Vcrystallization and Characterization of NLO Active Potassium Pentaborate Crystals by L-Threonine Doping

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Abstract

Effect of L-threonine (LT) doping enhanced the crystalline perfection, optical transparency, second harmonic generation (SHG) efficiency, functional groups, photoconductivity and Laser Damage Threshold in potassium pentaborate crystals grown by slow evaporation solution growth technique has been inspected. The crystal structure of KB5 (PotassiumPentaborate) was validated by X-ray diffraction analysis and due to the dopant L-threonine, an orderly change in the intensity of the peaks in parallel with morphology have been shown. FT-IR spectrum specifies the range of vibrations present in the crystal. The crystal holds transparency window from 240 nm to 1100 nm and its energy gap (Eg) found is 4.09 eV. Second harmonic generation studies expose that the crystal is fit for frequency conversion applications. Photoconductivity measurements show positive photoconducting nature of the crystalline material. Laser damage threshold has been analyzed.

Key Words: *Crystal growth, Characterization, Non linear optical material, Photoconductivity, LDT*

I. INTRODUCTION

The current epoch of information technology with swift and high data storage capacity, data retrieving, processing and transmission has claimed the investigation for new nonlinear optical (NLO) materials with unique optical properties [1]. In corresponding to the invention of new NLO materials for the tailor made applications the modification of the physical, optical and electrical properties are to be done centrally either by adding functional groups or incorporating the dopants [2]. Growth promoting factors like growth rate [3] and many of the useful physical properties like optical transparency, [4,5] second harmonic generation (SHG) efficiency [6], laser damage threshold (LDT) etc., get augmented by the presence of dopants. Borate compound materials are superior to other commonly used NLO materials for UV applications [7]. The present investigation deals with the growth of L-Threonine doped KB5 crystals by slow evaporation technique. The grown crystals are subjected to single crystal X-ray diffraction analysis,X-ray powder diffraction, FTIR and UV-Vis-NIR studies. Further SHG efficiency were examined using Nd:YAG Q-Switched laser. Photo conductivity studies and Laser Damage Threshold (LDT) were also carried out in the present case.

II. SYNTHESIS OF LT-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 1:10 ratio. KB5 salt was synthesized according to the reaction:

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

L-Threonine doped KB5 was also synthesized by adding 1 mole % of the dopant. The Calculated Quantity of L-Threonine was offered slowly to KB5 and stirred well for about 6 hours continuously in a magnetic stirrer and using micro wattmann filter paper, the completely reacted homogenous solution was filtered. It is then slowly evaporated to dryness at room temperature. Good Quality LTKB5 crystal seeds were attained on repeated recrystallisation using double distilled water. Bulk single crystals were prepared using defect free seeds. After a growth period of 45-60 days, single crystals of dimensions up to 15x9x6 mm^3 were achieved. Fig (1) shows the photograph of L-Threonine doped KB5 crystal.

Figure (1). Photograpgh of L-Threonine Doped KB5 Crystal

III. RESULTS AND DISCUSSION

A. Single Crystal XRD

The structural parameters and crystalline perfection of the as grown crystals were observed using ENRAF NONIUS CAD 4 single crystal x-ray diffractometer with MoKα (λ=0.71073Å). The obtained data revealed that the title compound belongs to orthorhombic system. The lattice parameters were found to be a=9.06Å, b=11.08Å and c=11017Å and α=β=γ=90˚.

B. X-ray Powder diffraction analysis

Powder X-ray diffraction studies of the as grown crystal were characterized using PAN analytical, XPert PRO Powder X-ray diffractometer taking up CuKα radiation (λ = 1.5418A^{o}) radiation at room temperature with a scanning range 0f 1^{o}/min and a scanning range of 10^{o} to 80^{o}. The Powder X-ray diffraction pattern is shown in Fig [2].

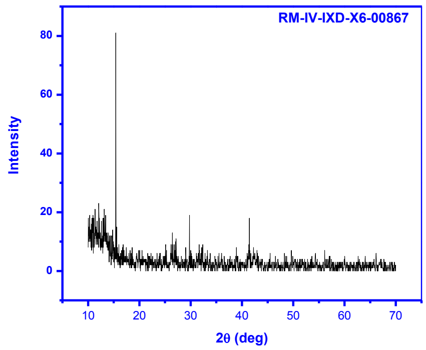

Figure (2). Powder XRD pattern of LTKB5 crystal

The diffraction patterns of L-Threonine doped KB5 crystals have been matched with the reported values of pure KB5 crystals [7] and L-Threonine doped KDP crystals [8]. Hence, the assimilation of L-Threonine in the crystal lattice of KB5 was substantiated clearly. Also, the sharp and well-defined Bragg's peaks obtained at specific 2ɵ angles specifies the ordered good crystalline nature of the as grown crystal.

C. FTIR Spectral Analysis

Fig (3) shows the FTIR spectrum of LTKB5 crystal. The Fourier Transform Infrared spectrum was carried out in KBr pellet phase using the instrument Perkin Elmer Spectrum-1 with

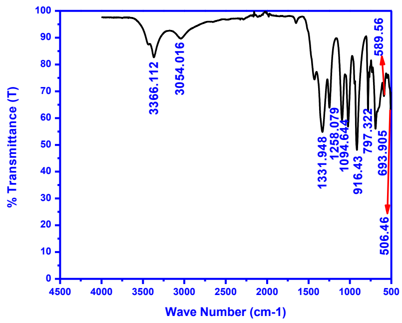

Figure (3). FTIR Spectrum of LTKB5 crystal

frequency range 500 cm^{-1} to 3500cm^{-1}. The spectrum recorded was compared with standard spectra of functional groups [9]. The spectral assignments are presented in Table-1.

TABLE 1. FREQUENCY ASSIGNMENTS OF LTKB5 CRYSTAL

Wavenumber(cm^{-1})	**Assignments**
3366.11	O-H stretching
3054.01	C-H stretching
1331.94	B-O asym stretching
1258.07	B-O stretching
1094.64	B-O asym stretching
916.43	B-O ring stretching
797.32	B-O ring stretching
693.90	OBO ring asym bending
589.56	OBO terminal bending
506.46	OBO ring bending

K.Thamizharasan et al., reported that the forces due to intermolecular hydrogen bond in each crystal are the specifications for molecular association in potassium pentaborate crystals [7]. Ample of contributions between hydroxyl groups of pentaborate anion and water are expected to occur to cling the molecules together in crystals through hydrogen bond.

Between 3500 and 3250 cm^{-1}, OH stretch of water occurs as an envelope. No observation of sharp signal around 3600 cm^{-1}. Hence it is revealed that the O-H stretch is not free and are hydrogen bonded. Also it could be stated that in the current study all the OH groups are forced to involve in hydrogen bond which is highly indispensible for rigid crystal formation. A peak projected at 3057 cm^{-1} is due to O-H stretch, also confirms that all the OH groups are entailed in hydrogen bonding. The lower wave number swing in comparison to that of OH stretch of water is due to the string hydrogen bond interaction with ring oxygen.B-O vibrations are being assigned between the wide envelope of 1245 and 1500 cm^{-1} and the relative bending modes are observed around 1095 cm^{-1}. The occurrence of bonds in the region between 450 cm^{-1}and 2000cm^{-1} with trivial change in the spectrum of doped KB5 supports the incorporation of dopant in the crystal lattice.

D. NLO Test

The nonlinear optical property of L-Threonine doped KB5 crystals were checked up Kurtz and perry powder technique using Quanta ray series Nd:YAG laser emitting first harmonics output of 1064 nm with a pulse width of 10ns [10]. The inclusion of microcrystalline LTKB5 crystal powder over the light path was introduced. An intense green radiation observed from the doped KB5 crystals confirmed the second harmonic generation (SHG). The SHG signals produced from the reference material KDP and the sample LTKB5 were 53mV and 84.1 mV respectively. The integration of dopant in KB5 increased the SHG efficiency of the crystal by 1.58 times that of the reference KDP, which is a productive nature of a NLO material.

E. UV-Vis-NIR Studies

The UV-VIS-NIR spectrum of LTKB5 crystal is shown in fig (4). The UV-Vis-NIR spectra of defect free single crystals of LTKB5 were recorded in the wavelength range 200nm to 1200nm using 5E UV-Vis-NIR spectrophotometer. The transparency of the as grown crystal is authenticated from the transmission spectrum in the range 240 nm to 1200 nm which is an essential parameter for NLO applications. The optical band gap of the crystal is calculated using the formula

$$Eg = \frac{1240}{\lambda} \quad (nm)$$

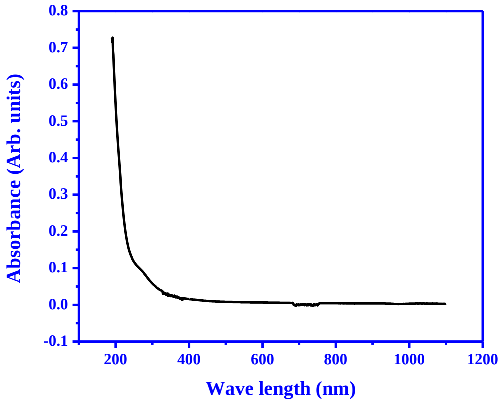

Figure (4). Absorption spectrum of LTKB5 crystal

and is found to be ~ 4.09 eV. The large optical transparency of NLO crystals is a key of essence for extensive photonic applications.

F. Photoconductivity

Fig (5) shows the field dependence of dark and photocurrents in LTKB5 crystal. It is observed that the dark and photocurrents of the crystals increases parallel with the applied electric field. Still the photocurrent of the sample is leading in advance to that of the dark current which is termed as positive photoconductivity. Hence this expression might be featured due to the presence of water molecules sustaining to high temperature. In the presence of radiation, the positive photoconductivity in the present case is characterized to the rise of number of charge carriers or their life time.

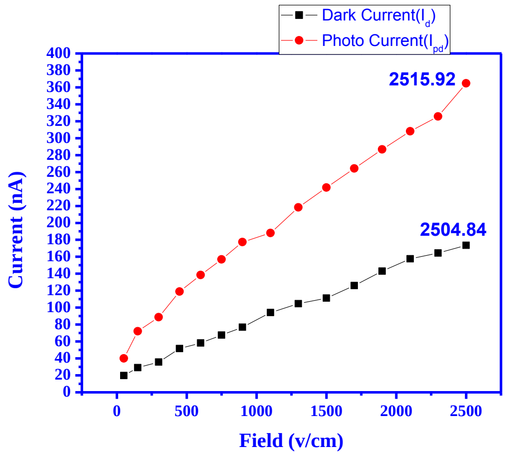

Figure (5). Field dependent photoconductivity of LTKB5 crystal

the orthorhombic structure of the crystal. The SHG efficiency confirms an appreciable NLO property.

G. Laser damage threshold (LDT)

In most of the transparent crystalline materials, various physical processes such as electron avalanche, multiphoton absorption and photoinonization are the causes behind laser induced breakdown. In case of high absorbing materials, the damage threshold is mainly due to the temperature rise, which leads to strain-induced fracture [11, 12]. Also it depends on specific properties of the material, pulse width and wavelength of laser used. For the long-pulse regime I>100ps, the damage process occur mainly by the rate of thermal conduction through the atomic lattice and for the short-pulse regime ι ≤ 10ps, the optical break down a non thermal process and various non linear ionization mechanisms (Multiphoton, avalanche multiplication and tunnelling) become important [12]. In the current investigation, 20ns pulsed laser has been used and consequently thermal effects are prominent. LDT values for (100) planes was recorded during the occurrence of clear visible spot on the sample surface with audible sound. To obtain the bulk LDT values, the beam was focused inside the crystal with a predetermined spot size of diameter 0.16mm in air close to the surface of the crystal. Since the spot size is very minute and which might vary inside the crystal due to change in the refractive index, there could be some error in the value of the actual spot size inside the crystal which in turn lead to error in the calculation of energy density. Taking an account on this factor, the relative LDT values have been given by measuring the LDT value of pure KB5 as one unit. The LDT value increased with 1 mole% doping. This feature indicates that LT doping has a greater influence on the enhancement in LDT irrespective of crystalline perfection. This character is a good sign for device fabrication application. accompanied in the crystal.

IV. CONCLUSION

Present investigation revealed the following conclusions. L-Threonine doping has a strong effect on growth rate. Optically transparent, defect free and good quality single crystals with significant dimensions were successfully grown by slow evaporation technique. XRD studies revelas the orthorhombic structure of the crystal. The SHG efficiency confirms an appreciable NLO property here in the crystal. FT-IR confirms the incorporation of dopant in the crystal lattice of KB5. The photoconductivity studies exhibit positive photoconductivity representing the increase of life time of the charge carriers. Laser damage threshold value of L-Threonine doped KB5 is stronger than pure KB5 crystal. All these characteristic studies represent that the as grown crystal is appropriately abled for frequency conversion and optoelectronic applications

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