Effect of Glycine on Crystal Growth Parameters and Properties of Ammonium Dihydrogen Orthophosphate crystals

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ABSTRACT: *Ammonium dihydrogen orthophosphate (ADP) crystals were grown with glycine as an additive. The solubility studies and metastable zonewidth of ADP solution with and without this additive was determined and compared. Nucleation studies show that metastable zonewidth of ADP are enhanced by the addition of this amino acid. Moreover, the addition of this amino acid improves the quality of the crystal and yields highly transparent crystals with well-defined features. The X-ray diffraction (XRD) analysis reveals that the crystalline perfection of these amino acid doped ADP crystals is extremely good without having any internal structural grain boundaries and mosaic nature. The effect of additives on the growth, nucleation kinetics, structural and optical properties has been investigated.*

Keywords: Crystal Growth, Nucleation, Optical Properties, Solubility

I.   INTRODUCTION

Growth and studies of ammonium dihydrogen phosphate (ADP) crystal is a favorite topic 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 acoustic-optical devices [1,2]. 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 [3-5]. ADP belongs to scalenohedral class of tetragonal crystal systems. ADP has unit cell parameters of a = b = 7.510 Å and c = 7.564 Å [6]. It is known that, very little amount of additives can strongly suppress the metal ion impurities and promote the crystal quality. Oxalic acid and amino acids as additives in ADP crystals give appreciable change in optical, thermal, dielectric and mechanical behaviors [7,8]. In a crystal metastable zone width is an essential parameter for the growth of good crystals from solution. Organic additives urea and thiourea increase the metastable zone width. In ADP crystal, using urea as additive, meta stable zone width increased by 3.7°C, saturated at 30°C [9].

Studies have also been made about the effect of additives on growth, habit modification and structure of ADP [10–11]. The capture of an additive in a crystal during its growth from a solution is the combined effect of various factors: the solubility of the host and the additive phase, the character of the mother phase, the interaction between the host and the additive molecules, the relative size of the additive and host ions, the similarity in the crystallographic structure of the two phases, the relative size of the additive and the host ions and other crystallization conditions [12]. The additive effect depends on the additive concentration, supersaturation, temperature, and the pH of the solution. The growth promoting effect is observed in the presence of organic additives [13,14] as well as inorganic additives [15]. 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 such as Glycine on nucleation studies, growth and properties of ADP crystals for both academic and industrial uses. The reason for choosing the dopants is that glycine is an efficient organic NLO compound under the amino acid category.

II.   EXPERIMENTAL

2.1. Crystal Growth:

The starting materials namely ADP and Glycine were of GR grade (Merck) and the growth process was carried out in aqueous solution. The calculated amount of salts of ADP and Glycine (2 mole%) was dissolved in Millipore water of resistivity 18.2MΩcm. This solution was then stirred well for more than six hours using a magnetic stirrer and filtered using Whatman filter paper. The solution was then poured into a Petri dish and allowed to evaporate at room temperature. Optically good quality single crystals of pure ADP and Glycine doped ADP were harvested in a period of 20 - 25 days. The photograph of the as grown crystal of pure ADP and Glycine doped ADP are shown in Figures 1(a) and 1(b).
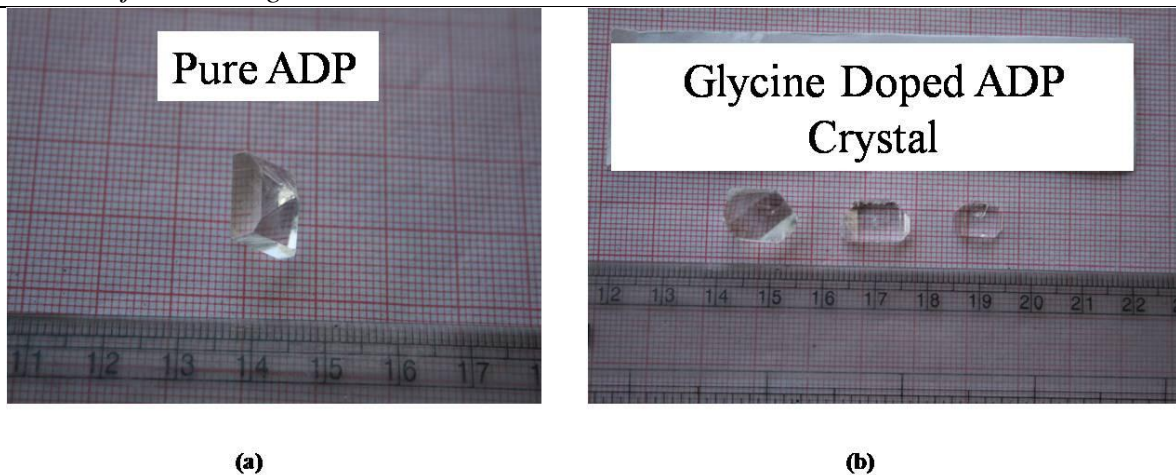
(a)   (b)

Fig.1. (a) Photograph of the as grown pure ADP crystal (b) Photograph of the as grown Glycine doped ADP crystals.

2.2. Solubility studies:

Ammonium dihydrogen orthophosphate (GR-grade) and glycine (Merck) and Millipore water of resistivity 18.2MΩcm were used for all studies. No further purification was done. The solubility studies were done for pure ADP and ADP doped with 2 mol% of glycine as an additive. Solubility studies were carried out in a constant temperature water bath having cryostat facility with an accuracy of $\pm0.01^o$C. Stirring was done using an immersible magnetic stirrer. The solution was stirred continuously for 6 h to achieve stabilization. Solubility was determined by gravimetric analysis for different temperatures (30–50°C). The solubility curve of pure ADP and glycine doped ADP is shown in Fig.2.

2.3. Determination of Metastable Zonewidth:

Metastable zone width is an essential parameter for the growth of large size crystals from solution since it is the direct measure of the stability of the solution in its supersaturated region. Metastable zone width is an experimentally measurable quantity which depends on number of factors, such as stirring rate, cooling rate of the solution and presence of additional impurities [16–18]. The metastable zone width studies of pure ADP, glycine added ADP solutions were carried out by adopting the polythermal method [17]. The ADP solution (200ml) saturated at 30°C was prepared according to the solubility diagram with continuous stirring using a magnetic stirrer. Then the solution was filtered by the filtration pump and Whatman filter paper of pore size 11µm. Two similar beakers with 100ml solution each were used, the first beaker contains pure ADP solution whereas the second beaker contain 2mol% Glycine doped ADP solutions respectively. Then pure and doped ADP solutions were kept in a constant temperature bath with cryostat facility. The solutions were stirred continuously for a period of 6 h for stabilization using magnetic stirrer. It was slowly cooled at a desired cooling rate of 4°C/h, until the first crystal appeared. Then the temperature was instantly recorded. The difference between the saturation temperature and nucleation temperature was taken to be the maximum under cooling Δt_{max}. This gives the metastable zone width of the system. The experiment is repeated for different saturation temperatures 35, 40, 45, 50˚C and the corresponding metastable zone widths are measured. Several nucleation runs (5–7 times) were carried out under controlled conditions.
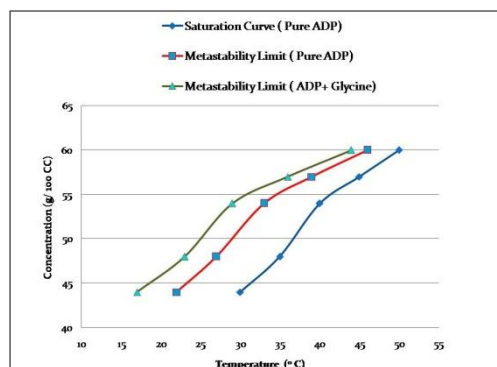
Fig. 2. Solubility curve and Metastability limit curves of pure and Glycine added ADP solutions.

III. RESULTS AND DISCUSSION

3.1. Metastable Zonewidth

The metastability limit of Glycine added solution is shown in Fig. 2 in comparison with the pure system. It is obvious from the figure that the zone widths for both the solutions decrease as the temperature increases. At the same time, the addition of dopants enhances the metastable zone width of ADP solutions for all the temperatures studied in this work, and makes the ADP solution more stable. Glycine enhances the metastable zone width of ADP. The addition of glycine can make ADP solution more stable and increase the growth rate of the ADP crystal under higher supercooling.

3.2. XRD Analysis

Lattice parameters were calculate during the single-crystal XRD, and the powder X-ray diffraction studies were done. The spectrum is shown in the Fig. 3. The prominent peaks of pure ADP are (101), (200), (112), (202), (301) and (312).The obtained peaks for the doped crystals are similar with the pure ADP crystal. Comparing the XRD spectrum of the pure and doped ADP crystal, slight variation in the intensity is observed. But no shift in the angle (2θ) is observed. It reveals that the structure of ADP is not distorted when 2mol% of Glycine is added with ADP. The unit cell parameters obtained from the single-crystal XRD for pure ADP are a=b=7.510A˚, c=7.564A˚, α=β=γ=90˚ and it belongs to tetragonal system, and for Glycine doped ADP the unit cell parameters are a=b=7.507A˚, c=7.557A˚ α=β=γ=90˚ V=425.9A˚^{3}. Fig. 3 shows X-ray powder diffraction patterns of pure ADP and ADP doped with Glycine (2 mol%) . X-ray powder diffraction patterns of pure ADP and doped ADP crystals are identical. As seen in the figure, no additional peaks are present in the XRD spectra of doped ADP crystals, showing the absence of any additional phases due to doping. Both single and powder crystal XRD studies show that the dopant has not entered into the lattice sites of ADP. The observed values are in good agreement with the reported values [19,21].
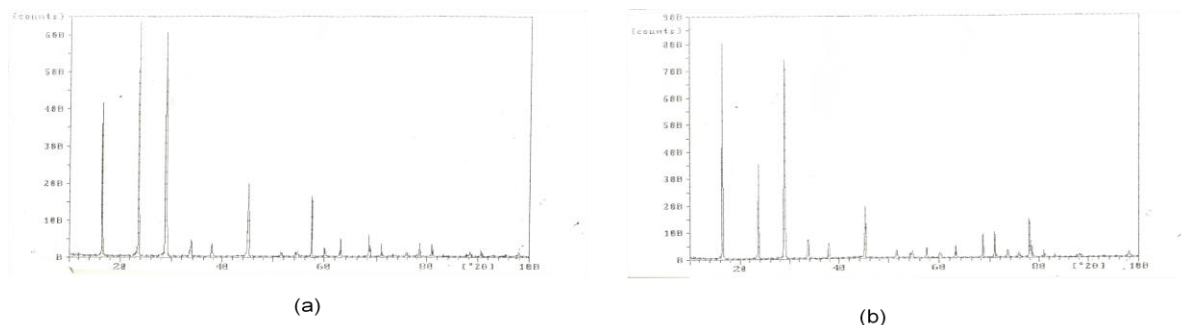

(a)

(b)

Fig. 3. Powder XRD spectra of (a) pure ADP crystal (b) Glycine doped ADP crystal

3.3. Optical transmission 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 reported value of the optical transparency for ADP is from 184 to1100 nm [22]. 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% where as glycine doped ADP has 83% respecively) 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 dopants in the optimum conditions to the solution is found to suppress the inclusions and improve the quality of the crystal with higher transparency.
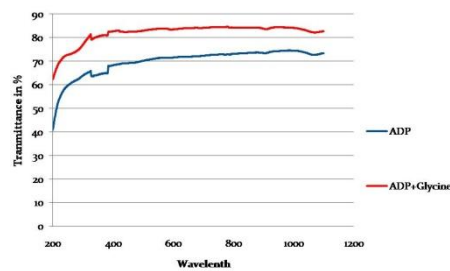
Fig. 4. UV–Vis transmission spectra of pure and doped ADP crystals

IV. CONCLUSION

New additive Glycine was added with ADP and found that this additive can affect the nucleation of ADP from aqueous solutions. The addition of this amino acid enhances the metastable zonewidth of pure ADP solution. Also, during the experiment it was observed that the number of tiny crystals formed by spontaneous nucleation was appreciably reduced in the case of additive added solution. It is believed that the addition of these amino acid suppresses the activities of the metal-ion impurities present in the solution which enables larger metastable zonewidth and faster growth rate. Single and powder XRD analysis indicates that the structure of the crystal remains same after the addition of 2 mol% of Glycine. 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 than the crystal grown by conventional method. The addition of Glycine will be helpful in growing high quality large size single crystals with faster growth rate.

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