CHAPTER 5

SINGLE CRYSTAL GROWTH AND PROPERTY STUDIES OF SEMIORGANIC NONLINEAR OPTICAL L-ARGININE HYDROCHLORIDE MONOHYDRATE

5.1 INTRODUCTION

In the recent years, an intense world wide effort has been focused on the design and development of materials with large optical non-linearity. Also, photonics is playing an ever-increasing role in our modern information society (Paresh Chandra Ray 2004). Interests have been centred on semiorganic crystals which have the combined properties of both inorganic and organic crystals like high damage threshold, wide transparency range, less deliquence and large non-linear coefficient, which make them suitable for device fabrication. Among these, semiorganic materials like L-arginine phosphate (Monaco et al 1987), L-histidine tetrafluoroborate (Agarwal et al 1999) and L-arginine acetate (Mohan Kumar et al 2005), play a significant role because of their high conversion efficiency, good thermal and mechanical strength, which are considered as the crucial factors for device applications.

Nonlinear optical materials have gained considerable attention due to their practical applications in the extension of the limited and fixed frequency outputs available from lasers (Franken et al 1961). In the recent years, amino acid family crystals are of interest due to their attractive nonlinear optical properties (Kitazawa et al 1994 and Misoguti et al 1996). Efforts have been made on the amino acid mixed organic and inorganic
complex crystals in order to make them suitable for device applications such as optical switches, optical modulators, optical bistable devices, electro optical devices, etc. Since the discovery of LAP (Xu et al 1983 and Eimerl et al 1989), many attempts have been made on the search of new polar materials with promising NLO properties. Monaco et al. tried synthesized L-arginine with 20 various organic and inorganic acids, of which they have succeeded in crystallizing 10 compounds and verified the linear and nonlinear optical properties and some other salts could not be crystallized due to difficulty in synthesizing the compounds. L-arginine hydrochloride monohydrate (LAHCl) was crystallized and reported that the crystal possesses monoclinic structure with space group P2₁. The unit cell parameters were a = 11.22 Å, b = 8.50 Å, c = 11.07 Å and β = 91°. Use of these crystals for nonlinear optical devices demands large size single crystals of extremely high quality.

Growth mechanism of L-arginine chloride monohydrate was reported by Rashkovich et al (1991). Mukerji et al (1998) reported the preliminary studies of LAHCl crystallization. Pal et al (2002) studied the mixed system of L-arginine chloride and L-arginine bromide in the equimolar ratio and reported that the mixed system is better than the parent crystals as far as the optical damage threshold is concerned. Mukerji et al (2000) reported the knoop hardness anisotropy and Young’s modulus of L-arginine hydrochloride and L-arginine hydrobromide. However, the detailed studies on bulk crystal growth and other physical properties of LAHCl have not been reported. In the present investigation, synthesis, solubility and bulk growth of LAHCl crystals from its aqueous solution by slow evaporation as well as slow cooling methods have been reported. The grown crystals have been characterized by single crystal X-ray diffraction, Infrared spectroscopy, thermal, linear, nonlinear optical and etching studies. Detailed studies on the dielectric properties of the grown crystal have also been presented.
5.2 L-ARGININE HYDROCHLORIDE

L-arginine hydrochloride monohydrate (LAHCl) is one of many L-arginine salts, and its single crystals attract attention because of their application in nonlinear optics (Monaco et al 1987).

In aqueous solution, L-arginine attaches one proton and forms the charged radical $R^+$

\[
\begin{array}{c}
HN = C - NH - (CH_2)_3 - CH - COO^- \\
\mid & \\
NH_3^+ & NH_3^+
\end{array}
\]

When L-arginine reacts with hydrochloric acid, it forms L-arginine hydrochloride $R^+ Cl^-$, which crystallizes in hydrated form (C$_6$ H$_{15}$ N$_4$ O$_2$ Cl. H$_2$O).

5.3 SYNTHESIS AND PURIFICATION OF LAHCL

L-arginine molecule, NH$_2$CNHNH(CH$_2$)$_3$CH(NH$_2$)COOH has two groups namely guanidyl and amino groups, which can be protonated. L-arginine hydrochloride monohydrate (LAHCl) was synthesized by the reaction between hydrochloric acid and the strongly basic amino acid, L-arginine taken in the ratio of 1:1 [higher ratios like two or more yields highly viscous solution]. The required amount of hydrochloric acid was added to the double distilled water. Then the calculated amount of L-arginine was added and dissolved in dilute hydrochloric acid. The following reaction takes place in this process

\[
NH_2CNHNH(CH_2)_3CH(NH_2)COOH + HCl + H_2O \rightarrow
\]

\[(H_2N)_2^+CNH(CH_2)_3CH(NH_3)^+ COO^- . Cl^- . H_2O\]
Purification of the synthesized salt was done by repeated recrystallization process until optically clear crystals were obtained. The purity of the synthesized salt was checked by measuring the melting point (222°C) after every crystallization. During the recrystallization process, the solution temperature was kept below 60°C in order to avoid any decomposition.

5.4 SOLUBILITY STUDIES

L-arginine hydrochloride was dissolved in double distilled water and kept in a constant temperature bath with a cryostat facility and stirring was achieved continuously for 6 h. Solubility studies for different temperatures (30, 35, 40 and 45 °C) have been carried out by gravimetric analysis and it has been observed that the solubility of LAHCl is high in water (140 g/100 ml of water at 30°C) compared to organic solvents. The solubility of LAHCl is shown in Figure 5.1.

![Figure 5.1 Solubility curve of LAHCl in water](image-url)
5.5  **GROWTH OF LAHCL CRYSTALS**

Initially, single crystals of LAHCl were grown from the saturated aqueous solution of LAHCl by solvent evaporation method at a constant temperature (35°C). Saturated aqueous solution of LAHCl was taken in a crystallizing vessel with perforated cover and placed in a constant temperature bath with the control accuracy of ± 0.01°C. Attempt was also made to grow large size single crystals of LAHCl from seeded solution by slow cooling method from 40°C at a cooling rate of 0.2°C/day during the initial and final stages of the experiment. Optical quality bulk crystal of dimension 26×13×11 mm³ has been harvested after a typical growth period of 20 days. As grown crystals of LAHCl is shown in Figure 5.2.

![As-grown single crystal of LAHCl](image)

**Figure 5.2**  As-grown single crystal of LAHCl
5.6 SINGLE CRYSTAL X-RAY DIFFRACTION

Single crystal X-ray diffraction studies were carried out to determine the lattice parameters using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK$_\alpha$ ($\lambda = 0.71069$ Å) radiation. The least square refinements of 25 reflections were carried out in the range 20-30º. The study reveals that the grown crystal belongs to monoclinic system with the unit cell parameters $a = 11.035$ (2) Å, $b = 8.479(1)$ Å, $c = 11.210$ (4) Å, $\beta = 91.42^\circ$, $Z = 2$, space group P2$_1$ and $Volume = 1049.5$ Å$^3$. The single crystal XRD results are in good agreement with the reported values and thus confirm the grown crystal (Monaco et al 1987).

5.7 OPTICAL PROPERTY STUDIES

5.7.1 Optical transmittance studies

Optical transmittance of LAHCl was measured in the range 200-800 nm using a Varian CARY 5E UV-VIS-NIR spectrophotometer and the transmittance spectrum is shown in Figure 5.3. The LAHCl possesses a good transparency of 65 % with the lower cut-off wavelength at 220 nm and hence the crystal can be used for second harmonic generation for Nd:YAG laser. There is no absorption in the entire visible range upto 300 nm, the material can find application as windows in spectral instruments in this region. From the high-energy edge of transmittance, when it is almost equal to zero, the forbidden energy gap of LAHCl is found to be around 5.64 eV.

5.7.2 Refractive index

The refractive index of the LAHCl crystal was determined by Brewster’s angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal of LAHCl was mounted on a rotating mount at an angle varied from 0 to 90 degrees. The angular reading on the rotary
stage was observed, when the crystal is perfectly perpendicular to the intra-cavity beam. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output. Brewster’s angle ($\theta_p$) for LAHCl is measured to be $58.5 \pm 0.1$ degree. The refractive index has been calculated using the equation $n = \tan \theta_p$; where $\theta_p$ is the polarizing angle and it is found to be 1.632.

5.7.3 FTIR analysis

The FTIR spectrum of LAHCl was recorded in the range 400 - 4000 cm$^{-1}$ using BRUKER IFS 66V FTIR spectrometer by KBr pellet technique to identify the functional groups present in the grown crystal. Figure 5.4 shows the IR spectrum of LAHCl and the characteristic deformation bands of the NH$_3^+$ group present in all amino acids appear at 1520 cm$^{-1}$. It was observed that two bands at 549.14 and 3169.54 cm$^{-1}$ correspond to the torsion and asymmetric stretching of the NH$_3^+$ group. The COO$^-$ asymmetric stretching and C=N stretching were seen to have intense.
peaks at 1591.88 and 1670.13 cm\(^{-1}\). The peaks at 1096.23 and 1401.85 cm\(^{-1}\) were assigned respectively to C-N stretching and COO\(^-\) symmetric stretching. The combination band in the region 2020-2100 cm\(^{-1}\) is due to the combination of NH\(_3^+\) deformation and NH\(_3^+\) torsion and it is a very good indicator band for the identification of the charged NH\(_3^+\) group. The symmetric stretching of water gives rise to the absorption band at 3328.74 cm\(^{-1}\). The chloride anion has got very intense vibration in the range 500-900 cm\(^{-1}\). Thus, on the basis of available data on the vibrational frequencies of several amino acids (Krishnan et al 1973), the characteristic IR bands for different molecular groups present in L-arginine hydrochloride monohydrate were identified.

![FTIR spectrum of LAHCl](image)

**Figure 5.4** FTIR spectrum of LAHCl

### 5.7.4 Non-linear optical studies

The SHG efficiency of LAHCl was measured by Kurtz and Perry powder technique (Kurtz et al 1968). The second harmonic output was generated by irradiating the powder sample using a pulsed laser beam of
Nd:YAG laser with a pulse width of 8 ns. The powder SHG efficiency of LAHCl is found to be 0.38 with respect to KDP.

5.8 THERMAL ANALYSIS

Thermal analysis was carried out using NETZSCH-Geratebu GmbH thermal analyzer to study the thermal behavior of the grown crystal. For thermal analysis, the sample was heated at a rate of 10°C/min in protected nitrogen gas flow. The TGA and DTA curves of LAHCl are shown in Figure 5.5(a) and Figure 5.5(b). The compound starts to lose single molecules of water of crystallization at about 98°C and the loss continues up to 142°C.

The weight loss in this temperature range is consistent with the weight of single molecule of water present in the crystal. A second dissociation occurred at 230-280°C. This weight loss may be attributed to the weight of two ammonia molecules, one being bonded to an α-carbon atom and the other attracted to the carbon atom of the guanidyl group. Decomposition of main carbon chain started at above 280°C, with the evolution of carbon dioxide. This decomposition process continues up to 500°C with the removal of almost all the compounds as gaseous products. The DTA curve showed a major endothermic peak corresponding to the melting point of the compound at 222.2°C. Summarized results of TGA and DTA analysis of the decomposition steps, the corresponding weight losses and the temperature at the peaks are given in Table 5.1.
Figure 5.5  Thermal studies of LAHCl (a) TGA and (b) DTA curves
Table 5.1 Summarized results of TGA and DTA

<table>
<thead>
<tr>
<th>Stage</th>
<th>Decomposition temperature range (°C)</th>
<th>Decomposition steps</th>
<th>Weight Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₆H₁₄N₄O₂. HCl. H₂O</td>
<td>Observed</td>
</tr>
<tr>
<td>1ˢᵗ</td>
<td>100 – 142</td>
<td>7.62</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2ⁿᵈ</td>
<td>230 – 280</td>
<td>C₆H₁₄N₄O₂. HCl</td>
<td>14.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₆H₈N₂O₂. HCl</td>
<td></td>
</tr>
</tbody>
</table>

5.9 ETCHING STUDIES

Etching studies were carried out on the (100) plane of the LAHCl crystal using water as an etchant, in order to investigate the growth mechanism and surface features. The nonlinear efficiency of the NLO material mainly depends on the quality of the grown crystal because the segregated impurities and dislocations occurring during growth results in the distortion of the optical beam to be processed. So, it is very much essential to study the microstructural imperfections or crystal defects in the as-grown crystal (Mukerji et al 1999a). Micromorphological studies of LAHCl crystal were carried out using water as etchant. Water is a superior etching solution for revealing dislocation etch pits and it is in-sensitive to surface orientation as it produced pits almost on all surfaces (Mukerji et al 1999b). LAHCl
crystals are highly soluble in water and hence water is selected as the etchant. In the present experiment, transparent crystal without cracks was selected and etching was carried out for 20 seconds at room temperature. Well defined rectangular etch pits were observed on the (100) plane of the crystal. These etch pits might be due to screw dislocations, which would have originated due to inclusion of water molecules (Mukerji et al 1999a). With increasing etching time, the size of the pits increased while the pit pattern remains the same. The rectangular etch pits observed on LAHCl crystal is shown in Figure 5.6. A similar morphology of rectangular etch pits were observed on L-arginine hydrobromide using alcohol and organic acid as etchants (Mukerji et al 1999d).

Figure 5.6  Rectangular etch pits observed on the (100) plane of LAHCl crystal
5.10 DIELECTRIC STUDIES

The dielectric constant and dielectric loss of LAHCl crystals were studied at different temperatures using HIOKI 3532 LCR HITESTER in the frequency region 100 Hz - 5 MHz in the temperature range 35-75ºC. For dielectric measurements, crystals were polished on a soft tissue paper with fine grade alumina powder (0.1 µm) dispersed in water.

Each sample was electroded on either side with air drying silver paste so that it behaved like a parallel plate capacitor. Typical sample thickness was in the range 0.7-2.6 mm. A cylindrical tube furnace with an Eurotherm temperature controller of accuracy ±0.01°C was used to heat the sample. The dielectric constant ($\varepsilon_r$) was calculated by using the relation

$$\varepsilon_r = \frac{C t}{\varepsilon_0 A}$$

where $\varepsilon_0$ is the permittivity of the free space, C is the capacitance, t is the thickness of the sample and A is the area of the cross section. The a.c conductivity of the crystal was calculated by using the relation

$$\alpha_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$

where $\omega$ is the angular frequency and $\tan \delta$ is the dielectric loss.

The variation of dielectric constant and dielectric loss of LAHCl crystal with frequency is shown in Figures 5.7 (a) and 5.7 (b). At room temperature (308 K), the value of $\varepsilon_r$ and $\tan \delta$ decreases with increasing frequency. The measured values of $\varepsilon_r$ and $\tan \delta$ at 1 kHz for LAHCl crystal were 702.5 and 0.75 and these values decrease to 394.5 and 0.024 respectively at 5 MHz. The magnitude of $\varepsilon_r$ depends on the degree of polarization of charge displacement in the crystals. The dielectric constant of a material is due to the contribution of electronic, ionic, orientational and space charge polarizations, which depend on the frequencies.
Figure 5.7  (a, b) Variation of εᵣ and tan δ as a function of frequency at different temperatures
Figure 5.7  (c, d) Variation of $\varepsilon_r$ and $\tan \delta$ with temperatures at different frequencies
Figure 5.7  (e) Variation of electrical conductivity (σ) with temperature at different frequencies

Figure 5.7  (f) Variation of electrical conductivity (σ) with frequencies at different temperatures
The space charge polarization will depend on the purity and perfection of the material. Its influence is large at higher temperature and is noticeable in the low frequency region (Goma et al 2006). The larger values of \( \varepsilon_r \) and \( \tan \delta \) at lower frequencies may be attributed to space charge polarization due to charged lattice defects. The increase in the capacitance at low frequencies is attributed to space charge polarization. The low value of \( \varepsilon_r \) at higher frequencies are important for these materials in the fabrication of photonic and NLO devices.

The variation of dielectric constant and dielectric loss as a function of temperature in the range from 308 to 348 K at different frequencies are shown in Figures 5.7 (c) and 5.7 (d). The increase of \( \varepsilon_r \) is continuous from the lowest to highest temperature range. At the lower temperature region, the variation of \( \varepsilon_r \) is frequency independent and at higher temperatures, the increase of \( \varepsilon_r \) is frequency dependent. The \( \tan \delta \) is frequency independent at low temperatures. The \( \varepsilon_r \) increases with temperature due to space charge polarization. The dielectric constant and dielectric loss of LAHCl were measured to be 702.5 and 0.75 at 308 K (1 kHz) and 717.92 and 0.82 at 348 K (1 kHz) respectively.

Figures 5.7 (e) and 5.7 (f) show the variations in a.c conductivity of LAHCl for different temperatures and different frequencies. The conductivity of LAHCl increases with increasing temperature. The electrical conduction in dielectrics was mainly a defect controlled process in the low temperature region. From the Figure 5.7 (e), it is observed that the electrical conductivity of LAHCl was low at lower temperature due to trapping of some carriers at defect sites. At any particular temperature, however, the Gibbs’s free energy of a crystal is minimal when a certain fraction of ions leaves the normal lattice. At higher temperatures, more and more defects were created and as a
result, the conductivity increases predominantly due to movement of defects produced by thermal activation (Srinivasan et al 2006a). The increase in conductivity at higher frequencies as shown in Figure 5.7 (f) could be due to the reduction in the space charge polarization.

5.11 CONCLUSIONS

Bulk single crystal of L-arginine hydrochloride was grown by the slow cooling method. The solubility curve showed that LAHCl has very high solubility in water. Lattice parameter values were determined by single crystal XRD analysis. Optical transmission studies showed that the grown crystal is optically transparent in the visible region with the lower cut-off at 220 nm and hence it is suitable for frequency conversion applications. The presence of various functional groups was confirmed by FTIR analysis. The SHG efficiency of LAHCl was found to be 0.38 with respect to KDP crystal. The thermal studies revealed the thermal stability of the crystal. Etching studies on the (100) plane of the crystal showed well defined rectangular etch pits. The low dielectric constant and dielectric loss of the crystal at high frequency region implies good quality crystals.