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Praseodymium doped KDP Single Crystal Grown by Different Techniques and its Optical, SHG and Dielectric Studies : A New NLO Crystal

Roopa V[1*], R.Ananda Kumari[2]

[1]Department of Physics, SreeSiddaganga College for Women, Tumkur, Karnataka, India.
2Department of Physics, SreeSiddaganga College of Arts, Science & Commerce, Tumkur, Karnataka, India.

Abstract : Praseodymium doped Potassium dihydrogen Orthophosphate (KDP) single crystals were grown using different techniques - SR method, Seed Rotation and Slow Evaporation. The single crystal grown by SR method on unidirectional {101} pyramidal face was around 150 mm in length and 16 mm in diameter. Kurtz powder technique is used to determine the SHG efficiency. It is observed that relative SHG conversion efficiency of crystal grown by SR method is greater compared to other techniques. Optical transmission spectra was recorded in the wavelength region 200 to 1100nm for the grown crystals using Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. It is found that percentage transmission of crystal grown by SR method is more as compared to other techniques. The electronic band transitions was studied from the plot of photon energy (hν) versus $(\alpha h\nu)^2$ and the value of band gap energy (E_g) has been calculated.

The dielectric constant, dielectric loss and a conductivity of the grown crystals were studied as a function of frequency and the results are discussed. The addition of Praseodymium improves the quality and transparency of crystals, which shows the suitability of the grown NLO material for optical applications.

Keywords: Single Crystal growth; SR method; SHG; Optical properties; Dielectric properties.

Introduction

The nonlinear Optical (NLO) material is widely studied for different optical device applications. Potassium dihydrogen orthophosphate (KDP) is a well known NLO material which can be used for laser frequency conversion, low repetition (<100 Hz) rate lasers, Q-switching applications, electro-optical modulation and for second harmonic generation of high pulse energy[1-3].Since it is having many significant applications, research hasbeen going on tofindefficientand novelNLOmaterial.

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Large size single crystals have a great demand for high power lasers in modern technical systems. The impurities are the most important factor which influences the growth rate and the surface morphology of crystal [4,5]. The growth of the crystal can be either enhanced, suppressed or stop completely by adding the impurities. In the modern period the growth process and properties of crystals can be varied by the effect of additives [6-8].

The most appropriate additives which can change the properties of solution such as surface tension, viscosity etc. without disturbing the optical qualities of crystals are reagents with metal ions that have the same properties as that of bulk solutions. Praseodymium is used in a wide variety of metallurgical applications like lasers, masers and in industrial glass production, as polishing agent and in thermoelectric and electronic components. It is having good electrical, chemical magnetic and optical properties.

Hence Praseodymium is selected as impurity in the KDP solution and doped KDP crystals were grown using aqueous solution with seed rotation technique, Sankaranarayanan-Ramasamy (SR) method and slow evaporation technique. The grown crystals are subjected to different characterizations like optical transmission, Second harmonicgeneration (SHG) efficiency, Dielectric studies and the studies are compared with different techniques.

Experimental

Crystal Growth

Good quality optically transparent crystals of 1 mol% of Praseodymium doped KDP were grown by slow evaporation technique as shown in Fig 1(a).Rare EarthPraseodymium used for the crystal growth is in the form of Nitrate.

A volume of 300ml of water was taken in a beaker and known quantity of the material determined from the solubility data was added till it attains saturation for our room temperatures at 27^0C. Sankaranarayanan-Ramasamy (SR) method was employed to grow the bulk size of Praseodymium doped KDP single crystals. The apparatus consists of ampoule of inner diameter 16mm, a 30x30x30 cm^3 size of glass container and two ring heaters. A <101> face of suitable seed crystal was selected for single crystal growth having a size of 4x4x4 mm3. The selected seed crystal without polishing the surface was slowly placed in the bottom of the ampoule. And then inside the glass water bath the ampoule was kept and constant ambient temperature is maintained. The prepared Super Saturated solution was poured into the ampoule carefully without disturbing the seed crystal. The two ring heaters are placed one at the top and another at the bottom of the ampoule. The growth was initiated with a suitable temperature applied across the ring heater under equilibrium condition at the top region of the saturated solution.

The nucleation was carefully controlled by maintaining the temperature difference between the top and bottom ring heaters of the ampoule. In the present work, the temperature around the top and bottom of the ampoule was maintained at 32^oC and 27^oC respectively. A very good transparent crystal starts growing within 10 days under this temperature condition. After a period of 90 days, a good quality crystal was carefully removed from the ampoule using diamond glass cutter. The crystal was grown with a size of 150 mm in length and 16 mm in diameter as shown in Fig.1(b). Fig. 1(c) shows the cut and polished crystals.

Stirring the solution by microcontroller based motor reduces the natural homogenizing mixing the bulk solution. The crystal also grows in bulk size with a short duration. Hence, the importance of optimum rates of rotation in crystal growth processes has gained recognition in the past decade [9]. The stirring techniques that most commonly used are the seed rotation technique and the rotation of the crystallizer. In our present work, Praseodymium doped KDP crystals were grown by continuously rotating the seed crystal at 40 rotations per minute (rpm). This apparatus consists of a stepper motor which is controlled by a microcontroller based drive that is coupled to a seed rotation controller. This microcontroller based drive rotates the seed holder in the crystallizer. The seed crystal mounted is at the center of the platform. The crystallizer platform rotates and mixes the solution very well, which results in better crystal quality. The prepared saturation solution at the temperature 40^0C was filtered to remove the extraneous solid and colloidal particles. Then at the temperature of 50^0C the solution was overheated for 24hrs, to make the solution stable against spontaneous nucleation under a high super saturation [10].

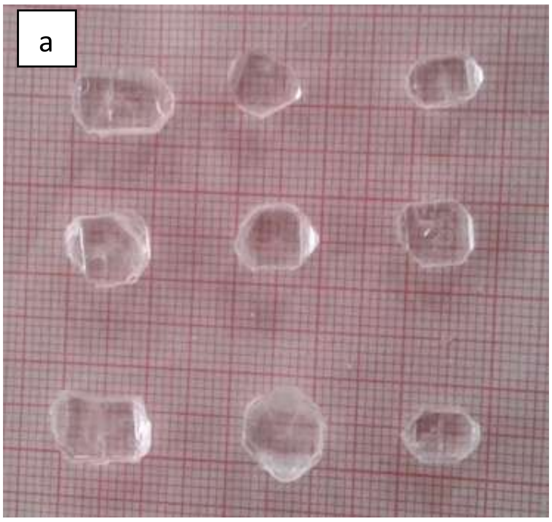

Fig. 1 a): Photograph of Praseodymium doped KDP crystals grown by Slow Evaporation technique

Fig.1 b) Praseodymium doped KDP <101> crystalgrown by SR method

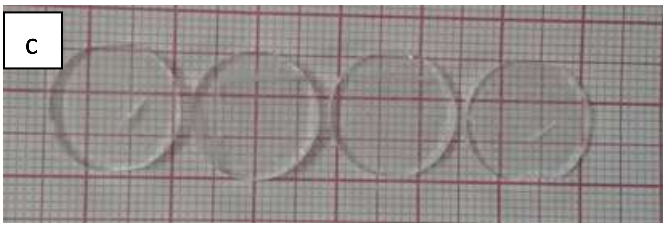

Fig. 1 c) The cut & polished crystals

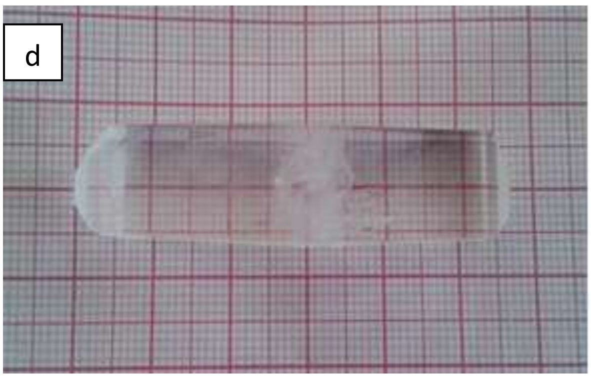

Fig. 1(d): Photograph of Praseodymium doped KDP crystal grown by Seed Rotation technique

After overheating, the temperature of the solution was reduced slightly and seed crystal was fixed on it. The temperature was decreased at the rate of 0.24^{0}C per day from the saturation point at the beginning of the growth. As the growth of the crystal is progressed, the temperature rate was decreased, when it reaches the room temperature, crystal was removed from the crystallizer platform. The grown crystal is shown in Fig.1(d).

Results and Discussion

1. UV-Visible Transmission

Pure KDP and Praseodymium doped KDP crystals plates were cut and polished without any coating for optical UV measurements. The size of the crystals were reduced in thickness around 1mm. Optical transmission spectra were recorded for the crystals in the wavelength region of 200 - 1100 nm using Perkin-Elmer Lambda *35* UV-Vis spectrometer. The measured UV-Visible spectrum is shown in the Figure 3. Lower cut off wavelength and Good optical transmittance are very essential properties for nonlinear optical (NLO) crystals [11]. It is observed from the fig. 3. that the Pure KDP grown by slow evaporation technique shows 45% of transmittance, Praseodymium doped KDP crystal by Slow Evaporation method, Seed Rotation method, SR method shows 65%, 70% and 85% of transmittance. In the entire visible region, it offers large transmission which enables this crystal to be a good material for electro-optical and NLO applications. The recorded results shows that the dopant Praseodymium to pure KDP has increased the percentage of transmittance for the crystal grown by SR method. It is also observed in the Fig. 2. that there is a non linear trend of transmittance between the wavelength range of 400 to 800nm shows that the light through the crystal is only transmitted and not absorbed in this visible region.

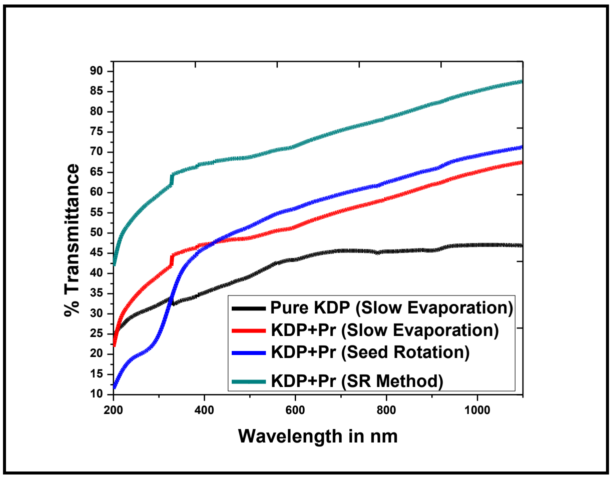

Fig 2. UV-Visible transmittance spectra of grown crystals

The graph of photon energy hυ versus $(\alpha h\upsilon)^2$ is plotted as shown in Fig.3. In order to find the value of Energy band gap Eg we make use of the relation (1)

$$\alpha = 2.303 \log (T/d) \qquad (1)$$

Where α is absorption coefficient, T is the transmittance and d is the thickness of the sample. The values of Eg have been determined by taking the intercept of the curve, at which it increases linearly. The optical band gap energy Eg of pure KDP crystal (Slow Evaporation) is 4.8eV, Praseodymium doped KDP crystals for different methods is found to be 5.2ev, 5.0eV, and 5.1eV for the grown crystals respectively suggests its suitability for optoelectronics applications.

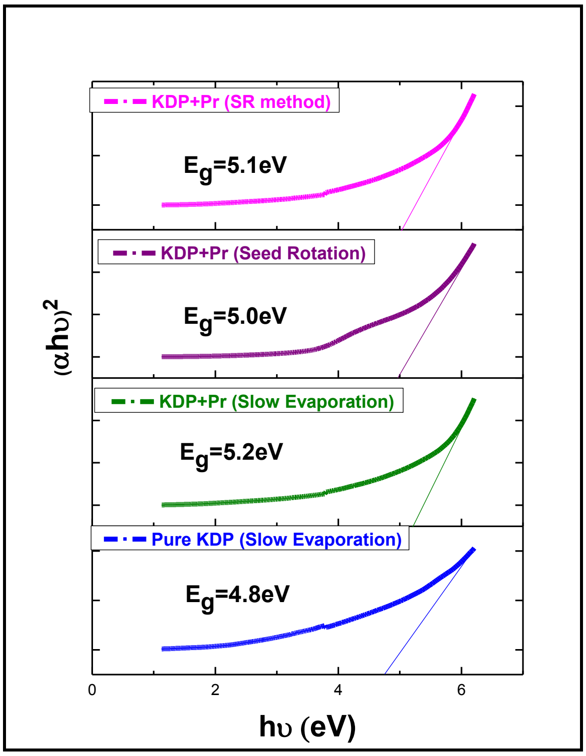

Fig 3. photon energy hυ versus $(\alpha h\upsilon)^2$ of the grown crystals

2. SHGStudies

The grown crystals were crushed to form fine powder and it is filled tightly without any air gap in a micro capillary tube. It was then placed in Q-switched Nd-YAG laser beam path having energy of 5mJ/pulse. The Second harmonic generation efficiency was determined by Kurtz powder technique [12]. The Laser beam coming from the source has very high intensity. So that its intensity has to be reduced by using the Neutral density (ND) filter and glass plates. ND filter which allows only 1064nm wavelength to be incident on the sample that is taken in a microcapillary tube. Output voltage coming from the sample tube is then allowed through the monochromator, which is intensified by photomultiplier tube and finally the signal is observed and readings are taken on the Cathode ray Oscilloscope. A Nd:YAG laser beam having 8ns pulse width and an input frequency rate of 10Hz was used to test the SHG effiency of the sample. Wavelength of 532nm green light Second harmonic signal was collected by a photomultiplier tube. The optical signal incident on the Photomultiplier tube was converted into voltage at the cathode ray oscilloscope.

The Potassium dihydrogen Orthophosphate (KDP) crystal was taken as a reference material, which produces a transmitted beam voltage of 4mV. The SHG signal generated for the Praseodymium doped KDP (Slow Evaporation method) crystal was 4.19mV, Praseodymium doped KDP (Seed Rotation method) crystal was 4.89mV, and for Praseodymium doped KDP (SR method) crystal was 5.33mV respectively.

SHG efficiency was calculated for all the grown crystals and it is found that for 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 shown in Table 1. From the table it is observed that Praseodymium doped KDP (SR method) crystal is having more SHG efficiency compared to all other techniques. SHG Output intensity gives relative values of NLO efficiency of the material. The relative SHG efficiency of the grown crystals is higher than that of reference material KDP which indicates the suitability of grown crystals for optoelectronic devices and in nonlinear optical applications. Due to higher polarizability of the material the SHG efficiency is relatively increased than that of KDP.

Table 1. SHG Signal and SHG efficiency of grown crystals

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

3. Dielectric Studies

Dielectric studies were performed for the grown crystals at various frequencies using LCR meter HEWLETT-PACKARD 4275A model. The crystals of pure and TGS mixed KDP in the molar ratio 9:1, 8:2 and 7:3 are finely cut and polished. And then the grown crystals were coated by air-drying silver paste to make a contact with the electrodes on both the sides. After coating the crystals acts like a capacitor plate. The dielectric constant (ε) and dielectric loss (tanδ) were calculated using the relations (2) & (3)

$$\varepsilon = \frac{Ct}{A\varepsilon_0} \qquad (2)$$

$$\tan\delta = D\varepsilon \qquad (3)$$

In the above relations C is called the capacitance, t is the thickness, A is the area of the grown crystal in contact with the electrode, ε_o is the permittivity of free space and D is the loss co-efficient respectively. At normal temperature the variations of dielectric constant (ε) and dielectric loss (tanδ) is measured for pure TGS and TGS mixed KDP in the molar ratio 9:1, 8:2 and 7:3 crystals and are shown in Fig. 4 and 5. From the figure it is seen that the dielectric constant (ε) is maximum at 100 Hz and it graduallydecreases as the frequency increases. At high frequencies due to the inertia of the ions and molecules, the orientation and ionic contributions of polarization decreases. The dielectric loss (tan δ) is directly proportional to the product of dielectric constant (ε) and loss co-efficient (D) that makes them to decrease. Tanδ the dielectric loss was found to be initially maximum and then it decreases gradually as frequency increases and later it becomes almost a constant over a range of frequencies.

The a.c. conductivity depends on the negative charges which happens due to leakage currents. This movement of negative charges results in polarization in the solid state dielectrics. But at higher temperature some of the negative ions come out from the crystal lattice sites due to ionic conduction [13].

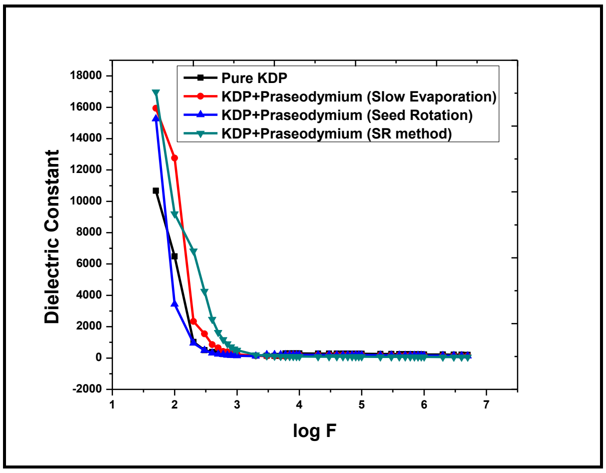

Fig. 4. Plot of log f vs. dielectric const. for the grown crystals

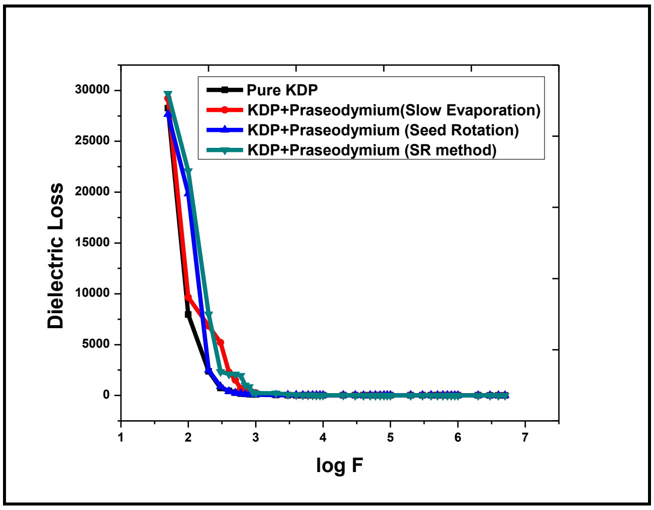

Fig. 5. Plot of log f vs. dielectric loss for the grown crystals

At low frequencies, Space charge polarization will be more, where as it is absent at high frequencies. Due to the uniform motion of ions in the variation of field, at high frequency the space charge polarization decreases. The conductivity and resistivity variation is plotted along with thefrequency for the grown crystals are shown in Fig.6&7. The relation used for calculating the a.c resistivity and a.c conductivity are given by (4 & 5)

$$\rho = \frac{A}{2\pi f C t} \quad (4)$$

$$\sigma\rho = \frac{1}{\rho} \quad (5)$$

From the above relation A corresponds to the area of the crystal, f is the frequency of the applied field, C is called the capacitance and t is the thickness of the grown crystal.From the graph it is observed that a.c resistivity decreases very fast as frequency increases.

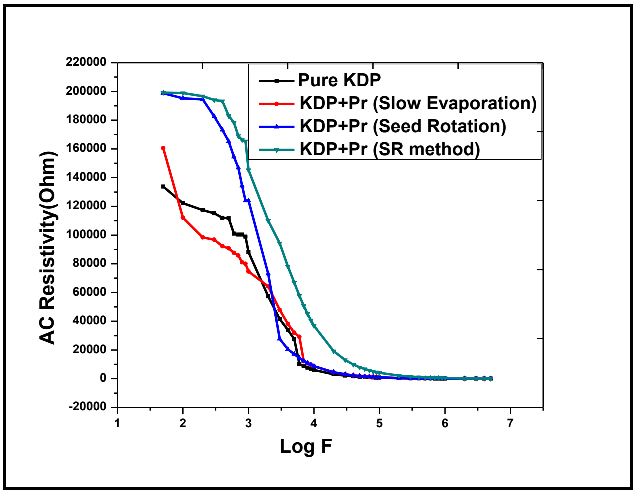

Fig 6. Plot of log f vs. AC resistivity for the grown crystals

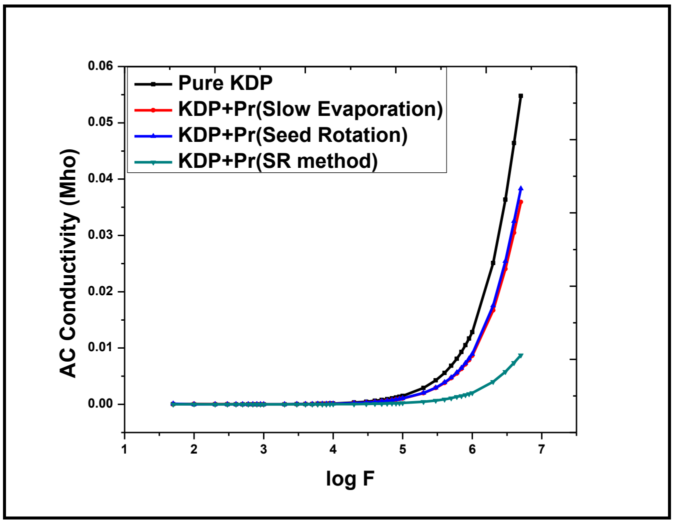

Fig 7. Plot of log f vs. AC Conductivity for the grown crystals

But in a.c conductivity studies, we see the reverse operation that is when frequency is increased for the grown crystals the a.c conductivity also increases, which shows a normal dielectric behavior [14].

Conclusion

A new rare earth additive Praseodymium was doped to KDP and crystals were grown by the technique of slow evaporation, microcontroller based Seed rotation technique and Sankaranarayanan-Ramasamy (SR) method. A wide band of transparency is observed in the UV-Visible transmission spectra without any absorption. Praseodymium doped KDP crystals grown by SR method shows highest percentage of transmission compared to all other techniques.Praseodymium doped KDP crystals generate optical second harmonic generation efficiency for an Nd:YAG laser. TheKurtzpowdertechniqueindicatesthatthePraseodymium doped KDP (SR method) crystal shows more SHG efficiency and 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 that the grown crystals are suitable in the field of nonlinear optical and optoelectronic device applications. Thedielectricstudies indicates that thegrowncrystalsdielectricconstant anddielectricloss decreases with increase in frequency. Sincethe grown crystal by the SR method is having more percentage transmission in UVvisibleregionand good SHG efficiency,impliesthatthiscrystal is a promising materialforopticalapplications.

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