International Journal of Luminescence and applications
Vol7 (1) April, 2017, **ISSN 2277 – 6362**

Comparative Study of Praseodymium doped KDP Single Crystals grown by different techniques

Roopa V[1] and R.Ananda Kumari[2]
[1,2] Sree Siddaganga Research Center, Sree Siddaganga College of Arts, Science and Commerce for Women, Tumkur, Karnataka, India.
Corresponding author: roopanaveen20@gmail.com
+91 9448111613

Abstract

Praseodymium doped Potassium dihydrogen Orthophosphate (KDP) single crystals were grown by different techniques - SR method, Seed Rotation and Slow Evaporation with the vision to improve the properties of the crystal. The objective of this study is to show how the dopant Praseodymium influences the growth, morphology and characteristics of KDP crystal. The crystal size grown by SR method on unidirectional {101} pyramidal face was around 150 mm in length and 16 mm in diameter. The Chemical composition of the grown crystals is confirmed by EDAX Analysis. The grown crystals are subjected to PXRD analysis using XrdwinPD 4-dectris computer based diffractometer with a characteristic Cu Kα (1.540598) radiations from 10^0 to 60^0 at a scan rate of 10^0/min, confirm the crystalline nature and shifts in peak positions due to doping is observed. Using Scherer's equation crystallite size has been calculated. Solubility of crystals grown by slow evaporation technique is determined using water as a solvent. The SHG efficiency is determined by Kurtz powder technique. It is found that relative SHG conversion efficiency of crystal grown by SR method is greater compared to other techniques. Optical transmission spectra are recorded for the crystals in the wavelength region 200 to 1100nm using Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. It is found that percentage transmission of crystals grown by SR method is more as compared to other techniques. The electronic band transitions is studied from the plot of $(\alpha h\nu)^2$ versus photon energy (hv) and the band gap energy has been calculated. The addition of Praseodymium improves the quality and transparency of crystals, which shows the suitability of the ingot for optical applications.

Keywords: *Crystal growth, SR method, SHG, Optical properties.*

1. INTRODUCTION

With the advanced research approach on efficient nonlinear optical material (NLO) is intensively studied for various optical device applications. Potassium dihydrogen orthophosphate (KDP) is a best known NLO material and has been used for second harmonic generation for high pulse energy, laser frequency conversion, low repetition (<100 Hz) rate lasers, electro-optical modulation and Q-switching applications [1-3]. As a result, significant efforts have been made to find novel and efficient NLO materials.

The Study of the crystallization behavior of KDP and the factors influencing its structural properties is still of great interest. The most important factor which influences the growth rate, the surface morphology of crystal is impurities [4,5]. An impurity can suppress, enhance or stop the growth of crystal completely. Modern technical tasks like high power laser systems have a great demand for very large size crystals. The use of special additives is an effective way to accelerate the growth rate. The beneficial effect of additives on the growth process and properties of crystals has been applied in recent years [6-8].

The most efficient additives are reagents with metal ions that have the same properties as that of bulk solutions which can change the properties of solution such as viscosity, surface tension, etc. without deteriorating the optical qualities of crystals. Hence Praseodymium is selected as additive in the KDP solution and doped KDP crystals were grown from the aqueous solution with seed rotation, SR method and slow evaporation technique and the grown crystals are subjected to different characterizations like powder X-ray diffraction, optical transmission, EDAX and second harmonic generation efficiency studies.

2. EXPERIMENTAL: CRYSTAL GROWTH

Good quality crystals of pure and Praseodymium doped KDP were grown by slow evaporation technique as shown in Fig 1(a). A volume of 200ml of water was taken in a beaker and known quantity of the material was added till it attains saturation for temperatures. Sankaranarayanan-Ramasamy (SR) method was employed to grow the bulk size of Praseodymium doped KDP single crystals. The apparatus consists of glass container of size 30x30x30 cm^3

and ampoule of inner diameter 10mm using two ring heaters. A suitable seed crystal grown by slow evaporation technique having a size of 4x4x3 mm^3 with <101> direction was selected for unidirectional crystal growth. The ampoule was kept in the glass water bath to maintain constant ambient temperature. Super Saturated solution was poured carefully into the ampoule without disturbing the seed crystal. The ring heaters are positioned one at the top and another at the bottom of the growth ampoule. The growth was initiated with a suitable temperature provided by the ring heater at the top region of the saturated solution under equilibrium condition. The temperature difference between the top and bottom ring heaters of the growth ampoule was carefully maintained to control the nucleation. In the present work, the temperature around the top and bottom of the ampoule was maintained at 32ºC and 27ºC respectively. Under this condition highly transparent crystal growth was seen after 10 days. After three months of the growth duration, a good quality crystal was harvested with size 140 mm in length and 16 mm in diameter as shown in Fig.1(b). Finally, the ampoule was detached from the growth system and the grown crystal was carefully removed from the ampoule using diamond glass cutter.

Stirring the solution reduces the natural convection-induced temperature oscillations by homogenizing the bulk solution. Hence, the importance of optimum rates of rotation in crystal growth processes has gained recognition in the past decade [9]. The two most widely used stirring mechanisms are the rotation of the seed and/or the rotation of the crystallizer. In the present work, KDP crystals doped with Praseodymium were grown from aqueous solution by continuously rotating the growing crystal at 40 rpm. This apparatus consists of a seed rotation controller coupled with a stepper motor which is controlled by using a microcontroller based drive. This controller rotates the seed holder in the crystallizer. The seed crystals mounted on the center of the platform made up of acrylic material and is fixed into the crystallizer. The seed mount platform mix the solution very well and makes the solution more stable, which resulted in better crystal quality.The aqueous solutions at the saturation temperature 40ºC was filtered in a closed system to remove extraneous solid and colloidal particles. Then the solution was overheated at 50ºC for one day, to make the solution stable against spontaneous nucleation under a high supersaturation [10]. After overheating, the temperature of the solution was reduced slightly above the saturation point and seed crystals were mounted on the platform. From the saturation point, the temperature was decreased at 0.1ºC per day at the beginning of the growth. As the growth of the crystal progressed, the temperature rate was decreased. After reaching the room temperature, crystals was harvested. The grown crystals are shown in Fig.1(c).

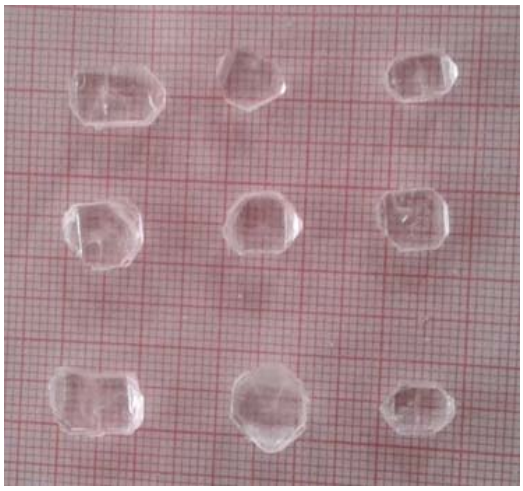

Fig. 1(a): Photograph of Praseodymium doped KDP crystals grown by Slow Evaporation technique

Fig. 1(b): Photograph of Praseodymium doped KDP crystals grown by SR method

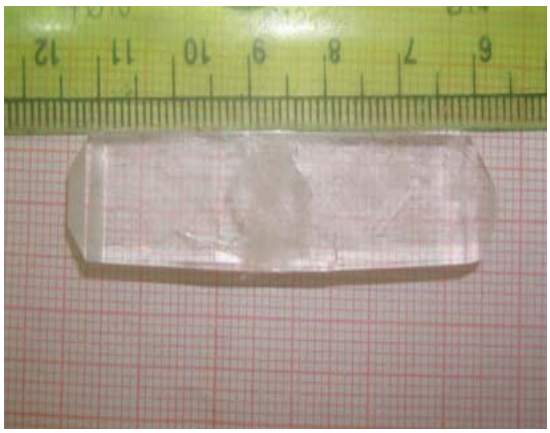

Fig. 1(c): Photograph of Praseodymium doped KDP crystals grown by Seed Rotation technique

3. RESULTS AND DISCUSSION

3.1DETERMINATION OF SOLUBILITY

The Solubility studies were carried out in a constant temperature water bath (CTB). The Solution was stirred continuously for 6 hours to achieve stabilization using an immersible magnetic stirrer. Solubility was determined by gravimetric analysis for different temperatures (25-50^{0}C). The Solubility curve of pure KDP & Praseodymium doped KDP crystals grown by slow evaporation technique is shown in Fig.2. It is observed from the solubility curve that the solubility of KDP doped Praseodymium increases with increase in the molar weight of KDP and has positive temperature co-efficient.

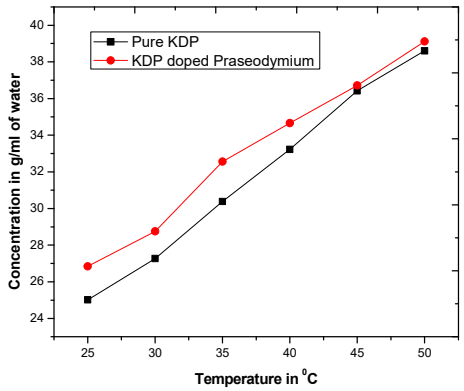

Fig 2. Solubility of grown crystals

3.2 EDAX ANALYSIS

In order to confirm the presence of the Praseodymium, the grown crystals was subjected to EDAX analysis. The EDAX spectra for KDP doped Praseodymium grown by Slow evaporation, Seed Rotation technique and SR method was recorded and analyzed. The spectrum shows the peaks of potassium, phosphate, oxygen, Nitrate and Praseodymium suggesting that the Praseodymium dopant has entered into the crystal lattice of KDP. The recorded spectrum for the grown crystals are shown in Fig. 3, 4 & 5. The Observed weight percentage of elements in the doped KDP crystal are given in the Table 1, 2 & 3.

Table 1. Shows the estimated Weight % of KDP doped Praseodymium Crystal (Slow Evaporation method)

Element	Weight %	Atom %
N	1.85	4.51
O	2.26	4.83
P	37.22	41.04
K	56.11	49.01
Pr	2.56	0.62
Total	100.00	100.00

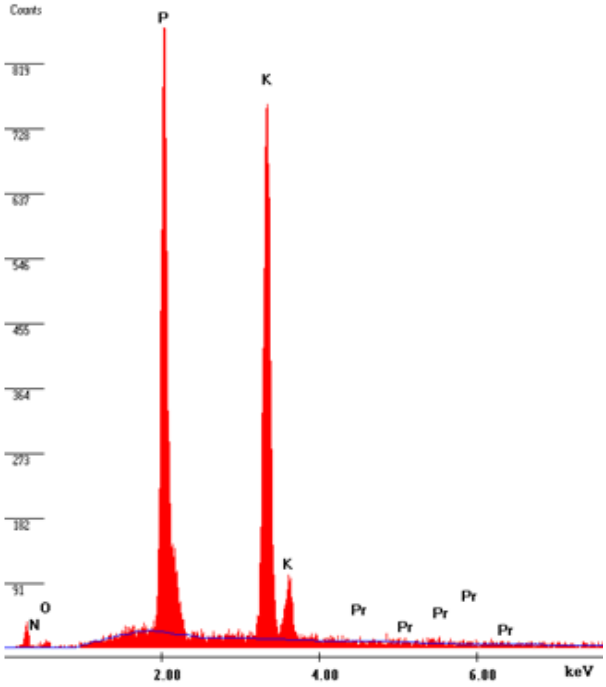

Fig. 3.EDAX Spectrum of Praseodymium-doped KDP crystals(Slow Evaporation)

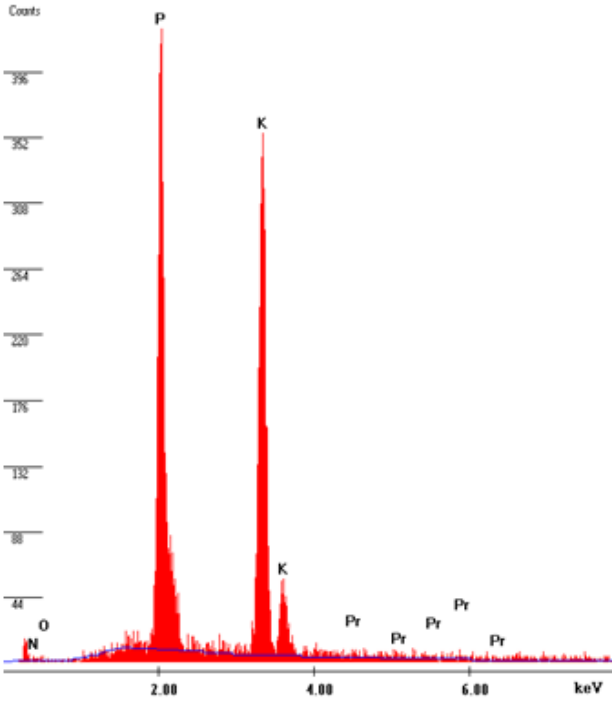

Fig. 4.EDAX Spectrum of Praseodymium-doped KDP crystals (Seed Rotation)

Table 2. Shows the estimated Weight % of KDP doped Praseodymium Crystal (Seed Rotation method)

Element	Weight %	Atom %
N	2.07	5.16
O	0.84	1.83
P	38.26	43.14
K	54.70	48.85
Pr	4.13	1.02
Total	100.00	100.00

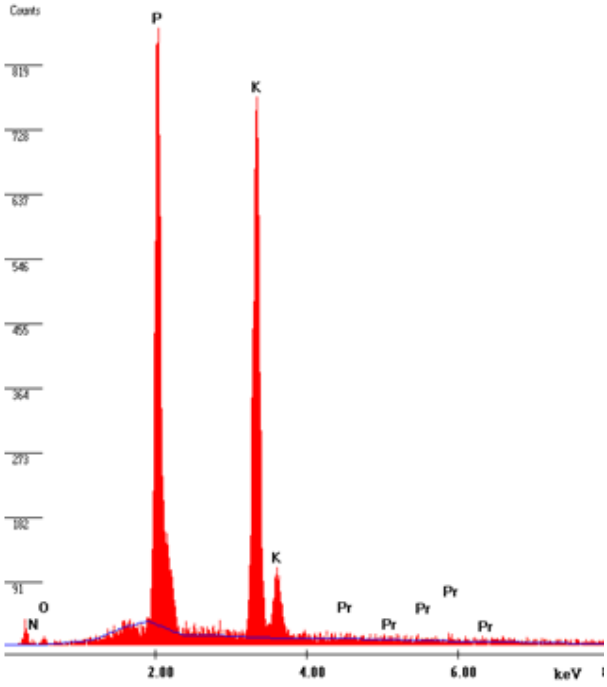

Fig. 5.EDAX Spectrum of Praseodymium-doped KDP crystals(SR method)

Table 3. Shows the estimated Weight % of KDP doped Praseodymium Crystal (SR method)

Element	Weight %	Atom %
N	1.85	4.55
O	1.66	3.58
P	37.70	41.90
K	55.97	49.28
Pr	2.81	0.69
Total	100.00	100.00

3.3 POWDER X-RAY DIFFRACTION STUDIES

Powder X-ray diffraction studies was performed on grown crystals to identify the phase formation and degree of crystal perfection. X-ray powder patterns of grown crystals was recorded using XrdwinPD 4-dectris computer based diffractometer with a characteristic Cu Kα (1.540598) radiations from 10^0 to 60^0 at a scan rate of 10^0/min. The Xrd pattern of the grown crystals are shown in Fig. 6.

The occurrence of sharp peaks at specific bragg's angle shows the crystallinity of the grown crystals. It is clear from the pattern that the entry of the dopant in the modified composition of KDP crystal lead to a change in the intensity of peaks when compared to the peaks of pure KDP crystals. Average crystallite size (D) was estimated using the following relation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where λ is wavelength of the X-ray radiation, β is full width at half maximum (FWHM) of diffraction peak (in rad), and θ is scattering angle. Further, the dislocation density (δ), Stacking fault (SF), and micro strain (ε) was estimated by the relation:

$$\delta = \frac{1}{D^2} \quad (2)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (3)$$

$$SF = \frac{2\pi^2}{\sqrt{3}tan\theta} \quad (4)$$

The obtained structural parameters were given in Table 4.Williamson and Hall (W-H) plots was used to estimate the micro strain in KDP doped Praseodymium crystal grown by different methods using the relation

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \quad (5)$$

where ε is strain associated with the crystal. Equation (5) represents a straight line between 4sinθ (X-axis) and βcosθ (Y-axis). The slope of line gives the strain (ε) and intercept (kλ/D) of this line on Y-axis gives grain size (D). Fig. 7. shows the W-H plots of grown crystals and the estimated strain values was shown in Table 4.

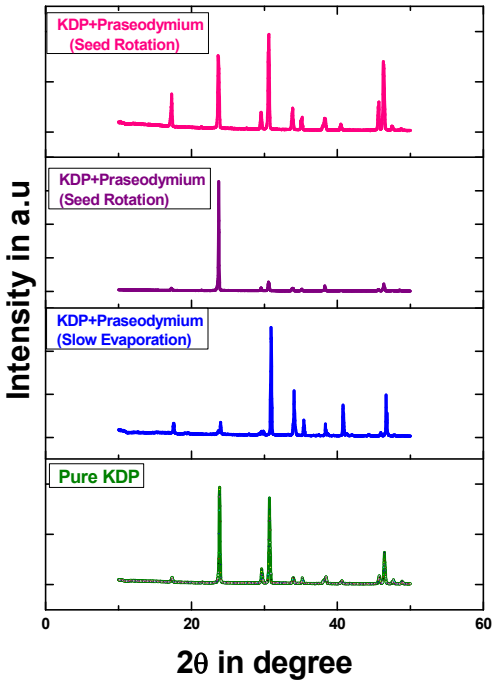

Fig 6. Xrd Pattern of grown crystal

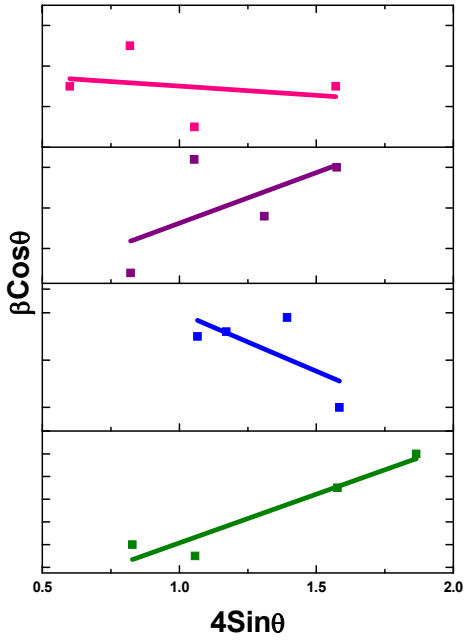

Fig 7. W-H plot of grown crystal

Table 4. Estimated crystalline size, strain, dislocation density and surface factor of grown crystals

Sample	Crystalline size (nm)		Strain	Stacking fault(SF)	Dislocation density $\delta(10^{14})m^{-2}$
	Scherer's formula	W-H plot			
Pure KDP	44.03	64.24	$8.55E^{-4}$	17.39	5.15
KDP+Pr (Slow Evaporation)	49.90	112.8	$1.28E^{-3}$	17.35	4.01
KDP+ Pr (Seed Rotation)	47.16	88.38	$1.24E^{-3}$	17.42	4.46
KDP+Pr (SR method)	36.30	34.77	$3.86E^{-4}$	17.42	7.58

3.4 UV-VISIBLE TRANSMISSION

Crystal plates of pure KDP and KDP doped Praseodymium crystals were cut and polished without any coating for optical measurements. The thickness of the crystals were around 1mm. Optical transmission spectra were recorded for the crystals in the wavelength region 200 - 1100 nm using Perkin-Elmer Lambda 35 UV-Vis spectrometer. The recorded UV-Vis spectrum is shown in the Figure 8. Good optical transmittance and lower cut off wavelength are very essential properties for nonlinear optical (NLO) crystals [11]. It is observed from the figure that the Pure KDP shows 45% of transmittance, KDP doped Praseodymium (Slow Evaporation method) shows 65% transmittance, KDP doped Praseodymium (Seed Rotation method) shows 70% of transmittance and KDP doped Praseodymium SR method) shows 85% of transmittance. The large transmission in the entire visible region enables it to be a good material for electro-optic and NLO applications. The above results indicate that the addition of Praseodymium to pure KDP increased the transmittance. There is a non linear trend in transmittance between 400 to 800nm wavelength shows that the light is only transmitted and not absorbed in this visible region. The plot of $(\alpha h\nu)^2$ versus photon energy hv is plotted as shown in Figure 9. In order to find the value of Eg we make use of the relation (6)

$$\alpha = 2.303 \log (T/d) \qquad (6)$$

α is absorption coefficient, d is the thickness of the sample and T is the transmittance. hν is the photon energy. Plot the graph of $(\alpha h\nu)^2$ versus hν. The values of Eg have been found by taking the intercept of the curve, at which it increases linearly. The wide optical band gap of KDP is 4.8eV, KDP doped Praseodymium crystals is found to be 5.2ev, 5.0eV, and 5.1eV for the grown crystals respectively suggests its suitability for optoelectronics applications.

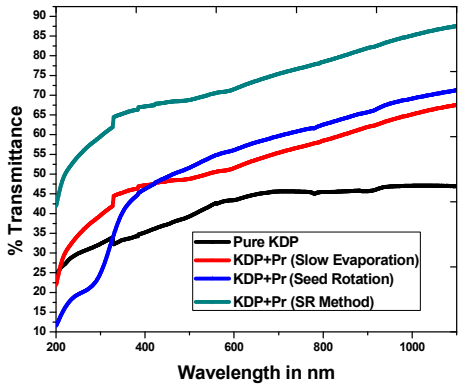

Fig 8. UV-Vis transmittance spectra of grown crystals

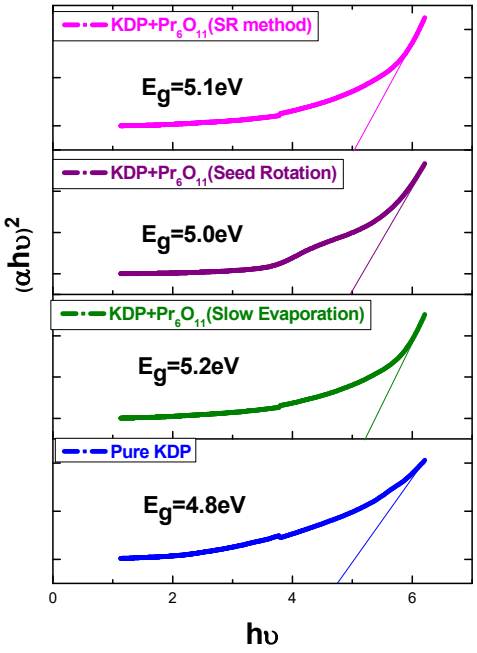

Fig 9. (αhv)^2 versus photon energy hv of the grown crystals

3.5 SHG STUDIES

The Second harmonic generation efficiency was determined by Kurtz powder technique [14]. Laser beam coming from the source has very high energy. Its intensity is reduced by using glass plates and Neutral density (ND) filter which reduces the intensity and it allows only 1064nm wavelength to incident on the sample taken in a microcapillary tube. Output from the sample is passed through the monochromator which is intensified by photomultiplier tube and finally the signal is observed and read on the Oscilloscope. A Q-switched Nd:YAG laser beam of wavelength 1064nm and 8ns pulse width with an input rate of 10Hz was used to test the NLO property of the sample. The second harmonic signal of 532nm green light was collected by a photomultiplier tube . The optical signal incident on the PMT was converted into voltage output at the cathode ray oscilloscope.

The grown crystals were crushed into fine powder and tightly packed in a micro capillary tube. It was mounted in the path of Nd-YAG laser beam of energy 5mJ/pulse. The KDP crystal was used as a reference material. The transmitted beam voltage for pure KDP crystal was 4mV, for the Praseodymium doped KDP (Slow Evaporation method) crystal was 4.19mV, Praseodymium doped KDP (Seed Rotation method) crystal was 4.89mV, Praseodymium doped KDP (SRmethod) crystal was 5.33mV respectively. It is found that the SHG efficiency of the Praseodymium doped KDP (SR method) crystal is 1.33 times greater than KDP, Praseodymium doped KDP (Seed Rotation method) crystal is 1.22 times greater than KDP, and Praseodymium doped KDP (Slow Evaporation method) crystal is 1.04 times greater than KDP. The measured values are given in Table 5. Output intensity of SHG gives relative values of NLO efficiency of the material. The relative SHG efficiency of the grown crystals is higher than that of KDP sample which indicates the suitability of crystals for application in nonlinear optical devices and optoelectronic devices. The increased SHG efficiency is due to higher polarizability of the material than that of KDP.

Table 5. SHG Signal and SHG efficiency of grown crystals

SHG Sample	SHG Signal	SHG Efficiency w.r.t KDP
Pure KDP	4.00 mV	1.00
KDP+Pr (Slow Evaporation)	4.19 mV	1.04
KDP+ Pr (Seed Rotation)	4.89 mV	1.22
KDP+ Pr (SR method)	5.33 mV	1.33

4. CONCLUSION

A new additive rare earth Praseodymium was added to KDP and crystals were grown by slow evaporation method, microcontroller based seed rotation technique and Sankaranarayanan-Ramasamy (SR) method. Powder XRD and EDAX analysis confirm the fact that the Praseodymium has gone into the lattice sites of the KDP crystals. The presence of additional peaks in the XRD spectrum of doped KDP crystals shows the presence of additional phases due

to doping. The UV-Vis-NIR transmission spectra show a wide transparency window without any absorption. KDP doped Praseodymium crystals generate optical second harmonic frequency of an Nd:YAG laser. The Kurtz powder technique indicates that the SHG efficiency Praseodymium doped KDP (SR method) crystal is 1.33 times greater than KDP, Praseodymium doped KDP (Seed Rotation method) crystal is 1.22 times greater than KDP, and Praseodymium doped KDP (Slow Evaporation method) crystal is 1.04 times greater than KDP, which indicates the suitability of crystals for application in nonlinear optical devices and optoelectronic devices. As the crystal has wide transparency in the UV and visible regions and with good SHG efficiency, implies that this crystal can be used as a potential material for optical applications.

Acknowledgements. The scientific supports extended by Department of IPC for SHG studies, Department of physics for Xrd analysis, Department of materials Engineering for UV-Visible analysis, IISC, Bangalore are gratefully acknowledged.

References:

1. A..Yokotani., T. Sasaki., K.Yamanaka, C.Yamanaka, Appl. Phys. Lett., 1986, 48, 1030.
2. S.SenGupta, T.Kar, S.P.SenGupta, Mater.Chem.Phys., 1999, 58, 227.
3. D. Xu. D. Xue, J. Rare Earth, 2006, 24, 228.
4. L. N. Rashkovich, KDP Family of Single Crystals, Adam Hilger, New York, 1991.
5. J. W. Mullin, Crystallization, third ed., Butterworth Heinemann, London, 1993.
6. K. Srinivasan, K. Meera, P. Ramasamy, Cryst. Res. Technol., 2000, 35, 291.
7. M. Jayaprakasan, N.P. Rajesh, V. Kannan, R. Bairava Ganesh, G. Bhagavannarayana, P. Ramasamy, Mater. Lett., 2007, 61, 2419.
8. G. Li, X. Liping, G. Su, X. Zhuang, Z. Li, Y. He, J. Cryst. Growth, 2005, 274, 555.
9. P.V. Dhanaraj, N.P. Rajesh, C.K. Mahadevan, G. Bhagavannarayana, Physica B, **2009,** 404, 2503-2508
10. M. Nakatsuka, K. Fujioka, T. Kanabe, H. Fujita, J. Cryst. Growth, **1997,** 171, 531.
11. G. W. Lu, and X. Sun, Cryst. Res. Technol., 2002, 37, 93.
12. B. W. Batterman and H. Cole, Rev. Mod. Phys., 1964, 36, 681
13. K. Balasubramanian , P. Selvarajan and E. Kumar, Indian Journal of Science and Technology, 2010,Vol. 3 No.1.
14. R. Priya, G. Bhagavannarayana, S. Krishnan and S. Jerome Das, Archives of Applied Science Research, 2010, 2 (4) , 111-118.
15. S.Suresh, A. Ramanand, P. Mani and K. Anand, Archives of Applied Science Research, 2010, 2 (4), 119-127.
16. S.K.Kurtz, T.T.Perry, J.Appl. Phys.., 1968, 39, 3798.