CHAPTER 5

GROWTH OF DL - MALIC ACID DOPED AMMONIUM DIHYDROGEN PHOSPHATE CRYSTAL AND ITS CHARACTERIZATION

5.1 INTRODUCTION

In recent years, various growth methods and apparatuses have been continuously developed to improve the crystal quality and the growth rate (Zaitseva et al 2002, Karnal et al 2006). One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Sankaranarayanan-Ramasamy method is an efficient method to grow the large size good quality single crystals (Sankaranarayanan and Ramasamy 2005). The slow evaporation method yields small-size single crystals with different crystallographic faces. For the phase-matching applications where the specimen should have more size along a particular direction, the crystals grown by this method are not economical (Balamurugan and Ramasamy 2006). In the case of VBT growth, although the size of the crystals is good with the desired orientation, the quality of the crystal is generally not up to mark, as these crystals grow with structural grain boundaries due to unavoidable thermal gradients, which affect the device performance and also it is not possible to grow ADP crystals by this method. The recently invented Sankaranarayanan-Ramasamy method has given the solution, and it is possible to grow bulk-size single crystals along a desired orientation needed for device fabrication (Sankaranarayanan and Ramasamy 2005, Vijayan et al 2008). The process of crystallization represents an important separation and
purification technique for the chemical industry (Ihinger 2000), so its control in the manufacture has been an intriguing field for a long time and has recently received considerable attention from both theoretical and experimental standpoints (Xu and Xue 2008)

In addition, the minute amounts of additives, such as KCl and EDTA, can effectively suppress the metal ions and promote the crystal quality (Podder 2002). Several researchers have carried out a lot of studies in pure and organic and metal ions doped crystals (Abdel-Kader 1991, Voronov et al 2007). DL-Malic acid (DLM) is an organic material, which crystallizes in combination with other materials. DL-Malic acid combined with ammonia solution gives ammonium malate single crystals and it is explained in the chapter 2. L-Malic acid with urea produces urea L-Malic acid single crystal (Dixit et al 2003). DL-Malic acid with boric acid and rubidium carbonate yields potential semiorganic materials Rubidium bis-dl-malato borate for second order NLO applications (Balasubramanian et al 2008).

There is no report available in literature on the effect of DL-Malic acid on the crystal growth and various properties of inorganic materials like ADP and KDP. 1 mol % of dopants has resulted in higher growth rate and has enhanced the various properties of the crystal (Bhagavannarayana et al 2008). Keeping this in our mind, in our laboratory it was proposed to grow ADP crystal added with 1 mol% of DL-Malic acid. In this work, we have presented the growth, structural, optical, thermal, mechanical, dielectric and SHG efficiency of DLM doped ADP single crystals grown by slow evaporation method and also by SR method. The effects of impurity atoms on the quality and performance of the crystals are analyzed. The results of the doped ADP crystals grown by slow evaporation method and SR method are compared with the results of the pure ADP grown by slow evaporation method.
5.2 CRYSTAL GROWTH

The commercially available ADP was used for growth, after repeated recrystallization. Single crystals of pure and DLM added ADP were grown using deionized water as a solvent by slow evaporation technique. According to the solubility data (Srinivasan et al 2000), 500 ml saturated solution of ADP was prepared and filtered at room temperature and the solution was divided equally into two beakers and it was named as A and B. The beaker A was kept closed with porously sealed cover, then 1 mol% of DLM was added into the beaker B and it was closed with the same type of cover. Solutions in both the beakers were allowed to evaporate in an identical condition. After seven days, tiny crystals were seen in the beaker B, whereas in A, it was observed one day later only. All crystals reached maximum size in 30 days. The colourless transparent pure ADP crystals harvested were of size up to 15x7x15 mm$^3$ and doped crystals of size up to 30x7x15 mm$^3$. It was observed that the growth rate of DLM added ADP is faster than the pure ADP and comparably big crystals were obtained in DLM added solution. Ammonium dihydrogen phosphate and DL-Malic acid used in the present study were bought from Merck, India and the deionized water got from Millipore water purification unit. The resistivity of the used deionized water is 18.2 M$\Omega$ cm.

5.3 SR METHOD ARRANGEMENT

SR method consists of ring heaters positioned at the top and bottom of the growth ampoule connected to the temperature controller, and the top heater provides the necessary temperature for solvent evaporation. SR method setup was arranged to grow ADP crystals with the addition of 1 mol% DL-Malic acid (Sankaranarayanan and Ramasamy 2005). The method is already explained in the 1st chapter. The habitual morphology of ADP is given in the Figure 5.1.
5.4 CRYSTAL GROWTH BY SR METHOD

Based on the quality of the crystals grown by slow evaporation technique, a suitable seed crystal having a size 4x4x3 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. Using the same material ingredients used in the slow evaporation method, ADP solution of optimized saturation was prepared and 1 mol% of DLM added into the solution and it was transferred carefully 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 on the top of the ampoule was 37 °C and the bottom 33 °C. The placement of ring heater at the top of the growth solution also 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 was harvested with size 10 mm in diameter and 100 mm in length.
Figure 5.2 DLM doped ADP crystals grown by slow evaporation method

Figure 5.3 SR method grown crystal with ampoule

Figure 5.4 Cut and polished SR method grown crystal
In the slow evaporation method using the same materials ingredients the achieved growth rate is 1 mm/day only. After 30 days of growth the grown crystal size is 30x7x15 mm$^3$. The DLM doped ADP is shown in Figure 5.2. This indicates that, it is possible to grow good quality crystals with higher growth rate in SR method. The quality of the crystal will be poor if a suspension thread is used in crystal growth. This situation is avoided in this method. A larger volume of ADP crystals added with dopants can be grown by slow cooling along with seed rotation method (Dhanaraj et al 2008). In this 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 maximum amount of solute will become a single crystal. The grown crystal is shown in the Figure 5.3. The cut and polished crystals are shown in the Figure 5.4. Pritula et al (2008) reported that in the presence of urea the growth rate of KDP is increased. The increase in the growth rate is obviously connected with the catalytic action of urea molecules on the surface of the growing face. Such an effect seems to be caused by the adsorption of the organic molecules and the decrease of the surface energy of the growth steps resulting in the rise of the growth rate. Dhanaraj et al (2008) reported that the presence of L-arginine monohydrochloride and L-analine enhances the growth rate of ADP single crystals.

5.5 CHARACTERIZATION

5.5.1 Single Crystal X-Ray Diffraction

The grown pure and DLM doped ADP crystals were subjected to single crystal X-ray diffraction studies using Enraf Nonius CAD4 single crystal X-ray diffractometer to determine the cell parameters. The cell parameters obtained for the pure ADP are $a = b = 7.510$ Å, $c = 7.564$, $\alpha = \beta = \gamma = 90^\circ$.
and it belongs to tetragonal system. The unit cell parameters for the doped ADP crystal are $a = b = 7.495(3)$ Å, $c = 7.540(1)$ Å, $\alpha = \beta = \gamma = 90^\circ$. It is seen from the above values that slight variation in the lattice parameters is observed and the grown crystal retains its original structure. This result reveals that, the DLM has entered into the lattice sites of ADP.

5.5.2 Powder X-Ray Diffraction Analysis

Powder X-ray diffraction studies were carried out using Rich Seifert X-ray diffractometer employing CuK$\alpha$ (1.54058 Å) radiation, scanning angle ranging from 10 °C to 50 °C at a scan rate 1°/min to study the crystallinity of the grown crystal.

![Figure 5.5 Powder XRD spectra of grown crystals](image_url)
The diffracted peaks are same in pure and doped ADP crystals. The observed prominent peaks of pure and doped ADP are (1 0 1), (2 0 0), (1 1 2), (2 0 2), (3 0 1) and (3 1 2) but the intensities of the diffracted peaks are found to be varied. The sharp peaks and low full width at half maximum (FWHM) values confirm that crystallinity of the grown crystals is good. This has been given in Figure 5.5. The observed values are in good agreement with the reported values in the previous chapters.

5.5.3 Fourier Transform Infrared Spectroscopy

FTIR spectra of pure and DLM doped ADP crystals were recorded using a JASCO FT-IR 410 spectrometer in the range 450–4000 cm\(^{-1}\) by KBr pellet technique. The spectra of pure and doped crystals are shown in Figure 5.6. The effect of DLM on the functional groups of the pure ADP crystal has been identified by the spectrum. The broad band in the high energy region is due to the O-H vibrations of water, P-O-H group and N-H vibrations of ammonium. The peaks at 1092 and 932 cm\(^{-1}\) represent P-O-H vibrations. The \(\text{PO}_4\) vibrations give their peaks at 544 and 470 cm\(^{-1}\). The broadness is generally considered to be due to hydrogen bonding interaction of \(\text{H}_2\text{PO}_4^-\), \(\text{COOH}^-\) and \(\text{NH}_3^+\) with adjacent molecules. By comparing the spectra of doped and undoped crystals, one can easily find missing absorptions for \(\text{N–H}\) stretching of \(\text{NH}_3^+\), \(\text{C–H}\) stretching of \(\text{CH}_2\) and \(\text{CH}\) and conclude that DLM doping was successfully achieved. The bending vibrations of water give its peak at 1646 cm\(^{-1}\).
The peak at 1402 cm\(^{-1}\) is due to bending vibrations of ammonium. In the structure of ADP strong bonding is there between P and O. The addition of DLM can make a small change in the hydrogen bonding of the crystals. The changes in the hydrogen bonds make some variations in the stretching vibrations and in the peak positions. Although this spectrum also carries similar features of that of ADP, there is a distinct evidence for the presence of DLM in the lattice of ADP. The peaks appearing at 2928 and about 2890 cm\(^{-1}\) are due to CH\(_2\) vibrations of DLM. 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 sites of ADP.

5.5.4 UV–Vis–NIR Spectral Analysis

Crystal plates of pure ADP, DLM doped ADP and SR method grown DLM doped ADP with a thickness of 2 mm were cut and polished at
face (0 0 1) without any coating for optical measurements. Optical transmission spectra were recorded for all the crystals in the wavelength region from 200 to 1100 nm using Perkin-Elmer Lambda 35 UV-Vis-NIR spectrometer. It is given in the Figure 5.7. It is observed from the figure that the pure ADP has 50% of transmittance and the conventional grown DLM doped ADP has 52%, and SR method grown DLM doped single crystal has transmittance of 60% in the visible region. 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 above results indicate that the addition of DLM has increased the transmittance and the SR method also plays important role to enhance the optical transmittance of the crystal. Similar results were reported in KDP (Balamurugan and Ramasamy 2008) and TGS (Senthil Pandian et al 2008) crystals.

Figure 5.7  UV-Vis-NIR Spectra of grown crystals
5.5.5 Thermal Analysis

Thermal analysis was performed using Perkin-Elmer diamond TG/DTA instrument in nitrogen atmosphere. Fig. 5.8 Shows the DTA spectra for pure and doped ADP crystals. The DTA curve shows a week endothermic at about 60 °C, which may be due to the presence of DLM inside the crystal and this is followed by a strong endothermic at 207 °C for the DLM doped ADP corresponding to the decomposition of the crystals. The decomposition temperature of the ADP is decreased by 6 °C when it is doped with DL-Malic acid. This appears to be in order as the DLM present inside the crystal could have partially out diffused damaging the lattice partially. The measurement was repeated several times and same results were observed. The melting point of the DLM is 130 °C [Science lab-material safety data sheet]. The presence of DLM appears to decrease the decomposition temperature.

![Figure 5.8 DTA spectra of grown crystals](image-url)
5.5.6 Vickers Hardness Analysis

The good quality crystals are needed for various applications not only with good optical performance but also with good mechanical behaviour. Vickers hardness studies have been carried out using the instrument MITUTOYO model MH 120. 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 5x5x3 mm$^3$ with (0 0 1) face was selected for microhardness studies. Indentations were carried out using Vickers indenter for varying loads.

![Figure 5.9 Vickers microhardness of grown crystals](image)

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. Vickers microhardness number was determined using $H_v = 1.8544 \frac{p}{d^2}$. A plot drawn between the hardness value and corresponding
loads is shown in Figure 5.9. 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 DLM doped crystal. The addition of DLM 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 (Balamurugan and Ramasamy 2008).

5.5.7 Dielectric Measurements

Dielectric properties are correlated with the electro-optic property of the crystals (Boomadevi and Dhanasekaran 2004). The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. The dielectric constant and dielectric loss was measured using Agilent 4284-A LCR meter. The dimensions of the used samples were 9x9x2 mm³. Two opposite surfaces across the breadth of the sample were treated with good quality silver paste in order to obtain good Ohmic contact. Using the LCR meter, the capacitance of these crystals was measured for the frequencies 100 Hz, 1, 10, 100 kHz and 1 MHz at various temperatures.

Figure 5.10 shows the dielectric constant of SR method grown DLM doped ADP crystal, conventional method grown DLM doped ADP crystal and conventional method grown pure ADP crystal as a function of temperature at the frequencies 1 kHz. It is observed from the figure that the
dielectric constant increases with increase of temperature. This is normal
dielectric behaviour of an antiferroelectric ADP crystal. The same has been
observed for all the frequencies (not shown in figure). The explanation for this
is already given in the previous chapters. It is seen from the Figure 5.10, that the
dielectric constant is higher in SR method grown DLM doped ADP crystal
than conventional method grown DLM doped ADP crystal and conventional
method grown pure ADP crystal at all frequencies.

Figure 5.11 shows the dielectric loss of the grown crystals for various
temperatures at the frequency 10 kHz. It is observed from the figure that the
dielectric loss increases with increase in temperature for the crystals grown by
both of the methods. At higher frequencies it is noted that the dielectric loss is
very low (not shown in the figure). It is also observed from the figure that
low dielectric loss is obtained at all frequencies in SR method grown ADP
crystal compared to the crystal grown by conventional method. The low
values of dielectric loss indicate that the grown crystal contains minimum
defects (Vijayan et al 2003)
The present study, in effect, indicates that high dielectric constant and low dielectric loss is obtained for the crystal grown by SR method compared to the crystal grown by conventional method. These results clearly indicate that the crystal grown by SR method has better quality than the crystal grown by conventional method.

The DLM doped crystal grown by SR method has higher transparency, higher dielectric constant, higher hardness and lower dielectric loss than the other crystals. This shows that the quality of the crystal is comparably higher than other crystals and the crystalline perfection of the SR method grown DLM doped ADP crystal has been increased. The increased crystalline perfection indicates that the dislocation is very low in SR method crystal. The generations of the dislocations are strongly correlated with the
formation of the inclusion of the crystals. Depending on the shape of the seed crystal inclusion may arise. The conventional method grown crystal has all the facets. The area between these facets develops terraces parallel to the habit faces. In these areas solvent is easily trapped into the crystal. It is also observed that dislocations can originate from the growth sector boundaries (Bhat 1985). In SR method, as the growth is only on one facet the dislocations of the above causes are avoided.

5.5.8 HRXRD Analysis

The high-resolution diffraction curve (DC) was recorded for a typical ADP crystal grown by slow evaporation method grown specimen using (200) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα₁ radiation. The DC of pure ADP contains a single peak and shows that this specimen is free from structural grain boundaries. It is interesting to see the asymmetry of the DC with respect to the peak position denoted by the dotted line at zero position. For a particular angular deviation (Δθ) of glancing angle with respect to the peak position, the scattered intensity is much more in the negative direction in comparison to that of the positive direction.

This feature clearly indicates that the crystal contains predominantly vacancy type of defects rather than interstitial defects. This can be well understood by the fact that due to vacancy defects or voids in the crystalline matrix, the lattice around these defects undergo tensile stress and the lattice parameter d (interplanar spacing) increases and leads to give more scattered (also known as diffuse X-ray scattering) intensity at slightly lower Bragg angles (θ_B) as d and sin θ_B are inversely proportional to each other in the Bragg equation (2d sin θ_B = nλ; n and λ being the order of reflection and wavelength respectively which are fixed). However, these point defects with
much lesser density as in the present case (if the concentration is high, the FWHM would be much higher and often lead to structural grain boundaries) hardly affect in the performance of the devices made by such crystals. However, the FWHM of this curve is more than that of DLM doped ADP.

Figure 5.11 shows the high-resolution DC recorded for 1 mol% DLM doped ADP specimen using (200) diffracting planes in symmetrical Bragg geometry by employing the same instrument and same MoKα₁ radiation. As seen in the figure the DC is quite sharp without any satellite peaks which may otherwise be observed either due to internal structural grain boundaries (Bhagavannarayana et al 2005) or due to epitaxial or a complexating layer which may sometimes form in crystals grown from solution using dopants (Bhagavannarayana et al 2006). The full width at half maximum (FWHM) of the diffraction curves is 11 arc s, which is quite low and close to that expected from the plane wave theory of dynamical X-ray diffraction (Betterman and Cole 1964). The single sharp diffraction curve with very low FWHM indicates that the crystalline perfection is quite good. The specimen is a nearly perfect single crystal without having any internal structural grain boundaries.

The DC for SR-grown specimen for the same set of diffracting planes i.e. (200) were made using the same instrument. This is also quite sharp having FWHM of 17 arc s. But the scattered intensity on both sides of the peak, the magnitude is slightly higher than that of Figure 5.12 which indicates that this specimen is grown with slightly more vacancies and interstitials. This may be due to fast growth rate which causes both vacancies and self interstitials.
Figure 5.12 HRXRD curves for 1 mol% DLM doped (a) conventional method (b) SR method grown ADP single crystal
5.5.9 SHG Studies

Quantitative measurement of the conversion efficiency of the crystals was determined using the powder technique developed by Kurtz and Perry (1968). ADP crystal powdered to the identical size was used as a reference material in the SHG measurement. The SHG conversion efficiency of DLM doped crystal grown by both the methods was found to be 1.5 times that of pure ADP. Though thiourea doped ADP is reported to have SHG efficiency 3 times that of pure ADP (Jayarama and Dharmaprakash 2006) DLM doped ADP has resulted in higher growth rate, large size and higher quality.

5.6 CONCLUSIONS

DL-Malic acid was successfully doped with ADP and found that the dopant can affect the various properties of pure ADP. Higher growth rate is achieved in SR method grown ADP. Single and powder XRD analysis indicates that the structure of the crystal remains same after the addition of 1 mol% of DL-Malic acid. The shift in the FTIR spectrum proves the presence of DL-Malic 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 method grown DLM doped crystal than the crystal grown by conventional method. Microhardness measurements reveal that the hardness value is increased in DLM doped crystal and further it is observed that the hardness value is higher in SR method grown DLM doped crystal than the crystal grown by conventional method. HRXRD analysis confirms the good crystalline perfection of the doped crystals. ADP crystals generate optical second harmonic frequency of an Nd:YAG laser. The SHG conversion efficiency of doped crystal is 1.5 times higher than that of pure ADP. The addition of 1 mol% DL-Malic acid in ADP will be useful to grow high quality, large size ADP crystals with faster growth rate.