Photoconductivity and dielectric studies of potassium pentaborate crystal (KB5)

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Abstract. Single crystal of potassium pentaborate (KB5) has been grown by solution growth technique. FTIR and laser Raman measurements are carried out to make a qualitative analysis on KB5 crystal. Dielectric behaviour of the KB5 crystal has been studied in the microwave region using K-band microwave bench equipped with the Gunn Oscillator guided with rectangular wave-guide. To confirm the suitability of this crystal as electro optic device, its dielectric behaviour with the change of frequency has also been investigated. Photoconductivity studies were also carried out on this material. It was interesting to observe that the KB5 crystal exhibited negative photoconductivity.

Keywords. Photoconductivity; dielectric constant; dark current.

1. Introduction

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 (NLO) frequency conversion materials can have a significant impact on laser technology (Belt *et al* 1985), optical communication (Clark 1988) and optical data storage technology (Gambino 1990). Materials with nonlinear 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 one such efficient nonlinear material which is used for second harmonic generation. The experiments conducted by Becker (1998) on NLO materials proved that 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 useful for type II second harmonic generation (SHG) (Voitsekhovskii *et al* 1982). KB5 is orthorhombic with four molecules in the unit cell of dimensions $a = 11·062$ Å, $b = 11·175$ Å, $c = 9·041$ Å. The dielectric properties of KB5 was not reported in the microwave region and the vibrational assignments were incomplete. In the present work, attention has been given to characterize this crystalline material through FTIR and laser Raman spectral measurements along with dielectric and photoconductivity studies.

2. Experimental

The starting material was synthesized by stoichiometric incorporation of potassium carbonate (AR grade) and boric acid (AR grade) taken in the appropriate ratio (Ramachandra Raja *et al* 1993). The calculated amount of salts was dissolved in deionized water at room temperature. KB5 salt was synthesized according to the reaction,

$$K_2CO_3 + 10H_3BO_3 \rightarrow 2[K(H_4B_5O_{10})\cdot 2H_2O] + 7H_2O + CO_2 \uparrow$$
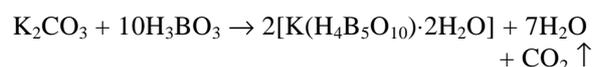
The purity of the synthesized salt was further increased by successive recrystallization process. Single crystals of KB5 are grown by slow and controlled evaporation of the solvent using a constant temperature bath. The supersaturated solution was kept in a constant temperature bath at 305 K in a polyethylene container with stirrer made of the same material. Crystals prepared by spontaneous nucleation were used as seed crystals. The period of growth ranged from 60 to 90 days.

3. Spectral analysis

The FTIR spectrum of KB5 was recorded on BRUKER IFS 66v Model FTIR spectrophotometer using KBr pellet. The laser Raman spectrum of KB5 was recorded on DILOR-Z24 Spectrophotometer. The spectra are presented in figures 1 and 2, and the observed frequencies with their assignments are summarized in table 1.

The B–O vibrations of borate crystals have their absorption bands in the frequency region 784–1438 cm^{-1} (Ross 1969; Clothup 1975; Chryssikos 1991; Chryssikos *et al*

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1991). The strong bands observed in the IR spectrum of KB5 at 784 cm^{-1} and 923 cm^{-1} have been assigned to ring B–O symmetric stretching vibrations. In the laser Raman spectrum these bands appear at 788 cm^{-1} and 918 cm^{-1}, respectively. The ring B–O asymmetric stretching vibrations appear at 1103 cm^{-1}, 1251 cm^{-1} and 1356 cm^{-1} with very strong intensity. The very strong peak at 1027 cm^{-1} in the infrared spectrum has been attributed to B–O terminal symmetric stretching vibration. The B–O terminal asymmetric stretching is observed in the IR spectrum at 1438 cm^{-1} with strong intensity. The very strong band observed at 3445 cm^{-1} has been assigned to OH stretching vibration.
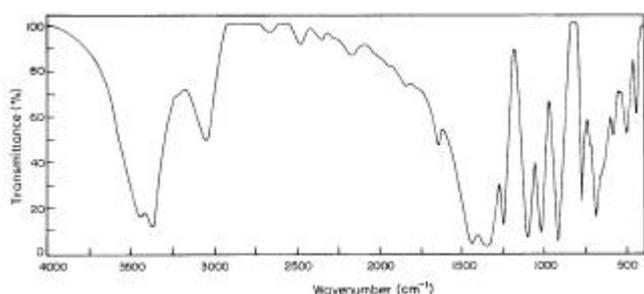

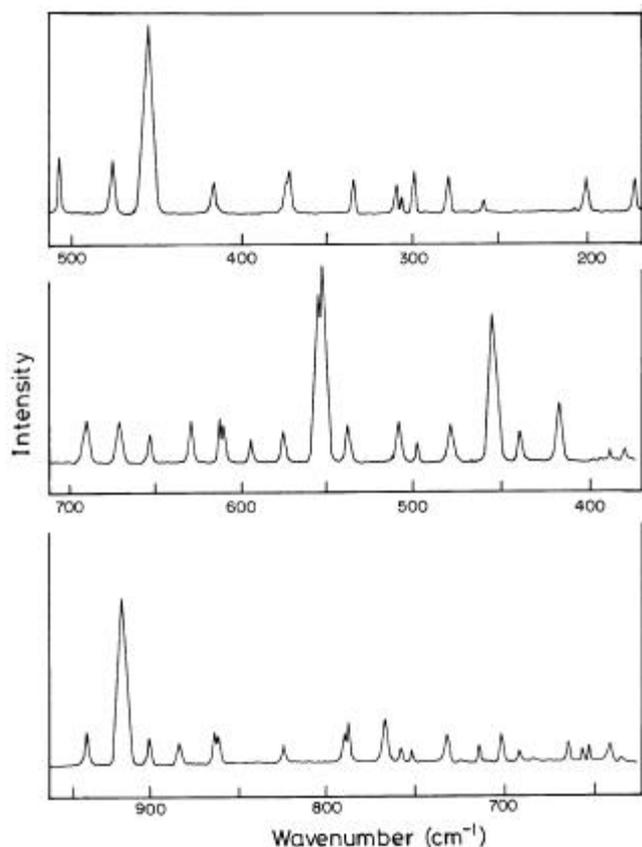**Figure 1.** FT-IR spectrum of KB5.

Figure 2. Laser Raman spectrum of KB5.

The bands observed in the Raman spectrum at 456 cm^{-1} and 504 cm^{-1} are assigned to ring OBO symmetric bendings. The corresponding frequencies in the IR spectrum are observed at 454 cm^{-1} and 509 cm^{-1}. The ring asymmetric bending vibrations are found at 655 cm^{-1} and 695 cm^{-1} with strong intensity. The medium intensity bands appearing at 552 cm^{-1} and 591 cm^{-1} are attributed to terminal ring OBO bendings. The terminal asymmetric bending vibration appears at 728 cm^{-1} and corresponding vibration in the Raman spectrum appears at 731 cm^{-1}.

4. Dielectric measurements

The K-band microwave test bench equipped with Gunn Oscillator was used to measure the dielectric constant of the sample. The dimension of the wave-guide used in the present case is $1·1 \times 0·4$ cm and hence the crystals are accordingly shaped to this size. Standing wave measurements have been carried out to determine the dielectric constants of the KB5 crystal. The functional block diagram of a microwave bench is shown in figure 3.

A direct and accurate method of Robert and Von-Hipple was used to measure the dielectric constant of the sample (Roberts and Von-Hipple 1956; Sisodia and Raghuvanshi 1990). The Von-Hipple method is based on the measurement of shift in the minimum of standing wave produced by a short circuit when a sample of

Table 1. FTIR and laser Raman frequencies of KB5 crystal and their assignments.

| FTIR (cm^{-1})	Laser Raman (cm^{-1})	Assignment
	373	OBO deformation
454	456	OBO ring bending
509	509	OBO ring bending
552	555	OBO terminal bending
591	–	OBO terminal bending
655	–	OBO ring asym. bending
695	–	OBO ring asym. bending
728	731	OBO ter. asym. bending
784	788	B–O ring stretching
923	918	B–O ring stretching
1027	–	B–O ter. stretching
1103	–	B–O asym. stretching
1251	–	B–O asym. stretching
1356	–	B–O asym. stretching
1438	–	B–O ter. asym. stretching
3445	–	OH stretching
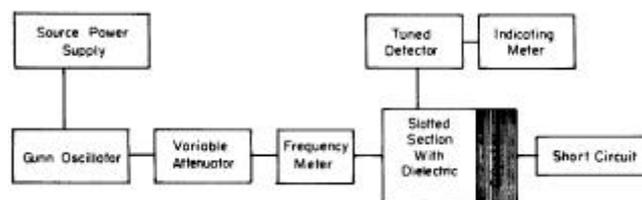
Figure 3. Functional block diagram of a microwave bench.

dielectric is placed in front of the short circuit. The shift, Δ, in the minimum of standing wave was caused due to the presence of the sample. To get common solution, measurements were carried out on the material with four different faces.

The dielectric constant (e_r) of the crystals is evaluated by using

$$b_d = \frac{2p}{l_0}\left[e_r m_r - \left(\frac{l_0}{2a}\right)^2\right]^{\frac{1}{2}},$$

where b_d is the phase constant of the wave in the dielectric medium, m_r the relative permeability of the material taken as unity for high frequency and l_0 the free space wavelength and a the wider dimension of the wave guide.

The dielectric constants of the KB5 crystal at different frequencies are listed in table 2.

5. Photoconductivity studies

The KB5 crystal was fixed on a glass plate and silver contacts were made over the sample to ensure good electrical contacts. The sample was connected in series to a d.c. power supply and a picoammeter (Keithley 480). The applied electric field to the sample was varied from 100 to 1100 V cm^{-1} without exposing the sample to any radiation and the corresponding dark current was recorded. The material was then exposed to radiation from a halogen lamp and the photocurrent was measured for various electric fields. Figure 4 shows the plot of dark current and photocurrent against the electric field. It is interesting to note that the photocurrent is less than the dark current, which is termed as negative photoconductivity.

The phenomenon of negative photoconductivity is explained successfully by Stockmann model (Joshi 1990). The negative photoconductivity in a solid is due to the reduction in the number of charge carriers or their life time, in the presence of radiation (Bube 1960). According to this model, the forbidden gap in the material contains two energy levels in which one is situated between the Fermi level and the conduction band while the other is located close to the valence band. The second state has high capture cross sections for electrons and holes. As it captures electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction band gets reduced and the current decreases in the presence of radiation.

Table 2. Dielectric constants of KB5 crystal at different frequencies.

Frequency (GHz)	Dielectric constant (e_r)
19·6	3·9589
	3·8440
	4·0185
	3·9590
22·7	3·8756
	3·7450
	3·9185
	3·8560

6. Conclusion

A satisfactory vibrational band assignment has been made available for KB5 crystal through FTIR and laser Raman spectroscopy. Dielectric behaviour of the KB5 crystal has also been investigated in the K-band microwave region. Further, the conductivity of the crystal was studied under dark and illuminated conditions and it was found to exhibit negative photoconductivity.

Figure 4. Plot of photocurrent/dark current vs applied electric field for KB5.

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