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# Growth and NLO Studies of Glycine Doped Ammonium Dihydrogen Phosphate, A Nonlinear Optical Crystal by Conventional, Rotation and SR Methods

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**ABSTRACT:**
*Ammonium Dihydrogen Phosphate (ADP) doped with Glycine has been grown by three different methods i.e. Conventional Slow Evaporation Method, Crystal Rotation Method and Sankaranarayanan Ramasamy (SR) Method. Crystals grown by Rotation and SR Methods are found to have Good SHG efficiency than the conventional method. SR Method grown crystals have higher NLO Property.*

***KEYWORDS:***
***ADP, NLO, Rotation, SR, SHG***

## INTRODUCTION:

Nonlinear optical crystals are very important for laser frequency conversion [1].. Nonlinear optical (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical storage technology. The ferroelectrics KDP and ADP used in electro-optical and acousto-optical devices were the first crystals applied for nonlinear frequency conversion. However some special nonlinear optical problems called for crystals with improved properties like high transparency in the UV region, higher nonlinearity, low hygroscopicity etc. The search for new NLO materials over the past decade has led to the discovery of many organic NLO materials with high nonlinear susceptibilities. However, their practical applications are limited by poor optical quality, lack of strength; low laser damage threshold properties [2].The difficulties are still remaining unaddressed in crystal growth with sufficient quality and hardness for applications, such as optical and electro-optical sampling devices.

Potassium dihydrogen phosphate $KH_2PO_4$ (KDP) and ammonium dihydrogen phosphate $NH_4H_2PO_4$ (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. The cell dimensions of ADP are a=b=7.510 Å and c=7.564 Å. 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. To improve the Second Harmonic Generation efficiency of ADP, researchers have attempted to modify ADP crystals by doping different type of impurities such as amino acids. The importance of amino acid for NLO application lies on the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in non-centrosymmetric space group. In solid state, many amino acids contain a depronated carboxylic acid group (COOH) and protonated amino groups ($NH^{3+}$). This dipolar nature exhibits peculiar physical and chemical properties in amino acid, thus making them ideal candidate for NLO application.

**EXPERIMENTAL GROWTH METHODS OF GLYCINE DOPED ADP CRYSTAL:**

**1. CONVENTIONAL SLOW EVAPORATION METHOD:**

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 ADP was dissolved in Millipore water of resistivity 18.2MΩcm. 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.

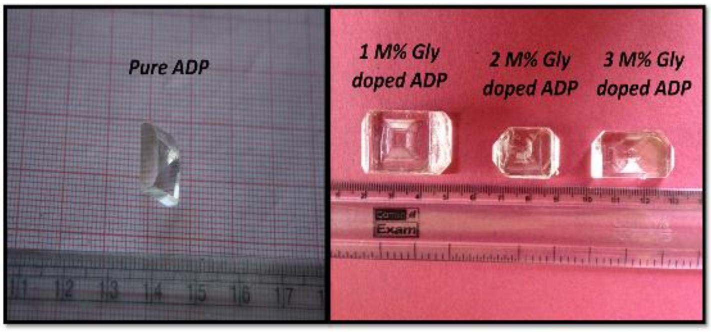


**Figure 1: Photographs of Grown Pure and Glycine Doped ADP Crystals**

The solution was then poured into a 500 ml beaker cover with a lid with small holes in it and 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 20 - 25 days [3]. The photograph of the as grown crystal of pure and Glycine doped ADP is shown in figure 1.

**2. CRYSTAL ROTATION METHOD:**

To achieve highly stable temperature, an active thermo-stating system with fine controlling accuracy is necessary. A general design of a thermostat with a control system is known as Constant Temperature Bath (CTB). Figure 2 shows the water bath used for the growth of crystals. It includes a thick-walled glass chamber filled with water, heating element, temperature sensor and control relay. A seed mount platform is made up of Acrylic sheet of 6 to 10 mm thickness, as it is transparent and does not react with ADP solution. Platform is suspended with the help of vertical post in the solution. The base of the platform is made circular. Surface of the platform including its axle rod were polished by buffing and all the sharp edges were blunted to avoid any secondary nucleation on them. Borosilicate glass beakers of 500 ml to 1000 ml in size containing the supersaturated solution are used for growing ADP crystals. At the lower side of the cover, glass beaker is fixed at its centre with its DC motor with gear arrangement to control speed to prevent dissolution of the seed, heater coil being distributed in a circular shape in the middle of the growth tank.

**Figure 2: Experimental Set-up of Rotation Method and Photograph of Grown Glycine Doped ADP Crystal**

Seed crystal is rotated clockwise and anticlockwise direction with rotation 30 rpm using electronic devices such as 555 timers, IC 4060 timer, microcontroller ATMEGA32, etc. Every minute rotation changes its direction and size of seed crystal looks bigger. After 12 hours temperature is reduced by one degree for maintaining saturation level in the solution. Growth rate along 'c' axis is 2 -3 mm per day and 1 mm per day along 'a' and 'b' axis. Growth of crystal is slower after some days i.e. after the maximum growth of crystal. The crystal was clear and no apparent defects were observed (figure 2).

## 3. SANKARANARAYANAN RAMASAMY (SR) METHOD:

SR method is one of the solution growth methods. The SR method experimental setup (figure 3) consists of a growth ampoule made up of glass with seed mounting pad. The top of the ampoule has bigger diameter compared to the middle, so that the surface of the solution and evaporation is increased. A ring heater positioned at the top of the growth ampoule facilitated solvent evaporation. The temperature around the growth ampoule was selected based on the solvent used and was controlled with the aid of temperature controller. The entire set up is kept in a water bath to avoid the temperature fluctuation. For controlled evaporation, the top portion was closed with some opening at the middle using thick plastic cover. The top cover is preventing the evaporation of water from bath and it allows the evaporation of the solvent. The seed crystals collected from the conventional slow evaporation technique were used for the unidirectional growth. The seed crystal with (100) plane was selected and mounted in the 2 cm diameter and 10 cm length ampoule. ADP material from Merck was used in this growth. The ampoule was filled with saturated solution of ADP doped with 1M% and 3M% Glycine. The temperature of the top and bottom portion was set as 38ºC and 34ºC, respectively. The Slow Evaporation grown crystals have different facets, growth sectors and growth sector boundaries. In conventional solution method, certain dislocations have a tendency to nucleate at growth sector boundaries. But in SR method, since the crystal is growing in selective growth orientation, the growth is on one facet only. There are no growth sector boundaries. Hence the dislocations associated with growth sector boundaries are absent in SR method grown crystal.

The effectiveness of this method was shown by the growth of large size benzophenone single crystal ingot with <110> orientation at room temperature by the authors of SR method [4]. The achievement of solute–crystal conversion efficiency of 100% reduces the preparation and maintenance of growth solution to a large extent because in conventional solution growth method, to grow such a large size crystal, a large quantity of solution in a large container is normally used and only a small fraction of the solute is converted into a bulk single crystal.


**Figure 3: Experimental Set-up for SR Method and Photograph of Glycine Doped ADP Crystal**

**RESULT AND DISCUSSION:**

**1. SECOND HARMONIC GENERATION (SHG)/ NLO STUDIES:**

The SHG measurement is carried out using Kurtz powder technique [1]. 1064 nm laser from Nd:YAG irradiates the sample, generating about 0.8 mJ and pulse width of 10 ns which was used for the present experimental study.

The input laser beam was passed through an IR reflector and then incident on the fine powder form of the KDP specimen, which was packed in a glass capillary tube. A photodiode detector integrated with oscilloscope assembly detected the output energy. The resultant second-harmonic signal (532 nm) was detected when the laser beam was passed through Glycine doped ADP specimen.

The second harmonic generation efficiency was measured with respect to KDP. After the 4 averages, the signal height was measured (peak to peak volts). The signal height for the standard was also measured. The intensity of SHG gives an indication of the nonlinear optical efficiency of the material. The doubling of frequency is confirmed by green radiation of 532 nm. SHG output signal values for pure and Glycine doped crystals are given in Table 1.

**Table 1. SHG Efficiency for Pure and Glycine Doped ADP (GADP) Crystal**

| Sr. No | Sample | Second Harmonic Signal Output (mV) | Signal Output Ratio with pure KDP |
|---|---|---|---|
| 1 | Pure KDP (Reference) | 96 mV | 1.00 |
| 2 | Pure ADP | 120 mV | 1.25 |
| 3 | 1 Mole% Slow GADP | 122 mV | 1.27 |
| 4 | 1 Mole% Rot GADP | 141 mV | 1.46 |
| 5 | 1 Mole% SR GADP | 160 mV | 1.67 |
| 6 | 3 Mole% Slow GADP | 136 mV | 1.42 |
| 7 | 3 Mole% Rot GADP | 158 mV | 1.64 |
| 8 | 3 Mole% SR GADP | 186 mV | 1.94 |

SHG efficiency is found to increase with dopant concentration. The efficiency of the 1 mole % Glycine doped ADP is 1.27 times greater than that of KDP while for 3 mole % Glycine doped ADP it is 1.42 times greater. From this measurement we found that the relative SHG efficiency of Glycine doped ADP increases than that of standard potassium dihydrogen phosphate and pure ADP [5]. Variation has been obtained between the crystals grown by different methods. SHG for 1M% and 3M% Rotation method grown Glycine doped crystals are 1.46 and 1.64 times greater than KDP while SHG for 1M% and 3M% SR grown Glycine doped crystals are 1.67 and 1.94 times greater than KDP.

**CONCLUSION:**

Glycine doped Ammonium Dihydrogen Phosphate (GADP) crystals were grown by conventional, rotation and SR method. Crystals grown from SR method are more transparent than conventional and rotation method. Addition of Glycine proved to be helpful in growing high quality large size single crystals with faster growth rate [6]. SHG efficiency for SR grown crystals is observed to be highest than crystals grown by other two methods, thus showing the better NLO property. The SHG studies therefore confirmed the NLO behaviour of the Glycine doped ADP crystals. Analogous results were observed in DLM doped ADP crystal by P. Rajesh.

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