Chemical Papers (2021) 75:5963–5969
https://doi.org/10.1007/s11696-021-01771-z

ORIGINAL PAPER

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

Özlem Karagöz[1] · **Soner Kuşlu**[1]

Received: 11 May 2021 / Accepted: 30 June 2021 / Published online: 11 July 2021

Abstract
In this study, after specifying theoretical reaction conditions required for the chemical reaction, potassium pentaborate (KB_5) was synthesized from the potassium dihydrogen phosphate (KH_2PO_4) solution and 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 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 ($KB_5O_8 \cdot 4H_2O$) mineral with ICSD: 96-026-1927 pdf code. As a result, the cost was reduced by using raw boron ore, colemanite, and KB_5 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 (B_2O_3) 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 ($Ca_2B_6O_{11} \cdot 5H_2O$), tincal ($Na_2B_4O_7 \cdot 10H_2O$), and ulexite ($NaCaB_5O_9 \cdot 8H_2O$) (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 ($KB_5O_8 \cdot 4H_2O$), 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 "KB_5" rather than potassium pentaborate tetrahydrate (Yang et al., 2005). 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 nonlinear materials. Latest research on effective nonlinear optical (NLO) materials shows that KB_5 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; Kıpçak et al., 2015; Kumar et al., 2013; Xue et al., 2000).

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 (Gürbüz et al., 2005). The chemical equation for the synthesis of KB_5 crystals using the traditional method is given in Eq. 1.

$$KOH(aq) + 5H_3BO_3(aq) \rightarrow KB_5O_8.4H_2O(aq) + 4H_2O(s) \quad (1)$$

Owing to the chemical and optical significance of potassium borates, many investigators displayed an interest in

✉ Özlem Karagöz
ozlemkaragoz@atauni.edu.tr

[1] Department of Chemical Engineering, Atatürk University, Erzurum, Turkey

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 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 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 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, 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. (2015) used KCl as a potassium source, NaOH as a hydroxide ion source, and B_2O_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 (KCl:NaOH:B_2O_3). Vigneshwaran et al. (2016) reacted K_2CO_3 and H_3BO_3 in the ratio of 1:10 mol 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. (2016) managed to obtain KB_5 crystal with 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 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 (KCl) as a source of potassium, and tincalconite, borax $\left(Na_2B_4O_7 \cdot 10H_2O\right)$, boric acid ($H_3BO_3$), and boron oxide $\left(B_2O_3\right)$ as sources of boron.

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 KOH, KNO_3, or K_2CO_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 (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 crystals under the conditions of low-temperature and short time. The optimum dissolution conditions were taken from our previous studies (Karagoz and Kuslu 2017; Karagöz and Kuşlu, 2017). Various slow evaporation times were trialed to obtain the best KB_5 single crystal.

Table 1 Chemical analysis of colemanite ore

Component	B_2O_3	CaO	H_2O	SiO_2 and others
%	44.20	26.75	22.20	6.85

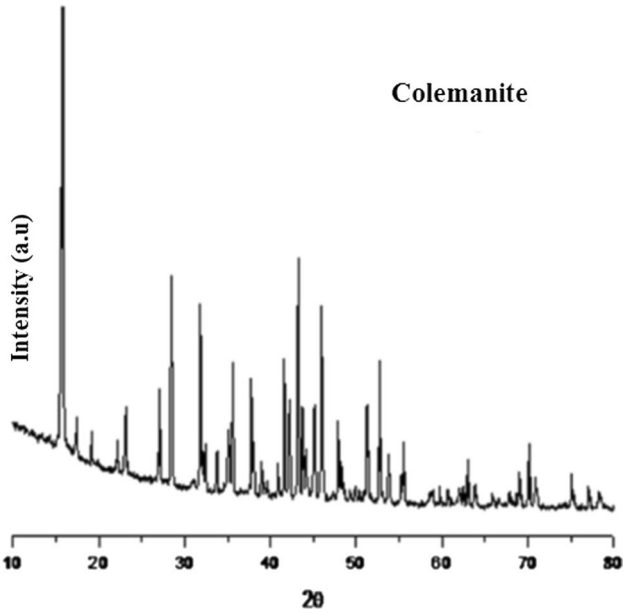

Fig. 1 X-ray diffraction pattern of colemanite ore

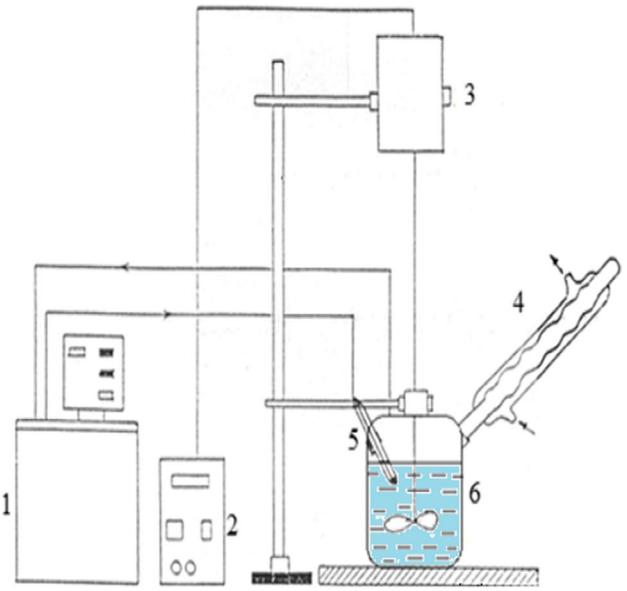

Fig. 2 The experimental setup

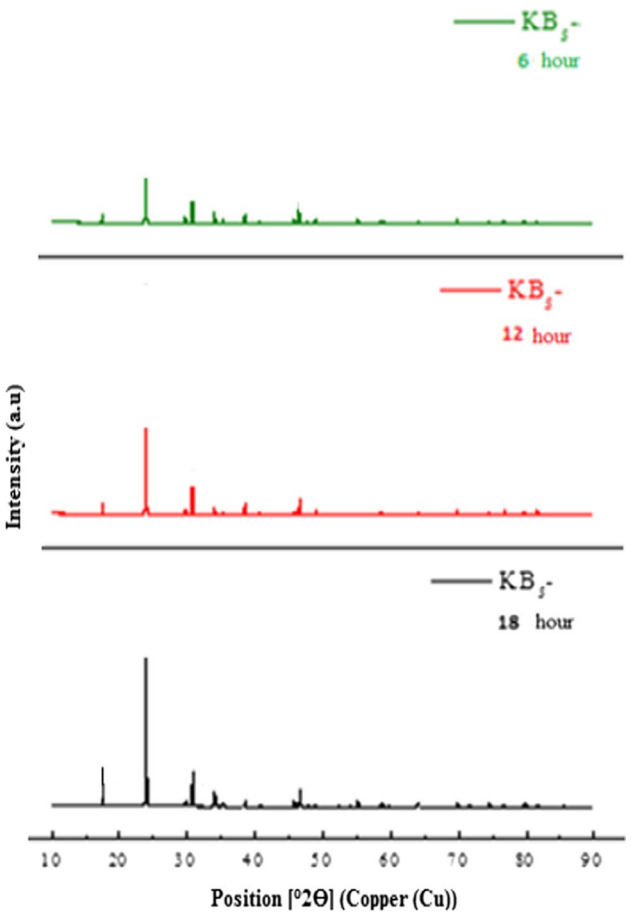

Fig. 3 Powder XRD patterns of KB_5 crystals obtained at different reaction times

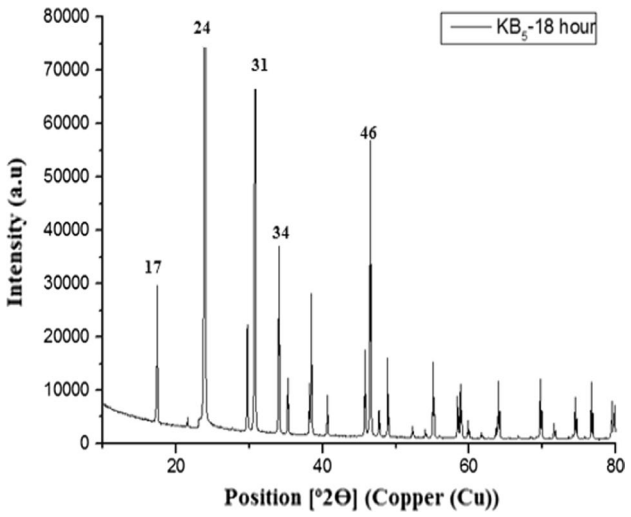

Fig. 4 Powder XRD pattern of KB_5 crystal obtained at 18 h

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 ($\lambda = 1.53$ 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 KH_2PO_4 solution were determined in our previous reports (Karagoz and Kuslu 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, KH_2PO_4 concentration; 2. 0 M, and time; 60 min. Firstly, 200 mL of KH_2PO_4 solution and colemanite was dissolved in deionized water at ambient temperature by using a magnetic stirrer at about 300 rpm. Then, 98% of B_2O_3 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 ($KB_5O_8 \cdot 4H_2O$) product. This solution obtained

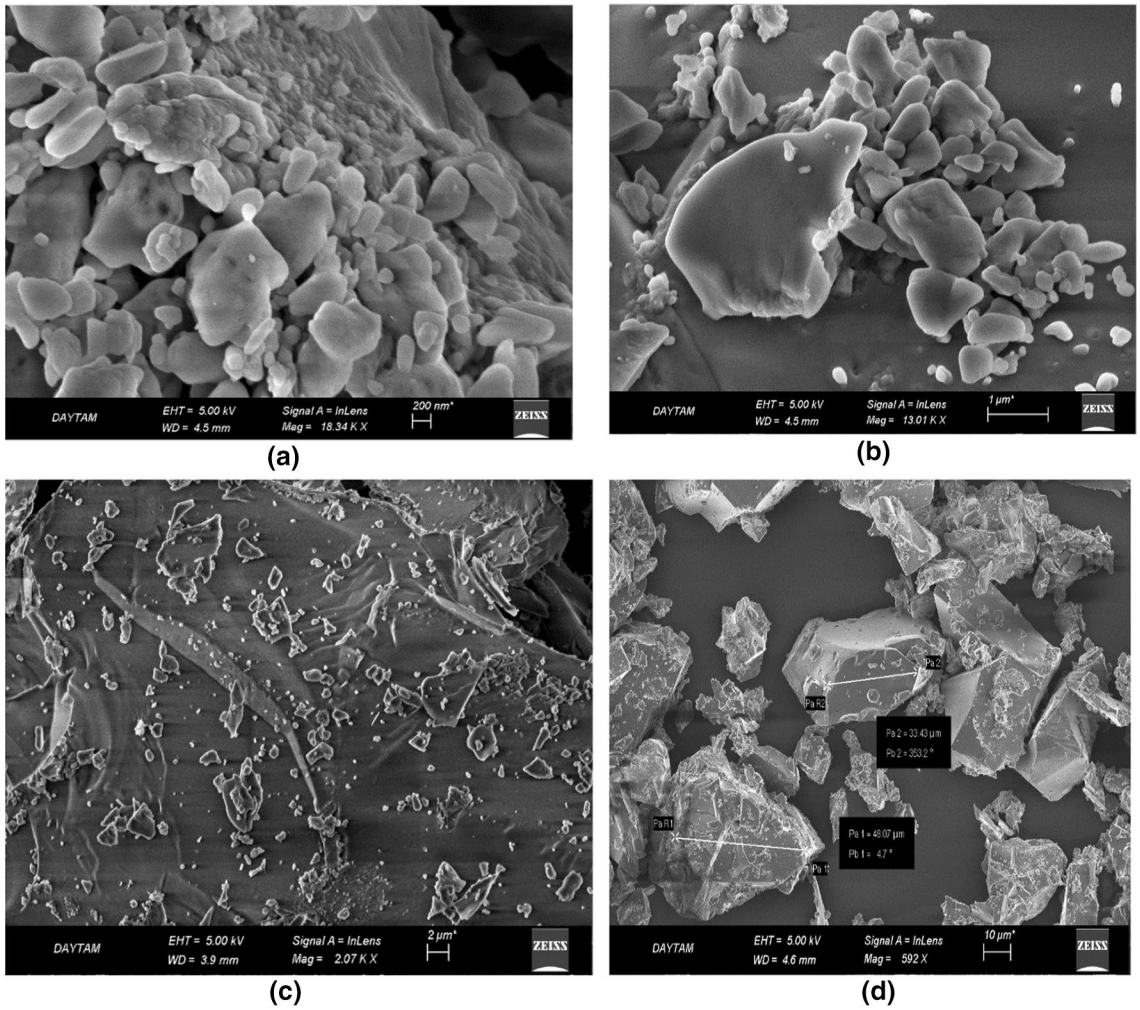

Fig. 5 SEM images of KB_5-18-h product **a** 200 nm, **b** 1 µm, **c** 2 µm, and **d** 10 µm size

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:

$$2CaO.3B_2O_3.5H_2O_{(k)} + 4KH_2PO_{4(k)} + 6H_2O_{(s)} \rightarrow 2[CaHPO_4.2H_2O]_{(k)} + 6H_3BO_{3(aq)} + 2K_2HPO_{4(aq)} \quad (2)$$

$$\frac{1}{2}K_2HPO_{4(aq)} + 5H_3BO_3(aq) \rightarrow K(H_4B_5O_{10}).2H_2O(aq) + \frac{7}{2}H_2O(l) + \frac{1}{2}HPO_3(aq) \quad (3)$$

As a result of the dissolution,$K(H_4B_5O_{10}) \cdot 2H_2O(aq)$ 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 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 KH_2PO_4 solutions were crystallized at 6, 12, and 18 h to ensure the formation of KB_5 single crystals which were named KB_5-6 h, KB_5-12 h, and KB_5-18 h. The powder XRD patterns 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 h. According to XRD results, the produced inorganic borate minerals are potassium pentaborate ($KB_5O_8 \cdot 4H_2O$) with ICSD: 96-026-1927 pdf code at 18 h. The powder XRD pattern of the KB_5 crystal obtained in 18 h can be seen clearly and in detail in Fig. 4.

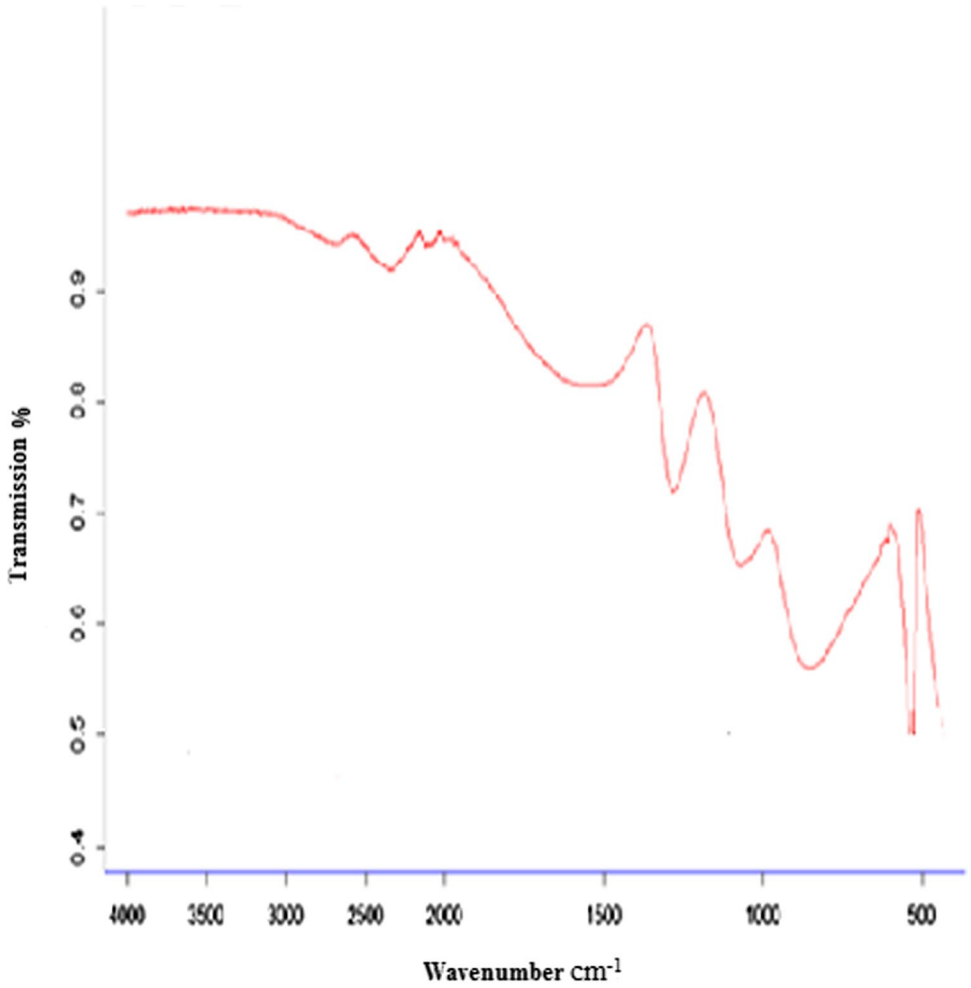

Fig. 6 FT-IR spectrum of potassium borates synthesized for KB_5-18-h product

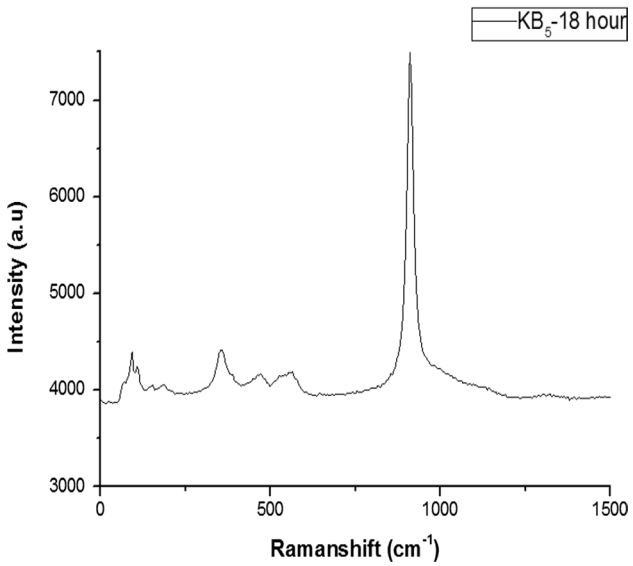

Fig. 7 Raman spectrum of KB_5-18 h

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_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 h) by the slow evaporation solution method, and a single crystal of KB_5 was obtained.
- Prepared samples were identified using the of 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 ($KB_5O_8 \cdot 4H_2O$) 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_2PO_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.

Funding There was no funding.

Availability of data and materials This manuscript has been registered as a preprint online in the Research Square Preprint Platform with the DOI number is 1XX0.21203/RS.3.RS-226838/V1.

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.

References

Apagyi Z, Csetenyi LJ (2001) Phase equilibrium study in the $CaO–K_2O–B_2O_3–H_2O$ system at 25 °C. Cem Concr Res 31(7):1087–1091

Arivuselvi R, Babu PR (2018) Investigation of inorganic nonlinear optical potassium penta borate tetra hydrate (PPBTH) single crystals grown by slow evaporation method. Phys B Condens Matter 533:17–21

Asensio MO, Yildirim M, Senberber FT, Kipcak AS, Derun EM (2016) Thermal dehydration kinetics and characterization of synthesized potassium borates. Res Chem Intermed 42(5):4859–4878

Derun EM (2018) Sodyum boratlardan potasyum borat sentezi: reaksiyon koşullarinin optimizasyonu. Dokuz Eylül Üni Eng Fac Sci Eng J 20(59):347–353

Gürbüz H, Badem G, Bulutçu A (2005) Determination of crystal growth kinetics of potassium pentaborate in a fluidized bed crystallizer. J Cryst Growth 283(1–2):222–229

Job CB (2015) Growth and characterization of sodium penta borate crystal. Int J Chem Technol Res 8:898–904

Joseph V, Gunasekaran S, Santhanam V (2003) Photoconductivity and dielectric studies of potassium pentaborate crystal (KB_5). Bull Mater Sci 26(4):383–386

Jun L, Shuping X, Shiyang G (1995) FT-IR and Raman spectroscopic study of hydrated borates. Spectrochim Acta A Mol Biomol Spectrosc 51(4):519–532

Kamatchi K, Umarani P, Radhakrishnan T, Raja CR (2018) Investigation on organic-inorganic hybrid NLO crystal L-valine potassium penta borate octa hydrate (LVPPB) for NLO applications. Optik 172:674–679

Karagöz Ö, Kuşlu S (2017) Dissolution kinetics of colemanite in potassium dihydrogen phosphate solution (KH_2PO_4). Int J Hydrog Energy 42(36):23250–23259

Karagöz Ö, Çopur M, Kocakerim MM (2018) Kinetic analysis of retention of SO_2 using waste ulexite ore in an aqueous medium. J Haz Mater 353:214–226

Karagoz O, Kuslu S (2017) Optimization of dissolution of colemanite ore in potassium dihydrogen phosphate solution (KH_2PO_4). Press Acad Proc 5(1):402–409

Kıpçak S, Günal M, Sibel I, Yıldırım M, Piskin M, Derun E (2015) Determination optimum B_2O_3, KCl and NaOH molar ratios in the synthesis of potassium borates. Celal Bayar Üniv Sci J 11(3)

Küçük Ö, Kocakerim MM, Yartasi A, Çopur M (2002) Dissolution of kestelek's colemanite containing clay minerals in water saturated with sulfur dioxide. Ind Eng Chem Res 41(12):2853–2857

Kumar RA, Arivanandhan M, Hayakawa Y (2013) Recent advances in rare earth-based borate single crystals: potential materials for nonlinear optical and laser applications. Progr Cryst Growth Charact Mater 59(3):113–132

Lakshmipriya M, Babu DR, Vizhi RE (2013) Nucleation kinetics, growth, and optical properties of potassium pentaborate single crystals. Phys B Cond Matter 430:6–9

Prabha K, Babu MR, Sagayaraj P (2013) Growth and characterization of pure and 1, 10 phenanthraline doped potassium penta borate (KB5) single crystals. Paper presented at the IOP Conference Series: Mater Sci Eng 43

Pye LD, Fréchette VD, Kreidl NJ (2012) Borate glasses: structure, properties, applications, vol 12. Springer, New York

Rajasekar SA, Thamizharasan K, Pragasam AJA, Julius JP, Sagayaraj P (2003) Growth and characterization of pure and doped potassium pentaborate (KB5) single crystals. J Crystal Growth 247(1–2):199–206

Şenberber FT (2018) The effect of the reaction conditions on the synthesis and characterization of potassium borate from potassium chloride. Akademik Platf Eng Sci J 6(3):92–96

Vigneshwaran A, Joseph AA, Raja CR (2016) A study on the properties of potassium pentaborate crystals. Optik Int J Light Electron Optics 127(13):5365–5369

Xue D, Betzler K, Hesse H, Lammers D (2000) Nonlinear optical properties of borate crystals. Solid State Commun 114(1):21–25

Yang G, Li Z, Zhang Y (2005) Dehydration of tetrahydrate potassium pentaborate in fluidized bed. Chem Eng Process Process Intensif 44(11):1216–1220

Yildirim M, Kipcak A, Senberber F, Asensio M, Derun E, Piskin S (2015) The determination of the potassium nitrate, sodium hydroxide and boric acid molar ratio in the synthesis of potassium borates via hydrothermal method. World Acad Sci Eng Technol Int J Chem Mol Nuclear Mater Metallurg Eng 9(5):605–608