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Optical Characterization Studies on boron doped KDP crystals

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ABSTRACT

Crystals of potassium dihydrogen phosphate (KDP) doped with boron has been grown by slow solvent evaporation method at room temperature. The presence of boron is confirmed by EDAX. The presence of the functional groups has been identified by Fourier transform infrared spectrum. The grown crystal was characterized by powder and single-crystal X-ray diffraction studies. The optical nature of the grown crystal is analyzed using the UV-Vis spectrum. The variation of photocurrent (I_p) and dark current (I_d) with applied field were determined. The SHG efficiency of boron doped KDP is higher than the pure KDP.

INTRODUCTION

KDP is among the most widely used NLO material. It is characterized by good UV transmission, high damage threshold but still their NLO coefficients are relatively low. In addition they are also excellent electro – optic crystals used as pocket cells, Q-switches etc [1-6]. Many methods have been tried to increase the growth rate and improve the NLO properties of the KDP crystal[7-8], The addition of dopants and their influence on the growth process and properties of crystals have been tried in recent years[9-11]. It is already well established that borate family crystals have a good power threshold figure of merit and have a proven track record of enhancing the non-linear optical nature of crystals. In the present work to further enhance the NLO property of KDP crystals an attempt is made to grow KDP crystals from the aqueous solution added with 0.1mol% Boric acid. The increase in the quality of the KDP crystal in the presence of Boron is analyzed.

MATERIALS AND METHODS

2. Crystal Growth

Single crystals of pure KDP and boric acid doped KDP were grown by slow evaporation of the saturated aqueous solution at room temperature. Analytical reagent grade (AR) samples of Potassium dihydrogen phosphate and Boric acid along with triple distilled water were used for the growth of single crystals. A solution of potassium dihydrogen phosphate and boric acid was prepared in the ratio 1:0.1 mol% using water as the solvent. The pH of the solution was 4. The solution was then filtered and allowed to evaporate at room temperature. After a period of 14 days, transparent colorless crystals of size 17 x 4 x4 mm^3 were harvested.

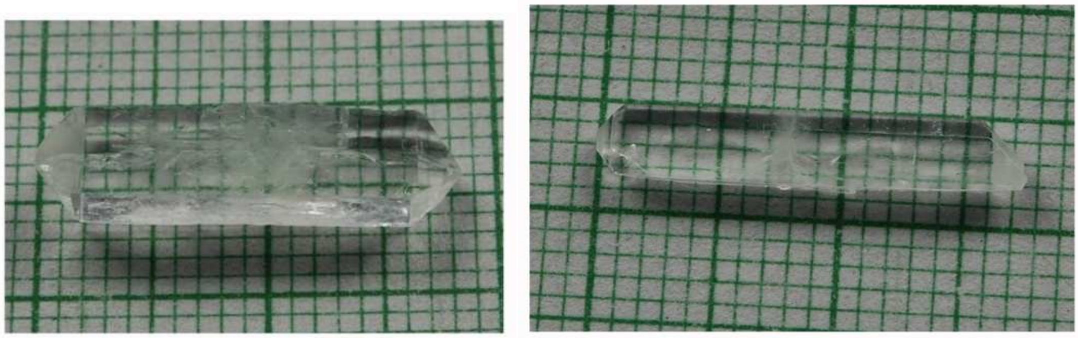

Fig.1. Photograph of the grown Pure KDP and boron doped KDP Crystals

The photographs of the as grown crystal of pure KDP along with the boron doped KDP crystal are shown in Fig.1. It is observed that the transparency of the doped crystal has improved and the as grown crystals have well defined faces and the growth is rapid along the 'X'- axis.

3. Characterization Studies

In order to confirm the presence of boron, the sample of grown crystals was subjected to EDAX analysis using the QUANTA 200 FEG Scanning Electron microscope. The Fourier transform infrared spectrum was recorded using Perkin Elmer model RXI Spectrometer in the range 400-4000cm^{-1} by KBr pellet technique. The crystals have been subjected to single crystal XRD studies using Bruker Kappa APEX II single crystal X-ray Diffractrometer to determine the unit cell dimensions. The powder x-ray diffraction has been recorded using Bruker-35kV Copper Kalpha Radiation . The UV-Visible transmission spectrum was recorded using Perkin Elmer Model-Lambda 35 spectrometer in the range 190nm to 1100nm. Photoconductivity of the crystal was studied using Keithley 485 picoammeter.

3.1 EDAX

The EDAX spectra for pure and 0.1mol% of boron doped KDP crystals were recorded and analysed. From the spectrum of pure crystals it is clear that there is no peak other than that of potassium, carbon, oxygen and phosphate, as expected from pure KDP crystals. The spectrum corresponding to boron doped KDP crystals shows peaks of potassium, carbon, oxygen, boron and phosphate suggesting thereby that the dopant has entered in to the crystal lattice of KDP and making it a new crystal. The recorded EDAX spectrums are shown in Fig.2. The observed weight percentage of elements in the pure KDP and boron doped KDP crystals are given.

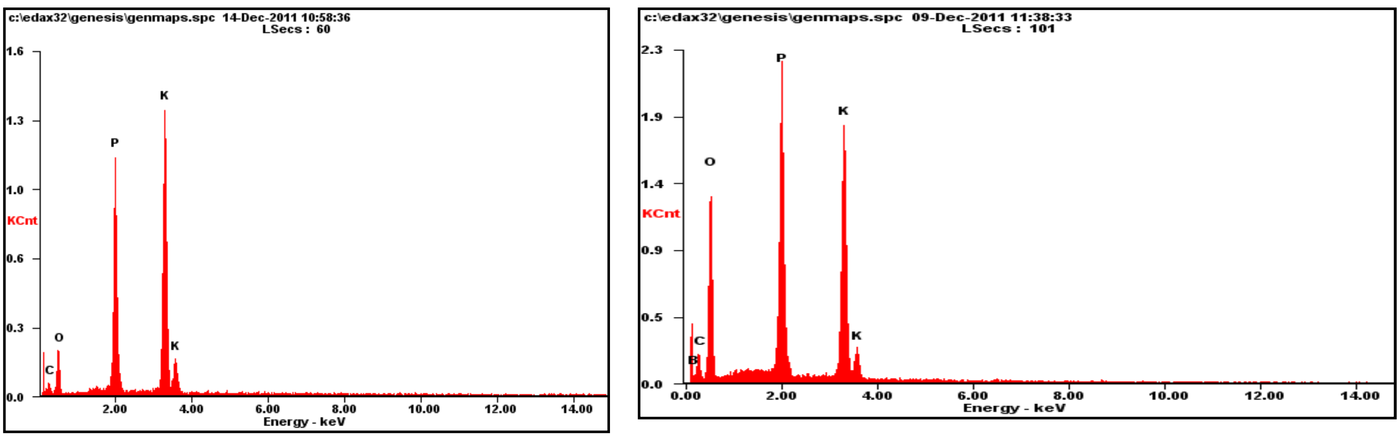

Fig.2. EDAX of Pure KDP and boron doped KDP Crystals

Element	*Wt%*	*At%*

CK	16.83	28.36
OK	34.60	43.76
PK	20.21	13.20
KK	28.36	14.68
Matrix	Correction	ZAF
Element	***Wt%***	***At%***
BK	35.51	50.45
CK	10.66	13.63
OK	23.75	22.80
PK	12.70	06.30
KK	17.38	06.83
Matrix	Correction	ZAF

3.2 FT-IR Spectral Studies

The FTIR recorded spectrum is given in Fig 3. Based on the chemical structure of KDP and boric acid the frequency assignment have been made to establish the functional groups present in the grown crystal. The broad band which appears in the range 3712 to 2439 cm^{-1} is due to free O-H stretching of KDP [12]. It is seen that these are very weak bonds. The peak at 2762cm^{-1} is due to P-O-H asymmetric stretching. The strong intensity band at 2439cm^{-1} is due to one of the P-O-H bending of KDP. The intense bands observed at 544 and 433 cm^{-1} are due to P-OH deformation. The OH groups in the boric acid and boronic acids in the solid state absorb broadly near 3300- 3200 cm^{-1} due to bonded O-H stretch. In the spectra of boric acid the peak at 3280 cm^{-1} is therefore assigned to the B-OH stretching. The peaks from B-O-H bending, B-O stretching all occurs in the 700-1000 cm^{-1} region [13]. In aqueous solution, the movement of H around the O atom of Boric acid is essentially unconstrained. Therefore for free boric acid the trigonal planar (YX_3) molecule has D_{3h} symmetry and should have one IR active peak in the range 1500-1300 cm^{-1} for the asymmetric B-O stretching or weakly IR active symmetric stretching band at 1100-950 cm^{-1}[14]. In the spectra of boric acid, the contribution from in plane B-O-H bending is excepted to be in the range 1300-1000 cm^{-1}, and out of plane bending at 850-700 cm^{-1} [15]. So , the peak at 1027 cm^{-1} and 618 cm^{-1} is assigned to the in plane bending and out of plane B-O-H bending respectively. There are a total of three B-O vibrations and as a free borate anion, the molecule has one broad asymmetric stretching band at approximately 950 cm^{-1} [16-17]. Therefore the peak at 932 cm^{-1} is due to asymmetric B-O stretching.

In order to analyze qualitatively the presence of the constituent elements in the crystal the FTIR spectrum has been recorded for the boron doped Potassium dihydrogen phosphate single crystal. It is seen that the spectrum of boron doped KDP, retains essentially the major peaks as observed in KDP, except for a slight change in frequencies and their intensity. The cluster of peaks observed in the range 3900- 2700 cm^{-1} is the leading evidence for the presence of boron in the KDP grown crystal, It is observed in the spectrum of Boric acid the bands in the range 3300-3200 cm^{-1} is due to the bonded B-OH stretching. These peaks are found to be present in the spectrum of boron doped KDP confirming the presence of the element boron in the as grown crystal. A detailed assignment of the frequencies observed in the FTIR spectrum is given Table 1.

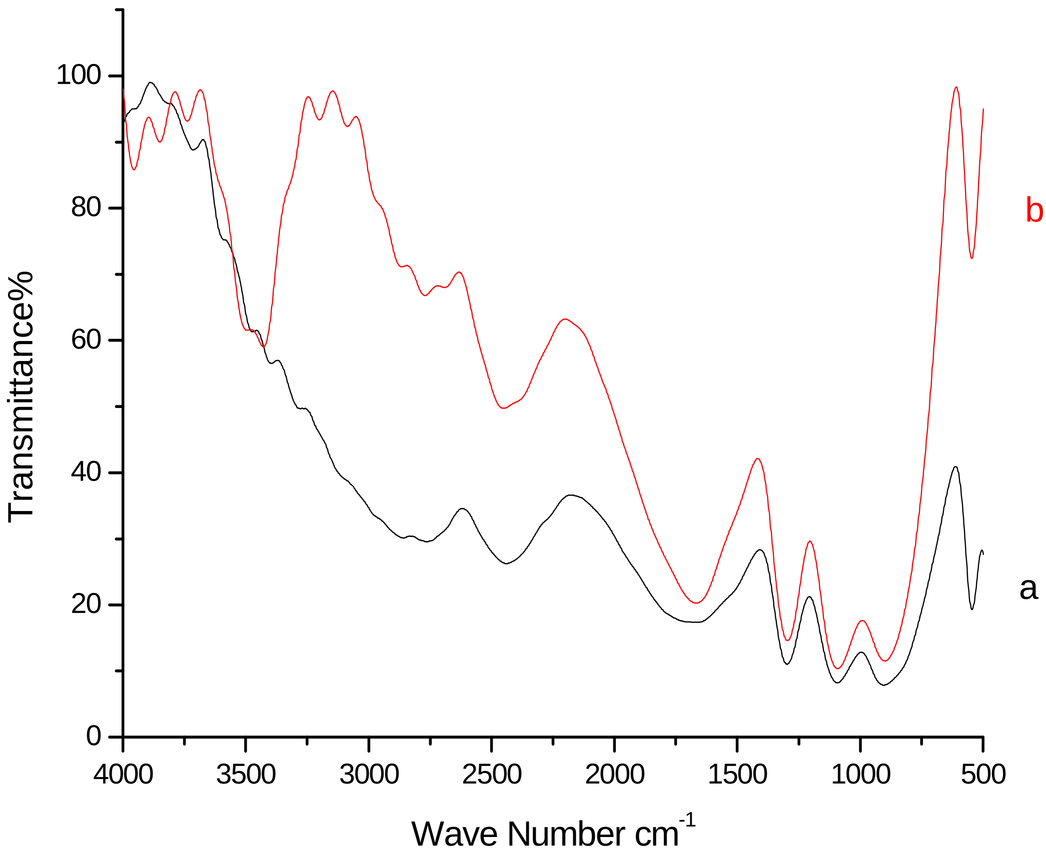

Fig.3. FT-IR Spectrum of (a) Pure KDP and (b) boron doped KDP crystal.

Table .1.Observed FT-IR frequencies (cm^{-1}) and Intensities of Pure KDP and boron doped KDP

Observed FT-IR frequencies (cm^{-1}) and Intensities		Assignments
Pure KDP	Boron Doped KDP	
3712 VW	3739 VW	Free O-H Stretching hydrogen bonded of KDP
-	3430 M	O-H Stretching hydrogen bonded of KDP
-	3202V W	B-OH Stretching
-	3088 VW	B-OH Stretching
2762 S	2772 W	P-O-H asymmetric stretching
2439 S	2453 M	P-O-H bending of KDP
1670 VS	1669 S	Asymmetric B-O Stretching
1297 VS	1297 VS	P-O stretching of KDP
1092 VS	1093 VS	P-O stretching
904 VS	901 VS	P-O-H stretching of KDP
544 VS	548 W	HO-P-OH bending
433 VS	435 VW	Torsional Oscillation

VS-very strong S- strong M-medium W-weak VW-very weak

3.3 X-Ray Diffraction Study

Single crystal x-ray diffraction studies were performed on grown crystals to identify the structural parameters and degree of crystal perfection. From the collected data, it is observed that from the cell parameters of both pure KDP and boron doped KDP belong to tetragonal crystal system [$\alpha = \beta = \gamma$ =90°;]; [a=b≠c] are tetragonal. The lattice parameter values of pure KDP are a=7.45 Å , b=7.45 Å, c= 6.97 Å, α=β=γ=90° and volume=387 $Å^3$. The lattice parameter values of doped KDP are a=7.42 Å, b=7.42 Å, c= 6.92 Å, α=β=γ=90° and volume=381 $Å^3$. It belongs to I-42d space group. The structural data for pure KDP and doped KDP crystals are presented in Table 2. The results are shown in Fig.4. It is seen that the x-ray pattern is almost similar indicating that the presence of boron has not affected the crystalline nature of the sample.

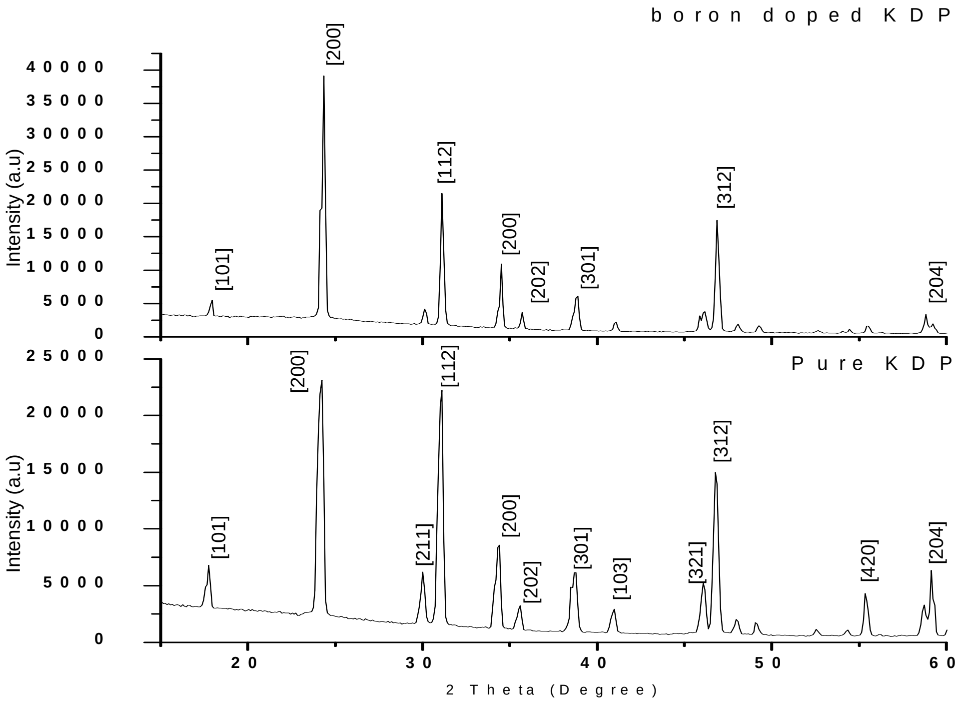

Fig.4. Powder XRD of Pure KDP and boron doped KDP

Table.2. Unit cell parameter values of Pure KDP and boron doped KDP

Sample	Lattice parameter a=b, c (Å)		Cell volume ($Å^3$)	α=β=γ	Structure
Pure KDP	7.45	6.97	387	90°	Tetragonal
Boron doped KDP	7.42	6.92	381	90°	Tetragonal

3.4 UV-Visible Spectroscopy

The optical properties of a material are important, as they provide information on the electronic band structure, localized state and types of optical transitions. Pure and boron doped KDP crystals plates with a thickness of 2mm without antireflection coating were cut and used for optical measurement. From the spectrum, Fig.5 it is observed that both the pure and boron doped KDP crystals show little absorbance in the entire visible region.

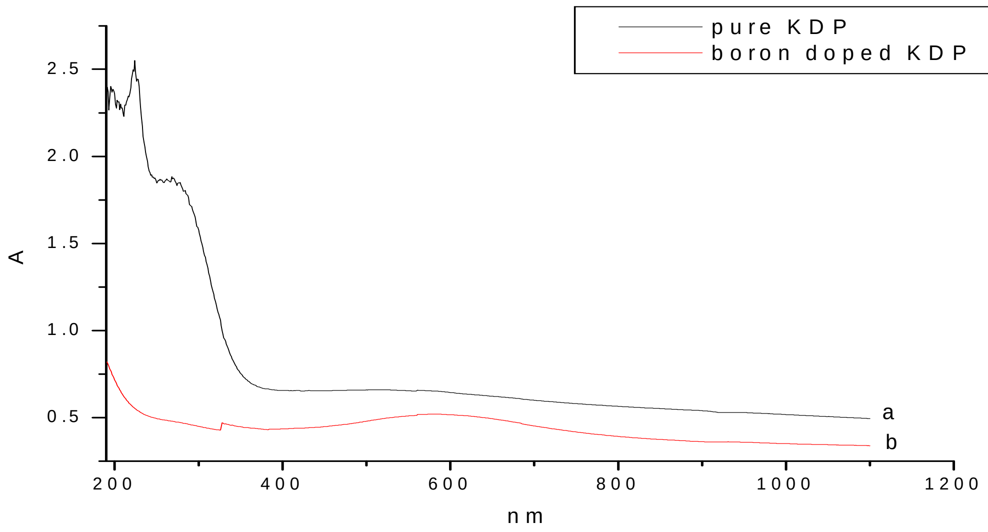

Fig.5. UV-VIS Spectra of (a) Pure KDP and (b) boron doped KDP crystal

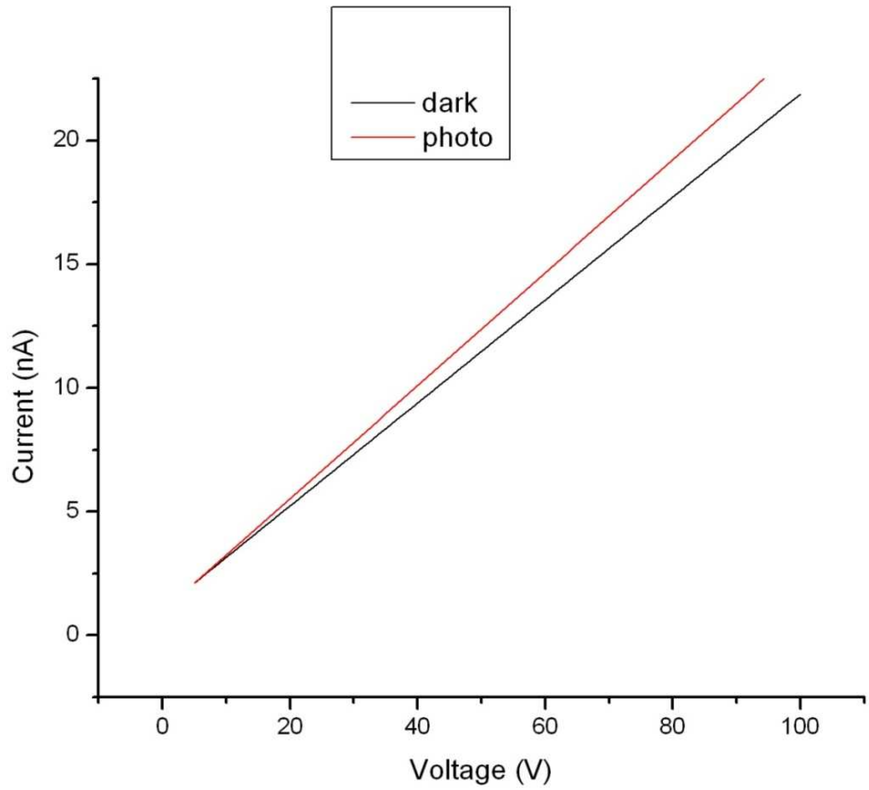

Fig.6. Variation of dark and photo current with applied field for boron doped KDP

The addition of boron seems to have increased the crystalline perfection in KDP thereby resulting in lesser absorbance when compared to pure KDP. The cut off wavelength is around (~220nm) for pure and doped KDP crystals. The UV-Vis data reveals that boron additives improve the optical transparency of the crystal and confirm the betterment of optical quality.

3.5 Photoconductivity

The Photoconductivity experiment was performed at room temperature. Dark conductivity of the sample was studied by connecting the sample in series to a DC power supply and a picoammeter. Electrical contacts were made at a spacing of about 1.5mm on the samples using silver paint.

The DC input was increased from 20 to 100V in steps and the corresponding dark currents were noted. For measuring the photocurrent, the sample was illuminated with a halogen lamp (100W) by focusing a spot of light on the sample with the help of a convex lens. The DC input was increased in the same range as done in the previous case and the corresponding photocurrent was measured. The variations of photocurrent (Ip) and dark current (Id) with applied field are shown in Fig.6. Both the photo and dark current of boron doped KDP crystal increase linearly with applied field. It is observed from the plot that the dark current is less than the photocurrent, thus implying that boron doped KDP exhibits positive photoconductivity. This phenomenon can be attributed to generation of mobile charge carriers caused by the absorption of photons [18].

3.6 Kurtz and Perry powder SHG test

Kurtz second harmonic efficiency test (SHG) is performed for the comprehensive analysis of second order nonlinearity. The non-linear optical property of the grown samples of KDP and boron doped KDP is determined. In the present work, a single shot mode of 8 ns laser with a spot radius of 1 mm was used. The experimental set up used a mirror and 50/50 beam splitter, to generate a beam with pulse energy of 0.68 Joules. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The second harmonic output was generated from the irradiated powder sample of doped KDP by a pulsed laser beam. The light emitted by the sample was detected by photodiode detector and oscilloscope assembly. The relative conversion efficiency was calculated from the output power of boron doped KDP crystals with reference to pure KDP crystal output power. When a laser input of 0.68 Joules was passed through pure and doped KDP, It is found that the output power is 2.8 mJ and 3.4mJ respectively. Thus the SHG efficiency of the boron doped KDP crystal is nearly 1.2 times than that of pure KDP.

CONCLUSION

Optical quality, colorless and transparent single crystals of pure and 0.1mol% boric acid added KDP were grown employing slow evaporation solution growth technique. EDAX studies confirm the presence of boron in the lattice of the crystal. The FT-IR and FT-Raman spectral studies confirm the presence of all the functional groups and also the presence of boron in the grown crystal. Single crystal X-ray diffraction studies reveal that the tetragonal structure of KDP is preserved and that the lattice parameters of boron doped KDP crystal is slightly changed due to the addition of boron. The optical transmission spectrum shows good transmission in the entire visible region for both the crystals with higher transmission for the boron added KDP crystal. TGA analysis reveals the different stages of decomposition. The thermal stability of the doped crystals is found to be improved due to presence of boron. Photoconductivity studies show that doped KDP crystal exhibits positive photoconductivity. The SHG efficiency of boron doped KDP is 1.2 times greater than that of pure KDP. This result indicates that the grown crystals are useful for NLO device application and the moderate SHG efficiency make boron doped KDP a potential candidate material for photonics device fabrication.

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