Synthesis of pure potassium pentaborate (KB₅) from potassium dihydrogen phosphate (KH₂PO₄) and colemanite

Özlem Karagöz · Soner Kuşlu

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Abstract
In this study, after specifying theoretical reaction conditions required for the chemical reaction, potassium pentaborate (KB₅) was synthesized from the potassium dihydrogen phosphate (KH₂PO₄) solution and raw colemanite (Ca₂B₆O₁₁·5H₂O) ore. The slow evaporation solution method was used at 25 °C. The effect of time (6–18 h) on crystallization was studied. Synthesized minerals were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), RAMAN spectroscopy, and scanning electron microscopy (SEM). The results according to XRD, FT-IR, RAMAN, and SEM analyses proved that the synthesized product was potassium pentaborate (KB₅O₈·4H₂O) mineral with ICSD: 96-026-1927 pdf code. As a result, the cost was reduced by using raw boron ore, colemanite, and KB₅ was obtained in a shorter time and at a lower temperature.

Keywords Potassium dihydrogen phosphate · Potassium pentaborate · Colemanite · Crystallization · Slow evaporation solution method · Optimization

Introduction

In recent years, there has been an increasing demand for the borate family for technological applications. Inorganic borates exist in numerous structural types. Among them, potassium pentaborate single crystals are significant compounds that can be used in 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 in free form, only forms complex borate structures as a result of the combination of boron oxide (B₂O₃) with the oxides of other elements (Pye et al., 2012). Borate compounds can generally be grouped into different subclasses such as calcium borates, calcium-sodium borates, sodium borates, and magnesium borates (Küçük et al., 2002). The most important of these and the most preferred in industry are colemanite (Ca₂B₆O₁₁·5H₂O), tincal (Na₂B₄O₇·10H₂O), and ulexite (NaCaB₅O₉·8H₂O) (Karagöz et al., 2018). However, many synthetic borate compounds have been selected and used in the industry apart from those found in nature. One of them, potassium pentaborate tetrahydrate (KB₅O₈·4H₂O), which contains 4 mol of structural water per mole of crystal, is one of the important borate compounds and is generally shown in the literature with the formula “KB₅” rather than potassium pentaborate tetrahydrate (Yang et al., 2005). KB₅ 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 nonlinear materials. Latest research on effective nonlinear optical (NLO) materials shows that KB₅ crystals are superior to other more commonly used NLO materials. That is why potassium pentaborate is successfully used to convert significant laser radiation and inorganic NLO crystals into UV and vacuum UV wavelength regions (Kamatchi et al., 2018; Kipcak et al., 2015; Kumar et al., 2013; Xue et al., 2000).

KB₅ crystals can usually be obtained by reacting boric acid and KOH in an aqueous medium by keeping the mole ratio of B₂O₃/K₂O around 5 (Gürbüz et al., 2005). The chemical equation for the synthesis of KB₅ crystals using the traditional method is given in Eq. 1.

\[ \text{KOH(aq)} + 5\text{H}_3\text{BO}_3(\text{aq}) \rightarrow \text{KB}_5\text{O}_8\cdot4\text{H}_2\text{O(aq)} + 4\text{H}_2\text{O(s)} \]

(1)

Owing to the chemical and optical significance of potassium borates, many investigators displayed 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. (2003) successfully obtained \( \text{KB}_5 \) by dissolving \( \text{K}_2\text{CO}_3 \) and \( \text{H}_3\text{BO}_3 \) in suitable proportions in double-distilled water. Growth conditions and surface morphology of the crystals of pure and magnesium-, calcium-, barium-, and copper-doped \( \text{KB}_5 \) were optimized, and magnified crystals were verified by XRD. Prabha et al. (2013) used the low-temperature slow solvent evaporation method and characterized pure and 1, 10 phenanthroline-doped \( \text{KB}_5 \) and determined their potential as a nonlinear optical material. Yıldırım et al. (2015) 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 h, \( \text{KB}_5 \) was produced by mixing different moles of \( \text{KNO}_3 \) as the potassium source, \( \text{NaOH} \) as the hydroxide ion source and \( \text{H}_3\text{BO}_3 \) as the boron source. Kıpçak et al. (2015) used \( \text{KCl} \) as a potassium source, \( \text{NaOH} \) as a hydroxide ion source, and \( \text{B}_2\text{O}_3 \) as a boron source and reacted them in different mole ratios. As a result of the experiment, they achieved optimum efficiency with a mole ratio of 1:1:7 (\( \text{KCl}:\text{NaOH}:\text{B}_2\text{O}_3 \)). Vigneshwaran et al. (2016) reacted \( \text{K}_2\text{CO}_3 \) and \( \text{H}_3\text{BO}_3 \) in the ratio of 1:10 mol and synthesized \( \text{KB}_5 \) 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. (2016) managed to obtain \( \text{KB}_5 \) crystal with 84.88% and 95.11% yield using \( \text{K}_2\text{CO}_3, \text{H}_3\text{BO}_3, \) and \( \text{B}_2\text{O}_3 \). The researchers, who found that the crystal they obtained lost the crystal water at 500–450 °C, also examined the crystalline thermal dehydration kinetics and characterized the crystals by using thermal gravimetry and differential thermal analysis. Derun (2018) used potassium chloride (\( \text{KCl} \)) as a source of potassium, and tincalconite, borax (\( \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \)), boric acid (\( \text{H}_3\text{BO}_3 \)), and boron oxide (\( \text{B}_2\text{O}_3 \)) as sources of boron.

\( \text{KB}_5 \) was synthesized at temperatures above 200 °C and in 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 \( \text{KOH}, \text{KNO}_3, \) or \( \text{K}_2\text{CO}_3 \) as a source of potassium (Apagyi and Csetenyi, 2001; Arivuselvi and Babu, 2018; Job, 2015; Joseph et al., 2003; Lakshmipriya et al., 2013; Şenberber 2018; Vigneshwaran et al., 2016). But boric acid is also a product and is more expensive than unprocessed raw ore.

In this study, a different potassium source (\( \text{KH}_2\text{PO}_4 \) solution) and different boron source (raw colemanite ore) were used for the first time in literature in order to obtain low cost \( \text{KB}_5 \) single crystals under the conditions of low-temperature and short time. The optimum dissolution conditions were taken from our previous studies (Karagoz and Kuşlu 2017; Karagöz and Kuşlu, 2017). Various slow evaporation times were trialed to obtain the best \( \text{KB}_5 \) single crystal.
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 (Retsch BB2/A) and ground (Brook Crompton Series, 2000). Then sieved by using ASTM standard sieves (Retsch5657, Haan, Germany) to obtain 165 µm average size fraction. The chemical composition of the ore was determined by volumetric and gravimetric methods. The purity of the colemanite ore was found to be 87%. The chemical analyses of colemanite ore are given in Table 1.

XRD analyses were performed with a PANalytical Empyrean X-ray diffractometer (XRD) by using Cu-Kα radiation. Operating parameters of the device were 2θ range of 10°–90°, 45 kV and 40 mA (λ = 1.53 nm). X-ray diffraction was used on the original sample. X-ray diffraction of colemanite ore can be seen in Fig. 1. A 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 analyses 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 researching the literature. For this reason, the 400–1800 cm⁻¹ spectral range was studied with FT-IR spectroscopy and Raman spectroscopy (Asensio et al., 2016; Kıpçak et al., 2015).

Experimental procedure

The kinetic mechanism and optimum dissolution conditions of colemanite in KH₂PO₄ solution were determined in our previous reports (Karagoz and Kuşlu 2017; Karagöz and Kuşlu, 2017). These optimum conditions are given as follows: reaction temperature; 333 K, grain size; 165 µm, solid/liquid rate; 0.02 g/mL, KH₂PO₄ concentration; 2.0 M, and time; 60 min. Firstly, 200 mL of KH₂PO₄ solution and colemanite was dissolved in deionized water at ambient temperature by using a magnetic stirrer at about 300 rpm. Then, 98% of B₂O₃ was dissolved as a result of the verification experiment carried out under the mentioned conditions. The experimental setup is shown in Fig. 2. In the second stage, the solution of the verification experiment was used to synthesize the potassium pentaborate tetrahydrate (KB₅O₈·4H₂O) product. This solution obtained
under optimum conditions was crystallized for different durations at 25 °C. In this study, the chemical Eqs. (2–3) governing the reaction are given as follows:

\[
\begin{align*}
2\text{CaO}.3\text{B}_2\text{O}_3.5\text{H}_2\text{O}(s) + 4\text{KH}_2\text{PO}_4(s) + 6\text{H}_2\text{O}(s) & \rightarrow 2[\text{CaHPO}_4.2\text{H}_2\text{O}]_4(s) + 6\text{H}_3\text{BO}_3(aq) + 2\text{K}_2\text{HPO}_4(aq) \\
& \text{(2)}
\end{align*}
\]

\[
\begin{align*}
\frac{1}{2}\text{K}_2\text{HPO}_4(aq) + 5\text{H}_3\text{BO}_3(aq) & \rightarrow \text{KB}_5\text{O}_8.4\text{H}_2\text{O}(s) + \frac{7}{2}\text{H}_2\text{O}(l) + \frac{1}{2}\text{HPO}_3(aq) \\
& \text{(3)}
\end{align*}
\]

As a result of the dissolution, \(\text{KB}_5\text{O}_8.4\text{H}_2\text{O}(s)\) was obtained in an aqueous medium as in Eq. (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 \(\text{KB}_5\) was crystallized at 25 °C using the slow evaporation solution technique for 6, 12, and 18 h.

**Results and discussion**

The solutions obtained three times by dissolving colemanite in \(\text{KH}_2\text{PO}_4\) solutions were crystallized at 6, 12, and 18 h to ensure the formation of \(\text{KB}_5\) single crystals which were named \(\text{KB}_5\)-6 h, \(\text{KB}_5\)-12 h, and \(\text{KB}_5\)-18 h. The powder XRD patterns of \(\text{KB}_5\) 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 h. According to XRD results, the produced inorganic borate minerals are potassium pentaborate (\(\text{KB}_5\text{O}_8\cdot4\text{H}_2\text{O}\)) with ICSD: 96-026-1927 pdf code at 18 h. The powder XRD pattern of the \(\text{KB}_5\) crystal obtained in 18 h can be seen clearly and in detail in Fig. 4.
SEM images obtained for the product crystallized by the slow evaporation method for 18 h were taken from different parts of the product. SEM images of KB$_5$-18 h product are given in Fig. 5 at different magnifications (a) 200 nm, (b) 1 μm, (c) 2 μm, and (d) 10 μm. As can be seen from Fig. 5, potassium borate particles are in the form of homogeneous, angularly arranged, and polyhedral aggregates. The images in the study by Asensio et al. (2016) confirm this sequence.

The FT-IR spectrum of potassium borates synthesized as KB$_5$-18-h product is given in Fig. 6. According Fig. 6, the IR peak at around 1360 cm$^{-1}$ is assigned to asymmetric stretching of B–O. The peak appearing at 1250 cm$^{-1}$ was attributed to the bending vibration of the B–O bond. The peaks at wavenumber 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$^{-1}$. The Raman spectrum of KB$_5$-18 h 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 (Jun et al., 1995).
Finally, at the end of 6 h and 12 h, it was observed that the crystals were not fully formed, and the particle size was small. However, after 18 h, it was observed that the crystallization efficiency increased with increasing particle size. In addition, it was seen that the crystalline particle size distribution obtained at the end of 18 h was more uniform than 6 h and 12 h.

Conclusion

- Raw boron ore colemanite was dissolved in KH$_2$PO$_4$ solution under optimum dissolution conditions.
- K$_2$HPO$_4$$_{(aq)}$ and H$_3$BO$_3$$_{(aq)}$, which were dissolved in the solution, were crystallized at different times (6, 12, and 18 h) by the slow evaporation solution method, and a single crystal of KB$_5$ was obtained.
- Prepared samples were identified using the XRD technique. XRD analysis results of KB$_5$ crystals obtained at different times showed that the best peaks were obtained with crystallization for 18 h. The same sample was characterized using the FT-IR and Raman spectroscopic methods. Morphological properties were investigated with SEM.
- The analyses were completed and the results according to the XRD, FT-IR, RAMAN, and SEM images confirmed that the synthesized product was potassium pentaborate (KB$_5$O$_8$ · 4H$_2$O) mineral with ICSD: 96-026-1927 pdf code.
- The cost was reduced by using raw boron ore, and KB$_5$ was obtained in a shorter time and at a lower temperature.

Author contributions Özlem KARAGÖZ finished her PhD thesis in 2018 about the Synthesis of pure potassium pentaborate (KB$_5$) from potassium dihydrogen phosphate (KH$_2$PO$_4$) and colemanite. Soner KUŞLU is the supervisor of Özlem KARAGÖZ. Soner KUŞLU and Özlem KARAGÖZ together contributed to the study conception and design of the thesis. Data collection, material preparations, and required analysis were also performed together by authors. The first draft of the manuscript was written by Özlem KARAGÖZ and Soner KUŞLU and the authors commented on the previous version of the manuscript.

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Code availability Microsoft word was used in writing manuscript and it is available. There is no custom code.

Declaration

Conflict of interest The authors declare that there are no conflict of interest and competing interests.

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