Effect of L-proline on the growth and NLO properties of KDP crystal

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L-proline doped potassium dihydrogen phosphate (KDP) single crystals are grown by solution growth technique. Slow cooling method was adopted for the growth. Due to variation in the doping concentration, there is a modification in the growth habit, nonlinear optical property and mechanical hardness of the doped crystals. Fourier transform infrared (FTIR) spectrum reveal strong absorption bands due to L-proline. UV – visible spectra shows an improvement in the optical transmittance. SHG studies have shown an enhancement in the NLO property due to doping. Mechanical hardness of the crystal also depends on the concentration of the dopant. The unit cell parameters and cell volume are obtained by single crystal X-ray diffractrometer CAD4/MACH 3 with MoK_α radiation of wavelength 0.71073Å, at room temperature (293 K). All the results are compared with as grown KDP crystals.

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1. Introduction

The rapid development in the field of science and technology necessitates the search for newer and efficient nonlinear optical materials. KDP crystal is extensively studied from various aspects and widely used NLO crystal. Its excellent qualities such as high nonlinear conversion efficiency, wide optical transmission range with low cut-off wavelength and high laser damage threshold [1] has drawn the attention of several crystal growers. Many research works has been resulted in the modification of KDP properties and growth rates by varying the growth conditions and by adding suitable impurities [2-9]. During the past decades, many organic and inorganic materials possing high nonlinear susceptibilities have been synthesized and used in various applications. However, from the application point of view, it is found that these materials involve only weak Vander Walls force and therefore shows poor optical quality, low laser damage threshold and mechanical hardness and also difficult to grow in size. These difficulties have been overcome by the introduction of semi organic crystals. In particular, amino acids possess electron donor and acceptor groups connected by extended π-electron pathways and shows large hyperpolarizabilities. Therefore amino acids are found to be more efficient candidates as dopants in growing semi organic crystals.

J.D. Dave et al. [10], have grown L-threonine doped KDP crystals with improved NLO properties, optical transmission and mechanical hardness. They also observe an incremental value of SHG efficiency with doping concentration. Kumaresan et al. [11] have grown KDP with L-glutamic acid, L-Histidine and L-Valine as dopants. They report the growth habit modification with pH variations, improved optical transmission and NLO property. They also observe an increase in the mechanical hardness with respect to the dopant concentration. Parikh et al. [12] have grown L-lysine doped KDP crystals with increasing NLO properties and optical transmission but with decreased thermal stability.

In the literature, no work has been reported in the modification of NLO properties of KDP by using L-proline as dopant. L-proline naturally possesses chirality and often crystallizes in noncentrosymmetric space group. They also possess zwitterionic nature [13, 14] in a moderate pH. Therefore large nonlinearities can be achieved in KDP by introducing L-proline as dopant. Peptide bonds formed with proline lack a free amino group to form hydrogen bonds and also it does not carry an ionizable group. Due to these potential sites, it was suggested to use L-proline as dopant.

In the present work, we report the growth of L-proline doped KDP single crystals by solution method. The doping concentration influences the growth habit of crystal. Fourier transform infrared (FTIR) spectrum reveal strong absorption bands due to L-proline. UV – visible spectra shows an increase in the optical transmittance with respect to L-proline concentration. The mechanical hardness was found to increase with increase in the dopant concentration. This suggests that the reported crystal is a potential candidate for nonlinear optical applications.

2. Experimental

2.1 Solubility study

The solubility of pure and doped KDP was studied for six different temperatures 30, 35, 40, 45, 50 and 60 °C as shown in figure 1. Initially, supersaturated solution was prepared at 30 °C in an air tight container of 250 ml inside the constant temperature bath maintained with an accuracy of ±0.01°C. After achieving the supersaturation, the solution was analysed gravimetrically and the solubility of pure KDP and doped KDP in 100ml of solvent was determined. This procedure was adopted for various temperatures and the solubility curves were drawn. It is observed from the solubility curves that the solubility increases with temperature. The solvent was able to accommodate fairly more solute between the temperature ranges of 45 to 50 °C. Therefore this temperature range was suggested for the growth by temperature lowering method.

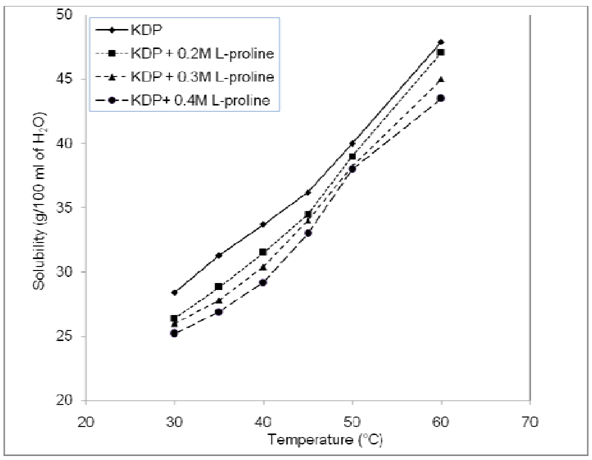

Fig. 1. Solubility curve of Pure and L-proline doped KDP.

2.2 Growth of L-proline doped KDP single crystals

Analytical grade (99.99% pure) KH_2PO_4 (KDP) and L-proline as purchased are used for the crystal growth. A saturated aqueous solution of KDP at 50 ºC was prepared to a volume of 1000 ml and allowed to equilibrate in a constant temperature bath. L-proline with a concentration of 0.2M, 0.3M and 0.4M were taken and homogenously mixed with the prepared saturated solution of KDP (each 500 ml). The growth solutions were taken inside identical crystallizers and kept inside the constant temperature bath. Seed crystals of KDP doped with L-proline were prepared in a Petri dish by conventional slow evaporation method. The seed crystals were analyzed in optical microscope. Optically good quality seed crystals were cut with preferred orientation and mounted in the crystallizer. The growth was carried out in a digitally controlled constant temperature bath with an accuracy of ±0.01 ºC by temperature reduction method. The growth run was initiated with a cooling rate of 0.24 ºC/day. Seed rotation was performed using a stepper motor to maintain the homogeneity of the growth solution throughout the growth period. After a period of 20 days, the L-proline doped KDP crystal was harvested and is shown in Fig. 2.

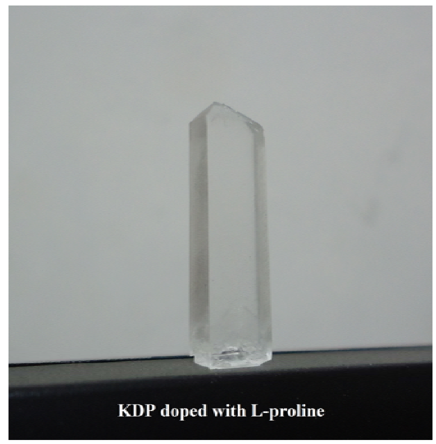

Fig. 2. KDP doped with L-proline crystal grown by temperature reduction method

3. Characterization

3.1. Single crystal XRD analysis

Single crystal X-ray diffraction analysis was performed using single crystal diffractrometer CAD4/MACH 3 and the data was collected using graphite-monochromated MoK$_\alpha$ radiation of wavelength 0.71073Å, at room temperature (293 K). Comparison of unit cell parameters (table 1) of pure and doped KDP crystal suggests that a slight distorsion has occurred as a result of doping with L-proline. The ‘c’ axis shows an enhanced growth which is also evident through the morphology of the crystal shown in the figure 2.

Table 1. Single Crystal X-ray diffraction results of cell parameters of Pure and doped KDP with L-proline.

Crystal	**Interplanar distance (Å)**			**Interfacial angles (˚)**			**Cell volume (Å)^3**
	a	**b**	**c**	**α**	**β**	**γ**	
KDP + 0.4M L-proline	6.313 (2)	6.304 (2)	10.548 (5)	90 (0)	112.97 (3)	90 (0)	386.5 (3)
Pure KDP	7.434 (3)	7.434 (3)	6.945 (2)	90 (0)	112.18(6)	90 (0)	383.8 (5)

3.2. Fourier transform infrared spectral study

FT-IR spectrum was recorded by Perkin-Elmer spectrum RXI spectrometer using KBr pellet technique between 400 cm^{-1} and 4000 cm^{-1} to determine the functional groups in the doped crystal. The observed FT-IR spectra of pure and doped KDP are shown in figure 3. The frequencies with their relative intensities obtained in FT-IR for pure and doped KDP and their most probable assignments are presented.

The broad intense envelope observed at 3500 cm^{-1} is due to P-OH stretching of H_2PO_4. A medium diffuse band with principal maxima of 2980 cm^{-1} and a shoulder at 2800 cm^{-1} shows up clearly the stretching vibration of CH group of the L-proline. These bands can therefore be assigned to overtones of deformation vibrations of both CH_2 and NH_2^+ groups. The deformation vibrations of CH_2 group includes asymmetric stretch CH_2, symmetric stretch CH_2 corresponding to different methylene groups. For a molecule containing methylene group, the electronic charge is back donated from the lone pair of nitrogen to the σ^* orbital of the C-H bonds, causing a weakening of the C-H bonds. This is followed by the increase in C-H force constant and can result in the enhancement of IR band intensity of C-H stretching modes.

The absorption between 2800 cm^{-1} and 3000 cm^{-1} supports the strong interaction of OH group of L-proline and the association of these ions into the KDP. The pure KDP shows a medium absorption at 2300 cm^{-1} which is due to P-OH stretching of H_2PO_4. In the spectrum of doped KDP, this peak becomes very weak and undergoes a shift towards 2450 cm^{-1}. It appears as a doublet due to deformation vibration of NH_2^+ of L-proline. The band at 1095 cm^{-1} are assigned to the C=O, C-O stretching mode of L-proline.

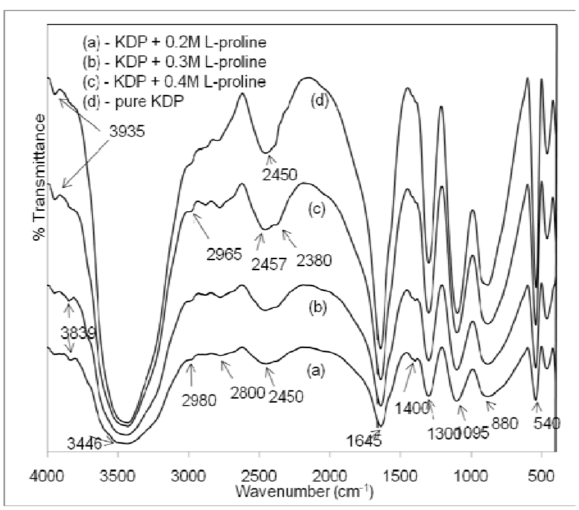

Fig. 3. FTIR spectrum of KDP doped with L-proline.

The bending mode of C-O-H give rise to a characteristic band near 1400 cm^{-1} for 0.2M of L-proline. This bending mode almost vanishes with increase in dopant concentration as a result of molecular interaction between COO^- and CH_3^+. The band of 880 cm^{-1} of doped KDP is assigned to bending modes of C-H and CH_2 groups of L-proline, which is absent in pure KDP. Moreover, this band envelopes the band of pure KDP at 930 cm^{-1}. This is due to the domination of C-H and CH_2 bending modes.

3.3. Optical transmission spectral study

Optical transmission spectra of pure and doped KDP single crystal are recorded in the range of 200-1100 nm and shown in figure 4.

It is observed from the spectrum that the maximum transmission percentage is for 0.4M concentration of L-proline. Transmittance percentage increases with the increase in dopant concentration. In general, the high conjugation and delocalized π bonding orbitals of L-proline are responsible for absorption in UV visible region. But, as the concentration of dopant increases, the zwitter ionic property decreases due to interaction between opposite charge ends of L-proline. This intern reduces the delocalization of π bonding orbitals. As a result, the electron jump takes high energy and hence absorption occurs in the shorter wavelength which is also evident from the spectrum.

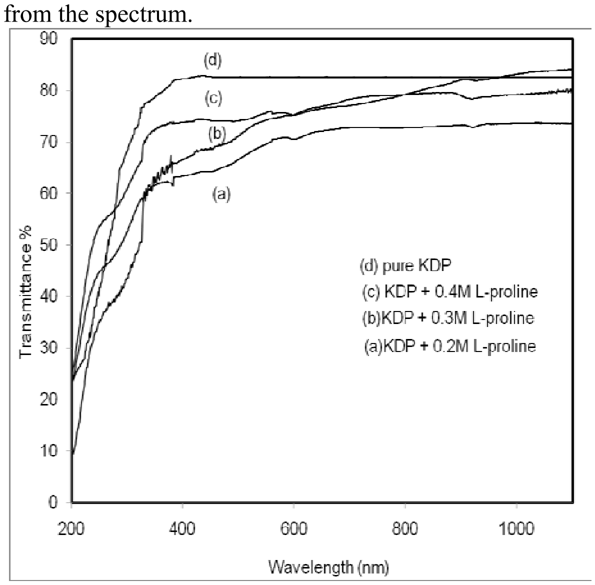

Fig. 4. UV-Vis Transmission spectrum of KDP doped with L-proline.

3.4. Kurtz and Perry powder SHG test

Kurtz and Perry powder technique [15] using Q-switched, mode locked Nd-YAG laser operating at the fundamental wavelength 1064 nm, generating input power of about 6.6 mJ/pulse and pulse width 8 ns with a repetition rate of 10 Hz was performed. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powder of uniform size of the crystal sample packed in a capillary tube of diameter 0.154mm. Second harmonic signal of 532 nm was produced and confirmed the nonlinear property. The second harmonic generation efficiency of KDP doped with

L-proline is presented in table 2. It is evident from the data that the SHG efficiency increases with increase in dopant concentration. This is because of the overlapping of π orbital which favours the electron transfer resulting in polarization effect under strong electric field component of the laser. It is therefore evident that the L-proline is a good candidate to be used as dopants for enhancing the NLO property of KDP crystal.

Table 2. Second Harmonic Generation efficiency with the dopant concentration in KDP

KDP + dopant	SHG efficiency w.r.t pure KDP
KDP + 0.2M L-proline	1.15 times
KDP + 0.3M L-proline	1.27 times
KDP + 0.4M L-proline	1.45 times

3.5 Microhardness measurements

KDP doped with L-proline (0.2M, 0.3M and 0.4M concentrations) were subjected to Vicker's static indentation test at room temperature using Shimadzu (Model HMV 2) hardness tester. Loads of different magnitudes ranging from 25g - 100 g were applied for duration of 5 seconds. The hardness was calculated using the relation HV= $1.8544P/d^2$ Kg/mm^2, where P is applied load in kilogram, d is the diagonal length of the indentation impression in micrometer, and 1.8544 is a constant of a geometrical factor for the diamond pyramid.

The plot of Vickers hardness (VHN) versus load (P) for the L-proline doped KDP crystal is shown in figure 5. It is seen from the figure that the hardness value increases with increase in the doping concentration. Also with increase in indenter load, the hardness increases. As L-proline possesses ring structure, which is a stable molecular structure and hence good mechanical hardness is observed in the doped crystals.

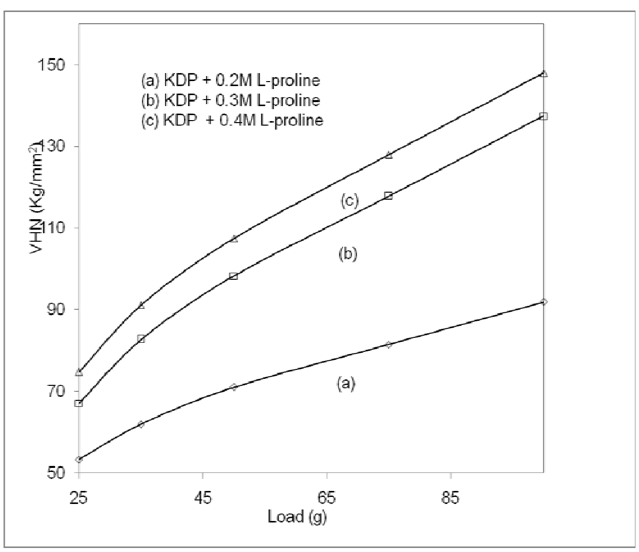

Fig. 5. Microhardness of KDP doped with L-proline

Further, as the load is increased, hardness also increases and reaches the saturation around 95 g of load and beyond which the crystal undergoes a fracture.

4. Conclusion

Pure and L-proline doped KDP crystals were grown from aqueous solution by temperature reduction methods. The functional groups present in the crystal have been confirmed by FTIR analysis. All the observed frequencies were assigned with respect to the different vibrational modes. The study also confirms the strong interaction of L-proline with the -OH group of KDP. Single crystal X-ray diffraction revealed the cell parameters of pure and doped crystals. A slight distorsion in the cell parameters suggests the incorporation of L-proline into KDP. SHG efficiency found to increase with the concentration of dopants. This is attributed to the delocalized π orbital of L-proline.

UV – visible spectrum has showed increase in the transmittance with doping concentration. Mechanical hardness has been found to change with different concentration of the dopant. The effect of L-proline as dopant has considerably enhanced the optical transparency, NLO property and mechanical property compared to pure KDP. It is suggested that doping of KDP with L-proline has made KDP much more efficient with improved qualities and facilitate its application in the field of nonlinear optics.

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