8.1 Introduction

Among organic crystals for nonlinear optical applications, amino acids display specific features of interest such as (i) molecular chirality which secures acentric crystallographic structures; (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (iii) zwitterionic nature of the molecule favours crystal hardness. Some crystals of amino acids with simple inorganic salts appear to be promising materials for optical second harmonic generations. The salts of amino acids like L - Arginine [1, 2], L-Histidine [3] and L -Alanine [4] are reported to have high Second Harmonic Generation (SHG) efficiency. Glycine, the simplest amino acid, has three polymorphic crystalline forms namely α, β and γ [5]. Very recently it was discovered that a crystal of glycine sodium nitrate exhibited SHG two times higher than that of KDP [6]. Nagaraja et al. [7] reported that the SHG efficiency of benzoyl glycine crystal was 1.5 times that of KDP. Further glycine combines with H₂SO₄ [8], CaCl₂ [9], CaNO₃ [10], BaCl₂ [11], SrCl₂ [11], CoBr₂ [12] and Li NO₃ [13] to form single crystals but none of these exhibit nonlinear optical property. Some complexes of glycine such as glycine silver nitrate [14], diglycine manganese chloride dihydrate [15] and glycine phosphate [16] exhibit ferroelectric properties. Hoshino et al. [17] reported about the dielectric and thermal properties of triglycine sulphate and triglycine fluroberyllate. In the present work transparent single crystals of glycine lithium chloride (GLC) were grown from slow cooling technique and the crystal was characterized for its structural, thermal, optical, mechanical, nonlinear optical and dielectric properties.
8.2 Experimental Procedure

8.2.1 Synthesis

In the present study aqua solution of glycine (E Merk) and lithium chloride (LOBA Chemie) was prepared by mixing them in stoichiometric ratio. Glycine lithium chloride salt was synthesized by the evaporation of the solvent at 50 °C. Then the purity of the salt was increased by successive recrystallization process.

8.2.2 Solubility and metastable zonewidth

To grow bulk crystals from solution growth technique, it needs selection of solvent in which the material is moderately soluble. The size of the crystal depends on the amount of the material available in the solution which in turn is decided by the solubility of the material in that solvent. It is found that the solubility of GLC in double distilled water is high when compared with a few glycine compounds. Further the aqua solution yields transparent well developed single crystal of GLC.

Solubility of the GLC salt was determined for six different temperatures of 30, 35, 40, 45, 50 and 55 °C by dissolving it in double distilled water in an air tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration was analyzed gravimetrically. This process was repeated to estimate the saturation concentration of this salt at various temperatures. Further following the above procedure the solubility of glycine (G), glycine lithium sulphate (GLS) and glycine lithium bromide (GLB) salt was also estimated and compared with that of glycine lithium chloride. This shows that the solubility of GLC (Fig. 8.1) is relatively higher than that of the above salts.

Metastable zonewidth of the GLC solution was estimated by conventional polythermal method. In polythermal method the equilibrium solution was cooled from the overheated temperature to the temperature at which the first speck of the solid particle is observed [18]. Since the
time taken for the formation of the first visible crystal after attainment of critical nucleus is very small the first crystal observed may be taken as the critical nucleus [19]. The solubility and metastable zonewidth estimated at different temperatures are presented in Fig. 8.2.

**Fig. 8.1** Comparison of solubility of Glycine Lithium Chloride with GLB, GLS and Glycine

**Fig. 8.2** Metastable zonewidth of GLC

### 8.2.3 Crystal growth

The synthesized and recrystallized GLC salt was used for crystal growth. The supersaturated solution was prepared with the help of
solubility diagram. From the solubility data 53.54 g was dissolved in 100 ml of double distilled water at 40 °C. The solution was filtered using Whatman filter paper. GLC crystal was grown by slow cooling method in a constant temperature bath having an accuracy of ± 0.01 °C. Crystal growth process was initiated in the solution prepared at 40 °C by suspending one of the good quality seed crystals obtained from the process of slow evaporation at room temperature. The temperature of the solution was reduced at a rate of 0.1 °C / day under constant stirring. The grown crystal of size 15mm ×14 mm× 8 mm was harvested after a growth period of twenty two days (Fig. 8.3).

![As grown GLC crystal](image)

**Fig. 8.3** As grown GLC crystal

### 8.3 Single crystal X-ray diffraction

Single crystal X-ray diffraction data recorded using Enraf Nonius CAD - 4 MACH3 X-ray diffractometer with Mo Kα radiation (λ = 0.71073 Å) reveal that GLC belongs to triclinic system. The cell parameters calculated are a = 7.4230 Å, b = 17.5394 Å and c= 8.0303 Å, α = 89.91°, β = 115.08° and γ = 90.21° and volume = 946.928 Å³.
8.4 FT-IR spectral analysis

The Fourier Transform Infrared (FTIR) Spectrum of GLC crystal was recorded at room temperature in the spectral range 4000 - 400 cm\(^{-1}\) by KBr pellet method using the Perkin Elmer grating Infrared spectrophotometer and is shown in Fig. 8.4. The bands observed at 675 and 908 cm\(^{-1}\) are attributed to carboxylate groups while the peaks absorbed at 1482 and 1127 cm\(^{-1}\) are attributed to NH\(_3\) group. Thus the carboxyl group is present as carboxylate ion and amino group exists as ammonium ion in glycine lithium chloride. The peak absorbed at 1033 cm\(^{-1}\) is assigned to C-N stretching vibration. The peak absorbed at 1631 cm\(^{-1}\) is assigned to C=O asymmetric stretching vibration [20, 21]. The observed frequencies are assigned and compared with the corresponding values of pure glycine in Table 8.1.

![FTIR spectrum of glycine lithium chloride](image)

**Fig. 8.4** FTIR spectrum of glycine lithium chloride
Table 8.1 Comparison of the vibrational frequencies of GLC with that of glycine (cm⁻¹)

<table>
<thead>
<tr>
<th>FTIR glycine</th>
<th>FTIR GLC</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3419</td>
<td>3415</td>
<td>(O-H) Asymmetric stretching</td>
</tr>
<tr>
<td>3282</td>
<td>3136</td>
<td>(O-H) Symmetric stretching</td>
</tr>
<tr>
<td>1593</td>
<td>1631</td>
<td>COO⁻ Asymmetric stretching</td>
</tr>
<tr>
<td>1502</td>
<td>1515</td>
<td>NH₃⁺ Scissoring vibration</td>
</tr>
<tr>
<td>1482</td>
<td>1443</td>
<td>CH₂ deformation scissoring</td>
</tr>
<tr>
<td>1407</td>
<td>1409</td>
<td>COO⁻ symmetric stretching</td>
</tr>
<tr>
<td>1345</td>
<td>1335</td>
<td>CH₂ wagging</td>
</tr>
<tr>
<td>1112</td>
<td>1127</td>
<td>NH₃ Rocking</td>
</tr>
<tr>
<td>1034</td>
<td>1033</td>
<td>C-N Asymmetric stretching</td>
</tr>
<tr>
<td>892</td>
<td>908</td>
<td>CH₂ Rocking</td>
</tr>
<tr>
<td>766</td>
<td>766</td>
<td>NH₂ Rocking</td>
</tr>
<tr>
<td>690</td>
<td>675</td>
<td>COO⁻ scissoring</td>
</tr>
<tr>
<td>607</td>
<td>527</td>
<td>NH₃ twisting</td>
</tr>
</tbody>
</table>

8.5 UV – vis– NIR spectral studies

Optically clear single crystal of thickness 3mm was selected to record the absorption spectrum by employing Varian Cary 5E UV – vis – NIR spectrophotometer in the region 230 - 2500 nm (Fig. 8.5). As the crystal is transparent in the entire visible range with a lower cutoff at 230 nm, it can be used as a potential material for frequency doubling. The optical absorption coefficient α is determined using the relation:

\[ \alpha = \frac{2.303 A}{t} \]  

where t is the thickness of the crystal and A is the absorbance. The relation between the photon energy and the optical absorption coefficient is

\[ \alpha h\nu = B (\alpha h\nu - E_g)^{1/2} \]
Growth, Structural, Optical, Thermal and Mechanical Properties

where $E_g$ is the energy gap. The optical absorption in the UV region is dominated by the optical band gap ($E_g$) of the materials which is related to the optical absorption coefficient ($\alpha$) and the incident photon energy ($h\nu$). The band gap energy was estimated from the plots of $(\alpha h\nu)^2$ vs $h\nu$ as shown in Fig. 8.6. Extrapolation of linear portion of the curve to zero absorption gives the value of optical band gap (3.9eV) for the GLC single crystal.

Fig. 8.5 UV -vis- NIR absorbance spectrum of GLC

Fig. 8.6 $(\alpha h\nu)^2$ vs $h\nu$ plots of GLC single crystal
8.6 Thermogravimetric analysis

Thermogravimetric analysis of the GLC crystal was carried out between 50 and 1200 °C in the nitrogen atmosphere at a heating rate of 10 °C / min by employing Perkin Elmer, US, TGA 7 Analyser. A small piece of crystal weighing 10.681 mg was used for this investigation. The compound is stable up to 235 °C. Then the material shows a sharp single weight loss after 235 °C ends at 320 °C. At 285 °C the crystal undergoes an irreversible endothermic transition and decomposes. The thermogravimetric analysis trace of GLC is shown in Fig. 8.7.

Fig. 8.7 Thermogravimetric analysis of glycine lithium chloride

8.7 SHG efficiency

Kurtz and Perry powder [22] SHG test was performed to study the NLO property of GLC crystal. The crystal was illuminated by Spectra Physics Quanta Ray DHS-2. Nd: YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repetition rate of 10Hz. The green radiation of 532 nm was collected by a photomultiplier tube (PMT- Philips Photonics - model 8563) after being monochromated (monochromator - model Triax – 550). The optical signal incident on the
PMT was converted into voltage output at the CRO (Tektronix- TDS 3052B). The input laser energy incident on the powdered sample was chosen to be 3.4 mJ. The powder SHG efficiency of this crystal is 2.25 times that of potassium dihydrogen orthophosphate.

### 8.8 Mechanical Hardness

Hardness, one of the important mechanical properties of the materials, is defined as the ability of a crystal to resist a structural breakdown under applied stress. The resistance offered by a crystal for the applied stress is the intrinsic property of the crystal. Employing REICHERT MD 4000E ULTRA microhardness tester Vickers microhardness values were estimated for different loads on the carefully polished (011) face of GLC crystal identified from single crystal X-ray diffraction. The dwell time of indentation was 2 sec for all the loads. Vickers microhardness number ($H_v$) was evaluated from the relation, $H_v = \frac{1.8544(P/d^2)}{kg/mm^2}$, where $P$ is the indenter load in kg and $d$ is the diagonal length of the impression in mm. Fig. 8.8 shows the variation of Vickers hardness values with load. The hardness value increases up to a load of 60 g. Cracks developed around the indentation mark for a load of 70 g and hence a decrease in the hardness value.

![Hardness Vs Load graph of the grown crystal on (011) face](image)

Fig. 8.8 Hardness Vs Load graph of the grown crystal on (011) face
8.9 Dielectric studies

The dielectric constant of the GLC single crystal was measured using LCR meter in the frequency region from 40Hz to 100 kHz. Carefully selected transparent good quality single crystal of GLC was cut and polished using fine grade alumina powder to obtain flat surface. Silver paste was applied on the opposite faces of the GLC single crystal of dimension 10mm×10mm×3mm. A two terminal copper electrode was used as sample holder and the sample was held between electrodes. The temperature of the sample was controlled and measured using a thermocouple. Thermocouple was fixed in the vicinity of lower electrode to measure the temperature of the sample. In this way a parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency. The dielectric constant (ε') was estimated at room temperature by using the formula \( \varepsilon' = \frac{C d}{\varepsilon_0 A} \), where \( C \) is the capacitance of the crystal, \( d \) is the thickness of the crystal, \( A \) the cross sectional area of the flat surface of the crystal and \( \varepsilon_0 \) the constant of permittivity of free space. Figure 8.9 shows variation of dielectric constant as a function of log frequency.

![Graph showing variation of dielectric constant as a function of log frequency.](image)

**Fig. 8.9** Frequency dependence of dielectric constant at room temperature
It is observed from the figure that the dielectric constant decreases with increasing frequency. This shows that the crystal exhibits the normal dielectric behaviour [23].

8.10 Conclusion

GLC crystal of size 15mm × 14mm × 8mm was grown by slow cooling method from aqueous solution of glycine lithium chloride. The solubility of GLC was estimated and compared with the solubilities of glycine, glycine lithium sulphate and glycine lithium bromide. The solubility of GLC is relatively higher than the above salts. Metastable zonewidth of GLC is estimated in aqueous solution by conventional polythermal method. The single crystal X-ray diffraction study reveals that the grown crystal belongs to triclinic system. Presence of various functional groups of GLC crystal was identified from the corresponding vibrational frequencies of the FT-IR spectrum. The optical absorbance spectrum recorded for this crystal confirms that it is suitable for NLO applications. The band gap value obtained is 3.9eV. Thermogravimetric analysis implies that the sample is stable up to 235 °C. Microhardness study reveals that the hardness value increases with the increase of applied load on (011) face up to a load of 60g. The SHG efficiency of the grown crystal is about 2.25 times that of potassium dihydrogen orthophosphate. The dielectric constant measured at room temperature shows normal dielectric behaviour.

References

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