

Growth and characterization of glycine doped KDP single crystal for optoelectronics applications

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Potassium dihydrogen phosphate (KDP) is a well known nonlinear optical (NLO) material for various optoelectronics applications. Since amino acids exhibits NLO property, it is of interest to dope them in KDP. In present study single crystal of pure and amino acid, Glycine doped Potassium dihydrogen phosphate (KDP) has been grown by slow evaporation solution growth technique. The SHG efficiency of pure and Glycine doped KDP crystal was confirmed by Nd:YAG pulsed Laser employing the Kurtz powder technique. The SHG efficiency of Glycine doped KDP crystal was found to be **1.36** times more than pure KDP. The crystallinity and cell parameters were characterized by X-ray diffraction analysis, the shifting in frequency assignment of different functional groups of KDP due to addition of Glycine were analyzed by FTIR analysis. The enhancement in transmittance of grown KDP crystal with addition of Glycine was determined by UV-Visible spectral analysis. The presence of dopant in the sample of grown crystal was confirmed by energy dispersive X-ray analysis (EDAX). The grown crystal was subjected to thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis to observe the thermal decomposition and weight loss.

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1. Introduction

Second order nonlinear optics (NLO) is widely used to convert the frequency of coherent sources. Applications such as laser based imaging, communication; remote sensing and counter measures system require improved nonlinear optical materials to accomplish such conversions. A strong need continues to exist for lower cost, more efficient, higher average power materials for optical parametric amplifier operation and second harmonic generation (SHG) through out the blue near UV spectral regions. Another area of growing need is materials for birefringent, phase matched optical parametric oscillators (OPO) for the generation of broadly tunable mid-wave and long wave infrared radiation. Intense attention has been paid to inorganic materials showing the second order nonlinear optical effect because of their higher nonlinearity. Among the nonlinear phenomenon, frequency doubling, frequency mixing and electro-optic modulations are important in the field of optical image and optical data storage [1-4].

The potassium dihydrogen phosphate (KDP) is the best known member of an important family of compound, where relevant nonlinear optical properties have made it, a widely used crystal in frequency converts, electro-optic switching and modulators and applications such as second harmonic generation and optical parametric oscillations. KDP is an interesting material and aroused considerable interest among the several researchers because of it wide frequency conversion, high damaged threshold against high power laser [4-8].

The amino acids are the famous organic materials, play a vital role in the field of nonlinear optical crystal growth. Many members of natural amino acids are individually exhibiting the nonlinear optical properties because they have a donor NH₂ and acceptor COOH group and the intermolecular charge transfer is also possible. Especially natural amino acids such as Arginine, Lysine and γ Glycine are evidently showing NLO activity because of an additional COOH group in first and NH₂ group in second. Therefore, amino acids may be used as dopants and it was observed that there is enhancement in the material properties such as nonlinear optical (NLO) and Ferro electrical properties [9]. The simplest or natural amino acid is Glycine, which has just a hydrogen atom as its side. In solution at neutral PH the Glycine is predominantly dipolar ion or Zwitterions. In Glycine the PK of the carboxylic (COOH) group is 2.3 and of the amino group is 9.6 [10,11].

The KDP crystals have disadvantages such as deliquescence, weak mechanical properties and a low damage threshold under higher power pulsed Nd:YAG laser light, which attracts the interest of many researchers to grow the KDP crystal with improved nonlinearity after addition of different impurities. Attempts have been made to dope KDP with inorganic additives to study the stability of the grown phase and compositional homogeneity of the existing crystal [12]. The SHG of KDP with addition of carbonates of Lithium Li, Sodium Na, Cesium Cs, and Rubidium Rb are reported by Rajasekaran [13]. The organic additives such as urea and thiourea were also doped in KDP and different properties were studied [13, 14]. The electrical conductivity measurements on KDP

crystals added with urea and thiourea were reported [15], but no attempts is made on large scale to dope amino acid into KDP. However only one report is available in which the doping of L-arginine in KDP was done and the SHG efficiency is reported to be increased and the thermal stability decrease with increase in impurities concentration [16].

In the present investigation the Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) was added in the KDP and it was observed that the SHG efficiency enhanced by that of Pure KDP. The thermal study revealed that the thermal stability of Glycine doped KDP is comparable to that of pure KDP hence may be used for laser fusion experiments with this enhanced SHG efficiency. The compound containing the 1 mole%, 2 mole% and 3 mole% Glycine doped in KDP were synthesized and subjected to Kurtz Perry Powder test to observe the SHG efficiency. It was observed that the SHG efficiency of KDP enhances after addition of Glycine but the highest enhancement was observed when it was doped with 1mole% of Glycine. It was found to be 1.36 times more than pure KDP. Therefore pure and the 1 mole% Glycine doped KDP crystals were grown by slow evaporation technique and subjected to X-ray diffraction, FTIR spectroscopy, EDAX analysis, and UV-Visible spectral analysis.

2. Experimental

2.1 Synthesis and growth

The KDP salt was dissolved in Millipore water. The purity of salt was obtained by repeated recrystallization. The solution of KDP salt was prepared in a slightly under saturation condition. The solution was stirred well for six hours constantly using magnetic stirrer, then solution was filtered using Whatmann filter paper. This solution was taken in three different beakers of 100 ml and the Glycine was added in each beaker in molar percent (1 mole%, 2 mole% and 3 mole%) and the same was kept for crystallization at room temperature. The spontaneous nucleation takes place and seed crystals in all three beakers were obtained. These seeds were crushed to get their microcrystalline form in order to subject them for NLO test by using Kurtz powder method. It was observed that the SHG efficiency of 1mole% Glycine doped KDP crystal is 1.36 times more than pure KDP.

A super saturated solution of pure KDP and 1mole% Glycine doped KDP at temperature 32°C was obtained by constant stirring up to six hours and then filter. These solutions were loaded in constant temperature bath set at 32°C . After twenty four hours the good quality seeds were suspended in respective beakers using the nylon thread. Slow evaporation method was employed for the growth. After completion of growth run, the crystal were harvested. The photograph of grown crystals are shown in Fig. 1(a,b).

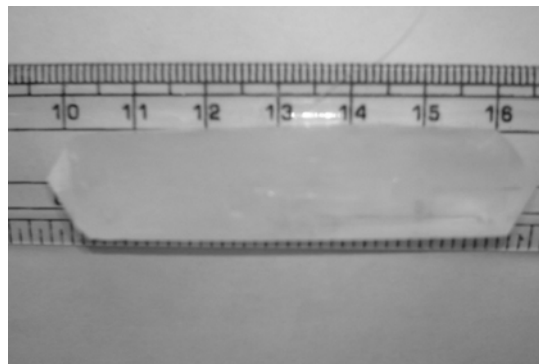


Fig. 1(a). Pure KDP crystal.

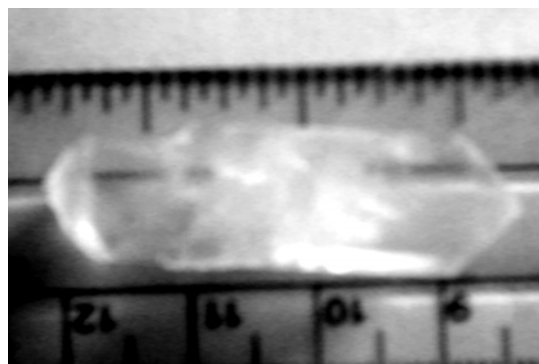


Fig. 1(b). 1mole% Glycine doped KDP crystal.

2.2 Characterization

The grown Glycine doped KDP crystal was subjected to various characterizations viz. NLO test, Powder and single crystal X-ray diffraction, FTIR analysis, UV-visible spectral study, Energy dispersive X-ray analysis(EDAX), Thermal study by TGA and DSC analysis and the results were compared with that of pure KDP.

3. Results and discussion

3.1 NLO Studies

The Kurtz's powder SHG test was performed to study the enhancement in nonlinearity of KDP due to addition of Glycine. The Glycine was added in three different mole percent in under saturated solution of pure KDP. The crystalline powder was illuminated by Nd:YAG laser of wavelength 1064nm with in put beam energy of 3 mJ/p with pulse width of 8ns and repetition rate of 10 Hz. The second harmonic signals generated in the crystalline sample were confirmed from emission of green radiation by the sample. It was found that the SHG efficiency of KDP increases with addition of Glycine in different mole percent but maximum enhancement was observed with addition of 1mole% Glycine. It was 1.36 times more than pure KDP. This increase in SHG of KDP with addition of Glycine is due to the fact that the Glycine has one Zwitter ion and it may be connected with KDP by short O-H-O

hydrogen bonds. In Glycine there is more dipole moment due to presence of polar NH_3 amino group [17]. When Glycine react with KDP the optically active amino group may replaces some potassium ion and increases its non centrosymmetry which results in increase of nonlinearity of grown crystal. Hence this Glycine doped KDP crystal with large SHG efficiency may be useful for laser fusion experiment and frequency conversion applications. This experiment was performed in the laboratory of Prof P.K.Das, Dept of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

3.2 X-ray diffraction analysis

The single crystal XRD data of Glycine doped KDP crystal has been collected using ENRAF NONIUS CAD4X-ray diffractometer and calculated cell parameters values are $a=7.4490 \text{ \AA}$, $b= 6.9666 \text{ \AA}$, $c= 7.4486 \text{ \AA}$ and $V= 386.5366 \text{ \AA}^3$ [3]. The powdered sample of Glycine doped KDP crystal was also subjected for powder X-ray diffraction analysis using X¹Pert PRO powder X-ray diffractometer. The data obtained by powder XRD analysis is in accordance with the single crystal XRD data. The powder X-ray diffraction pattern of sample of grown crystal is shown in Fig. 2. It was confirmed from the result that due to the incorporation of Glycine in KDP cell parameters and cell volume have been changed slightly [18].

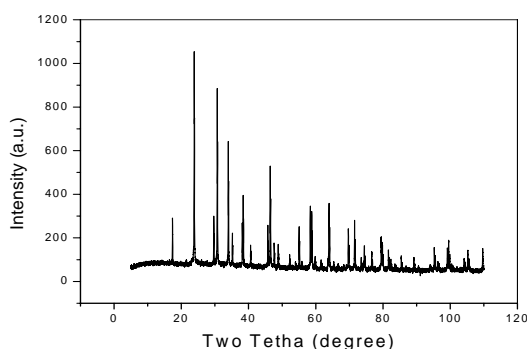


Fig. 2. Powder X-ray diffraction pattern.

3.3 FTIR analysis

The FTIR spectrometry measurement was done using Perkin Elmer Spectrum FTIR spectrometer in the region $4000\text{--}450 \text{ cm}^{-1}$ at room temperature to analyze the incorporation of different functional groups in Glycine doped KDP crystal. A free $(\text{PO}_4)^{3-}$ ion has four fundamental vibrations: a non degenerate mode $\nu_1(\text{XY})$ at 938.4 cm^{-1} in XY plane but in Glycine doped KDP crystal this ion is bonded with neighbours and absorption appears at 916.37 cm^{-1} . The broad band at the frequency 3703.29 cm^{-1} and 3318 cm^{-1} may represents the OH stretching of unchanged COOH group of the amino acid. A broad absorption in FTIR spectra of Glycine doped KDP crystal at 1761.32 cm^{-1} is assigned to $\text{C}=\text{O}$ stretching vibration. The strong absorption bands appeared

at 1286.69 cm^{-1} and 1086.46 cm^{-1} in Glycine doped KDP crystal were assigned to P=O and P-O stretching mode of vibration respectively. The band at 2736.26 cm^{-1} and 2418.35 cm^{-1} are assigned to O-H stretching vibration. The O-P-O bending appears at 537.78 cm^{-1} to 592.65 cm^{-1} in the FTIR spectrum of glycine doped KDP crystal. The involvement of NH_3^+ in hydrogen bonding is evident by the fine structure of the band at lower energy region [19].

The FTIR spectrum of Glycine doped KDP crystal contain all functional groups with slightly shift in frequency. By comparing the spectras of pure and Glycine doped KDP, one can easily find missing absorption for N-H stretching of NH_3^+ , C-H stretching of CH_2 , it conclude that the Glycine is successfully incorporated in the material of grown crystal. The FTIR spectrum of Glycine doped KDP crystal is shown in Fig. 3.

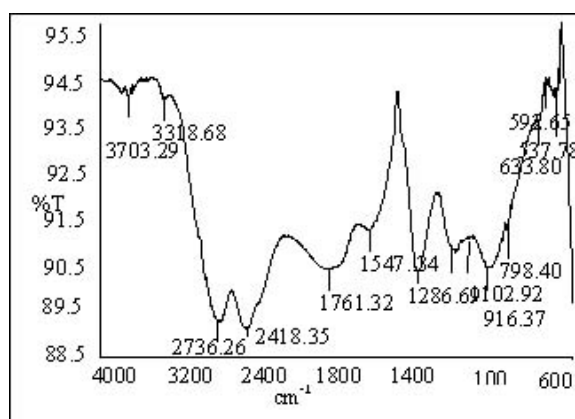


Fig. 3. Powder X-ray diffraction pattern.

3.4 UV-Visible spectral study

The UV-Visible spectral analysis was carried out using Perkin Elmer Lambda 35 UV Spectrophotometer in the range between 200 nm to 800 nm. The Figure 4(a) shows the plot of absorption vs wave length (nm). The crystal is found to be transparent in the entire visible region. There is strong absorption near the wave length of 300 nm, it may be assigned to electronic excitation in the Glycine doped KDP crystal. The lower cut off wavelength in Glycine doped KDP crystal is slightly shifted toward higher wave length side from pure KDP, which may be due to incorporation of Glycine. The absence of absorption in the region between 300 nm to 800 nm is advantageous as it is the key requirement for materials having NLO properties [20-22]. It is also clear from the transmission spectra shown in Fig. 4(b), that the percentage of transmission is 100% from 400 to 800 nm wavelength via KDP with glycine.

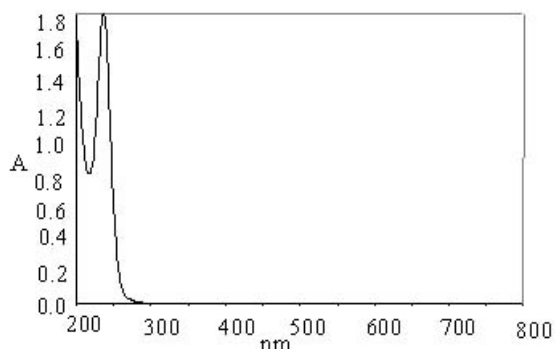


Fig. 4(a) UV Transmittance spectra.

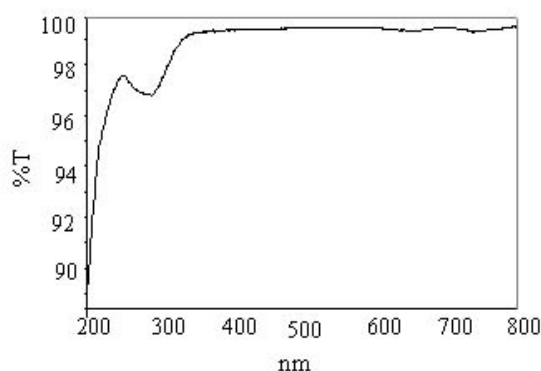


Fig. 4(b). UV Transmittance spectra.

3.5 EDAX analysis

Energy dispersive X-ray analysis (EDAX) used in conjunction with all type of electron microscope has become an important tool for characterizing the elements present in the crystals. In order to confirm the presence of glycine, the sample of grown crystal was subjected to Energy dispersive X-ray analysis using JEOL-6360 Scanning Electron Microscope. The recorded EDAX spectrum is shown in Fig. 5.

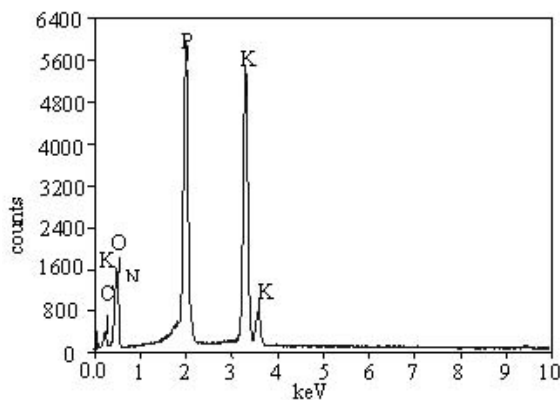


Fig. 5. EDAX spectra of Glycine Doped KDP crystal.

3.6 Thermal analysis

3.6.1 Thermogravimetric analysis (TGA)

The single crystal of Glycine doped KDP was subjected to thermogravimetric analysis (TGA) using TA Q-500 thermogravimetric analyzer at heating rate $25^{\circ}\text{C}/\text{min}$ to 800°C in nitrogen inert atmosphere to study the weight loss and thermal stability of KDP crystal after addition of Glycine. The thermogram and DTG trace are shown in Fig. 6(a). Although the TGA trace appears nearly straight up to the temperature of 200°C , a careful examination of thermogram indicates that short weight loss is at temperature near 190°C , it may be due to physically adsorbed water. The comparison of thermogram of Glycine doped KDP crystal with reported thermogram values of pure KDP revealed that the Glycine doped KDP crystal undergoes the weight loss in same stage as that of pure KDP. The decomposition temperature was 204.93°C .

3.6.2 Differential scanning calorimetry (DSC)

The Glycine doped KDP crystal was also subjected to Differential Scanning Calorimetry (DSC) to study phase transition and to measure the decomposition temperature. The DSC curve shown in Fig. 6(b) indicates that there is no phase transition up to 192.05°C . There is second weight loss at temperature of 195.34°C and after that one distinct anomaly of heat was observed at 204.93°C . The first endothermic curve corresponds to loss of water. The thermogram also shows the decomposition temperature (Td) of Glycine doped KDP crystal at 204.93°C while in pure KDP this value was 207.91°C . The reduction in decomposition value of Glycine doped KDP crystal as compared to pure KDP may be attributed to the decrease in bond energy caused by addition of dopant [23].

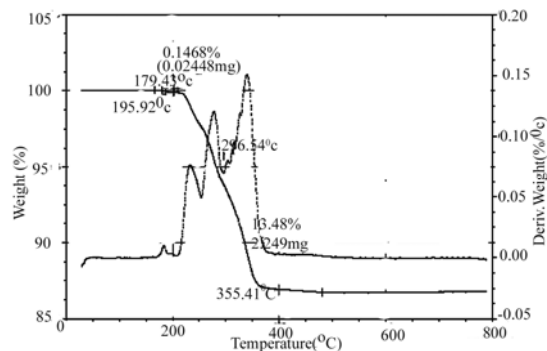


Fig. 6(a). TGA thermogram of Glycine Doped KDP crystal.

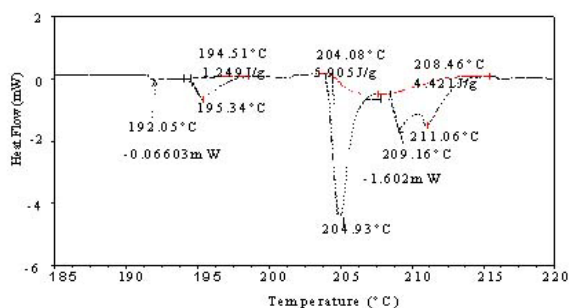


Fig. 6(b). DSC thermogram of Glycine Doped KDP crystal.

5. Conclusions

Single crystal of Glycine doped by potassium dihydrogen Phosphate (KDP) has been grown using the solvent evaporation method. The powder X-ray diffraction confirms the crystal structure of grown crystal. The cell parameters were determined from the single X-ray diffraction study. The EDAX study show that presence of Glycine in the sample. The FTIR analysis confirmed the presence of all functional groups and the addition of Glycine dopant in KDP. The absence of absorption and excellent transmission in entire visible region makes this crystal a good candidate for optoelectronic application. The thermal study by thermogravimetric analysis and Differential Scanning Calorimetry of grown Glycine doped KDP crystal indicated that this crystal can be exploited for NLO applications up to the temperature of 204.93°C.

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