



XRD, FTIR & UV-VISIBLE STUDIES OF GLYCINE DOPED ADP CRYSTAL

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Abstract

Ammonium dihydrogen orthophosphate (ADP) crystals were grown with amino acid Glycine as an additive in different molar concentrations. Addition of Amino acid has increased the quality of the crystals and yields highly transparent crystals. XRD analysis reveals that the crystalline perfection of Glycine doped crystals is extremely good without having any internal structural grain boundaries. FTIR studies were performed to identify various functional groups present in the crystal. The large optical transmission in the entire visible region enables it to be a good candidate for electro-optic and NLO applications.

Index Terms: ADP, FTIR, Glycine, XRD

I. INTRODUCTION

Crystals are the unacknowledged backbone of advanced technology. Without crystals, there would be no electronic industry, no fiber optic communications, no photonic industry, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject

covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications.

Potassium dihydrogen phosphate KH_2PO_4 (KDP) and ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP) continue to be interesting materials both academically and industrially. KDP and ADP are representatives of hydrogen bonded crystals which possess very good electro-optic and nonlinear optical properties. ADP is antiferroelectric and KDP is ferroelectric due to the difference in the number of hydrogen bonds. An additive can suppress, enhance or stop the growth of crystal completely and its effects depend on the additive concentration, supersaturation, temperature and pH of the solution. Some dopants are added to suppress the effect of metal ion impurities on ADP and KDP crystals. For example, EDTA and KCl reduces the effect of metal ion impurities and enhance the metastable zone width and increases the growth rate of the crystals [1]-[2]. Studies have also been made about the effect of additives on growth, habit modification and structure of ADP [3]-[4]. To improve the Second Harmonic Generation efficiency of ADP, researchers have attempted to modify ADP crystals by doping different type of amino acids. In solid state, many amino acids contain a deprotonated

carboxylic acid group (COOH) and protonated amino groups (NH³⁺). This dipolar nature exhibits peculiar physical and chemical properties in amino acid, thus making them ideal candidate for NLO application. In the light of research work being done on ADP crystals, to improve their growth and other characteristics, it was thought interesting and worthwhile to investigate the effects of amino acid Glycine on growth and properties of ADP crystals for both academic and industrial uses.

II. EXPERIMENTAL ARRANGEMENT AND GROWTH OF CRYSTAL

A. Solution Preparation

Submit your manuscript electronically for review. The starting materials namely Ammonium Dihydrogen Phosphate (ADP) and Glycine were of GR grade (Merck) and the growth process was carried out in aqueous solution. The calculated amount of ADP was dissolved in Millipore water of resistivity 18.2(MΩcm). Solution was prepared according to solubility curve of ADP at the constant growth temperature under saturation condition. This solution was then stirred well for more than six hours using a magnetic stirrer and filtered using Whatman filter paper of pore size 11(μm).

B. Crystal Growth

The solution was then poured into a beaker cover with a lid with small holes in it and was allowed to evaporate at room temperature in a dust free environment. The procedure was repeated for different mole percentage of Glycine as a dopant in ADP. Optically good quality single crystals of pure ADP and glycine doped ADP crystals were harvested in a period of 15 - 25 days.

The glycine doped ADP crystals were observed to be more transparent and bigger in size than the conventional grown crystals. The photograph of the as grown crystal of pure and glycine doped ADP is shown in Fig. 1.

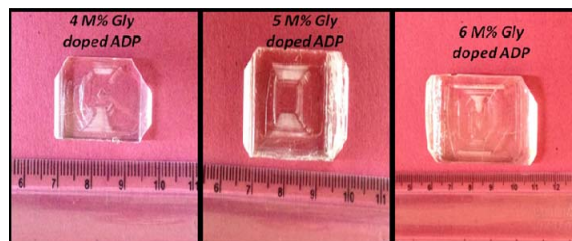
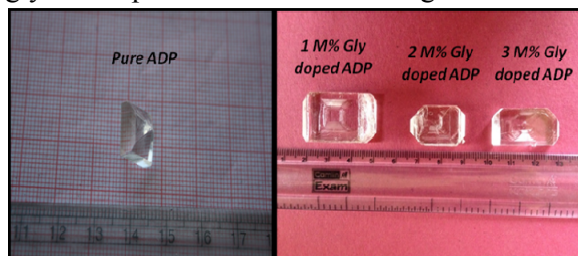


Figure 1 Photographs of Pure and Glycine Doped ADP (GADP) Crystals with different concentration

III. RESULT AND DISCUSSION

A. Powder X-ray Diffraction

The X-ray powder diffraction analysis was used to confirm the physical phase of the product. Grown crystals were ground using a porcelain mortar - pestle in order to determine the crystal phases by X-ray diffraction (XRD). Powder X-ray diffraction studies were carried out using a Bruker AXS D8 Advance ($\lambda=1.5406 \text{ \AA}$) X-ray diffractometer. The powder sample scanned over the range 5-80° at a scan rate of 1°/min. The recorded Powder X-ray diffraction patterns of pure and doped ADP crystals for different concentration of Glycine dopant as 1 mole %, 2 mole %, 3 mole %, 4 mole %, 5 mole% and 6 mole % are shown in Fig. 2.

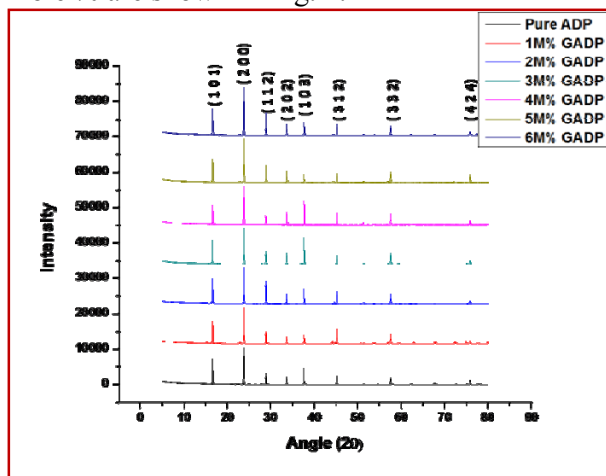


Figure 2 Powder XRD Pattern of Pure and Glycine Doped ADP (GADP) crystals

Well defined Bragg peaks are obtained at specific 2θ angles indicating that crystals are ordered. The powder XRD results reveal that the obtained diffracted peaks are same with pure ADP crystal. The observed prominent peaks of pure and glycine doped ADP are (101), (200), (112), (202), (103), (312), (332), (424) but the intensities of the diffracted peaks are found to be varied.

B. FTIR Spectral Analysis

The Fourier Transform Infra Red (FTIR) investigations were also carried out on the powdered samples of ADP. The spectrum was observed from Thermo Nicolet, Avatar 370 spectrophotometer in the region 400 to 4000 cm^{-1} using KBr pellet. The functional groups of pure and doped ADP has been identified by the spectrum and matched with the standard spectrum of functional groups. The spectrum confirms the interaction between ADP and organic amino acid by additional peaks corresponds to the functional groups of Glycine [9]. The FTIR spectra of pure ADP and Glycine doped ADP crystals are shown in Fig. 3. All functional group were present and verified with FTIR standard spectrum data.

Amino acid doped ADP crystals were studied by many researchers [10]-[11]. The authors confirmed the interaction between ADP and organic amino acids by observing shift in the peak positions of P-O-H and PO_4 vibrations compared to pure ADP. In this research work the FTIR spectra of pure ADP and Glycine doped ADP crystals are shown in Fig. 3. In the FT-IR spectrum of pure ADP the O-H stretching vibration of water happened at 3258.13 cm^{-1} and CH_2 stretching mode just below 3000 cm^{-1} , bending vibrations of water at 1651.48 cm^{-1} , P-O-H stretching at 1098.25 cm^{-1} , N-H stretching of ammonia at 2363.52 cm^{-1} and the PO_4 vibrations give their peaks at 548.28 and 405 cm^{-1} and are in good agreement with the reported values [12]-[13].

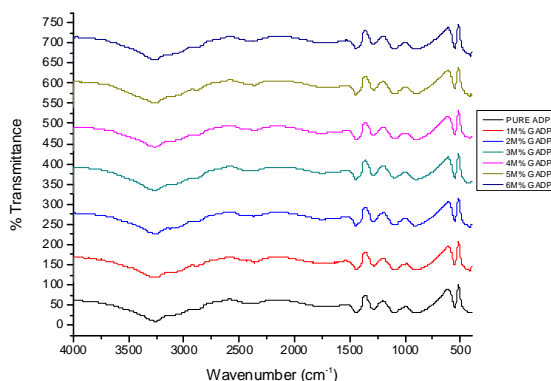


Figure 3 FTIR Spectrum of grown crystals

C. UV-Visible Studies

Optical transmission spectra were recorded for the samples obtained from pure as well as

additive added crystals grown by the slow evaporation method. The spectra were recorded in the wavelength region from 200 to 1100 nm using Lambda 35 spectrophotometer. C-cut crystal plates with 2mm thickness were used for the study.

The UV-Vis spectra recorded for pure and additive added ADP crystals is shown in Fig. 4. It is clear from the figure that the crystals have sufficient transmission in the entire visible and IR region. The optical transparency of the ADP crystal is increased by the addition of Glycine [8]. It has also been observed that the cut off wavelength is the same for pure and additive added ADP crystals [14].

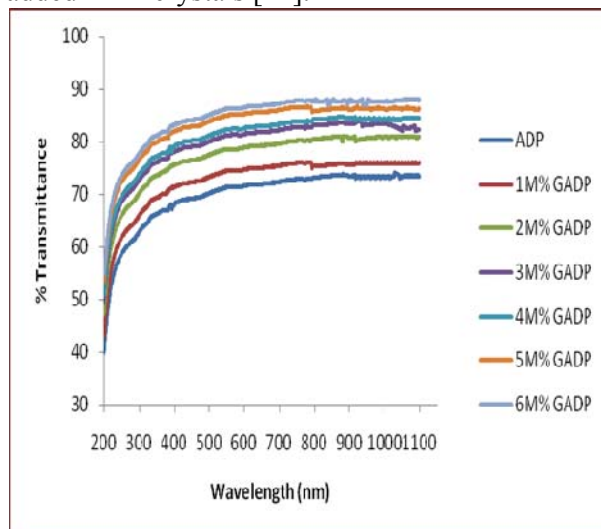


Figure 4 UV Spectrum of Conventionally Grown Pure and Glycine Doped ADP (GADP) Crystals with Different Concentrations

The addition of the amino acid dopants (1M%, 2M%, 3M%, 4M%, 5M%, 6M%) in the optimum conditions to the solution is found to suppress the inclusions and improve the quality of the crystal with higher transparency.

The transmission spectrum of the crystal reveals that the grown crystal has sufficient transparency in the entire visible region and it is noted that the transparency is higher in Glycine doped crystal (76% for 1M%, 80% for 2M%, 82% for 3M%, 84% for 4M%, 86% for 5M%, 87% for 6M%) than the pure ADP. The large transmission in the entire visible region enables it to be a good candidate for electro-optic and NLO applications [8].

IV. CONCLUSION

The powder XRD results reveal that the obtained diffracted peaks are same as that of pure ADP crystal but the intensities of the diffracted peaks are found to be varied. The observed values are in good agreement with the reported values. This suggests that the crystals retain almost the same structure and exhibit very slight variation in the unit cell parameters on doping of Glycine. The Fourier Transform Infra Red (FTIR) spectrum confirms the interaction between ADP and organic amino acid by additional peaks corresponds to the functional groups of Glycine. The peaks analogous to C = O stretching of –COOH group and CH₂ vibrations of glycine confirms the incorporation of dopant into the ADP crystal. The optical transmission spectrum of the crystal reveals that the grown crystal has sufficient transparency in the entire visible region and it is noted that the transparency (87%) is higher in Glycine doped crystal than the pure ADP. The large transmission in the entire visible region enables it to be a good candidate for electro-optic and NLO applications.

REFERENCES

- [1] N. P. Rajesh, K. Meera, K. Srinivasan, P. Santhana Raghavan, & P. Ramasamy, *Journal of Crystal Growth*, vol. 213, pp.389-394, 2000.
- [2] J. Podder, *J. Cryst. Growth*, vol. 237-239, pp. 70-75, 2002.
- [3] R. J.Davey, & J. W. Mullin, *J. Cryst. Growth*, vol. 26, pp. 45-51, 1974.
- [4] A. Boukhris, M. Souhassou, C. Lecomte, B. Wyneke & A. Thalal, *J. Phys.: Condens. Matter*, vol. 10, pp. 1621-1626, 1998.
- [5] Dongli Xu, Dongfeng Xue, Henryk Ratajczak, *J. Mol. Struct.*, vol. 740, pp. 37, 2005.
- [6] Dongli Xu, Dongfeng Xue, *Journal of Alloys and Compounds*, vol. 449, pp. 353, 2008.
- [7] P. Rajesh, P. Ramasamy, *Journal of Crystal Growth*, vol. 311, pp 3491–3497, 2009.
- [8] P. Rajesh and P. Ramasamy, *Optical Materials*, vol. 42, pp. 87–93, 2015.
- [9] B. Narayana Moolya, S.M. Dharmapraksh, *Materials Letters* 61 (2007) 3559–3562.
- [10] P. V. Dhanaraj, G. Bhagavannarayana and N. P. Rajesh, *Materials Chemistry and Physics*, 112 (2008) 490-495

- [11]N. Pattanaboonmee, P. Ramasamy , R. Yimnirun , P. Manyum, *Journal of Crystal Growth*, 314 (2011) 196-201.
- [12]C. N. Banwell, E.M. Mc Cash, *Fundamentals of Molecular Spectroscopy*, fourth ed., McGraw-Hill, NewYork, (1994).
- [13]A. Jegatheesan, B. Neelakantaprasad, J. Murugan, G. Rajarajan, *International Journal of Computer Applications* (0975 – 8887), 53 (2012) 15-18.
- [14]R.N.Shaikh, S.R. Mitkar, Mohd Anis, Mahendra D.Shirsat and S.S.Hussaini, *International Journal of Chem Tech Research CODEN (USA)*, 6(2014) 1617-1620.