Determination Optimum B_2O_3, KCl and NaOH Molar Ratios in the Synthesis of Potassium Borates

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Abstract

Borates are attention getting chemical compounds because of their properties which leads them a wide usage area. Being sub-group of borates, potassium borates show non-linear optical properties and owing to this they can find applications in optical modulation, optical switching, optical logic and memory, signal processing. Potassium borates can be used in welding, insulation, metal refining and lubricating oil production applications, also.

In this study, potassium borates were produced from potassium chloride (KCl), sodium hydroxide (NaOH) and boron oxide (B_2O_3) when different molar ratios of B_2O_3 were used to find out the optimum ratio for the synthesis at 80°C and 1 hour of reaction time. The molar ratios of reactants were examined as 1:1:3 (as KCl:NaOH: B_2O_3), 1:1:4, 1:1:5, 1:1:6 and 1:1:7. The identification of products and the effects of different molar ratios on the final product were determined by X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR) methods. According to experimental results, the Santite ($KB_5O_8{\cdot}4H_2O$) mineral with powder diffraction file number (pdf) code of 01-072-1688 was produced for all molar ratios whereas the optimum ratios in which highest XRD score was obtained was 1:1:7.

Keywords-potassium borates, hydrothermal sythesis, XRD, FT-IR.

1 Introduction

Borates are naturally occurring chemical compounds especially in the volcanic-tectonic belts of western North and South America, the eastern Mediterranean, and Asia [1]. Having biggest deposits, Turkey has approximately 72% of world boron reserves [2]. However, potassium borate is a very rare borate compound which occurs just the regions of Larderello, Italy and Eagle Borax Spring, California, USA [3]. There are mainly two types of potassium borates which are potassium tetraborate $K_2B_4O{\cdot}4H_2O$ and potassium pentaborate. When potassium borate can be found in nature, potassium tetraborate is synthesized in laboratories by the reaction of a boron and a potassium source. Potassium tetra borate has wide usage areas such as treatment of contact lenses, glass industry and lubricating oil additive. Being one of the popular second-harmonic generation (SHG) at short wavelengths, potassium pentaborate shows significant non-linear optic properties which lead them to convert laser radiation to UV and vacuum UV wavelength region [4-6]. Potassium pentaborate crystals are uncolored, optically biaxial and chemically stable compounds. Because of the optical and chemical importance of potassium borates, many researchers show an interest in their synthesis and application in different fields [4-12].

In literature studies, Yang and Zhang [4] produced $KB_5O_8{\cdot}4H_2O$ with a reaction of K_2CO_3 and H_3BO_3 at 70°C for 6 hour when Senthilkumar [9] prepared saturated solution of $KB_5O_8{\cdot}4H_2O$ at room temperature using KOH and H_3BO_3 with a molar ratio of 7:10 at room temperature than obtain $KB_5O_8{\cdot}4H_2O$ crystals. Gürbüz, Badem, and Bulutcu [5] synthesized potassium pentaborate by adding a seed crystal in the bulk solution of boric acid and potassium hydroxide in the fluidized bed crystallizer Wang, Sun, Zheng and Yang [13] obtained $KB_3O_4(OH)_2$ hydrothermally by the reaction of $K_2B_4O_7{\cdot}4H_2O$, DMF and H_2O at room temperature and

crystallization at 165°C for 10 days. Zhu et. al. [14] prepared solutions of KOH and H_3BO_3 with the molar ratio between 3 and 5 at 50-60ºC to get potassium pentaborate precipitate.

In this study, a different potassium source of KCl and boron source of B_2O_3 was used to obtain potassium pentaborate compound. To reveal optimum molar ratios of raw materials various B_2O_3 ratios were attempted at 80°C of reaction time and 1 hour of reaction time. Determination optimum molar ratio of reactants will be light the way of further studies.

2 Experimental Studies

2.1 Raw material preparation

The reactants of KCl and NaOH were procured from Merck Chemicals and used without any further treatment when the boron source of B_2O_3 was obtained from Bandırma Boron Works, Turkey and crushing, grinding through agate mortar and sieving through shaker sieve processes applied to have a particle size below 75µm.

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) methods were conducted to raw materials for identification. Philips PANalytical XRD instrument was used with CuKα radiation at the parameters of 45kV and 40mA. Perkin Elmer Spectrum One Fourier Transform Infrared Spectroscopy (FT-IR) was used to record infrared spectra of raw materials between 650 cm^{-1} and 1800cm^{-1}.

2.2 Synthesis and Characterization Studies of Potassium Pentaborate

To determine optimum raw material molar ratio for synthesizes of potassium borate compounds, the molar ratio of B_2O_3 was varied from 3 to 7 when amounts of the other reactants were kept constant. The reaction temperature was adjusted at 80°C and the reactions were carried out for 1 hour.

Distilled water was chosen for hydrothermal synthesis procedure which can dissolve all reactants. For the synthesis, a closed glass reaction vessel which was combined with a thermocouple to ensure temperature control was used. With the end of the reaction, the reaction slurry was placed to a crystallizer and excess water was removed by the help of an incubator maintained at 40°C. Following obtainment of potassium borate crystals, the products were washed with ethanol to purify from the excess amount of reactants and by-product of NaCl. The washed products were dried in an incubator which is at 40°C. Aforementioned synthesis process is illustrated in Fig. 1.

The characterization studies of produced potassium borate compounds were carried out by XRD and FT-IR spectroscopy methods. The XRD analyses were performed at 45kV and 40 mA by using Cu-Kα radiation (λ=1.53 cm^{-1}) in the 2θ range of 7-90°. The spectrum ranges for infra-red vibrational spectroscopy of FT-IR were recorded in the ranges of 650-1800 cm-1 because literature studies showed that literature the characteristic peaks of borate compounds were observed in the ranges between 500 - 1500cm^{-1} [15].

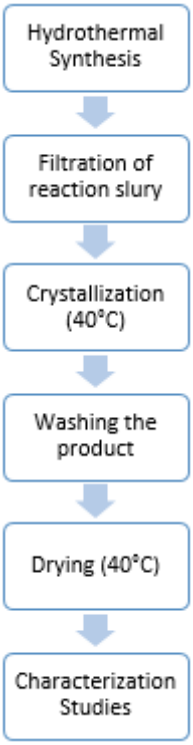

Figure 1. Synthesis process

3 Experimental Results

3.1 Characterization Results of Raw Materials

XRD patterns of B_2O_3 and KCl are given in Fig. 2. According to XRD results the boron source was defined as Boron oxide (B_2O_3) with powder diffraction code (pdf) of 00-006-0297 and 00-041-1476 pdf coded Sylvite (KCl) was defined as potassium source.

The FT-IR spectra of raw materials are given in Fig. 3.

3.2 Characterization Results of Synthesized Potassium Borates

Fig. 4 shows the XRD patterns of experimental products of various B_2O_3 molar ratios between 1:3 and 1:7. When XRD patterns are examined thoroughly, characteristic XRD peaks of potassium borates cannot be seen until the B_2O_3 ratio reached to 1:5. According to XRD results, the produced potassium borates are a potassium pentaborate ($KB_5O_8{\cdot}4H_2O$) type of Santite with pdf code of 01-072-1688.

As given in Table I, the gain in the B_2O_3 ratio ensured an increase of XRD scores of the synthesized Santite compounds. The highest crystallinity was achieved at the molar ratio of 1:1:7 ($KCl:NaOH:B_2O_3$) with XRD score of 70.

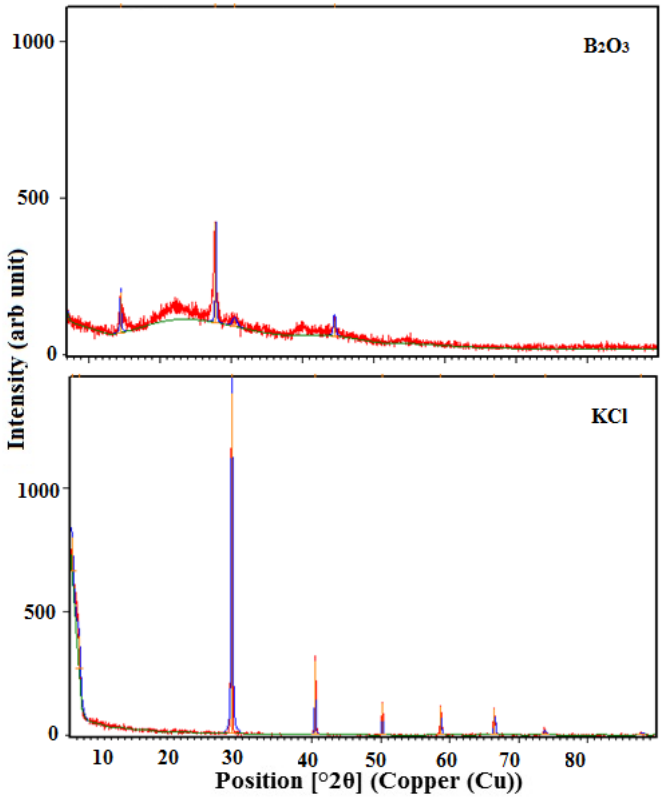

Figure 2. XRD patterns of boron and potassium source

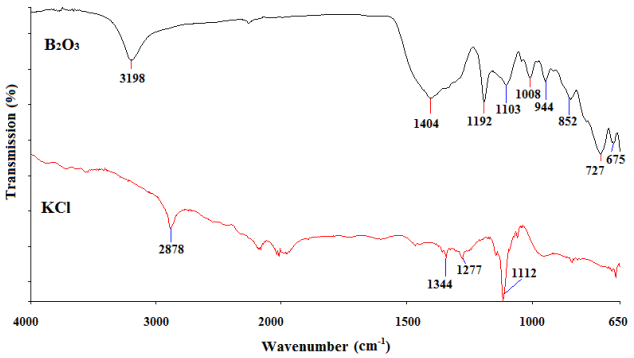

Figure 3. FT-IR spectra of raw materials

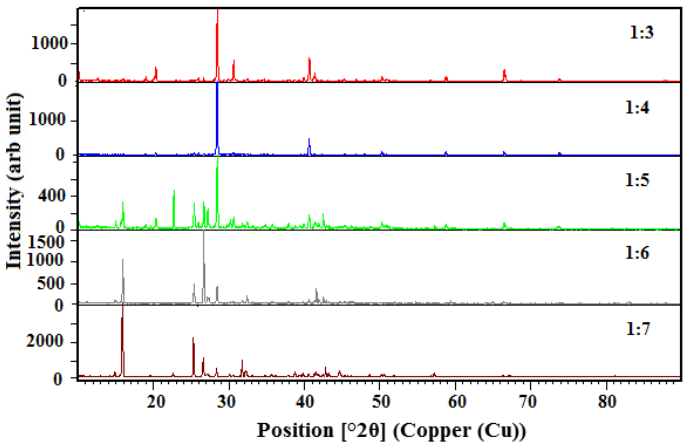

Figure 4. XRD patterns of products

Table 1. XRD Results of products

Molar ratio	XRD scores
1:3	15
1:4	14
1:5	51
1:6	61
1:7	70

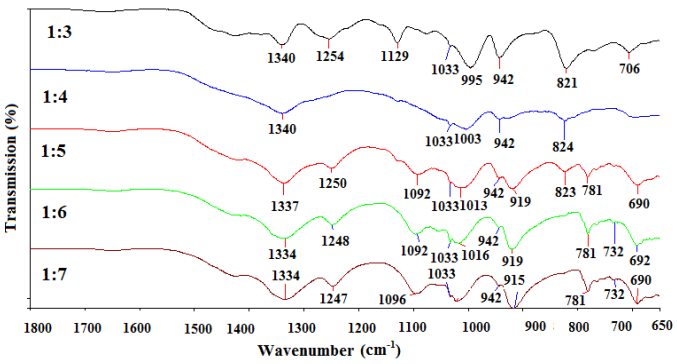

Figure 5. FT-IR spectra of synthesized potassium borates

FT-IR spectra of synthesized potassium borates for various molar ratios are shown in Fig. 5. FT-IR spectra of products of experiments, which were started with higher boron ratios (between 1:5 and 1:7), have conformity with literature studies According to FT-IR spectra, the IR peaks around 1340 cm^{-1} are assigned to asymmetric stretching of $B_{(3)}$–O when the peaks around 1250 cm^{-1} corresponded to the bending mode of B–O–H. Asymmetric stretch of $B_{(4)}$–O is observed in the range of 1129 - 1013 cm^{-1}. The peaks between wavenumbers of 942 cm^{-1} and 915 cm^{-1} belongs to symmetric stretching of $B_{(3)}$–O. The peaks between 824 cm^{-1} and 781 cm^{-1} are assigned to symmetric stretching of $B_{(4)}$–O. In-plane bending vibrations of $B_{(3)}$–O are observed between 732 cm^{-1} and 680 cm^{-1}.

4 Conclusion

Potassium borates are important nonlinear optical materials which find a usage especially in laser application. The importance of this borate group makes their cheap, safe and environment friendly production inevitable.

The present study was focused on the determination optimum molar ratio of raw materials for the synthesis of potassium pentaborate with hydrothermal method. By varying molar ratio of boron source, several experiments were occurred and the product were characterized by XRD and FT-IR spectroscopy methods.

Experimental results showed that the synthesized compound was the Santite ($KB_5O_8{\cdot}4H_2O$) mineral with pdf code of 01-072-1688 for all experiments. However, according to XRD scores the most appropriate ratio is 1:1:7 (KCl:NaOH:B_2O_3).

In further studies by using the determinated molar ratio, lower reaction temperatures and reaction times can be examined for a green chemistry approach.

5 References

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