GROWTH, SOLUBILITY AND METASTABLE ZONE WIDTH OF GLYCINE DOPED AMMONIUM DIHYDROGEN PHOSPHATE CRYSTAL

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Abstract— Glycine doped Ammonium Dihydrogen Phosphate (ADP) crystals are grown by conventional slow evaporation method. The Solubility and Metastable zone width of pure ADP and Glycine doped ADP crystals are determined and compared. Metastable zone width of ADP is improved by the addition of amino acid Glycine. Crystalline perfection and transparency are enhanced by the addition of this dopant.

Index Terms— ADP, Glycine, solubility, metastable zone width.

I. INTRODUCTION

ADP crystals are widely used as the second, third and fourth harmonic generators for Nd: YAG, Nd: YLF lasers and for electro-optical applications such as Q-switches for Ti: Sapphire, Alexandrite lasers, as well as for acousto-optical applications. ADP crystal has found applications in NLO, electro-optics, transducer devices and as monochromators for X-ray fluorescence analysis. The cell dimensions of ADP are a=b=7.510 Å and c=7.564 Å. 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. EDTA and KCl reduces the effect of metal ion impurities and enhance the metastable zone width and increases the growth rate of the crystals [1-3].

Studies have also been made about the effect of additives on growth, habit modification and structure of ADP [4-5]. 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, metastable zone width increased by 3.7°C, saturated at 30°C [6]. 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. This research module is an extension to the work done on ADP with 2 Mole% of glycine as a dopant [7].

II. EXPERIMENTAL

A. *Solubility Studies*

Solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process. Ammonium dihydrogen phosphate and glycine of GR-grade (Merck) and Millipore water of resistivity 18.2MΩcm were used for the studies. The solubility study was done for pure ADP. Solubility study was carried out in a constant temperature water bath having cryostat facility with an accuracy of ±0.01°C. Stirring was done using an immersible magnetic stirrer. The solution was stirred continuously for 6 hours to achieve stabilization. Solubility was determined by gravimetric analysis for different temperatures (30–50^{o}C). The solubility curve of pure ADP is shown in Fig.1.

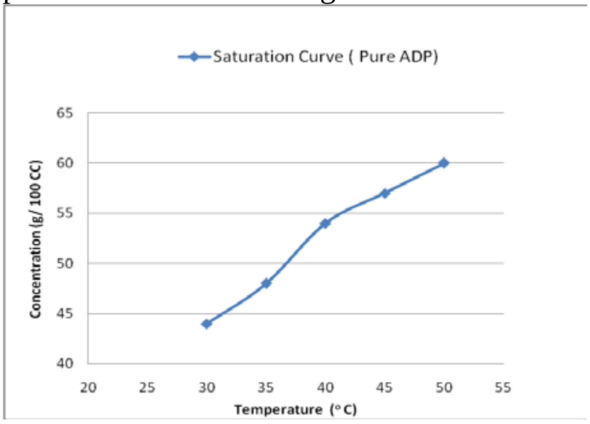

Figure 1: Solubility Curve of Pure ADP

B. Metastable Zone Width

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 [8-10]. The metastable zone width studies of pure ADP, glycine added ADP solutions were carried out by adopting the polythermal method [9].

The ADP solution (700ml) saturated at 30^{o}C was prepared according to the solubility diagram with continuous stirring using a magnetic stirrer. The solution was then filtered by the filtration pump and Whatman filter paper of pore size 11μm. Seven similar beakers with 100ml solution each were used. One beaker contains pure ADP solution whereas the other beakers contain 1, 2, 3, 4, 5 and 6 mole% Glycine doped ADP solutions respectively. Then pure and all the doped ADP solutions were kept in a constant temperature bath with cryostat facility. The solutions were stirred continuously for a period of 6 hours for stabilization using magnetic stirrer. It was slowly cooled at a desired cooling rate of 5^{o}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.

C. Crystal Growth

Ammonium dihydrogen phosphate (ADP) and Glycine of GR grade (Merck) were the initial materials and the growth process was carried out in aqueous solution. On the basis of solubility and metastable zone width the calculated amount of solute of ADP and Glycine (1, 2, 3, 4, 5 and 6 mole%) was dissolved in Millipore water of resistivity 18.2MΩcm.

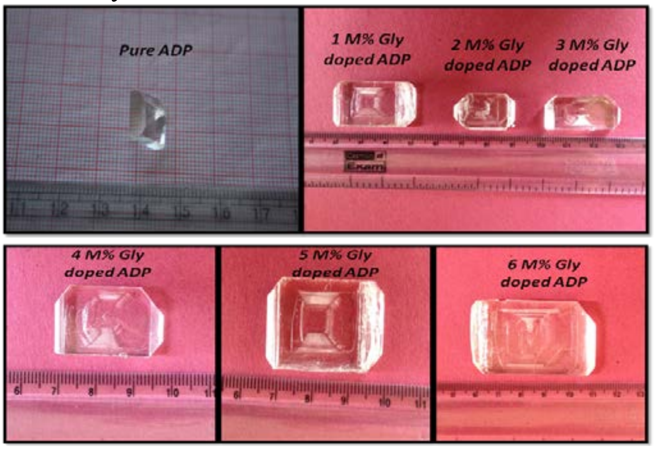

Figure 3: Photographs of Pure and Glycine Doped ADP Crystals

The prepared solution was then stirred well for more than six hours using a magnetic stirrer and filtered using Whatman filter paper. The solution was then 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 grown crystals of pure ADP and Glycine doped ADP are shown in Figures 3.

III. RESULTS AND DISCUSSION

The solubility curve for pure ADP shows that the concentration of the solute increases with increase in temperature. The metastability limit of Glycine added ADP solution is shown in Fig. 2 in comparison with the pure ADP solution. It is observed that the zone widths for all the solutions decrease as the temperature increases. At the same time, the addition of glycine enhances the metastable zone width of ADP solutions for all the temperatures studied in this research module, and makes the ADP solution more stable. These results are in good agreement with the research work done by the author [7]. It is also observed that metastable width increases with increase in dopant concentration. This result is in good agreement with the effect of urea on meta-stable zone width, induction period and nucleation parameters of ADP crystals were reported by Rajesh et al [11]. They evaluated the critical parameters based on classical theory and concluded that the parameters increased on increasing doping concentration.

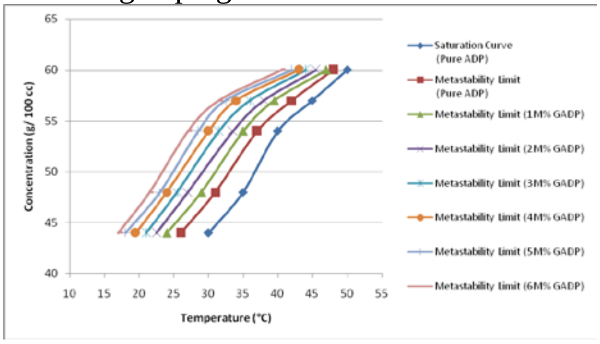

Figure 2: Metastability Limit of Pure and Glycine Doped ADP

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. The addition of glycine make ADP solution more stable and increase the growth rate of the ADP crystal under higher supercooling. 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 reduces with increase in concentration. It is believed that the addition of this amino acid suppresses the activities of the metal-ion impurities present in the solution which enables larger metastable zonewidth and faster growth rate. The addition of Glycine will be helpful in growing high quality large size single crystals with faster growth rate.

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