FTIR spectral analysis of glycine doped ammonium dihydrogen phosphate (ADP) crystal

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Abstract. Ammonium Dihydrogen Phosphate crystals doped with Glycine (GADP) has been grown by slow evaporation method, Rotation method and Sankaranarayanan - Ramasamy (SR) methods with different molar concentration. The Fourier Transform Infra-Red (FTIR) studies have been investigated on the as grown GADP crystals. The FTIR spectrum shows the interaction between ADP and the dopant by the additional peaks which corresponds to the functional groups of Glycine. The standard spectrum statistics of FTIR confirms the presence of all the functional groups. The spectrum for ADP crystals doped with Glycine grown by Rotation and SR methods have similar peaks with slight variation as that of conventional slow evaporation method grown Glycine doped ADP crystals.

1. Introduction
Crystal growth is an elementary component of material science and engineering. The immense majority of work done on crystal growth has been concerned with practical methods rather than with hypothetical investigation. Advancement in the growth of crystal is extremely needed for the production of higher efficiency PV cells for surrogate energy. Crystals of an appropriate dimension and precision are essential for initial data acquirement and for devices used for practical purpose such as IC’s and sensors etc. Adding tiny formerly prepared crystals offer nucleating sites to the prepared solutions. Single seed crystal would results in the crystal of larger size [1-2]. Depending on the phase conversion method, techniques of crystal growth can be classified as growth from solid, vapour, melt and solution [3]. The various methods of solution growth are studied by many researchers [4]. As the crystal growth is conceded at the room temperature, the structural impurities in the crystals grown by solution method are quite less [5].

Ammonium Dihydrogen Phosphate crystals have been extensively used as the 2nd, 3rd and 4th harmonic generators for different laser applications which require short pulses of laser. ADP crystals have found many applications in Nonlinear optics, electro-optics, and transducer devices. It is also used as Monochromator in X-ray fluorescence investigation. Numerous researchers have studied properties of pure and doped Ammonium dihydrogen phosphate crystals [6-7]. Amino acids with various molar concentrations have been used as an additive to grow ADP crystals [8]. Glycine (NH₂CH₂COOH) is considered to be the simplest amino acid among the 20 protein amino acids. In this research module; we have used amino acid Glycine as an additive in ADP in different molar
concentrations. We have employed slow evaporation growth method, crystal rotation method and Sankaranarayana-Ramasamy method to grow pure and glycine doped ADP (GADP) crystals.

2. Synthesis of G-ADP Crystals
ADP crystals have been grown by the method of conventional slow evaporation. Calculated amount of Ammonium Dihydrogen Phosphate (GR-grade) was dissolved in the water. Aqueous solution containing Ammonium dihydrogen phosphate was made based on the solubility curve of salt at the constant temperature under saturation state. Magnetic stirrer was used for stirring the solution. The solution was then stirred constantly for 8 hours to attain stability. Filter paper of 11μm dimension and filtration pump was used to filter the prepared solution.

The above process was repeated for calculated mole % of Glycine (Merck) dopant which was dissolved in Ammonium dihydrogen phosphate solution. Crystals of ADP and GADP with optically superior quality have been grown in the span of 20 - 30 days. The photographs of ADP and GADP crystals have been shown in figure 1.

![Figure 1. Photographs of GADP (left) and ADP (right) Crystals.](image)

G-ADP crystals have been also grown by crystal rotation method and Sankaranarayanan-Ramasamy (SR) method [9].

3. FTIR Spectral Analysis
The grown crystals were grounded in pestle mortar to get fine powder. The fine powdered samples were then utilized for FTIR Spectral Analysis. Fourier Transform Infrared (FTIR) spectrum shows a fingerprint of the material with the peaks that correspond to the vibrational frequencies amongst the bonds of the atoms building up the substance. In IR spectroscopy, Infrared rays are allowed to pass through a target material. Several IR rays are absorbed by the material but few of them are transmitted through it. The ensuing spectrum thus represents the structural fingerprint of the material. Similar IR spectrum could not be produced by two distinctive molecular structures thus making IR spectroscopy helpful for various types of quantitative examinations.

3.1. Results and Discussion
The Fourier Transform Infrared (FTIR) studies have been done on the crushed samples of pure Ammonium Dihydrogen Phosphate and Glycine doped ADP crystals. The FTIR spectra were observed in the region 400 to 4000 cm⁻¹ with the use of KBr pellet. The standard spectra of functional group were used to match the functional groups of pure and doped ADP crystals have been acknowledged. Functional groups of Pure ADP and Glycine doped ADP (GADP) crystals developed by conventional slow evaporation methods with different concentrations [1M% - 6M%] are shown in figure 2.
Figure 2. FTIR Spectrum of ADP and GADP with Various Concentrations.

The spectra reveal the interface between ADP and protein amino acid through the supplementary peaks which correspond to the functional groups of Glycine [10]. Standard FTIR spectrum statistics verifies all the functional groups present in the crystal. The above FTIR graph shows variations in the absorption frequencies due to variation in the bond length between O-H and P=O. Owing to the variation in the bond length between P=O and O-H, change in the wave number (cm\(^{-1}\)) was observed in FTIR spectrum. Owing to the feeble force of attraction amongst the P=O and O-H bonds, optical characteristics of pure
and doped Ammonium Dihydrogen Phosphate crystals are modified [11]. Amino acid doped ADP crystals were studied by many researchers [12-13]. Observed reallocation in the positions of the peak of PO$_4$ and P-O-H vibrations in the FTIR spectra confirms the interaction of ADP and amino acids. The FTIR spectra of pure ADP and GADP crystals have been shown in figure 2. In this research module, the FTIR spectrum of ADP shows that the O-H stretching vibration of H$_2$O was observed at 3258.17 cm$^{-1}$ and CH$_2$ stretching mode just below 3000 cm$^{-1}$. Stretching of P-O-H at wave number 1098.29 cm$^{-1}$ and ammonia N-H stretching at wave number 2363.55 cm$^{-1}$ was observed. The peaks at 548.29 and 405.5 cm$^{-1}$ show PO$_4$ vibrations and these results agree with the reported results [14-15].

The FTIR spectrum of Glycine (1, 2, 3, 4, 5 and 6 moles %) doped ADP (GADP) crystals disclose that due to the existence of Glycine into Ammonium Dihydrogen Phosphate, the position of the peaks have been moved to other wave numbers. The PO$_4$ vibration of the ADP is moved from 405.5 cm$^{-1}$ to a maximum value of 416.29 cm$^{-1}$. Likewise, vibrations of P-O-H at 1098.29 and 905.36 cm$^{-1}$ of the ADP are moved to lower side i.e., 1095.35 and 899.69 cm$^{-1}$, which confirms the existence of Glycine in the ADP crystal lattice.

![Figure 3. FTIR Spectrum of Glycine (1M%) Doped ADP Crystal by Different Methods.](image-url)

Functional groups of Glycine doped ADP crystals grown by different methods are shown in figure 3. C = O stretching of –COOH group is assigned in the absorption range 1700-1800 cm$^{-1}$ and CH$_2$ vibrations of glycine give their peak in the range 2872.11 to 2876.88 cm$^{-1}$ which are missing in pure ADP spectrum [16]. Due to high concentrations of dopant, the -NH group hydrogen stretching which was observed at
wave number 3500 - 3000 cm$^{-1}$ is broadened to some extent. Some kind of interaction amongst -NH group of the ADP and the dopant is indicated by the shifting of peak from 2363.55 cm$^{-1}$ to a maximum value of 2366.97 cm$^{-1}$ [12]. The spectrum for Glycine doped (1M%) ADP crystals (figure 3) grown by Rotation (Rot-GADP) and SR (SR-GADP) methods also have similar peaks with minor difference as that of slow evaporation (Slow-GADP) method grown Glycine doped ADP crystals with slight variations. The PO$_4$ vibration of 1M% GADP crystal developed by slow evaporation, rotation and Sankaranarayan-Ramasamy methods are found to be at 404.86, 416.50 and 423.91 cm$^{-1}$ respectively. Also, the P-O-H vibrations are found at 1097.84 and 905.62 cm$^{-1}$ for 1M% Slow GADP, 1096.56 and 900.81 cm$^{-1}$ for rotation and 1097.25 and 900.95 cm$^{-1}$ for SR method grown GADP crystals, which again confirms that Glycine is present in ADP crystals. CH$_2$ vibrations of glycine give their peak at 2872.11, 2879.89 and 2888.72 cm$^{-1}$ for slow, rotation and SR grown GADP crystals respectively. The vibration frequencies shows that hydrogen bonding results in O-H group stretching frequencies of ADP and COOH group of Glycine [17].

4. Conclusion
The Fourier Transform Infra-Red (FTIR) analysis was performed on the grown ADP samples. The effect of Glycine used in this research module on the vibration frequency assignments of functional groups of ADP and GADP crystals have been recognized by Fourier Transform Infrared (FTIR) Spectroscopy. Matching of functional groups with the standard spectrum was done. The FTIR spectra validate the interaction between ADP and the dopant by the extra peak which corresponds to the functional groups of Glycine. The peaks analogous to C = O stretching of –COOH group and CH$_2$ vibrations of glycine confirms the incorporation of dopant into the ADP crystal lattice. The variation in the values of SR grown GADP crystal shows that it can modify the transparency and strength of the Ammonium Dihydrogen Phosphate crystals, better than the crystals grown by slow evaporation and rotation methods. Fourier Transform Infrared (FTIR) spectra of the specimens validate the presence of functional groups in them.

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