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Synthesis of pure potassium pentaborate (KB_5) from potassium dihydrogen phosphate (KH_2PO_4) and colemanite

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ABSTRACT

In this study, after specifying theoretical reaction conditions required for chemical reaction, potassium pentaborate (KB_5) was synthesized from the potassium dihydrogen phosphate (KH_2PO_4) solution and the raw colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) ore. The slow evaporation solution method was used at 25 °C. The effect of time (6-18 hours) on crystallization was studied. Synthesized minerals were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), RAMAN spectroscopies, and scanning electron microscopy (SEM). The results according to the XRD, FT-IR, RAMAN, and SEM analyses proved that the synthesized product was the potassium pentaborate ($KB_5O_8 \cdot 4H_2O$) mineral having the **ICSD:** 96-026-1927 pdf code. As a result, the cost was reduced by using raw boron ore, colemanite and KB_5 could be obtained in a shorter time and at a lower temperature.

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1. Introduction

In recent years, there has been an increasing demand for borates family for technological applications. Inorganic borates exist in numberless structural types. Among them, potassium penta borate single crystals are the significant compounds that can be used in the industry. Containing approximately 72% of the world's boron reserves, Turkey is the country that has the largest boron deposits. Boron element, which is never found free, only forms the complex borate structures as a result of the combination of boron oxide (B_2O_3) with the oxides of other elements [1]. Borate compounds can generally be grouped into different sub classes such as calcium borates, calcium-sodium borates, sodium borates, and magnesium borates [2]. The most important of these and the most preferred in the industry are respectively colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), tincal ($Na_2B_4O_7 \cdot 10H_2O$) and ulexite ($NaCaB_5O_9 \cdot 8H_2O$) [3]. However, many synthetic borate compounds have been preferred and used in the industry apart from those found in nature. One of them, potassium pentaborate tetrahydrate ($KB_5O_8 \cdot 4H_2O$), which contains 4 moles of structural water per mole of crystalline, is one of the important borate compounds and generally shown in the literature with the formula “ KB_5 ” rather than potassium pentaborate tetrahydrate [4]. KB_5 crystals are uncolored, chemically stable and optically biaxial compounds. Potassium pentaborate, can be used in welding, insulation, lubricating oil additives, metal refining, cement, textile, fiberglass, and non-linear materials. Last researches on effective nonlinear optical (NLO) materials show that KB_5 crystals are superior to other mostly used NLO materials. That is why potassium pentaborate, is successfully used to convert significant laser radiation and inorganic NLO crystal into UV and vacuum UV wavelength region [5-8].

KB_5 crystals can usually be obtained by reacting boric acid and KOH in an aqueous medium by keeping the mole ratio of B_2O_3 / K_2O around 5 [9]. The chemical equation for the synthesis of KB_5 crystal using the traditional method is as given in equation 1.

Owing to the chemical and optical significance of potassium borates, many investigators show an interest in their synthesis and application in different fields. There are some studies in the literature where potassium pentaborate is produced by changing the potassium and boron sources. The literature summary of these studies is given below.

Rajasekar et al. [10] have achieved to obtain KB_5 by dissolving K_2CO_3 and H_3BO_3 in suitable proportions in double-distilled water. Growth conditions and surface morphology of the crystals of pure and magnesium, calcium, barium, and copper doped KB_5 have been optimized and magnified crystals have been verified by XRD. Prabha et al. [11] used the low-temperature slow solvent evaporation method and characterized pure and 1, 10 phenanthroline doped KB_5 and determined their potential as a non-linear optical material. Yıldırım et al. [12] aimed to produce potassium borate compounds by the hydrothermal method. In the study where the reaction temperature and reaction time were determined as 80 °C and 1 hour, KB_5 was produced by mixing different moles of KNO_3 , as the potassium source, NaOH as the hydroxide ion source and H_3BO_3 as the boron source. Kıpçak et al. [5] used KCl as a potassium source, NaOH as a hydroxide ion source, B_2O_3 as a boron source and reacted to them in different mole ratios. As a result of the experiment, they achieved optimum efficiency in a mole ratio of 1:1:7 (KCl: NaOH: B_2O_3). Vigneshwaran et al. [13] reacted K_2CO_3 and H_3BO_3 in the ratio of 1:10 moles and synthesized KB_5 crystals. The obtained crystals were kept in a 32 °C constant temperature bath for 50-60 days using pure water. Thus, the crystals were grown by a slow evaporation solution growth technique. Asensio et al. [14] managed to obtain the KB_5 crystal in 84.88% and 95.11% yield using K_2CO_3 , H_3BO_3 and B_2O_3 . The researchers, who found that the crystal they obtained lost their crystal water at 500-450 °C, also examined the crystalline thermal dehydration kinetics and characterized them by using thermal gravimetry and differential thermal analysis. Derun, [15] used potassium chloride (KCl) as a source of potassium, and tincalconite, borax ($Na_2B_4O_7 \cdot 10H_2O$), boric acid (H_3BO_3) and boron oxide (B_2O_3) as a source of boron.

KB_5 was synthesized at temperatures above 200 °C and more than 1 week using the conventional hydrothermal method in the literature. In these studies, researchers generally preferred pure boric acid as a boron source and KOH , KNO_3 , K_2CO_3 as a source of potassium [13, 16-21]. But boric acid is also a product and is more expensive than unprocessed raw ore.

In this study, different potassium source (KH_2PO_4 solution) and different boron source (raw colemanite ore) were used for the first time in literature in order to obtain low cost KB_5 single crystal under the conditions of low temperature and short time. The optimum dissolution condition was taken from the our previous studies [22, 23]. Various slow evaporation times were tried to obtain the best KB_5 single crystal.

2. Materials and Methods

The boron source of colemanite was obtained from Emet-Mine in Kütahya, Turkey. The potassium source of potassium dihydrogen phosphate (Merck reagent of 99.9% purity) was used in the experiments. The colemanite samples were crushed, ground, and then sieved by using ASTM standard sieves to obtain 165 μm average size fraction. The chemical composition of the ore was determined by volumetric and gravimetric methods. The chemical analyses of colemanite ore are given in Table 1.

Table 1. Chemical analysis of colemanite ore

Component	B ₂ O ₃	CaO	H ₂ O	SiO ₂ and others
%	44,20	26,75	22,20	6,40

XRD analyzes were performed. by a PANalytical Empyrean X-ray diffractometer (XRD) by using Cu-K α radiation. Operating parameters of the device were 2 θ range of 10° - 90°, 45 kV and 40 mA (λ = 1.53 nm). X-ray diffraction was used in the original sample. X-ray diffraction of colemanite ore can be seen in Fig. 1. Scanning Electron Microscope with Sistem Zeiss brand and Sigma 300 model was used to take SEM images. Fourier Transform Infrared Spectroscopy (FT-IR) with Bruker VERTEX 70w was used for FT-IR analyzes and WTech alpha 300 R brand Raman spectroscopy was used for RAMAN analysis. The characteristic peaks of borate compounds were found in the range of 500-1500 cm^{-1} from the researches in the literature. For this reason, 400-1800 cm^{-1} spectral range for FT-IR spectroscopy and RAMAN Spectroscopy was studied [5, 14].

3. Experimental Procedure

The Kinetic mechanism and optimum dissolution conditions of colemanite in KH_2PO_4 solution were determined in our previous reports [22, 23]. These optimum conditions were given respectively as the following: reaction temperature; 333 K, grain size; 165 μm , solid/liquid rate; 0, 02 g/mL, KH_2PO_4 concentration; 2, 0 M, and time; 60 minute. Firstly the 200 mL of KH_2PO_4 solution and colemanite was dissolved in deionized water at ambient temperature by using a magnetic stirrer for about 300 rpm. 98 % of B_2O_3 was dissolved as a result of the verification experiment carried out under the mentioned conditions. The experimental setup was shown in Fig. 2.

At the second stage, the solution of the verification experiment was used to synthesize potassium pentaborate tetrahydrate ($KB_5O_8 \cdot 4H_2O$) product. This solution obtained under optimum conditions was crystallized at different times at 25 °C. In this study, the chemical equations (2-3) governing the reaction were given as follows,

As a result of the dissolution, $K(H_4B_5O_{10}) \cdot 2H_2O(aq)$ could be obtained in an aqueous medium as in equation (3). Hot filtering was done at 333 K with Whatman filter papers to remove impurities. The filtered solution was covered with porous papers and kept in a dust-free environment for crystallization. The effect of time on crystallization was examined. The solution containing the remaining KB_5 was crystallized at 25°C using the slow evaporation solution technique for 6, 12, and 18 hours.

4. Result and Discussion

The solutions obtained three times by dissolving colemanite in the KH_2PO_4 solutions were crystallized at 6, 12, and 18 hours to ensure the formation of KB_5 single crystals which were named as KB_5 – 6 hour, KB_5 – 12 hour, KB_5 – 18 hour. Powder XRD pattern of KB_5 crystals obtained at different times can be seen in Fig. 3. When XRD patterns are examined thoroughly, characteristic XRD peaks of potassium borates cannot be seen until the time reached 18 hour. According to XRD results, the produced inorganic borate minerals are potassium pentaborate ($KB_5O_8 \cdot 4H_2O$) having the ICSD: 96-026-1927 pdf code at 18 hour. The powder XRD pattern of the KB_5 crystal obtained in 18 hour can be seen clearly and in detail in Fig. 4.

SEM images obtained on the product crystallized by slow evaporation method for 18 hour were taken from different parts of the products. SEM images of KB_5 -18 hour product at different magnifications a) 200 nm, b) 1 μm c) 2 μm and d) 10 μm were given in Fig. 5. As can be seen from the Fig. 5. Potassium borate particles are in the form of homogeneous, angularly arranged, and polyhedral aggregates. The images in the study of Asensio et al. Confirm this sequence [14].

FT-IR spectrum of potassium borates synthesized for KB_5 – 18 –hour product is given in Fig. 6. According Fig. 6 the IR peak at around 1360 cm^{-1} are assigned to asymmetric stretching of B–O. The peak appears at 1250 cm^{-1} has been attributed to the bending vibration of the B–O bond. The peaks wavenumber of at 922 cm^{-1} belong to the ring stretching of B–O. The O–B–O terminal bending appears at 592 cm^{-1} . In-plane O–B–O ring bending of B–O is observed at 510 cm^{-1} . Raman spectrum of KB_5 -18 hour is given in Fig. 7. FT-IR and Raman spectra of the products appear to give typical potassium borate peaks in both the infrared and visible regions [24].

5. Conclusions

- The raw boron ore colemanite was dissolved in KH_2PO_4 solution under optimum dissolution conditions.
- $K_2HPO_{4(aq)}$ and $H_3BO_{3(aq)}$, which were dissolved in the solution, were crystallized at different times (6, 12 and 18 hour) by slow evaporation solution method and a single crystal KB_5 was obtained.
- Prepared samples were identified using the technique of X-ray diffraction (XRD). XRD analysis results of KB_5 crystals obtained at different times showed that the best peaks were obtained with 18 hours. The same sample was characterized using the spectroscopic methods of Fourier transform infrared (FT-IR) and Raman. Morphological properties were investigated with a scanning electron microscope (SEM).
- The analyses were made and the taken results according to the XRD, FT-IR, RAMAN, and SEM images confirmed that the synthesized product was the potassium pentaborate ($KB_5O_8 \cdot 4H_2O$) mineral having the **ICSD**: 96-026-1927 pdf code.
- The cost was reduced by using raw boron ore, and KB_5 could be obtained in a shorter time and at a lower temperature.

Declaration of Competing Interest

No potential conflict of interest was reported by the authors.

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Figures

Figure 1

X-ray diffraction of colemanite ore.

Figure 2

The experimental setup

Figure 3

Powder XRD pattern of KB_5 crystals obtained at different times.

Figure 4

Powder XRD pattern of KB₅ crystal obtained at 18 hour

Figure 5

SEM images of KB5-18-hour product a)200 nm, b) 1 μm c)2 μm and d) 10 μm size

Figure 6

FT-IR spectra of potassium borates synthesized for KB5-18-hour product

Figure 7

Raman spectrum of KB5-18 hour