Chapter 3

Nucleation kinetics, growth and characterization of nonlinear optical $\gamma$-glycine single crystal in the presence of Lithium Nitrate

3.1 INTRODUCTION

Nonlinear optical (NLO) materials have received consistent attention owing to their practical application in the domain of optoelectronics and photonics. In the present investigation, single crystals of $\gamma$-glycine have been grown in the presence of lithium nitrate by slow evaporation method. With the objective of optimizing the growth parameter, solubility of the grown crystal was analyzed gravimetrically. Metastable zonewidth and induction period were determined experimentally. The thermodynamical parameters involved in the crystal growth like interfacial energy, Gibbs free energy change were computed. The other nucleation parameters such as radius of critical nuclei, nucleation rate and number of molecules or ions in critical nuclei were estimated. Powder X-ray diffraction analysis was carried out to identify the crystalline nature and cell parameter. FT-IR and FT-Raman spectrum revealed the presence of various functional groups. Vickers microhardness test were carried out for different loads, the result shows that the material exhibits Reverse Indentation Size Effect and mechanical related constants were also calculated. The grown crystal was subjected to TGA/DTA to confirm the thermal stability. The dielectric behavior of the sample was analyzed for different temperature and frequency. UV-Vis –NIR studies of $\gamma$-glycine single crystal possesses maximum transparency in ultraviolet as well as in visible region and the other optical constants were determined. SHG test was confirmed by Q-switched Nd: YAG laser.

3.2 EXPERIMENTAL

3.2.1 MATERIAL SYNTHESIS

Growth solution was prepared by dissolving 3:1 ratio of glycine and lithium nitrate. The prepared solution was stirred about 30 minutes and then filtered. The
saturated solution was poured into a petri dish and the same was closed by a perforated paper. The solution was kept at room temperature. After 20 days high quality $\gamma$-glycine single crystal was harvested (Figure 3.1).

![Figure 3.1 As grown $\gamma$-glycine single crystal in the presence of lithium nitrate](image)

3.2.2 SOLUBILITY AND METASTABLE ZONEWIDTH

Solubility is one of the important factors which decide the growth of crystals. Solubility of the grown crystal was determined over a temperature range of 35 °C – 50 °C by gravimetric analysis. Figure 3.2 shows the concentration increases and temperature also increases. It is clear that the crystal has positive temperature coefficient of solubility.

![Figure 3.2 Metastable zonewidth of $\gamma$-glycine](image)
The difference between the saturated temperature and the nucleation temperature was taken to be the metastable zonewidth of the system. Metastable zonewidth of \( \gamma \)-glycine was measured by conventional polythermal method. Saturated solution was prepared based on the solubility data. In this method, the equilibrium saturated solution was cooled from overheated temperature until the first speck was observed (Figure 3.2). The figure clearly shows that the solution exhibits broader metastable zonewidth at lower temperature and a narrower one at higher temperature. We know that the concentration and the intermolecular distance between the solutes decide the extent of nucleation. The growth solution’s stability corresponding to a wider metastable zonewidth helps in growing bulk crystals (Suvitha et al., 2013). The same procedure was adopted for 40 °C, 45 °C and 50 °C.

### 3.2.3 INDUCTION PERIOD MEASUREMENT

Induction period was determined by isothermal method. The time taken for the formation of the critical nucleus is called induction period. The experiment was executed in different supersaturation (\( S=C/C^* \)) on 1.1, 1.2, 1.3, 1.4 and 1.5 at temperatures 35 °C, 40 °C, 45 °C and 50 °C. Figure 3.3 shows that the induction period decreases with increase in supersaturation which confirmed that the nucleation rate increases exponentially. This could lead to an increasing the number of critical nuclei formation which results in spurious nucleation. From figure 3.4, it is clear that the steeper linear curve represents homogeneous nucleation at higher supersaturation, while the other part of the curve represents heterogeneous nucleation at low supersaturation. At high supersaturation, the homogeneous nucleation rate is high, and therefore it dominates nucleation (Maheswata Lenka et al., 2014).

The induction period (\( \tau \)) is written by (Balu et al., 2009)

\[
\tau \propto \exp\left[\frac{\Delta G^*}{kT}\right] \tag{3.1}
\]

\[
\ln \tau = \ln B + \frac{\Delta G^*}{kT} \tag{3.2}
\]

The critical free energy is given by
The bulk energy change per unit volume is given by

$$\Delta G_v = -\Delta \mu / V$$  \hspace{2cm} (3.4)$$

Where

$$\Delta \mu = kT \ln S$$  \hspace{2cm} (3.5)$$

and

$$k = \frac{R}{N_A}$$  \hspace{2cm} (3.6)$$

The critical nucleation parameters have been calculated using the classical theory for the homogeneous formation of spherical nuclei

$$\ln \tau = \ln B + \frac{16\pi \gamma^3 V^2 N_A^3}{3R^3 T^3 (\ln S)^2}$$  \hspace{2cm} (3.7)$$

The relation between $1/(\ln S)^2$ versus $\ln (\tau)$ with slope $m$ is given by

$$m = \frac{16\pi \gamma^3 V^2 N_A^3}{3R^3 T^3}$$  \hspace{2cm} (3.8)$$

The interfacial energy ($\gamma$) is given by

$$\gamma = \frac{3R^3 T^3 m}{16\pi V^2 N_A^3}$$  \hspace{2cm} (3.9)$$

![Figure 3.3 Supersaturation vs induction period](image-url)
3.2.4 INTERFACIAL ENERGY

Interfacial energy between a solid crystal and surrounding supersaturated solution is an important parameter involved in the theory of nucleation and growth kinetics. (Mekala Daniel et al., 2009). From the experimental study it was seen that the interfacial energy value ranged from 1.2731 to 2.1388 mJ/m^2. Experimentally determined interfacial energy values were compared with the theoretical values as shown in Table 3.1. The small variation in theoretically determined interfacial energy may be due to the variation in hydration number. The interfacial energy values increases with an increase in temperature. It can be explained that when there is an increase in temperature, the concentration of the solution will be increased. So the probability of entering into the labile zone will be decreased, leading to a decrease in nucleation rate which in turn alters the interfacial energy inversely.

Several relations for the interfacial energy using physico-chemical data have been reported in literature.

A. E. Neilsen and Sohnel, (1971) proposed a relation between interfacial energy and solubility as
\[ \gamma = \left( \frac{kT}{h_\alpha^2} \right) \ln \left( \frac{C_s}{C_i} \right) \]  

(3.12)

Where, \( h \) – Hydration number

\( C_s \) – Actual concentration of the solution

\( C_i \) – Equilibrium concentration of the solution

\( d \) – Mean diameter of ions

Based on surface nucleation theory, J. Chrisoffersen et al., (1991) predicted the relation

\[ \gamma = 0.282 \left( \frac{kT}{h_\alpha^2} \right) \ln \left( \frac{C_s}{C_i} \right) \]  

(3.13)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Theoretical</th>
<th>Experimental (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neilson &amp; Sohnel 1971 (mJ/m²)</td>
<td>Christoffersen, et al., 1991 (mJ/m²)</td>
</tr>
<tr>
<td>35</td>
<td>0.3535</td>
<td>0.0994</td>
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<td>1.0631</td>
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<tr>
<td>45</td>
<td>0.3650</td>
<td>1.0801</td>
</tr>
<tr>
<td>50</td>
<td>0.3707</td>
<td>1.0893</td>
</tr>
</tbody>
</table>

Using the interfacial energy values, various nucleation parameters such as radius of critical nuclei, nucleation rate and the number of molecules in the critical nuclei are evaluated at various supersaturation and presented in (Table 3.2). Figure 3.5 and 3.6 shows that the radius of critical nuclei and critical free energy of the nucleus were decreases with increase in supersaturation and temperature. As a result, the nucleation rate increases considerably with increase in supersaturation at a fixed temperature.
Radius of critical nucleus ($r^*$) ($10^{-10}$ m) vs Supersaturation (S)

Figure 3.5 Supersaturation vs radius of critical nuclei

Critical free energy of the nucleus ($\Delta G$) ($10^{-21}$ J) vs Supersaturation (S)

Figure 3.6 Supersaturation vs critical free energy of the nucleus
Table 3.2 Nucleation parameters of γ-glycine

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>S=C/C*</th>
<th>τ (sec)</th>
<th>ΔGv×10^6 (J/m^3)</th>
<th>r* (Å)</th>
<th>J×10^28 (nuclei/s/vol)</th>
<th>i*</th>
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<td>5.5132</td>
<td>54.3155</td>
<td>3.0110</td>
</tr>
</tbody>
</table>

3.3 POWDER X-RAY DIFFRACTION ANALYSIS

Finely crushed powder of γ-glycine crystal was scanned in the 2θ values ranging from 10° to 50° at the rate of 1° per min (Figure 3.7) Appearance of sharp and strong peak confirms the good crystallinity of the grown crystal. The characteristic peak at 25.5° (2θ) corresponds to γ-glycine (Srinivasan 2008). The
calculated cell parameters values are \( a = 7.04 \, \text{Å}, \ b = 7.04 \, \text{Å}, \ c = 5.58 \, \text{Å}, \ \alpha = \beta = 90^\circ, \ \gamma = 120^\circ \) and the crystal belongs to hexagonal system. The observed peaks were found to be good agreement with the data available in JCPDS file no: 006-0230 (Iitaka 1954). Further it is evident that the lithium nitrate is not incorporated into the grown crystal but in the presence of lithium nitrate, \( \gamma \)-glycine was yielded.

![Figure 3.7 Powder XRD pattern of \( \gamma \)-glycine](image)

### 3.4 SPECTRAL ANALYSIS

#### 3.4.1 FT-IR SPECTRUM

The spectrum was recorded in the wave number range of 500 – 4000 cm\(^{-1}\) for the identification of functional group of the grown crystal and the obtained spectrum is shown in Figure 3.8. The peaks are observed at 686, 607 and 503 cm\(^{-1}\) indicated the presence of carboxylate group. The peak observed at 3111 cm\(^{-1}\) is due to \( \text{NH}_3^+ \) group. A peak at 929 cm\(^{-1}\) is assigned for \( \text{CH}_2 \) rocking. These observation confirms that glycine exists in zwitterion form, in which the carboxyl group is present as a carboxylate ion and the amino group is present as an ammonium ion. All these observation peaks demonstrate the existence of \( \gamma \)-glycine. The identified functional groups and their assigned wavenumbers were tabulated (Table 3.3) and
they are in good agreement with the reported values in literature (Esthaku Peter et al., 2010, Dillip et al., 2012).

3.4.2 FT-RAMAN SPECTRUM

The FT-Raman spectrum of \(\gamma\)-glycine crystals were recorded in the wavenumber region 4000-500 cm\(^{-1}\) (Figure 3.9). The frequency and assignment of vibration were tabulated (Table 3.3).
Table 3.3 Wavenumber assignment of $\gamma$-glycine

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-IR</td>
<td>FT-Raman</td>
</tr>
<tr>
<td>3111</td>
<td>3092</td>
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<tr>
<td>1668</td>
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<tr>
<td>1371</td>
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<td>1323</td>
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<td>1126</td>
<td>1128</td>
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<td>929</td>
<td>892</td>
</tr>
<tr>
<td>686</td>
<td>686</td>
</tr>
<tr>
<td>607</td>
<td>604</td>
</tr>
<tr>
<td>503</td>
<td>502</td>
</tr>
</tbody>
</table>

3.5 THERMAL ANALYSIS

Thermal analysis were performed on the grown crystals to study the thermal stability and melting point on the sample. The $\gamma$-glycine powdered sample was scanned between the temperatures of 30 °C to 850 °C in nitrogen atmosphere at a heating rate of 10°C/min (Figure 3.10). TGA curve shows that $\gamma$-glycine is stable up to 215 ºC and weight loss starts above this temperature. The resulting residue gives a weight loss for a wide range of temperature between 215 °C and 850 ºC. Differential thermal analysis reveals a minor endothermic peak at 213 ºC, which may be due to conversion of $\gamma$-glycine into $\alpha$-glycine. The sharp endothermic peak appears at 258 ºC represents the melting point of the sample and this value is observed to be in good agreement with the $\gamma$-glycine single crystal obtained by using other additives (Dillip et al., 2011).
3.6 MECHANICAL STUDIES

Microhardness testing is one of the best methods of understanding the mechanical properties of materials such as fracture behavior, brittleness index, crack length and elastic stiffness constant. The microhardness of γ-glycine crystals were determined using Vickers hardness tester at room temperature. For each load (P), an average of two impressions were recorded and the average of diagonal length (d), of the indentation mark after unloading were measured using a calibrated micrometer attached to the eyepiece of the microscope (Ezhil Vizhi et al., 2010). The Vickers hardness number (H_v) was calculated using this formula

\[ H_v = \frac{1.854 + P}{d^2} (kg \, mm^{-2}) \]  

(3.14)

Where,

P - Applied load in (in kg)

d - Diagonal length of the indentation in (in mm)
Vickers hardness number increases with increase in load (Figure 3.11) and it is termed as Reverse Indentation Size Effect (RISE).

![Figure 3.11 Plot of P vs H_v](image)

The work hardening coefficient \((n)\) is measure of the strength of the crystal. The plot of \(\log P\) versus \(\log d\) yields a straight line and its slope gives the work hardening coefficient (Figure 3.12). According to Onitsch and Hanneman, \(n\) should lie between 1 and 1.6 for hard materials and above 1.6 for soft materials (Susmita Karan et al., 2005). The value of \(n\) is found to be 4.3. It is identified that \(\square\)-glycine single crystal belongs to soft materials. The Meyer’s law, gives an expression regarding load and size of indentation,

\[
P = k_1d^n
\]  
(3.15)

Where, \(k_1\) is Material constant, \(n\) is Meyer index. The material constant \(k_1\) is computed as 3.0798 kg/mm from the Figure 3.13.
3.6.1 ELASTIC STIFFNESS CONSTANT ($C_{11}$)

The elastic stiffness constant ($C_{11}$) was calculated for various loads by using Wooster’s relation (Wooster, 1953) and the values are tabulated (Table 3.4). The
elastic stiffness $C_{11}$ gives the measure of resistance to deformation by applied load on flat crystal surface. These are two factors, the first factor is the tightness of the bonding between neighboring atoms. The second factor is the rate of variation with position of the atoms of the forces of attraction and repulsion between them (Sudharsana et al., 2012).

3.6.2 FRACTURE MECHANICS

The resistance to fracture indicates the toughness of a material and the fracture toughness $K_c$ determines how much fracture stress is applied under uniform loading and is given by a relation (Bamzai et al., 2000).

$$K_c = \frac{P}{\beta_0} \frac{c^{3/2}}{a} \quad \text{for } c/a \geq d/2$$

For Vickers indenter, $\beta_0$ is equal to 7. The calculated value of $c/a$ is 1.6943 and $K_c$ is 3.3751 MNm$^{-3/2}$ at 200 g load. The type of crack occurred in the material can be determined by $c/a$ values. Here, $c$ is the crack length measured from center of the indentation mark to the crack end and $a$ is the half diagonal length. If $c/a < 2.5$ median (or) half penny crack and if $c/a > 2.5$ palmqvist crack occurred in the materials. The crack length was measured from the center of indentation mark up to the tip of crack in □m (Figure 3.14). The nature of crack is palmqvist crack.

![Figure 3.14 Indentation photo on γ-glycine](image)
3.6.3 BRITTLENESS INDEX

Brittleness is an important property that affects the mechanical behavior of the material and gives an idea about the fracture induced in a material without an appreciable deformation. The value of brittleness index $B_i$ is computed using the given relation and the values are tabulated (Table 3.4)

$$B_i = \frac{H}{K_c}$$  \hspace{1cm} (3.17)

Table 3.4 Mechanical related constant for $\gamma$-glycine

<table>
<thead>
<tr>
<th>Load (g)</th>
<th>C_{11}X10^{14} (Pa)</th>
<th>c/a</th>
<th>Nature of crack</th>
<th>Fracture mechanics (MNm^{-3/2})</th>
<th>Brittleness index (m^{-1/2})</th>
</tr>
</thead>
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<tr>
<td>10</td>
<td>18.8266</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>100</td>
<td>185.0455</td>
<td>-</td>
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<td>Palmqvist</td>
<td>3.3751</td>
<td>217.930</td>
</tr>
</tbody>
</table>

3.7 DIELECTRIC MEASUREMENTS

The dielectric parameters like dielectric constant and dielectric loss are the basic electrical properties of solids. Dielectric measurements were carried for $\gamma$-glycine crystal having a thickness 1.785 mm and area 55 mm$^2$. Figure 3.15 and 3.16 shows the dielectric constant and dielectric loss as a function of frequency. Figure 3.15 dielectric constant decreases with increase in frequency. The higher value of dielectric constant and dielectric loss at lower frequency may be attributed to the space charge polarization. The high value of dielectric constant at low frequency may be due to the presence of four types of polarization namely ionic, electronic, orientational and space charge polarizations. Figure 3.16 shows that the low dielectric loss at higher frequency of $\gamma$-glycine which is desirable property for nonlinear optical applications.
Figure 3.15 Dielectric constant for γ-glycine crystal

Figure 3.16 Dielectric loss for γ-glycine crystal
3.8 OPTICAL STUDIES

3.8.1 UV-Vis-NIR SPECTRUM

The UV–Vis-NIR spectrum of the grown crystal was recorded using Perkin-Elmer Lambda 35 spectrophotometer in the wavelength region of 200–800 nm. UV-visible spectral analysis is an efficient tool to determine the optical transparency of the crystals an important property for a material to be optically active (Ashok Kumar et al., 2011). Figure 3.17 shows that the lower cut off wavelength nearly 238 nm. The low absorption in the entire UV and visible region is a potential requirement for NLO applications. Large absorption was found at around 300 nm for all crystals due to \( n-\pi^{*} \) transition of the carbonyl group of the carboxyl function (Ashok Kumar et al., 2011).

![Figure 3.17 Absorbance spectrum of \( \gamma \)-glycine](image)

3.8.2 OPTICAL BAND GAP ENERGY \((E_g)\) CALCULATION

The optical absorption coefficient \((\alpha)\) was calculated using the following relation (Ashok Kumar et al., 2012)
As a direct band gap, the crystal under study has an absorption coefficient \( \alpha \) obeying the following relation for high photon energies \( (h\nu) \)

\[
\alpha = \frac{A(h\nu - E_g)^{3/2}}{h\nu} \tag{3.19}
\]

Where \( E_g \) – optical band gap of the crystal,

\( A \) – Constant

\( \alpha \) – is optical absorption coefficient

\( h\nu \) – is the energy of the incident photon.

Using the Tauc’s relation a graph has been plotted between \( h\nu \) and \((\alpha h\nu)^2\) to estimate the direct band gap of the \( \gamma \)-glycine crystal as shown in Figure 3.18. The energy gap \( (E_g) \) is determined by extrapolating the straight line portion of the curve \((\alpha h\nu)^2 = 0\). From the plot, the band gap of \( \gamma \)-glycine value was found to be 5.6 eV. Which is an agreement with the reported values [25].

\[
\alpha = \frac{2.303}{d} \log \left( \frac{1}{\tau} \right) \tag{3.18}
\]
3.8.3 DETERMINATION OF OPTICAL CONSTANTS

The optical constants (n, k) are determined from the transmittance (T) and reflectance (R) spectrum based on the following relations (Denton et al., 1972)

\[
T = \frac{(1-R^2)\exp(-\alpha t)}{1-R^2\exp(-2\alpha t)}
\]  

(3.20)

Where t is the thickness and \(\alpha\) is related to extinction coefficient k is given by

\[
k = \frac{\alpha \lambda}{4\pi}
\]  

(3.21)

The reflectance in terms of absorption coefficient can be written as

\[
R = 1 \pm \sqrt{1 - \exp(-\alpha t) + \exp(-2\alpha t)}/1 + \exp(-\alpha t)
\]  

(3.22)

Figure 3.19 Plot of photon energy vs extinction coefficient
Figure 3.20 Plot of photon energy vs reflectance

Figure 3.19 and 3.20 has shown the variation of the extinction coefficient (k) and reflectance (R) as a function of photon energy respectively. From the graphs, it is clear that both the reflectance and extinction coefficient of the grown crystals depends on the photon energy. Since the internal energy of the device also depends on the photon energy, by tailoring the photon energy one can achieve the desired material to fabricate the optoelectronic devices.

3.8.4 SHG CONFIRMATION

The second harmonic generation behavior of powdered γ-glycine was tested using Q-switched Nd:YAG laser. A high-intensity Nd:YAG laser (λ=1064 nm) with a pulse duration of 8ns was passed through the powdered sample. The SHG behaviour was confirmed from the output of the laser beam having the bright green emission (λ=532 nm). The SHG signal of 7.45 mJ/pulse was generated for γ-glycine for input energy 0.68 J/pulse. But the standard KDP crystalline powder gave a SHG signal of 8.8 mJ/pulse for the same input energy. So thus it was observed that the SHG efficiency of γ-glycine single crystal in the presence of lithium nitrate was comparable that of KDP.
3.9 CONCLUSION

The γ-glycine single crystal in the presence of lithium nitrate was grown by a slow evaporation method. The solubility and metastable zonewidth of γ-glycine were estimated. It is observed that the solubility of material increases with an increase in temperature and nucleation temperature increases with the increase in concentration. Induction period was measured isothermally over the saturation temperature range by varying the degree of supersaturation. The interfacial energy was calculated by using the experimentally determined induction period values. The calculated interfacial energy values at different temperature were compared with theoretical values. The nucleation parameters such as Gibbs volume free energy change (ΔGv), critical free energy change of the nucleus (ΔG*), radius of critical nuclei (r*), nucleation rate (J) and number of molecules in the critical nucleus (i*) of γ-glycine single crystal for different temperatures were calculated. The lattice parameters were calculated by Powder X-ray diffraction analysis. The functional groups were confirmed by FT-IR and FT-Raman spectrum analysis. Thermal stability and decomposition point of the sample was confirmed by TG/DTA analysis. The Vickers hardness were carried out by applying the load. It was observed that the hardness increases with increasing load is normally termed as reversed indentation size effect (RISE). Dielectric measurement indicates that the dielectric constant and dielectric loss of γ-glycine single crystal decreases with increasing frequency, it is fact that the material is suitable for NLO applications. Optical absorption spectrum shows that the lower cut off wavelength is 238 nm and energy gap value of 5.6 eV. The other optical constants such as extinction coefficient and reflectance were also calculated. The second harmonic generation of γ-glycine single crystal in the presence of lithium nitrate is comparable that of KDP.