The Determination of the Potassium Nitrate, Sodium Hydroxide and Boric Acid Molar Ratio in the Synthesis of Potassium Borates via Hydrothermal Method

M. Yildirim, A. S. Kipcak, F. T. Senberber, M. O. Asensio, E. M. Derun, S. Piskin

Abstract—Potassium borates, which are widely used in welding and metal refining industry, as a lubricating oil additive, cement additive, fiberglass additive and insulation compound, are one of the important groups of borate minerals. In this study the production of a potassium borate mineral via hydrothermal method is aimed. The potassium source of potassium nitrate (KNO3) was used along with a sodium source of sodium hydroxide (NaOH) and boron source of boric acid (H3BO3). The constant parameters of reaction temperature and reaction time were determined as 80ºC and 1 h, respectively. The molar ratios of 1:1:3 (as KNO3:NaOH:H3BO3), 1:1:4, 1:1:5, 1:1:6 and 1:1:7 were used. Following the synthesis the identifications of the produced products were conducted by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR) and Raman Spectroscopy. The results of the experiments and analysis showed in the ratio of 1:1:6, the Santite mineral with powder diffraction file number (pdf no.) of 01-072-1688, which is known as potassium pentaborate (KB5O8·4H2O) was synthesized as best.

Keywords—Hydrothermal synthesis, potassium borate, potassium nitrate, sanidine.

I. INTRODUCTION

Boron minerals are naturally present in a huge family of over 200 different crystal structures, in addition to the ones that can be synthesized at laboratory [1]. Classification of these structures can be handled in base of the polymerization of boron trioxide (BO3) triangular and boron tetraoxide (BO4) tetrahedral (T) groups into polyanions, which constitute the polynuclear anions sharing vertices.

The combinations of these groups in different forms release a molecule of water (H2O), which forms the wide variety of boron minerals known [2]. Dozens of these polyborates exist in aqueous solution can be found in previous studies; several methods are used combined with different raw materials concentrations. Rajasekar et al [7] synthesized KB5 dissolving potassium carbonate (K2CO3) and H3BO3 in double distilled water at 35ºC. Gürbüz et al [8] together with Zhu et al [9] prepared an aqueous solution of potassium hydroxide and boric acid and between 3-5 respectively. Gürbüz used a fluidized bed at 35ºC, while Zhu prepared the sample in a mixed solution of H3BO3 and potassium hydroxide (KOH) between 50-60ºC.

In the present study it was aimed to determine of a proper ratio between compounds for a high yield reaction in which the crystal formation of synthesized potassium borate is in a high degree. Therefore, starting with KNO3, NaOH, H3BO3 as raw materials, hydrothermal synthesis of potassium borate at 80ºC was investigated for different boric acid ratios.

II. EXPERIMENTAL STUDIES

A. Raw Material Preparation

The starting materials of KNO3 and NaOH were commercial...
grades and used without further purification. The boron source of H$_3$BO$_3$ was procured from Bandirma Boron Works and processed by crushing, grinding through agate mortar and sieving through shaker sieve to reduce particle size below 75μm. In the sequel, the prepared raw materials were identified by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) methods. Philips PANalytical XRD instrument (Fig. 1 (a)) with CuKα radiation at the parameters of 45kV and 40mA was used. Infrared spectra were recorded in the range 650-1800cm$^{-1}$, with Perkin Elmer Spectrum One Fourier Transform Infrared Spectroscopy (FT-IR) (Fig. 1 (b)).

**C. Experimental Results**

XRD patterns and results of reagents of KNO$_3$ and H$_3$BO$_3$ are given in Fig. 3.

![Production process of potassium borate](image)

Fig. 2 Production process of potassium borate

![XRD patterns of raw materials](image)

Fig. 3 XRD patterns of raw materials

According to XRD results, raw materials are defined as Niter (KNO$_3$) with pdf code of 00-005-0377 and Sassolite (H$_3$BO$_3$) with pdf code of 01-073-2158.

![FT-IR spectra of raw materials](image)

Fig. 4 FT-IR spectra of raw materials

FT-IR spectra of raw materials are shown in Fig. 4.

The XRD patterns of products of experiments for different boron molar ratio are given in Fig. 5. Table I shows the XRD results of products. According to XRD results for all boric
acid ratios, potassium borate synthesis has been accomplished. The synthesized mineral is Santite with powder diffraction file number (pdf no.) of 01-072-1688, which is known as potassium pentaborate (KB$_5$O$_8$·4H$_2$O). However, for the molar ratios of 1:1:6 (KNO$_3$·NaOH·H$_3$BO$_3$), the XRD score of Santite reaches to the highest value of 57.

### TABLE I

<table>
<thead>
<tr>
<th>Molar ratio</th>
<th>XRD score</th>
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<tbody>
<tr>
<td>1:1:3</td>
<td>22</td>
</tr>
<tr>
<td>1:1:4</td>
<td>41</td>
</tr>
<tr>
<td>1:1:5</td>
<td>52</td>
</tr>
<tr>
<td>1:1:6</td>
<td>57</td>
</tr>
<tr>
<td>1:1:7</td>
<td>47</td>
</tr>
</tbody>
</table>

According to FT-IR spectra, IR peaks around 1340 cm$^{-1}$ are assigned to asymmetric stretching of B$_{3y}$-O when the bending mode of B–O–H is observed 1247 cm$^{-1}$. The peaks in the range of 1093-1022 cm$^{-1}$ belongs to symmetric stretch of B$_{4y}$-O. The peaks at wavenumber of 917 cm$^{-1}$ belongs to symmetric stretching of B$_{3y}$-O. The peaks between 825 cm$^{-1}$ and 781 cm$^{-1}$ are corresponded to symmetric stretching of B$_{4y}$-O. The peaks between 736 cm$^{-1}$ and 680 cm$^{-1}$ is ascribed to in-plane bending vibrations of B$_{3y}$-O [10].

In Fig. 7, Raman spectra of synthesised potassium borate compounds are shown.

### III. CONCLUSION

In this study, it was intended to synthesize potassium borates using KNO$_3$, NaOH, H$_3$BO$_3$ as raw materials by hydrothermal method. Starting out to investigate the influence of boric acid molar ratio on the final product, the experimental conditions were set to 80°C of reaction temperature and 1 hour reaction time. Several boric acid molar ratios were used while molar ratios of other raw materials were kept constant. According to characterization analysis, it was observed that for all molar ratios, potassium borate synthesis was completed with success. The synthesized potassium pentaborate compound was potassium pentaborate (KB$_5$O$_8$·4H$_2$O). XRD results showed that, with increasing molar ratio of boric acid, the crystallinity of synthesized minerals were increasing up to 1:1:7. In consideration of analysis results, the most appropriate molar ratios of raw materials were determined as 1:1:6.

### REFERENCES


Meral Yildirim was graduated from B.Sc. in 2011, M.Sc. in 2013 from Chemical Engineering Department in Yildiz Technical University, Istanbul. She is currently continuing her Ph. D. education at the same university. She is interested in synthesis and characterization of borate minerals, waste management and cement-concrete production.

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Fatma Tugce Senberber was graduated from B.Sc. at Yildiz Technical University in 2010. After she completed her M.Sc. studies at Yildiz Technical University in 2012, she started to Ph.D. studies at the same year and same department of university. She is interested in boron technologies such as alternative synthesis methods of boron minerals and evaluation of industrial wastes in synthesis process. She also studied the characterization methods by instrumental analysis, kinetic studies of minerals and alternative application areas of synthesized minerals.

Miguel Ortega Asensio studied at University of Valladolid in the Industrial Engineering faculty, specializing in Energetic Engineering. He is under the Erasmus+ program, developing his final master thesis at Yildiz Technical University on the study of borate minerals synthesis, characterization and instrumental analysis.

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