CHAPTER 3

THIOUREA DOPED L-GLUTAMIC ACID HYDROCHLORIDE: SYNTHESIS, CRYSTAL GROWTH AND ITS CHARACTERIZATION

3.1 AMINO ACIDS: A BRIEF INTRODUCTION

Amino acids are presently explored very extensively for the opto electronic, NLO and many more applications. These amino acids even being organic molecules possess relatively high melting point (usually above 200 °C) which makes them more stable than some organic complexes. Aliphatic amino acids characteristically transmit down to 220 nm and also conversion of these compounds to acid salts generally increases the magnitude of the non-linear optical co-efficient, while simultaneously minimizing absorption in the ultraviolet (Prasad and Williams 1991 and Saleh and Teich 1991)

In recent years, semi organic materials based on amino acid groups have gained a wide range of attention in the field of non linear optics due to their mechanical strength and chemical stability. Semi-organic crystals exhibit excellent electro-optical and nonlinear optical properties and are commonly used in frequency conversion applications such as second, third, and fourth harmonic generation and in electro-optic modulation (Marder et al 1991). Some of the well known semi-organic complexes are Tri Glycine Sulphate (TGS) (Meera et al 2005), Bis Thiourea Zinc Chloride (BTZC), L- arginine hydrobromide (L-AHBr) (Haussuhl et al 1990), L-histidine tetrafluoroborate
(L-HFB) (Aggarwal et al 1999, Gokul Raj et al 2005), L-arginine tetrafluoroborate (L-AFB) (Owens et al 2001), L – alanine tetrafluoroborate (L-AlFB) (Rajan Babu et al 2002), L-arginine acetate (LAA) (Meera et al 2001 and Muralidharan et al 2003), L-alanine sodium nitrate (LASN) (Sethuraman et al 2008), Bis thiourea cadmium chloride (BTCC), L-arginine phosphate (LAP), etc., are reported. Growth of thiourea-doped TGS crystal was also reported (Meera et al 2004). Easy growth of large single crystals, a broad transparency range, a high optical damage threshold, and relatively low production cost are all qualities that make these amino acid based semi-organic crystals attractive for and well-suited to a variety of optical applications.

3.1.1 Effect of Doping

Nonlinear optical crystals significantly enhance the laser performance by making possible wavelength shifting and tunability and higher power. Technical progress has been made in developing several crystals which together cover the spectral range from middle ultraviolet to far infrared (Chen et al 1995). Selective crystallization of polymorphs requires control and manipulation of nucleation and growth process and may be achieved using additives (Blagden 2001). Currently, it is believed that additives operate by adsorption onto crystal facets, which consequently changes the surface free energy and may block sites which are necessary for incorporation of solute into the crystal lattice. This may ultimately result in kinetic and morphological changes (Davey 1976).

Impurities which are used to control polymorphism can also induce morphological changes which cannot be avoided (Kitamura and Nakamura 2001). Generally, impurities in the semi-organic materials are of considerable importance, not only because of their influence on the physical and chemical properties of the resulting crystal, but also since they can play a dominant role
in controlling crystal growth behavior. In the later case impurities, can modify crystal morphology (Buckley 1951) and growth rates, as well as alters the stability of growth, during constitutional supercooling.

The influence of impurities on the growth behavior has attracted intensive studies; impurities have various effects both in habit modification and crystal quality (Chen Jianzhong et al 1997, Kuznetsov et al 1998, Guohui Li et al 2005). In this present work, thiourea is doped with the L-gluHCl and the crystal growth is carried out to find the effect of dopant on the crystal. The characterization results of the crystals are presented and discussed.

3.2 CRYSTAL GROWTH: THIOUREA DOPED L-gluHCl

In the present study, stoichiometrically synthesized L-gluHCl was taken as the starting material for growth. Saturated solution of L-glutamic acid hydrochloride has been prepared at room temperature and the solution is filtered and 2 wt% of thiourea is doped. After adding the dopant, the solution is again stirred well in a closed vessel for more than 1 hour and then solution is filtered and is dried in a dust free atmosphere.

The crystals were grown by solvent evaporation method and the crystals were harvested after a week’s time. As grown thiourea doped L-gluHCl crystals were also found to be transparent and slightly hygroscopic in nature. There are no observable morphological changes in thiourea doped crystals. Figure 3.1 show the as grown thiourea doped L-gluHCl crystals.
Figure 3.1 As grown crystals of Tu doped L-gluHCl in water
3.3 CHARACTERIZATION

3.3.1 Powder X-ray Diffraction Analysis

X-ray powder pattern of the crystal was recorded on a SIEFERT X-ray diffractometer using CuKα (Kα = 1.540 Å) radiation. The sample was scanned for a 2θ range 10 - 70 degree and at a scan rate 1 degree /min at the room temperature. The indexed powder XRD spectra for the pure and thiourea doped L-gluHCl single crystals are as shown in Figure 3.2. Thiourea doped crystal shows a slight peak shift in the powder XRD pattern. L-glutamic acid hydrochloride crystals exhibit an orthorhombic bisphenoidal habit having well-defined prism faces (Delfino et al 1976). The crystal parameters of thiourea doped L-gluHCl are given in Table 3.1.

Table 3.1 Crystal parameters of Tu doped L-glutamic acid hydrochloride

<table>
<thead>
<tr>
<th>S. No</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chemical formula HOOC (CH₂)₂CH (NH₂) COOH HCl</td>
</tr>
<tr>
<td>2</td>
<td>Cell parameters a = 5.151 Å, b = 11.79 Å, c = 13.35 Å</td>
</tr>
<tr>
<td>3</td>
<td>Volume 810.4897 Å³</td>
</tr>
<tr>
<td>4</td>
<td>Molecular weight 147.13</td>
</tr>
<tr>
<td>5</td>
<td>System Orthorhombic</td>
</tr>
<tr>
<td>6</td>
<td>Space group P2₁2₁2₁</td>
</tr>
</tbody>
</table>
3.3.2 Fourier Transform Infrared (FTIR) Analysis

The powdered crystal of thiourea doped 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\(^{-1}\) and is shown in the Figure 3.3. Appearance of bands in the frequency region of 1213 cm\(^{-1}\), 1253 cm\(^{-1}\), 1276 cm\(^{-1}\) and 1426 cm\(^{-1}\), 1448 cm\(^{-1}\), 1509 cm\(^{-1}\) corresponds to the symmetric and asymmetric stretching of O – H and C = O groups respectively. The peaks corresponding to 635 cm\(^{-1}\), 675 cm\(^{-1}\) and 1610 cm\(^{-1}\), 1677 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 1981 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\(^{-1}\).
3.3.3 Energy Dispersive X-ray Analysis (EDAX)

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals. In the present study, the crystal was analyzed by INCA 200 energy dispersive X-ray micro analyzer equipped with LEO – Stereoscan 440 Scanning electron microscope. From the EDAX analysis of thiourea doped L-gluHCl crystal, it is determined that 0.05 weight % of thiourea is incorporated in the L-gluHCl crystal as shown in Figure 3.4 which confirms that thiourea has gone into the crystal lattice.
3.3.4 UV-Vis-NIR Spectral Analysis

The optical transmission spectra of both pure and thiourea doped L-gluHCl single crystals of thickness 2 mm were recorded in the range 200 nm to 1100 nm as shown in the Figures 3.5 (a) and (b) respectively. The transmission percentage of pure L-gluHCl crystal is found to be more than 50 % in the UV region. Also, it is observed from the UV-Vis-NIR spectrum that the transmission percentage decreases after doping thiourea. The thiourea doped L-gluHCl crystal shows more than 40 % transparency in the UV region. Both the pure and thiourea doped crystals have got transmission in the entire visible region, with the cutoff wavelength near 235 nm. With its transmission comparable to CDA, L-glutamic acid hydrochloride can be considered as an alternative of CDA, which may be grown easily from
solution and possesses a comparable transparency as that of CDA in the UV region.

![UV-Vis-NIR transmission curve of pure and Tu doped L-gluHCl crystals](image)

Figure 3.5  UV-Vis-NIR transmission curve of pure and Tu doped L-gluHCl crystals

### 3.3.5 HRXRD Analysis

The multicrystal X-ray diffractometer with the schematic as shown in the Figure 2.10 was also used for the present investigation. The experimental setup and the conditions are same as recorded for the pure L-gluHCl single crystal. The well-collimated and monochromated MoKα\text{1}\ beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal, Tu doped L-gluHCl is aligned in the (+,-,-,+\) configuration. The diffraction curve (DC) was recorded in the \(\omega\) scan mode wherein the detector was kept at the same angular position \(2\theta\text{h}\) with wide opening for its slit. Before recording the diffraction curve, to remove the impurities present on the surface of the crystal and also to ensure surface planarity, the
specimens were first lapped and chemically etched in a non-preferential etchant.

The diffraction curve recorded on the Tu doped L-gluHCl crystal is shown in Figure 3.6. The DC for the crystal recorded for the same planes (121) as that of the pure L-gluHCl is shown in Figure 2.11 and the FWHM value of thiourea doped L-gluHCl is found to be 28 arc s (whereas for pure L-gluHCl crystal it is 12 arc s), which is an indication of good crystalline quality. The much heavy scattering at higher glancing angles (with respect to Bragg peak position) shows that thiourea occupied the interstitial positions in the lattice and elucidate the ability of the crystal to accommodate thiourea in the crystalline matrix, which is a sign that thiourea may possibly affect the optical and the second harmonic properties of the crystal.

![Figure 3.6](image)

**Figure 3.6** High resolution X-Ray Diffraction curve recorded for thiourea doped L-gluHCl
3.3.6 Vickers Micro Hardness

L-glutamic acid hydrochloride has been doped with thiourea to know its effect on microhardness. The variation of hardness with indenter load for thiourea doped L-glutamic acid hydrochloride crystals is given in the Figure 3.7. The hardness of the crystal is found to decrease on doping the material. Thiourea doped L-glutamic acid hydrochloride crystals are found to break at an applied load of 70 g whereas the pure L - glutamic acid hydrochloride crystals could withstand up to an applied load of 90 g.

![Figure 3.7 Vickers microhardness studies on Tu doped L-gluHCl](image-url)
3.3.7 Powder SHG Measurement

The effective second order susceptibility at 1064 nm fundamental wavelength was evaluated using Kurtz-Perry powder technique, 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 thiourea doped 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 frequency doubled SHG signal was separated from fundamental ones by a filter. The Photo multiplier tube (Philips Photonics) was used as the detector. Thiourea doped L - glutamic acid hydrochloride crystals were found to possess SHG, and the SHG efficiency is similar to that of pure L-gluHCl crystal.

3.3.8 Etching Studies

To find the growth pattern of Tu doped L-gluHCl, etching analysis was carried out. The crystals were etched for time periods of 1 s and 3 s. From the etching analysis, we can observe that the crystals possess step growth pattern as shown in Figure 3.8 (a) and (b). Etch pits were observed from the surface micrographs of the etch patterns. The concentration of the etch pits was found to increase in the thiourea doped crystals as compared to pure L-gluHCl crystal. Thiourea in the crystal lattice did not alter the step growth pattern of pure L-gluHCl crystal.
Figure 3.8 Etchpatterns of Tu doped L-gluHCl for (a) 1 s and (b) 3 s
3.4 SUMMARY

Semi organic crystals of thiourea doped L-glutamic acid hydrochloride were synthesized. These crystals were grown by low temperature solution growth by solvent evaporation technique at room temperature. Studies such as infra red spectroscopy and X-ray diffraction confirm the formation of the material and their crystalline nature respectively. The presence of thiourea has been confirmed by the EDAX analysis. The UV-Vis-NIR spectrum shows that both the pure and Tu doped crystals are transparent in the UV region. Comparing the pure L-gluHCl, the transmission percentage is found to decrease for the Tu doped L-gluHCl crystal. From the HRXRD analysis, it is determined that the grown crystals are of good quality. It is also determined that Tu was present in the L-gluHCl crystal lattice. Similarly the hardness of Tu doped L-gluHCl was found to decrease in comparison to the pure L-glutamic acid hydrochloride crystals. By Kurtz powder method, it is observed that, the powder SHG of the Tu doped L-gluHCl possesses NLO property.