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RESEARCH ARTICLE

EFFECT OF PRASEODYMIUM ON THE OPTICAL, STRUCTURAL AND DIELECTRIC PROPERTIES OF <101>DIRECTEDKDP CRYSTALS GROWNBYSRMETHOD

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ABSTRACT

The Praseodymium doped potassium dihydrogen orthophosphate (KDP) crystals were grown by Sankaranarayanan-Ramasamy (SR) method and slow evaporation technique with the vision to improve the properties of the crystal. The chemical composition of the grown crystals is confirmed by EDAX Analysis. The grown crystal was characterized by PXRD analysis confirm the crystalline nature and shifts in peak positions due to doping is observed. Using Scherer's equation particle size has been calculated. 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 technique. The UV-Vis spectrum shows that percentage transmission of crystals grown by SR method is greater compared to slow evaporation. The electronic band transition is studied from the plot of $(\alpha h\nu)^2$ versus photon energy (hv) and the band gap energy has been calculated. The dielectric constant, dielectric loss and ac conductivity of the crystal were studied as a function of frequency and the results are discussed. The functional groups are identified by FT-Raman analysis. The Optical transmission and SHG studies shows the suitability of the ingot for optical applications.

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INTRODUCTION

Advanced research on efficient nonlinear optical material (NLO) is intensively studied for various optical device applications. Potassium dihydrogen orthophosphate (KDP) KH2PO4 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 (Yokotani Sasaki, et al., 1986; SenGupta et al.,1999; Xu. Xue, et al., 2006). 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 (Rashkovich, 1991; Mullin, 1993). 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.

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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 (Srinivasan, et al., 2000, Jayaprakasan, et al., 2007; Li, Liping, et al., 2005). 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 an additive in the KDP solution and doped KDP crystals were grown from the aqueous solution with SR and slow evaporation technique and the grown crystals are subjected to different characterizations like powder X-ray diffraction, FT-Raman analysis, optical transmission, dielectric study, EDAX and second harmonic generation efficiency(SHG) studies.

MATERIALS AND METHODS

Crystal growth

Good quality crystals of pure and Praseodymium doped KDP were grown by slow evaporation technique. 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.

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 32^{o}C and 27^{o}C 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 150 mm in length and 16 mm in diameter as shown in fig. 1. Finally, the ampoule was detached from the growth system and the grown crystal was carefully removed from the ampoule using diamond glass cutter.

Fig. 1. Photograph of Praseodymium-doped KDP crystals

RESULTS AND DISCUSSION

EDAX ANALYSIS

In order to confirm the presence of the Praseodymium, the grown crystals was subjected to EDAX (Energy dispersive X-ray analysis). The EDAX spectra for KDP doped Praseodymium grown by Slow evaporation 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. 2 & 3. The Observed weight percentage of elements in the doped KDP crystal are given in the Table 1 & 2.

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.

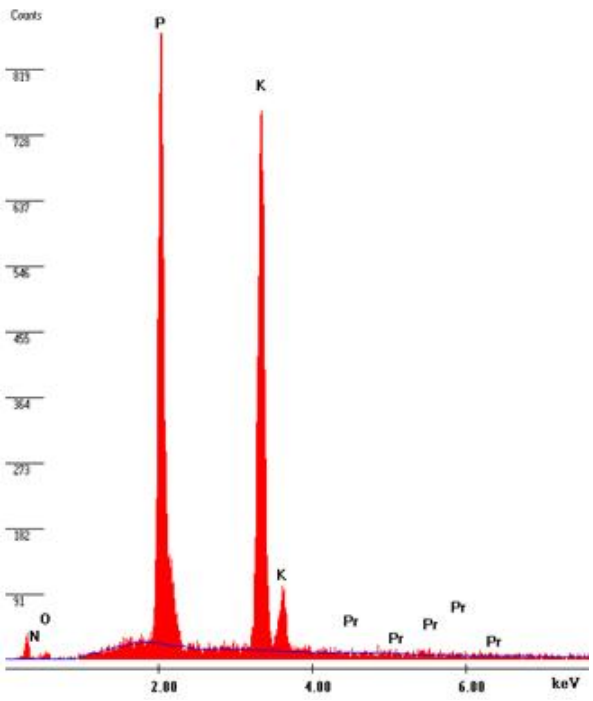

Fig. 2.EDAX Spectrum of Praseodymium-doped KDP crystals(Slow Evaporation)

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

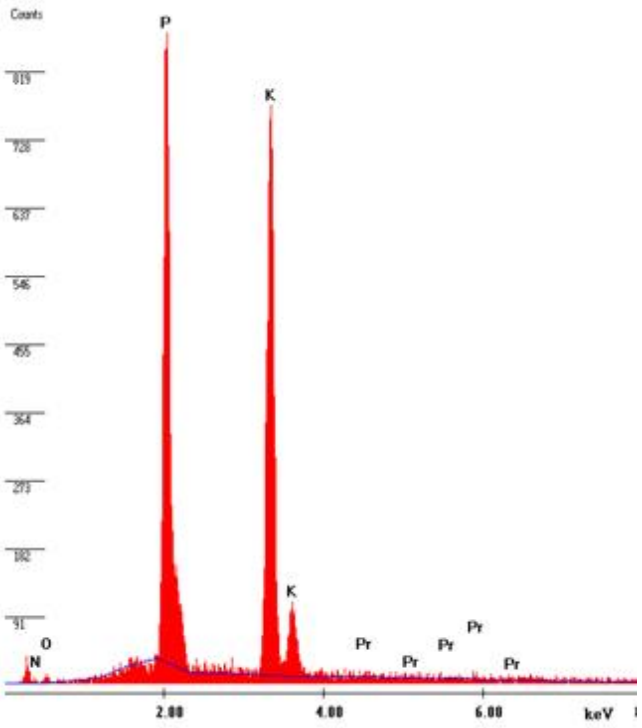

Fig. 3.EDAX Spectrum of Praseodymium-doped KDP crystals(SR method)

Table 2. Shows the estimated Weight % of KDP doped Praseodymium Crystal (SR 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

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. 4.

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 crystalline size (D) was estimated using the following relation:

$$D = \frac{0.9^{a}}{\cos^{-}} \quad (1)$$

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:

Table 3. Estimated crystalline size, strain, dislocation density and surface factor of grown crystals

Sample	Crystalline size (nm)		Strain	Stacking fault(SF)	Dislocation density $\delta(10^{14})m^{-2}$
	Scherrer's formula	W-H plot			
Pure KDP	44.03	64.24	$8.554E^{-4}$	17.39	5.15
KDP+Pr (Slow Evaporation)	49.90	112.81	$1.28E^{-3}$	17.35	4.01
KDP+Pr (SR method)	36.30	34.77	$3.86E^{-4}$	17.42	7.58

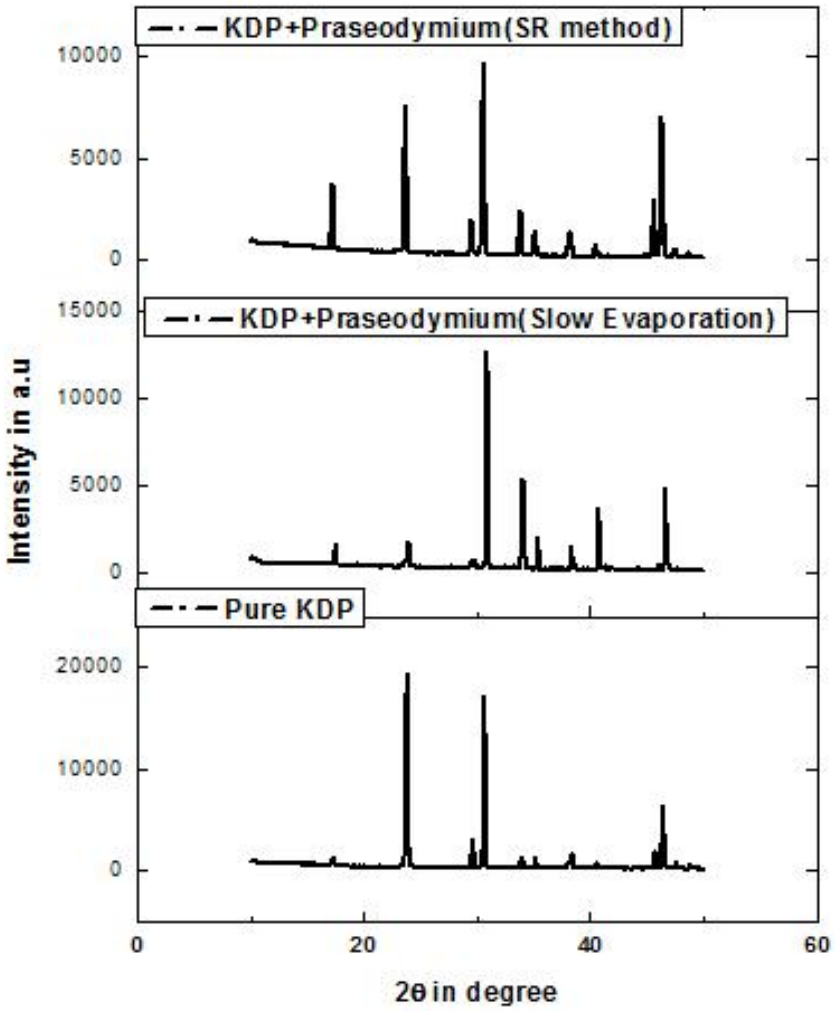

Fig. 4. Xrd patterns of pure and Praseodymium-doped KDP crystals

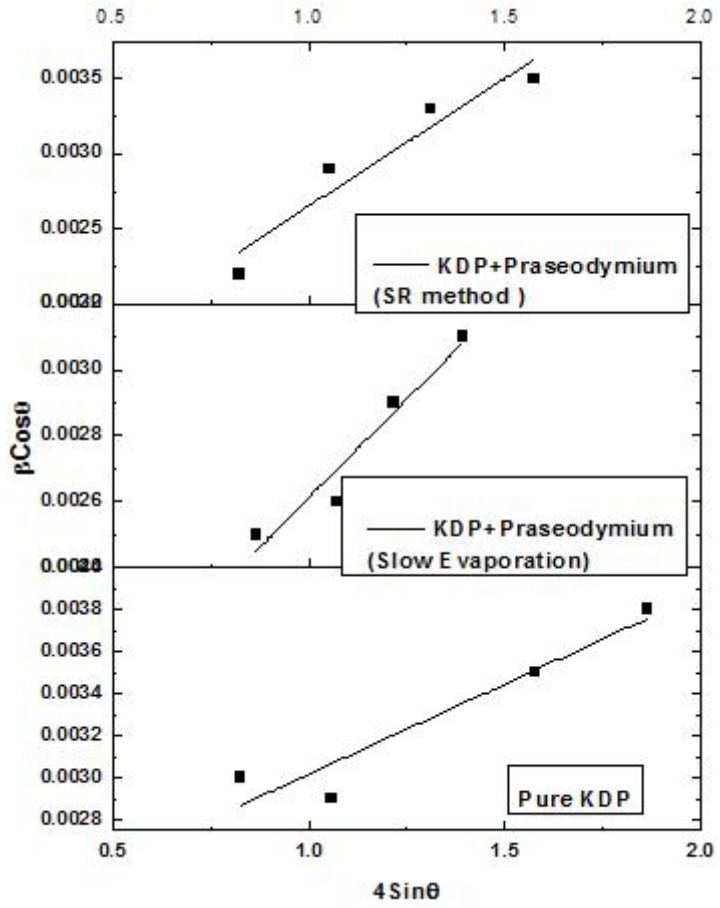

Fig. 5. W-H Plot of grown crystals

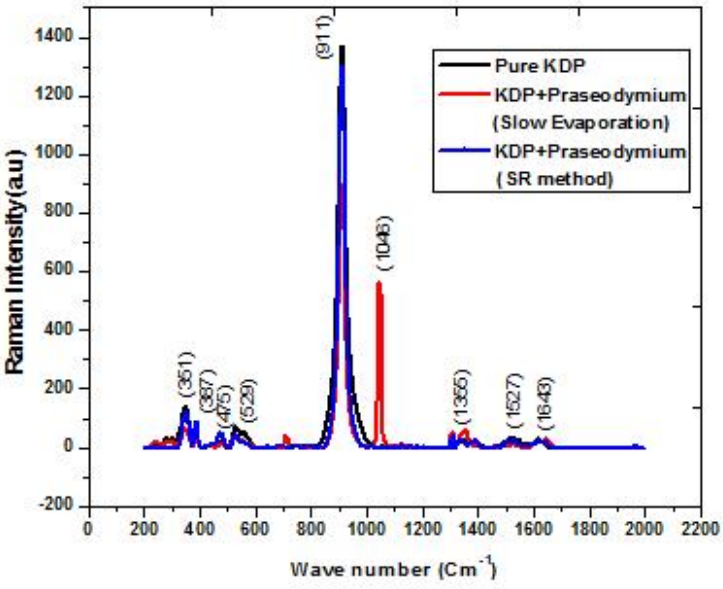

Fig. 6. FT-Raman Spectrum of grown crystals

Reference (Cm^{-1})	Pure KDP		KDP+Pr (Slow Evaporation)		KDP+ Pr (SR method)	
	FWHM (Γ in Cm^{-1})	Phonon life (μs)	FWHM (Γ in Cm^{-1})	Phonon life (μs)	FWHM (Γ in Cm^{-1})	Phonon life (μs)
351	31.42	50.65	25.63	62.09	23.8	66.87
387	16.43	96.86	16.67	95.47	17.09	93.12
529	56.95	27.94	51.42	30.95	43.51	36.57
911	45.99	34.60	30.98	51.37	26.99	58.96
1046	-	-	15.79	10.07	-	-
1527	55.74	28.53	54.65	29.12	55.56	28.64
1643	37.28	42.69	68.17	23.34	91.54	17.38

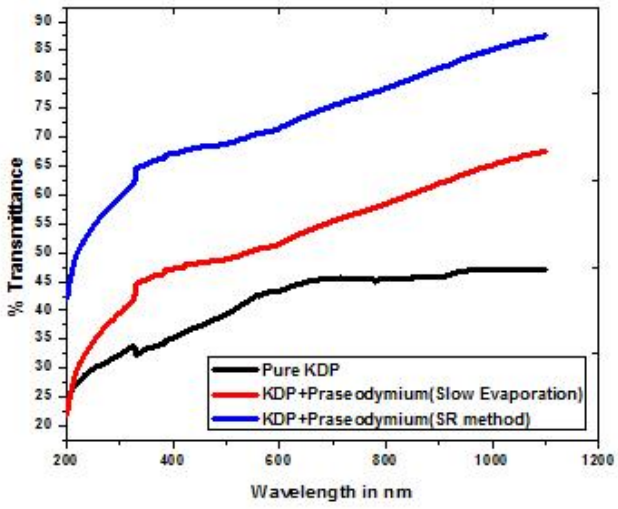

Fig. 7. UV-Visible Spectrum of grown crystals

$$¢ = \frac{1}{D^2} \quad (2)$$

$$£ = \frac{\cos^{-}}{4} \quad (3)$$

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

The obtained structural parameters were given in Table 3.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

$$\cos^{-} = \frac{k^{a}}{D} + 4£ \sin^{-} \quad (5)$$

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. 5. shows the W-H plots of grown crystals and the estimated strain values was shown in Table 3.

FT-RAMAN ANALYSIS

The Raman spectra of grown crystals were recorded for (101) planes at room temperature in the wave number range of 200 to 2000 cm-1. Raman spectra in the range of 200 to 2000 cm-1 is shown in Fig. 6. The spectra of pure, Praseodymium doped KDP single crystal grown by different methods contain the internal modes of vibrations (Lu *et al.*, 2002, Batterman *et al.*, 1964) of $H_2PO_4^{-1}$ in KH_2PO_4 at 911cm^{-1} (ν1), 529 cm^{-1} (ν2), 478 cm^{-1} (ν3), 387 cm^{-1} (ν4) and 351 cm^{-1} (ν5). The peaks with very small intensity at around 1366 cm^{-1}, 1527cm^{-1} and 1643 cm^{-1} are corresponding to the lattice vibrations of crystals through the absorption or emission of optical phonons. It is clearly observed from the figure that doping of Praseodymium did not influence the internal vibrational modes of crystals as there is no shift or broadness of the main peak at 911 cm^{-1} corresponding to the asymmetric stretching vibration of $H_2PO_4^{-}$ anions at all concentrations. The same nature of all spectra confirms no deviation in tetragonal phase and also reveals the absence of any additional phase with praseodymium doping. The Phonon life time (τ) can be deduced from the Raman scattering by using energy time uncertainty relation:

$$\frac{1}{\tau} = \frac{\Delta E}{h/2\pi} = 2\pi\,\Gamma \quad (6)$$

where E is the uncertainty in the energy of the phonon mode, h/2π is the Planck constant, and Γ is the FWHM of the Raman modes in cm^{-1}.

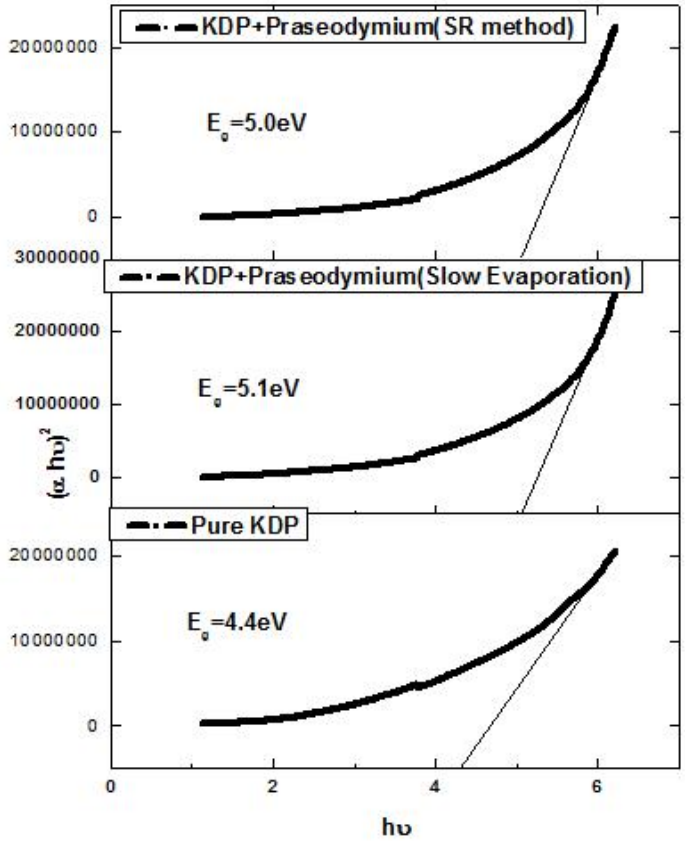

Fig. 8. (αhv)^2 versus photon energy hv of the grown crystals

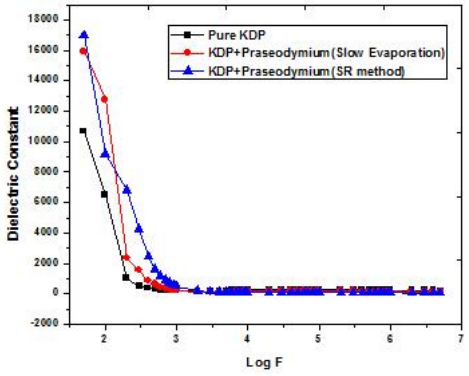

Fig. 9. Variation of dielectric constant with log frequency for grown crystals

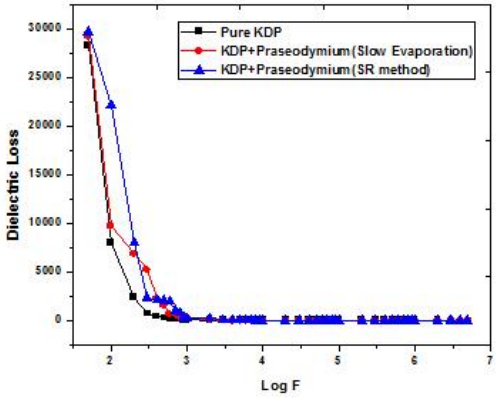

Fig. 10. Variation of dielectric Loss with log frequency for grown crystals

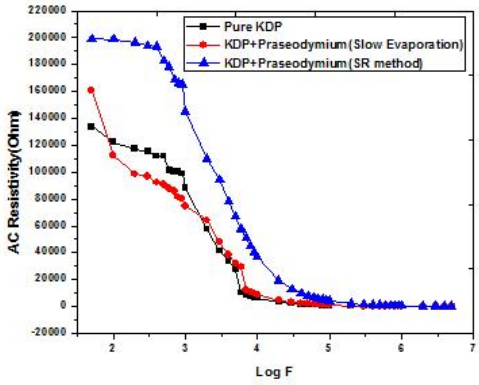

Fig 11. Variation of AC resistivity with log frequency for grown crystals

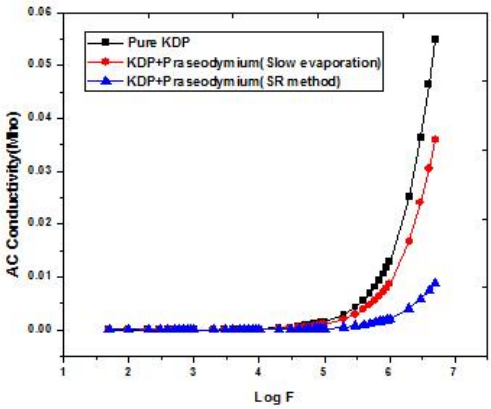

Fig 12. Variation of AC Conductivity with log frequency for grown crystals

The phonon life time is a combination of two characteristic decay time such as an harmonic decay of the phonon into two or more phonons so that energy and momentum are conserved (τ_A) and perturbation of translational symmetry of the crystals due to the presence of impurities, defects and isotropic fluctuations (τ_1). So the calculated phonon life time is an addition of two characteristic decay time. $\left(\frac{1}{\tau} = \frac{1}{\tau a} + \frac{1}{\tau 1}\right)$. The calculated phonon life time values are listed in Table 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 Fig. 7. Good optical transmittance and lower cut off wavelength are very essential properties for nonlinear optical (NLO) crystals (Balasubramanian *et al.*, 2010). It is observed from the figure that the Pure KDP shows 45% of transmittance, KDP doped praseodymium (Slow Evaporation method) shows 65% and KDP doped praseodymium (SR method) shows 87% 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 Fig. 8. In order to find the value of Eg we make use of the relation:

$$\alpha = 2.303 \log (T/d) \quad (7)$$

α is absorption coefficient, d is the thickness of the sample and T is the transmittance. hv is the photon energy. 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 pure KDP is found to be 4.4eV, and for KDP doped praseodymium crystals is 5.1eV and 5.0eV respectively suggests its suitability for optoelectronics applications.

DIELECTRIC STUDIES

Suitably cut and polished crystals section of pure and praseodymium doped KDP crystal grown by different methods was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A 4275A, multi frequency LCR meter (Hewlett-Packard) was used to measure capacitance (C) and dissipation factor (D) of the sample as a function of frequency. The dielectric constant (ε) and dielectric loss (tanδ) were calculated from C and D using the relations:

$$\varepsilon = \frac{Cd}{A\varepsilon_0} \quad (8)$$

$$\tan\delta = D\varepsilon \quad (9)$$

where C is the capacitance of the sample, d the thickness of the sample, A is the area of the face in contact with the electrode and ε_o the permittivity of free space. The variations of dielectric constant (ε) and dielectric loss (tanδ) at room temperature for pure KDP and praseodymium doped KDP crystal grown by different methods are shown in Fig. 9 and 10.

Table 6. SHG Signal and SHG efficiency of grown crystals

Details of the Sample	SHG Signal	SHG Efficiency w.r.t KDP
Pure KDP	4.00 mV	1.00
KDP doped Praseodymium (Slow Evaporation)	4.19 mV	1.04
KDP doped Praseodymium (SR method)	5.33 mV	1.33

It is observed that the dielectric constant (ε) decreases with the increase in the frequency. The dielectric constant of a material is generally composed of four types of contributions, viz ionic, electronic, orientational and space charge polarizations. At low frequencies all polarizabilities are operative hence ε is high. As frequency increases one polarization mechanism after another is frozen out. The first to stop contribution to ε is orientational component, then the ionic and lastly the electronic. The dielectric loss (tan δ) is due to the resistive component that makes them to decrease, so that they dissipate some of the applied ac energy. Tanδ in the present study was found initially to decrease with frequency and later almost a constant over a range of frequencies.

It is seen that a.c. conductivity is governed by the presence of a small number of free charges which result in small leakage or conduction currents and by the displacement of bound charges that give rise to polarization or displacement currents in the solid state dielectrics whereas in the d.c. conductivity there is no contribution from localized charges. Further ionic conduction plays a major role at higher temperatures for both a.c and d.c conductivity because at higher temperatures some ions detach from the sites of crystal lattices (Priya et al., 2010). At low frequency space charge polarization is dominant mechanism in the transport processes which is absent at high frequencies. The space charge polarization decreases with increase in frequency due to inertia of the ions to follow the variation in field. The variation in resistivity and conductivity with the frequency for the grown crystals are shown in Fig. 11 & 12. The a.c resistivity and a.c conductivity were calculated using the relation:

$$\rho = \frac{A}{2\pi f C d} \quad (10)$$

$$\sigma\rho = \frac{1}{\rho} \quad (11)$$

Where C is the capacitance, d is the thickness, A is the area of the crystal and f is the frequency of the applied field. It is observed that a.c resistivity decreases rapidly as frequency increases. Obviously reverse trend was observed for a.c conductivity of the grown crystals which is considered to be a normal dielectric behavior (Suresh et al., 2010).

SHG STUDIES

The Second harmonic generation efficiency was determined by Kurtz powder technique (Kurtz *et al.,* 1968). 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 (SR method) crystal was 5.33mV respectively. It is found that the SHG efficiency of the praseodymium doped KDP (SRmethod) crystal is 1.33 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 6. 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.

Conclusion

A new additive rare earth Praseodymium was added to KDP and crystals were grown by 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 presence of various functional groups was confirmed by FT-Raman spectrum. The UV-Vis 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 of praseodymium doped KDP (SR method) crystal is 1.33 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. The dielectric studies show that the grown crystal has low dielectric constant and low dielectric loss. As the crystal has wide transparency in the UV and visible regions, low dielectric constant and dielectric loss, implies that this crystal can be used as a potential material for optical applications.

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