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Comparative Study on Two Different Methods for the Synthesis of Hydrated Sodium Metaborates

Sulu Sodyum Metaboratların Sentezi İçin İki Farklı Yöntemin Karşılaştırmalı Çalışması

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Abstract

This work is focused on the comparison of the synthesis of sodium metaborate hydrates using classical and ultrasound-assisted methods. For this purpose kernite, water, and sodium hydroxide were reacted at 80˚C for 2 hours under mechanical stirring or ultrasonic irradiation. At the end of the reactions, the obtained samples were characterized by X-ray diffraction (XRD) analysis. It was found that the sample synthesized under the ultrasonic irradiation was identified as sodium borate hydrate ($NaB(OH)_4.2H_2O$) condition, while it was found as sodium boron hydroxide ($NaB(OH)_4$) synthesized under the mechanical stirring condition.

Keywords: Classical method, Hydrated sodium metaborates, Kernite, Synthesis, Ultrasound-assisted method

Öz

Bu çalışma, sodyum metaborat hidrat sentezinin klasik ve ultrason yardımlı yöntemlerle karşılaştırılmasına odaklanmıştır. Bu amaçla kernit, su ve sodyum hidroksit 80˚C'de 2 saat mekanik karıştırma veya ultrases ışınlaması altında reaksiyona girdirilmiştir. Reaksiyon sonunda elde edilen örnekler X-ışınları difraktometresi (XRD) ile karakterize edilmişlerdir. Ultrases ışınlaması altında üretilen örneğin sodyum borat hidrat ($NaB(OH)_4.2H_2O$), mekanik karıştıma altında üretilen örneğin ise sodyum bor hidroksit ($NaB(OH)_4$) olduğu bulunmuştur.

Anahtar Kelimeler: Klasik yöntem, Sulu sodyum metaboratlar, Kernit, Sentez, Ultrases-yardımlı yöntem

1. Introduction

Sodium metaborate ($NaBO_2$) are divided into three main groups based on their water amount which include tetrahydrate, dihydrate and anhydrous (Perry and Phillips 1995). $NaBO_2$ is commonly used in chemical and metallurgical industries such as production of sodium perborate tetrahydrate, sodium borohydride, photographic-textile chemicals, detergents and cleaners (Garret 1998). $NaBO_2$ is the hydrolytic by-product of sodium borohydride ($NaBH_4$). The hydrolysis reaction is as follows:

$$NaBH_4+(2+n)H_2O \rightarrow NaBO_2.nH_2O+4H_2+Heat \quad (1)$$

where *n* is the excess hydration factor, representing the fact that the solid by-product can exist in varying degrees of hydration (i.e. hydrated metaborates). The hydration state of the by-product depends on the conditions under which the reaction occurs. These hydrated forms of by-product are sodium metaborate dihydrate and sodium metaborate tetrahydrate (Marrero-Alfonso et al. 2007, Marrero-Alfonso et al. 2009).

It was reported in the literature sodium metaborate was synthesized from different boron minerals such as concentrated tincal (Kanturk and Piskin 2010), borax (Yılmaz Sarı et al. 2012) and anhydrous borax (Kanturk et al. 2008). To our knowledge there is no study has been found related to use of kernite mineral in the synthesis of sodium metaborate.

All the efforts in optimizing experimental conditions/ techniques for faster and accurate production of sodium metaborates are quite essential from application point of view and also to vaticinate the transition to a hydrogen energy economy. In order to improve hydrogen storage capacity as well as recyclability of the borate, an understanding of thermal stability and dehydration processes of hydrated metaborates is essential (Beaird et al. 2011).

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In the present study the objective is to compare the synthesis of sodium metaborate hydrates using classical and ultrasound-assisted methods. The synthesis methods were undertaken at the same conditions using kernite as a boron source and the synthesized samples were compared in terms of structural characteristics.

2. Materials and Method

Kernite ($Na_2B_4O_6(OH)_2.3H_2O$) used in the experiments was supplied by Eskişehir Kırka Eti Mine Works. The mineral was cleaned, dried, crushed and sieved to a particle of <63 μm using the ASTM standard sieve. Sodium hydroxide (NaOH) was purchased from Merck (purity, 99%).

Crystal structures of the synthesized samples were identified by XRD (PANalytical X'Pert PRO) equipped with CuKα radiation (45 kV, 40 mA). The morphologies of the samples were observed by using a CamScan Apollo 300 scanning electron microscope (SEM). The thermal analyses (TG/DTG) were carried out on a Perkin Elmer Pyris Diamond thermal analyzer in nitrogen atmosphere at a heating rate of 10°C.min^{-1}. The infrared spectra of the samples were collected with a Fourier transform infrared spectrometer (FTIR, Perkin Elmer Spectrum One).

$Na_2B_4O_6(OH)_2.3H_2O$ and NaOH were prepared for the synthesis of sodium metaborate tetrahydrate, which is a type of hydrated sodium metaborates, by adding the appropriate amount of water based on the following reaction:

$$Na_2B_4O_6(OH)_2.3H_2O+2NaOH+11H_2O \rightarrow 4NaB(OH)_4.2H_2O \quad (2)$$

In the ultrasound-assisted method (UM), the reactant powders weighted according to the mole ratio of $NaOH:Na_2B_4O_7.4H_2O$=2:1 and a given amount of water were loaded in a batch reactor. The reactor was immersed in an ultrasonic bath (filled with distilled water to be heated at 80°C). Then, the mixture was irradiated under ultrasonic wave (35 kHz) for two hours. During the reaction, the samples were taken periodically from the solutions to investigate the formation of sodium metaborate hydrates. At the end of the reaction, the solution was allowed to cool down to 25°C and white color solid was formed immediately. Afterwards, the obtained solid was dried at 40°C.

In the classical method (CM), the sample was prepared following the same procedure as for ultrasonically treated sample, except that the mixture was kept in a water bath at 80°C and mechanically stirred for homogenous mixing during the reaction.

3. Results and Discussion

The XRD patterns of the obtained samples that were taken from the solution for different times during ultrasonic synthesis are shown in Figure 1. At the 5th minute, the XRD investigation showed the presence of $NaB(OH)_4{\cdot}2H_2O$ (PDF:01-076-0756), $NaB(OH)_4$ (PDF No: 01-081-1512), and sodium borate hydrate hydroxide ($Na_2B_4O_6(OH)_2(H_2O)_3$) (PDF No: 01-071-1549). Then the reaction proceeded, peak intensities of $NaB(OH)_4.2H_2O$ increased. The conversion of obtained sample to $NaB(OH)_4.2H_2O$ was completed at 60 min.

Figure 2 represents the XRD patterns of the obtained samples that were taken from the solution for different times during classical synthesis. At the 5th minute, the XRD investigation showed the presence of $NaB(OH)_4$ (PDF No: 01-081-1512) and $NaB(OH)_4{\cdot}2H_2O$, (PDF:01-076-0756). Then the reaction proceeded, peak intensities of $NaB(OH)_4$ increased. The conversion of the obtained sample to $NaB(OH)_4$ was completed at 60 min.

TG/DTG curves of the synthesized samples by different methods were given in Figure 3. From the Figure 3(a), it can be seen that the decomposition process of the synthesized sample by UM occurred in one dehydration stage and three dehydroxylation stages. The dehydration stage (<100 °C) attributed to the removal of 1.77 mole of crystalline water. The last three stages (100-473°C) corresponded to the removal of 1.94 mole of structural water in the sample. The total weight loss was found as 3.71≈ 4 mol of H_2O per

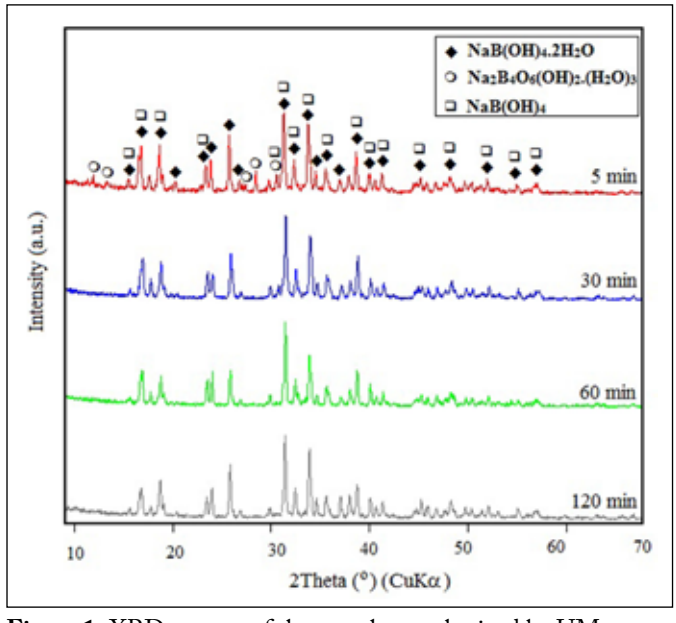

Figure 1. XRD pattern of the samples synthesized by UM.

formula unit of $NaB(OH)_4.2H_2O$ product as expected. The dehydration and dehydroxylation reactions were proposed to take place according to the following mechanisms:

$$NaB(OH)_4.2H_2O \longrightarrow NaB(OH)_4 + \approx 2H_2O \quad \text{(Dehydration reaction)} \quad (3)$$

$$NaB(OH)_4 \longrightarrow NaBO_2 + \approx 2H_2O \quad \text{(Dehydroxylation reaction)} \quad (4)$$

From the Figure 3(b), it can be observed that the thermal decomposition of the sample synthesized by CM, occurred within the temperature range 33-477°C with one dehydration stage followed by two dehydroxylation stages. The first stage occurred in the temperature range from 30°C to 50°C due to the removal of physically adsorbed water (0.07 mole). The total weight loss during the dehydroxylation corresponded to the removal of 1.95 ≈ 2 mol of H_2O per formula unit of $NaB(OH)_4$ product as expected, which was occurred by the following mechanism.

$$NaB(OH)_4 \longrightarrow NaBO_2 + \approx 2H_2O \quad \text{(Dehydroxylation reaction)} \quad (5)$$

FTIR spectra of the obtained samples by UM and CM were demonstrated in Figure 4. The bands at 3141 cm^{-1} and 1258 cm^{-1} are due to the stretching mode of O-H and inplane bending band of B-O-H, respectively. The bands between 1128 cm^{-1} and 907 cm^{-1} can be assigned to the asymmetric stretching of B-O vibrations. The band at 766 cm^{-1} corresponds to the out-of-plane bending of O-H and symmetric stretching band of B-O (Pişkin 1983). There are only a few differences between the IR spectrum of the synthesized samples by UM and CM. In the spectrum region of 1350-1050 cm^{-1} of the sample synthesized by CM was divided into three peaks, while it was divided into two peaks in the sample synthesized by UM. In addition, the H-O-H stretching band at 1654 cm^{-1} disappeared, while the B-O band at 1080 cm^{-1} observed in the sample synthesized by CM.

SEM investigation was carried out to reveal the particle shape and size. The SEM images of the samples under different stirring techniques are illustrated in Figure 5. It can be seen that the shapes of the particles were very similar to each other, but the crystal size of the samples was different. The particles of the sample synthesized at 80°C by UM were bigger in size than CM.

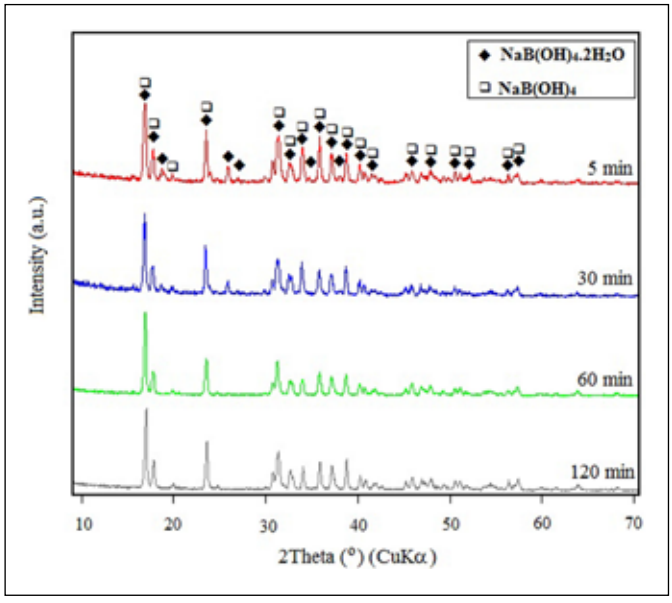

Figure 2. XRD pattern of the samples synthesized by CM.

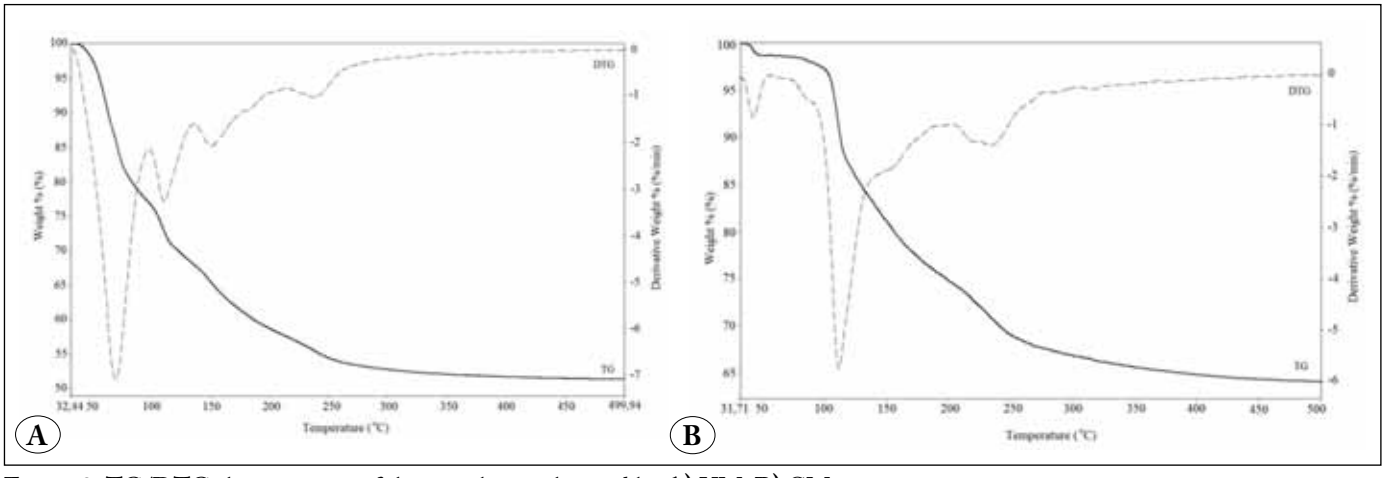

Figure 3. TG/DTG thermograms of the samples synthesized by **A)** UM, **B)** CM.

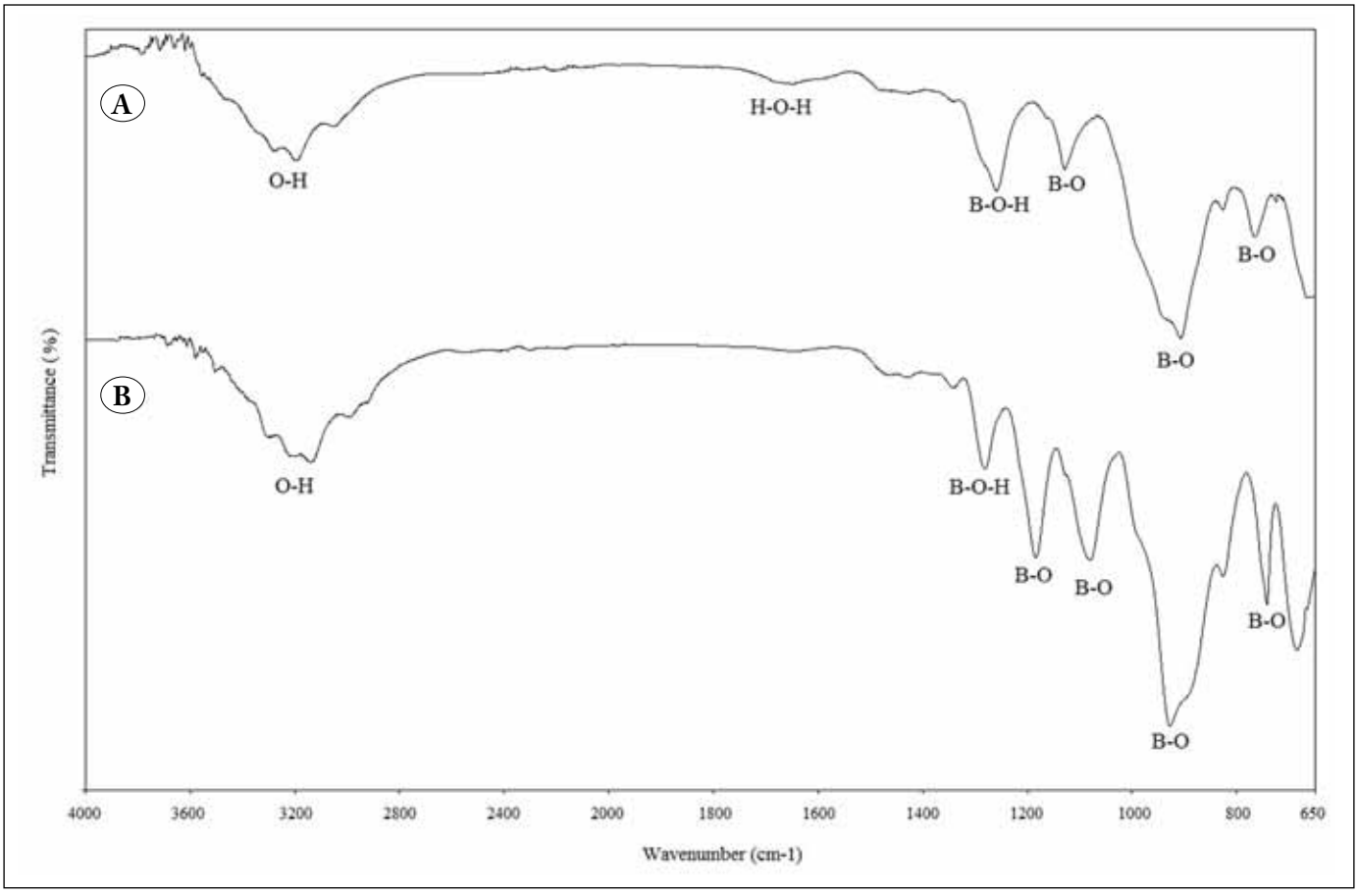

Figure 4. FTIR spectra of the samples synthesized by **A)** UM, **B)** CM.

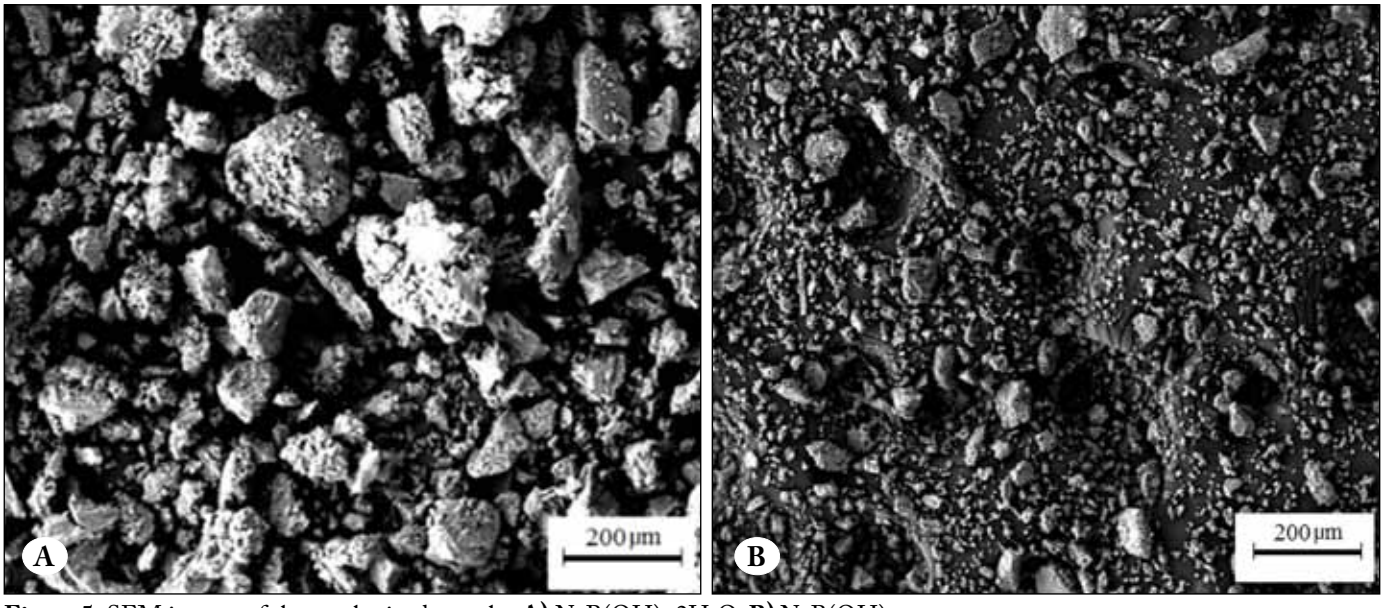

Figure 5. SEM images of the synthesized samples **A)** $NaB(OH)_4.2H_2O$, **B)** $NaB(OH)_4$

4. Conclusion

In this study, hydrated sodium metaborates from kernite mineral were successfully synthesized by ultrasonic and classical procedures. It was obtained that the synthesized sample was sodium boron hydroxide by the classical methods, while it was sodium borate hydrate by the ultrasonic methods. It can be seen that the sonochemical synthesis of sodium borate hydrate can be accelerated by irradiating the solution. Moreover, the reaction temperature is inadequate for the synthesis of sodium borate hydrate in the classical methods.

5. References

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