CHAPTER 2

GROWTH OF SEMIORGANIC BASED L-GLUTAMIC ACID HYDROCHLORIDE SINGLE CRYSTAL AND ITS CHARACTERIZATION

2.1 INTRODUCTION TO SEMI - ORGANICS

Today, nonlinear optics is a vast area, and undoubtedly one of the most important areas of physics with a diverse range of applications in many other areas of science (Munn Umist and Ironside 1997). Since the first demonstration in 1961, nonlinear frequency conversion has been a materials-limited field, with practical advances largely controlled by progress in making available improved NLO materials (Bordui and Fejer 1993). The recent research activities focus mainly on materials exhibiting excellent second order nonlinear optical (SONLO) properties because of their potential applications in optoelectronic technologies, telecommunication, computer and optical signal processing (Long 1995 and Nalwa 1991).

Ionic salt materials offer an important and extremely flexible approach for the development of new materials applicable over a broad range of frequencies. For visible to near-UV wavelengths (400 – 200 nm), new materials were developed using simple solution-grown organic-inorganic complexes (‘semiorganics’) (Warren 1990 and Newman et al 1990). Semi organic crystals have been proposed as a new approach for materials with interesting nonlinear optical properties (Debrus et al 2002). These
‘semiorganics’ are salts in which the typically high optical nonlinearity of a purely organic ion is combined with the favorable mechanical and thermal properties of an inorganic counter ion (Masse and Zyss 1991 and Kotler et al. 1992). In this new approach to high efficiency, optical quality organic based non-linear optical materials are considered as compounds in which a polarizable organic molecule can be bonded to an inorganic host. An alternative and closely related strategy is to form metal-coordination complexes of highly polarizable organic molecules. These materials are known as semi organics and the principal approach to such kind of crystals is based on finding of metal-coordination complexes favoring substantial charge transfer and enhancement of charge density, non- centrosymmetry determining the corresponding second-order hyper-polarizabilities and susceptibilities. In addition to retaining the high optical nonlinearities of the organic molecules, where chromophore molecular complexes interacting with the surrounding background play the principal role (Kityk et al. 2004) they also possess favorable physical properties. An added advantage is that large single crystals can be grown from low temperature solutions (Brahadeeswaran et al. 1998). Allyl thiourea cadmium chloride (ATCC) (Sun et al. 2003), bis-glycine sodium nitrate (BGSN) (Sankar et al. 2007) are some examples of semi-organic crystals which are employed in devices. The advantage of semi organic materials is that the crystals can be grown from aqueous solutions and they form three-dimensional crystals which can be easily cut and polished (Min-hua Jiang and Qi Fang 1999).

Complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation (SHG), as they tend to combine the advantage of organic amino acids with that of inorganic salt. L-glutamic acid hydrochloride [HOOC (CH)₂CH (NH₂) COOHHCl] is an acid salt of L-glutamic acid, a mono amino dicarboxylic a-amino acid
(Delfino et al 1976), also known as α-amino glutaric acid hydrochloride or 2-aminopentanedioic acid hydrochloride. It is one of the members of 20 amino acids, which has an acidic carboxyl group on its side chain, which serves as both an acceptor, and a donor of ammonia, and is the main NLO active chromophore. Aliphatic amino acids characteristically transmit down to 220 nm and the conversion efficiency of these compounds to their acid salts generally increases the magnitude of the nonlinear optical coefficients while simultaneously minimizing absorption in the ultraviolet region. In this chapter the synthesis, growth and characterization of nonlinear optical material L-glutamic acid hydrochloride from the amino acid family is presented.

2.2 SYNTHESIS

L-glutamic acid hydrochloride was synthesized stoichiometrically. L-glutamic acid (Extra pure grade Merck) and hydrochloric acid (GR grade) of purity 99 % were commercially bought and L-glutamic acid hydrochloride was synthesized by reacting aqueous solutions of L-glutamic acid and hydrochloric acid according to stoichiometry. The synthesized material was then recrystallised from water and dried. The recrystallized material was then treated with a solution of 50 % volume ethanol - water solvent to assist the removal of non-polar contaminants (Delfino et al 1976, Delfino et al 1978). The molecular structure of L-glutamic acid hydrochloride is shown in the Figure 2.1.

![Figure 2.1 Molecular structure of L-gluHCl](image-url)
2.3 SOLUBILITY

In solution growth technique, the solubility of the material in a given solvent plays a vital role in growing large size single crystals. Recrystallized material was used for the solubility studies. Solubility of L-glutamic acid hydrochloride in water was determined by dissolving the solute in water taken in an air-tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility of the synthesized L-glutamic acid hydrochloride as a function of temperature for five different temperatures 30-50 °C in water is determined and plotted as shown in Figure 2.2. It was determined that the material possesses a positive gradient of solubility with a good solubility.

![Figure 2.2 Solubility of L-gluHCl in water](image-url)
2.4 BULK GROWTH OF L-gluHCl SINGLE CRYSTALS

In the present study L-glutamic acid hydrochloride was grown by low temperature solution growth, using solvent evaporation method. Stoichiometrically synthesized material was taken as the starting material for growth. Saturated solution of L-glutamic acid hydrochloride was prepared at room temperature with water as solvent and the prepared solution was filtered using a micro-filter. The filtered solution was taken in the vessels and dried in dust-free atmosphere with perforated covering. L-gluHCl crystals were grown during the process of solvent evaporation from a Petri dish. The crystals are harvested with good dimensions after a few days as shown in Figure 2.3. The harvested crystals were found to be transparent and are little hygroscopic in nature.

Figure 2.3 As grown crystals of L-gluHCl
2.5 CHARACTERIZATION OF THE L-gluHCl CRYSTALS

2.5.1 X-ray Diffraction Analysis

X-ray powder diffraction pattern of the L-gluHCl crystal was recorded by SIEFERT X-ray diffractometer using CuKα (Kα = 1.540 Å) radiation. The X-ray studies were carried out at room temperature. The sample was scanned for a 2θ range 10-70 degree at a scan rate 1 degree /min. The formation of L-gluHCl compound is confirmed through the powder XRD pattern. The indexed X-ray diffraction pattern of the material is shown in Figure 2.4.

The X-ray diffraction data of the L-gluHCl single crystal was collected using an Enraf-Nonius CAD – 4 diffractometer, with graphite monochromated CuKα radiation source. From single crystal X-ray diffraction analysis, it is determined that the material crystallizes in a tetra molecular cell in orthorhombic space group P2₁2₁2₁. The term ‘tetra molecular cell’ refers to the number of glutamic acid hydrochloride molecules by which the unit cell is being built up (i.e) four molecules.

Actually the unit cell contains two free Glutamic acid hydrochloride molecules and the portions of the same L-gluHCl molecule corresponding to two more molecules of the unit cell and the obtained cell parameters are similar to the values available for the L-gluHCl crystal in earlier reports (Sequeira et al 1972). The crystallographic parameters are given in the Table 2.1.
Table 2.1 Crystal data of L-glutamic acid hydrochloride

<table>
<thead>
<tr>
<th></th>
<th><strong>Chemical formula</strong></th>
<th>HOOC (CH$_2$)$_2$CH (NH$_2$) COOH HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td><strong>Cell parameters</strong></td>
<td>a = 5.151 Å, b = 11.79 Å, c = 13.35 Å</td>
</tr>
<tr>
<td>3</td>
<td><strong>Crystal system</strong></td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>4</td>
<td><strong>Space group</strong></td>
<td>P2$_1$2$_1$2$_1$</td>
</tr>
<tr>
<td>5</td>
<td><strong>Molecular weight</strong></td>
<td>147.13</td>
</tr>
<tr>
<td>6</td>
<td><strong>Cell volume</strong></td>
<td>810.4897 Å$^3$</td>
</tr>
<tr>
<td>7</td>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td><strong>Density</strong></td>
<td>1.524 g/cm$^3$</td>
</tr>
</tbody>
</table>

![XRD pattern](image)

Figure 2.4 Powder XRD pattern of L-gluHCl
2.5.2 Infrared and Raman Spectral Analysis

The presence of the functional groups was qualitatively analyzed by the Infrared spectrum. The powdered crystal of L-gluHCl was subjected to FTIR studies to confirm the presence of functional groups and coordination of ligands. The spectrum was recorded in the range 400 - 4000 cm\(^{-1}\) as shown in the Figure 2.6. The main absorption peaks of amino acids, carboxylic acids, amines and amino carboxylic acids were observed in L-gluHCl. Appearance of bands in the frequency region of 1212 cm\(^{-1}\), 1253 cm\(^{-1}\), 1275 cm\(^{-1}\) and 1425 cm\(^{-1}\), 1508 cm\(^{-1}\) correspond to the symmetric and asymmetric stretching of O – H and C = O groups respectively. The peaks corresponding to 634 cm\(^{-1}\), 674 cm\(^{-1}\) and 1610 cm\(^{-1}\), 1679 cm\(^{-1}\), 1721 cm\(^{-1}\) are the N-H deformation of amino acids and amines respectively. The C-H stretching mode of amino acid hydrochloride was observed at the frequency of 1982 cm\(^{-1}\). Also N-H stretching mode vibrations for the amino acid were observed at the frequencies 2501 cm\(^{-1}\), 2624 cm\(^{-1}\), 2721 cm\(^{-1}\) and 2895 cm\(^{-1}\).

Raman spectral study is a complementary of IR spectroscopy and gives information about the internal molecular vibrations. Raman activity tends to be a function of the covalent character of bonds. A Raman spectrum reveals information about the backbone structure of the molecule, whereas the strong infrared features are indicative of polar segments (Willard et al 1986). Powdered sample of L-gluHCl was subjected to Raman spectral analysis in the range 200 cm\(^{-1}\) to 2000 cm\(^{-1}\) and the corresponding spectrum is shown in Figure 2.5.

The Raman peaks at 920 cm\(^{-1}\) and 1008 cm\(^{-1}\) are assigned to C-C symmetric and asymmetric stretching vibration modes respectively. The
-O-C=O stretching vibration mode appears at 1400 cm\(^{-1}\). The NH\(_2\) symmetric
and asymmetric stretching vibrations occur near the bands 700 cm\(^{-1}\), 530 cm\(^{-1}\).
The CH\(_2\) twisting of amino acids appears at the frequency 830 cm\(^{-1}\). Thus the
FTIR and Raman spectra of L-gluHCl crystal show all the fundamental
vibrations and confirm the formation of L-gluHCl compound. The functional
group assignments for both the FTIR and Raman spectra are given in the
Table 2.2.

![FTIR spectrum of L-gluHCl](image)

**Figure 2.5** FTIR spectrum of L-gluHCl
Figure 2.6 Raman spectrum of L-gluHCl crystal

Table 2.2 Functional group assignments of L-gluHCl

<table>
<thead>
<tr>
<th>S. No</th>
<th>Functional group</th>
<th>FTIR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bond assignment</td>
<td>Wavenumber (cm(^{-1}))</td>
<td>Bond assignment</td>
<td>Wave number (cm(^{-1}))</td>
</tr>
<tr>
<td>1.</td>
<td>Amino acid</td>
<td>N–H deformation</td>
<td>634,674</td>
</tr>
<tr>
<td>2.</td>
<td>Carboxylic acids</td>
<td>O – H stretching</td>
<td>1212,1253,1275</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C = O stretching</td>
<td>1425,1508</td>
</tr>
<tr>
<td>3.</td>
<td>Amines</td>
<td>N–H deformation</td>
<td>1610,1679,1721</td>
</tr>
<tr>
<td>4.</td>
<td>Amino acid</td>
<td>N – H stretching</td>
<td>2501, 2624, 2721, 2895</td>
</tr>
</tbody>
</table>
2.5.3 Optical Transmission Features

Nonlinear optical effects can be used for the generation of new optical frequencies, not available with existing lasers, in particular compact blue coherent light sources (Bosshard et al 1995). It was reported earlier (Delfinio et al 1976) that the transmission and nonlinear optical property of L-glutamic acid hydrochloride was found to be comparable with that of Cesium dihydrogen arsenate, CsH₂AsO₄ (CDA). It has been reported that the transmission range of the crystal is from 235.4 nm to 1700 nm which makes it a very potential material for blue light emission. With its transmission comparable to Cesium dihydrogen arsenate, L-glutamic acid hydrochloride can be considered as an alternative of CDA, which may be grown relatively easier from solution and possesses a comparable transmission as that of CDA, which is a well-known nonlinear optical material. The recorded transmission spectrum is shown in Figure 2.7. The transmission percentage of the crystal is found to be more than 50 % with the cutoff wavelength near 235 nm. The transmission of L-glutamic acid hydrochloride is found to extend over the entire visible region.

![Figure 2.7 UV-Vis-NIR spectrum of L-gluHCl crystal](image.png)
2.5.4 Vickers Micro Hardness Test

As the hardness of the crystal determines the applicability of the crystal in devices, it is an inevitable parameter to be determined. Here the micro hardness of the material was measured by using the REICHERT MD 4000 E Ultra micro hardness tester fitted with a Vickers diamond pyramidal indentor attached to a REICHERT POLYVAR 2 MET microscope. Indentations were made on the (0 1 0) plane and the micro hardness measurements were made for the applied loads varying from 5 to 90 g for a dwell time of 1s. The hardness of the crystal can be calculated using the relation \( H_v = 1.8544 \frac{p}{d^2} \) where \( H_v \) is the Vickers hardness number, \( p \) is the indenter load in g and \( d \) is the diagonal length of the impression in mm. The micro hardness value is taken as the average of the several impressions made with both diagonals being measured. The variation of hardness with indenter load for L-glutamic acid hydrochloride crystals is given in the Figure 2.8. From the analysis, it is observed that the L-glutamic acid hydrochloride crystals can withstand up to an applied load of 90 g.

![Figure 2.8 Vickers microhardness studies L-gluHCl](image-url)
2.5.5 HRXRD Analysis

A multicrystal X-ray diffractometer was used to study the crystalline perfection of the single crystal (Lal and Bhagavannarayana 1989). Figure 2.9 shows the schematic diagram of the multicrystal X-ray diffractometer. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm × 8 mm; 2kW Mo) is first reduced by a long collimator fitted with a pair of fine slit assemblies. This collimated beam is diffracted twice by two (Bonse and Hart 1965) types of monochromator crystals and thus the diffracted beam contains well resolved MoKα₁ and MoKα₂ components.

![Diagram of Multi crystal X-ray diffractometer]

Figure 2.9 Schematic diagram of Multi crystal X-ray diffractometer

The MoKα₁ beam is isolated with the help of fine slit arrangement and allowed to further diffract from a third (111) Si monochromator crystal set in the dispersive geometry (+, -, -). Due to the dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the dispersion broadening in the diffraction curve of the specimen
does not arise. Such arrangement disperses the divergent part of the MoKα₁ beam away from the Bragg diffraction peak and thereby gives a good collimated and monochromatic MoKα₁ beam at the Bragg diffraction angle, which is used as incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+,-,-) and non-dispersive (+,-,+), configuration. This arrangement improves the spectral purity ($\Delta \lambda/\lambda < 10^{-5}$) of the MoKα₁ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be $<< 3$ arc s. Hence, specimen occupies the fourth crystal stage in symmetrical Bragg geometry for diffraction in (+, -, -, +) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc s.

The diffracted intensity is measured by using an in-house (National Physical Laboratory) developed scintillation counter. To provide two-theta (2θ_B) angular rotation to the detector (scintillation counter) corresponding to the Bragg diffraction angle (θ_B), it is coupled to the radial arm of the goniometer of the specimen stage. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle. The detector was kept at the same angular position 2θ_B with wide opening for its slit, the so-called θ scan.

The well-collimated and monochromated MoKα₁ beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration was used as the exploring X-ray beam. The L-gluHCl specimen crystal was aligned in the (+,-,-,+), configuration. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with
minimum angular interval of 0.4 arc s. The diffraction curve (DC) was recorded in the $\theta$ scan mode, wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit.

Before recording the diffraction curve, to remove the non-crystallized solute atoms which remained on the surface of the crystal and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a nonpreferential etchant of water and acetone mixture in 1:2 volume ratio. Figure 2.10 shows the high-resolution rocking or diffraction curve (DC) recorded for a typical L-gluHCl specimen grown by solvent evaporation method in symmetrical Bragg geometry by employing a multicrystal X-ray diffractometer described above with MoK$_\alpha$ radiation and the value of FWHM was 12 arc s which reveals good crystallinity of the grown crystals. The diffracting plane chosen to record the DC is (121).

The full width at half maximum (FWHM) of the diffraction curves is 12 arc s, which is close to that expected from the plane wave dynamical theory of X-ray diffraction (Betterman and Cole 1964). The single sharp diffraction curve with low FWHM indicates very good crystalline perfection. The specimen is a nearly perfect single crystal without having any internal structural grain boundaries and dislocations (or very low density of dislocations which could not be detected by high-resolution X-ray topography). However, the relatively higher values of diffuse scattered intensity along the tails on higher diffraction angle with respect to the exact Bragg diffraction peak position indicates interstitial type of point defects and their aggregates (Lal and Bhagavannarayana 1989 and Bhagavannarayana et al 2005), which may be due to impurities or solvent molecules occupied interstitially in the crystalline matrix.
2.5.6 Powder SHG Measurement

The effective second order susceptibility at 1064 nm fundamental wavelength was evaluated using Kurtz-Perry powder technique (Kurtz and Perry 1968), which is considered to be a valuable technique for initial screening of materials for second harmonic generation. The fundamental beam 1064 nm from Q switched Nd: YAG laser (Pro Lab 170 Quanta ray) is used to test the Second Harmonic Generation (SHG) property of the crystals by using Kurtz powder technique. Pulse energy of 4-mJ/pulse and pulse width of 10 ns and repetition rate of 10 Hz is used. 90° geometry was employed. The output SHG signal was separated from the fundamental beam by filter. The Photo multiplier tube (Philips Photonics) was used as the detector.

L-glutamic acid hydrochloride crystals were found to possess SHG. It was already reported by Delfinio et al that L-glutamic acid hydrochloride [HOOC (CH₂)₂ CH (NH₂) COOH·HCl] is phase matchable for optical second harmonic generation at 1.06 μm with their nonlinear optical coefficients.
comparable to CsH$_2$AsO$_4$. It has also been found that the material possesses $d_{36} \approx d_{36}$ CDA $\pm$ 30 %. Transmission and the order of magnitude of walk off angle correction were also found to be comparable with CDA (Delfino et al 1976).

### 2.5.7 Etching Studies

Etching studies were carried out for the as grown samples of L-gluHCl single crystals to understand the growth mechanism and to assess the perfection of the grown crystals. The crystal was selected and polished by gently rubbing with a feltly cloth wetted with 50 % ethanol and 50 % water and the final polishing was carried out using a thick wet cloth. The crystals were etched for a time periods of 3 s and 5 s and the etch patterns of L-gluHCl crystals are presented in Figures 2.11 and 2.12 respectively. From the etching analysis, etch pits were observed from the surface micrographs of the etch patterns and it is observed that the crystals possess step growth pattern

![Figure 2.11 Surface Micrograph of L – GluHCl etched for 3 s](image)

**Figure 2.11** Surface Micrograph of L – GluHCl etched for 3 s
2.6 SUMMARY

Semi organic material L-glutamic acid hydrochloride was synthesized and the crystal growth is optimised. Solubility of L-glutamic acid hydrochloride was found in the temperature range 30-50 °C, it was found to possess fairly good solubility in this range with a positive solubility gradient. These crystals were grown by low temperature solution growth by solvent evaporation technique at room temperature. The indexed powder XRD pattern and the FTIR spectrum confirm the formation of the L-gluHCl compound. From the single crystal XRD analysis, crystal system, lattice parameters, and space group were identified. The internal molecular vibrations of L-gluHCl compound were analyzed by Raman analysis. The UV-Vis-NIR spectrum shows that the crystal are having a cut-off wavelength near 235 nm and is more than 50 % transparent in the UV region. The hardness number (Hₜ) of L-gluHCl is found to increase with increase in the applied indenter load and the crystal was found to break at the load of 90 g. From the HRXRD results, it
is observed that the crystals possess very good crystalline nature with FWHM value of 12 arc s. By Kurtz powder method it was determined that these crystals possess fairly good SHG efficiency and the non linear optical co-efficient comparable to that of CDA. The as grown L-gluHCl crystals were subjected to etching analysis and the step growth pattern was observed from the surface micrographs.