4.1 Introduction

The search for new materials possessing high optical nonlinearity is an important task because of their practical applications in harmonic generation, switching and other optical signal processing devices. Some complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation [1-3]. Among the amino acids glycine is the simplest one. Unlike other amino acids it has no asymmetric carbon and is optically inactive. It has three polymorphic crystalline forms of α, β and γ under ambient conditions. Narayan Bhat and Dharmaprakash [1] had grown the glycine sodium nitrate and reported that the second harmonic generation efficiency (SHG) of this crystal was two times that of potassium dihydrogen orthophosphate (KDP). Nagaraja et al. [4] reported that the SHG efficiency of benzoyl glycine crystal was 1.5 times that of KDP. Ferroelectric properties were reported for glycine silver nitrate (5), diglycine manganese chloride [6] and glycine phosphate [2]. Hoshino et al. [7] reported about the dielectric properties of triglycerine fluoroberyllate. It was also reported that glycine combines with H2SO4 [8], CaCl2 [9], CaNO3 [10], BaCl2 [11], SrCl2 [11], CoBr2 [12] and LiNO3 [13]. But none of these are reported to have nonlinear optical property.

Michael Fleck et al. [14] carried out X-ray single crystal structure solution of glycine zinc sulphate and reported that a = 8.440(2) Å, b = 8.278(2) Å, c = 12.521(3) Å, V = 874.8(4) Å³. As no reports are available on the growth and characterization of glycine zinc sulphate (GZS) single crystals we have estimated the solubility, metastable zonewidth and growth of glycine zinc sulphate crystals from aqueous solution by solvent evaporation method. These crystals were
characterized by X-ray diffraction, infrared spectroscopy, UV-vis-NIR optical transmittance and absorption, thermal analysis, microhardness, SHG efficiency and Dielectric studies and the results are discussed in this chapter.

4.2 Experimental

4.2.1 Synthesis

Glycine zinc sulphate salt was synthesized by dissolving analytical grade reagent glycine and zinc sulphate heptahydrate in the stoichiometric ratio in double distilled water. According the reaction

\[
\text{Zn SO}_4\cdot\text{7H}_2\text{O} + \text{CH}_2\text{NH}_2\text{COOH} \rightarrow \text{Zn [CH}_2\text{NH}_2\text{ COOH} \text{ SO}_4\cdot\text{5H}_2\text{O} + 2 \text{ H}_2\text{O}
\]

GZS salt was obtained by the evaporation of the solvent at 50 °C and then it was purified by repeated recrystallization process.

4.2.2 Solubility and metastable zonewidth

The solubility of GZS was determined for five different temperatures viz., 35, 40, 45, 50 and 55 °C. The solubility at 35 °C was determined by dissolving the GZS salt in 100 ml double distilled water taken in an air tight container with continuous stirring. After attaining the saturation the concentration of the solute was estimated gravimetrically. The same procedure was repeated to estimate the solubility for different temperatures.

Saturated solution of GZS was prepared in accordance with the presently determined solubility data for the determination of metastable zone width. The nucleation studies were carried out in a constant temperature bath controlled to an accuracy of ± 0.01 °C. A constant volume of 100 ml of salt solution was used in all the experiments. The solution was preheated to 5 °C above the saturated temperature for homogenization and left at the superheated temperature for about an hour before cooling. Metastable zonewidth of GZS was measured using
the conventional polythermal method [15]. The same experimental procedure was repeated with solutions saturated at 40, 45, 50 and 55 °C. The variation of solubility along with metastable zonewidth for different temperatures is shown in Fig. 4.1.

![Graph showing solubility and metastable zonewidth of GZS](image)

**Fig. 4.1** Solubility and metastable zonewidth of GZS

### 4.2.3 Crystal Growth

Bulk growth of GZS single crystal was carried out from aqueous solution by solvent evaporation technique, in a constant temperature bath having an accuracy of ± 0.01°C. 200 ml of the solution was saturated at 35 °C and then filtered to remove any insoluble impurities. An optically good transparent single crystal obtained by slow evaporation at room temperature was used as seed crystal. The crystals harvested after a growth period of 15 days are shown in Fig. 4.2 (a). Morphology of the grown GZS crystal is shown in Figure 4.2b.
4.3 XRD analysis

The grown crystal was subjected to single crystal X-ray diffraction study using BRUKER NONIUS CAD 4 single crystal X-ray diffractometer with CuKα radiation (λ=1.5405Å) to estimate the cell parameters. At room temperature GZS crystal belongs to triclinic system and the cell parameters are a =5.954(2) Å, b=6.812(2) Å, c = 13.272(8) Å, α=85°, β = 83° and γ=82.92° and V = 529.1(4) Å³.

Fig. 4.2(a) As grown crystal of GZS (b) Morphology of GZS single crystal

4.4 FT-IR studies

FT-IR spectrum of GZS recorded at 300 K employing JASCO FT-IR 460 plus spectrophotometer following the KBr pellet technique is shown in Fig. 4.3. The intense sharp peak at 3181 cm⁻¹ is due to NH₂ asymmetric stretching. The absorption due to carboxylate group of free glycine was observed at 1593 cm⁻¹. In GZS this peak was shifted to 1631 cm⁻¹. The sulphato group in GZS is unidentate ligand since it gives three (S-O) stretching at 1113, 981 and 618 cm⁻¹. The peaks observed at 1505 and 1479 cm⁻¹ are due to (C-O) asymmetric and symmetric stretching vibrations respectively. The peak observed at 1317 cm⁻¹ is due to the CH₂ wagging vibration [16].
4.5 **UV-vis – NIR transmittance and absorption studies**

The UV visible NIR spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in the $\sigma$ and $\pi$ orbital from the ground state to higher energy states. Transmission and absorption spectra of GZS recorded in the range of 200-1100 nm using Varian Cary 5E UV-vis-NIR spectrophotometer are shown in Fig. 4.4. A crystal of thickness 3 mm was used. The UV transparency lower cut off occurs at 350 nm. There is no absorption of light to any appreciable extent in the visible range of the electromagnetic spectrum. As there is no absorption in the whole of the visible region GZS can be used as a potential material for second harmonic generation (SHG) in the visible and near infrared region.
4.6 Thermal analysis

4.6.1 Thermogravimetric Analysis

Thermogravimetric Analysis of GZS crystal carried out by employing Perkin Elmer Thermal Analyzer (Pyris Diamond TG/DTA) between 50 °C and 1215 °C is given in Fig. 4.5. The sample was heated at a rate of 10 °C /min in the inert nitrogen atmosphere. The weight of the sample taken for investigation was 14.843 mg. The weight loss was observed in three steps. In the first step the weight loss starts at 50.2 °C and completes at 285 °C. This results in a weight loss of 27.5%. In this step elimination of all the seven water molecules takes place. At this stage the material gets reduced to anhydrous glycine zinc sulphate. On further heating the second weight loss starts at 285 °C and ends at 1040 °C. In this temperature interval a total weight loss of 50.5% is observed which corresponds to further removal of two molecules of glycine. The final step of weight loss is observed on heating beyond 1040 °C and ends at 1215 °C resulting in a weight loss of 11.5 % of the total weight of the material taken. In this step the material gets reduced to zinc sulphite by the loss of oxygen. The weight losses calculated compare well with the
Structural, Thermal and Optical

corresponding experimental values. The decomposition steps were given below.

\[
\begin{align*}
\text{ZnSO}_4 \ (\text{CH}_2\text{NH}_2\text{COOH})_2 \cdot 7\text{H}_2\text{O} & \xrightarrow{(-7\text{H}_2\text{O})} \text{ZnSO}_4[\text{CH}_2\text{NH}_2\text{COOH}]_2 \\
\text{ZnSO}_4 \ (\text{CH}_2\text{NH}_2\text{COOH})_2 & \xrightarrow{(-\text{CH}_2\text{NH}_2\text{COOH})_2} \text{Zn SO}_4 \\
\text{ZnSO}_4 & \xrightarrow{(-\text{O})} \text{Zn SO}_3
\end{align*}
\]

\[\text{Fig. 4.5 Thermogravimetric curve of GZS}\]

4.6.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) study was performed using NETZSCH-Geratebau Gmbh Thermal analysis instrument (Model DSC 200PC) is shown in Figure 4.6. 14.800 mg of sample was placed in the Alumina crucible. The differential scanning calorimetry analysis of the grown GZS single crystal was carried out between 30 °C and 525 °C in the nitrogen atmosphere at a heating rate of 10 °C /min. This material shows three endothermic peaks at 81 °C, 128.8 °C and 321.4 °C. These peaks correlate well with the thermogravimetric curve which shows weight loss at these temperatures.
4.7 SHG studies

Kurtz [17] SHG test was performed to estimate the NLO property of GZS crystal. The crystal was illuminated using 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 10Hz. The second harmonics signal of 532 nm green light 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 Cathode Ray Oscilloscope (Tektronix- TDS 3052B). The input laser energy incident on the powdered sample was chosen to be 3.4 mJ. The result obtained for GZS shows a powder SHG efficiency of about 0.7 times that of KDP crystal.

4.8 Microhardness studies

Vickers Microhardness measurements were carried out on GZS crystal using Ultra Microhardness Tester fitted with a diamond indentor. The indentations were made using a Vickers pyramidal indentor for various loads from 2 to 18 g. The diagonals of the impressions were measured using a Reichert Polyvar 2 MET Microscope with a Microduromat 4000E hardness controller. The measurements were made
on the well developed (01-1) face. Vickers microhardness number was evaluated from the relation \( H_v = 1.8544 \left( \frac{P}{d^2} \right) \) kg/mm\(^2\), where \( H_v \) is Vickers hardness number, \( P \) is the indenter load in kg and \( d \) is the diagonal length of the impression in mm. The variation of microhardness values with applied load is shown in Fig. 4.7. For loads above 18 g cracks started developing around the indentation mark.

![Figure 4.7 Variation of Hardness with load](image)

**4.9 Dielectric studies**

The dielectric constant of the GZS single crystal was measured using LCR meter in the frequency region 40Hz to 100 kHz. Cut and polished transparent good quality single crystal of dimension 10mm\( \times \)10mm\( \times \)3mm was used. Silver paste was applied on the opposite faces of the sample. 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 \( (\varepsilon') \) in the frequency range 40Hz - 100kHz was estimated at the temperature 30, 35, 40 and 50 °C 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.

![Graph showing frequency dependence of dielectric constant for various temperatures](image)

**Fig. 4.8** Frequency dependence of dielectric constant for various temperatures

Figure 4.8 shows variation of dielectric constant with applied frequency. The dielectric constant of the sample was calculated for various temperatures. It is observed from the figure that the dielectric constant decreases with increasing frequency which is due to space charge polarization [18]. In the low and high frequencies the dielectric constant depends on both temperature and frequency.

### 4.10 Conclusion

Large, optically transparent GZS crystal with dimensions upto $19 \times 16 \times 15$ mm$^3$ was grown by solvent evaporation method. Solubility and metastable zonewidth were estimated for different temperatures. Solubility test indicates that water is a suitable solvent for growing single crystals. The unit cell constants of GZS crystals were determined by the single crystal XRD technique. Presence of various functional groups was confirmed by FT-IR analysis. Optical transmittance and the lower cutoff
wavelength identified through UV-vis-NIR spectrum reveal that GZS is a potential candidate for NLO application. Thermogravimetric analysis indicates the three stage decomposition process of GZS. DSC curve well supports the three stage weight loss as explained in the thermogravimetry. The powder SHG efficiency of this glycine zinc sulphate crystal is 0.7 times that of KDP. Vickers microhardness study shows that the hardness values of GZS increases with the increase of load. In the low and high frequencies the dielectric constant depends on both temperature and frequency.

References