CHAPTER IV
EFFECT OF INORGANIC ACIDS (H$_3$PO$_4$, H$_3$PO$_3$ and HNO$_3$) ON GLYCINE CRYSTAL

4.1 Introduction

Aminoacid family crystals are gaining importance as highly feasible second order NLO materials. The α-aminoacid, glycine forms addition compounds with a number of inorganic materials, especially inorganic acids. Complexes of glycine with inorganic acid/salts are promising materials for optical second harmonic generation as they tend to combine advantages of the organic aminoacid with that of the inorganic acid/salt. These materials exhibit promising structural background in view of their zwitterionic, protonated forms and structural stabilization with hydrogen bonding. These factors account for the delocalization and corresponding enhancement in second order NLO activity. Some of them show phase transitions with interesting dielectric and elastic properties. Typical examples of these families of crystals include the well-known glycine compounds such as triglycine sulphate (TGS), triglycine selenate (TGSe) [89], triglycine fluroberyllate (TGFBe) etc. In the present investigation, large sized optical quality γ-glycine single crystals have been grown in presence of inorganic acids (H$_3$PO$_3$, H$_3$PO$_4$ and HNO$_3$) by slow evaporation technique. Thus the crystal growth and characterization of the γ-glycine crystals are outlined in this chapter.

4.2 Effect of orthophosphoric (H$_3$PO$_4$) and orthophosphorus acid (H$_3$PO$_3$) on glycine crystal

Glycine is known to react with the phosphoric acid (H$_3$PO$_4$) leading to the formation of monoglycine dihydrogen phosphate (GP) [90] and triglycine sulpho phosphate (TGSP) [91, 92]. Baran et al. [90] synthesized GP by mixing stoichiometric amount of glycine and H$_3$PO$_4$. The GP crystallized into centrosymmetric $P2_1/c$ space group of the monoclinic system. Ravi et al. [91] grew H$_3$PO$_4$ substituted TGS crystals and studied their dielectric properties. The Curie transition temperature of TGS has improved from 49°C to 51.5°C due to phosphoric acid substitution. Saxena et al. [92] reported that the dopant concentration of 20 mol% H$_3$PO$_4$ leads to TGSP crystals with large $ac$ plane which makes it suitable for IR detector applications. Glycine phosphite
[NH₃CH₂COOH₃P0₃], abbreviated as GPI, is a recent ferroelectric crystal in this category and is composed of phosphorous acid and glycine [93-94]. At room temperature, GPI has monoclinic symmetry with space group P2₁/a. Single crystal of GPI undergo a continuous ferroelectric-paraelectric phase transition at 224K [95-96]. Phosphoric acid (H₃PO₄) shows different chemical and physical property from phosphorous acid (H₃PO₃) due to presence of extra oxygen atom. The difference between H₃PO₄ and H₃PO₃ is given in Table 4.1.

Table 4.1 Difference between H₃PO₄ and H₃PO₃

<table>
<thead>
<tr>
<th>Properties</th>
<th>H₃PO₄</th>
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</thead>
<tbody>
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<td>Structure</td>
<td><img src="image" alt="Structure_H₃PO₄" /></td>
<td><img src="image" alt="Structure_H₃PO₃" /></td>
</tr>
<tr>
<td>Molar Mass</td>
<td>98.00 g/mol</td>
<td>82.00 g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>white solid or colourless, viscous liquid (&gt;42 °C)</td>
<td>white solid</td>
</tr>
<tr>
<td>Density</td>
<td>1.885 g/ml (liquid)</td>
<td>1.651 g/ml</td>
</tr>
<tr>
<td></td>
<td>1.685 g/ml (85 % solution)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.030 g/mol (crystal at 25°C)</td>
<td></td>
</tr>
<tr>
<td>Melting Point</td>
<td>42.35°C</td>
<td>73.6°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>158°C</td>
<td>200°C (decomp)</td>
</tr>
<tr>
<td>Solubility</td>
<td>548 g/100 ml</td>
<td>310 g/100 ml</td>
</tr>
<tr>
<td>Oxidation state</td>
<td>+5</td>
<td>+3</td>
</tr>
</tbody>
</table>

In view of these significant impacts of and H₃PO₄ and H₃PO₃ on glycine family crystals, we have studied the influence of H₃PO₄ and H₃PO₃ at lower concentration (0.1M and 0.2M) on growth, spectral, thermal and NLO behavior of glycine single crystals.
4.2.1 Solubility studies and crystal growth

Initially, γ-glycine was synthesized by mixing 1M glycine (99%) with two different concentration of phosphoric acid (0.1M and 0.2M). Impurity content in γ-glycine was minimized by successive recrystallization process. The pH value of the mixed solutions was found to be 3.38 and 3.15 for 0.1M and 0.2M of H₃PO₄ respectively. These values are lower than that of pure glycine (pH = 4). The solubility of the glycine was determined in water in the temperature range of 35-60°C. The solution was prepared in double distilled water and maintained at 35°C with continuous stirring to ensure homogeneity of temperature and concentration over the entire volume of the solution. On reaching saturation the concentration of the solution was analyzed gravimetrically. The procedure was repeated at each temperature was calculated and plotted with respect to corresponding temperature and it is shown in the Fig. 4.1. This shows that the solubility of α-glycine was higher than that of γ-glycine which indicates that γ-form was thermodynamically stable phase than α-form [97]. Similarly, γ-glycine was synthesized by taking 1M glycine (99%) with two different concentration of phosphorous acid (0.1M and 0.2M). The solubility of glycine in presence of H₃PO₃ was found to be similar to that of glycine synthesized in presence of H₃PO₄.

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Fig. 4.1 Solubility curves of glycine grown in presence of H₃PO₄; (a) 0M, (b) 0.1M and (c) 0.2M
Supersaturated solution of glycine was prepared by mixing synthesized salt in double distilled water. The final solution was filtered using 0.1 micron porosity filter papers and kept in beakers covered with perforated sheets and the beakers placed in constant temperature bath set at 35°C. The controlled evaporation of solvent yields crystals in the time span of 15-20 days. The grown crystals were carefully harvested and then subjected to characterization studies.

In aqueous solution glycine molecules primarily exists as zwitterionic cyclic dimers, which usually crystallize in α-glycine. Pure aqueous solution yielded α-glycine with prismatic morphology. To induce crystallization of the γ-polymorph of glycine it is necessary to destroy the dimers present in the solution [66]. Addition of polar molecule, H₃PO₄ in glycine solution prevents the formation of dimers. Thus incorporation of H₃PO₄ in glycine solution inhibits the growth of metastable α-polymorph and leads to crystallization of γ-polymorph. It should be mentioned that the α-polymorph grew when the pH value was 4 and the γ-polymorph crystallized at reduced pH values of 3.38 and 3.15 for 0.1M and 0.2M H₃PO₄ added solution [98]. As grown γ-glycine crystals have pyramid-like morphology with approximate dimensions of 9x9x2 mm³ and they were found to be transparent (Fig. 4.2a). However, these crystals tend to lose their transparent nature and became opaque and white in color (Fig. 4.2b) after about 2-3 weeks. But still it was in γ-polymer according to powder XRD results. This may be due to the presence of certain amount of H₃PO₄ in γ-glycine crystal. Since H₃PO₄ is hygroscopic, the crystal may lose its transparency after exposure to atmosphere. Glycine crystals grown in presence of H₃PO₃ have bipyramid-like morphology with approximate dimensions of 6x6x2 mm³ and they were found to be transparent (Fig. 4.3). Close observation of the crystals revealed that there is tiny crystal inside the large one. Powder XRD pattern of these crystals confirmed the crystal to be of biphasic nature. Contrary to the γ-glycine grown in presence of H₃PO₄, these crystals didn’t lose transparency even after several months. The additive H₃PO₃ is known to interact with the crystalline phase stereochemically, and in the process, they influence the nucleation and growth kinetics. Based on an adsorption- based mechanism, the impact of impurities on nucleation could be twofold, first the adsorption on specific crystal faces could influence the interfacial
tension between the crystal nuclei and the supersaturated solution and therefore, alter the nucleation kinetics; second, the impurities could block the active growth sites on the embryonic nucleus surface and hence inhibit its development to the critical size. In some cases, impurities could alter the solution thermodynamics (primarily the solubility) and, therefore, influence the effective supersaturation available for nucleation. In a crystallization system, these effects acting either independently or coupled with each other can bring about nucleation of more than one polymorph.

Fig. 4.2(a) γ-Glycine crystal grown in presence of H₃PO₄ (0.2M); (b) crystals become opaque after two weeks

Fig. 4.3 γ-Glycine crystals grown in presence of H₃PO₃ (0.2M)

4.2.2 X-ray diffraction analyses

The γ-glycine crystallizes in hexagonal structure with space groups of $P\bar{3}_2$. Powder X-ray diffraction patterns of the grown crystals are shown in Figs. 4.4 & 4.5.
Appearance of sharp and strong peaks confirmed the good crystallinity of the grown samples. The results agree well with the simulated XRD pattern of γ-glycine and the characteristic peak has appeared at around 25.3° (2θ). The estimated lattice parameters of γ-glycine grown in presence of H₃PO₄ are given in Table 4.2. There is no significant change in the lattice constants. Powder XRD patterns of crystals grown in presence of H₃PO₃ were found to be a mixture of α- and γ-polymorphs. α-glycine has characteristic peaks at 2θ values of 15, 19, 24 and 29.9° and γ-glycine peaks correspond to 2θ values of 21, 25.3 and 29.2° [99]. Most of these peaks could be observed in the XRD pattern shown in Fig. 4.5. Thus the crystals grown in presence of H₃PO₃ are biphasic in nature but percentage of γ-polymorph was more than that of α-polymorph.

Fig. 4.4 Calculated and experimental powder XRD pattern of γ-glycine grown in presence of (a) 0 M; (b) 0.1M and (c) 0.2M of H₃PO₄
Fig. 4.5 Powder XRD pattern of glycine grown in presence of (a) 0.1M and (b) 0.2M of H₃PO₃

Table 4.2 Lattice parameters of γ-glycine grown with various concentration of H₃PO₄

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a = b (Å)</td>
</tr>
<tr>
<td>γ-glycine⁷⁺⁺</td>
<td>7.02</td>
</tr>
<tr>
<td>γ-glycine grown in presence of 0.1M H₃PO₄</td>
<td>7.03</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-glycine grown in presence of 0.2M H₃PO₄</td>
<td>7.03</td>
</tr>
</tbody>
</table>

a, Ref [62]; b, present work
4.2.3 Thermal analysis

Figs. 4.6 (a), (b) & 4.7 illustrate the TG-DTA curves of glycine crystals grown in presence of H₃PO₄ and H₃PO₃ respectively. The experiments were done in the temperature range of 30-1100°C with heating rate of 20°C/min in nitrogen atmosphere. The TG curve shows no change in weight upto 216°C, which eliminate the possibility of hydrate or solvate formation of crystals. The major weight loss in the temperature range 216-282°C (~42%) and minor weight loss in the temperature range 282-382°C (~13%) could be attributed to the sublimation and decomposition of the glycine grown in presence of H₃PO₄ resulting in the release of CO and NH₃ molecules. The peak at 270°C in DTA curve indicated the decomposition of the glycine. In addition to that DTA curve shows an endothermic peak at 174°C and 191°C for γ-glycine grown in presence of 0.1M and 0.2M H₃PO₄ respectively. These peaks correspond to the transformation of γ-glycine into α-phase. This transition temperature is known to depend on the nature of the dopant and are reported to be 172°C for crystals grown from a mixture of glycine and sodium hydroxide [65] and 182°C for crystals grown from a mixture of glycine and lithium acetate [83] respectively. But Perlovich et al. [100] reported that the transition temperature of γ and α-glycine can range between 165 and 201°C depending on the growth medium. Thus, there is a significant improvement of transition temperature in γ-glycine crystal grown in presence of 0.2M H₃PO₄ when compared to crystals grown from other additives.

The DTA curve reveals no endothermic/exothermic reaction curves below 191°C in glycine crystal suggesting its structure stability in the temperature range. This ensures the suitability of the material for possible application in laser, where the crystal is required to withstand high temperature. TG-DTA results of H₃PO₃ grown crystals were found to be nearly identical to that of H₃PO₄ grown crystal, except that the transition temperature remained at 173°C for both 0.1M and 0.2M H₃PO₃. Further experiments such as UV, NLO and hardness studies were done on γ-glycine grown in presence of 0.2M of H₃PO₄ since it has high transition temperature.
Fig. 4.6 (a) TG-DTA curve of γ-glycine crystal grown in presence of H₃PO₄ (0.1M)

Fig. 4.6 (b) TG-DTA curve of γ-glycine crystal grown in presence of H₃PO₄ (0.2M)
4.2.4 FTIR and FT-Raman analyses

The FTIR and FT-Raman spectra of powdered glycine grown with H$_3$PO$_4$ and H$_3$PO$_3$ are shown in Figs. 4.8 and 4.9 respectively. The observed wave numbers, relative intensities obtained from the recorded spectra and the assignments proposed for grown crystals are found to be in good agreement with the assignment reported in literature [83-84, 101-102] and they are listed in Table 4.3. The broad envelope in the higher wavenumber region between 3700-2100 cm$^{-1}$ was due to hydrogen interaction with other atoms such as N-H stretching of NH$_2$ and C-H of CH$_2$ stretching. The N-H stretching vibration occurred at 3112 and 3106 cm$^{-1}$ for γ-glycine grown in presence of 0.1M and 0.2M H$_3$PO$_4$ respectively. The sharp band at 2897 and 2989 cm$^{-1}$ in IR and Raman spectra was attributed to the symmetric stretching of CH$_2$ group. The prominent bands at 2173 cm$^{-1}$ endorsed to the combination of the asymmetrical NH$_3^+$ bending vibration and the torsional oscillations of the NH$_3^+$ group [103]. Two overlapped bands at around 1593 and 1395 cm$^{-1}$ in γ-glycine grown in presence of 10 mol % H$_3$PO$_4$ were attributed to the asymmetric and symmetric stretch mode of the COO$^-$ group. While increasing additive concentration (0.2M) these peaks were shifted to 1628 cm$^{-1}$ and 1401 cm$^{-1}$ respectively.
Other bands of COO⁻ deformation mode were observed at 690 and 503 cm⁻¹. These results confirmed that the glycine molecule existed as zwitterions form inside the crystal. This caused an antiparallel arrangement, which contributed to non-centrosymmetric crystalline growth. The stretching vibration CCN skeleton gave a peak at 1042 cm⁻¹. The C-C stretching vibration was observed at 927 cm⁻¹ in sample grown in presence of H₃PO₄. This is the characteristic peak of γ-glycine crystal [66]. FTIR and FT-Raman spectroscopic studies H₃PO₃ grown crystals were found to be similar to that the H₃PO₄ grown crystals. As expected, the characteristic peak corresponding to γ-phase not seen in samples grown in presence of H₃PO₃.

Fig. 4.8 FTIR spectra of γ-glycine crystal grown in presence of (a) 0.1M and (b) 0.2M of H₃PO₄
Fig. 4.9 FT-Raman spectra of γ-glycine crystal grown in presence of (a) 0.1M and (b) 0.2M of H₃PO₄
Table 4.3  IR and Raman wave numbers of γ-glycine grown in presence of H₃PO₄

<table>
<thead>
<tr>
<th>γ-glycine grown in presence of 0.1M H₃PO₄(cm⁻¹)</th>
<th>γ-glycine grown in presence of 0.1M H₃PO₄(cm⁻¹)</th>
<th>Tentative assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR</td>
<td>FT-Raman</td>
<td>FTIR</td>
</tr>
<tr>
<td>3430s</td>
<td>3417vs</td>
<td>3433vs</td>
</tr>
<tr>
<td>3112s</td>
<td>-</td>
<td>3106s</td>
</tr>
<tr>
<td>2895m</td>
<td>2989w</td>
<td>2892m</td>
</tr>
<tr>
<td>2604m</td>
<td>2561m</td>
<td>2607m</td>
</tr>
<tr>
<td>2173m</td>
<td>-</td>
<td>2172m</td>
</tr>
<tr>
<td>1593vs</td>
<td>-</td>
<td>1628vs</td>
</tr>
<tr>
<td>1491s</td>
<td>-</td>
<td>1492s</td>
</tr>
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<tr>
<td>1125m</td>
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<td>1124m</td>
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<tr>
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<tr>
<td>927 m</td>
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<tr>
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<td>857w</td>
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<td>338m</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>320w</td>
<td>-</td>
</tr>
</tbody>
</table>

ν, stretching; ρ, rocking; δ, deformation; ω, wagging; τ, torsion; w, weak; m, medium; s, strong; vs, very strong.
4.2.5 Optical transmission studies

UV - Visible spectrum was recorded on a PerkinElmer Lambda 25 spectrometer in transmission mode. The grown crystal was dissolved in solvent i.e., water. The saturated solution was taken in quartz tube and exposed to UV- Visible source. The UV transmission spectrum of γ-glycine grown in presence of H₃PO₄ is shown in Fig. 4.10. The absorption was not registered due to its excellent optical behavior until the wavelength from 350 to 800 nm. This means that the material possesses a good non-absorbance band in the visible region and this was an advantage as it was key requirement for materials having NLO properties. The lower cut-off at 230 nm for both glycine samples combined with the very good transmittance above 80% attests the usefulness of this material for optoelectronics applications, the generation of the second and the third harmonic of the Nd:YAG laser fundamental and for the generation of the higher harmonics of the GaAlAs diode lasers emitting fundamental in the vicinity of 800nm for the achievement of blue lasers.

Fig. 4.10 UV- Visible spectrum of γ-glycine grown in presence of H₃PO₄ (0.2M)
4.2.6 Powder SHG measurement

Second harmonic generation efficiency of the samples was determined by Kurtz powder method. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation ($\lambda=534$ nm) from the crystal. The measured amplitude of second harmonic green light for $\gamma$-glycine grown in presence of $\text{H}_3\text{PO}_4$ and $\text{H}_3\text{P}0_3$ was 125mV and 104mV respectively against 95mV for KDP crystal. This result shows a powder SHG efficiency of $\gamma$-glycine grown in presence of $\text{H}_3\text{PO}_4$ and $\text{H}_3\text{P}0_3$ was about 1.3 and 1.1 times respectively that of potassium dihydrogen orthophosphate. Due to zwitterionic nature $\gamma$-glycine crystal have high dipole moment and high melting point which leading to high optical non-linearity. The main contributions of the higher nonlinear optical properties of $\gamma$-glycine are the presence of the hydrogen bond and the vibrational part of the hydrogen bond vibrations [83]. The good second harmonic generation efficiency indicates that the $\gamma$-glycine crystals can be used for application in nonlinear optical devices.

4.2.7 Dielectric studies

From the analysis of dielectric constant as a function of frequency, different polarization mechanism can be understood. Dielectric study on the single crystal was carried out using the instrument HIOKI 3532 LCR HITESTER at room temperature. The samples with approximate dimension of the order of $6.78 \times 4.85 \times 1.77 \text{ mm}^3$ were used for measurement. Graphite was applied on opposite sides of the crystal and the samples were placed between two copper electrodes and thus parallel plate capacitors were formed. The capacitances of the samples were measured for various frequencies in the range of 500Hz to 5MHz. The dielectric constant was calculated using the relation:

$$\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot A}$$

where $C$ is the capacitance, $d$ is the thickness of the sample, $\varepsilon_0$ is the permittivity of the free space and $A$ is the area of the cross section [104]. The variation of dielectric constant with frequency at different temperature of the glycine crystal are shown in Figs. 4.11 & 4.13 The dielectric constant have high value at low frequency region and then it decrease with the increase in applied frequency. The high value of $\varepsilon_r$ at low frequencies may be due to the presence of all the four polarization namely, space charge,
orientational, ionic and electronic and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. It also indicates that the value of dielectric constant increases with increase in temperature. Space charge polarization is generally active at lower frequencies and higher temperatures and indicates the perfection of crystals [75]. The variation of dielectric loss with frequency at different temperature was shown in Figs. 4.12 & 4.14. The behavior dielectric loss with frequency at different temperature was similar to that of dielectric constant. However, the low values of dielectric loss suggest that the grown crystals possess good optical quality. This parameter is of vital importance for nonlinear optical materials in their application [105]. Since H₃PO₄ is a polar molecule, the dielectric constant of glycine grown in presence of H₃PO₄ is higher than that of H₃PO₃.

![Graph showing variation of dielectric constant with frequency for γ-glycine grown in presence of H₃PO₄ (0.2M)](image)

Fig. 4.11 Variation of dielectric constant with frequency for γ-glycine grown in presence of H₃PO₄ (0.2M)
Fig. 4.12 Variation of dielectric loss with frequency for γ-glycine grown in presence of H₃PO₄ (0.2M)

Fig. 4.13 Variation of dielectric constant with frequency for γ-glycine grown in presence of H₃PO₃ (0.2M)
4.2.8 Vickers microhardness studies

The mechanical property of γ-glycine crystals grown in presence of H₃PO₄ and H₃PO₃ was studied by Vickers hardness test. The measurements were carried out on the grown crystals using Shimadzu tester. Hardness is a measure of materials’ resistance to localized plastic deformation. It plays key role in device fabrication. The applied loads were 25, 50, 100 and 200 grams.

The micro hardness was calculated using the relation

\[ H_v = 1.8544 \frac{P}{d^2} \text{ (kg/mm}^2) \]

where \( P \) is the applied load and \( d \) is the diagonal length of the indentation impression.

The calculated Vickers hardness values for γ-glycine crystal grown in presence of 0.2M H₃PO₄ and H₃PO₃ as a function of load were shown in Fig. 4.15. It can be noticed that the γ-glycine crystal grown in presence of 0.2M H₃PO₄ has higher \( H_v \) value (70 kg/mm\(^2\)) which is in good agreement with the value reported by Narayan Bhat et al. [65]. Interestingly, the γ-glycine crystal grown with H₃PO₄ withstands higher loads than reported value [65]. Further, the hardness values increase with increasing load which can be understood based on the reverse indentation size effect [79].
4.3 Effect of nitric acid (HNO₃) on glycine crystal

The glycine reacts with a number of compounds resulting in glycine based materials such as glycine nitrate [106], glycine potassium sulphate [107], glycine sodium nitrate [108], glycine zinc sulphate [109] and glycine lithium sulphate [110] etc. These materials have been grown and are reported to possess non linear optical (NLO) property. There are only limited number of papers dealing with the crystal growth and optical studies of glycine nitrate (GN). Baran et al. [101] reported the spectral properties of γ-glycine single crystals grown from the aqueous solution containing some amount of the HNO₃. Recently Britto et al. [106] reported that the GN possesses NLO property with SHG efficiency of 50mV which is much lower than that of KDP. The molecular structure of GN is shown in Fig. 4.16. Sato et al. [111] reported that the diglycine nitrate (DGN) was grown from glycine and HNO₃ in the ratio 2:1 respectively.

Growth of crystals from solution consists of basically three steps; achievement of supersaturation or supercooling, formation of crystal nuclei of microscopic size and successive growth of crystals to yield distinct faces. Nucleation is the first stage in the crystal growth process. It takes place in a supersaturated system and can be considered as
kind of phase transition, namely from an unstable, usually disordered state to a crystalline one. It consists of spontaneous aggregation of growth units into clusters of greater size. The process can take place as a consequence of exclusive molecular collisions (homogenous nucleation) or in the presence of some substrates, which favorably acts as catalytic support (heterogeneous nucleation).

The growth rate of a face depends on the internal and external factors. Internal factors are surface structure of the faces, and external factors are supersaturation, temperature, solution composition, mechanical condition, presence of impurities, magnetic and gravitational fields. The crystal growth of a face is therefore a succession of complex processes, which take place at the interface between the liquid and the solid phase. The growth of crystals requires knowledge of the nucleation parameters. In the present investigation the fundamental crystal growth parameters, such as solubility and induction period have been measured for glycine nitrate crystals. From the values of induction period, supersaturation ratio and interfacial tension has been determined. The morphology, optical properties and microhardness studies are also discussed.

Fig. 4.16 Molecular structure of glycine nitrate

4.3.1 Solubility studies

Glycine nitrate (GN) was synthesized by taking the analar grade 1M glycine (99%) and 1M nitric acid. The calculated amount of salt was mixed in distilled water at room temperature. The reaction between glycine and nitric acid is given below

\[(\text{NH}_2\text{CH}_2\text{COOH}) + \text{HNO}_3 \rightarrow (\text{NH}_2\text{CH}_2\text{COOH})\cdot\text{HNO}_3\]

Purity of synthesized salt was further improved by successive recrystallization process. Solubility corresponds to saturation i.e. to equilibrium between a solid and its solution at
a given temperature and pressure. Thermodynamically, this means that the chemical potential of the pure solid is equal to the chemical potential of the same solute in the saturated solution. The growth rate of a crystal depends on its solubility and temperature. Solubility data of a material governs the amount of material, which is available for the growth and hence defines the total size limit. Solvent and solubility factors define the supersaturation which is driving force for the rate of crystal growth. Hence for a material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion. The solubility of GN has been determined at various temperatures in double distilled water. For this, a saturated solution was prepared in a well-controlled thermal environment with excess of solute. Solubility was then measured gravimetrically (Fig. 4.17).

![Fig. 4.17 Solubility curve of glycine nitrate](image)

4.3.2 Induction period measurements, nucleation kinetics and crystal growth

Induction period ($\tau$) is defined as the time taken for the formation of nucleus after the attainment of supersaturation. Induction period measurements were performed at
selected degree of supersaturation (S), viz, 1.1, 1.2, 1.3, 1.4 and 1.5 at constant temperature of 30°C by isothermal method. Since time required for the growth of critical nucleus to a detectable size is negligibly small, the induction period has been measured as the time interval between the achievement of supersaturation and the appearance of a crystal of a detectable size. The appearance of first speck of the nucleus was seen at the bottom of the container. The nucleation can be observed only after the nucleus has grown to a sufficient size. The time taken to achieve this size is much closer to the formation of the critical nucleus. The induction period values at various supersaturation ratios (S) are shown in Fig. 4.18.

![Fig. 4.18 Plot of S Vs \( \tau \)](image)

Generally, crystal growth process takes place by the achievement of supersaturation, formation of crystal nuclei followed by the growth of a crystal. The critical parameter involved in between a growing crystal and the surrounding mother liquor is the interfacial tension. This complex parameter has been determined by conducting nucleation experiments using the saturated solution of glycine nitrate. The induction period is determined experimentally for glycine nitrate solution at different
supersaturation. According to the classical theory of homogenous formation of spherical nucleus

\[
\ln \tau = -\ln B + \frac{16\sigma^3 v^2 N_A}{3R^3 T^3 (\ln S)^2}
\]  

(3.1)

where \( v \) is molar volume of the crystals. \( N_A \) is the Avogadro number, \( R \) is the gas constant, \( \tau \) induction period of glycine nitrate at temperature \( T \) and \( B \) is constant. \( S \) is the supersaturation \( (S= C/C^*) \) where \( C \) is the actual concentration and \( C^* \) is the equilibrium concentration. The function, \( \ln B \) weakly depends on the temperature and hence there is a linear dependence between \( \ln \tau \) and \( 1/ (\ln S)^2 \) at constant temperature. The interfacial tension \( \sigma \) of the solid relative to the solution has been calculated from the slope of the line (m) as

\[
\sigma^3 = \frac{3R^3 T^3 m}{16\nu^2 N_A}
\]  

(3.2)

The energy of formation of a critical nucleus has been evaluated from the experimental data as

\[
\Delta G^* = RT m/ (\ln S)^2
\]  

(3.3)

The radius of the nucleus in equilibrium with its solution has been computed as [Ref. 81]

\[
r^* = \frac{2\sigma v}{RT \ln S}
\]  

(3.4)

![Fig. 4.19 Plot 1/(ln S)^2 vs ln (\tau)](image-url)
Initially, glycine nitrate solution was prepared by mixing it in double distilled water. This solution was stirred using a magnetic stirrer until the salt dissolves. The impurity content in the GN was minimized by successive recrystallization process. The solution was then filtered using Whatmann filter paper of 0.1 micron porosity. The final solution was taken in the beaker and it was covered with perforated sheets and kept in dust free environment. After 2-3 days of solvent evaporation, the solution becomes supersaturated and tiny crystal was found at the bottom of the beaker. It was allowed to grow for maximum possible dimension and then harvested after 20 days.

It was observed that the induction period decreases with increase in supersaturation as shown in Fig. 4.18. The interfacial tension \( \sigma \) was obtained from the slope of \( \ln \tau \) and \( 1/ (\ln S)^2 \) curve (Fig. 4.19) using equation (3.2) and it was estimated as 1.8mJ/m\(^2\) for glycine nitrate solution. Using the interfacial tension value, the radii of the critical nuclei were calculated. The graph plotted between supersaturation and critical radius (\( r^* \)) is shown in Fig. 4.20. It is noted that the increase in supersaturation results in
the decrease of the critical radius. This favors the easy formation of critical nuclei of glycine nitrate at higher supersaturation.

Fig. 4.21 Picture of a typical glycine nitrate crystal

Fig. 4.21 shows the picture of a typical glycine nitrate (GN) crystal. As seen in the picture, large transparent platelet crystals with approximate dimension of 27x21x2 mm$^3$ have been grown by slow evaporation of solvent over a period of about 20 days. The platelet shape is the characteristic morphology of glycine nitrate crystal. As shown in the figure, large size GN crystals could be grown only under specific supersaturation range (1.2-1.5). At higher supersaturation, there were more number of tiny crystals. This observation is in accordance with the theoretical findings that the nuclei formed at lower supersaturation grow to large size when compared to the nuclei formed at higher supersaturation.

4.3.3 X-ray diffraction analysis

Single crystal XRD was recorded on ENRAF NONIUS CAD 4 to confirm crystal quality and to estimate the cell parameters. The result confirmed that the GN crystal is orthorhombic with non-centrosymmetric space group of $P\bar{2}_12_12_1$ and the lattice parameters are $a = 6.10\,\text{Å}$, $b = 16.37\,\text{Å}$ and $c = 5.61\,\text{Å}$. This result agrees well with the literature value [62].
4.3.4 Thermal analysis

Thermogravimetry of samples was performed using TA instruments NETZSCHSTA409. Fig. 4.22 illustrates the TG curves of glycine nitrate recorded in the temperature range of 30-800°C at the rate of 10°C/min in nitrogen atmosphere. The TG curve shows two stage weight losses in the temperature range between 210-312°C and 312-560°C with actual weight loss of 48% and 15% respectively. The possible reaction during heating is given by

$$\text{NH}_2\text{CH}_2\text{COOH}.\text{HNO}_3 \rightarrow \text{NO}_3\uparrow + \text{CO}\uparrow + \text{remaining product}$$

The mass loss in the first two stages can be attributed to the liberation of NO3 and CO respectively. The actual weight loss of 48% and 15% is in agreement with the estimated mass of CO and NO3 respectively. On further heating, the remaining compound such as methamide (NH2COH) and hydrogen gas may liberate.

![Fig. 4.22 TGA curve of glycine nitrate crystal](image)
4.3.5 FTIR analysis

The FTIR spectrum was recorded on a Perkin Elmer (Spectrum RXI) spectrometer in transmission mode. The infrared spectrum of powdered GN is shown in Fig. 4.23. FTIR spectrum in the mid region for the glycine nitrate sample agrees well with standard result [69]. The observed peak positions and their assignments for GN are given in Table 4.4. In glycine, the amino group exists as ammonium ion while carboxyl group exists as carboxylate ion. The stretching vibrations of the NH$_3$ groups are known to occur at 3112 cm$^{-1}$ in GN crystal. Peaks corresponding to the NH$_3^+$ symmetric bend mode have been observed around 1498 cm$^{-1}$ in the samples. CH$_2$ twisting is observed at 1386 cm$^{-1}$ for GN crystal. The ammonium ions and carboxylate ion are observed around 1121 and 889 cm$^{-1}$ respectively. The presence of carboxylate ion and ammonium ion clearly indicates that the glycine molecule exists as zwitter ion (NH$_3^+$CH$_2$COO$^-$) in GN crystals. In addition to that the peaks at 1624 cm$^{-1}$ for GN crystal correspond to antisymmetric stretching of COO$^-$ bend which indicates the presence of glycine zwitter ion.

![FTIR spectrum for glycine nitrate crystal](image)
Table 4.4 Vibrational assignment of glycine nitrate

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3450s</td>
<td>NH₃(^+) stretching</td>
</tr>
<tr>
<td>3112m</td>
<td>NH₃(^+) stretching</td>
</tr>
<tr>
<td>2604m</td>
<td>CH₂ stretching</td>
</tr>
<tr>
<td>1995m</td>
<td>-</td>
</tr>
<tr>
<td>1716m</td>
<td>-</td>
</tr>
<tr>
<td>1624m</td>
<td>Antisymmetric stretching of COO(^-)</td>
</tr>
<tr>
<td>1498vs</td>
<td>NH₃(^+) asymmetric bend</td>
</tr>
<tr>
<td>1386w</td>
<td>CH₂ twisting</td>
</tr>
<tr>
<td>1121w</td>
<td>NH₃ rocking</td>
</tr>
<tr>
<td>1028w</td>
<td>CH₂ wagging &amp; NO₃ symmetrical stretching</td>
</tr>
<tr>
<td>912w</td>
<td>CH₂ rocking</td>
</tr>
<tr>
<td>886w</td>
<td>COO(^-) stretching</td>
</tr>
<tr>
<td>671w</td>
<td>C-C stretch</td>
</tr>
<tr>
<td>578w</td>
<td>COO(^-) bend</td>
</tr>
</tbody>
</table>

4.3.6 Optical transmission spectral analysis

The UV-Visible spectrum gives information about the structure of the molecule that the absorption of ultraviolet and visible light involves promotion of electrons in σ and π orbital from the ground state to higher energy state. The grown crystal was dissolved in solvent i.e., water. The saturated solution was taken in quartz tube and
exposed to UV-Visible source. The UV-Visible transmission spectrum of GN crystal is shown in Fig. 4.24. It shows the lower cutoff wavelength to be nearly 325 nm. The absence of absorption in the visible region clearly indicates that these crystals can be used as potential material for frequency doubling. The peak around 325 nm is due to the n-π* transition [71]. High transmittance % is observed from 400nm which clearly indicates that the crystal possesses good optical transparency for SHG of Nd³⁺: YAG laser.

![Transmittance vs Wavelength Graph](image)

**Fig. 4.24 UV-Visible spectrum for glycine nitrate crystal**

4.3.7 Powder SHG measurement

Second harmonic generation efficiency of the samples was determined using Kurtz powder method. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation (λ = 534 nm) from the crystal. The second harmonic signal of GN crystal was only 19mV while the standard KDP crystal gave a SHG signal of 360mV for same input energy. This value is much lower than the results reported by Britto et al. [106].

4.3.8 Dielectric studies

The capacitance and dielectric loss measurement of the glycine nitrate was studied at room temperature using HIOKI 3532 LCR HITESTER in the frequency region
500 Hz to 5 MHz. Glycine crystal (dimensions: area 6.7392 mm\(^2\) and thickness 2.02 mm) was coated with graphite to provide good electrical contact. The capacitance was measured with varying frequency for a fixed applied voltage. The dielectric constant \(\varepsilon_r\) is calculated using the formula

\[
\varepsilon_r = \frac{C d}{\varepsilon_0 A}
\]

where \(C\) is the capacitance, \(d\) is the thickness, \(A\) is the area and \(\varepsilon_0\) is the permittivity of the free space having the value \(8.854 \times 10^{-12} \text{ F/m}\) [83].

Fig. 4.25 shows the plot of dielectric constant \(\varepsilon_r\) versus applied frequency. The very high value of \(\varepsilon_r\) at low frequency may be due to the presence of all the four polarizations namely; space charge, orientational, electronic and ionic polarization and its low value at high frequencies may be due to the loss of significance of these polarizations gradually. In accordance with the lower value of dielectric constant is a suitable parameter for the enhancement of SHG coefficient. The variation of dielectric loss with frequency is shown in Fig. 4.26. The characteristic of low dielectric loss with high frequency for a given sample suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application.

![Fig. 4.25 Variation of dielectric constant with frequency for glycine nitrate crystal](image)
4.3.9 Vickers microhardness studies

Microhardness studies were carried out on the grown crystals using Shimadzu tester. The mechanical property of the glycine nitrate crystal was studied by Vickers hardness test. The applied loads were 25, 50 and 100 grams. The micro hardness was calculated using the relation

\[ H_v = 1.8544 \frac{P}{d^2} \text{ (kg/mm}^2) \]

where \( P \) is the applied load and \( d \) is the diagonal length of the indentation impression. The Vickers hardness for GN crystals was shown in the Fig. 4.27 (inset).

The work hardening efficiency (n) for a given material in relation to load (P) is given by Meyer law

\[ P = Ad^n \]

where \( A \) is arbitrary constant for a given material. The coefficient ‘n’ of the samples has been determined from the slope of the log P vs. log d plot (Fig. 4.27). The coefficient ‘n’ is found to be 1.5 for glycine nitrate crystal. If n is above 1.6, then the material is soft [Ref. 112]. Since n is below 1.6 for GN, it is relatively hard material.
4.4 Conclusion

Optically transparent γ-glycine single crystals were grown by slow-evaporation method using H$_3$PO$_4$ and H$_3$PO$_3$ as additives. Powder XRD result of glycine crystal grown in presence of H$_3$PO$_3$ confirmed to be of mixed phase i.e., both α and γ-form. On the other hand, crystals grown with H$_3$PO$_4$ were found to be phase pure γ-glycine. TG-DTA curves revealed that the transition temperature corresponding to phase transition from γ to α-glycine has improved in crystal grown in presence of H$_3$PO$_4$. Kurtz powder SHG test confirmed the frequency doubling of the γ-glycine grown in presence of H$_3$PO$_4$ and H$_3$PO$_3$ was about 1.3 and 1.1 times respectively higher than that of KDP. Since H$_3$PO$_4$ is a polar molecule, the dielectric constant of glycine grown in presence of H$_3$PO$_4$ is higher than that of H$_3$PO$_3$. Owing to its single phase, wide transparency range, high thermal stability, high hardness value with relatively high SHG efficiency, γ-glycine grown in presence of H$_3$PO$_4$ becomes a promising material for laser application and fabrication of electro-optic devices. Still, the main drawback of this crystal is that it became opaque and loses its transparency when exposed to atmosphere.

Glycine nitrate single crystals were grown by slow evaporation method. The values of critical radius of nucleus have been evaluated. It is noted that the increase in
supersaturation results in the decrease of the critical radius. This favors the easy formation of critical nuclei of glycine nitrate at higher supersaturation. FTIR studies confirm the formation and presence of functional groups of glycine nitrate crystals. UV-Visible spectrum shows that the crystals possess high % of transparency. Vickers microhardness studies show the anisotropy nature of GN crystal and Meyers plot reveals that it is relatively hard material. A second harmonic signal of GN crystal was 19mV while the standard KDP crystal gave a SHG signal of 360mV for same input energy. The low value of dielectric loss indicates that the grown crystal of glycine nitrate was of reasonably good quality.