CHAPTER 3

GROWTH OF TRIGLYCINE ZINC CHLORIDE CRYSTAL
AND ITS CHARACTERIZATION

3.1 INTRODUCTION

Amino acids are compounds containing an amino group, -NH₂, and a carboxylic acid group, -COOH. The biologically important amino acids have the amino group attached to the carbon atom next door to the -COOH group. The two simplest of these amino acids are 2-aminoethanoic acid and 2-aminopropanoic acid. Because of the biological importance of molecules like these, they are normally known by their traditional biochemical names: 2-aminoethanoic acid, for example, is usually called glycine, and 2-aminopropanoic acid is usually known as alanine. Nonlinear optical (NLO) materials are playing an important role in laser science technology, and the search for new NLO materials, particularly for UV and far-IR applications (Sasaki et al 2000). In general amino acid organic materials show a good efficiency of second harmonic generation. But most of the organic NLO crystals have poor mechanical and thermal stability. In order to increase the mechanical strength and thermal stability organic compounds are added with inorganic compounds. Glycine is the simplest form of amino acid which reacts with other inorganic compound to give a good mechanical and thermal stability.
Optical nonlinearity is defined simply as any deviation from the linear relationship between a material’s polarization response and an applied electromagnetic field. A nonlinear polarization can result from the application of a DC electric field, from a modulation in the intensity of the applied electromagnetic field, or from a combination of both. The type of nonlinear optical behavior exhibited by each material depends upon its atomic structure and composition. The velocity of electromagnetic wave is affected by the local polarization processes. There are many polarization processes; some are important to nonlinear optical behavior, and others are not. The polarization processes due to interaction of the wave with outer, loosely bound, valence electrons of a dielectric material affect the transparency of a material and its refractive index. This intensity dependence in the absorption and index of refraction of the material is a nonlinear optical process. Nonlinear optical behavior is observed in materials that have permanent polarization anisotropies. This is found in noncentrosymmetric crystals (Joseph Simmons and Kelly Potter 2000).

3.2 PRESENT WORK ON TRIGLYCINE ZINC CHLORIDE

Single crystals of the title compound (point group mm2) have been grown from aqueous solution of glycine and zinc chloride in the molar ratio 3:1 at 39 °C by slow controlled evaporation of the solvent (Fleck et al 2008). The growth of compounds such as glycine zinc chloride, bisglycine zinc chloride and triglycine zinc chloride were already reported (Tepavitcharova et al 2008) with the starting molar ratio 1:3, 1:1 and 3:1 respectively by the method of isothermal evaporation of the solvent. The preparative temperature for the first compound was 50 °C and for the others 25 °C. In this chapter we are presenting a report for the synthesis and growth of triglycine zinc chloride (TGZC) by slow solvent evaporation method with the starting molar ratio 2:1 at the preparation temperature of 50 °C. It crystallizes in the non-centrosymmetric
space group Pbn21. The characterization studies such as powder X-ray diffraction, fourier transform infrared (FTIR) and UV-Vis-NIR spectroscopic analysis, thermogravimetric and differential thermal analysis (TGA, DTA), dielectric and mechanical studies have been carried out on triglycine zinc chloride.

3.3 GROWTH OF TRIGLYCINE ZINC CHLORIDE

3.3.1 Metastable Zonewidth Measurement

To grow bulk crystals from solution by slow solvent evaporation technique, it is desirable to select a solvent in which it is moderately soluble. The size of a crystal depends on the amount of material available in the solution, which in turn is decided by the solubility of the material in the solvent. The solubility of a solute is the maximum mass of the solute that one can dissolve in a specified mass of the solvent. The growth rate of a crystal depends on its solubility and temperature.

The solubility of triglycine zinc chloride was assessed as a function of temperature from 25 °C to 53 °C in Millipore water. It was carried out in a constant temperature bath controlled to an accuracy of ± 0.01 °C, provided with a cryostat for cooling below room temperature. Saturated solution of triglycine zinc chloride was prepared at 25 °C in the constant temperature bath and the solution was continuously stirred using a motorized magnetic stirrer to ensure homogeneous temperature and concentration throughout the entire region of the solution. The concentration of the solute was determined gravimetrically. Then the solution was slightly warmed above the saturation temperature so as to dissolve the suspended solute particles present in the solution. In order to find the temperature at which nucleation is formed, the solution was cooled at a constant rate (4 °C/h) until nucleation occurred. For the solution which is saturated at 25 °C, the nucleation occurred at 19 °C.
This procedure was repeated at 34, 43 and 53 °C temperatures and the corresponding nucleation temperature was found. Figure 3.1 shows the metastable zone width of triglycine zinc chloride crystal. From the graph, it is observed that when the solubility increases, metastable zone width decreases with the increase of temperature.

![Solubility Curve and Nucleation Curve](image)

**Figure 3.1 Metastable zonewidth of triglycine zinc chloride crystal**

### 3.3.2 Growth

Triglycine zinc chloride crystals were grown by dissolving glycine and zinc chloride in the molar ratio 2:1 in Millipore water. The pH value of the prepared solution was 3.3 and it was allowed to evaporate at the ambient temperature. During the mixing of zinc chloride with the saturated solution of glycine, the solution temperature increases to 50 °C due to the exothermic reaction. After 45 days, good optically transparent single crystals of triglycine...
zinc chloride of size 45 x 23 x 18 mm$^3$ were harvested. The grown crystals were stable under standard conditions. The photograph of the as grown crystals is shown in the Figure 3.2. Due to large lattice force, an extra glycine molecule in its switterionic form is retained in the lattice, so that the title compound forms from the starting 2:1 molar ratio solution of glycine and zinc chloride. The expected chemical reaction is as follows:

$$4\text{NH}_2\text{CH}_2\text{COOH} + 2\text{ZnCl}_2 \rightarrow (\text{NH}_3^+\text{CH}_2\text{COO}^-)_3\text{ZnCl}_2$$

$$+\text{NH}_2\text{CH}_2\text{COOHZnCl}_2 \text{ ( in solution )} \quad (3.1)$$

The ORTEP diagram (Figure 3.3) shows the formation of triglycine zinc chloride precisely. Figure 3.4 is the morphology of the crystal, which shows typically orthorhombic pyramid.

Figure 3.2 Photograph of as grown triglycine zinc chloride crystals
3.4 CHARACTERIZATION STUDIES

3.4.1 Single Crystal X-ray Diffraction

In order to reveal the crystal structure, x-ray diffraction studies were carried out and data were collected. The unit cell parameters obtained are $a = 11.221(2)\, \text{Å}$, $b = 15.270(3)\, \text{Å}$, $c = 15.561(3)\, \text{Å}$, $\alpha = \beta = \gamma = 90.00(0)^\circ$, and $V = 2666.2(8)\, \text{Å}^3$. It exhibits orthorhombic crystal structure and is noncentrosymmetric with the space group of $Pbnm$. When the unit cell parameters were compared, they are analogous to the reported values (Fleck et al. 2008, Tepavitcharova et al. 2008).

![ORTEP diagram of triglycine zinc chloride crystal](image)

Figure 3.3 ORTEP diagram of triglycine zinc chloride crystal
3.4.2 Powder X-ray Diffraction

Figure 3.4 Morphology of triglycine zinc chloride crystal

Powder X-ray diffraction pattern of the triglycine zinc chloride crystal was recorded using Seifert Dyz 2002 model powder X-ray diffractometer with CuKα (λ = 1.540598 Å) radiation to study the crystallinity of the grown crystal. This powder pattern is a one dimensional recording of the intensity of diffracted radiation from all the sets of parallel planes as a function of the angle 2θ within the angular range measured. Finely crushed powder of the grown triglycine zinc chloride crystalline sample was used for the analysis. Then it was scanned over the range of 10-70° at a scanning rate of 1°/minute. The intensity of the diffracted beam was recorded as a function of 2θ and the peaks were indexed. It is seen from the powder XRD pattern that the sharp peak indicates the good crystallinity of the crystal. The XRD pattern for the grown crystal is shown in the Figure 3.5.
Figure 3.5 Powder XRD pattern of triglycine zinc chloride crystal

3.4.3 Fourier Transform Infrared Analysis

Fourier transform infrared spectrometry has been extensively developed over the past decade and provides a number of advantages. Radiation containing all IR wavelengths (5000-400 cm$^{-1}$) is split into two beams. One beam is of fixed length, the other of variable length (movable mirror). The varying distances between two pathlengths result in sequence of constructive and destructive interferences and hence variations in intensities: an interferogram. Fourier transformation converts this interferogram into complete IR spectrum. The FTIR analysis of TGZC was carried out between 4000 and 450 cm$^{-1}$ using Perkin Elmer spectrum one FT-IR spectrometer. The resulting spectrum is shown in the Figure 3.6.
The functional groups present in the molecules are identified by the absorption peak. In this spectrum the broad band between 2614 and 3180 cm\(^{-1}\) is due to the NH\(_3^+\) stretching vibration (Robert Silverstein and Francis Webstar 1998, Sharma 2007). Multiple combination and overtone bands extend the absorption to about 1941 cm\(^{-1}\). A weak asymmetrical NH\(_3^+\) bending band is obtained at 1641 cm\(^{-1}\) and a strong symmetrical bending occurs at 1561 cm\(^{-1}\) and 1500 cm\(^{-1}\). The strong absorption of carboxylate ion group COO\(^-\) is obtained at 1602 cm\(^{-1}\) and more weakly at 1412 cm\(^{-1}\). These bands result, respectively, from asymmetrical and symmetrical C(=O)\(_2\) stretching. The vibrations obtained at 1325 cm\(^{-1}\) and 562 cm\(^{-1}\) are due to CO stretching and bending respectively. Vibrations at 1034 cm\(^{-1}\) and 918 cm\(^{-1}\) denote CN stretching and CH\(_2\) rocking, and 490 cm\(^{-1}\) is due to Zn-N asymmetric stretching (Balakrishnan and Ramamurthi 2008). This observation confirms that glycine exists in zwitterionic form.

### 3.4.4 Optical Transmission Spectrum

Transmission spectrum is very important for any nonlinear optical (NLO) material, because a nonlinear optical material can be of practical use only if it has wide transparency window. The optical transmission spectrum of TGZC single crystal of 2mm thickness is recorded in the range 200 to 1100 nm using Perkin Elmer Lamda 35 UV/VIS spectrometer. The transmittance graph is shown in the Figure 3.7 in which the lower cut off region is obtained at 233 nm and almost there is a steady transmittance in the visible region. From the UV-Vis-NIR spectrum, it is found that the triglycine zinc chloride single crystal is conveniently transparent from 400 to 1100 nm with about 40% of transmittance.
Figure 3.6 FTIR spectrum of triglycine zinc chloride crystal

Figure 3.7 UV-Vis-NIR transmittance spectrum of triglycine zinc chloride crystal
3.4.5 NLO Studies

In order to find NLO property, the grown TGZC crystal was subjected to second harmonic generation studies by Kurtz powder technique. The sample was ground into very fine powder and tightly packed in a microcapillary tube. Then it was mounted in the path of Nd:YAG laser beam of energy 1.95 mJ/pulse. When KDP crystal was used as a reference material, it produced 62 mV as output beam voltage. But it was about 33 mV for the grown sample and hence it is confirmed that the triglycine zinc chloride has NLO efficiency about 0.5 times that of the KDP crystal.

3.4.6 Thermal Studies

Thermogravimetric and differential thermal analysis of TGZC crystals were carried out between 25 °C and 1200 °C in nitrogen atmosphere at a heating rate of 10 °C/min using NETZSCH STA 409 TG/DTA instrument. The respective TGA trace for triglycine zinc chloride crystal is shown in the Figure 3.8, which precisely shows that there is no weight loss up to 231 °C. Hence the crystal is devoid of any physically adsorbed water on it. It is observed in the graph that about 37 % weight loss occurs at the temperature of 244.6 °C. In the second step, weight decreases gradually up to the temperature of 1000 °C. The DTA response curve also shows a sharp endothermic peak at 231 °C. Thus from the thermal analysis, triglycine zinc chloride crystal is stable up to approximately 231 °C and it can be utilized for device application till 231 °C.

3.4.7 Dielectric Studies

Dielectric studies of triglycine zinc chloride crystal were carried out at various frequencies and temperatures using Precision LCR meter AGILENT 4284A model. The sample was prepared from the transparent part
of the triglycine zinc chloride crystal and its both surfaces were coated by carbon paste to make a contact with the electrodes. Then the prepared sample was mounted and heated from room temperature to 150 °C within the frequency range 100 Hz to 1MHz. Dielectric constant was calculated from the measured capacitance, dielectric loss values for finding dielectric properties of the grown crystal. Its maximum dielectric constant value was calculated as 7.8. Figures 3.9 and 3.10 represent the graph of dielectric constant and dielectric loss respectively. From the graph it is observed that dielectric constant is maximum at 100 Hz since all microscopic polarizations (electronic, ionic, orientation and space charge polarization) occur at lower frequency. Dielectric loss was found to increase with the increase of temperature. Because of the inertia of the molecules and ions, the dipolar and ionic contributions are small at high frequencies (Charles Kittel 1993). Hence the dielectric constant increases with the decrease of frequencies.

Figure 3.8  TG/DTA curves of triglycine zinc chloride crystal
Figure 3.9 Dielectric constant of triglycine zinc chloride crystal

Figure 3.10 Dielectric loss of triglycine zinc chloride crystal
3.4.8  Microhardness Studies

In order to reveal surface hardness of the as grown TGZC crystal, Vicker’s microhardness was measured on the (110) plane from 25 to 200 g load using HMV Microhardness tester. Vickers microhardness number was evaluated from the relation \( H_v = 1.8544 \frac{P}{d^2} \text{ kg/mm}^2 \), where \( H_v \) is Vickers hardness number, \( P \) is the indenter load in kg and \( d \) is the diagonal length of the impression in mm. Vicker’s microhardness of the triglycine zinc chloride crystal was calculated as 192 kg/mm\(^2\) at 200 g applied load. The trace is shown in the Figure 3.11, which shows that the hardness increases with the increase of load. To find the work hardening coefficient or Meyer index (n) of the grown crystal, a graph (Figure 3.12) was drawn between log \( P \) and log \( d \). It was calculated from the Meyer’s law \( P = ad^n \) connecting the applied load and diagonal length of the impression. In this relation, ‘a’ is the constant for a given material.

![Figure 3.11 Hardness Vs load of the triglycine zinc chloride crystal](image_url)
The work hardening coefficient was found to be 3.33 by taking slope in the straight line of the graph. According to Onitsch (Onitsch 1947) \( n \) lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials. Moreover if \( n > 1.6 \), then the microhardness increases with increase of load (Ramesh Babu et al 2003, Rajesh et al 2004). Yield strength can also be calculated using the relation (Ramesh Babu et al 2003) \( \sigma_y = (H_v/3)(0.1)^{n-2} \), where \( \sigma_y \) is the yield strength, \( H_v \) is the Vicker’s microhardness of the material and \( n \) is the logarithmic exponent. According to the relation, the yield strength was found to be 3.21 MPa and hence the grown triglycine zinc chloride crystal has relatively low mechanical strength.

![Figure 3.12 Plot of log P and log d of triglycine zinc chloride crystal](image)

**Figure 3.12 Plot of log P and log d of triglycine zinc chloride crystal**
3.5 CONCLUSION

Single crystals of Triglycine zinc chloride have been grown from the aqueous solution containing glycine and zinc chloride in 2:1 molar ratio by slow solvent evaporation technique. This is possible due to more lattice energy benefit for the coordination of triglycine zinc chloride crystal from 2:1 starting molar ratio of glycine and zinc chloride compound. The unit cell parameters determined in this experimental work agree well with the reported values. Optical studies show that the grown crystal is 40% transparent from 400 to 1100 nm. It has NLO efficiency half of that of KDP crystal. Thermogravimetric and differential thermal analysis show that triglycine zinc chloride crystal is stable up to 231 °C. Dielectric constant was found to be 7.8 at 140 °C. The grown TGZC crystal is soft material and having low yield strength.