CHAPTER 4

STUDIES ON THE GROWTH AND PROPERTIES OF TRIS THIOUREA GLYCINE - AN ORGANIC NONLINEAR OPTICAL CRYSTAL

4.1 INTRODUCTION

The engineering of new nonlinear optical (NLO) materials, structures, and devices with enhanced figures of merit has emerged as the major force to drive nonlinear optics from the laboratory to real applications. Due to its potential applications in photonic devices, a lot of experimental (Sukhorukov et al 2002) and theoretical efforts (Maroulis 2003, Schoonveld et al 2000) are focused on the NLO properties of organic molecules. Organic materials with large second order optical nonlinearities find wide applications in the area of laser technology, laser communication and data storage technology.

Amino acids have proton donor carboxylic acid (COO\(^-\)) groups and proton acceptor amino (NH\(_2\)) groups. The importance of amino acids in NLO applications is due to the fact that all amino acids have a chiral symmetry and crystallize in noncentro-symmetric space groups. Amino acids and their complexes belong to a family of organic materials that have NLO applications (Kitazawa et al 1994). The salts of amino acids like L-arginine (Eimert et al 1989) and L-histidine (Aggarwal et al 1999) are reported to have high second harmonic conversion efficiency.
Glycine is the simplest of all amino acids. Glycine forms crystal with H$_3$PO$_3$ (Deepthy and Bhat 2001), K$_2$SO$_4$ (Shanmugavadivu et al 2006), NaNO$_3$ (Narayan Bhat and Dharmaprakash 2002, Sankar et al 2007), and AgNO$_3$ (Mohan Rao and Vishwamitra 1972). The growth and properties of glycine with thiourea (Diglycinyl thiourea) was reported (Ezhil and Kalainathan 2008). Diglycinyl thiourea crystal was found to exhibit better nonlinear optical property compared to Glycine zinc sulphate and Bis glycine sodium nitrate.

This chapter deals with the synthesis and growth of Tris thiourea glycine by the slow evaporation technique. The grown crystals have been subjected to single crystal X-ray diffraction (XRD), powder X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, optical absorption, thermal, dielectric, micro hardness, etching and second harmonic generation (SHG) efficiency studies.

4.2 EXPERIMENTAL
4.2.1 Synthesis and solubility

Tris thiourea glycine (TTG) was synthesized from thiourea and glycine taken in the stoichiometric ratio of 3:1.

$$3\text{CH}_4\text{N}_2\text{S} + \text{NH}_2\text{CH}_2\text{COOH} \rightarrow (\text{NH}_2\text{-CS-NH}_2)_3\text{NH}_2\text{CH}_2\text{COOH}$$

Thiourea  Glycine  Tristhiourea Glycine

The synthesized compound was dissolved in doubled distilled and was kept in a constant temperature bath at 303 K. After attaining supersaturation the equilibrium concentration of the solute was analyzed gravimetrically. The same process was repeated at four different temperatures
303 K, 308 K, 313 K, and 318 K and the solubility curve is shown in Figure 4.1. From the graph, it was observed that the solubility increases linearly with temperature and the material has high solubility.

![Figure 4.1 Solubility curve of TTG](image)

4.2.2 Crystal Growth

Thiourea and glycine were taken in the stoichiometric ratio of 3:1 and dissolved in double distilled water. The solution was stirred well using a magnetic stirrer for 1 hr to ensure homogeneous concentration over the entire volume of the solution. The solution was filtered using a filter paper of porosity 0.1 micron and transferred to a clean petri dish. Care was taken to minimize thermal variations and mechanical disturbances. Crystallization takes place by slow evaporation of the saturated solution. The synthesized salt was then purified by repeated crystallization. Transparent colourless crystals
were harvested in a period of 2 weeks. The photographs of the TTG crystals are shown in Figure 4.2.

![Figure 4.2 Single crystals of TTG](image)

### 4.3 RESULTS AND DISCUSSION

#### 4.3.1 Single Crystal X-Ray Diffraction

Crystalline materials scatter X-rays at well defined angles. The intensities of the scattered X-rays provide information about the atomic positions and the arrangement of atoms within the crystal structure.

The single crystal X-ray diffraction analysis of the tris thiourea glycine has been carried out using the Enraf-Nonius CAD-4 diffractometer. TTG crystal belongs to the monoclinic system with the lattice parameters $a = 5.142$ Å, $b = 12.056$ Å, $c = 5.514$ Å, $\alpha = 90.00^\circ$, $\beta = 111.75^\circ$ and $\gamma = 90.00^\circ$ and $V = 341.82$ Å$^3$. 
4.3.2 Powder X-Ray Diffraction Studies

Finely crushed particles of the TTG were subjected to Powder X-ray diffraction using the Siemens Rich-Seifert diffractometer with CuKα (λ = 1.5418) radiation. The sample was scanned over the range of 10°–70° at a scan rate of 2°/min. The prominent peaks obtained from the powder X-ray diffraction were indexed for the lattice parameters, which confirm the crystalline property of the grown crystals. The recorded powder X-ray diffraction pattern is shown in Figure 4.3.

![Figure 4.3 Powder X-ray diffraction pattern of TTG](image)

4.3.3 UV-Vis-NIR Spectra

UV-Vis-NIR spectroscopy is usually applied to molecules and inorganic ions or complexes in solution. The concentration of an analyte in
the solution can be determined by measuring the absorbance at some wavelength by applying the Beer-lamberts law.

The UV-Vis-NIR absorption spectrum is an essential tool to analyze the optical transmittance in crystals. The absorption spectrum of the TTG was recorded using a Varian Cary UV-Vis-NIR spectrophotometer in the spectral region of 200 nm–800 nm as shown in Figure 4.4. The lower optical cut-off is observed at 310 nm. The lower cut off wavelength for Diglycinyl thiourea is at 290 nm.

![Figure 4.4 Absorption spectrum of TTG](image)
4.3.4 FTIR Analysis

The absorption due to the bonding of the various functional groups present in the TTG crystal was analyzed by Fourier Transform Infrared FTIR spectroscopy. The spectrum was recorded in the wave number range of 500–4000 cm$^{-1}$ as shown in Figure 4.5.

![Figure 4.5 FTIR spectrum of TTG](image)

The peak observed at about 3428 cm$^{-1}$ due to O–H symmetric stretching clearly indicates the presence of hydrogen bonding and water molecule in the crystal lattice. The vibrations at 2307 cm$^{-1}$ are considered as overtones or combinations. The sharp band observed at 1623 cm$^{-1}$ is due to the N–H bending vibration. The peak observed at about 1410 cm$^{-1}$ is assigned to the C–C stretching. The peak observed at about 1331 cm$^{-1}$ is assigned to the
C–N symmetric stretching and the peak at 1107 cm\(^{-1}\) is due to C–O symmetric stretching. The peak at about 893 cm\(^{-1}\) is observed for N-H wagging. Also, an absorption band was observed at about 710 cm\(^{-1}\) which is due to the wagging vibration of CO\(_2\) structure. The rocking of the CO\(_2\) mode of band is assigned at wave number 512 cm\(^{-1}\). The observed vibrational frequencies and their assignments are given in Table 4.1.

**Table 4.1 Frequency assignments for TTG crystal**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Mode</th>
<th>Wave number cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>Symmetric stretching</td>
<td>3428</td>
</tr>
<tr>
<td>N-H</td>
<td>Bending</td>
<td>1623</td>
</tr>
<tr>
<td>C-C</td>
<td>Symmetric stretching</td>
<td>1410</td>
</tr>
<tr>
<td>C-N</td>
<td>Symmetric stretching</td>
<td>1331</td>
</tr>
<tr>
<td>C-O</td>
<td>Symmetric stretching</td>
<td>1107</td>
</tr>
<tr>
<td>N-H</td>
<td>Wagging</td>
<td>893</td>
</tr>
<tr>
<td>C=O</td>
<td>Wagging</td>
<td>710</td>
</tr>
<tr>
<td>C=O</td>
<td>rocking</td>
<td>512</td>
</tr>
</tbody>
</table>

### 4.3.5 Thermal Analysis

The thermal behaviour of the TTG crystal was studied by the ZETZSCH–Geratebau GmbH thermal analyzer. The sample was heated in a nitrogen atmosphere in an alumina crucible at the rate of 30 K/min. The TGA and DTA thermograms of the crystal are shown in Figures 4.6 (a) and 4.6(b). The thermogram illustrates the absence of weight loss from 303 K to 483 K. Hence the crystal is devoid of any water of crystallization. At 483.8 K, a
major weight loss is noted due to the degradation of the thiourea glycine. The DTA trace shows an endotherm starting at 437.8 K, which matches with the melting point of the crystal determined by the capillary method. It is followed by an intense endotherm due to the decomposition of the components in the crystal. The TG-DTA studies reveal that the crystal is thermally stable up to 437.8 K. The thermal stability of Diglycinyl thiourea was 453 K.

Figure 4.6 (a) TGA thermogram of TTG
4.3.6 Microhardness Studies

The hardness of a material is a measure of the resistance it offers to deformation (Mott 1956). Transparent crystals free from cracks were selected for the microhardness measurements. The indentations were made on the grown surface with the load ranging from 10 to 110 g using the Vickers microhardness tester. Leitz–Wetzlar was fitted with a Vickers diamond pyramidal indenter and attached to an incident light microscope. For each load, several indentations were made and the average value of the diagonal length was used to calculate the microhardness. The indentation time was kept as 5s for all the loads.
The plot of hardness (Hv) versus load for the TTG crystal is shown in Figure 4.7. From the plot it is observed, that the hardness number was found to increase with the load. After a load of 110 g, the hardness number (Hv) suddenly decreases as cracks developed in the material. This may be due to the release of internal stresses generated locally by indentation.

![Graph showing variation of hardness number with load of TTG](image)

**Figure 4.7 Variation of hardness number with load of TTG**

### 4.3.7 Etching Studies

The nonlinear efficiency of the NLO material depends mainly on the quality of the grown crystals because the segregated impurities and dislocations occurring during growth, result in the distortion of the optical beam to be processed. Hence, it is very essential to study the defects in the
grown crystals. Water is a superior etching solution for revealing dislocation etch pits and is insensitive to surface orientation, since it produced pits almost on all surfaces.

The etching study of the TTG crystal was carried out using deionized water as an etchant at room temperature for etching times of 10 s, 20 s, 30 s and 50 s. A transparent crystal free from inclusions and cracks was selected. The etching of the crystal surface was carried out by dipping the crystal in water for few seconds at room temperature and then wiping it with dry filter paper. The etched patterns were examined by an optical microscope (Chou et al 2006). The elongated etch patterns observed for an etching time of 10 s, 20 s, 30 s and 50 s are shown in Figures 4.8(a), 4.8(b), 4.8(c) and 4.8(d) respectively. The size of the pits increases with the increase of etching time, while the pit pattern remains the same. The observed etch pits, due to layer growth, confirmed the two-dimensional nucleation (2D) mechanism with less dislocations.
Figure 4.8 Etch patterns of TTG with water as an etchant for (a) 10 s (b) 20 s (c) 30 s and (d) 50 s
4.3.8 NLO Test

The NLO property of the crystal was confirmed by the Kurtz and Perry powder technique. A Q-switched Nd:YAG laser beam of wavelength 1064 nm was used with an input power of 2.0 mJ and pulse width of 10 ns, the repetition rate being 10 Hz. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample of the TTG packed in a capillary tube of diameter 0.154 mm. The assembly of an oscilloscope and photodiode detector is employed to measure the light emitted by the sample. The SHG behavior is confirmed from the output of the laser beam having a bright green emission ($\lambda=532$ nm) from the crystal. The SHG efficiency of tris thiourea glycine was found to be 0.8 times that of KDP crystal. The comparison of SHG efficiency of tris thiourea glycine with other organic crystals Diglycinyl thiourea, Glycine zinc sulphate and Bis glycine sodium nitrate with respect to KDP are presented in Table 4.2

Table 4.2 Comparison of SHG efficiency of tris thiourea glycine with other organic crystals with respect to KDP

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>NLO Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diglycinyl thiourea (Ezhil and Kalainathan 2008)</td>
<td>2.6</td>
</tr>
<tr>
<td>Glycine Zinc Sulphate</td>
<td>0.7</td>
</tr>
<tr>
<td>(Balakrishnan and Ramamurthi 2007)</td>
<td></td>
</tr>
<tr>
<td>Bis glycine sodium nitrate (Sankar et al 2007)</td>
<td>2.0</td>
</tr>
<tr>
<td>Tris thiourea glycine (Title compound)</td>
<td>0.8</td>
</tr>
</tbody>
</table>
4.4 CONCLUSION

Good quality single crystals of tris thiourea glycine were grown by the slow evaporation technique. Single crystal X-ray diffraction studies confirm the monoclinic structure of the grown crystal. The UV-vis-NIR absorption spectrum showed good transparency in the entire visible region. The functional groups were confirmed by the FTIR analysis. The DTA and the TGA analyses reveal that the melting point of the crystal is 437.8 K. From the hardness measurement, the crystal is mechanically stable up to 110 g. Etching studies reveals that the crystal grows by the two dimensional layer growth mechanism. The powder SHG efficiency of tris thiourea glycine is 0.8 times that of KDP.