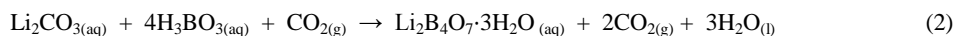
Figure 1. Flow sheet of lithium tetraborate production

The reaction between boric acid and lithium carbonate was studied in the temperature range of 30-50°C, for different reaction time (1-2 h), at different CO₂ pressure in an autoclave. The details of the experimental conditions are shown in Table 1. The stirring rate (200 rpm) and the solid-liquid ratio in the reaction were held constant for all the experiments.

Table 1. The reaction conditions for lithium tetraborate synthesis

Runs	Temperature (°C)	Pressure (bar)	Reaction time (hour)
1	50	40	2
2	50	25	2
3	50	10	2
4	50	10	1
5	50	10	1.5
6	40	10	2
7	30	10	2

At the end of the reaction, water was evaporated at 100 °C, at atmospheric pressure to crystallize the precursor. After this step, the precursor was placed into the furnace for thermal treatment. After the thermal treatment of the sample for 1 hour at 300-400 °C in the furnace, the final products were stored in a desiccator to avoid moisture adsorption from the air. Both the precursor obtained in aqueous phase reaction and the powder product obtained after thermal treatment were characterized. The expected reaction between lithium carbonate and boric acid in CO₂ pressurized aqueous phase is given in Equation 2. The dehydration reaction that takes place in the thermal treatment is given Equation 3.



2.3. The characterization of semi-product and final product

Both products obtained at the end of thermal treatment and precursor crystallized from an aqueous phase were examined by Fourier Transform Infrared (FTIR) spectroscopy, X-Ray powder diffraction (XRD), thermal gravimetric analysis (TGA) and Scanning Electron

Microscope (SEM). The crystal structures of the lithium tetraborates were analyzed by X-Ray diffractometer (Philips Xpert-Pro) in which registration was performed in the 2θ range of $5-80^\circ$ with CuK_α radiation at 45 kV and 40 mA. Fourier Transform Infrared Spectrometer (Perkin Elmer Spectrum BX) having wavenumbers of 400 and 4000 cm^{-1} was used to determine the vibrational modes of the materials produced. KBr pellets including lithium tetraborate samples were prepared by mixing in an agate mortar and then pressed at 8 tons. TGA (Thermal gravimetric analyses) were conducted using SETARAM Labsys TG. Powder samples (10-15 mg) were placed into an alumina pan and heated from 30°C to 1000°C with N_2 flow ($40\text{ ml}\cdot\text{min}^{-1}$) at $10^\circ\text{C}\cdot\text{min}^{-1}$. SEM (Scanning electron microscope) (Philips XL30 SFEG) with Energy Dispersive X-ray fluorescence (EDX) utility was used for identification of particle size, morphology and composition of both powder products obtained after thermal treatment and precursor crystallized from an aqueous phase. The density of samples and reference lithium tetraborate was determined using helium pycnometer (Quantachrome Ultrapycnometer 1000). The mean value of the sample's density was calculated using the average of three measurements.

3. RESULTS AND DISCUSSION

Lithium tetraborate was synthesized by the reaction of boric acid and lithium carbonate in an aqueous phase using a high-pressure autoclave. The effects of pressure by CO_2 , reaction time and temperature were investigated on lithium tetraborate synthesis in the first step. The influence of thermal treatment temperature was also investigated in the second step. The precursor, hydrated lithium tetraborate, was obtained as a dissolved product at the end of the reaction in the first step. The solubility of reactants is critically important in aqueous phase reactions. Since the solubility of Li_2CO_3 is low ($1.30\text{ g}/100\text{ g H}_2\text{O}$) given by Lide [18] and it is inversely proportional to temperature, the use of CO_2 in the aqueous phase reaction increases the solubility of the reactants. Before thermal treatment, the solution was crystallized at 100°C and 1 atm. The precursor was exposed to thermal treatment at the temperature range of $300-400^\circ\text{C}$ in the furnace.

Pekpak and her coworkers (2012) studied the lithium tetraborate production at atmospheric pressure by using a stoichiometric ratio of Li_2CO_3 : H_3BO_3 (1:4) in a water-solution assisted method. Thermal treatment was performed by increasing temperature from 150°C to 750°C . Lithium tetraborate obtained at 750°C was doped with copper (Cu), silver (Ag) and indium (In). It was reported that the glow curves of these samples were applicable for using in thermoluminescence dosimetry [13]. Lithium tetraborate (LTB) was synthesized from the reaction of boric acid and lithium carbonate using high-temperature solid-state reaction and solution assisted method. The effects of the synthesis and doping method on the thermoluminescence glow curves of lithium tetraborate having different amounts of manganese (Mn) were investigated. Lithium tetraborate sample (Mn 1.0%, in mass) synthesized using high-temperature solid-state reaction produced better glow curves than those powders with different synthesis and doping methods and those with different Mn contents. Microstructures of samples prepared by using solid-state reaction and solution assisted methods are different from each other. Lithium tetraborate produced by solution assisted method has large single crystal which is doped with Mn [19].

3.1. FTIR analysis of semi-product and final product

FTIR spectra of precursor samples produced from the reaction of boric acid and lithium carbonate in an aqueous phase at CO_2 pressure of 10, 25 and 40 bar are shown in Fig. 2a, 2b, and 2c, respectively. The broad peak between 3600 and 3000 cm^{-1} indicates the presence of B-OH groups in the sample structure. The shoulder peak around 1650 cm^{-1} belongs to the H-O-H bending in H_2O . The characteristic modes of chemical bonds in hydrated lithium tetraborate were determined as the asymmetric stretching vibration band of B-O in a BO_3 unit at 1367 cm^{-1} ,

asymmetric stretching bands of B-O in BO_4 unit at 1018 cm^{-1} . The shoulder peak at 873 cm^{-1} and small absorption peak at 774 cm^{-1} were assigned to symmetric stretching vibration of B-O bonds in BO_3 and BO_4 units, respectively. The medium absorption peak at 690 cm^{-1} indicates the out of plane bending of BO_3 structure. The small peak at 567 cm^{-1} is due to the tetraborate anion symmetric pulse vibration [9, 20, 21, 22].

It was observed that the increase of CO_2 pressure has no effect on the synthesis of lithium tetraborate precursors for all experiments which were carried out for 2 h and at 50°C (Fig. 2). Even for the reaction carried out at 5 bar CO_2 pressure, the desired precursor (hydrated lithium tetraborate) was produced. However, the solubility of CO_2 in the aqueous phase is directly proportional to the pressure applied. Increasing CO_2 pressure decreases the pH of the media thereby accelerating the solubility of the reactants.

In solid-state synthesis, the reaction between lithium carbonate and boric acid is carried out at a high temperature (700°C) so that lithium carbonate can easily react with boron compound after it has decomposed at that temperature [16]. In an aqueous phase reaction, lithium carbonate dissolves in water and then reacts with boric acid. The amount of hydrated lithium tetraborate is greatly influenced by the amount of lithium carbonate dissolved in an aqueous phase since lithium carbonate has low solubility and its solubility decreases with increasing temperature. Thus, the use of CO_2 in an aqueous phase increases the amount of reactant in the reaction media. Moreover, the effect of reaction temperature on the synthesis of the precursor was investigated. Precursors produced at 30 and 40°C have a different structure than the semi-product obtained at 50°C . The effect of reaction time on precursor formation was also investigated. Precursors synthesized for 1 and 1.5 h reaction times have a different structure than the one produced for 2 h. Thus, a minimum reaction time of 2 h is required for the desired lithium tetraborate precursor. Semi-products produced for 2 h of reaction time and at 50°C and at 10 bar CO_2 pressure were used in the second step of this method.

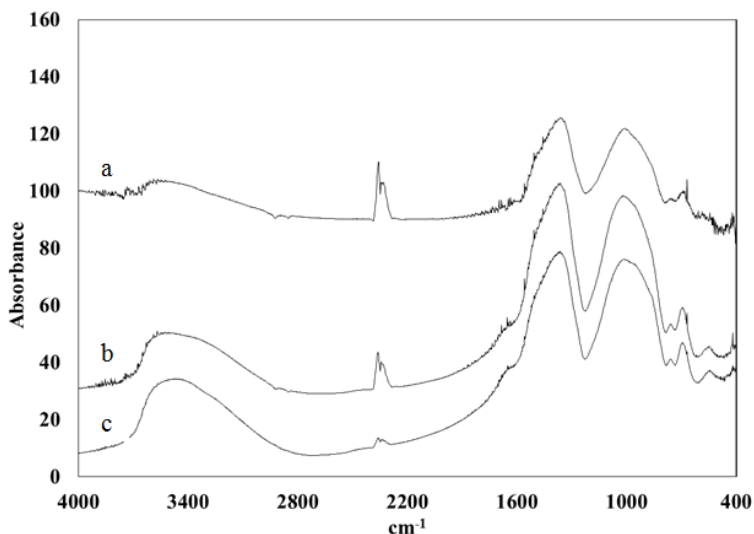


Figure 2. FTIR spectra of semi-product prepared at the CO_2 pressure of a) 10 bar, b) 25 bar and c) 40 bar

The semi-product crystallized after aqueous phase reaction was exposed to thermal treatment at $300\text{--}400^\circ\text{C}$ for 1h. The spectra of the final product and the reference lithium tetraborate are

shown in Fig. 3a and Fig. 3b, respectively. The peaks at 1136 and 900 cm^{-1} , which did not exist in the structure of precursor samples in Fig. 2, appeared after thermal treatment as it can be seen in Fig. 3a. The strong absorption peak between 1390 and 1350 cm^{-1} can be assigned to the asymmetric stretching vibration of B-O bond in trihedral BO_3 structure. The medium peak at 1136 cm^{-1} is due to the asymmetric stretching vibration of B-O bond in a tetrahedral BO_4 structure. The strong peak at 980 cm^{-1} and medium peak 900 cm^{-1} indicate the stretching vibrations of B-O in a BO_3 structure. The small absorption peak at 770 cm^{-1} is due to the symmetric stretching vibration of B-O bond in a BO_4 structure. The symmetric pulse vibration frequency of the tetraborate anion is observed at 550 cm^{-1} [20]. The peaks between 688 and 418 cm^{-1} are assigned to the O-B-O deformation mode of BO_4 structure in $\text{Li}_2\text{B}_4\text{O}_7$. It was also determined that hydroxyl groups and water being in the crystal lattice system was eliminated in the thermal treatment as the broad band between 3000 and 3600 cm^{-1} and the shoulder peak at 1650 cm^{-1} were eliminated as seen by the comparison of Fig. 2a and 3a.

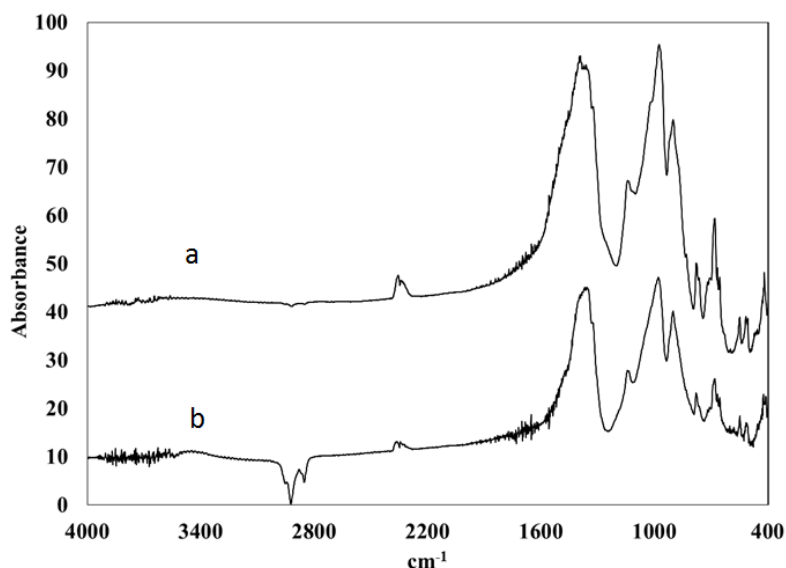


Figure 3. FTIR spectra of a)- the final product thermally treated at 400°C and b)- the reference lithium tetraborate

3.2. XRD analysis of semi-product and final product

Fig. 4 indicates XRD patterns of semi-product (Fig. 4a) and final products thermally treated at different temperature (300-400 °C), (Fig. 4b-4d). The peaks with the highest intensity found in the structure of lithium tetraborate were assigned to the JCPDS card no 79-0963 in which crystal lattice system was determined as tetragonal and dimensions of the unit cell were $a = 9.477$, $b = 9.477$ and $c = 10.286$ Å [13]. The XRD pattern of semi-product prepared utilizing CO_2 at 10 bar has been shown in Fig. 4a, where the amorphous structure was observed due to the presence of a broad peak, while the small sharp peaks belong to the formation of the crystalline phase [9, 21]. Final products that were thermally treated at 300°C and °C and 350°C begin to crystallize as shown in Fig. 4b and Fig. 4c., respectively. The XRD patterns of final product thermally treated at 400°C indicated that fully crystalline anhydrous lithium tetraborate was produced as main peaks in those patterns are compatible with those given in the literature and JCPDS of 79-0963 (2θ , 21.80°,

25.63°, 33.60°, 34.61°) [13, 19] shown by red lines on Fig. 4. XRD patterns revealed that lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) was successfully produced from the two-step method (aqueous phase reaction and thermal treatment). When it is compared to the nano-sized lithium tetraborate which was synthesized using single-step thermal treatment at the temperature range of 650-750 °C, the product having the same XRD pattern was synthesized at a lower temperature (400°C) and a shorter reaction period (3 h).

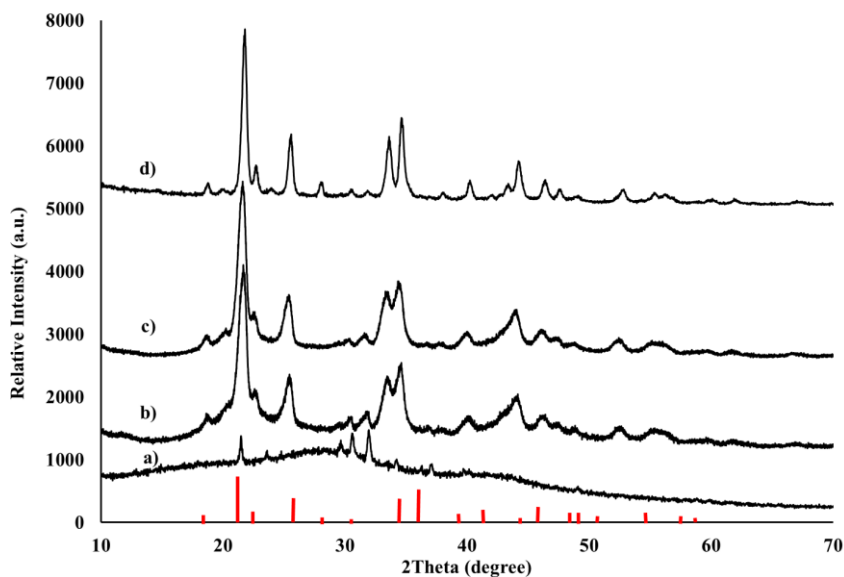


Figure 4. XRD patterns of a-) semi-product and final-products treated at b)- 300°C, c)- 350°C, d)-400°C

3.3. SEM analysis of semi-product and final product

Scanning Electron Microscopy (SEM) was used to compare the morphology and particle size of semi-product prepared at 10 bar CO_2 pressure and the final product produced by thermal treatment of the same sample as shown in Fig. 5a and Fig. 5b, respectively. As it can be seen in Fig. 5, SEM images of both samples are different from each other. Since semi-product was obtained by evaporation of the formed compound from the aqueous phase at 100°C and 1 atm. it has a smooth surface as in Fig. 5a [13]. Dehydration of semi-product occurred when sample powder was thermally treated. Because the water molecules formed by condensation of hydroxyl groups or the diffusion of H_2O in the crystal lattice out of the solid matrix, the flat surface seen in Fig. 5a was completely broken down and converted into smaller particles (Fig. 5b). The particle size of thermally treated lithium tetraborate is uniform and an average size varies between 2 and 5 micron as depicted in Fig. 5b.

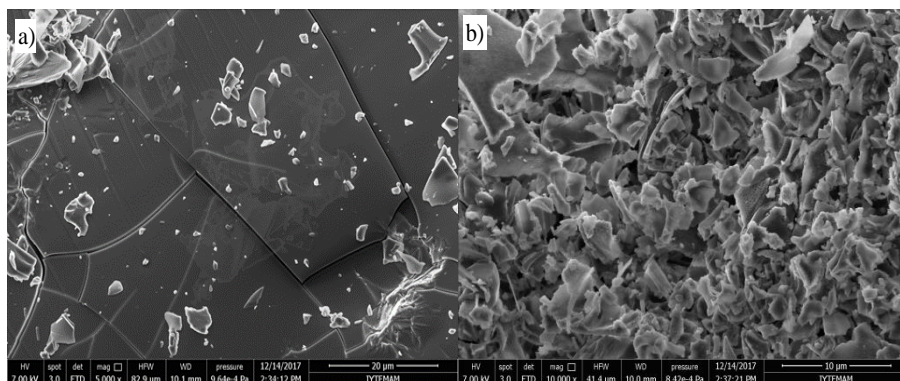


Figure 5. SEM images of a-) semi-product and b-) final-product prepared at 400°C

3.4. TGA analysis of the powder samples

Thermal analysis of lithium tetraborate samples produced in a two-step process is shown in Fig. 6a and 6b. The structure of lithium tetraborate with 3 moles of water is defined as $\text{Li}(\text{H}_2\text{O})\text{B}_2\text{O}_3(\text{OH})$ in which tetrahedral (BO_4) and trihedral (BO_3) coordination occurs to form infinite chains. Li atoms have tetrahedral coordination with two oxygen atoms, one hydroxyl group (OH) and one water molecule [4]. The semi-product synthesized in the aqueous phase at 50°C and 10 bar CO_2 pressure (Fig. 6b) decomposed thermally in three steps. The first step is related to the removal of the water from the sample which started at 76°C and has a peak at 112°C. In the second step, water molecules which are entrapped in the crystal lattice system were released between the temperatures 187°C and 300°C as shown in Equation 4. In the last step, hydroxyl groups in the structure of the semi-product polymerized to form water and removed from the structure above the 305 °C as given in Equation 5. Dehydration reactions of amorphous semi-product could be given as following:



The total mass loss occurred in the semi-product is about 23% which is very close to the theoretical amount of water (24%) in the lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7 \cdot 3\text{H}_2\text{O}$). Anhydrous lithium tetraborate did not undergo thermal degradation or decomposition when heated. Thus, no mass loss was recorded as shown by Fig. 6a. The small variation in mass loss is related to the moisture adsorbed by lithium tetraborate from the atmosphere [7].

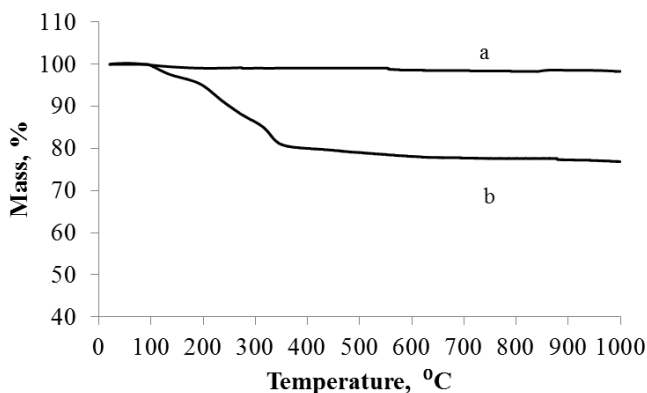


Figure 6. TG thermograms of a-) final product prepared at 400°C and b-) semi-product

3.5. Density measurements of the powders

The volume of samples increased during the thermal treatment step. As a result of this observation, the true densities of the semi-product, final product, and the reference lithium tetraborate were measured by the pycnometer and the results are shown in Table 2.

Table 2. True density values of semi-product, final product and the reference lithium tetraborate.

Exp. No.	Ref. Lithium tetraborate (g.cm ⁻³)	Semi- product (g.cm ⁻³)	Final product (g.cm ⁻³)
Run 1	2.365	1.630	1.553
Run 2	2.343	1.622	1.561
Run 3	2.351	1.634	1.539
Mean density	2.353	1.629	1.551

The true densities of the final products were quite low compared to the reference sample and the one given in the literature (2.45 g.cm⁻³) [23]. This difference was induced by the removal of the water trapped in the crystalline structure of the product when heated to 400 °C. Voids formed during the thermal treatment increased the volume of the powder product. Therefore, thermal treatment significantly reduced the density of the lithium tetraborate samples. The flat surfaces of the semi-product formed after the crystallization step expanded when exposed to heating. The morphology of the particles after thermal treatment supports the expansion of the solid matrix and cracked particles were observed in SEM microphotographs, as well.

4. CONCLUSION

Lithium tetraborate was produced in the two-step method. Amorphous Li₂B₄O₇·3H₂O was synthesized as a semi-product from the reaction of lithium carbonate and boric acid in the aqueous phase in the first step. The use of CO₂ in the aqueous phase reaction increased the amounts of reactants that dissolved in the reaction medium due to the carbonic acid formed when CO₂ dissolved in the H₂O. Crystalline lithium tetraborate (Li₂B₄O₇) was produced by the thermal treatment of the semi-product at 400°C. The formation of lithium tetraborate was obtained at a lower temperature compared to the one produced at 750°C in solid-state reaction. Mass transfer limitation in the solid-state reaction due to the large particle size of the reactants was removed.

The sublimation problem of boric acid in the solid-state reaction was also hindered because only dehydration of semi-product was carried out in thermal treatment.

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