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Enhancement of Optical, Thermal and Hardness in KDP crystals by Boron Doping

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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 unit cell dimensions are recorded by single crystal X ray diffraction. The crystalline nature of the grown crystal is verified by powder x-ray diffraction studies. The presence of the functional groups has been identified by both Fourier transform infrared and FT-Raman spectrum. The optical nature of the grown crystal is analyzed using the UV-Vis spectrum. The temperature stability of the crystal has been confirmed by TGA. The hardness of the crystal has been determined.
KeyWords : Slow Evaporation, Doping, Boron, Optical transmission , EDAX, Hardness, FT-IR, Thermal analysis.

1. 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 [9-10]. 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.

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 x 4 mm^3 were harvested. The photographs of the as grown crystal of boron doped KDP along with the pure KDP crystal is shown in Fig.1 and Fig.2 respectively. It is observed that the transparency of the doped crystal has improved, the as grown crystals have well defined faces and the morphology is shown in Fig 3. The

morphology reveals that the growth rate is more along the crystallographic 'a' axis.

3. Characterization Studies

3.1 FT-IR and FT-Raman Spectral Studies

The Fourier transform infrared spectrum of pure KDP and boron doped Potassium dihydrogen phosphate (KDP) crystals were recorded using Perkin Elmer model RXI Spectrometer in the range 400-4000cm^{-1} by KBr pellet technique. The recorded spectrum is given in Fig 4. The Raman spectrum was recorded using Bruker RFS 27 FT-Raman Spectrometer in the range 50-5000 cm^{-1}. A laser source working at 532nm with an average power of 63.02mW was used during the experiment. The spectrum recoded is shown in Fig 5.

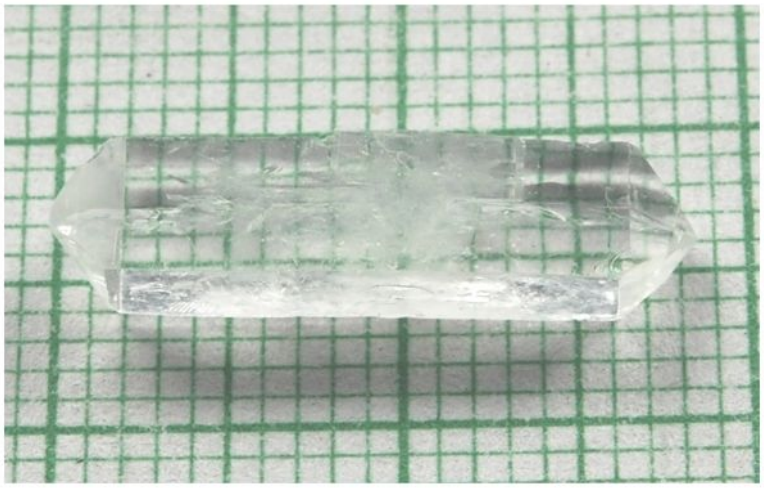

Fig.1. Photograph of the grown Pure KDP

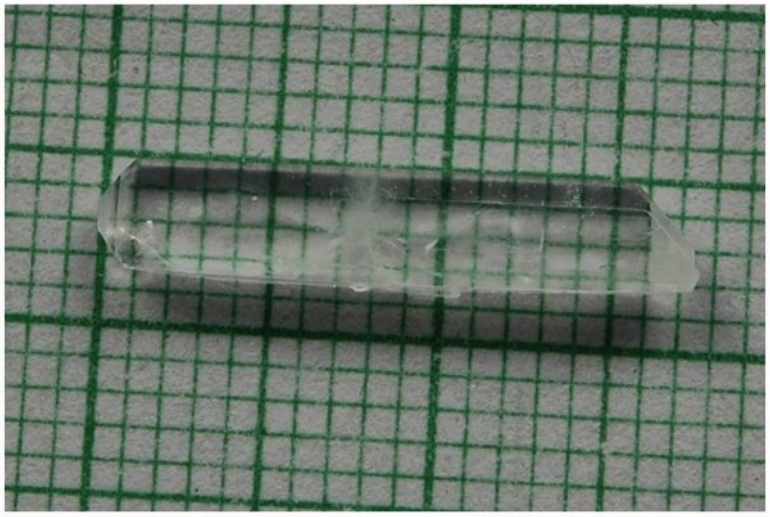

Fig.2. Photograph of the as grown boron doped KDP Crystal

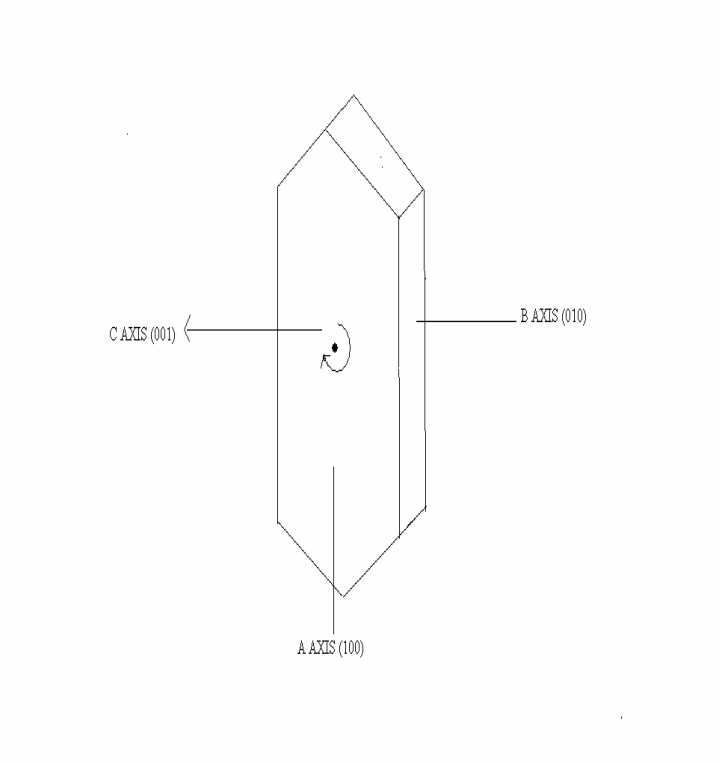

Fig.3. The Morphology of boron doped KDP crystal

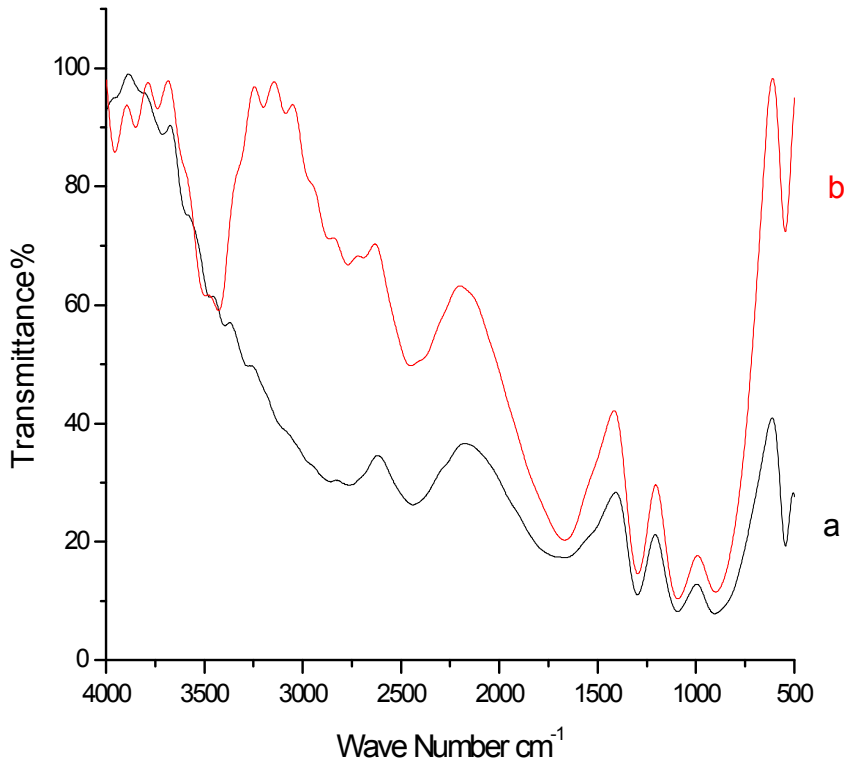

Fig.4. FT-IR Spectrum of (a) Pure KDP and (b) boron doped KDP crystal

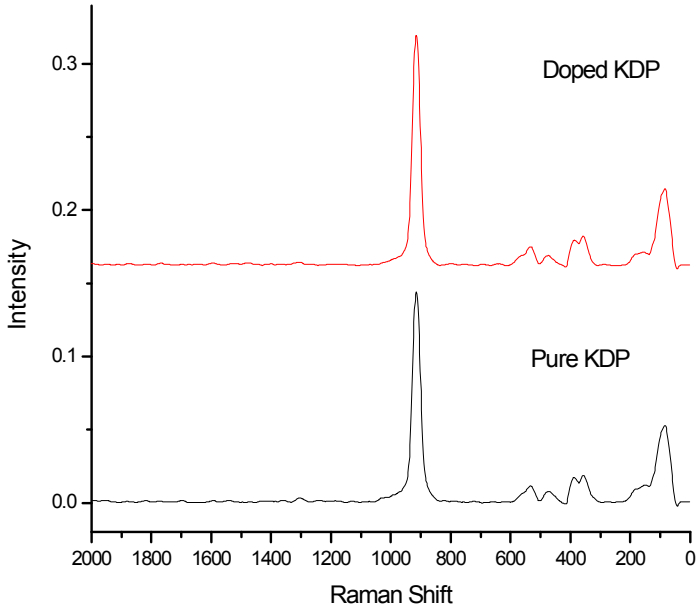

Fig. 5. FT-RAMAN Spectrum of Pure KDP and (b) boron doped KDP crystal

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 [11]. 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 occur in the 700-1000 cm^{-1} region [12]. 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} [13]. 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} [14]. 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}.[15-16] 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. Also in the recorded Raman spectrum a peak of moderate intensity is observed at 2129 cm^{-1} which is definitely related to B-O bond. Raman spectrum shows an additional peak at 914cm^{-1}.This is attributed to P-O-H stretching of KDP. From the comparative study on the FTIR spectrum of pure KDP and Boron doped KDP, clearly indicate the effect of dopant, which has led to the change in the intensity of absorption of IR frequencies and a slight shift in some of the frequencies. A detailed assignment of the frequencies observed in the FTIR spectrum is given Table 1.

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

3.2 EDAX

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 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 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[18]. The recorded EDAX spectrum is shown in Fig**,** 6 and Fig, 7. The observed weight percentage of elements in the pure KDP and boron doped KDP crystals are given.

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. 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. From the collected data, it is observed that from the cell parameters of both KDP and boron doped KDP belong to tetragonal crystal system. It belongs to I-42d space group. The structural data for pure KDP and doped KDP crystals are presented in Table 2. The powder x-ray diffraction also has been recorded for pure and doped KDP using Bruker-35kV Copper K-alpha Radiation and the results are shown in Fig. 8. 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.

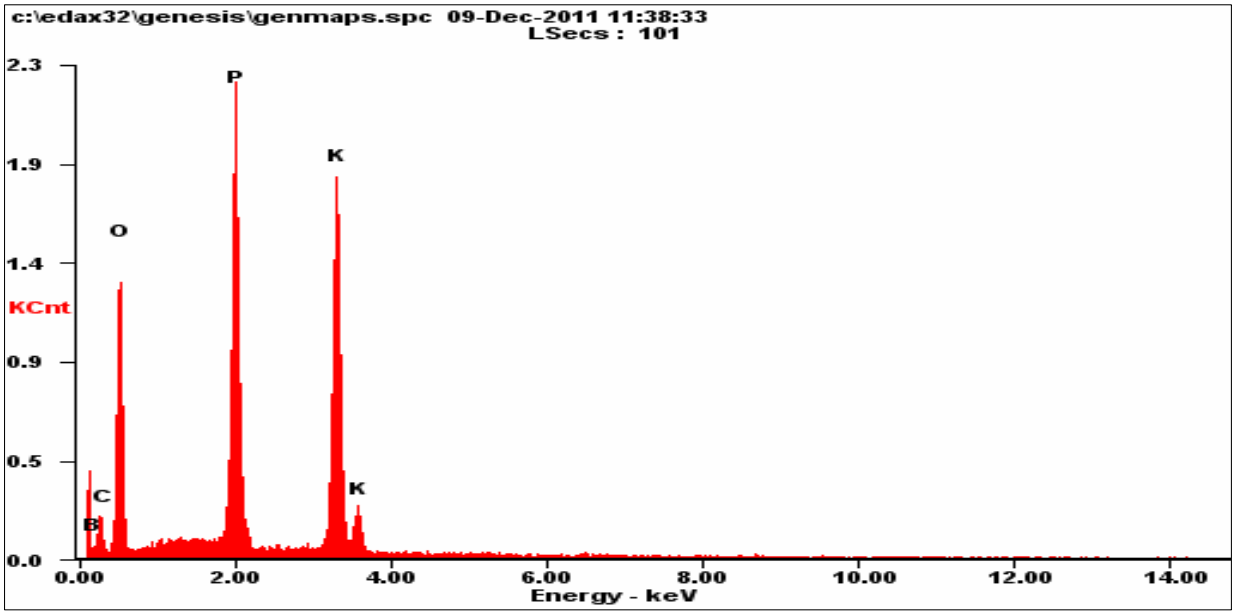

Fig.6. EDX of

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

Pure KDP Crystal

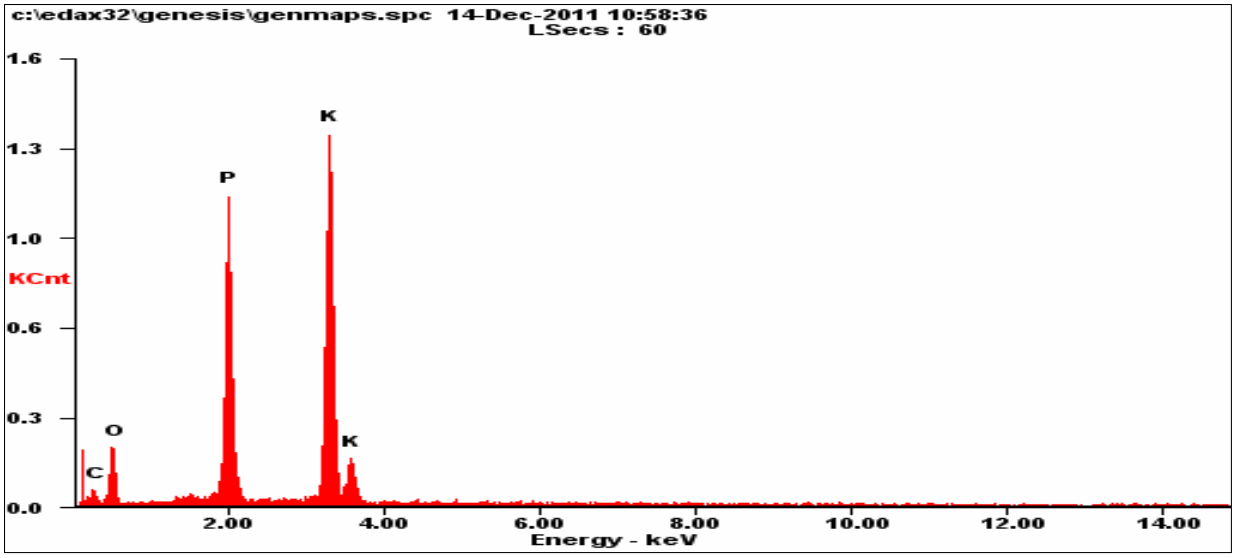

Fig.7. EDX of doped KDP Crystal

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

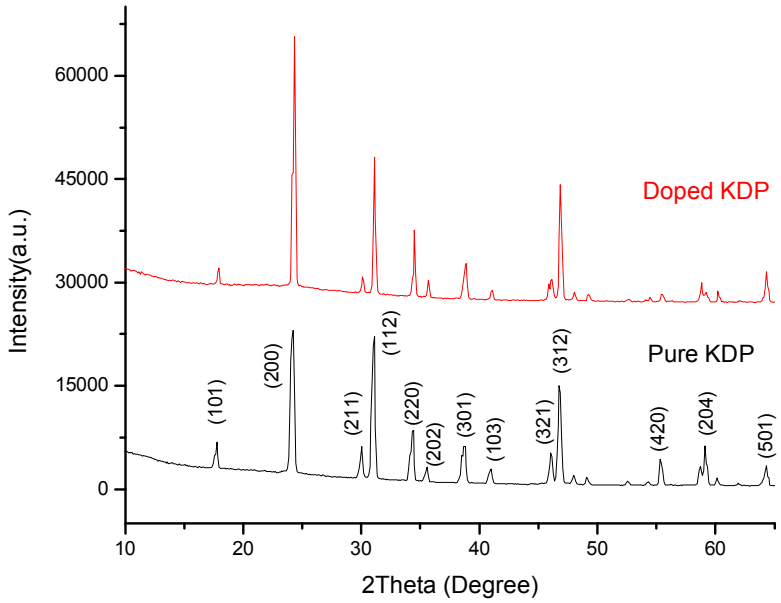

Fig.8. Powder XRD of Pure KDP and Doped KDP

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. The UV-Visible transmission spectrum was recorded using Perkin Elmer Model-Lambda 35 spectrometer in the range 190nm to 1100nm. From the spectrum, Fig.9 it is observed that both the pure and boron doped KDP crystals show little absorbance in the entire visible region. 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 Microhardness Study

Hardness test is useful to find the mechanical hardness of the crystal and to estimate the threshold mechanical stress. Vicker's hardness measurement of pure KDP and Boron doped KDP crystals were noted by applying loads of 25g, 50g and 100g for an indentation time of 7sec, for each trial. Repeated trials were performed to ascertain the correctness of the observed results. The collected data is presented in Table 3. The Vickers's microhardness number (H_v) was calculated using the relation $Hv=1.8544\ P/d^2$ (kg/mm^2), where P is the indenter load in kg and d is the diagonal length of the impression in mm. The plot of Vickers hardness versus load for the pure KDP and boron doped KDP crystals are shown in Fig.10.

From the fig. it is seen that the hardness value of the doped KDP crystal is higher than the hardness of the pure KDP crystal. The addition of boron increases the hardness of the crystal. Microhardness value of the pure KDP crystal increases with doping of boron. This is because of the incorporation of the boron ions into superficial crystal lattice and removing defect centers which reduce the weak lattice stresses on the surface.[17].

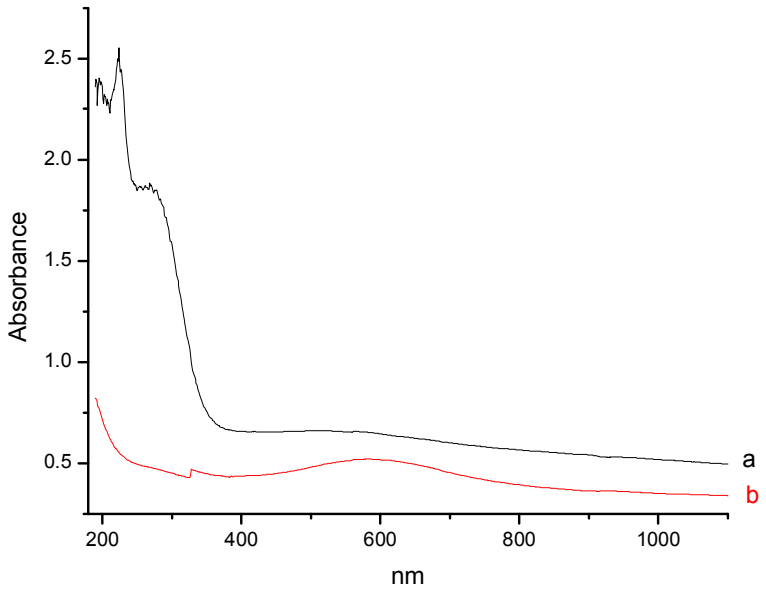

Fig.9. UV-VIS Spectra of (a) Pure KDP and (b) boron doped KDP crystal

Table.3. Microhardness values of Pure KDP and boron doped KDP

Sample	Load (gm)		
	25gm	50gm	100gm
Pure KDP	52.1	77.2	94.6
Boron doped KDP	62.7	82.3	98.4

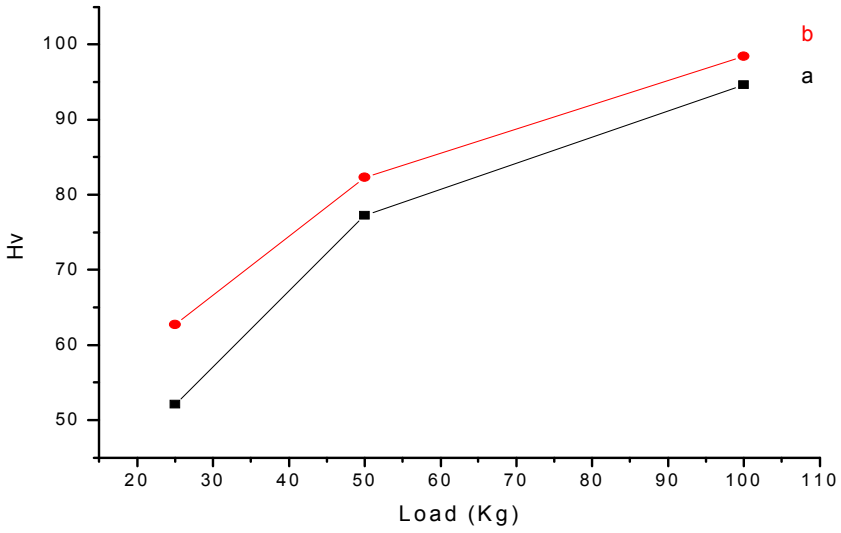

Fig.10. Plot for Vickers Hardness of (a) Pure KDP and (b) boron doped KDP crystal

3.6 Thermal analysis

The thermal analysis of the boron doped KDP and pure KDP crystals were recorded on Perkin Elmer TGA7 at a heating rate of 20° C/min under nitrogen atmosphere to determine the thermal stability of the crystal.

The recorded TGA curve of pure KDP exhibits negligible weight loss in the region 40˚C to 200˚C as shown in Fig.11. The decomposition of pure KDP crystals begins at 230°C and terminates at 350˚C. The weight loss starts due to the liberation of volatile substances, probably water molecule of decomposed KDP. The TGA curve for boron doped KDP crystal is given in Fig.12.The experimental results show that the initial weight loss starts at about 250˚C and ends at 390°C with about 12% weight loss, which is possibly due to the decomposition of KDP and remaining boron. It is observed that the crystal of pure KDP is stable upto 350 ˚C whereas in boron doped KDP crystal the thermal stability is slightly increased 370 ˚C .This study confirms the increase in the thermal stability of doped KDP crystal. Thus the thermal stability of the crystal has improved due to the presence of the dopant boron.

3.7 SEM Studies

The morphology of the crystallites grown in the pure KDP and boron doped KDP crystals is observed from the scanning electron microscope (SEM) studies done using JSM – 6700F. It can be confirmed by SEM images of KDP, that the growth conditions are unconstrained and the crystallites obtained are on the whole and as seen in Fig.13. KDP crystallites are seen have much bigger planes. Due to the different atom interaction among additives, in boron doped KDP the effect of boron on the crystal morphology influences the volume of crystallites. Consequently the dopant boron affects the expanded capacity of crystallographic plane resulting in numerous crystallites as seen in Fig 14.

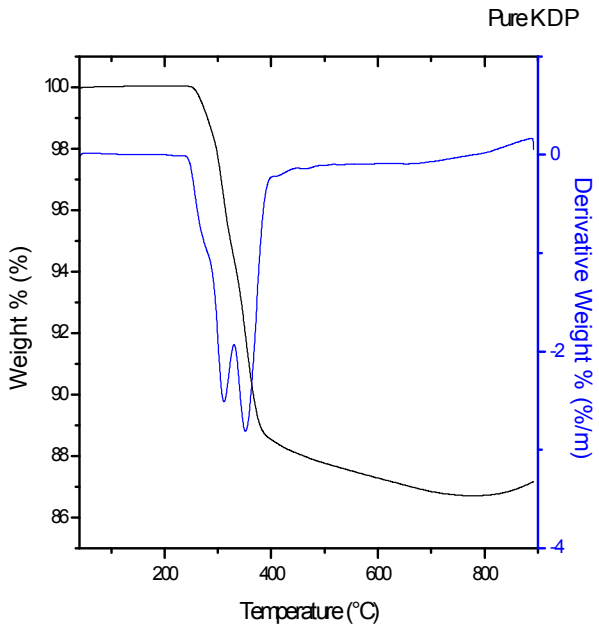

Fig.11. Thermo-gravimetric curve of Pure KDP

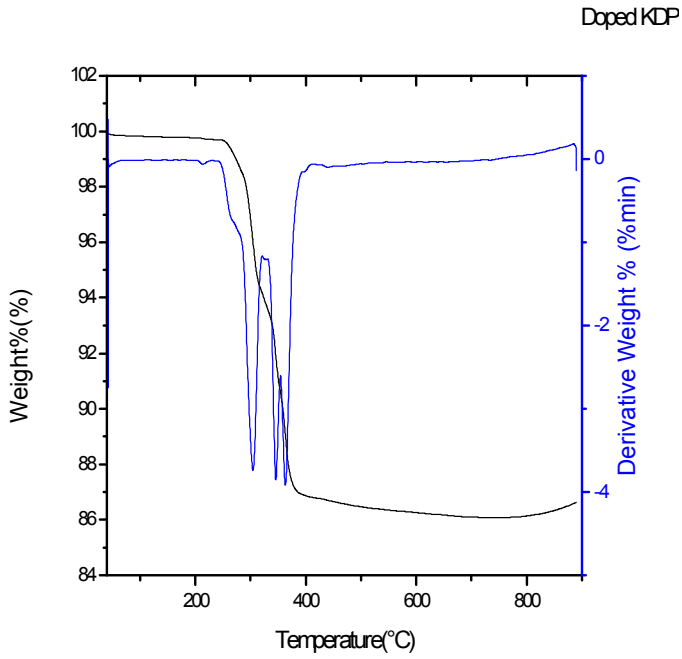

Fig.12. Thermo-gravimetric curve of boron doped KDP crystal

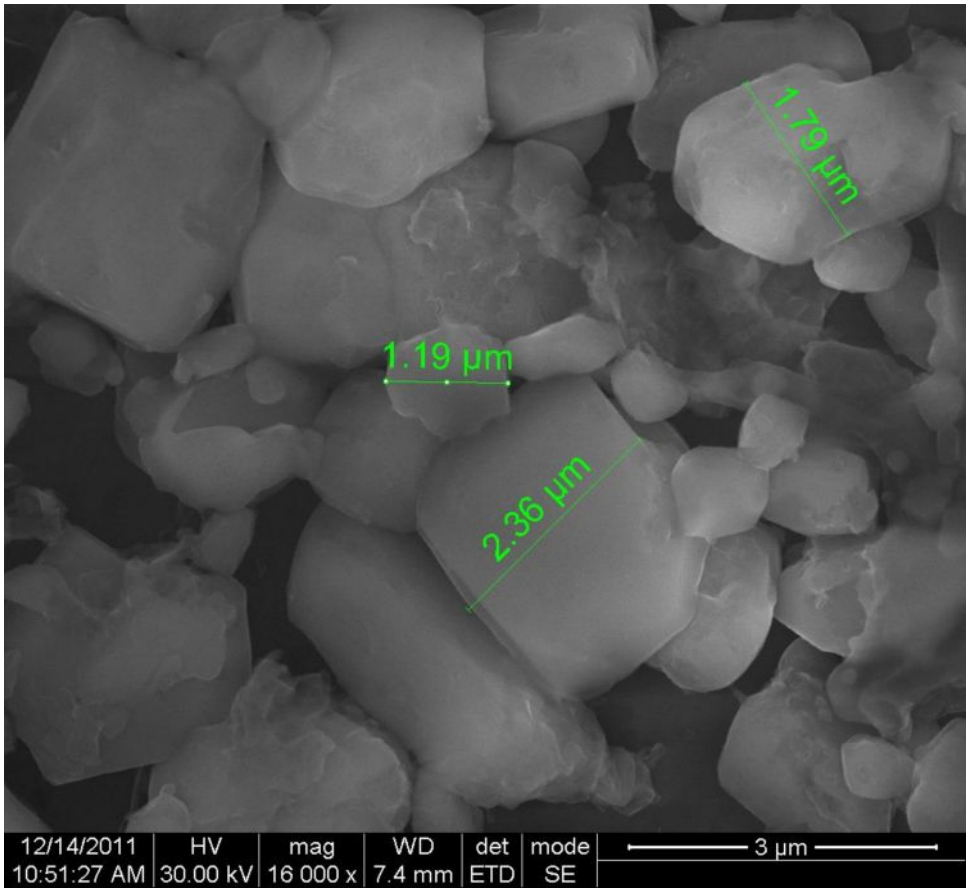

Fig.13 SEM Image of Pure KDP

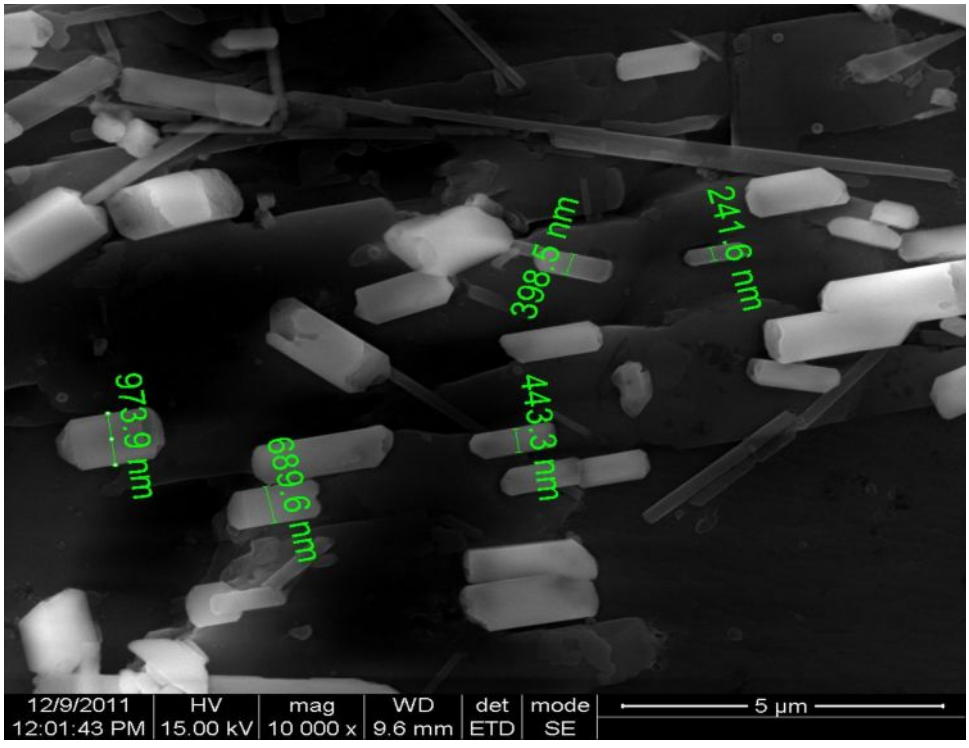

Fig.14 SEM Image of boron doped KDP

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. 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 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. 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. The microhardness values of doped KDP crystals are found to be increased by the presence of the dopant boron. This result indicates that the grown crystals are useful for device application.

References

[1] J.Podder,,Journal of Crystal Growth,237-239,70 (2002).
[2] Sonal S. Gupte, Ranjit D.Pradhan, J.Appl.Phys.91, 3125(2002).
[3] Shukin Lin ,Liting Li,J.Cryst. Growth, 249,341 (2003).
[4]Tiffany N.Thomas, Terry A Land, Michael Johnson, William H Casey, Journal of Colloid and interace Science 280, 18-26(2004).
[5] H.F.Robey, J. Crystal Growth 259, 388-403(2003).
[6] H.V. Alexandru, S.Antohe, J.Crystal Growth 258, 149-157(2003).
[7]H.M. Muncheryan, *Lasers and Opto-electronic Devices*, Hemisphere Pub.Co, New York 1991.
[8] Y.R. Shen, *The Principles of the Nonlinear Optics*, Wiley, New York 1984.
[9] P. Meystrey, M. Sargent II, *Elements of Quantum Optics*, Springer-Verlag, Berlin 1991.
[10] Jun-Ichi Sakai, *Phase Conjugate Optics*, McGraw Hill, Inc., New York, London 1992.
[11] P. Santhana Raghavan, P. Ramasamy, *Recent Trends in Crystal Growth*, Pinsa 68, New Delhi 2002, p.235.
[12]Goldberg S. and Johnston C. T. (2001) Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling. *J. Colloid Inter - face Sci.* 234, 204-216.
[13]Keren R. and Bigham F.T. (1982) Effect of exchangeable ions and ionic strength on boron adsorption by montmorillonite and illite. *Clays Clay Miner.* 30, 341-346.
[14]Keren R. and Bigham F.T. (1985) Boron in water, soils, and plants. In *Advances in Soil Science.* (Stewart B. E., ed) Springer-Verlag. 229-276.
[15]Keren R. and Sparks D.L. (1994) Effect of pH and ionic strength on boron adsorption by pyrophytllite. *Soil Sci. Soc. Am. J.* 58, 1095-110.
[16]McBride M. B. (1997) A critique of diffuse double layer models applied to colloid and surface chemistry. Clays Clay Miner. 45(4), 598-608.
[17]Sun,X.; Xu,X. G.; Sun,D.L.; Wang,Z.P.; Wang ,S.L.;Fu, Y.J.; Zeng, H.; Li,Y.p.; Yu,X.L.; Gao,Z.S.J.Cryst.Growth 2001,226,529-533.

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