CHAPTER 7

COMPARATIVE STUDY ON L-ASPARAGINE MONOHYDRATE DOPED ADP CRYSTALS

7.1 INTRODUCTION

As we have discussed in the chapter 5 and 6, many methods are available to grow single crystals. Compared to other crystal growth techniques, the slow evaporation technique has been widely used to grow several types of crystals at ambient temperature. Orientation control during bulk crystal growth is one of the important development targets for crystal growers. Effective control of growth direction has attracted a great deal of attention. Therefore, technology for preparing bulk materials with effective orientation control has been required for achieving significant applications in the field of optoelectronics.

Asparagine is one of the 20 most common natural amino acids in living organisms. It is stable in both hydrated (with one water molecule) and anhydrous forms, and contains carboxamide as the side chain function group (Neacsu et al. 2008). In Asparagine monohydrate there is a total of seven hydrogen bonds per hydrated molecule, three of which involving the water molecule. L-asparagine monohydrate (LAM) single crystal is orthorhombic, belongs to the space group P2₁2₁2₁ and contains four molecules in a unit cell (Kripal and Singh 2007). It is mentioned in the previous chapters that the addition of amino acids enhances the various properties of the crystal. It is expected that the addition of LAM can also enhance the properties of the
ADP crystal. 1 mol % of doping helps the crystal to grow with higher growth rate and enhance the various properties of the crystal. There is no report available in literature on the effect of L-Asparagine monohydrate (LAM) in crystal growth and various properties of ADP.

Keeping this in our mind, in our laboratory it was proposed to grow ADP crystal added with 1 mol% of LAM. In this chapter the growth rate, optical, thermal, mechanical, dielectric properties, crystalline perfection and SHG efficiency of LAM doped ADP single crystals grown by slow evaporation, slow evaporation along with seed rotation (SESR) and Sankaranarayanan-Ramasamy method are presented. The effects of impurity atoms on the quality and performance of the crystals are analyzed. The results of the crystals grown by different methods are compared with one another.

7.2 PREPARATION OF SOLUTION

The commercially available ADP was used for growth, after repeated recrystallization. 4000 ml saturated solution of ADP was prepared at 33 °C. 1 mol % of LAM was added into the beaker and stirred well and filtered. The prepared solution was divided into three parts to grow the crystals by three different methods i.e 500 ml for slow evaporation method, 3000 ml for SESR method and 500 ml for SR method. Ammonium dihydrogen phosphate and L-Asparagine monohydrate used in the present study were bought from M/S. Merck (GR grade), India and the deionized water got from Millipore water purification unit. The resistivity of the used deionized water is 18.2 Meg ohm cm.
7.3 SLOW EVAPORATION METHOD

Single crystals of 1 mol % of LAM added ADP were grown by slow evaporation technique. The prepared 500 ml saturated solution of 1 mol % LAM added ADP was taken in a 1000 ml beaker. The beaker was closed with a porously sealed cover and the solution in the beaker was allowed to evaporate. Few days after, tiny crystals were seen in the beaker. After 30 days of growth, colourless transparent crystals harvested were of size up to 15x7x15 mm$^3$. The grown crystal is shown in the Figure 7.1 (a).

7.4 SLOW EVAPORATION ALONG WITH SEED ROTATION METHOD

The crystal growth is carried out in a 5000 ml standard crystallizer. The crystallizer temperature is controlled using an external water bath, and the temperature fluctuations are less than 0.01 °C. The prepared 3000 ml saturated solution of 1 mol % LAM added ADP was taken in the crystallizer. The seed holder was attached to the crystallizer and it was driven by a stepper motor of torque 2 kg/cm$^2$. The stepper motor is energized through a microcontroller based drive controller. 35 rpm was fixed to carry out the experiment. 4x3x3 mm$^3$ size pure ADP crystal was fixed in the center of the crystallizer and it was kept inside a constant temperature bath. Next day onwards the crystal started to grow. Approximately after 25 days a good quality crystal of size 20x20x25 mm$^3$ was harvested. The grown crystal is shown in the Figure 7.1 (b).
7.5 SR METHOD

Based on the quality of the crystals grown by slow evaporation technique, a suitable seed crystal of size $5 \times 5 \times 5 \text{ mm}^3$ was selected for single crystal growth of $(0 0 1)$ face. To control the spurious nucleation, care has been taken while preparing the growth vessel and the solution. The chosen $(0 0 1)$ plane of the seed crystal was mounted in the bottom of the ampoule without polishing the surface. 500 ml saturated solution of 1 mol % LAM added ADP was used for growth. The solution was prepared at $33 \, ^\circ\text{C}$ and it was overheated to $35 \, ^\circ\text{C}$ for a few hours and again reduced to $33 \, ^\circ\text{C}$. The solution was filtered using Whatman filter paper. Filtered solution was carefully transferred into the growth vessel. The growth vessel was porously sealed and placed in a dust free chamber.

The growth was initiated with a suitable temperature provided by the ring heater at the top region of the saturated solution under equilibrium condition. The applied temperature at the top of the ampoule was $38 \, ^\circ\text{C}$ and at the bottom $33 \, ^\circ\text{C}$. The ring heater at the top of the growth solution controls the spurious nucleation near the surface region of the solution during the entire growth period. Under optimized condition highly transparent crystal growth was seen. The growth rate was 2 mm/day for the given ampoule of diameter 10 mm. After 50 days of the growth a good quality crystal of size 10 mm in diameter and 85 mm in length was harvested. The quality of the crystal is poor if a suspension thread is used in crystal growth. This situation is avoided in this method. Also, generally in solution growth method large quantity of solution in large container is normally used and only a small fraction of the solute is converted into a bulk single crystal. In SR method this drawback has been eliminated. The SR method grown crystal is shown in the Figure 7.1 (c).
Figure 7.1  L-Asparagine monohydrate doped ADP crystal grown by
(a) slow evaporation (b) slow evaporation along with seed rotation (c) SR method

7.6  GROWTH RATE

The growth rate of 1 mol% of LAM doped ADP crystals grown by slow evaporation method was approximately 0.5 mm per day, the SESR method grown crystal was approximately 1 mm per day and SR method grown crystal has higher growth rate than the other two, it is 2 mm per day. The growth rate of SR method is four times higher than the slow evaporation method. The observed growth rates are along “c” direction.
The slow evaporation method is controlled by free convection. By free convection a surface boundary layer develops in which the diffusion takes place. In the SESR method, due to the rotation, the boundary layer gets much thinner, which leads to an enhanced transport of solute toward the crystal surface, whereas in the case of SR method due to the gravity driven concentration all the solutes are approaching the crystal surface directly and hence the surface attracts the atoms easily and resulted in the higher growth rate compared to the other two methods.

There are two important parameters affecting growth rate, they are impurities and mass transfer, or hydrodynamic conditions. The growth rate can be increased by purification of the raw material, as well as by shifting the growth process into the kinetic regime by increasing velocity of the solution flow relative to the surface of a growing crystal. Unfortunately, wide variations due to the content of impurities and hydrodynamic conditions are limited because of their influence on the optical quality of the growing crystals. Therefore, the biggest increase in growth rate due to changing such factors as chemical purity, dislocation structure and hydrodynamic conditions, typically does not exceed a factor of two. Larger acceleration of the growth rate obviously can be obtained by increasing supersaturation. However, low-temperature solution growth had been traditionally performed at very low supersaturation because any significant increase in the growth rate typically resulted in spontaneous nucleation from the solution and formation of macro defects (liquid inclusions, disoriented blocks and cracks) in the crystals. To proceed with the investigation in the almost completely unknown field of one-two orders of magnitude, higher growth rates were possible only if the growth process could be performed under stable, controllable conditions (Zaitseva et al 2001). In SR method the growth was achieved by stable and controlled evaporation.
7.7 CHARACTERIZATION

7.7.1 UV-Vis-NIR Spectroscopy

The recorded optical transmittance spectra are given in the Figure 7.2. It is observed from the figure that all the crystals have good transmission in the entire visible region. The transmission window in the UV region and visible region enables good optical transmission of the second harmonic frequencies of Nd:YAG laser (Anandha babu et al 2008). In order to confirm the reproducibility, the whole experiment was repeated several times for the crystal plates cut from the different parts of the grown crystals and the same results were observed. The crystals grown by SESR and SR method have higher transmittance than the other method grown crystals.

![Figure 7.2 UV-Vis-NIR spectra of grown crystals](image.jpg)
7.7.2 Thermal Analysis

Figure 7.3 shows the DTA spectra for pure and doped ADP crystals. The DTA curve shows an endothermic peak at 213 °C for the pure ADP and at 223 °C for the LAM doped ADP. It is observed from the figure that the decomposition temperature of the ADP is increased by 10 °C when it is doped with LAM. This appears to be in order as the LAM present inside the crystal could have strengthened the lattice partially. The measurement was repeated several times and same results were observed. The melting point of the LAM is 236 °C (Science lab-material safety data sheet). The presence of LAM appears to increase the decomposition temperature of ADP.

![Figure 7.3 DTA curves of grown crystals](image)

Figure 7.3 DTA curves of grown crystals
7.7.3 Vickers Microhardness

The Vickers Microhardness plots are shown in the Figure 7.4. It is observed from the figure that hardness increases with increase in load for all the crystals and at 200 g cracks have been observed. The addition of LAM enhanced the hardness of the crystal. It is also observed that the mechanical strength of the SR method grown crystal is good compared to the other solution growth 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 several crystals.

![Figure 7.4 Vickers microhardness of grown crystals](image-url)
7.7.4 Dielectric Measurements

Figures 7.5 and 7.6 show the temperature dependence of dielectric constant of LAM doped ADP crystals at the frequencies 1, 100 kHz, respectively. It is observed from the figures that the dielectric constant increases with increase in temperature and decreases with increase in frequency. This effect can be attributed to the effect of charge distribution by mean carrier hopping on defects.

![Graph showing temperature dependence of dielectric constant at 1 kHz](image)

**Figure 7.5 Temperature dependence of dielectric constant at 1 kHz**

At low frequency, the charge on the defects can be rapidly redistributed so that defects closer to the positive side of the applied field become negatively charged, while defects closer to the negative side of the applied field become positively charged. This leads to a screening of the field and overall reduction in the electric field. Because capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased capacitance observed as the frequency is lowered. At high
frequency, the defects no longer have enough time to rearrange in response to the applied voltage, hence the capacitance decreases (Zukowski et al 1989).

![Figure 7.6 Temperature dependence of dielectric constant at 100 kHz](image)

**Figure 7.6 Temperature dependence of dielectric constant at 100 kHz**

Dielectric loss of the grown crystals for various temperatures at frequency 10 kHz was measured. It is shown in the Figure 7.7. It is observed that the dielectric loss increases with increase in temperature for the crystals. The low values of dielectric loss indicate that the grown crystal contains minimum defects. The study, in effect, indicates that lower dielectric loss is obtained for the crystal grown by slow evaporation along with seed rotation. Results of crystal grown by slow evaporation with and without seed rotation reveals that the seed rotation helps to a significant extent in improving the crystalline perfection. It seems that due to the seed rotation, the complex layers containing impurities and dopants are not allowed to stay on the surface of the growing crystal due to the centrifugal force and also helps to keep a
homogeneous saturated solution at the liquid-solid interface and thereby the crystal grown under seed rotation has good crystalline perfection.

![Graph showing dielectric loss vs temperature for different methods](image)

**Figure 7.7 Temperature dependence of dielectric loss at 10 kHz**

### 7.7.5 HRXRD Analysis

In order to verify the crystalline perfection of the crystal, it was subjected to HRXRD analysis. Figure 7.8 depicts the high-resolution rocking or diffraction curve (DC) recorded for typical ADP single crystal specimens doped with LAM grown respectively by slow evaporation with seed rotation (SESR) using (200) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer described above with MoKα₁ radiation. As seen in the figure the DC is quite sharp without any satellite peaks, which may otherwise be observed due to internal structural grain boundaries. The full width at half maximum (FWHM) of the curve is 8 arc s which is quite low as expected for a nearly perfect crystal. The single sharp diffraction curve with very low FWHM indicates that the crystalline
perfection is very good. The specimen is a nearly perfect single crystal without having any internal structural grain boundaries.

The reason for bulk of the inclusions getting trapped could be due to fluctuations in supersaturation close to the crystal or due to transition from dissolution to growth. A number of parameters such as variation in supersaturation during the growth, non-uniform growth rates, etc., are responsible for the formation of inclusions. Liquid inclusions getting trapped parallel to the interfaces are due to drastic changes in growth condition (Bhat et al 1985, Kishnan Rao and Surender 2001). In general, it is observed that almost all the conventional method grown crystals (ADP, KDP, NaBr, BaNO₃, KAl(SO₄)₂, LAHF) contain inclusions (Bhat 1992, Maiwa et al 1990, Pal and Kar 2005). In SR method as there are no such growth fluctuations or non-uniform growth rates the dislocations of the above causes are avoided.

![HRXRD curve for LAM doped ADP single crystal grown by SESR](image)

**Figure 7.8** HRXRD curve for LAM doped ADP single crystal grown by SESR
7.7.6 SHG Measurements

It is found from the SHG measurements that the addition of 1 mol% of LAM slightly enhanced SHG efficiencies of the crystal. 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 LAM doped crystals are given in Table 7.1. Not much variation has been obtained between the crystals grown by different methods. All the crystals exhibit the same SHG efficiency. Similar results were observed in DLM doped ADP crystal and it is given in the chapter 5.

Table 7.1 SHG output signal values of the different method grown ADP crystals

<table>
<thead>
<tr>
<th>Method</th>
<th>Output signal height (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>400 - 440</td>
</tr>
<tr>
<td>Slow evaporation (with LAM)</td>
<td>460 - 485</td>
</tr>
<tr>
<td>Slow Evaporation with seed rotation (with LAM)</td>
<td>465 - 485</td>
</tr>
<tr>
<td>Sankaranarayanan – Ramasamy (with LAM)</td>
<td>465 - 490</td>
</tr>
</tbody>
</table>

7.8 CONCLUSIONS

Optically transparent crystals of L-asparagine monohydrate doped ADP crystals were grown successfully by three methods. The growth rate of slow evaporation along with seed rotation method grown crystal is two times and Sankaranarayanan–Ramasamy method grown crystal is four times higher than the slow evaporation method. Higher crystalline perfection, good transmission in the entire visible region and low dielectric loss of different temperatures depicts that the Sankaranarayanan–Ramasamy method and slow evaporation along with seed rotation method grown L-asparagine
monohydrate doped ADP crystal is suitable for device fabrications. Similarly the higher growth rate, growth along a direction, higher hardness and higher thermal stability indicate that the crystals have suitability for various applications. The second harmonic relative efficiency of L-asparagine monohydrate doped ADP crystal is higher than the pure ADP and there is not much difference between the crystals grown by different methods.