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Contents

Page

Growth Mechanism, XRD, Raman and FTIR Spectroscopic Studies of Potassium Pentaborate (KB5) Crystal

Zin Min Tun[1] and Win Kyaw[2]

Abstract

Single crystal of potassium pentaborate (KB5) has been grown by solution growth technique. Structural investigation of the crystal was examined by powder XRD method. FTIR and laser Raman measurements were carried out to study the vibrational characterizations of those crystals. The B–O vibrations of ring B–O symmetric stretching, ring B–O asymmetric stretching and the B–O terminal asymmetric stretching have been assigned in the recorded frequency band of 700 cm^{-1} to 1500 cm^{-1} region. Furthermore, ring OBO symmetric bending, OH stretching and terminal asymmetric bending vibrations were also observed and studied in this research. In addition, thermal analysis has been investigated by TG-DTA method to study the high temperature phases of the crystal.

Key words: Potassium pentaborate (KB5), ring B–O symmetric, ring B–O asymmetric, B–O terminal asymmetric stretching, thermal analysis.

Introduction

Non-Linear Optical (NLO) materials play a major role in non-linear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of non-linear optics (Arivuoli, 2001).

The fast development in the field of optoelectronics has stimulated the search for highly new non-linear optical crystals for efficient signal processing. New Non-Linear Optical (NNLO) frequency conversion materials can have a significant impact on laser technology, optical communication and optical data storage technology. Materials with non-linear electro optic properties have a role in modern optoelectronics that is analogous to that of non-linear electronic circuit elements in conventional electronics. Potassium pentaborate (KB5) is such an efficient non-linear material which is used for second harmonic generation. The borate compound materials are superior to other commonly used materials for UV applications. KB5 is a desirable NLO material which exhibits a low angular sensitivity and hence, proved to be useful for type II Second Harmonic Generation (SHG). KB5 is

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orthorhombic with four molecules in the unit cell of dimensions a = 11·062 Å, b = 11·175 Å, and c = 9·041 Å respectively (Becker, 1998; Joseph, 2003).

In this paper, X-Ray Diffraction (XRD), laser Raman, Fourier Transform Infrared (FTIR) and Thermo Gravimetric and Differential Thermal Analysis (TG-DTA) analyses of KB5 crystals were reported to study the structural, vibrational and thermal properties of the crystal.

Materials and Methods

Growth of KB5 Crystals

The starting material was synthesized by stoichiometric incorporation of potassium carbonate (AR grade) and boric acid (AR grade) taken in the molar ratio. The calculated amount of salts was dissolved in deionized - water (DI – water) at room emperature (Ravikumar et al., 1999; Win Kyaw et al., 2004). KB5 salt was synthesized according to the reaction,

$$K_2CO_3+10H_3BO_3 \rightarrow 2[K(H_4B_5O_{10})\cdot 2H_2O]+7H_2O\uparrow+CO_2$$

The purity of the synthesized salt was further increased by successive recrystallization process. Single crystals of KB5 are grown by slow and controlled evaporation of the solvent using a constant temperature bath. The supersaturated solution was kept in a constant temperature bath at 305 K in a glass container with a temperature-controller to get the constant temperature as shown in Fig. 1. Crystals prepared by spontaneous nucleation were used as seed crystals. The period of growth ranged from 60 to 90 days. Finally, enough size of the KB5 crystals were selected for measurements.

XRD, Laser Raman and FTIR Measurements

Structural analysis and lattice parameters determination of KB5 crystals were performed using a RIGAKU, MULTIFLEX X-ray diffractometer using Ni-filter with CuK_α radiation, λ = 1.54056 Å. The main reflections in the range $10° < 2\theta < 70°$ were observed, and the collected data were used to refine the unit cell parameters from the observed 2θ values with Joint Committee on Powder Diffraction Standards (JCPDS).

Raman spectra of KB5 crystals were recorded by RSI-2001S Raman Spectrometer within the Raman shift range 300 cm^{-1} – 4000 cm^{-1} region at room temperature. Experimental conditions were used as follows:

Laser source	: Solid-state diode laser
Colour	: Green
Wavelength	: 532 nm
Scattering geometry	:180° back-scattering
Integration time	: 20 s.

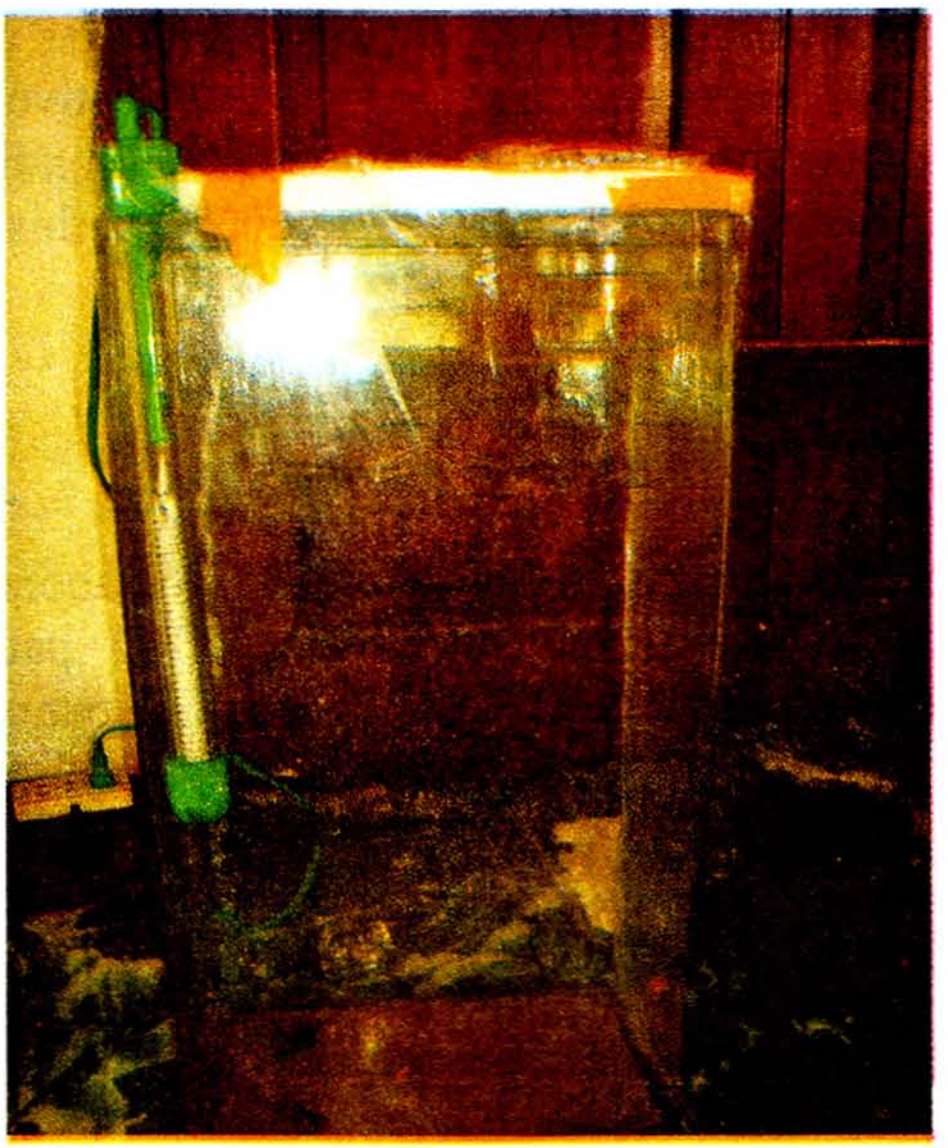

Figure 1. Photograph of the crystal growth condition of KB5 in water bath with temperature-controller

In the present work, IR transmission spectrum of KB5 crystal with the ratio of each of (1:100 wt) Potassium Bromide, KBr have been recorded on *Perkin Elmer-600* FTIR Spectrometer to analyse the vibrational modes molecules at room temperature. The experimental conditions were used as follows:

Measurement mode : %T

Wave number range : 400 cm^{-1} – 4000cm^{-1}

Number of scan : 60 s

Method : KBr disc.

TG-DTA Measurement

Thermal analysis of KB5 crystal was investigated by using (SHIMADZU) DTG-60H simultaneous Thermogravimetric and Differential Thermal Analyzer (TG-DTA). Powdered crystal sample of 6.629 mg weight were used. Aluminium (Al) pan was used as the standard sample. All measurements were carried out by heating run under N_2 atmosphere with the flow rate of 50 ml/min. The speed of heating was chosen at the rate of 20 °C/min and kept constant in the respective runs. TGA-DTA measurements were done under the experimental conditions. The start and end temperatures were used from 30 °C to 600°C in this work.

Results and Discussion

XRD Study

Powder XRD pattern of potassium pentaborate, KB5 crystal is shown in Fig. 2. According to powder XRD patterns, KB5 crystal analogous to orthorhombic lattice and their lattice parameters are evaluated by the equation of $\frac{1}{d^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}=\frac{4\sin^2\theta}{\lambda^2}$ where θ is the diffraction angle, (hkl) is the Miller indices, λ is the wavelength of incident X-rays, d is the atomic spacing, a, b and c are the lattice constants of a unit cell of the crystal (Clegg, 2003). The lattice parameters are obtained as a = 11·35 Å, b = 11·44 Å and c = 8.97 Å respectively.

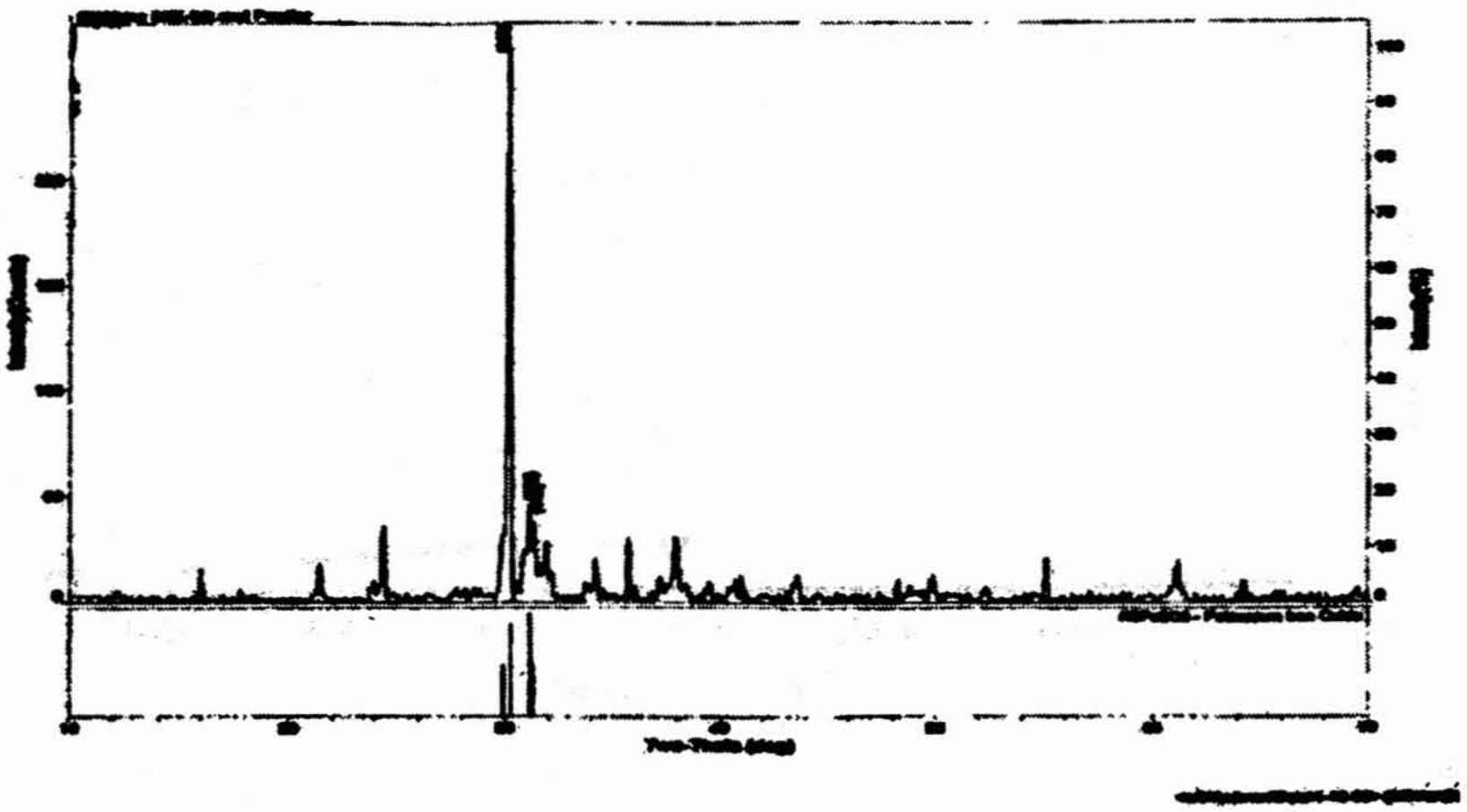

Figure 2. XRD pattern of potassium pentaborate, KB5 crystal

Laser Raman and FTIR Spectroscopic Study

Raman spectrum of KB5 crystals was measured by RSI-2001S Raman spectrometer as shown in Fig. 3. The observed Raman shifts and corresponding vibrational mode assignments are tabulated in Table 1 (Raj et al., 2007).

IR transmission spectrum of KB5 crystals with KBr disc method was recorded by Perkin-Elmer 600 FTIR spectrometer as shown in Fig. 4. The observed absorption lines, corresponding frequency assignments and types of molecular vibrations are tabulated in Table 1. The B–O vibrations of borate crystals have their absorption bands in the frequency region 784 – 1438 cm^{-1} (Raj et al., 2007). The strong bands observed in the laser Raman spectrum of KB5 at 788 cm^{-1} and 913 cm^{-1} have been assigned to ring B–O symmetric stretching vibrations. The ring B–O asymmetric stretching vibrations appear at 1131 cm^{-1}, 1251 cm^{-1}, 1282 cm^{-1}, 1343 cm^{-1} and 1382 cm^{-1} with very strong intensity.

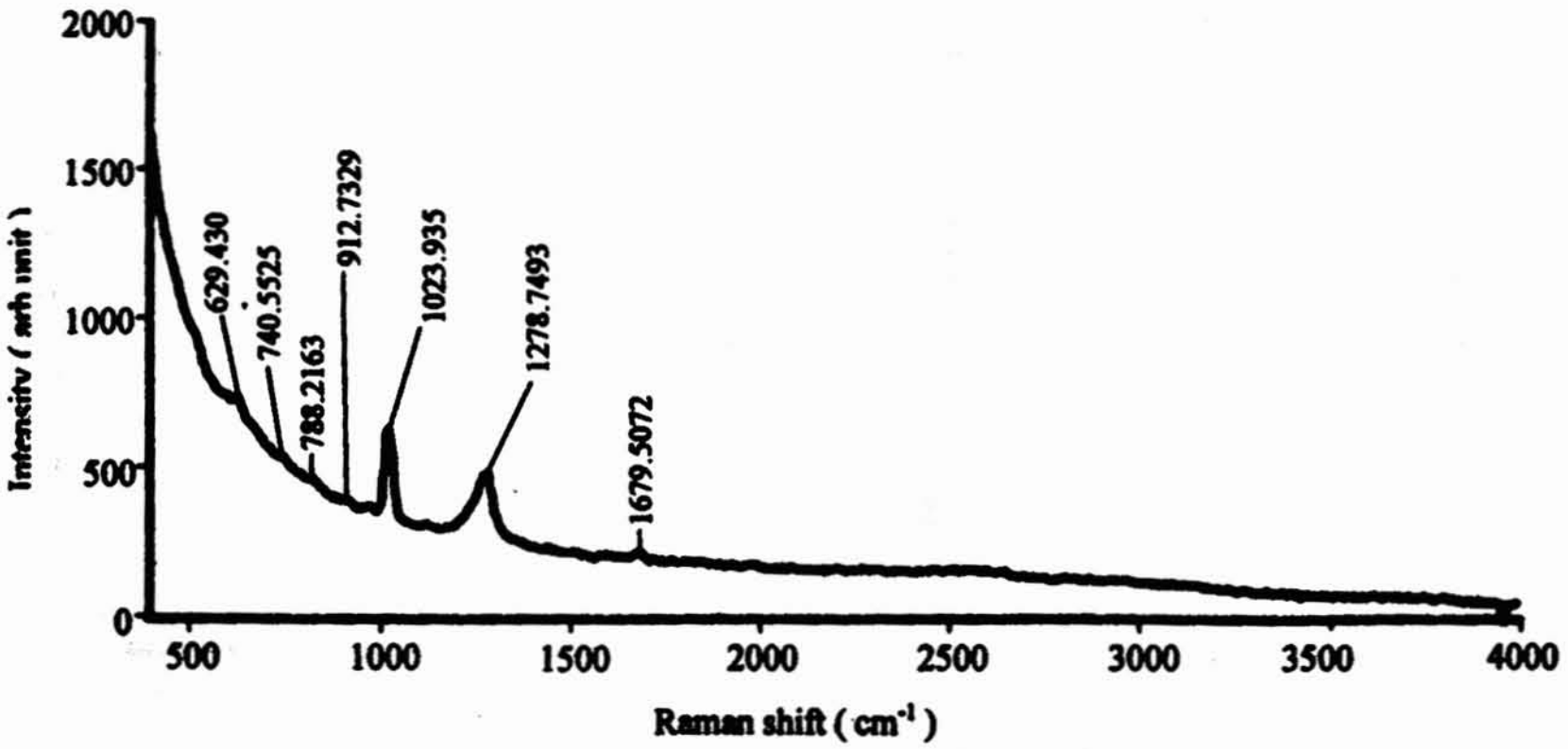

Figure 3. Laser Raman spectrum of KB5 crystal at room temperature

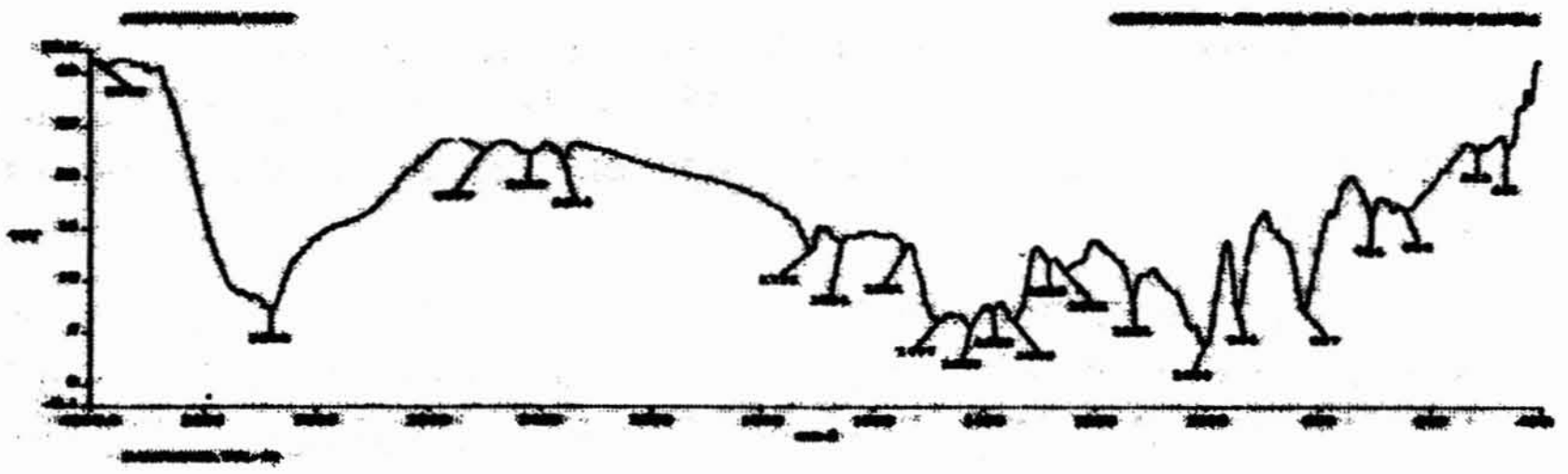

Figure 4. IR transmission spectrum of KB5 crystal with KBr pellet method

The very strong peak at 1004 cm^{-1} in the infrared spectrum and 1024 cm^{-1} in the Raman spectrum has been attributed to B–O terminal symmetric stretching vibration. The B–O terminal asymmetric stretching bands are observed in the IR spectrum at 1422 cm^{-1} and 1477 cm^{-1} with strong intensity. The very strong band observed at 3356 cm^{-1} has been assigned to OH stretching vibration in the FTIR spectrum.

The bands observed in the FTIR spectrum at 461 cm^{-1} and 513 cm^{-1} are assigned to ring OBO symmetric bendings. The ring asymmetric bending vibrations are found at 644 cm^{-1} and 704 cm^{-1} with strong intensity. The corresponding OBO ring asymmetric bending vibration in laser Raman spectrum is found at 629 cm^{-1}. The terminal asymmetric bending vibration appears at 728 cm^{-1} and corresponding vibration in the Raman spectrum appears at 741 cm^{-1}.

Table 1. Laser Raman and FTIR frequencies of KB5 crystal and their corresponding vibrational mode assignments

FTIR (cm^{-1})	Laser Raman (cm^{-1})	Assignment
461	-	OBO ring bending
513	-	OBO ring bending
644	629	OBO ring asym. bending
704	-	OBO ring asym. bending
728	741	OBO ter. asym. bending
-	788	B–O sym. stretching
827	-	B–O ring stretching
-	913	B–O sym. stretching
944	-	B–O ring stretching
1004	1024	B–O ter. stretching
1131	-	B–O asym. stretching
1251	-	B–O asym. stretching
1282	1278	B–O asym. stretching
1343	-	B–O asym. stretching
1382	-	B–O asym. stretching
1422	-	B–O ter. asym. stretching
477	-	B–O ter. asym. stretching
1634	1680	OH bending
1711	-	B–O ter. asym. bending

FTIR (cm^{-1})	Laser Raman (cm^{-1})	Assignment
2314	-	OCO bending
2432	-	OCO bending
2597	-	OCO bending
3356	-	OH stretching

TG-DTA Result

Simultaneous TG-DTA curves of KB5 crystal is shown in Fig. 5. The TGA curve shows the mass variation (weight loss) recorded during the measurement (heating). In the present work, the TG analysis shows that between 150°C and 290°C, the weight loss is about 14.89 %. This indicates the dehydration of $K(H_4B_5O_{10})\cdot 2H_2O$ compound to $K(H_4B_5O_{10})$. The strong endothermic peak in DTA curve around 177°C with the associated shoulders indicates the step-wise removal of water during this temperature range. When the crystal is heated above 290°C, the constitutional water on the surface that produced during growth evaporates. Finally, when the temperature reaches 300°C, the sample melts.

Conclusion

Crystals of potassium pentaborate, KB5 were grown by solution growth technique at 305 K. In this paper, structural analysis and vibrational characterizations of potassium pentaborate, KB5 crystals have been reported by means of XRD, laser Raman and FTIR spectroscopic techniques. XRD pattern indicates the KB5 crystal analogous to orthorhombic structure. Vibrational characterizations of B-O stretching, B-O terminal stretching, B-O terminal bending, O-B-O terminal asymmetric bending, O-B-O ring asymmetric bending and O-B-O ring bending of borate molecules in KB5 crystals were observed and precisely assigned. According to TG-DTA analysis, the dehydration of water from $K(H_4B_5O_{10})\cdot 2H_2O$ compound was changed to $K(H_4B_5O_{10})$ or loss of double-hydrate to anhydrous compound.

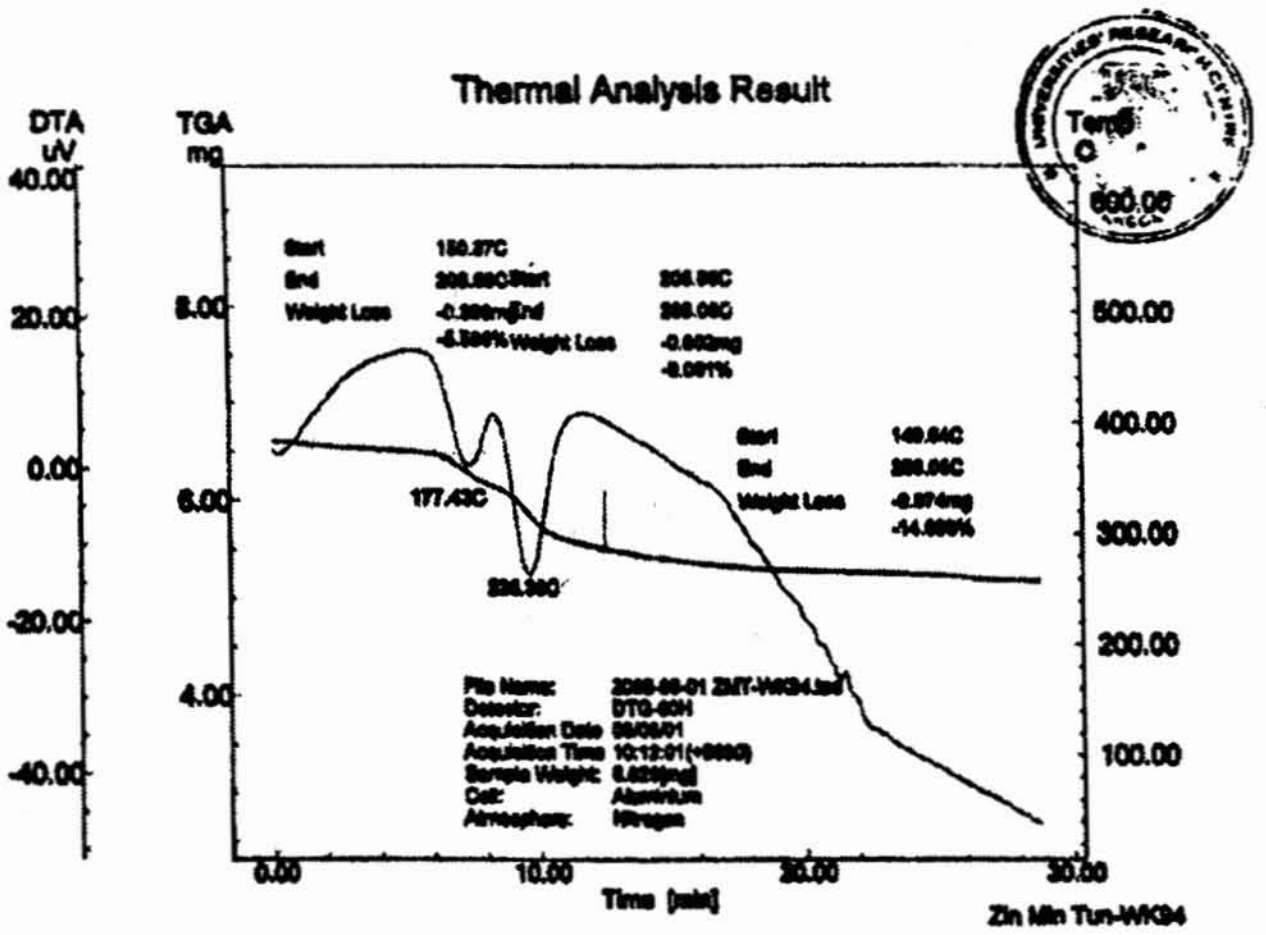

Figure 5. TG-DTA curves of KB5 crystal

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