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Potassium Pentaborate Single Crystals for nonlinear optical applications

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ABSTRACT

In the present investigation, influence of rare earth Neodymium (Nd^{3+}) on the thermal, linear and nonlinear optical properties of Potassium Pentaborate (KB5) crystal have been studied systematically. The exact weight percentage of the metal dopant was determined by Inductively Coupled Plasma analysis. Powder X-ray diffraction studies were carried out for the pure and doped crystals to confirm the structure of the grown crystals. Dielectric and photoconductivity studies were made on the grown crystals. Mechanical and thermal stability of the grown crystals were determined by Vickers microhardness and thermal studies. Nonlinear optical properties were analyzed by SHG studies.

INTRODUCTION

Borate family of crystals plays an indispensable role in frequency conversion as they possess a wide transparency, high damage threshold, higher order harmonic generation, moderate birefringence and sharp UV absorption edge at shorter wavelength. Borate compound materials are superior to other commonly used NLO materials for UV applications [1]. Potassium pentaborate (KB5) is a desirable inorganic nonlinear optical material which exhibits a low angular sensitivity and hence, proved useful for second harmonic generation (SHG) [2]. High-damage threshold and wide transparency make it a better alternative for KDP crystals in frequency doubling and laser fusion experiments [3]. Kato attributed the primary advantage of KB5 over KDP to its slightly large birefriengence, which permitted generation of shorter wavelengths. Further his experiments confirmed the fifth harmonic generation for KB5 crystals at room temperature, whereas the other NLO crystals like ADP and KDP can achieve the same only at high temperature [4, 5]. Using the Bond-Valence theory of complex crystals, the origin of non linearities of the KB5 crystals was investigated by Xue Dongfeng etal and its larger NLO coefficients were also estimated [6]. The growth of single and twinned crystals of KB5 by low temperature solution growth was reported by several workers [7, 8, 9]. The present investigation deals with the growth of pure KB5 and metal doped KB5 crystals by slow solvent evaporation technique. The grown crystals are subjected to powder XRD to estimate the crystal structure and space group. The content of the dopant was determined by ICP analysis. FT-IR, UV-Vis-NIR, thermal and microhardness studies were carried out for the grown pure and doped crystals. The SHG efficiency of the pure and doped KB5 crystals were also studied using Nd:YAG Q-switched laser.

2 Synthesis of pure and doped KB5

The synthesis of potassium pentaborate with chemical formula $K(H_4B_5O_{10}).2H_2O$ was done by stoichiometric incorporation of potassium carbonate and boric acid taken in the appropriate ratio. KB5 salt was synthesized according to the reaction:

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

Nd^{3+} doped KB5 salt was also synthesized by adding 2 mole % of the dopant. To increase the purity of the crystal, recrystallisation was carried out using double distilled water more than three times.

3 Solubility and growth of pure and doped KB5

The growth rate of a crystal depends on its solubility and temperature. The solubility data of a material governs the amount of material, which is available for the growth, hence defines the total size. Solvent and solubility factors define super saturation, which is the driving force for the rate of crystal growth. Hence, for a material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion.

A 250 ml capacity glass beaker containing 100 ml of solvent was placed in the temperature bath. Initially the temperature was set as 30 ^{o}C. The beaker was closed with an acrylic sheet containing a hole at the center through which the stirrer was dipped into the solution. The addition of powdered sample of pure KB5 to the solution in small amount and subsequent stirring of the solution by a motorized stirrer was continued till the excess salt was deposited at the bottom of the beaker. The stirring was further continued, to ensure homogeneous temperature and concentration throughout the entire volume of the solution. After confirming the saturation, the content of the solution was analyzed gravimetrically. A 20 ml of the saturated solution of the sample was withdrawn by means of a warmed pipette and the same was poured into a cleaned, dried and weighed petri dish. The solution was then kept for slow evaporation in a heating mantle till its complete evaporation. The mass of pure KB5 in 20 ml of solution was determined by weighing the petri dish with salt and hence the solubility was determined. The solubility of pure and doped KB5 in double distilled water was determined for five different temperatures (30, 35, 40, 45 and 50 °C). Figure 1 shows the solubility curves of pure and doped KB5.

The saturated solutions of KB5 and doped KB5 salts were prepared separately using solubility data and allowed for slow evaporation. The period of growth ranged from 45-60 days. During the growth experiments, it was observed that the presence of dopant in general, increases the dimensions of the grown crystals. The photographs of as grown crystals of pure and Nd^{3+} doped KB5 are shown in Figure 2. The single crystals of pure and doped KB5 were grown with dimensions up to 14 x 8 x 6 mm^3 and 16 x 10 x 6 mm^3 respectively.

RESULTS AND DISCUSSION

4.1 Powder XRD studies

Powder X-ray diffraction studies of pure and doped KB5 crystals were carried out using Rich Seifert, XRD 3000P, X-ray diffractometer with Cu Kα (λ = 1.541Å) radiation. The samples were scanned for 2θ values from 10° to 40° at a rate of 2° per min. Figure 3 shows the Powder XRD pattern of the pure and doped KB5 crystals. The diffraction patterns of the crystals have been indexed by least square fit method. The lattice parameter values of the pure and doped KB5 crystals have been calculated and matched with the reported values [8]. KB5 crystal belongs to orthorhombic crystal system and its lattice parameters are presented in Table.1.

4.2 Inductively coupled plasma analysis

In order to determine the weight percentage of dopant in doped KB5 crystal, 10 mg of fine powder of the doped crystal was dissolved in 100 ml of triple distilled water. This prepared solution was taken for the ICP analysis. The results obtained from ICP show that 1.22% of Nd^{3+} (122 μg/100 ml) was present in the solution. It is observed that the amount of dopant incorporated into the crystal lattice is below its original concentration (2%) in the solution.

4.3 NLO test

The nonlinear optical property of the pure and doped KB5 crystals were tested by passing the fundamental beam of Q-switched, mode locked Nd:YAG laser operating at 1.06 μm and pulse width of 8 ns laser pulse with spot radius of 1mm Kurtz and Perry (1968) [10]. The input laser beam with pulse energy of 6.2 mJ was passed through IR reflector and then directed on to the samples. An intense green radiation observed from the pure and doped KB5 crystals confirmed the second harmonic generation (SHG). The second harmonic signals generated from pure and doped KB5 were 167.8 and 285.35 mW respectively with reference to KDP (275 mW). It is interesting to note that the incorporation of dopant has increased the SHG efficiency of the KB5 crystal.

4.4 UV-Vis-NIR studies

The UV-Vis-NIR spectra of defect free single crystals of pure and doped KB5 crystals were recorded using Varian Carry 5E model spectrophotometer in the region 200nm – 2000 nm. The transmission spectra (Figure 4) show that the crystals are transparent in the range 200 nm – 1400 nm, which is an essential parameter for NLO applications. The various bands appear in the infrared region are due to overtones and combinations. The spectra also reveal that the dopant has enhanced the transparent nature of the pure KB5 crystal. This wide optical transparency of NLO crystals is a vital factor for a wide range of photonic applications.

Using the recorded absorbance (A)–wavelength (λ) data of the crystal of thickness 1mm, absorption coefficient (α) is calculated using the relation,

$$\alpha = \frac{2.303}{t} \log_{10}\left({}^{1}\!/_{T}\right)$$

where t is the sample thickness and $\log_{10}(1/T)$ is defined as absorbance (A) of the sample. The value of α is used to determine the optical energy band gap from Tauc's relation. By plotting graphs of $(\alpha h\nu)^2$ versus hν and $(\alpha h\nu)^{1/2}$ versus hν (Figure 5), it is possible to determine the band gap. The band gap is obtained by extrapolating the linear part of the curve to the zero of the ordinate. The band gaps of pure and doped crystals are found to be 3.654 eV and 3.185 eV respectively.

4.5 FT-IR studies

Crushed powder of pure and doped KB5 crystals was mixed separately with KBr in the ratio 1:10 and pelletized using a hydraulic press and subjected to the FT-IR studies. The spectra were recorded in the range 450 cm^{-1} – 4000 cm^{-1} employing Bruker Model IFS 66V FT-IR spectrometer. The spectra of pure and doped KB5 crystals are shown in Figure 6 and Figure 7 respectively. The spectral assignments are presented in Table 2. In potassium pentaborate crystals, the molecular association in each crystal occurs through forces due to intermolecular hydrogen bond. Hydroxyl groups of pentaborate anion and water are expected to contribute substantially to hold the molecules together in crystals through hydrogen bond. The OH stretch of water occurs as an envelope between 3500 and 3250 cm^{-1}. The doublet structure of OH stretch in this region requires the existence of unequal hydrogen bonds for the two hydrogens of water with two ring oxygen of the pentaborate anion. There is no sharp signal around 3600 cm^{-1}. It would generally arise for O-H stretch if it is free and unhydrogen bonded. Hence, in this compound all the OH groups irrespective of its nature is forced to involve in hydrogen bonding as it is a very essential driving force for the formation of rigid crystals. Similarly the OH stretch of $(B_5O_6(OH)_4)^-$ which occurs at 3057 cm^{-1} also reveals that all the OH groups are involved in hydrogen bonding. The shift to lower wave number compared to the OH stretch of water is due to strong hydrogen bonding interaction with ring oxygen. The broad envelope between 1245 and 1500 cm^{-1} is assigned to B-O vibrations and the corresponding bending modes are seen around 1000 cm^{-1}. The significant change in the appearance of bands in the region between 450 cm^{-1} and 2000 cm^{-1} in the spectrum of doped KB5 supports the incorporation of dopant in the crystal lattice.

4.6 Microhardness studies

Microhardness behavior of the pure and doped crystals were tested by employing Vickers micro hardness test on the (001) plane. Measurements were taken by varying the applied loads from 5 to 50 g. Microcracks were developed at higher loads; therefore the maximum applied load was restricted to 50 g only. The plot of variation of Vickers hardness number (Hv) with applied load for (001) plane of pure and doped KB5 is shown in Figure. 8. From the plot, it is noted that the hardness number (Hv) of the crystal decreases with increasing load. This type of behavior wherein the hardness number decreases with increasing applied load is called normal indentation size effect (ISE). The work hardening coefficient, n is calculated using log p versus log d graph, shown in Figure 9. The value of work hardening coefficient, n is found to be less than 2 for both pure and doped crystals. This further confirms the normal ISE behavior.

4.7 Thermal studies

The thermo gravimetric analysis of KB5 was carried out between 23˚C and 1200˚C in nitrogen atmosphere at a heating rate of 10 K/min. The TGA traces of pure and doped KB5 are shown in Figure 10 and Figure 11 respectively. The corresponding DTG curves are also shown in the respective figures. In the case of pure and doped KB5, the decomposition temperatures are observed respectively at 173.5^{o}C, and 184 ^{o}C respectively. The final residues for pure and doped KB5 observed after decomposing at three different stages are respectively 69% and 62%. It is observed that the dopant slightly increases the decomposition temperature and alter the weight loss of KB5 crystals. The difference in decomposition temperature of pure and doped KB5 crystals confirms the incorporation of dopant in the crystal lattice. The increase in the decomposition temperature may be attributed to the decreased bond energy caused by the addition of dopant.

4.8 Dielectric Studies

Freshly polished crystals of pure and doped KB5 were cut into samples of known dimensions. In order to ensure good electrical contact between the crystal and the electrodes, the crystal faces were coated with silver paint. Proper care was taken to avoid the spreading of silver paint to the sides of the crystal. The prepared samples were mounted between the copper platforms and electrodes. The dielectric measurement for KB5 sample was made on (100) plane, which happens to be the predominant plane [8]. At low frequency range there is steep fall of dielectric constant with the increase of frequency. At high frequency range the dielectric constant remains almost constant at all frequencies. At any frequency the dielectric constant of the doped crystal is lower than that of pure crystal. The effect of inclusion of dopant is found to decrease the dielectric constant. The behaviour of doped crystals is very similar to that of undoped crystal except having lower values of dielectric constant. The variation of dielectric constant with frequency for pure and Nd^{3+} doped KB5 single crystals are shown in Figure 12.

The dielectric loss was also studied as a function of frequency. The curves are shown in Figure 13, suggesting that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of the dielectric constant. The low value of dielectric loss at high frequency can be taken as a proof for the good optical quality of the crystals. The trend of variation of dielectric constant and dielectric loss as a function of frequency is the same for both pure and doped crystals of KB5.

4.9 Photoconductivity Studies

Figures 14 and 15 shows the field dependence of dark and photo currents in pure and doped KB5 crystals. It is observed that both dark and photo currents of crystals increase linearly with the applied electric field but the photocurrent of both pure and doped crystals is less than the dark current which is termed as negative photoconductivity. The loss of water molecules can also lead to decrease in conductivity. However, in the present case the contribution of water molecules to negative photoconductivity is ruled out as the loss of water molecules for pure and doped KB5 crystals begins at 173.5˚C and 184˚C respectively. Hence, the negative photoconductivity in the present case is attributed to the reduction in the number of charge carriers or their life time, in the presence of radiation [8].

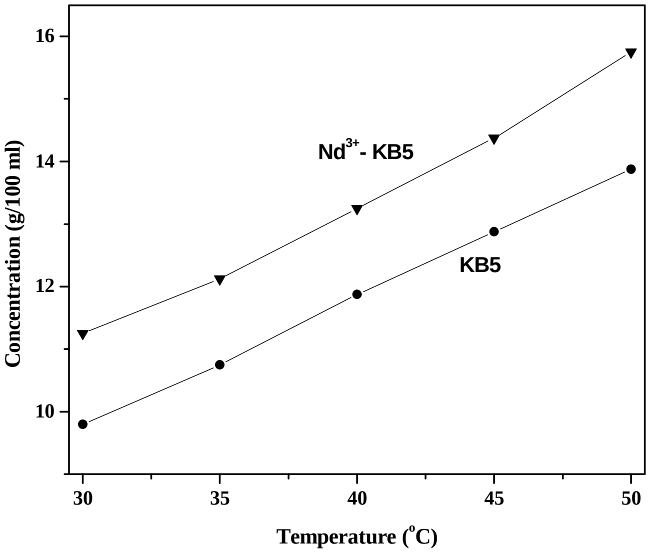

Figure 1 Solubility curves of pure and Nd^{3+} doped KB5 crystal

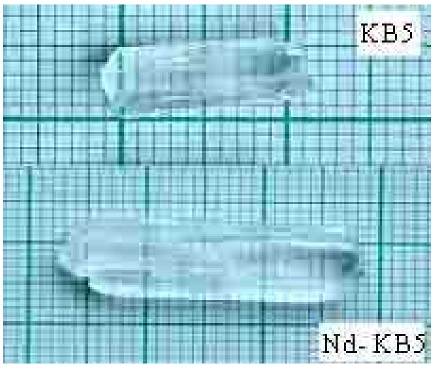

Figure 2 Photograph of as grown pure and Nd^{3+} doped KB5 crystal

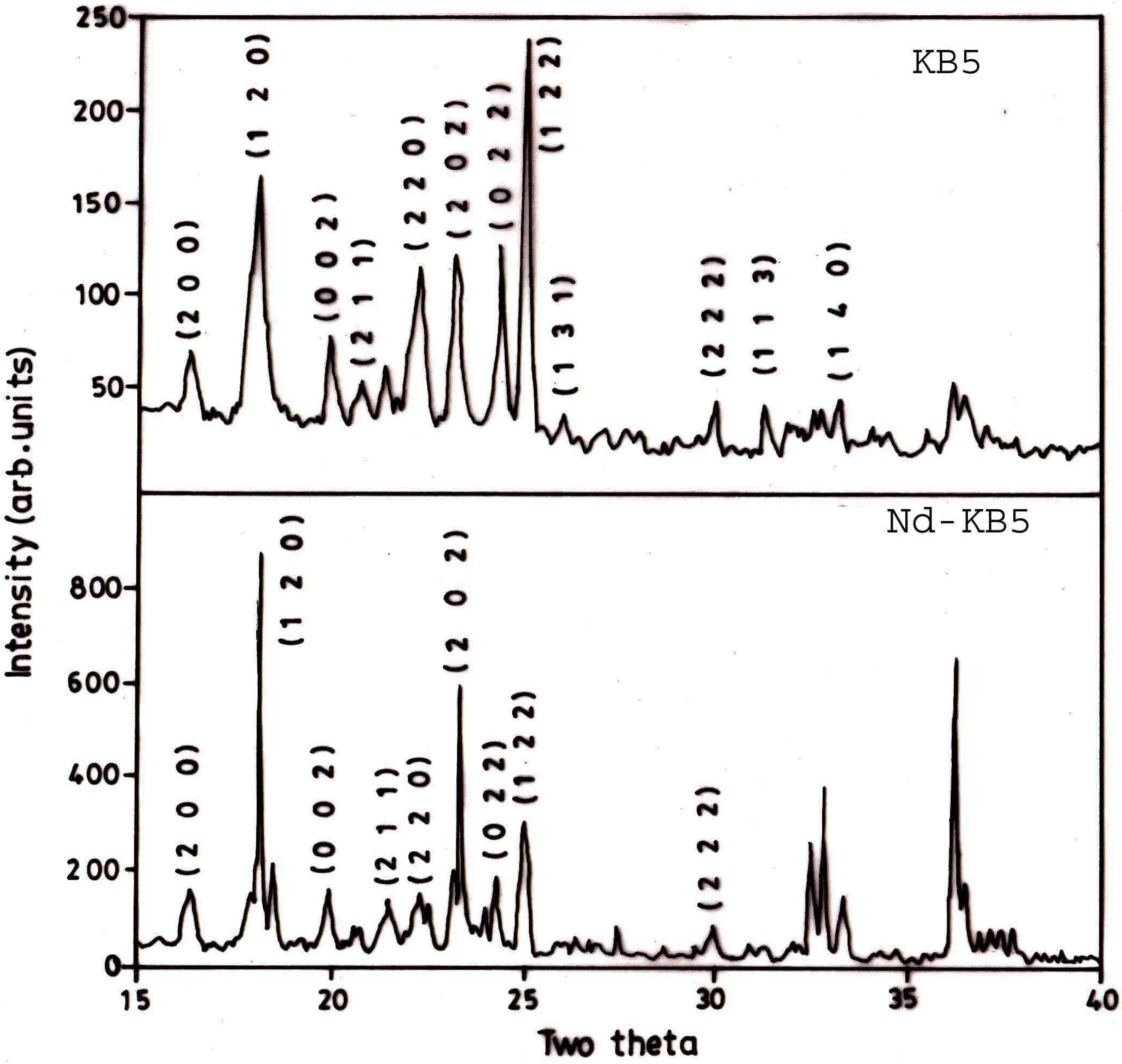

Figure 3 Powder XRD pattern of pure and Nd^{3+} doped KB5 crystal

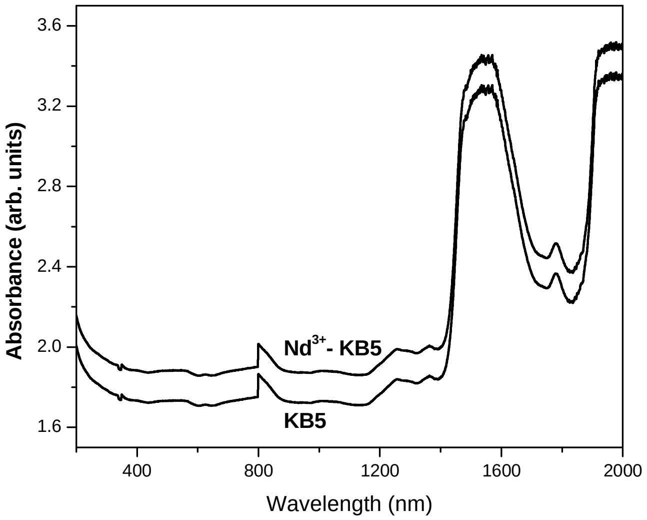

Figure 4 Absorption spectrum of pure and Nd^{3+} doped KB5 crystals

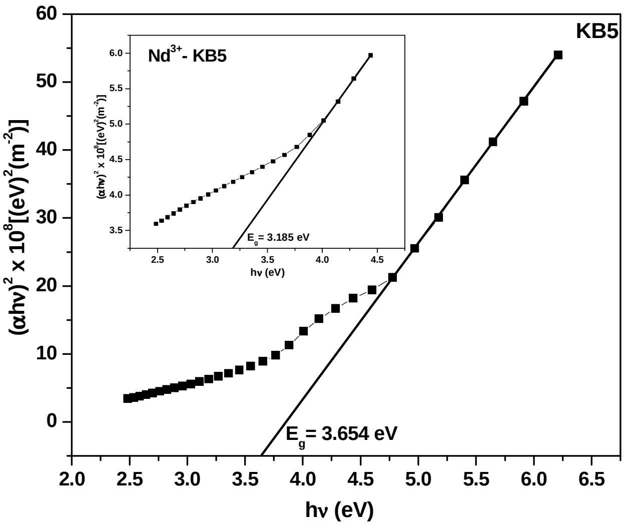

Figure 5 Band gap of pure and Nd^{3+} doped KB5 crystals

Table 1 Lattice parameters of pure and Nd^{3+} doped KB5 crystals

Lattice parameters	**Pure KB5**	**Nd^{3+} - KB5**
a (Å)	9.312	9.385
b (Å)	11.112	11.167
c (Å)	11.312	11.714
α(°)	90.00	90.00
β(°)	90.00	90.00
γ(°)	90.00	90.00
Crystal System	Orthorhombic	Orthorhombic
Space group	Aba2	Aba2
Volume (Å^3)	1170.509	1227.654

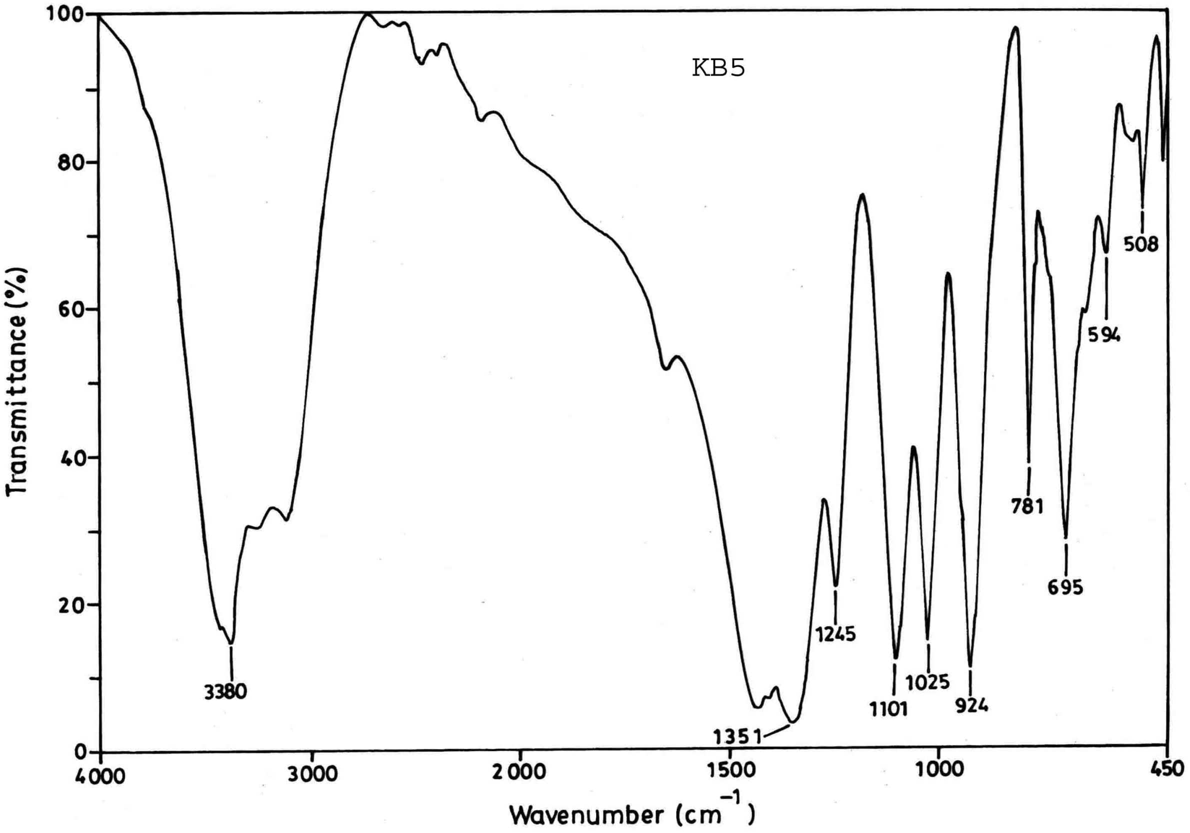

Figure 6 FT-IR spectrum of pure KB5 crystal

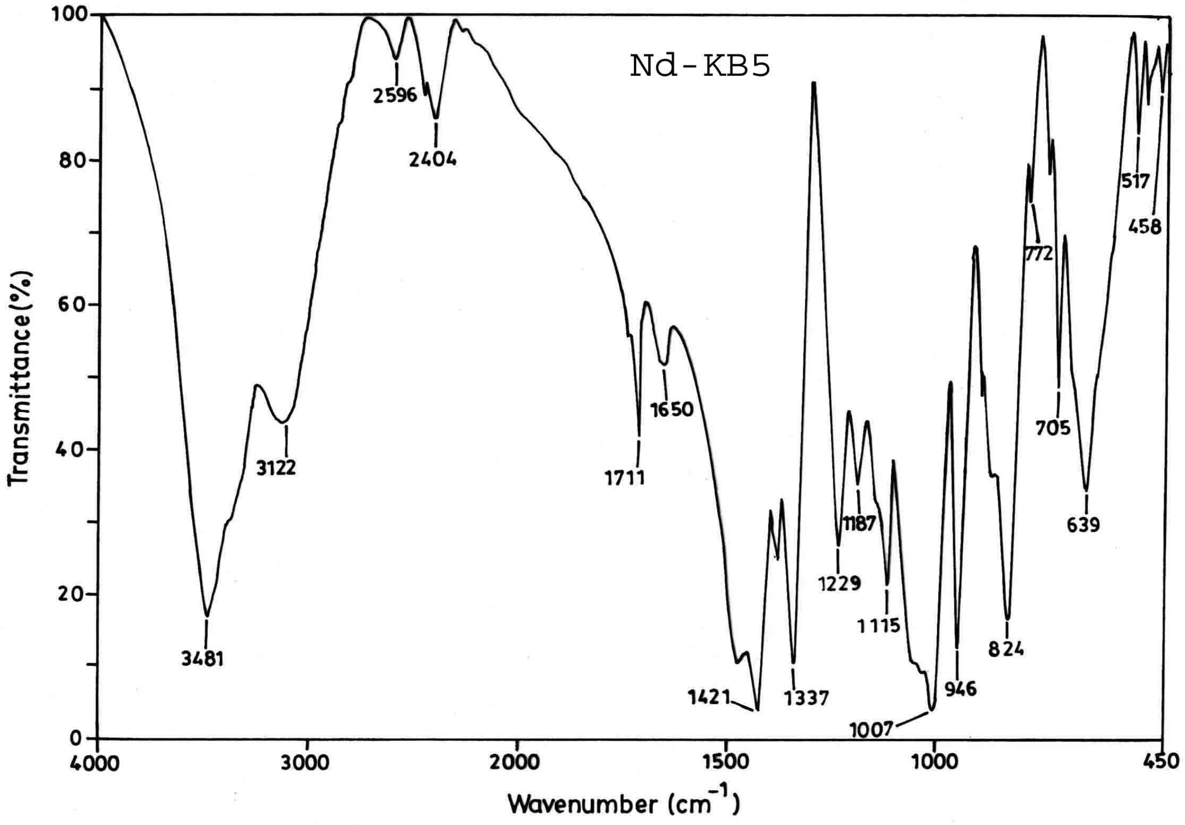

Figure 7 FT-IR spectrum of Nd^{3+} doped KB5 crystal

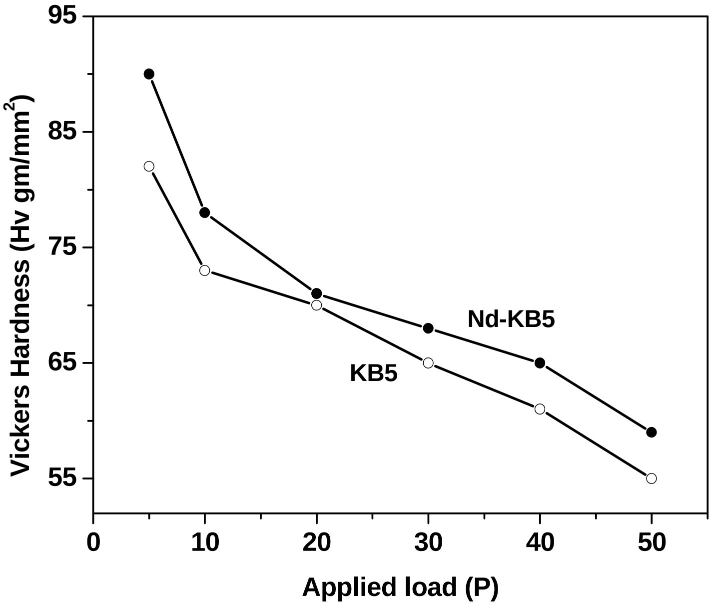

Figure 8 Variation of Vickers hardness number with load on (001) orientation for pure and doped KB5 crystals

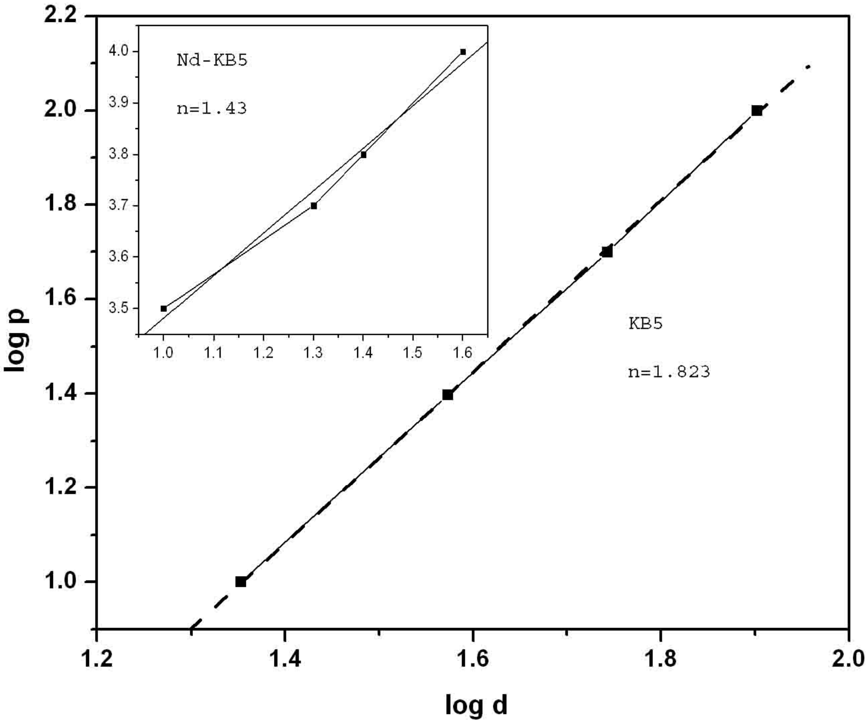

Figure 9 Plot of log d versus log p for pure and doped KB5 crystal

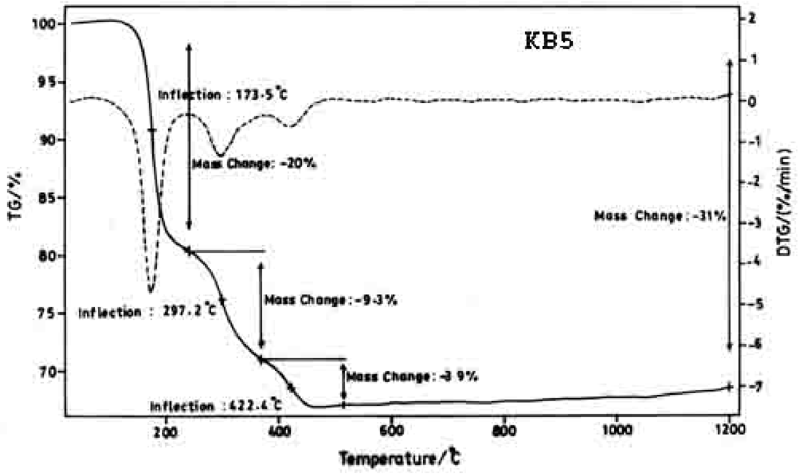

Figure 10 TGA and DTG curves of pure KB5 crystal

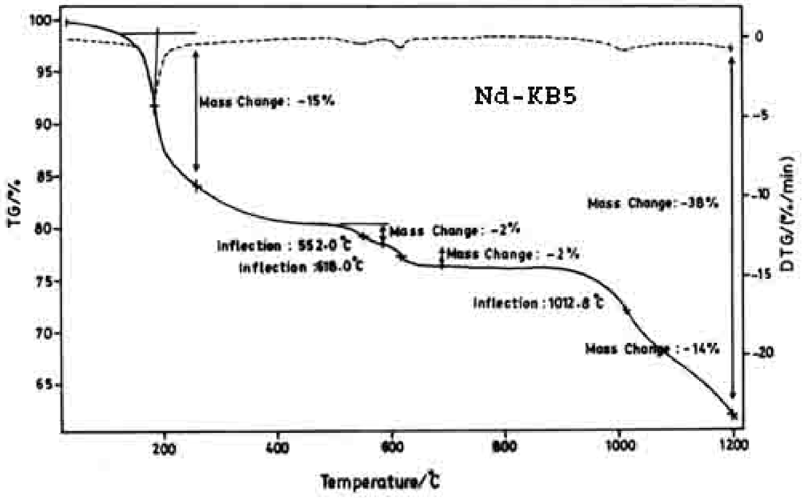

Figure 11 TGA and DTG curves of Nd^{3+} doped KB5 crystal

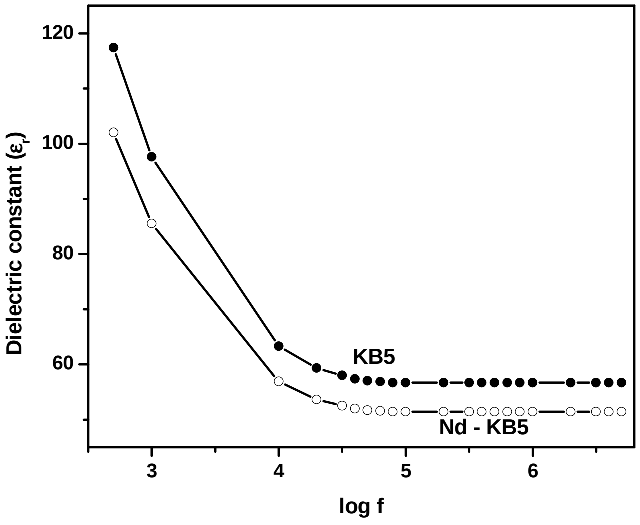

Figure 12 Variation of dielectric constant with frequency for pure and Nd^{3+} doped KB5 single crystals

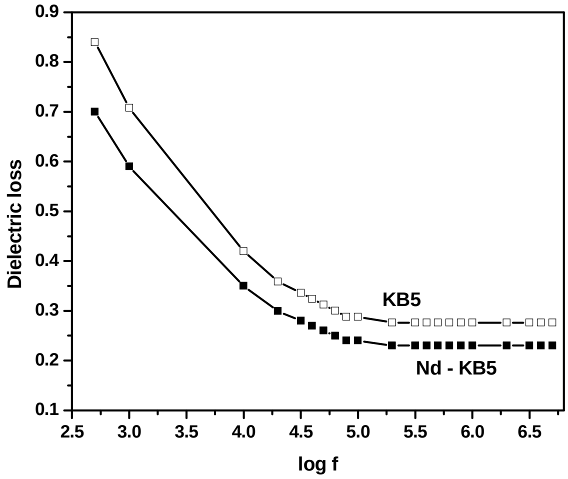

Figure 13 Variation of dielectric loss with frequency for pure and Nd^{3+} doped KB5 single crystals

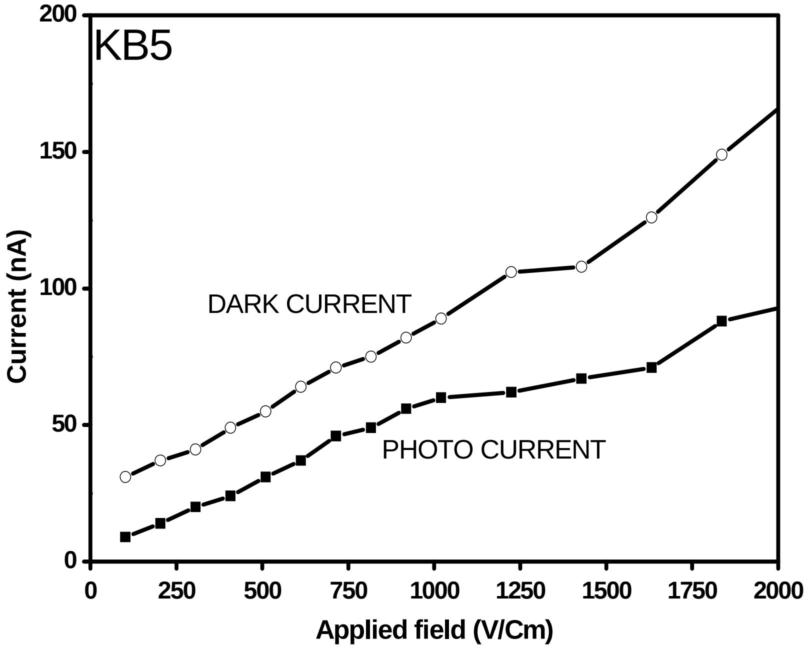

Figure 14 Field dependent photoconductivity of pure KB5

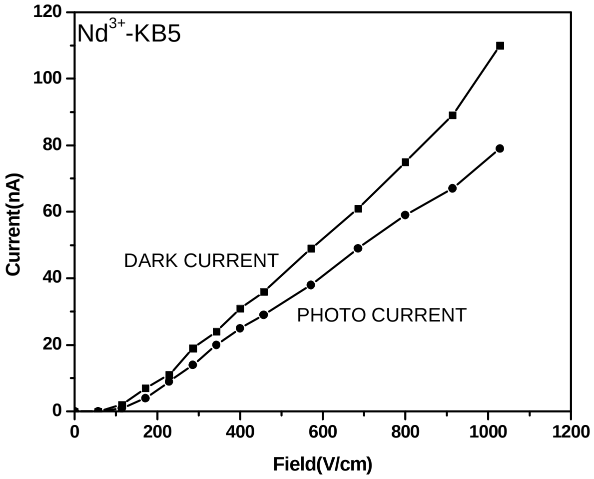

Figure 15 Field dependent photoconductivity of doped KB5

Table 2 FT-IR spectral assignments of pure and Nd^{3+} doped KB5 crystals

Wave number (cm^{-1})		**Assignments**
Pure KB5	**Nd^{3+} KB5**	
3380	3481	O-H stretching
1351	1337	B-O asym. stretching
1245	1229	B-O vibrations
1101	1115	B-O asym. stretching
1025	1007	B-O terminal stretching
924	946	B-O ring stretching
781	772	B-O ring stretching
695	705	OBO ring asymmetric bending
594	639	OBO terminal bending
508	517	OBO ring bending

CONCLUSION

Pure and doped potassium pentaborate (KB5) salts were synthesized using double distilled water. Synthesized salts were used to study their solubility behaviour. For both pure and doped KB5, the solubility increases with temperature and thereby possess positive solubility coefficient. Optically transparent, defect free and good quality single crystals of pure and doped KB5 crystals with considerable dimensions were successfully grown by slow evaporation technique. XRD studies on pure and doped KB5 crystals revealed that the basic orthorhombic structure of the parent is not altered by the incorporation of dopant. The slight variation in cell parameters of doped crystal confirmed the incorporation of dopant in the crystal lattice. The results of Kurtz powder technique confirmed the SHG and enhancement of NLO property in doped KB5 crystals. Significant change in the appearance of bands in the region between 400 and 2000 cm^{-1} in FT-IR spectra of doped crystals confirmed the incorporation of dopant in the crystal lattice of KB5. The microhardness studies on pure and doped KB5 crystals revealed that the microhardness number decreases linearly with increasing load for both pure and doped KB5 crystals. The work-hardening coefficients of pure and doped KB5 crystals were calculated and found to be greater than two for both pure and doped crystals of KB5. The TGA and DTG analysis confirmed that both pure and doped KB5 crystals are thermally stable up to 173.5˚C and 184˚C respectively. The dielectric constant and the dielectric loss of pure and doped crystals of KB5 were measured. At low frequency range both dielectric constant and dielectric loss are found to decrease with the increase of frequency and are independent of frequency at higher frequency range. In general, KB5 shows higher dielectric constant and dielectric loss than its doped system. The crystals with low dielectric constant lead to minimum losses as they have less number of dipoles per unit volume and hence doped crystals will be more useful for high speed electro optic modulations as compared to pure crystals. Photoconductivity studies were carried out for pure and doped KB5 crystals. It is observed that both pure doped crystals exhibit negative photoconductivity. Both the dark and photo currents of doped KB5 are found to be more than that of pure ones.

REFERENCES

[1] Becker P, *Advanced Materials*, 10, pp. 979–992 (**1998**).
[2] Voitsekhovskii V.N., *Sov. Phys. Crystal*, 27, pp. 322-323 (**1982**).
[3] Newman P.R., Warren L.F., Cunningham P., Chang T.Y., Copper D.E., Burdge G.L., Polak dingels P. and Lowe-Ma C.K., "Advanced Organic Solid State materials", Ed. 173, pp. 557-561 (**1990**).
[4] Kato K., *J. Quantum Electron*, 13, pp. 544-547 (**1977**).

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[5] Kato K., *J. Quantum Electronics*, 8, pp.544-545 (**1977**).
[6] Xue D. and Zhang S. *J. Appl. Phys*. A, 65, pp. 451-456 (**1997**).
[7] Ramachandra Raja C., Gobinathan R., Gnanam F.D., *Cryst. Res. Tech*., 28, pp.735-741 (**1993**).
[8] Rajasekar S.A., Thamizharasan K., Joseph Arul Pragasam A., Packiam Julies J and Sagayaraj P, *J.Crystal Growth*, 247, pp 199-206 (**2003**).
[9] Thamizharasan K., Xavier Jesuraja S., Francis P. Xavier and Sagayaraj P., *J. Crystal Growth*, 218, pp. 323-326 (**2000**).
[10] S.K. Kurtz, T.T. Perry, *J. Appl. Phys*. 39 3798 (**1968**).