

## FTIR, Electrical and SHG Studies of Single Crystals of KDP Doped With Phenylalanine

Sandhya Ravi<sup>1</sup>, S.Chenthamarai<sup>2</sup>, R.Jayavel<sup>3</sup>

<sup>1,2</sup> (Research Department of Physics, SDNB Vaishnav College for Women, Chromepet, Chennai- 600 044, India)

<sup>3</sup> (Centre for Nano Science and Technology, Anna University, Chennai- 600 025, India)

**Abstract:** In recent years study of Non linear optical (NLO) materials is gaining rapid momentum due to their increased need in several device applications. Potassium dihydrogen phosphate (KDP) is a well known NLO material, whose non linearity is enhanced by doping with amino acids. In the present study single crystals of Phenylalanine doped KDP have been grown by slow evaporation solution growth technique. The crystallinity and cell parameters were characterised by X-ray diffraction analysis (XRD), the shift in frequency assignments of various functional groups of KDP due to the addition of phenylalanine was analysed by Fourier transform infrared (FTIR) spectroscopic studies. The dielectric constant and dielectric loss of the single crystals were studied as a function of frequency at different temperatures and the activation energies were determined from Conductivity studies. Kurtz-Perry powder technique was employed to determine the SHG efficiency of Phenylalanine doped KDP single crystals.

**Keywords:** NLO, XRD, SHG efficiency, Dielectric studies, Kurtz- Perry.

### I. Introduction

Extensive studies have been made on the synthesis and crystal growth of nonlinear optical (NLO) materials over the past decade because of their potential applications in the field of telecommunications, optical signal processing and optical switching [1]. Potassium dihydrogen phosphate (KDP) is one of the most widely used commercial Non linear optical (NLO) materials. KDP exhibits good homogeneity over large volumes and has a high damage threshold. It is an effective angle tuned dielectric medium for optical harmonic generation in and near visible region [2]. The physical, chemical and non linear optical properties of KDP are enhanced by adding optically active amino acids as dopants. These amino acids are organic compounds that possess large second order non linear susceptibilities due to delocalized  $\pi$  electrons [3].

The growth and characterization of Single crystals of KDP doped with amino acids namely glycine, arginine, alanine, tryptophan, histidine have been reported earlier [4-6]. In the present work single crystals of Phenylalanine doped KDP have been grown by slow evaporation technique with deionized water as solvent at room temperature (28.4 °C) with a doping concentration of one mole percent. Powder XRD studies were employed to analyze the crystalline nature and single XRD studies to determine the cell parameter values of phenylalanine doped KDP single crystals. The FTIR study was carried out to identify the shift in frequency of functional groups in KDP as a result of doping. The dielectric and conductivity studies were carried out to investigate the NLO character of the crystals. The SHG efficiency of phenylalanine doped KDP was found to be higher than pure KDP, thereby establishing it as an excellent material for non linear applications.

### II. Growth Procedure

Calculated amount of analytical grade KDP and 1 mole percent of phenylalanine were first mixed thoroughly and uniformly and added slowly into deionized water accompanied by constant stirring with a magnetic stirrer to ensure uniform and homogenous distribution throughout the entire volume of the solution. Upon reaching saturation, the solution was filtered and transferred to a Petri dish, covered with a thick paper with fine pores in order to minimize the rate of evaporation. Upon complete evaporation of solvent, single crystals of size 6.45mm x 1.85mm were harvested within three days (Fig 1).



**Fig 1 :** As grown crystals of Phenylalanine doped KDP single crystals

### III. Characterization

#### 3.1 Single and Powder X-ray diffraction studies

The single crystal X-ray diffraction analysis was performed using an Enraf Nonius CAD4-F single crystal X-ray diffractometer. Phenylalanine doped KDP single crystals possess tetragonal geometry. The cell parameter values are  $a = b = 7.494 \text{ \AA}$ ,  $c = 6.995 \text{ \AA}$  with angles  $\alpha = \beta = \gamma = 90^\circ$ . The a, b, c values vary as compared to that of pure KDP. This clearly indicates that doping changes the cell axes and hence the cell volume [7].

The grown single crystals were subjected to Powder XRD analysis using Rich Seifert X-ray diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation. The samples were scanned for  $2\theta$  values from  $10^\circ$  to  $60^\circ$  at a rate of  $2^\circ/\text{min}$ . The prominent peaks observed in the diffraction pattern confirm the single crystalline nature of the phenylalanine doped KDP crystals. While change in intensity of peaks is observed when compared to diffraction pattern of pure KDP [8], no additional peaks are observed indicating the absence in variation of structure due to doping [5].

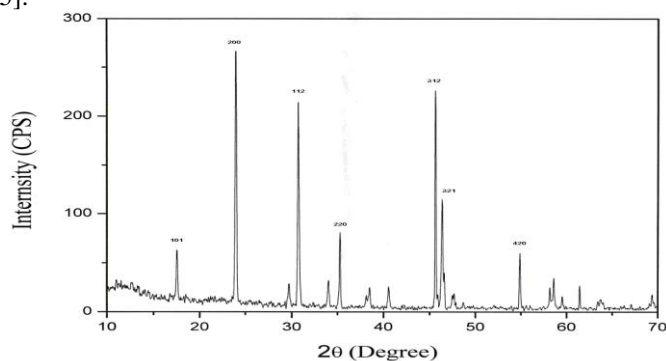


Fig 2: Powder diffraction pattern of Phenylalanine doped KDP

#### 3.2 FTIR Study

The FTIR analysis of the single crystals of Phenylalanine doped KDP was performed by employing a 66V model spectrophotometer by KBr pellet method in the wave-number range  $4000\text{--}450 \text{ cm}^{-1}$ . The FTIR spectrum of the doped crystal (Fig 3) is compared to the spectrum of pure KDP which is already reported by various authors [7, 9-10] and analyzed. The inclusion of phenylalanine into KDP has been strongly verified. The bending vibrations due to  $(\text{H}_2\text{PO}_4)$  in both pure and doped KDP are observed in the region  $400\text{--}600 \text{ cm}^{-1}$ . The P=O symmetric bending vibration gives a strong band at  $538.54 \text{ cm}^{-1}$  in pure KDP while it is slightly shifted to  $539 \text{ cm}^{-1}$  in the doped crystal. The absorption band at  $914 \text{ cm}^{-1}$  is due to P-O-H bending vibration in the doped crystal while it is present at  $909.14 \text{ cm}^{-1}$  in pure KDP. At a frequency of  $1304 \text{ cm}^{-1}$  and  $1306 \text{ cm}^{-1}$  P=O stretching vibration occurs in phenylalanine doped KDP and pure KDP respectively. The broad absorption peak at  $1670 \text{ cm}^{-1}$  in the doped crystal is due to C=O carbonyl stretching vibration of phenylalanine which is absent in the spectrum of pure KDP. The frequency  $1097 \text{ cm}^{-1}$  in the doped crystal corresponds to C-H in plane bending vibration. The absorption peaks at  $2753 \text{ cm}^{-1}$  and  $2426 \text{ cm}^{-1}$  correspond to  $\text{NH}_2$  and NH stretching vibrations which are again absent in pure KDP spectra.

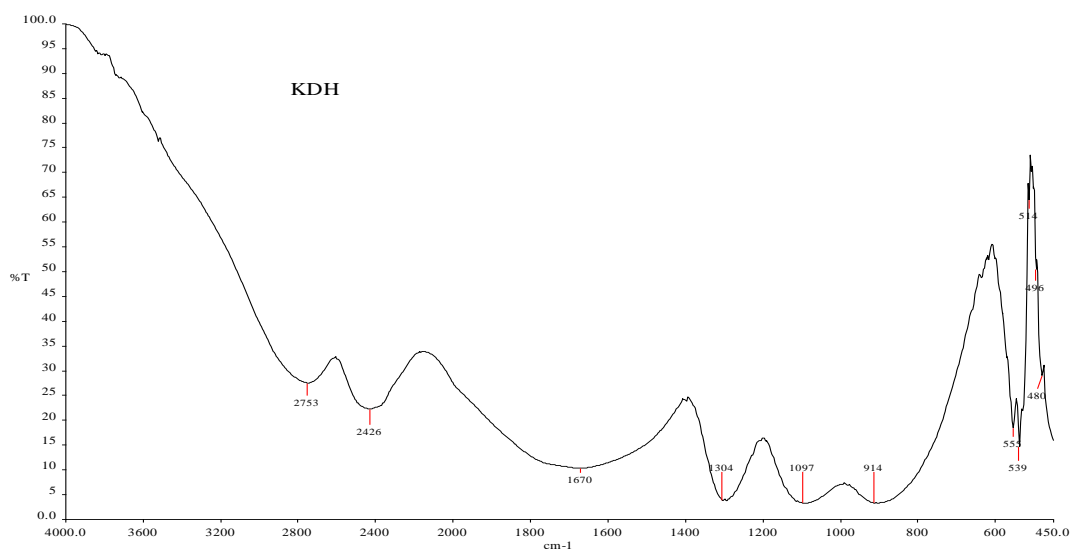


Fig 3: FTIR Spectrum of Phenylalanine doped KDP

### 3.3 Electrical Study

The electrical parameters of phenylalanine doped KDP single crystals were measured using the instrument HIOKI 3532-50 LCR HITESTER over a frequency range 50 Hz to 5 MHz. The crystal sample of dimension 6.45mm x 1.85mm having silver coating on opposite faces was placed between two copper electrodes to form a parallel plate capacitor. The dielectric constant and dielectric loss of the doped crystals were plotted as a function of frequency at temperatures 373 K, 393 K and 413 K respectively (Fig 4 and Fig 5). The high value of dielectric constant at low frequency can be attributed to the presence of all four types of polarizations namely ionic, electronic, space-charge and orientation and the low value at higher frequencies may be due to the loss of significance of these gradually[11]. The dielectric loss also exhibits a similar behavior. The low value of dielectric loss at high frequency proves that the doped single crystals possess enhanced optical quality with lesser defects. This property is an important characteristic which is of prime importance for NLO materials and their applications [12].

AC conductivity ( $\sigma_{ac}$ ) studies yields useful information regarding the mobility and production of lattice defects [13]. The bulk resistance of the crystalline sample is also determined from this study [14]. The plot of AC conductivity against frequency at temperatures 373 K, 393 K, 413 K is shown in Fig 6. There is a general rise in conductivity with increasing frequency and the  $\sigma_{ac}$  values of doped crystals are higher compared to those of pure KDP [13] which may be attributed to the occupation of interstitial sites of KDP by the amino acid molecules leading to an enhancement of the conductivity [15]. The study of DC electrical conductivity ( $\sigma_{dc}$ ) sheds light on the behavior of charge carriers under a DC field, their mobility and mechanism of conduction. The plots of  $\ln \sigma_{ac}$  vs.  $1000/T$ , (Fig 7, Fig 8, Fig 9, Fig 10) and  $\ln \sigma_{dc}$  vs.  $1000/T$  (Fig 11, Fig 12, Fig 13, Fig 14) for frequencies 2 KHz, 50 KHz, 100 KHz and 4 MHz were found to be linear and hence they were fitted into the Arrhenius relationship for AC/DC conductivity [16]:

$$\sigma_{ac/dc} = \sigma_0 \exp(-E_a/kT) \text{-----(1)}$$

Where  $\sigma_0$  is the pre exponent factor,  $E_a$  the activation energy for AC/DC conduction,  $k$  the Boltzmann constant and  $T$  the temperature. The slope of the curve gives  $(-E_a/k)$  value from which the activation energy ( $E_a$ ) for AC/DC conduction can be evaluated. The activation energy for AC conduction at frequencies 2 KHz, 50 KHz, 100 KHz and 4 MHz were 0.026 eV, 0.058 eV, 0.088 eV and 0.17 eV respectively. The activation energy for DC conduction at frequencies 2 KHz, 50 KHz, 100 KHz and 4 MHz were 0.04 eV, 0.057 eV, 0.085 eV and 0.167 eV respectively.

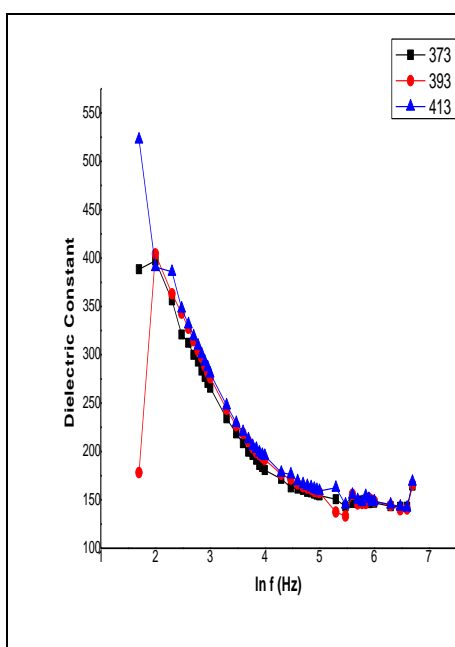


Fig 4: Dielectric Constant vs.  $\ln f$  for phenylalanine doped KDP

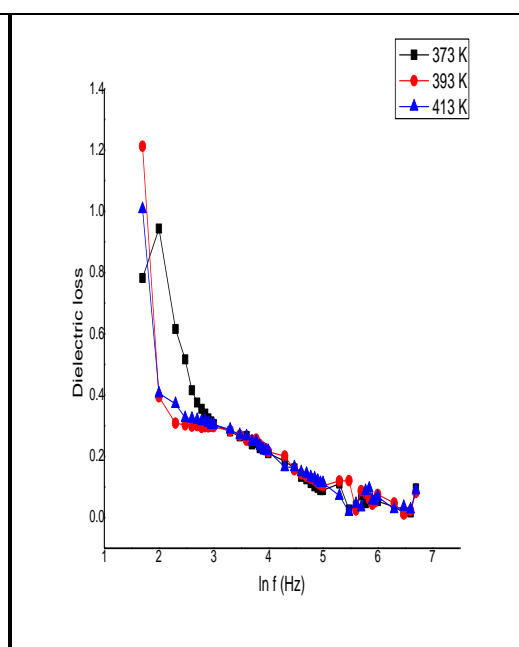


Fig 5: Dielectric loss vs.  $\ln f$  for phenylalanine doped KDP

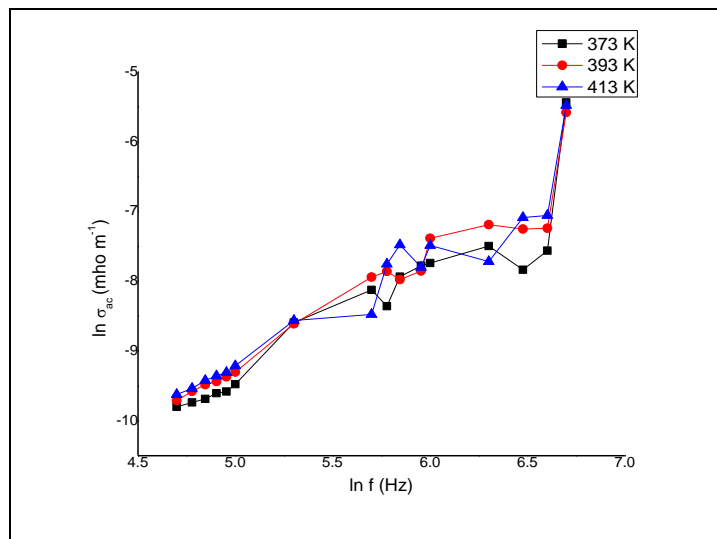


Fig 6: AC conductivity vs. frequency for phenylalanine doped KDP

Arrhenius AC Conductivity plots for phenylalanine doped KDP

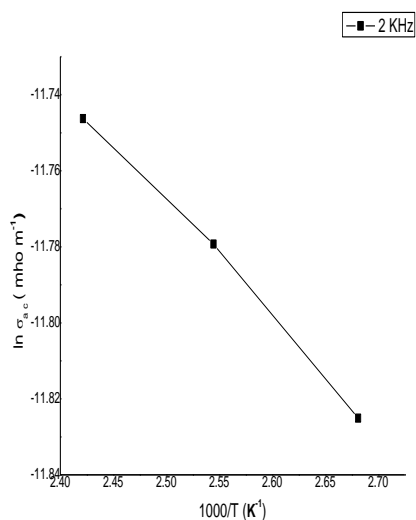


Fig 7:  $\ln \sigma_{ac}$  vs.  $1000/T$  (2 KHz)

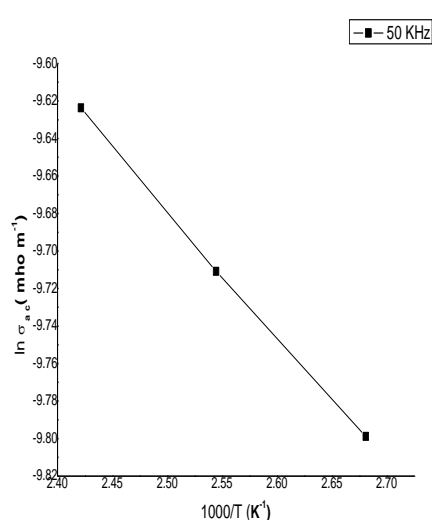


Fig 8:  $\ln \sigma_{ac}$  vs.  $1000/T$  (50 KHz)

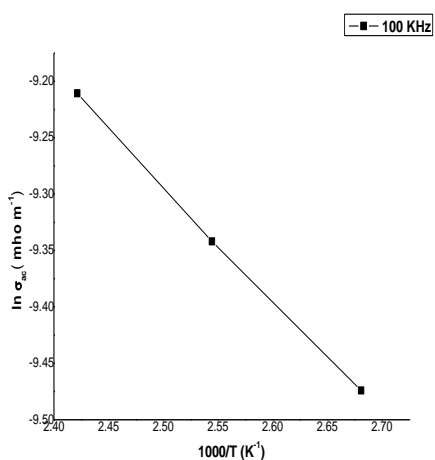


Fig 9:  $\ln \sigma_{ac}$  vs.  $1000/T$  (100 KHz)

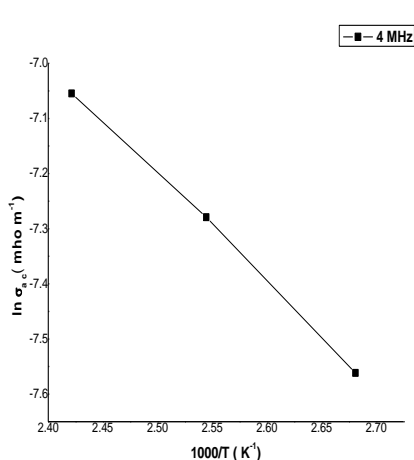


Fig 10:  $\ln \sigma_{ac}$  vs.  $1000/T$  (4 MHz)

Arrhenius DC Conductivity plots for phenylalanine doped KDP

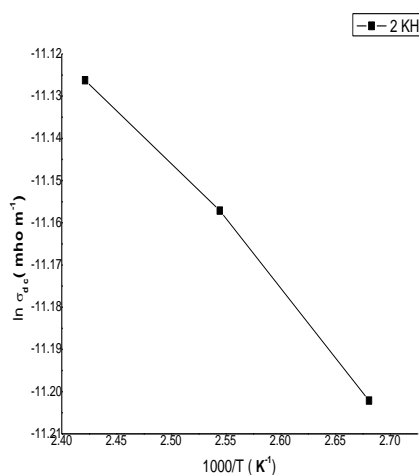


Fig 11:  $\ln \sigma_{dc}$  vs.  $1000/T$  (2 KHz)

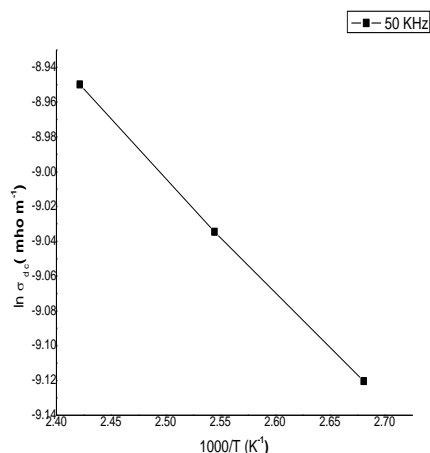


Fig 12:  $\ln \sigma_{dc}$  vs.  $1000/T$  (50 KHz)

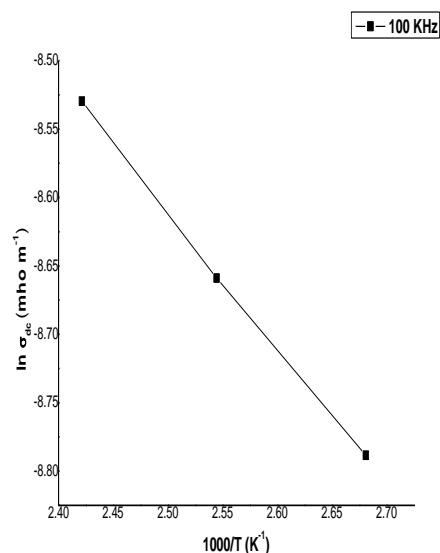


Fig 13:  $\ln \sigma_{dc}$  vs.  $1000/T$  (100 KHz)

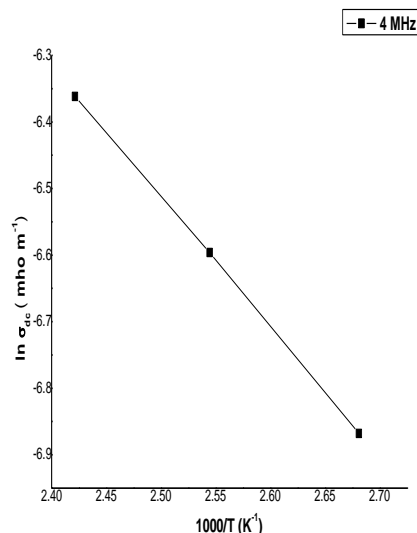


Fig 14:  $\ln \sigma_{dc}$  vs.  $1000/T$  (4 MHz)

### 3.4 SHG Analysis

The second harmonic frequency generation efficiency of the single crystals of KDP doped with phenylalanine was analyzed by the Kurtz-Perry powder technique. Q-switched Nd: YAG laser (QUANTA RAY ICR 11) of wavelength 1064 nm and pulse width of 8 ns with a repetition rate of 10 Hz was employed. The second harmonic signal generated in the crystals was confirmed from the emission of green radiation. The NLO SHG efficiency of the crystals was found to be 2.18 times more than pure KDP [17]. The results show that by doping KDP with amino acid, the NLO efficiency of KDP can be enhanced. Due to the substantial number of defects formed as a result of doping one can expect enhancement of SHG signals. The phosphate ( $\text{PO}_4$ ) group of KDP makes a significant contribution to the SHG effect and hydrogen bonds help in enhancing the birefringence. The possibility of hydrogen bond formation between oxygen unit of  $\text{PO}_4$  group of KDP and the amino group  $\text{NH}_3$  of the amino acid may have led to an increase in non-linearity of KDP [6] which in turn increases the SHG efficiency.

### IV. Conclusion

Single crystals of phenylalanine doped KDP were grown by slow evaporation solution growth technique and characterized. The single crystalline nature of the crystals was confirmed by powder XRD and cell parameters; geometry was determined by single XRD studies. FTIR analysis confirmed the inclusion of the dopant into KDP and identified the shift in frequency bands due to doping. The plots of dielectric constant and

dielectric loss against frequency proved the good optical quality of the crystals and the low value of dielectric loss at high frequencies meant that the crystals have a very high NLO efficiency. The activation energies for AC and DC conductivities were determined from the Arrhenius plots. The second harmonic frequency generation efficiency of the phenylalanine doped KDP crystals was found to be 2.18 times that of pure KDP. Thus it is concluded that phenylalanine doped KDP single crystals can be effectively used as a promising NLO material.

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