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

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***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 (KNO_3) was used along with a sodium source of sodium hydroxide (NaOH) and boron source of boric acid (H_3BO_3). The constant parameters of reaction temperature and reaction time were determined as 80°C and 1 h, respectively. The molar ratios of 1:1:3 (as KNO_3:NaOH:H_3BO_3), 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 ($KB_5O_8 \cdot 4H_2O$) was synthesized as best.

***Keywords*—**Hydrothermal synthesis, potassium borate, potassium nitrate, santite.

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 (BO_3) triangular and boron tetraoxyde (BO_4) 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 (H_2O), which forms the wide variety of born minerals known [2]. Dozens of these polyborates exist in aqueous solutions, its formation depending on temperature, cation type, pH and composition of the primary solution. When dissolved in water, boron normally is present as undissociated boric acid, depending on the pH composition and concentration of the sample to produce either mononuclear $B(OH)_3$ or the monoborate anion $B(OH)_4^-$ [3]-[5].

One of the important borate type is potassium borates which are widely used in metal refining, welding, cement, insulation, fiberglass and non-linear materials. Also potassium borates improve the anticorrosion and antiwear properties of industrial and automotive gear lubricants so they are used as lubricating oil additives. Like other borate compounds, potassium borates are good neutron absorbers and can be used in nuclear energy plants [6].

There are mainly two important potassium borate minerals; potassium tetraborates and potassium pentaborates. Potassium tetraborates ($K_2B_4O_7 \cdot 4H_2O$) are produced the reaction of potassium hydroxide, water and boric acid. Potassium tetraborates belong to the orthorhombic crystal system, being a positive biaxial element and its lattice parameters are: a=12,899 Å, b= 11,774 Å and c= 6,859 Å. Potassium pentaborates ($KB_5O_8 \cdot 4H_2O$, or KB_5) belong to the orthorhombic crystal system, too. Its lattice parameters are: a=11,065 Å, b= 11,171 Å and c= 0,054 Å [3].

Preparation of potassium borates in aqueous solution can be founded in previous studies; several methods are used combined with different raw materials concentrations. Rajasekar et al [7] synthesized KB_5 dissolving potassium carbonate (K_2CO_3) and H_3BO_3 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 B_2O_3/K_2O with ratio 5 and between 3-5 respectively. Gürbüz used a fluidized bed at 35ºC, while Zhu prepared the sample in a mixed solution of H_3BO_3 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 KNO_3, NaOH, H_3BO_3 as raw materials, hydrothermal synthesis of potassium borate at 80°C was investigated for different boric acid ratios.

II. Experimental Studies

A. Raw Material Preparation

The starting materials of KNO_3 and NaOH were commercial

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grades and used without further purification. The boron source of H_3BO_3 was procured from Bandırma Boron Works and processed by crushing, grinding through agate mortar and sieving through shaker sieve to reduce particle size below 75 μm. 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)).

Fig. 1 (a) Philips PANalytical XRD, (b) Perkin Elmer Spectrum One FT-IR

B. Hydrothermal Synthesis

In hydrothermal synthesis of potassium borates, the reaction parameters were set to 80°C of reaction temperature and 1 hour of reaction time. The molar ratio of H_3BO_3 was varied from 3 to 7 for determination appropriate ratio.

In synthesises, raw materials were dissolved in distilled water solution at 80°C. The reaction cell was controlled by a thermocouple to ensure constant temperature. At the end of the reaction time, the mixture was placed to a crystallizer glass and the crystallizer was situated into an incubator maintained at 40°C until the excess water evaporated and potassium borate minerals were crystallized. After crystallization process, the excess raw materials were removed from products by washing with ethanol. The washed products were dried in an incubator maintained at 40°C.

The illustration of production process of potassium borates which is aforementioned above is given in Fig. 2.

The characterization studies of synthesized potassium borate compounds were conducted by using XRD, FT-IR and Raman spectroscopy analysis methods. XRD analyses were performed at 45kV and 40 mA by using Cu-Kα radiation. According to literature the characteristic peaks of borate compounds were observed in the ranges between 500 - 1500 cm^{-1}[3]. For this reason the spectrum ranges for vibrational spectroscopy of FT-IR were recorded in the range 650-1800 cm^{-1} when for Raman spectroscopy the spectrum ranges were selected between 250 cm^{-1} - 1800 cm^{-1}.

C. Experimental Results

XRD patterns and results of reagents of KNO_3 and H_3BO_3 are given in Fig. 3.

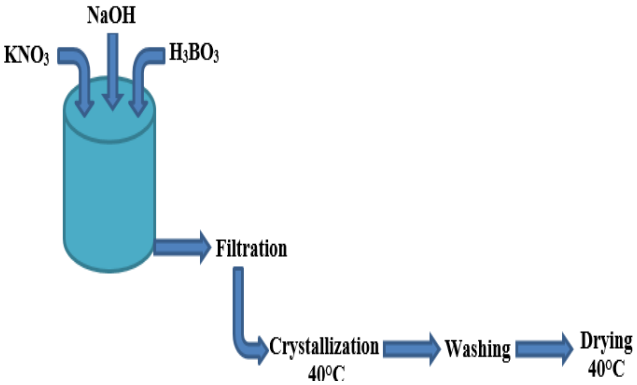

Fig. 2 Production process of potassium borate

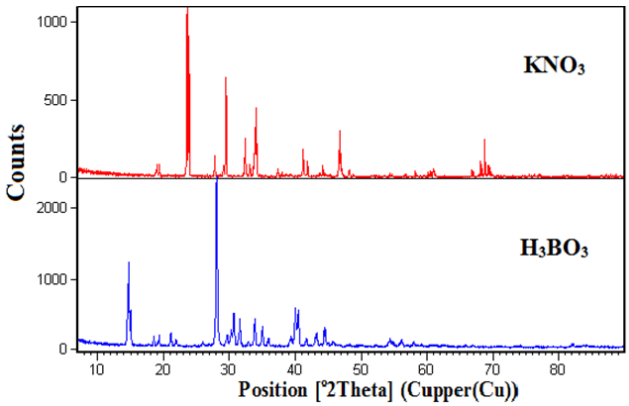

Fig. 3 XRD patterns of raw materials

According to XRD results, raw materials are defined as Niter (KNO_3) with pdf code of 00-005-0377 and Sassolite (H_3BO_3) with pdf code of 01-073-2158.

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

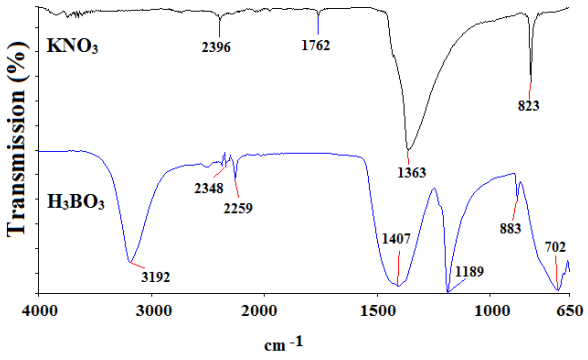

Fig. 4 FT-IR spectra of raw materials

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 ($KB_5O_8{\cdot}4H_2O$). However, for the molar ratios of 1:1:6 (KNO_3:NaOH:H_3BO_3), the XRD score of Santite reaches to the highest value of 57.

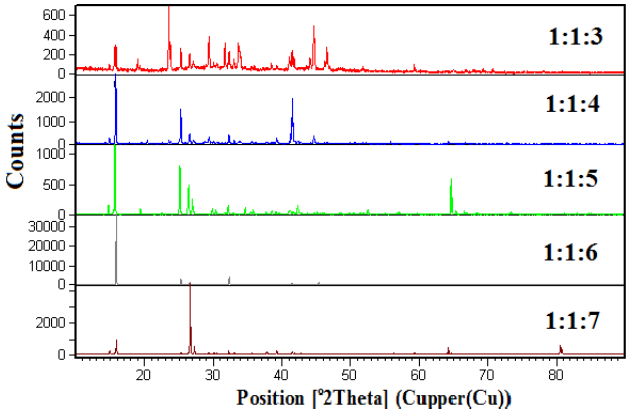

Fig. 5 XRD patterns of raw materials

TABLE I
XRD RESULTS OF SYNTHESIZED SANTITE MINERAL

Molar ratio	XRD score
1:1:3	22
1:1:4	41
1:1:5	52
1:1:6	57
1:1:7	47

FT-IR analysis results of synthesized minerals are given in Fig. 6.

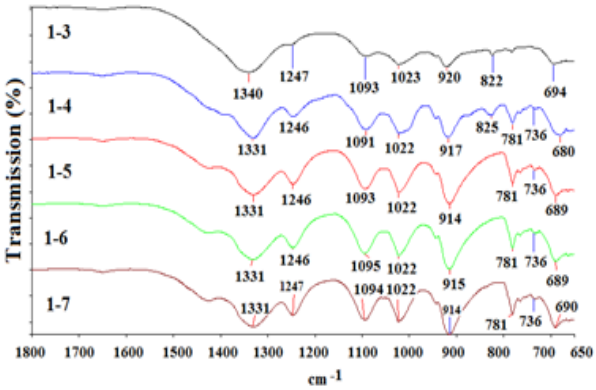

Fig. 6 FT-IR spectra of synthesized minerals

According to FT-IR spectra, IR peaks around 1340 cm^{-1} are assigned to asymmetric stretching of $B_{(3)}$–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 asymmetric stretch of $B_{(4)}$–O. The peaks at wavenumber of 917 cm^{-1} belongs to symmetric stretching of $B_{(3)}$–O. The peaks between 825 cm^{-1} and 781 cm^{-1} are corresponded to symmetric stretching of $B_{(4)}$–O. The peaks between 736 cm^{-1} and 680 cm^{-1} is ascribed to in-plane bending vibrations of $B_{(3)}$–O [10].

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

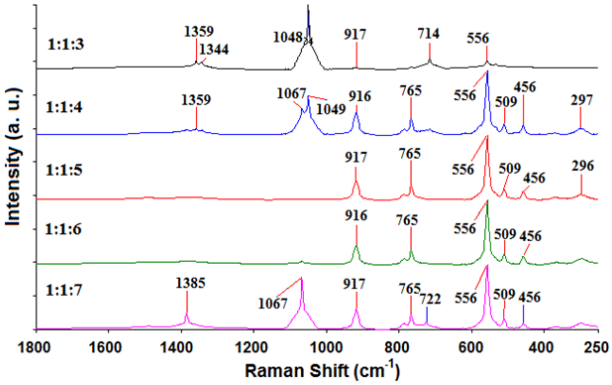

Fig. 7 Raman spectra of synthesized minerals

According to Raman spectra, asymmetric stretching of $B_{(3)}$–O is observed between 1344-1385 cm^{-1} when the peaks between 1049-1067 cm^{-1} are assigned to asymmetric stretching of $B_{(4)}$–O. Around 918 cm^{-1} the peaks are caused by symmetric stretching of $B_{(3)}$–O). The frequencies between 785-714 cm^{-1} are symmetric stretching of $B_{(4)}$–O. The peak at 556 cm^{-1} can be belong to the symmetric pulse vibration frequency of the pentaborate anion $[(B_5O_6(OH)_4)^-]$. The frequencies between 509 cm^{-1} and 296 cm^{-1} are assigned to bending of four coordinate boron $B_{(4)}$ –O.

III. CONCLUSION

In this study, it was intended to synthesize potassium borates using KNO_3, NaOH, H_3BO_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 borate compound was potassium pentaborate ($KB_5O_8{\cdot}4H_2O$). 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.

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