Growth & Study of Pure and SR Grown Glycine doped Ammonium Dihydrogen Orthophosphate Crystal

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Abstract— *Ammonium dihydrogen orthophosphate (ADP) crystals doped with Glycine were grown by conventional & Sankaranarayan-Ramasamy (SR) method. The addition of this amino acid improves the quality of the crystal and yields highly transparent crystals with well-defined features. Fourier transform infrared (FTIR) spectral analysis was performed to identify the presence of various functional groups in the crystals. The UV-Visible-NIR spectral analysis was carried out to confirm the improvement in the transparency of the ADP crystal on the addition of Glycine. Thermal studies indicate that the decomposition temperatures of the crystal decreases in Glycine added ADP crystals. Vicker's microhardness study reveals that the addition of Glycine increases the hardness of the crystal. The studies performed have revealed the incorporation of Glycine into the lattice of ADP crystal.*

Keywords- *Crystal Growth, FTIR, Optical Properties*

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I. INTRODUCTION

Ammonium Dihydrogen Phosphate (ADP) is a representative of hydrogen bonded materials that have excellent dielectric, piezoelectric, antiferroelectric, electro-optic and nonlinear optical properties. Growth and studies of ammonium dihydrogen phosphate is a centre of attraction to researchers because of its unique properties and wide applications. Single crystals of ADP are used for frequency doubling and frequency tripling of laser systems, optical switches in inertial confinement fusion and acousto-optical devices [1]. ADP crystallizes in a body centered tetragonal structure with the space group I 4 2d and has tetra molecular unit cell [2] with unit cell parameters a = b = 7.510 Å and c = 7.564 Å.

ADP has been the subject of a wide variety of investigations over the past decades. Reasonable studies have been done on the growth and properties of pure ADP [3-10]. In recent years, efforts have been taken to improve the quality, growth rate and properties of ADP, by employing new growth techniques, and also by the addition of organic, inorganic and semiorganic impurities [11-18]. Organic nonlinear optical materials have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power as compared with inorganic materials.

Amino acids are interesting materials for NLO applications as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino ($-NH_2$) group in them [19]. Amino acids, when added as impurities, have improved material properties [20]. Amino acid has formed several complexes, which are promising materials for second harmonic generation [21-22]. In the light of research work being done on ADP crystals, to improve the properties, it was thought interesting and worthwhile to investigate the effect of Glycine on ADP. In this work, the structural spectral and nonlinear optical behavior of single crystals of Glycine doped ADP against pure ADP has been studied and reported.

Crystals of different orientations with different morphology are grown by conventional solution growth technique but from application point of view, specific orientation with good quality is needed. The crystal with specific orientation and bulk size can be grown from solution by Sankaranarayanan–Ramasamy (SR) method [23–25]. In this communication we report the growth of unidirectional Glycine doped ADP single crystal by SR method. The growth conditions and experimental details have been presented.

II. EXPERIMENTAL PROCEDURE AND CRYSTAL GROWTH

Growth of Glycine doped ADP crystals were carried out by conventional as well as SR method by using Millipore water of resistivity 18.2MΩ cm^{-1}. The ADP seed crystal was fetched from conventional slow evaporation technique and a (100) face was selected in the present study to inflict the orientation in the growing crystal.

The saturated solution of Glycine (2 mole%) doped ADP was prepared using water as the solvent and fed into the SR method glass ampoule. The crystallizer was kept in a water bath to avoid the temperature fluctuation of the daily variation. In the freshly prepared solution, the concentration of solute is intentionally kept slightly under saturated in order to avoid any physical and chemical instability at the growth interface. After one day there is more concentration in bottom portion due to gravity.

A suitable cover was placed on the top of the ampoule, the water vapor was condensed on the top cover and seeps into the solution via the wall. This keeps the inner wall wet which avoids the dried solute particle from falling into the solution. With a thin plate as seed a large size crystal can be grown. A suitable temperature is provided by ring heater at the top and the bottom of the glass ampoule. The temperature

around the growth region is maintained at 34°C with ±0.05°C accuracy. The temperature for the top portion of the ampoule was 40°C and bottom portion temperature was 34°C. In this condition, growth of highly transparent crystal was observed (Figure 1). Due to the transparent nature of the solution and the experimental setup, real time close-up observation revealed the solid– liquid interface which was found to be flat.

The crystals of 20 mm diameter and 18 mm length have been grown in a period of 40 days. The average growth rate was about 1mm/day. This was found to be higher than average growth rate in conventional method under similar conditions. The shape of the crystal depends on the shape of the crucible used. By this method desired shapes are possible. The photograph of the conventional grown and SR grown Glycine doped ADP are shown in Figures 1(a) and 1(b).

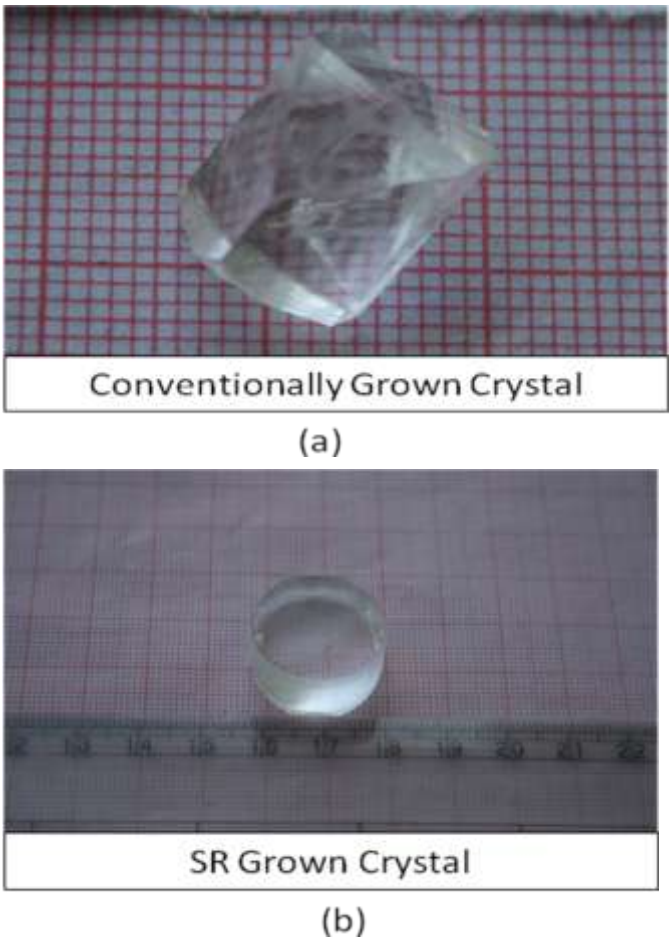

Figure 1. (a) Photograph of the conventionally grown glycine doped ADP crystal (b) Photograph of the SR grown Glycine doped ADP crystals.

III. RESULTS AND DISCUSSION

A. *Measurement of microhardness*

The good quality crystals are needed for various applications not only with good optical performance but also with good mechanical behavior. Vicker's hardness studies have been carried out using the instrument. The indentation hardness was measured as the ratio of applied load to the surface area of the indentation. The conventional- and SR method- grown pure and doped crystal of size 5×5×3 mm^3 with (1 0 0) face was selected for microhardness studies. Indentations were carried out using Vicker's indenter for varying loads. For each load (p), several indentations were made and the average value of the diagonal length (d) was used to calculate the microhardness of the crystals. Vicker's microhardness number (Hv) was determined using

$$Hv=1.8544p/d^2$$

A graph drawn between the hardness value and corresponding loads is shown in Figure 2. It is observed from the figure that hardness increases with increase in load for all the crystals and up to 100 g no cracks have been observed for the SR-method-grown Glycine-doped ADP crystal. The addition of Glycine has enhanced the hardness of the crystal and it is also observed that the mechanical strength of the SR-method grown crystal is good compared to the conventional-method grown crystals.

Hardness is the resistance offered by a solid to the movement of dislocation. Practically, hardness is the resistance offered by a material to localized plastic deformation caused by scratching or by indentation. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of the indentation.

Higher hardness value for SR-method grown crystal indicates that greater stress is required to form dislocation thus confirming greater crystalline perfection. Similar results were reported in KDP crystal [26].

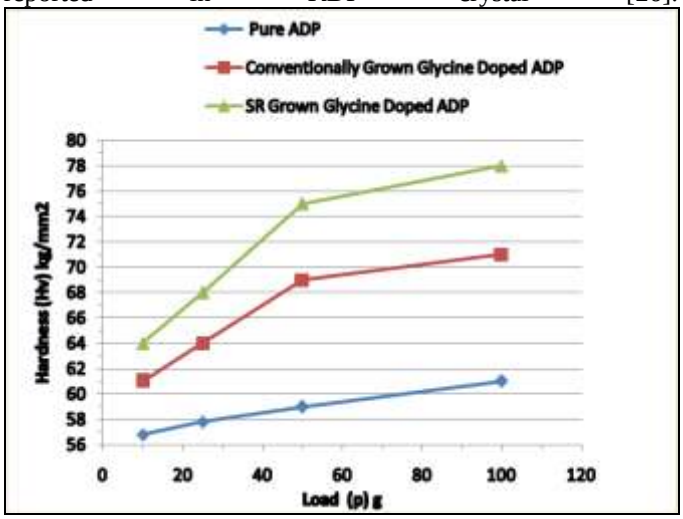

Figure 2. Vicker's microhardness of grown crystals

B. *Optical transmission studies*

Optical transmission spectra were recorded for the samples obtained from pure as well as glycine added crystals grown by the slow evaporation method and SR 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 reported value of the optical transparency for ADP is from 184 to1100 nm [27]. 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 (pure ADP has 73%, glycine doped ADP has 83% while SR grown crystal has 98% respectively) in the entire visible and IR

region. The optical transparency of the ADP crystal is increased by the addition of Glycine. It has also been observed that the cut off wavelength is the same for pure and additive added ADP crystals. The addition of the amino acid dopant in the optimum conditions to the solution is found to suppress the inclusions and improve the quality of the crystal with higher transparency. From the spectrum it is observed that the transmittance percentage of SR grown crystal is higher than that of the conventional solution grown crystal.

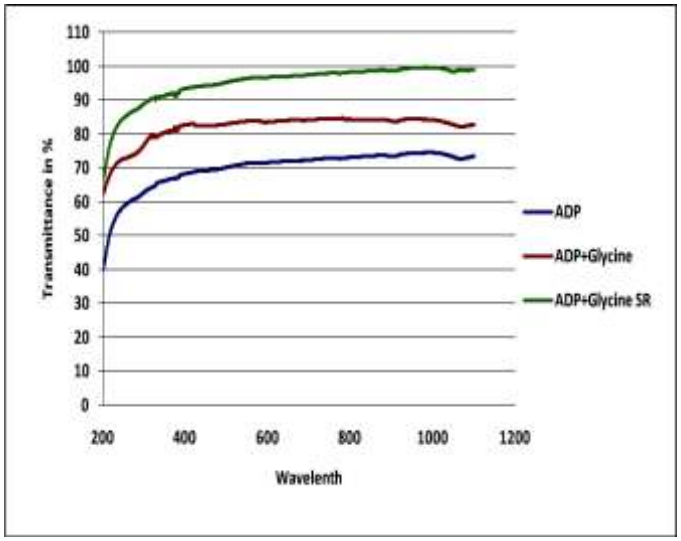

Figure 3. UV–Vis transmission spectra of pure and doped ADP crystals

C. *TGA-DTA*

The effect of Glycine doping on thermal stability of ADP crystals is studied from the simultaneous TGA & DTA curves shown in the Figure 5. In order to study the influence of dopant on the thermal stability of ADP, the temperature corresponding to the first stage of decomposition is taken into account for comparison.

The endothermic peaks of the DTA curves for Glycine doped ADP crystals is 226.21°C. These endothermic peaks correspond to the decomposition temperature of the crystals. The TGA curve exhibited negligible weight loss in the region 40°C to 150°C as shown in the Figure 4. The weight loss observed from TGA graph for glycine doped ADP in the temperature range 205.72°C.

The weight loss of the crystal might be devoid of any physically entrapped water or water of crystallization, which confirms the absence of water molecules in the grown crystals. The weight loss in these temperatures is consistent with the decomposition temperature of the compounds. It is observed from the reported values of pure ADP that the decomposition temperature (215°C) of pure ADP is decreased by 10°C. Compared with the JCPDS data, these results reveal that the Glycine has entered as an impurity into ADP crystals. Similar results were reported in L-arginine-doped KDP crystals [28].

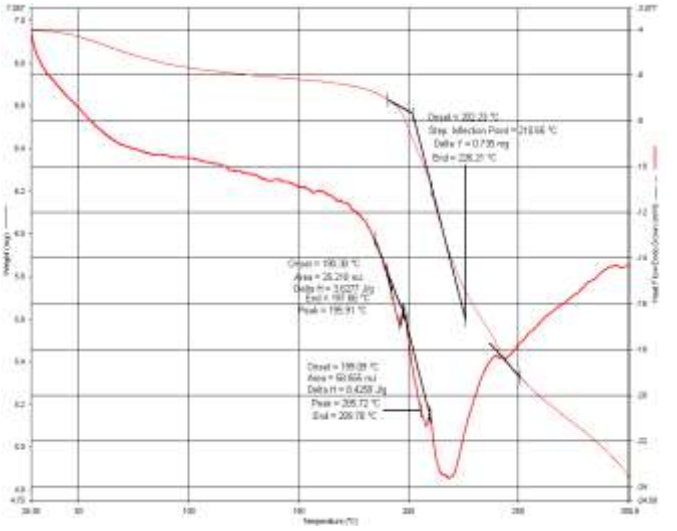

Figure 4. TG/DTA spectra of glycine doped ADP crystal

D. *Fourier transform infrared (FTIR) spectral studies*

The influence of additives used in this work on the vibration frequencies of functional groups of pure ADP crystal has been identified by FTIR spectroscopy. The FTIR spectra were recorded in the regions 400–4000cm^{-1} using a Perkin Elmer FTIR Spectrum RXI spectrometer by KBr pellet technique. Fig. shows the FTIR spectra of Glycine doped ADP crystal.

The broad band in the high energy region is due to O–H vibrations of water, P–O–H group and N–H vibrations of ammonium. The peak at 2371cm^{-1} is due to the combination band of vibrations occurring at 1293 and 1290cm^{-1}. The bending vibrations of water give its peak at 1658cm^{-1}.

The peak at 1409cm^{-1} is due to bending vibrations of ammonium. The P–O–H vibrations give its peaks at 1099 and 921cm^{-1}.The PO_4 vibrations give their peaks at 547 and 478 cm^{-1}. In the spectrum of ADP doped with Glycine, the intense band appearing at 3298cm^{-1} includes O–H vibrations and N-H vibrations of amino acid.

Although this spectrum also carries analogous features as that of ADP, there is a distinct evidence for the presence of Glycine in the lattice of ADP. In addition, shift in the peak positions of P–O–H and PO_4 vibrations compared to ADP established the presence of the additive in the lattice of ADP. For example, the PO_4 vibration of the parent is shifted from 478 to 462 cm^{-1}.

Similarly the P–O–H vibrations at 1099 and 921cm^{-1} of the parent are shifted to 1092 and 919 cm^{-1}. Such a shift establishes the presence of Glycine in the lattice of ADP. There is a slight evidence of CH_2 vibrations of Glycine just below 3000cm^{-1}. All these support the presence of Glycine in the lattice of ADP.

 ISSN: 2321-8169
026– 029

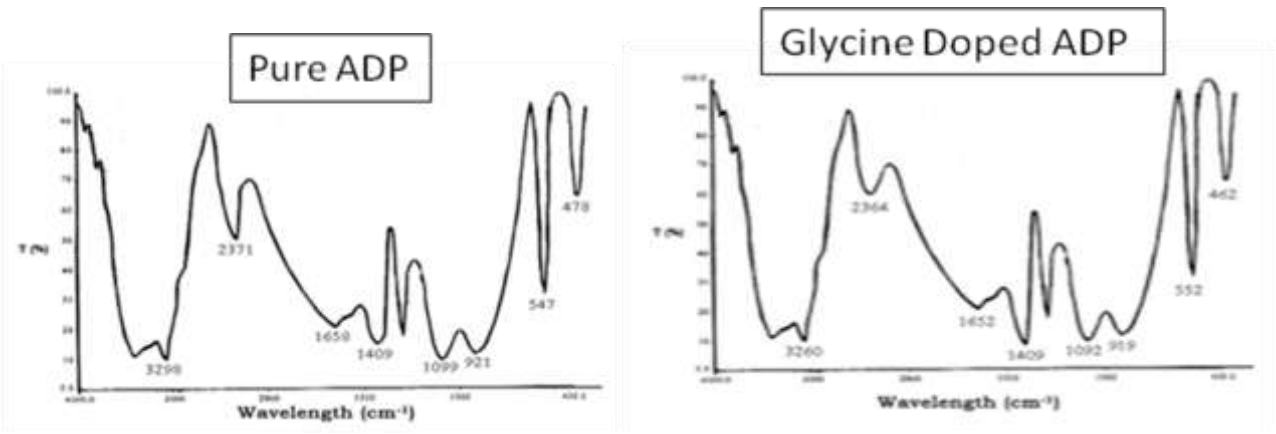

Figure 5. FTIR spectrum of pure and glycine doped ADP

IV. CONCLUSION

Good-quality conventional and SR grown ADP crystals were grown from 2 mol% of Glycine added solution. The optical studies show that the crystal is transparent in the region of 400–1100 nm and the decomposition temperature is decreased. The shift in the FTIR spectrum proves the presence of Glycine acid in the ADP crystal. 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 SR grown crystal than the crystal grown by conventional method. The addition of Glycine proved to be helpful in growing high quality large size single crystals with faster growth rate. Higher hardness value is obtained for SR grown Glycine added ADP crystal than the conventional grown pure and doped ADP crystal.

REFERENCES

[1] N. Zaitseva, L. Carman, Prog. Crystal Growth Charact. 43 (2001) 1.

[2] L. Tenzer, B.C. Frazer, R. Pepinsky, Acta Cryst. 11 (1958) 505.

[3] H.V. Alexandru, J. Cryst. Growth 10 (1971) 151.

[4] W.J.P. Van Enckevort, R. Janssen-van Rosmalen, W.H. Van der Linden, J. Cryst. Growth 49 (1980) 502.

[5] F. Lefaucheux, M.C. Robert, E. Manghi, J. Cryst. Growth 56 (1982) 141.

[6] R. Ledzion, M. Izdebski, K. Bondarczuk, W. Kucharczyk, Opto Electronics Review 12 (2004) 449.

[7] Zhengdong Li, Xiangjin Huang, Dexiang Wu, Kemin Xiong, J.Cryst. Growth 222 (2001) 524.

[8] A. Abdel-Kader, A.A. Ammar, S.I. Saleh, Thermochimica Acta 176 (1991) 293.

[9] P. Rajesh, P. Ramasamy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 74 (2009) 210.

[10] P. Rajesh, P. Ramasamy, G. Bhagavannarayana, Binay Kumar, Current App. Phy. 10 (2010) 1221.

[11] P. Rajesh, P. Ramasamy, Materials Letters 63 (2009) 2260.

[12] P. Rajesh, P. Ramasamy, Physica B 404 (2009) 1611.

[13] A. Claude, V.Vaithianathan, R.Bairava Ganesh, R. Sathyalakshmi, P. Ramasamy J. Appl. Sciences 6(1) (2006) 85.

[14] N.Joseph John, C.K. Mahadevan, Materials and Manufacturing Processes 23 (2008) 809.

[15] N.P. Rajesh, C.K. Lakshmana Perumal, P. Santhana Raghavan, P. Ramasamy, Cryst. Res. Technol. 36 (2001) 55.

[16] P. Rajesh, P. Ramasamy, J. Cryst. Growth 311 (2009) 3491.

[17] P. Rajesh, P. Ramasamy, C.K. Mahadevan J. Cryst. Growth 311 (2009) 1156.

[18] P. V. Dhanaraj, G. Bhagavannarayana, N. P. Rajesh Mat. Chem. Phy. 112 (2008) 490.

[19] P.Selvarajan, J.Glorium Arul Raj, S.Perumal, J. Crystal Growth 311 (2009) 3835.

[20] P. Kumaresan, S. Moorthy Babu, P.M. Anbarasan, Optical Materials 30 (2008) 1361.

[21] S.A. Martin Britto Dhas, G. Bhagavannarayana, S. Natarajan, J. Cryst. Growth 310 (2008) 3535.

[22] G. Anantha Babu, P. Ramasamy, Mater. Chem. Phys. 113 (2009) 727.

[23] Balamurugan N, Ramasamy P. Cryst Growth Des 2006;6:1642–4.

[24] Sankaranarayanan K, Ramasamy P. J Crystal Growth 2005;280:467–73.

[25] Balamurugan N, Lenin M, Ramasamy P. Mat letters 2007;61:1896–8.

[26] S. Balamurugan, P. Ramasamy, Mater. Chem. Phys. 112 (2008) 1.

[27] V.G. Dmitriev, G.G. Gurzadyan, D.N .Nikogosyan, Handbook of Non-linear Optical Crystal (Springer, Berlin, 1991).

[28] K.D. Parikh, D.J. Dave, B.B. Parekh, M.J. Joshi, The Bulletin of Materials Science 30 (2007) 105.