CHAPTER III
GROWTH OF α AND γ-GLYCINE CRYSTALS FROM AQUEOUS AND GEL MEDIUM AND THEIR CHARACTERIZATION

3.1 INTRODUCTION

Glycine is the simplest, achiral (symmetry) and is optically inactive amino acid. Great efforts have been made to the research and design of highly efficient non-linear optical (NLO) materials due to the widespread applications such as high speed information processing, optical communication and optical data storage [1]. Materials based on amino acids are widely utilized because they not only contain chiral carbon atoms directing the crystallization in non-centrosymmetric space group, but also possess zwitterionic nature favoring crystal hardness [2]. While glycine can exist as a neutral molecule in the gas phase, it exists as a zwitterion in solution and in the solid state. Glycine crystallizes in three polymorphic forms, viz. α, β and γ. The polymorphs have similar structure but differ in the way molecules are packed (the space group P2₁/n, P2₁ and P3₁ for α, β and γ glycine, respectively) [3]. The carboxylic groups present in the molecule donates its proton to the amino group to form the structure (NH₃⁺CH₂COO⁻). Thus in the solid state γ-glycine exist as a dipolar ion in which carboxyl group is present as carboxylate ion and amino group present as ammonium group. The dipolar nature exhibits peculiar physical and chemical properties in glycine, thus
making it as ideal candidate for NLO, piezoelectric and pyroelectric applications. Another advantage of glycine is the presence of chromophores namely amino group and carboxyl group which makes it as transparent in the ultraviolet-visible region [4]. The γ-form transforms to α-form on heating around 172°C. An ordinary α-form, Marsh et.al [5] determined its structure, in which the hydrogen bonded double layers of molecules packed by Vander Waals forces. An unsuitable β-form, whose internal arrangement is same as in α-form, and each single molecular layers are held together by hydrogen bond throughout the crystal. The α- and β forms crystallize in the monoclinic system with centrosymmetric space groups P2₁/n and P₂₁ respectively, and the γ-form crystallizes in the trigonal-hexagonal system with non-centrosymmetric space group of P₃₁ [6-8]. This makes γ glycine a candidate for non-linear optical applications and reported that it showed a second harmonic efficiency of about 1.5 times that of KDP [9].

3.2 SOLUBILITY STUDIES

The growth rate of a crystal depends on its solubility and growth temperature. Solubility of a material governs the amount of material, which is available for the growth and hence defines the total size limit. The analar grade 3M glycine (99%) with 1M orthophosphoric acid and 3M glycine with 1M concentrated nitric acid were taken for the synthesis of α- glycine and γ-glycine respectively. The solubility of glycine has been determined at various temperatures in triple distilled water. For this, a saturated solution was prepared in
a well-controlled thermal environment with excess of solute. After 2 hours of stirring, the solution kept idle for 30 minutes. Then the supernatant solution was taken and subjected to gravimetric analysis to know the solubility at particular temperature. The same method was employed to find solubility for different temperatures. The graph was then plotted for various temperatures verses concentration. The solubility curves for $\alpha$ and $\gamma$ glycine are shown in figure 3.1.

Figure 3.1 solubility curves of $\alpha$ and $\gamma$ glycine
3.3 GROWTH OF $\alpha$ AND $\gamma$-GLYCINE FROM SOLUTION

$\alpha$-glycine crystals were grown in aqueous solution by taking the analar grade glycine (NH$_2$CH$_2$COOH) and concentrated orthophosphoric acid in stoichiometry ratio 3:1 respectively. For the preparation of 200 g of $\alpha$-glycine, 39.52 ml of concentrated H$_3$PO$_4$ diluted with 750 ml of triple distilled water were taken. Then 139.37 g of glycine salt was slowly dissolved in the diluted H$_3$PO$_4$. The solution was heated below 60°C until the salt crystallizes. The crystals obtained from the solution are found to be opaque (figure 3.2).

$\gamma$-glycine was grown by taking the analar grade glycine and concentrated nitric acid in stoichiometry ratio 3:1 respectively. For the preparation of 200 g of salt, 44.34 ml of concentrated HNO$_3$ diluted with 750 ml of triple distilled water was prepared. Then 156.13 g of glycine salt was slowly dissolved in the diluted HNO$_3$. The $\gamma$-glycine crystals grown from solution are also found to be opaque (figure 3.2). Since both $\alpha$ and $\gamma$ glycine crystals were opaque after harvesting from solution, an attempt has been made to grow these crystals by gel method.
3.4 GROWTH OF α AND γ-GLYCINE CRYSTALS FROM GEL

The stock solution was prepared as reported by Henisch [10]. The specific gravity of this solution was adjusted between 1.06-1.08 g/cm³. Silica gel prepared from an aqueous solution of sodium metasilicate (Na₂SiO₃·5H₂O) was used as the crystal growth medium. Analytical grade glycine and orthophosphoric acid were taken in the optimized ratio 3:1 and dissolved in triple distilled water. The solution was filtered and heated in a water bath at a constant temperature. The gelation was achieved by mixing this solution with sodium metasilicate solution of density 1.06-1.08 g/cm³. After making several trials, the optimized pH was found to be 3.6. The growth experiments were performed with straight test tubes of length 21 cm and diameter 4.5 cm.

The gel was found to be perfectly set within 48 hours and kept one more day for proper gel setting. In order to initiate the solubility reduction process, methanol was gently added on top of the set gel without affecting the gel structure. The period of growth for growing good sized quality crystals is 15 days.
The gel grown $\alpha$ glycine crystal of size $12 \text{ mm} \times 7 \text{ mm} \times 5 \text{ mm}$ is shown in figure 3.4. Glycine is a biological nutrient and hence microbes grow easily in its aqueous solution. Microbial growth plays havoc in the growth of good quality crystals [11]. Due to three dimensional cross linked network of the gel, quality of crystal are highly transparent and microbial growth is completely eliminated which is a major problem in aqueous growth. Performing growth in gel medium is easier because the whole experiment is carried out at room temperature.

\[
\text{NH}_2\text{CH}_2\text{COOH} + \text{Orthophosphoric acid} \rightarrow \text{NH}_2\text{CH}_2\text{COOH} \\
\text{Glycine} \quad \rightarrow \quad \alpha\text{-Glycine}
\]

--------------- 3.1

The same experiment is repeated for the growth of $\gamma$-glycine, instead of using orthophosphoric acid concentrated nitric acid is used. The selected pH of the gel for the growth is 4.0. The maximum size of $\gamma$ glycine crystals obtained is $12 \times 8 \times 6 \text{ mm}^3$ and harvested crystals are shown in figure 3.4. Figure 3.3 is the photograph of $\alpha$ and $\gamma$ glycine crystals growing near the interface and gel.

\[
\text{NH}_2\text{CH}_2\text{COOH} + \text{Conc. nitric acid} \rightarrow \text{NH}_2\text{CH}_2\text{COOH.} \\
\text{Glycine} \quad \rightarrow \quad \gamma\text{-Glycine}
\]

--------------- 3.2
Figure 3.3 Photograph of $\alpha$ and $\gamma$ glycine crystals near the interface and inside the gel
Figure 3.4 Gel grown crystals of $\alpha$ and $\gamma$ glycine
Table 3.1
Optimum pH for the growth of α and γ glycine

<table>
<thead>
<tr>
<th>Crystal</th>
<th>pH of the gel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
</tr>
<tr>
<td>α-glycine</td>
<td>3.2</td>
</tr>
<tr>
<td>γ-glycine</td>
<td>2.8</td>
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3.5 CHARACTERIZATION STUDIES

3.5.1 CHN analysis

α and γ-glycine are made up of the elements carbon, hydrogen, nitrogen and oxygen. In order to determine the exact percentage of elements in unknown substance, CHN analytical method is performed. The substance to be analysed is decomposed through oxidative combustion. 100 mg of substance is heated at temperature of 950 to 1050°C. α and γ-glycine has molecular formula C₂H₅NO₂ (NH₂CH₂COOH). The percentage of carbon, hydrogen and nitrogen found from CHN analysis is given in the table 3.2. It is understood from the table that the determined elemental values are very much comparable to theoretical values.
Table 3.2

Chemical analysis of α and γ-Glycine

<table>
<thead>
<tr>
<th>Elements</th>
<th>Theoretical %</th>
<th>α-Glycine Measured %</th>
<th>γ-Glycine Measured %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>31.97</td>
<td>32.62</td>
<td>32.36</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.66</td>
<td>6.40</td>
<td>6.33</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>18.65</td>
<td>19.46</td>
<td>19.38</td>
</tr>
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</table>

3.5.2 Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction data were recorded for the grown crystals using MACH 3 Nonius CAD-4 X-ray diffractometer with Mo Kα radiation (λ = 0.71073 Å). The cell parameters are as tabulated in table 3.3. These values compare well with the corresponding values reported previously [12-14].

The crystal structure of glycine was also reported by Dawson et.al. [15]. He quoted that the α - and γ-glycine crystallizes in monoclinic and hexagonal structure with space groups of P2₁/n and P3₁ respectively. The lattice parameters of α-glycine are reported as a = 5.11Å, b = 11.98 Å, c = 5.47 Å and β = 111.78.
Table 3.3
Lattice parameter values of $\alpha$ and $\gamma$-glycine

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>$\alpha$-glycine</th>
<th>$\gamma$-glycine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P2$_1$/n(Monoclinic)</td>
<td>P3$_1$(Hexagonal)</td>
</tr>
<tr>
<td><strong>Lattice parameters</strong></td>
<td><strong>Literature</strong></td>
<td><strong>Experimental</strong></td>
</tr>
<tr>
<td>a(Å)</td>
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<td>5.10</td>
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<tr>
<td>b(Å)</td>
<td>11.96</td>
<td>11.95</td>
</tr>
<tr>
<td>c(Å)</td>
<td>5.45</td>
<td>5.46</td>
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<tr>
<td>$\beta$ (°)</td>
<td>111.70</td>
<td>111.76</td>
</tr>
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</table>

3.5.3 Powder X-ray diffraction analysis

Powder XRD pattern of $\alpha$ and $\gamma$-glycine crystals grown are shown in figure 3.5 and 3.6 respectively. The $\alpha$ glycine exhibits its 100% peak corresponding to (130) plane at an angle approximately 29° of 2$\theta$ in its XRD spectrum whereas the $\gamma$ glycine exhibits its 100% peak corresponding to (110) plane at an angle approximately 25° of 2$\theta$ in its XRD spectrum. This is the fingerprint distinction between these two polymorphs of glycine. The results agree well with previously reported XRD pattern [15]. Appearance of sharp and strong peaks confirms the good crystallinity of the grown samples [16].
Figure 3.5 Powder XRD pattern of $\alpha$ glycine

Figure 3.6 Powder XRD pattern of $\gamma$ glycine
3.5.4 FTIR spectral analysis

The Fourier Transform Infrared (FTIR) spectra for $\alpha$ and $\gamma$-glycine crystals (Figure 3.7) were recorded at room temperature in the spectral range 450–4000 cm$^{-1}$ by KBr pellet method using the Thermo Nicolet 380 spectrophotometer. An advanced inbuilt software EZOMNIC was utilized for crosschecking the molecular vibrations of both glycine molecules. FTIR spectra in the mid region for the glycine samples agree well with reported result [17-20]. The observed frequencies and their assignment of the $\alpha$ and $\gamma$ glycine crystals are given in table 3.4, which shows the close agreement with the literature values and confirms the presence of glycine molecule in the crystals.

![FTIR spectra of $\alpha$ and $\gamma$ glycine](image)

Figure 3.7 FTIR spectra of $\alpha$ and $\gamma$ glycine
Table 3.4
Frequency assignment of α and γ-glycine

<table>
<thead>
<tr>
<th>Frequency in wave number (cm⁻¹)</th>
<th>α-glycine</th>
<th>γ-glycine</th>
<th>Assignment of vibrations</th>
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<td>Experimental</td>
<td>Literature</td>
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<td>694, 606, 504</td>
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</tr>
</tbody>
</table>
3.5.5 UV–Vis–NIR spectral studies

Optically transparent single crystal of thickness 1mm was used to record the absorption spectrum by employing Varian Cary 5E UV–vis–NIR spectrophotometer in the range 200 and 1200 nm (figure 3.8). As there is no absorption in the entire UV–vis–NIR range with a lower cutoff at 250 nm, γ-glycine can be used as a potential material for frequency doubling.

![UV absorption spectrum of α and γ glycine](image)

Figure 3.8 UV absorption spectrum of α and γ glycine

3.5.6 Thermal analysis

Grown single crystals of α and γ glycine were subjected to TG and DTA analysis in the temperature range of 40- 1200°C at heating the rate of 20°C/min in nitrogen atmosphere using a NETZSCH STA 409 C/CD system. The TG and DTA curve of the grown α glycine (figure 3.9) does not indicate any change in the heat flow until the melting temperature that occurs at 255.7 °C. The melting transition starts at 220 °C and ends at 255.7 °C. Also no appreciable weight loss was
observed until the melting transition. Whereas the TG and DTA curve of γ glycine (figure 3.9) shows an endothermic peak at 172 °C before its melting transition. This peak represents certainly a phase transformation of this crystal from γ to possibly the α glycine form. Except this, there is no big change in the thermal behaviour this crystal until the melting transition that occurs at 254.9 °C.

Figure 3.9 TG/DTA curve of α and γ glycine
3.5.7 Dielectric studies

In order to carry out dielectric measurements, carefully selected samples of \( \alpha \) and \( \gamma \)-glycine were cut and later polished to obtain a good surface finish. Dielectric studies were carried out with the silver coated sample placed inside a dielectric cell subjected to various temperatures in the frequency range 100Hz to 1MHz. Figure 3.10 shows the plot of dielectric constant \( \varepsilon' \) as a function of log frequency and figure 3.11 shows a plot of dielectric loss \( \varepsilon'' \) as a function of log frequency. It is observed that both \( \varepsilon' \) and \( \varepsilon'' \) show similar variation with frequency. Broadly speaking the graph exemplifies the fact that the dielectric constant and dielectric loss are both inversely proportional to frequency. This is a normal dielectric behaviour [21] that both \( \varepsilon' \) and \( \varepsilon'' \) decrease with increasing frequency. This can be understood on the basis that the mechanism of polarization is similar to that of conduction process. The electronic exchange of the number of ions in the crystals gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. As the frequency increases, the point is reached where the space charge cannot sustain and comply with the external field and hence the polarization decreases, giving rise to diminishing values of \( \varepsilon' \) and \( \varepsilon'' \). Continuous gradual decrease of \( \varepsilon' \) as well as \( \varepsilon'' \) suggest that \( \gamma \) and \( \alpha \) glycine crystals are like any normal dielectric may have domains of different sizes and varying relaxation times.
Figure 3.10. Frequency dependence of dielectric constant of α and γ glycine.
Figure 3.11 Frequency dependence of dielectric loss of $\alpha$ and $\gamma$ glycine
3.6 RESULTS AND DISCUSSION

Glycine is the simplest optically inactive (possess centre of symmetry) compound. While glycine can exist as a neutral molecule in the gas phase, it exits as a zwitterions in solution and in the solid state. In the solid state, glycine crystallizes into three forms \( \alpha \), \( \beta \), and \( \gamma \). The \( \alpha \) and \( \beta \)-forms crystallizing into monoclinic system with centrosymmetric space group of \( P2_{1/n} \) and \( P2_1 \) respectively, and \( \gamma \)-form crystallizes in the trigonal-hexagonal system with non-centro symmetric space group \( P3_1 \). The dipolar nature exhibits peculiar physical and chemical properties of glycine, thus it is ideal for nonlinear optic, piezoelectric and pyroelectric applications. Presence of chromophores namely amino and carboxyl groups makes it transparent in the UV-Visible region.

The powders of \( \alpha \) and \( \gamma \)-glycine were synthesized by mixing 3:1 molar ratio of analar grade glycine and orthophosphoric acid and concentrated nitric acid respectively. Both the crystals were grown using the synthesized salts. In solution growth method, the grown \( \alpha \) and \( \gamma \)-glycine crystals turned opaque and the problem of microbial incorporation was encountered. To overcome these problems selecting gel method is the suitable one for the growth of \( \alpha \) and \( \gamma \)-glycine crystals. For the growth of \( \alpha \) glycine, 3:1 molar ratio of glycine and orthophosphoric acid were dissolved in triple distilled water and then sodium meta silicate stock solution of density 1.06 g/cm\(^3\) was added at a pH 3.6. The above procedure was also adopted for the growth of \( \gamma \)-glycine instead of using orthophosphoric acid, nitric acid was used and pH of the solution was maintained at pH 4. Transparent \( \alpha \)
and γ-glycine crystallized at the interface and inside the gel. 12 mm × 7 mm × 5 mm and 12 mm × 8 mm × 6 mm size of α and γ-glycine crystals were harvested respectively.

The single crystal X-ray diffraction studies confirm that α and γ-glycine crystallizes in *monoclinic* and *hexagonal* systems respectively. The lattice parameters of both the crystals were determined from the single crystal X-ray diffraction and compared with the reported values [12-14]. The powder X ray diffraction pattern recorded for the grown α and γ-glycine crystals show marked distinctions and used to confirm the form of crystallization of glycines in polymorphic forms.

FTIR spectrum confirms the presence of various functional groups and corresponding frequencies of the vibrational modes. This spectrum also reveals the presence of carboxylate and ammonium ions that clearly indicates the glycine molecule exists in zwitterionic forms i.e., in α and γ-glycine forms. Optical absorption spectra were recorded in the wavelength range of 200-1200 nm and shows no absorption peak over this range, which is essential parameter for NLO crystals. The grown crystal has an absorption edge in the lower wavelength region at 220 nm and 222 nm for α and γ glycine respectively.

The thermal stability of the grown crystals was studied by TG and DTA analysis. The endothermic peak at 254 °C corresponds to melting of the α glycine. In the case of γ glycine, endothermic peaks at 172 °C and 255.7 °C correspond to the phase transformation from γ phase to α phase and its melting point
respectively. Dielectric constant and loss of both α and γ glycine decreases with increase in frequency. The very high value of $\varepsilon'$ at lower frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The nature of decrease of $\varepsilon_r$ and tan δ ($\varepsilon''$) with frequency suggests that the α and γ glycine crystals contain dipoles of continuously varying relaxation times.
REFERENCES


