# Growth, Optical, Mechanical, Dielectric and Theoretical Studies on Potassium Pentaborate Tetrahydrate ($KB_5O_8 \cdot 4H_2O$) Single Crystal by Modified Sankaranarayanan-Ramasamy Method

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A nonlinear optical single crystal of potassium pentaborate tetrahydrate ($KB_5O_8 \cdot 4H_2O$) has been grown from aqueous solution by using unidirectional crystal growth method of Sankaranarayanan-Ramasamy (SR) with a due modification in the growth assembly. Potassium pentaborate crystal of 60 mm length and 10 mm diameter has been grown along (100) plane with a growth rate of 3 mm per day within a period of 20 days. The grown crystal was subjected to single crystal X-ray diffraction analysis to confirm that the crystal belongs to the orthorhombic system. Some fundamental data such as valance electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal were calculated. The presence of borate in the grown crystal was confirmed by Fourier transform infrared (FTIR) spectroscopy. The optical transmission property of the grown crystal was analyzed using ultra violet (UV) visible spectral analysis. Surface morphology of the growth plane was observed using scanning electron microscopy (SEM). The mechanical strength of the crystals was found out using Vickers microhardness test along the growth axis. Frequency dependent dielectric constant of the grown crystal was studied for various temperatures along (100) plane.

**KEY WORDS: Crystal growth; Characterization; Nonlinear optic materials**

## 1. Introduction

Borate family complexes are excellent nonlinear optical (NLO) materials, as they possess high chemical stability, damage threshold, optical quality and wide range of transparency. In particular, inorganic crystals like lithium triborate (LBO), $\beta$-barium meta borate (BBO) and potassium pentaborate tetrahydrate ($KB_5O_8 \cdot 4H_2O$, Simplified as KB5) have been widely used and assumed great impetus for NLO devices in ultra violet (UV) laser generation[1–3]. 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). It belongs to orthorhombic system having space group $Aba_2$ and point group mm2, which is colorless, optically biaxial positive[4–8]. Recently, Sankaranarayanan-Ramasamy (SR) solution growth method attracted the researchers due to the growth of defect free transparent bulk single crystals along a particular axis[9–11]. This method is advantageous due to the low temperature gradient involved in the growth, which minimizes thermal stress on the crystal in growth. This method gains 100% solute-crystal conversion efficiency and free from microbial growth, which mainly alters the growth of crystals[12,13]. In this work, optically good quality single crystal of KB5 was grown using the modified unidirectional growth assembly of SR method[14,15]. The grown crystal was characterized by single crystal X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultra violet (UV), scanning electron microscopy (SEM) analysis. Microhardness and dielectric studies were carried out along the growth axis. Fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal were calculated for the first time.

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## 2. Experimental

Starting materials, potassium carbonate and boric acid (AR grade) in the appropriate amount were dissolved in deionized water for the synthesis of potassium pentaborate mixture. In order to obtain seed crystals of good quality, synthesized homogenous solution was subjected to several times of recrystallization. The seed crystals of KB5 were obtained within a week by slow evaporation at room temperature. Since the grown seeds possess a perfect external morphology along the plane (010), this plane was selected for the unidirectional growth. The modified version of SR growth setup is shown in Fig. 1. In this growth setup, ring heater was replaced by assemblies of alternating 60 W filament lamps. A vertical bottom-seed ampoule placed along the axis of the growth assembly was rotated 90°/s using a stepper motor for maintaining steady temperature around the ampoule. The temperature gradient was adjusted according to the requirement by varying the spacing

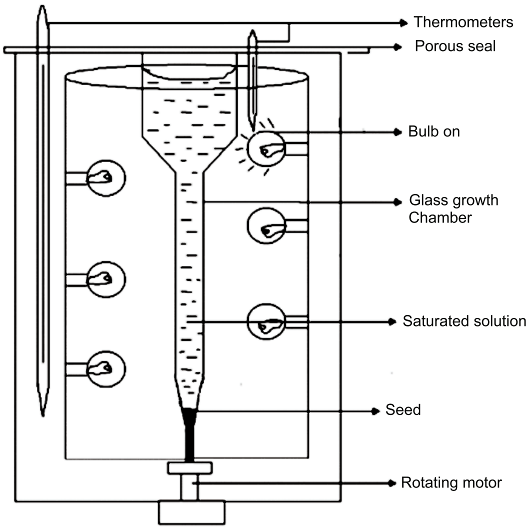


**Fig. 1** Crystal growth assembly

between the lamps, which are facing opposite and alternatively. The seed-fitted ampoule was filled with saturated solution prepared at room temperature. The temperature at top of the ampoule was maintained at 45°C using a temperature controller setup for the evaporation of the saturated solution. The temperature gradient makes the concentration gradient maximum at the bottom and minimum at the top of the ampoule for avoiding the spurious nucleation along the length of the ampoule. The growth rate of the crystal was 3 mm per day. The crystals of 60 mm length and 10 mm diameter have been grown successfully within a period of 20 days. The grown crystal shows a cylindrical morphology as that of the growth vessel. The grown crystal was carefully harvested from the ampoule using diamond cutter and polished for further characterization. The photographs of the as-grown and polished sections of the crystal are shown in Figs. 2 and 3.

## 3. Results and Discussion

### *3.1 Single crystal XRD and fundamental parameters*

Single crystal data collection was performed by using ENRAF NONIUS CAD-4 X-ray diffractometer. The XRD study reveals that the crystal belongs to orthorhombic system with lattice parameters $a$=1.1067 nm, $b$=1.1180 nm, $c$=0.90550 nm and $V$=1.115725 $nm^3$, which is in agreement with that of reported values[16]. The molecular weight of the grown crystal is $M$=293.0 g, and total number of valance electron $Z$=62. The density of the grown crystal was found to be $\rho$=1.74 $g\cdot cm^{-3}$ and dielectric constant at 1 MHz is $\varepsilon_\infty$=143.8. The valence electron plasma energy, $\hbar\omega_p$ is,

$$\hbar\omega_{\rm p} = 28.8\Big(\frac{Z\rho}{M}\Big)^{1/2} \quad (1)$$

where $Z$ is the total number of valence electrons, $\rho$ the density and $M$ the molecular weight of KB5 crystal. Explicitly the factors depending on $\hbar\omega_p$ are the Penn gap, $E_p$ and the Fermi energy, $E_F$[17], given by

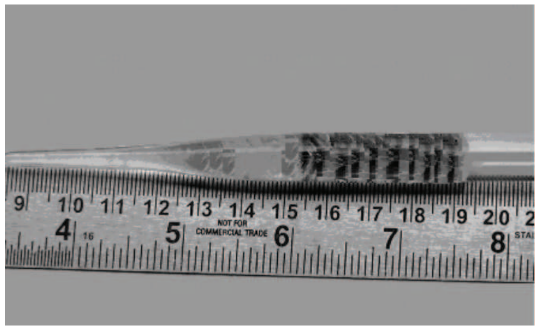

**Fig. 2** Photograph of as-grown crystal of KB5

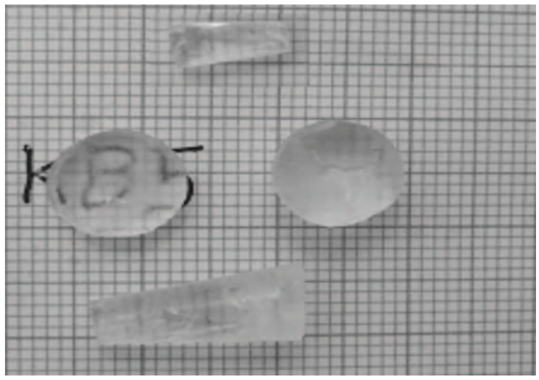

**Fig. 3** Photograph of polished portion of KB5 crystal

$$E_{\rm p} = \frac{\hbar\omega_{\rm p}}{(\varepsilon_\infty - 1)^{1/2}} \quad (2)$$

Electronic polarizability $\alpha$ was obtained using the relation[18–20],

$$\alpha = \Big[\frac{[(\hbar\omega_{\rm p})^2 S_0]}{(\hbar\omega_{\rm p})^2 S_0 + 3E_{\rm p}}\Big] \times \frac{M}{\rho} \times 0.396 \times 10^{-24}\ {\rm cm}^{-1};$$

$$S_0 = 1 - \Big[\frac{E_{\rm p}}{4E_{\rm F}}\Big] + \frac{1}{3}\Big[\frac{E_{\rm p}}{4E_{\rm F}}\Big] \quad (3)$$

The value of $\alpha$ so-obtained agrees with that Clausius-Mossotti relation,

$$\alpha = \frac{3}{4}\frac{M}{\pi N_{\rm a}\rho}\Big[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\Big] \quad (4)$$

where the symbols have their usual significance. $N_a$ is Avagadro number and the calculated fundamental data on the grown crystal of KB5 are listed in Table 1.

### *3.2 FTIR analysis*

The FTIR spectrum (Fig. 4) of KB5 was recorded with IFS BRUKKER 66v spectrophotometer using KBr pellet technique. The B–O vibrations of borate crystals have their absorption bands in the frequency region of 784–1438 $cm^{-1}$. The strong bands observed at 784 and 923 $cm^{-1}$ have been assigned to B–O symmetric stretching vibrations. The B–O asymmetric stretching is observed at 1438 $cm^{-1}$ with strong intensity. The very strong band observed at 3445 $cm^{-1}$ has been assigned to OH stretching vibration[21–24].

### *3.3 Optical transmission spectral analysis*

The optical transmission spectrum was recorded using the instrument VARIAN CARY 5E UV-Vis

**Table 1** Theoretical parameters of KB5 crystal obtained at room temperature

| Plasma energy /eV | Penn gap /eV | Fermi energy /eV | Polarizability/cm$^2$ | |
|---|---|---|---|---|
| | | | Penn analysis | Clausious-Mossotti |
| 17.475 | 1.462 | 13.368 | $65.353\times10^{-24}$ | $65.537\times10^{-24}$ |

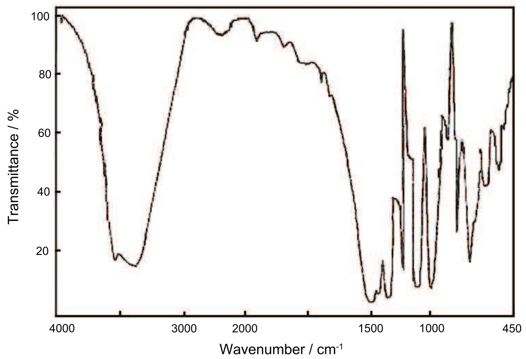


**Fig. 4** FTIR spectrum of the KB5 single crystal

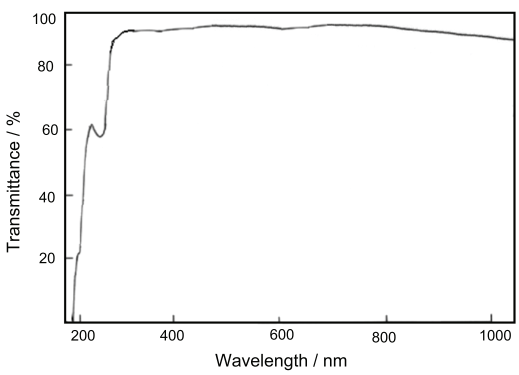


**Fig. 5** Optical transmission spectrum of KB5 crystal

-NIR spectrophotometer, and the obtained spectrum is shown in Fig. 5. The transparency is around 95% within the range of 240 to 1000 nm. Very high transmission of crystal through out the visible region of the spectrum is due to the delocalization of electronic cloud through charge transfer (CT) axis. This is the most desirable property of the materials possessing NLO activity. The grown crystal shows equal transmission as that of conventional grown crystals[25].

*3.4 Surface analysis*

The SEM image of the as-grown KB5 crystal was recorded along (100) plane. The resultant image is shown in Fig. 6. A few dislocation networks are observed on the surface of the crystal. Moreover small crack of very low depth was observed on the surface of the growth plane. However, major part of the crystal surface is free from dislocation networks and visible inclusions.

*3.5 Microhardness test*

The microhardness measurements were carried out with a load range from 25 to 200 g on growth plane (100) using Vicker′s hardness tester (LEITZ WETZLER) fitted with a diamond pyramidal indenter and attached to an incident light microscope. The Vickers microhardness number was calculated using the

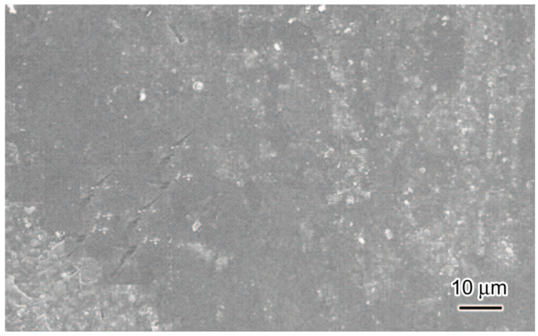


**Fig. 6** SEM image of KB5 single crystal along (101) plane

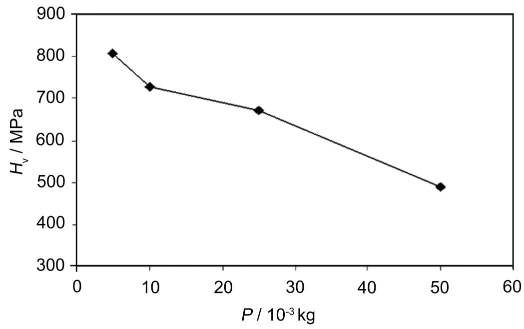


**Fig. 7** Variation of $H_v$ with load $P$ along growth axis (010)

relation,

$$H_v = (1.8544\ P/d^2) \quad (5)$$

where $P$ is the indenter load and $d$ is the diagonal length of the impression. Figure 7 shows the variation of $P$ with Vickers hardness number ($H_v$) for KB5. It is evident from the plot that the Vickers microhardness number decreases with increasng applied load and it is in good agreement with the concept proposed in literature [26,27]. According to Meyer′s law, the relation connecting the applied load is given by

$$P = k_1 d^n \quad (6)$$

where $n$ is the Meyer index or work hardening exponent and $k_1$, is the constant for a given material. By plotting log $P$ against log $d$, the values of work hardening coefficient was calculated as 1.67, which is less than 2, establishing the crystal to be a hard material. Large value of $n$ indicates large effect of dislocations[27]. For a material with $n$ less than 2, the resistance of the slip planes may be small and move easily due to inertia.

*3.6 Dielectric studies*

The dielectric constant and the dielectric loss of the KB5 crystals were studied along the growth (100) plane at four different temperatures (308, 328, 348 and 388 K) using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. Figure 8 shows

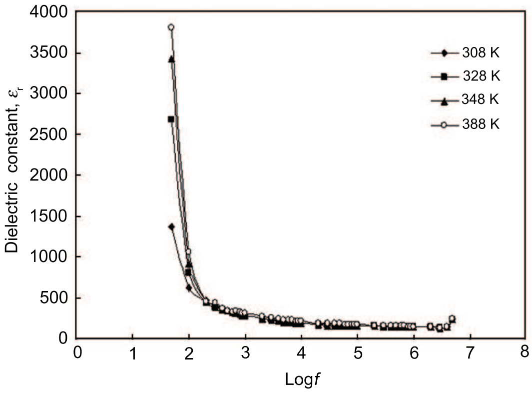


**Fig. 8** Variation of dielectric constant with log frequency

the plot of dielectric constant ($\varepsilon_r$) *vs* log frequency. The dielectric constant has high values in the lower frequency region and then decreases with the applied frequency. The very high value of $\varepsilon_r$ at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. From the plot, it is also observed that dielectric constant increases with increasing temperature, attributed to space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample[28].

## 4. Conclusion

An optically good quality and bulk single crystal of potassium pentaborate tetrahydrate ($KB_5O_8{\cdot}4H_2O$) was grown by modified unidirectional Sankaranarayanan-Ramasamy (SR) solution growth method. The crystal shows morphology of the growth vessel with 60 mm in length and 10 mm in diameter, maximum growth rate of 3 mm per day. Single crystal XRD analysis confirms that the crystal belongs to orthorhombic system. Fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. The FTIR spectral analysis confirms the presence of functional groups in the crystals. The optical transmission spectral analysis confirms the device fabrication property of the grown crystal. SEM analysis shows less defect along the growth plane. From the hardness test, work hardening coefficient for the grown crystal was found to be $n$=1.67 and hardness decreases with load along the growth plane. The frequency dependence of dielectric constant decreases with increasing frequency at different temperatures. The nonlinearity, excellent mechanical strength and growth along a required plane favour the material for the fabrication of optoelectronic devices.

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