CHAPTER 4

STUDIES ON THE GROWTH ASPECTS AND
CHARACTERIZATION OF L-ARGININE
PERCHLORATE SINGLE CRYSTALS

4.1 INTRODUCTION

Nonlinear optical (NLO) materials capable of generating second harmonic frequency play an important role in the domain of optoelectronics and photonics. Nonlinear optical crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications. Within the last few years, much progress has been made in the development of nonlinear optical organic materials for second harmonic generation. However, most of the organic NLO crystals are constituted by weak van der Waals and hydrogen bonds with conjugated π electrons. Hence they are soft in nature and it is difficult to cut and polish the crystals and also to have intense absorption in the UV region. In view of these difficulties, a new type of NLO materials have been built from organic-inorganic complexes which form strong ionic bond than the van der Waals and hydrogen bonds, thus increasing the mechanical strength of these semiorganic crystals.

One of the essential requirements for a material to exhibit second order optical susceptibilities described by third rank polar tensor is that the crystal should have noncentrosymmetric space group. In amino acids, except glycine, all the other possess non-centrosymmetric space group. The
semiorganic materials possess higher mechanical strength compared to organic materials. The research on the synthesis of semiorganic crystals has increased enormously in the last few years (Koshima et al 2001 and Anwar et al 2000). Specifically, amino acids and strong inorganic acids are good raw materials to produce semiorganic crystals because amino acid crystals are having good optical properties (Razzetti et al 2002). Amino acids are interesting material for NLO applications as they contain a proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH$_2$) group. For example, L-arginine phosphate has shown promising results as efficient second harmonic generator and is being applied in devices such as optical parametric amplifiers (Monaco et al 1987).

An improved harmonic generator, L-arginine phosphate monohydrate (LAP), a semiorganic NLO material for laser fusion experiments to replace conventional KDP crystals was discovered by Xu et al (1983). LAP and its deuterated analog (DLAP) are phase matchable for all nonlinear processes, where KDP is phase matchable, and, with the possible exception of harmonic generation to wavelengths shorter than 270 nm, they are substantially more efficient than KDP. LAP is three times more nonlinear than KDP, its damage threshold also two to three times higher than that of KDP, less deliquescent and more angularly sensitive compared to KDP (Sasaki et al 1989 and Yokotani et al 1989). LAP has considerable absorption at 1.06 $\mu$m due to overtones of the molecular vibrations of the hydrophilic functional groups such as – OH, - NH$_3^+$, = NH, - NH$_2$, = NH$_2^+$ etc. Hence deuteration of these functional groups leads to the reduction in the absorption (Yokotani et al 1989).

Monaco et al (1987) synthesized the chemical analogs of LAP with strong basic amino acids and various other organic and inorganic acids. All the compounds in this class contain an optically active carbon atom, therefore
all of them form acentric crystals and hence offer the possibility of large nonlinearity, with less angular sensitivity in the phase matching conditions. About ten compounds were synthesized, crystallized and proved to have nonlinear optical properties, one such compound is L-arginine perchlorate (LAPC). It has a transmission range extending from 230 nm. Therefore, bulk single crystals of LAPC are potential materials throughout the visible and UV spectral region.

Mallik and Kar (2005d) reported the preliminary studies of L-arginine perchlorate (LAPC) crystallization and Aruna et al (2007) reported the basic characterization of LAPC crystals. Vibrational spectra of L-arginine tetrafluoroborate and L-arginine perchlorate were studied by Petrosyan et al (2006). However there is no report on the bulk growth of LAPC crystal. In the present work, an attempt has been made to grow bulk single crystal of LAPC suitable for physical property measurements. A systematic investigation has been made on the growth of L-arginine perchlorate crystals and the grown crystals have been subjected to X-ray diffraction, optical, thermal, infrared, etching and NLO property studies.

4.2 CRYSTAL STRUCTURE

L-arginine is a linear chain of molecules with amino acid and guanidyl groups at opposite ends. The crystal structure of L-arginine phosphate is shown in Figure 4.1 (Aoki et al 1971). The crystal structure consists of alternate layers of phosphate groups and arginine molecules stacked along the a-axis and held together by hydrogen bonds. Xu et al (1983) reported that the nonlinear optical properties of phosphate ion do not contribute significantly to the d coefficient of the macroscopic crystal and Eimerl et al (1989) showed that large birefringence and nonlinearity is possible in other analogs of L-arginine. In view to this, L-arginine perchlorate was crystallized.
Figure 4.1  Crystal structure of LAP

The structural formula of L-arginine is

\[
HN = C - NH - (CH_2)_3 - CH - COOH \\
| \quad \quad | \\
NH_2 \quad \quad \quad \quad \quad \quad \quad NH_2
\]

In aqueous solution, arginine binds protons and forms a charged radical \((R^+)\)

\[
HN = C - NH - (CH_2)_3 - CH - COO^- \\
| \quad \quad | \\
NH_3^+ \quad \quad \quad \quad \quad \quad \quad NH_3^+
\]
When L-arginine reacts with the perchloric acid it forms L-arginine perchlorate with $R^+\text{COO}^-$, which crystallizes in anhydrous form.

L-arginine perchlorate crystallizes in the orthorhombic structure (Monaco et al 1987) with space group $P2_12_12_1$, $Z = 4$ and the unit cell parameters $a = 13.854$ Å, $b = 16.573$ Å, $c = 5.083$ Å, $\alpha = \beta = \gamma = 90^\circ$. The linear and nonlinear optical properties of LAPC were studied using crystals of size 50-100 µm. In the crystal, the guanidyl and amino groups are protonated and hence they have positive charges, which balance the negative charges of the carboxylate and perchlorate ions.

### 4.3 SYNTHESIS AND PURIFICATION OF LAPC

Equimolar amounts of strongly basic L-arginine amino acid, and perchloric acid were dissolved in Millipore water to synthesize LAPC as per the following reaction,

$$\text{(H}_2\text{N) NH CNH (CH}_2\text{)}_3 \text{ CH (NH}_2\text{) COOH + HClO}_4 -> (H}_2\text{N)}_2^+ \text{ CNH (CH}_2\text{)}_3 \text{ CH (NH}_3\text{)}^+ \text{ COO}^- \cdot \text{ClO}_4^-$$

The synthesized LAPC salt was then purified by repeated recrystallization process and each time the melting point was measured in order to ascertain the purity of the synthesized material.

### 4.4 SOLUBILITY STUDIES

The solubility of LAPC was determined for different temperatures, viz., 30, 35, 40, 45 and 50°C. The solubility at 30°C was determined by dissolving the LAPC salt in 100 ml of millipore water taken in an air-tight container with continuous stirring. After attaining the saturation, the concentration of the solute was estimated gravimetrically. The same
procedure was repeated to estimate the solubility for different temperatures. The solubility curve of LAPC is shown in Figure 4.2. It is observed that the solubility of LAPC increases significantly with increasing temperature.

![Solubility curve of LAPC in aqueous solution](image)

**Figure 4.2  Solubility curve of LAPC in aqueous solution**

4.5 CRYSTAL GROWTH

At the initial stage, L-arginine perchlorate solutions of different pH values were tried for crystallization. pH of the mother solution (pH = 2) was increased by the addition of dilute NaOH. Crystals grown at higher pH values (4, 6, and 8) were poor in quality with opaque nature. Better crystals were obtained for pH 2 at room temperature. It was observed that the growth rate of the crystals for pH 2 was increased with repeated recrystallization process. Hence the optimized pH value 2 was used for the bulk growth. The as-grown single crystals are transparent without hygroscopic nature.
The starting material of L-arginine perchlorate was dissolved in Millipore water in accordance with the solubility data. The saturated solution of LAPC (150 ml) was prepared at 40°C and the solution was filtered using filter paper of porosity 0.1 μm. Good optical quality transparent seed crystals obtained by slow evaporation method were used for the bulk growth. The growth was carried out in a constant temperature bath of controlling accuracy ±0.01°C. A cooling rate of 0.2°C/day was employed during the initial and final stages of the growth experiment. Optical quality crystal of dimension 50 × 7 × 4 mm³ has been grown over a typical growth period of 15 days. As grown single crystal of LAPC is shown in Figure 4.3.

![Figure 4.3](image)

**Figure 4.3** As-grown single crystal of LAPC by slow cooling technique

### 4.6 SINGLE CRYSTAL X-RAY DIFFRACTION STUDIES

Single crystal X-ray diffraction study was carried out to determine the lattice parameters using ENRAF NONIUS CAD 4 X-ray diffractometer with MoKα radiation (λ = 0.71069 Å). The least square refinement for 25 reflections was done in the range of 20-30°. This study reveals that the grown
crystal belongs to orthorhombic system with the space group P2₁2₁2₁. The calculated lattice parameter values are listed in Table 4.1. The single crystal XRD results are in good agreement with the reported values and thus confirm the structure of the grown crystal (Monaco et al 1987).

Table 4.1 Crystal data of LAPC

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>C₆H₁₅N₄O₆Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight</td>
<td>274.66</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁2₁2₁</td>
</tr>
<tr>
<td>a</td>
<td>5.079 (1) Å</td>
</tr>
<tr>
<td>B</td>
<td>13.827 (5) Å</td>
</tr>
<tr>
<td>c</td>
<td>16.556 (9) Å</td>
</tr>
<tr>
<td>α = β = γ</td>
<td>90°</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1162.8 (8)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (By experiment)</td>
<td>1.555 g/cm³</td>
</tr>
<tr>
<td>Density (By calculation)</td>
<td>1.568 g/cm³</td>
</tr>
</tbody>
</table>

4.7 MORPHOLOGY OF LAPC CRYSTALS

The typical growth morphology of LAPC single crystal is shown in Figure 4.4. The crystal has eight visible faces out of which four are well defined, namely {10 1}, {101}, {010} and {001}. Among them, (10 1) is the smallest triangular plane and (101) is the bigger triangular plane. These two faces have its Friedel parallel faces at the bottom. In the a-direction, (010) and (001) are the prominent morphological planes. The a-direction (a-axis) is along the length of the crystal. The b and c-axes are normal to (010) and (001) planes and the c-axis also coincides with one of the edges of the crystal.
4.8 OPTICAL STUDIES

4.8.1 Optical absorption studies

For optical device applications, the transparency in the near IR region is significant because 1.3 and 1.5 μm wavelengths are used in optical telecommunication system (Kaino et al 2000). The UV-Vis spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves the promotion of electrons in the σ and π orbitals from the ground state to a higher energy state. Figure 4.5 shows the UV-Vis-NIR spectrum recorded in the region 200-1100 nm using a Varian Cary 5E UV-Vis-NIR spectrometer for a highly transparent LAPC single crystal of thickness 2 mm. It is observed from the absorption spectrum that the crystal is transparent not only in the visible range, however, also in the
near UV part of the spectra, which is an essential parameter for NLO applications. It is further observed that UV cut-off of LAPC is 230 nm and it is suitable for applications in the blue region. The absence of absorption in the visible region is an intrinsic property of all amino acids.

Figure 4.5  Optical absorption spectrum of LAPC crystal

4.8.2  Refractive index measurement

The refractive index of the LAPC crystal was determined by Brewster’s angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal of LAPC 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 LAPC is measured to be $56.9 \pm 0.5$ 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 1.534.
4.9 FTIR ANALYSIS

Figure 4.6 shows the FTIR spectrum recorded in the range 400-4000 cm\(^{-1}\) using Bruker IFS 66V by KBr pellet technique to identify the functional groups present in LAPC. The peak at 3189 cm\(^{-1}\) is assigned to NH\(_3^+\) asymmetric stretching. The peaks at 2972 and 2882 cm\(^{-1}\) correspond to C-H stretching. Ratajczak et al. (2000) reported that the lack of any strong IR band at 1700 cm\(^{-1}\) clearly indicates the existence of the COO\(^-\) ion in zwitterionic form. The bands above 2000 cm\(^{-1}\) correspond to the absorption due to CH\(_2\) grouping. The characteristic deformation bands of NH\(_3^+\) group present in the amino acid appeared at 1629 and 1491 cm\(^{-1}\). The existence of carboxyl group is confirmed by absorption at 1380 cm\(^{-1}\). The presence of perchlorate anion as the counter ion can be proved by the absorption at 1116 cm\(^{-1}\). FTIR spectrum of LAPC is in good agreement with the FT-IR ATR spectrum of LAPC (Petrosyan et al. 2006). The observed vibrational frequencies and their tentative assignments are given in Table 4.2.

![FTIR spectrum of LAPC](image)
Table 4.2  Assignment of IR band frequencies (cm\(^{-1}\)) observed for L-arginine perchlorate

<table>
<thead>
<tr>
<th>Band frequencies for LAPC</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3189</td>
<td>NH(_3^+) asymmetric stretching</td>
</tr>
<tr>
<td>2972</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>2528</td>
<td>combination band of NH(_3^+) bending vibration</td>
</tr>
<tr>
<td>above 2000</td>
<td>absorption due to –CH(_2) grouping</td>
</tr>
<tr>
<td>1629</td>
<td>NH(_3^+) asymmetric deformation</td>
</tr>
<tr>
<td>1654</td>
<td>C = N stretching</td>
</tr>
<tr>
<td>1491</td>
<td>NH(_3^+) symmetric deformation</td>
</tr>
<tr>
<td>1380</td>
<td>COO(^-) symmetric stretching</td>
</tr>
<tr>
<td>1356</td>
<td>C-CH in plane deformation</td>
</tr>
<tr>
<td>1323</td>
<td>wagging CH(_2)</td>
</tr>
<tr>
<td>1116</td>
<td>presence of perchlorate ion</td>
</tr>
<tr>
<td>844</td>
<td>rocking NH(_2)</td>
</tr>
<tr>
<td>744</td>
<td>wagging NH</td>
</tr>
<tr>
<td>626</td>
<td>COO(^-) in plane deformation</td>
</tr>
<tr>
<td>550</td>
<td>wagging COO(^-)</td>
</tr>
</tbody>
</table>

4.10  MELTING POINT AND DENSITY MEASUREMENT

The finely powdered L-arginine perchlorate single crystal was taken in a capillary tube and placed in the melting point measurement apparatus. The temperature was increased at a rate of 2\(^\circ\)C/min and the melting of material was noted at 236\(^\circ\)C. The error in the measurements was ±1\(^\circ\)C. The most efficient method namely, the flotation technique (Andreev 1989) was used to measure the density of the grown crystals. In this analysis, toluene and CCl\(_4\) were used for the measurements. The experimentally determined value
is in good agreement with theoretically estimated value using the formula
\[
\rho = \frac{M Z}{N_A V};
\]
where \( M \) is the molecular weight, \( Z \) is the number of molecules per unit cell, \( N_A \) is the Avogadro’s number and \( V \) is the volume of the unit cell. The experimental and theoretical density values are 1.555 g/cm\(^3\) and 1.568 g/cm\(^3\) respectively.

### 4.11 THERMAL ANALYSIS

Thermal studies were carried out using NETZSCH-Geratebu GmbH thermal analyser to study the thermal behavior of the grown crystal. The characteristic curves of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for LAPC are shown in Figure 4.7. A powder sample was used for the analysis in the temperature range of 28ºC to 1000ºC with a heating rate of 10ºC/min in inert nitrogen atmosphere.

![Figure 4.7 DTA and TGA curves of LAPC](image-url)
The alumina (Al$_2$O$_3$) crucible was used as a reference. It is inferred that the LAPC crystal is thermally stable upto 153ºC. TGA curve shows that there is a sharp weight loss at 235ºC and the sample undergoes gradual weight loss till 1000ºC. In the DTA curve, the endothermic peak at 237ºC corresponds to melting point of the substance and then it undergoes an exothermic peak at 280ºC, which is associated with weight loss as observed from the TGA curve. TGA curve shows complete weight loss of 99.5 % due to the elimination of volatile substance like carbon dioxide, ammonia and oxide of chlorine.

4.12 MICROHARDNESS STUDIES

Microhardness measurements on LAPC crystal were carried out on the two well developed faces {010} and {001} using Wetzlar Vicker’s microhardness tester fitted with a diamond pyramidal indenter attached to an optical microscope. The static indentations were made at room temperature with a constant indentation time of 15 sec for all indentations. Indentations were made by varying the loads from 10 to 50 g, above this load microcracks were observed. The Vicker’s microhardness number was calculated using the relation

$$H_v = 1.8544 \times \frac{P}{d^2} \text{ (kg/mm}^2\text{)}$$

where P is the indentation load and d is the diagonal length of the impression. Figure 4.8 shows the variation of load (P) versus Vicker’s hardness number (H$_v$) for LAPC. It was observed that microhardness value of LAPC increases with the applied load. Similar hardness behavior is exhibited by BTCC (Jayakumari et al 2004), LADI (Thomas et al 2006). The values of hardness were found to be 68 kg/ mm$^2$ for (010) plane and 57 kg/ mm$^2$ for (001) plane. It is observed that the (010) plane is harder than the (001) plane. This shows
that the LAPC crystal have anisotropic mechanical properties along different crystallographic directions.

![Figure 4.8 Variation of Vicker’s hardness number with load on (010) and (001) planes of LAPC crystal](image)

4.13 ETCHING STUDIES

Micromorphology studies of LAPC crystal were carried out on the (001) plane by chemical etching with water as an etchant. Water is an effective etching solution for revealing dislocation etch pits and it is insensitive to surface orientation as it produced pits almost on all surfaces (Mukerji et al 1999). In the present work, the etching study was carried out on the selected polished samples, which were transparent and free from visible inclusions or cracks. During etching, the crystal surface was dipped at room temperature in the etchant for 20 seconds and then wiped with dry filter paper. Etch patterns were observed and photographed under an optical microscope in the reflected light mode. The surface microscopic study of the grown crystals
showed that the (001) plane consists of elliptical etch pits as shown in Figure 4.9, which is similar to the etch patterns observed on the \{001\} face of LAHBr crystals (Mukerji et al. 1999).

![Figure 4.9](image)

**Figure 4.9** Elliptical etch pits observed on the (001) plane of LAPC crystal [400x]

### 4.14 DIELECTRIC STUDIES

Dielectric properties are correlated with the electro-optic property of the crystals (Boomadevi et al. 2004). The dielectric constant of LAPC sample was measured using HIOKI 3532-50 LCR meter. Figure 4.10 shows the plot of dielectric constant versus applied frequency at room temperature. The decrease in dielectric constant of LAPC crystal at low frequencies may be attributed to the contribution of the electric, ionic, orientation and space charge polarizations which depend on the frequencies (Dharmaprakash et al. 1989). At low frequencies, all the four contributions are active. The low value of $\varepsilon_r$ at high frequencies is important for these materials in photonic and NLO devices. The dielectric loss is also studied as a function of frequency at room temperature, as shown in Figure 4.11. It is observed that the dielectric loss decreases with increasing frequency. The low value of dielectric loss indicates
that the grown crystals are good quality (Benet Charles et al 1994). The larger values of dielectric loss at lower frequencies may be attributed to space charge polarization owing to charged lattice defects (Smyth et al 1995).

Figure 4.10 Dielectric constant ($\varepsilon_r$) as a function of frequency

Figure 4.11 Dielectric loss as a function of frequency
4.15 POWDER SHG STUDIES

The study of NLO conversion efficiency of LAPC has been carried out in accordance with the classical powder method developed by Kurtz and Perry (Kurtz et al 1968). A DCR 11 Quanta ray of spectra physics Nd:YAG laser producing a pulse width of 8 ns and repetition rate of 10Hz were used. The crystal of LAPC was powdered with a particle size of 100-150 µm and then placed in a microcapillary and exposed to laser radiation. The output from the sample was monochromated to collect the intensity of 532 nm component, and to eliminate the fundamental wavelength. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photomultiplier tube. The generation of the second harmonic was confirmed by the emission of green light. Urea crystal was powdered to the same particle size as the experimental sample and it was used as a reference material for this measurement. The SHG conversion efficiency of LAPC was found to be 0.17 with respect to urea, and it is comparable with the reported values (Monaco et al 1987 and Mallik et al 2005). For NLO crystals, the principal role for second order susceptibilities determining the optical SHG depends on the number of defects, which requires detailed study on the defect structure (Kityk et al 2001).

4.16 CONCLUSIONS

Optical quality LAPC single crystal was grown by temperature lowering growth technique. The single crystal XRD study was carried out to determine the cell parameters. The morphology of the LAPC crystal indicates that (010) and (001) are the most prominent planes. UV-Vis-NIR spectrum revealed that the LAPC crystal is transparent in the entire visible region. FTIR spectrum confirmed the functional groups present in the grown crystal. DTA and TGA analyses revealed that LAPC is stable up to 153°C. Hardness
anisotropy for both planes has been observed in accordance with the orientation of the crystallographic planes. Well defined elliptical etch pits were observed on (001) plane of the LAPC crystal. The dielectric constant and dielectric loss were studied with varying frequency at room temperature. The SHG efficiency of LAPC was found to be 0.17 times that of urea. With wide transparency range and high second harmonic efficiency, the LAPC crystal can be used for NLO device applications.