CHAPTER 8

EFFECT OF AMINO ACID ADDITIVES ON CRYSTAL GROWTH PARAMETERS AND PROPERTIES OF AMMONIUM DIHYDROGEN PHOSPHATE CRYSTALS

8.1 INTRODUCTION

The isomorphous ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP) are technologically important crystals grown in large size for various applications. ADP crystal is of more appeal due to its piezo-electric property (Tukubo et al 1989). Studies on ADP crystals attract interest because of their unique nonlinear optical, dielectric and antiferroelectric properties (Gunning et al 2001). 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 room temperature structure of ADP determined by X-ray diffraction analysis was reported by Ueda (1948). Tenzer et al (1958) and Hewat (1973) examined the structure by neutron diffraction analysis. The projection of the structure onto the b, c plane is shown in Figure 8.1.
ADP differs from KDP by having extra N–H–O hydrogen bonds which connect PO$_4$ tetrahedra with neighbouring NH$_4$ group. Each oxygen atom is connected with another oxygen atom in the neighboring PO$_4$ ion and with a nitrogen atom in a neighbouring NH$_4$ ion by two kinds of bonds: (O–H–O) and (N–H–O). According to the positional refinements of each atom in ADP by X-ray diffraction study (Srinivasan 1997), both above and below the phase transition point, each NH$_4$ ion at the potassium position in KDP structure is shifted to the off-center position by forming two shorter and two longer bonds with four PO$_4$ tetrahedra at low temperature phase. When an oxygen is connected with the shorter N–H–O bond, it tends to keep the other proton off in the O–H–O bond and when with the longer N–H–O bond it
tends to take the acid proton nearby. Thus the extra hydrogen bonds produce a
distorted NH$_4$ ion lattice at low temperature and co-operate with the acid
protons in causing proton configurations different from those found at low
temperature in KDP (Matsushita et al 1987). As a representative hydrogen
bonded material, ADP has attracted extensive attention in the investigation of
hydrogen bonding behaviors in crystal and the relationship between crystal
structure and their properties.

Several researchers have carried out a lot of studies in pure and
doped ADP crystals (Zaitseva et al 2001, Ren et al 2008). In ADP and KDP
crystal growth, the metallic cations present in the solutions, especially
materials with high valency were considered to strongly affect the growth
habit and optical properties of the crystals. The most dangerous impurities
which affect the growth habit are trivalent metals Cr$^{3+}$, Fe$^{3+}$ and Al$^{3+}$
(Alexandru et al 2003). Even after repeated recrystallization, the presence of
small amount of those kinds of impurities in the solution suppresses the
crystal quality and growth rate. Here comes the importance of beneficial
effects of additives in the crystal growth. 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. For example, EDTA and KCl reduces the effect of metal ion
impurities and enhance the metastable zone width and increases the growth
rate of the crystals (Rajesh et al 2000, Podder 2002, Meenakshisundaram et al
2009). The addition of such kind of dopants does not remove the impurities
present in the solution; it just reacts with the metal ions and is making
complexes. By making complex, the ions become bigger in size and it is not
possible to enter into the growing crystal (Li et al 2005, Asakuma et al 2007).
Studies have also been made about the effect of additives on growth, habit
The adsorption of impurities at different sites can cause growth inhibitions, even block the growing surface and in consequence stop the growth process. However, the adsorbed impurities may simultaneously lead to a reduction in the edge free energy, which results in an increase in crystal growth rate (Rak et al 2005). Several dopants help in the growth of ADP crystals with higher growth rate and enhancement in the various properties of the crystals. The growth promoting effect is observed in the presence of organic additives (Kern et al 1992, Bhagavannarayana et al 2006) as well as inorganic additives (Shantha et al 1997, Podder et al 2001).

Amino acid family crystals exhibit excellent nonlinear optical and electro-optical properties. Reports are available in literature on the doping of amino acids in technologically important crystals and the enhancement of the material properties like nonlinear optical and ferroelectric properties. For example, enhancement of SHG efficiency has been reported in L-arginine doped KDP crystals (Parikh et al 2007). Kumaresan et al (2008) reported the doping of amino acids (L-glutamic acid, L-histidine, L-valine) with KDP and studied its properties. The effects on various properties of L-theronine, DL-theronine and L-methionine admixed TGS crystals were studied and the authors reported that the admixed TGS crystal has different properties compared to pure TGS crystal (Meera et al 2004). Batra et al (2005) investigated the growth kinetics of KDP and TGS crystals doped with L-arginine phosphate monohydrate. The addition of L-arginine decreases the value of dielectric constant of KDP crystals (Meena et al 2008).

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 materials L-arginine monohydrochloride ($C_6H_{15}N_4O_2Cl$) and L-alanine ($C_3H_7NO_2$) on nucleation studies, growth and properties of ADP crystals for both academic and industrial uses. The reason for choosing the dopants is that
L-arginine monohydrochloride and L-alanine are efficient NLO materials under the amino acid category. Monaco et al (1987) discovered NLO material L-arginine monohydrochloride, which belongs to space group \( P2_1 \) of monoclinic system with two molecules in the asymmetric unit. L-alanine crystallizes in orthorhombic system with noncentrosymmetric space group \( P2_12_12_1 \) (Razzetti et al 2002).

### 8.2 DETERMINATION OF SOLUBILITY AND METASTABLE ZONE WIDTH

Ammonium dihydrogen phosphate, L-arginine monohydrochloride (LAHCl) and L-alanine of GR grade from Merck and Millipore water of resistivity 18.2 MΩcm were used for all studies. The solubility was determined gravimetrically for pure ADP and ADP doped with small amount (5 mol\%) of LAHCl and L-alanine separately as additives. Polythermal method (Nyvlt et al 1970) was adopted for the metastable zonewidth studies of pure and doped ADP solutions. The ADP solution (600 ml) saturated at 30 °C was prepared according to the solubility diagram with continuous stirring using a magnetic stirrer and the solutions were filtered. Three similar beakers with 200 ml solution each were used; the first beaker contains pure ADP solution whereas the second and the third beakers contain 5 mol\% LAHCl and 5 mol\% L-alanine doped ADP solutions respectively. Then pure and doped ADP solutions were kept in a CTB with cooling facility. After stirring for 6 h, the solution was slowly cooled at a desired cooling rate of 4 °C/h, until the first crystal appeared. The experiments were repeated for different saturation temperatures (30–50) °C with the interval of 5 °C and the corresponding metastable zonewidths were measured. Several nucleation runs (5–7 times) were carried out under controlled conditions. The metastability limit of LAHCl added solution and L-alanine added solution is shown in Figure 8.2 in comparison with the pure system.
Figure 8.2 Saturation and metastability limit curves of pure, LAHCl and L-alanine added ADP solutions

The figure shows that the zone widths for all the solutions decrease as the temperature increases. At the same time, the addition of dopants enhances the metastable zonewidth of ADP solutions for all the temperatures studied in this work, and makes the ADP solution more stable. During the experiment, the number of tiny crystals formed by spontaneous nucleation was appreciably reduced in the case of the doped solutions compared with the pure one. Among the two additives, the additive L-alanine enhances the metastable zonewidth of ADP than the other additive LAHCl especially at lower temperatures. The addition of these amino acid additives can make ADP solution more stable.

8.3 DETERMINATION OF INDUCTION PERIOD

Isothermal method (Zaitseva et al 1995) was employed to determine the induction period for ADP solutions with and without the presence of additives at different supersaturations. The “direct vision method” by naked eye is used for measuring induction period. Glass beaker without scratches on the walls was used to avoid the heterogeneous nucleation due to
scratches. Solutions of equal volume (100 ml) were taken and the experimental temperature is 35 °C. Experiments were performed at selected degrees of supersaturation ($c/c_0$), viz., 1.25, 1.275, 1.3, $c$ being the mole fraction of solute in supersaturated solution and $c_0$ is the equilibrium concentration. Several trials (4–6) were conducted under controlled conditions and reproducible results with the accuracy of ±0.25% were obtained. Figure 8.3 depicts the experimental results of induction period versus supersaturation for the pure and additive added ADP solutions.

![Figure 8.3 Values of induction period against supersaturation](image)

Considering the principles of homogeneous and heterogeneous nucleation theories, the free energy of formation of a nucleus under heterogeneous nucleation is less than that of a homogeneous condition (Sangwal 1996, Srinivasan et al 1999). Considering the additive added system it can be noticed that the induction period of doped ADP is higher than that of pure and it increases with the increase in the additive concentration. Among the additives, L-alanine has a higher induction period than LAHCl at every concentration. The presence of additives in the system affects the nucleation
behavior very considerably. This may be due to the suppression of chemical activity of the metal ions present in the ADP solution (Mullin 1993).

8.4 GROWTH RATE MEASUREMENTS

The influence of additives on the growth rate of ADP crystals is determined by the weighing method (Kubota et al 1995). By this method, the growth rate of a crystal is determined by $G_g = (m - m_o)/m_o \Delta \theta$, where $m_o$ is the initial mass of the crystal (kg), $m$ is the final mass of the crystal (kg), and $\Delta \theta$ is the growth time. In the experiment, growth time is taken as 1 h and size of the seed crystal is 5–10 mm. The seed crystal (of mass $m_o$) was suspended in the solution in 500 ml glass vessel (working volume: 400 ml) for 1 h ($\Delta \theta$) for growth. The solution was continuously stirred throughout the process. Supercooling was varied from 2 to 10 °C by changing the growth temperature. The same procedure is done for pure, LAHCl doped ADP and L-alanine doped ADP crystals. Growth rates of pure and doped ADP crystals are shown in the Figure 8.4.

![Figure 8.4 Variation of mass growth rates for pure and doped ADP crystals](image-url)
The presence of additives is found to have an influence on the growth rate. The role of additives during the growth process could be visualized as follows. The additives LAHCl and L-alanine have higher solubility than that of the crystallizing substance (ADP). The additives might have changed the thermodynamic parameters, i.e. the surface concentration of the growth species and the surface energy. An increase in solubility by the addition of LAHCl and L-alanine may lead to decrease in the surface energy, which consequently decreases the rates of layer displacement that cause an increase in the growth rate (Sangwal 1996).

8.5 CRYSTAL GROWTH

In the present work, ADP crystals doped with 5 mol% LAHCl and L-alanine separately were grown from aqueous solution with an apparatus that rotates the growing crystal. The seed mount platform in this experiment stirs the solution very well and makes the solution more stable, which resulted in better crystal quality. The crystal growth was carried out in a 5000 ml standard crystallizer used for conventional crystal growth by using the method of temperature reduction. The aqueous solutions at the saturation temperature 50 °C were filtered by filtration pump and Whatman filter paper under slight pressure in a closed system to remove extraneous solid and colloidal particles. Then the solutions were overheated at 70 °C for 24 h, to make the solution stable against spontaneous nucleation under a high supersaturation (Nakatsuka et al 1997). Then the temperature of the solution was reduced to 3–5 °C higher than saturation point (50 °C) at 1 °C/h. After that temperature was reduced to saturation point at 1 °C/day and the seed crystal was mounted on the platform. The rotation rate of the platform was 40 rpm. From the saturation point, the temperature was decreased at 0.1 °C/day at the beginning of the growth. As the growth progressed, the temperature lowering rate was increased up to 1 °C/day. After the growth period of 30 days, crystals were harvested. The as–grown crystals are shown in Figure 8.5. In the figure, (a) is ADP doped with L-Alanine and (b) is ADP doped with LAHCl.
For various characterization techniques, pure and doped (in concentrations 1 and 5 mol %) ADP crystals were grown by slow cooling method under identical conditions.

8.6 POWDER XRD STUDIES

The X-ray powder diffraction analysis was used to confirm the physical phase of the product. Grown crystals were ground using an agate mortar and pestle in order to determine the crystal phases by X-ray diffraction. The XRD analysis (SAIFERT, 2002 DLX model) was performed using a tube voltage and current of 40 kV and 30 mA respectively. Figure 8.6 shows X-ray powder diffraction patterns of ADP doped with LAHCl (5 mol%) and ADP doped with L-alanine (5 mol%) compared with that of pure ADP crystal. 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.
8.7 HRXRD ANALYSIS

A multicrystal X-ray diffractometer has been used to reveal the crystalline perfection of the grown crystals. Figure 8.7 shows the high-resolution diffraction curve (DC) recorded for LAHCl doped (5 mol%) ADP specimen and figure 8.8 shows the DC recorded for L-alanine doped (5 mol%) ADP specimen using (200) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα₁ radiation. The curves are very sharp having full width at half maximum (FWHM) of 8 arc s for LAHCl doped ADP and 5 arc s for L-alanine doped ADP crystals as expected for nearly perfect crystals from the plane wave dynamical theory of X-ray diffraction (Batterman et al. 1964). The absence of additional peaks and the very sharp DC shows that the crystalline perfection of the specimen crystals is extremely good without having any internal structural grain boundaries and mosaic nature. The high reflectivity (∼ 50% in LAHCl doped and ∼ 60% in L-alanine doped) and the very small value of FWHM indicate that even the unavoidable point defects like self interstitials and vacancy
defects (Lal et al 1989)) are also extremely low. However, the quality of L-alanine doped ADP specimen is better than that of LAHCl doped specimen.

Figure 8.7 Diffraction curve recorded for LAHCl doped ADP single crystal using (200) diffracting planes

Figure 8.8 Diffraction curve recorded for L-alanine doped ADP single crystal using (200) diffracting planes
The influence of additives used in this work on the vibration frequencies of functional groups of pure ADP crystal has been identified by FTIR spectroscopy. The FTIR spectra were recorded in the region 400–4000 cm\(^{-1}\) using a Perkin-Elmer FTIR Spectrum RXI spectrometer by KBr pellet technique. Figure 8.9 shows the FTIR spectra of the pure ADP, ADP doped with LAHCl (1 mol%) and ADP doped with L-alanine (1 mol%). The broad band in the high energy region is due to O–H vibrations of water, P–O–H group and N–H vibrations of ammonium. The peak at 2370 cm\(^{-1}\) is due to the combination band of vibrations occurring at 1293 and 1290 cm\(^{-1}\). The bending vibrations of water give the peak at 1646 cm\(^{-1}\). The peak at 1402 cm\(^{-1}\) is due to bending vibrations of ammonium. The P–O–H vibrations give the peaks at 1090 and 930 cm\(^{-1}\). The PO\(_4\) vibrations give their peaks at 544 and 470 cm\(^{-1}\).

Figure 8.9 FTIR spectra of pure ADP, ADP doped with LAHCl and ADP doped with L-alanine
In the spectrum of ADP doped with LAHCl, the intense band appearing at 3442 cm\(^{-1}\) includes O–H vibrations and N–H vibrations of ammonium and amino acid. Although this spectrum carries similar features as that of ADP, there is a distinct evidence for the presence of LAHCl in the lattice of ADP. The peaks appearing at 2928 cm\(^{-1}\) and about 2890 cm\(^{-1}\) are due to CH\(_2\) vibrations of LAHCl. 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 of ADP. In the spectrum of ADP with L-alanine also, there is a significant shift in the peak positions. For example, the PO\(_4\) vibration of the parent is shifted from 470 to 419 cm\(^{-1}\). Similarly the P–O–H vibrations at 1090 and 930 cm\(^{-1}\) of the parent are shifted to 1101 and 913 cm\(^{-1}\). Such a shift establishes the presence of L-alanine in the lattice of ADP. As the vibrations of L-alanine are not clearly resolved from the spectrum of the parent, it might be in a trace amount below the deductibility limit. There is a slight evidence of CH\(_2\) vibrations of L-alanine just below 3000 cm\(^{-1}\). All these support the presence of L-alanine in the lattice of ADP.

8.9 DIELECTRIC STUDIES

The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. Using Agilent 4284A LCR meter, the capacitances of the pure and doped ADP crystals were measured for temperatures from 313 to 423 K with frequency (f) of 1 kHz. Good quality transparent crystals of size 7 × 7 × 2 mm\(^3\) were used for the measurements. The dimensions of the samples were determined using a traveling microscope (LC = 0.001 cm). Samples were coated with good quality graphite in order to obtain a good ohmic contact. The measurements were done on a–b directions of the crystals. The samples were annealed up to 423 K to remove water molecules if present. Several trials of experiments were conducted.
Figure 8.10 shows the temperature dependence of dielectric constants of pure and LAHCl doped (1 and 5 mol%) ADP crystals. Temperature dependence of dielectric constants of pure and L-alanine doped (1 and 5 mol%) ADP crystals are depicted in Figure 8.11.

**Figure 8.10**  Variation of dielectric constant with temperature for pure and LAHCl doped ADP crystals

**Figure 8.11**  Variation of dielectric constant with temperature for pure and L-alanine doped ADP crystals
It is observed from the figures that the dielectric constant increases with increase in temperature. This is normal dielectric behaviour of an antiferroelectric ADP crystal. In the present study, it has been observed that the LAHCl and L-alanine doped ADP crystals have lower $\varepsilon_r$ values compared to pure. Among these, 5 mol% doped crystals have lower $\varepsilon_r$ values than 1 mol% doped ones. Suitable dopants added in suitable concentrations can reduce the $\varepsilon_r$ value to a lower one as observed in the case of KDP single crystals added with urea (Goma et al 2006). Thus, in effect, the present study indicates that LAHCl and L-alanine doped ADP crystals are not only potential NLO materials but also low $\varepsilon_r$ value dielectric materials, which will be useful for microelectronic industries and electro-optic modulators. The dielectric loss of the grown crystals for various temperatures at the frequency (1 kHz) is shown in Figures 8.12 and 8.13. It is observed that the dielectric loss increases with increase in temperature for the crystals. It shows that doped crystals have low dielectric loss values than pure.

![Figure 8.12 Variation of dielectric loss with temperature for pure and LAHCl doped ADP crystals](image-url)
Figure 8.13  Variation of dielectric loss with temperature for pure and L-alanine doped ADP crystals

8.10  OPTICAL TRANSMISSION STUDIES

Optical transmission spectra were recorded for the samples obtained from pure as well as doped crystals grown by the slow cooling method. The spectra were recorded in the wavelength region 200–1100 nm using Lambda 35 spectrophotometer. Crystal plates with 2 mm thickness were used for the study. The reported value of the optical transparency for ADP is from 184 to 1500 nm (Dmitriev et al 1991). The UV–vis–NIR spectra recorded for pure and doped ADP crystals are shown in Figure 8.14. It is clear from the figure that the crystals have sufficient transmission (pure ADP has 70% whereas LAHCl and L-alanine doped ADP have 78% and 82% respectively) in the entire visible and IR region. The optical transparency of the ADP crystal is increased by the addition of LAHCl and L-alanine. 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.
To determine the SHG conversion efficiency of doped crystals, pure and doped crystals were ground into powder and densely filled into the cells. A fundamental wave with a pulse width of 8 ns, repetition frequency of 10 Hz and a wavelength of 1064 nm radiated from Nd: YAG laser source was focused on the samples by a lens with focal length of 120 mm. The input laser energy incident on the powdered sample was 1.35 mJ/pulse. An emission of green light was seen in all the samples. The transmitted fundamental wave was absorbed by a CuSO₄ solution and the SHG signal was detected by a photomultiplier tube and displayed on a storage oscilloscope. It was observed that the measured SHG efficiency of L-alanine doped (5 mol%) ADP was 1.75 and LAHCl doped (5 mol%) ADP was 1.5 that of pure ADP.

8.12 PIEZOELECTRIC MEASUREMENTS

Piezoelectricity is the ability of certain crystals to generate an electric charge when subjected to mechanical stress. The piezoelectric...
property is related to the polarity of the material (Ge et al. 2008). The piezoelectric studies were made using piezometer system. A precision force generator applied a calibrated force (0.25 N) which generated a charge on the piezoelectric material under test. An oscilloscope gives the output in $d_{33}$ coefficient of unit pC/N. Piezoelectric measurements were conducted for the grown crystals by without poling of the crystal. Pure ADP crystal gives the piezoelectric coefficient ($d_{33}$) value of 0.37 pC/N. The obtained piezoelectric coefficient ($d_{33}$) values for LAHCl doped (5 mol%) ADP and L-alanine doped (5 mol%) ADP crystals are 0.68 and 0.8 pC/N. Thus $d_{33}$ value of 5 mol% LAHCl doped ADP crystal is 1.84 and 5 mol% L-alanine doped ADP crystal is 2.16 times that of pure ADP crystal. Greater crystalline perfection may be the reason for the increase in piezoelectric efficiency.

8.13 CONCLUSIONS

New additives L-arginine monohydrochloride and L-alanine were added with ADP and found that these additives can affect the nucleation of ADP from aqueous solutions. The addition of these amino acid materials enhances the metastable zone width and induction period 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 doped solution. It is believed that the addition of these amino acid materials suppresses the activities of the metal ion impurities present in the solution which enables larger metastable zone width and faster growth rate. HRXRD curves recorded for 5 mol% doped crystals have excellent crystalline perfection. The FTIR spectrum shows that amino acid additives have entered into the ADP crystals. The transmission spectrum reveals that the crystal has sufficient transmission in the entire visible and IR region. The SHG conversion efficiency and piezoelectric coefficient values of doped crystals are higher than that of pure.