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Physical properties of γ- Glycine crystal grown using Aqueous Solution of α-Glycine and P- Chlorobenzophenone.

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Abstract: An organic nonlinear optical single crystal of Gamma (**γ**) glycine (GGLY) has been Grown by slow evaporation of the saturated solution at room temperature. Single crystal of γ- glycine (GGLY), an organic nonlinear optical (NLO) material, has been grown by slow solvent evaporation technique. Good optical quality single crystals with dimension up to 32 × 31 × 7 mm^3 are obtained. The crystals are characterized by optical absorption Spectrum, FTIR and X-ray diffraction studies. The dielectric response of the sample is Studied as a function of frequency and temperature. The mechanical, Dielectric behavior and Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) study of the grown crystals is also investigated.

Keywords: NLO materials; Crystal growth; X-Ray diffraction, FTIR, Dielectric measurement; Conductivity; TGA, Mechanical and thermal properties.

1. INTRODUCTION

The NLO materials are always high due to its practical applications in optical modulation, switching and other signal processing devices. The research on organic and semi-organic crystals was started in 1980s. Organic materials offer good optical response time, non-resonant susceptibility, second harmonic generation and high phase-conjugate reflectivity [1] materials.

The Amino acids and their complexes belong to a family of organic materials that have been

Considered for photonic applications [2]. Amino acids are essential materials for NLO applications.

The importance of amino acids in NLO applications is due to the fact that all the amino acids have chiral symmetry and crystallize in non Centro-symmetric space groups. Out of 20 amino acids glycine is the simplest of all. The Glycine family crystals have been subjected to extensive research by several researches for their efficient NLO properties [3-6]. Glycine is the only protein forming amino acid and is optically inactive too. It exists as dipolar ions in which the carboxyl group is present as a carboxyl ate ion and the amino group as an ammonium ion. Its high melting point is due to its dipolar nature. Under different conditions, glycine crystallizes in 3 kinds of polymorphs with different thermal stabilities [7]. Also α, β and γ glycine exhibit different characteristics. Both α and β forms are crystalline in centrosymmetric space group P21/c that is not feasible for optical second harmonic generation [8-9]. But γ glycine crystallizes in non centrosymmetric space group P31 & P32 enabling itself ideal for piezo electric and NLO applications. Due to the presence of

chromophores namely amino groups, carboxyl group, γ glycine (Gamma Glycine) finds itself absolutely transparent in the U-V visible region.

Even though many researchers reported that single crystals of GGLY (gamma glycine) can be grown from aqueous solutions of glycine which can be acidic as well as basic [10-12]. The growth of single crystals of Gamma glycine from aqueous solution incorporated with sodium chloride (NaCl) has been reported recently by Srinivasan and Arumugam employing slow solvent evaporation technique [13]. Ambujam et al [14] and Ramachandran et al [15] have successfully crystallized GGLY (Gamma glycine) via gel technique. Scaled quantum mechanical force field calculations on the Gamma Crystal polymorph have confirmed the effect of hydrogen bond stretching in vibrational analysis. Gamma Glycine is actually grown by many conventional methods like slow cooling, slow evaporation as well as gel method. Though there are numerous reports on this title compound wherein mixed solvents like water with sodium acetate, sodium hydroxide, ammonium sulphate, ammonium hydroxide, potassium chloride, lithium bromide, lithium acetate etc are used, still the indispensable characteristics of gamma glycine urges the researches to implant deeper studies on its properties. Bharaniraj et al have been reported the growth of gamma glycine from the aqueous solutions of alpha glycine and sodium acetate with deionised water. The present article also addresses the growth of Gamma glycine (GGLY) crystals in the presence of the aqueous solution of α -Glycine and P-Chlorobenzophenone. The crystals of Gamma glycine grown with P-Chlorobenzophenone are characterized by single crystal and powder XRD, FT-IR, NLO test, optical, micro hardness, dielectric, thermo gravimetric analysis (TGA) studies and impedance analysis .

Materials and Methods

2. Experimental procedure

2.1 Synthesis

The single crystals of Gamma glycine (GGLY) crystals were grown by slow evaporation method

at ambient room temperature. The commercially available analar grade Glycine (99.5%) and P-Chlorobenzophenone mixture of 1:1 molar ratio was dissolved in de-ionized water and was stirred at 50 ºC then the solution was filtered in room temperature (30 ºC). Light brownish transparent crystals of the title compound were formed by slow evaporation technique after four to nine weeks.

2.2 Solubility determination

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 solubility curve of Gamma Glycine (Glycine and P-Chlorobenzophenone) was determined by dissolving the synthesized product in Millipore water in an airtight container kept in a constant temperature bath, the content was continuously stirred for 1-2 hours. After attaining the saturation, the equilibrium concentration of the solute was estimated gravimetrically. The same process was repeated for different temperatures (30, 35, 40, 45, 50 and 55 ºC). The variation of solubility with

temperature Fig. 1 indicates that Gamma glycine (Glycine with P-Chlorobenzophenone) have high positive solubility-temperature co-efficient values.

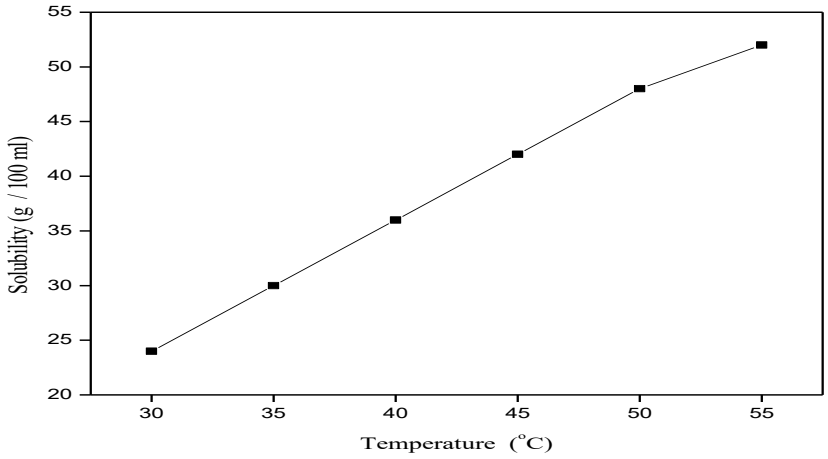

Fig 1. Solubility curve for Gamma glycine GGLY (Glycine and P-Chlorobenzophenone)

3. Crystal Growth

Single crystals of γ-Glycine (GGLY) crystals were grown from the aqueous solution of α-Glycine and P-Chlorobenzophenone compounds procured from Merck KGaA, Germany. The purity of the procured compounds was 99 % and was further enhanced by recrystallization.

Recrystallized α-Glycine and P-Chlorobenzophenone were taken in 2:1 molar ratio, mixed and crushed into a fine powder. This powder was dissolved in demineralised water and ethyl alcohol of very high resistivity, and stirred for 2 hours using a hot plate magnetic stirrer at 60 °C to prevent any possible degradation.

In order to prevent the undissolved solid substances from the solution, the prepared solution was filtered using Whatman filter paper of pore size 11 µm into a beaker. The pH value of the solution was 5.3. The beaker was covered with a perforated polythene sheet and kept on a solid platform. Yellow-brownish Crystals of reasonable size were harvested after a period of 20 days. Two of the grown crystals of Gamma Glycine are shown in Figure 2.

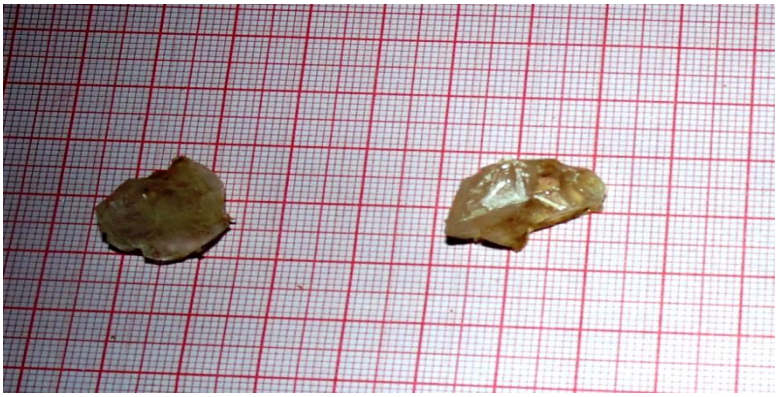

Figure 2. Photograph of the Gamma glycine crystals (GGLY) from Glycine and P-Chlorobenzophenone

4. Result and Discussion

4.1Single-Crystal X-ray Diffraction (SC-XRD)

The Single-crystal X-ray diffraction data of Gamma glycine was collected with the help of Bruker Kappa Apex II single-crystal diffract meter. The unit cell parameters obtained from the SC-XRD are listed in Table 1.

4.2 Powder X-ray Diffraction (PXRD)

The powder X-ray diffraction data of single crystals was collected using Bruker AXS D8 Advance powder X-ray diffracto meter. The powder X-ray diffractogram was indexed using the unit cell parameters (Table 1) of the crystal obtained from single-crystal X-ray diffraction. The diffractogram of GGLY and that of the indexed (Gamma glycine) GGLY is shown in Figure3. It depicts the powder XRD pastern of the Glycine with P-Chlorobenzophenone crystals and is found to be in good agreement with literature

Table 1 Crystal data of GGLY(Glycine and P-Chlorophenzophenone)

Cell Parameters	Gamma glycine crystals (present study)	Gamma Glycine Reported
a (Å)	7.028	7.037
b (Å)	7.028	7.037
c (Å)	5.520	5.483
α, β and γ (°)	90°, 90°, 120°	90°, 90°, 120°
Crystal System, Space group	Hexagonal ,P31	Hexagonal, P31
Density D_x, D_m $v(A)^3$	1.584, 1.6 236.05	1.587, 1.6 235.2(4)

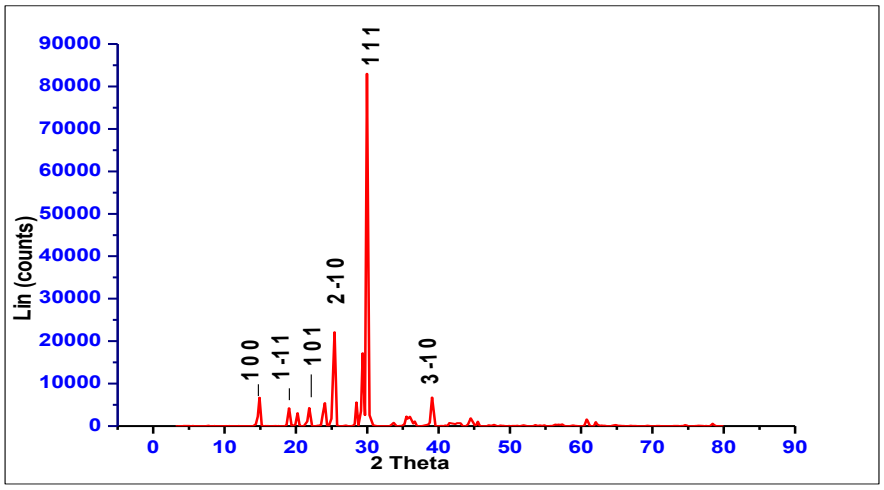

Figure 3. Powder X-ray diffractogram of GGLY (Glycine and P-Chlorobenzophenone)

4.3 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectral analysis on the grown GGLY crystal was performed with the help of Perkin Elmer RX 1 FTIR Spectrophotometer in order to investigate the functional groups and vibrational modes present in the grown crystal. The FTIR spectrum of Glycine with P-

Chlorobenzophenone crystal is shown in Figure 4 and the FTIR assignments are listed in table 2.

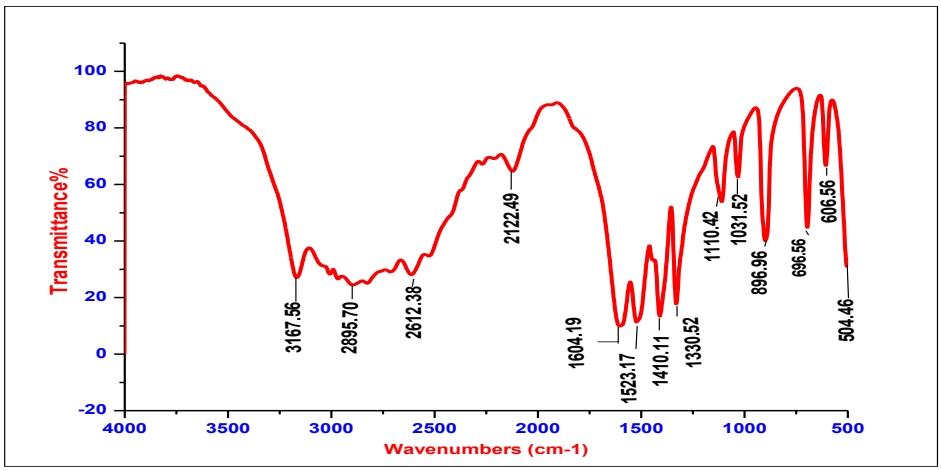

Figure 4. FTIR spectrogram of GGLY

Table 2. FTIR assignments of GGLY

S.No.	Wave no. (cm^{-1})	Assignment
1	3167.56	NH_3^+ stretching vibration
2	2895.70	CH stretching vibration
3	2612.38	N-H-O stretching
4	2122.49	Combination bonds
5	1604.49	COO^-stretching
6	1523.17	NH_3^+ deformation
7	1410	CH_2 Bending
8	1330.53	CH_2 Twisting
9	1110.42	NH_3^+ Rocking
10	1031.52	CCN stretching
11	896.6	C-C Rocking
12	696.56	COO^- bending
13	606.58	COO^- wagging
14	504.46	COO^- rocking

4.4 UV-Vis Spectroscopy

4.4.1 Absorption Spectroscopy

The optical absorption spectrum of GGLY (Glycine and P-Chlorobenzophenone) crystal of thickness 2 mm was measured in the 190-1100 nm range and the spectrum is shown in Figure 5. Low absorbance is observed throughout the visible and IR region. The cut-off wavelength of the GGLY crystal is found to be 195 nm.

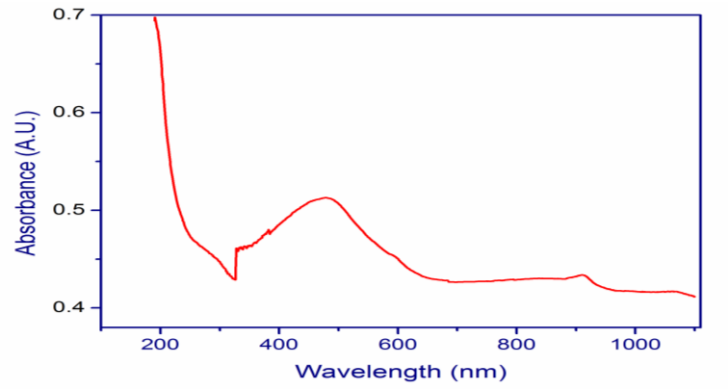

Figure 5. UV-Vis absorbance spectrum of GGLY

4.4.2Transmission Spectroscopy

The UV-Vis transmittance study on GGLY was carried out using PerkinElmer's LAMBDA 35 UV-Vis Spectrophotometer for the wavelength range of 190-1100 nm. The thickness of the crystal was 2 mm. The observed transmittance spectrum of GGLY is shown in Figure 6. The crystal shows moderate transmittance in the entire visible range. However there is reduction in the transmittance around 479.9 nm.

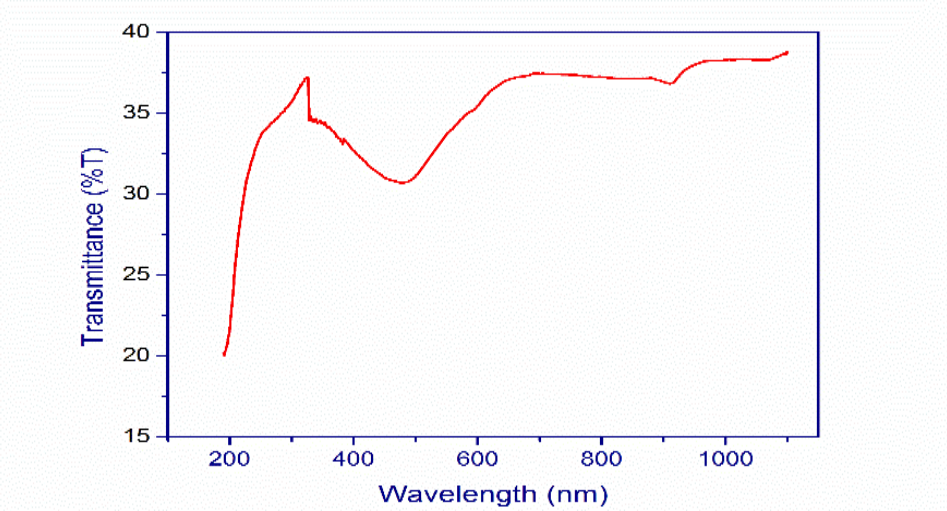

Figure 6. UV-Vis transmission spectrum of GGLY

4.4.3 Diffused Reflectance Spectroscopy (DRS)

The diffused reflectance spectrum of GGLY was studied for a frequency range of 200-800 nm.. The DRS spectrum of GGLY is shown in Figure 7.

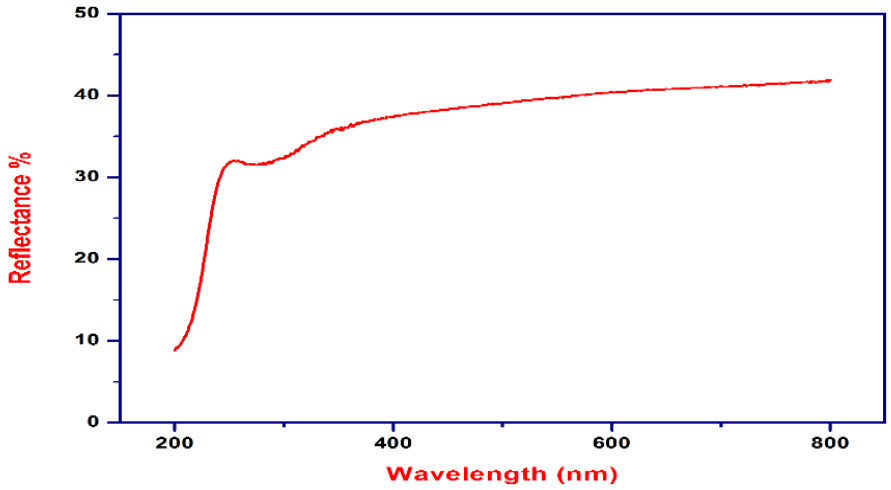

Figure7. DRS graph showing wavelength versus reflectance of GGLY

4.5 Second Harmonic Generation by Kurtz Powder Technique

Second harmonic test on GGLY (Glycine and P-Chlorobenzophenone)sample was done by Kurtz and Perry [16] powder technique. The microcrystalline powdered sample was packed in a capillary tube of diameter 0.154 mm. The powder sample with an average particle size of 100-150 µm was illuminated using a Q-switched mode-locked Nd: YAG laser of pulse width 8 ns at a wavelength of 1064 nm and 10 Hz fundamental radiation. For SHG efficiency measurements, microcrystalline sample of KDP of the same particle size was used for comparison. When a laser input of 0.8 J was passed through the sample and KDP, the output signal obtained from the GLCBP was 4.9 mJ whereas the output for the pure KDP of the same particle size it was 3.39 mJ. Thus it is concluded that the SHG efficiency of GGLY is 1.4 times that of KDP.The sample of chlorobenzophenone which is qualitatively higher intensity to the reference of KDP crystal.

4.6. Micro hardness Analysis

The Vickers micro hardness of the grown GGLY crystal is determined using SHIMADZU HMV-2T micro hardness tester. The indentations are made on the polished crystal for the loads of 25, 50 and 100 g. The indentation time was kept as 5 s for all the loads. The Vickers micro hardness number, H_V was calculated. The graph showing variation in H_V with load is shown in Figure 8. It belongs to soft material category [17].

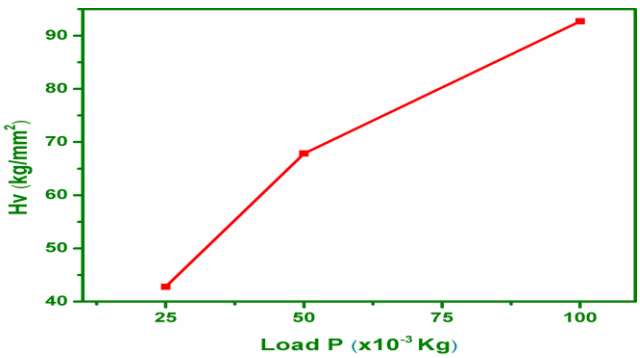

Figure 8. Variation in the Vickers hardness H_V with load P of GGLY

4.7. Dielectric Studies

The dielectric properties of the GGLY crystals were studied using N4L impedance analyser. The experiment was conducted for various temperatures from 26 °C to 150 °C over a frequency range of 1 kHz to 1 MHz. The variation of dielectric constant with frequency at different temperatures is shown in

Figure 9 and the variation of dielectric loss with frequency is shown in Figure10. It is observed that the inclusion of α-Glycine in the pure P-Chlorobenzophenone has reduced its dielectric constant to a considerable level [18]. The dielectric constant remains high at frequencies up to 30 kHz and reduces rapidly up to 150 kHz and remain low up to 1 MHz. This transition signifies the absence of orientational polarisation at higher frequencies [19]. The temperature dependency of the dielectric loss (tan δ) is more at frequencies below 30 kHz.

The frequency dependent AC conductivity of GGLY is shown in Figure11. The AC conductivity of the crystal is high at higher frequencies (above 30 kHz). There is appreciable variation in AC conductivity due to temperature [20-23]. The conductivity decreases with decrease in temperature [24-26]. This tendency is observed in the entire frequency range.

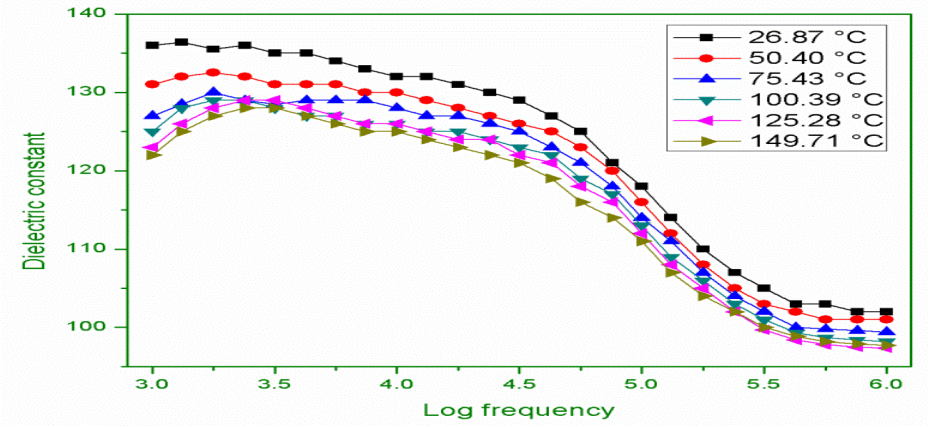

Figure 9. Variation of dielectric constant with log frequency

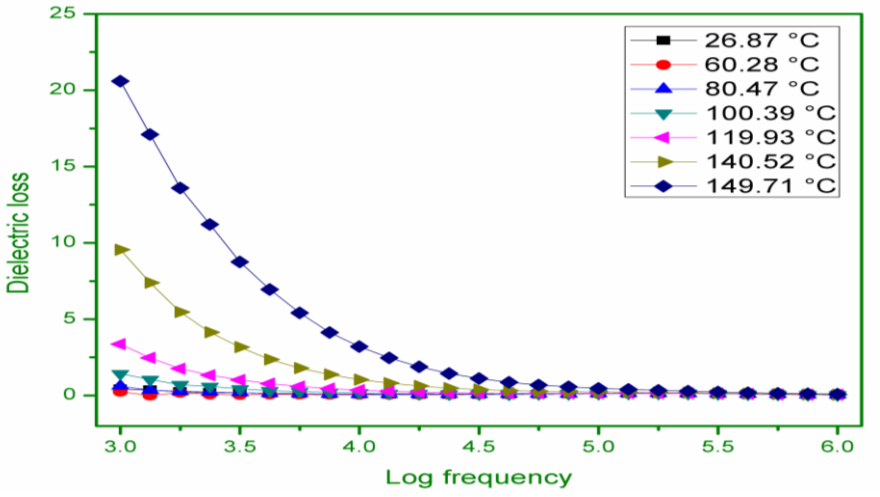

Figure10. Variation of dielectric loss with log frequency

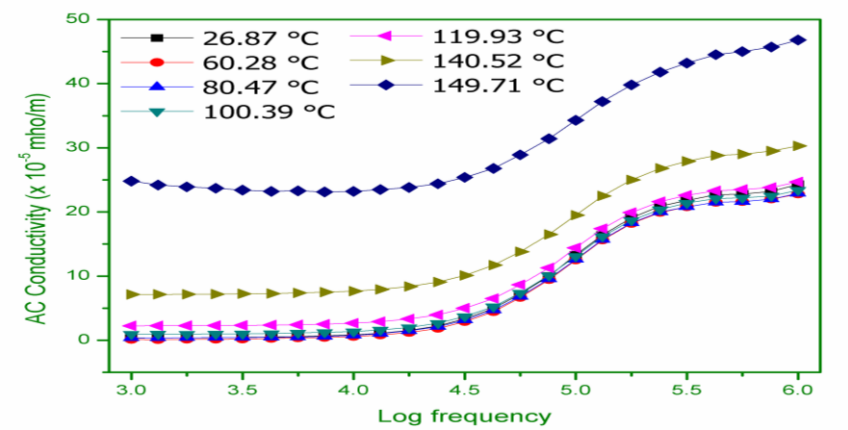

Figure11. The frequency dependent AC conductivities (x 10^{-5} mho/m) of GGLY

4.8 Thermal Analysis

4.8.1 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetric study on BADP was conducted with the help of NETZSCH DSC 200 PC for a temperature range of 30 to 750 °C. The DSC thermo gram of GGLY is shown in

12. There are two endothermic peaks, one at 261.47 °C. These peaks represent decomposition of the sample.

4.8.2 Thermo gravimetric Analysis (TGA)

The Thermo gravimetric analysis on GGLY was performed with the help of PerkinElmer Pyris 6 TGA in Nitrogen atmosphere with a rate of flow of 20 ml/min for a temperature from 30 °C to 750 °C at 10 °C/min. The thermo gram of GGLY is shown in Figure 8 and the TGA/DTA thermo gram is shown in13.

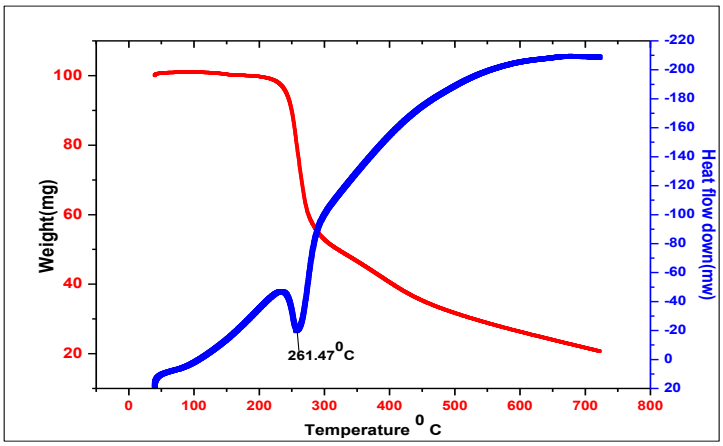

Figure. 12. DSC thermo gram of GGLY

In the thermo gram of GGLY the 5.05 % weight loss of 162 °C is due to the evaporation of water trapped in the lattice. The sample decomposes in stage with a weight loss of 31.63 %, includes the endotherms, 251.7 °C and 299.1 °C. The second stage of decomposition, leading to a weight loss of 49.21 %, occurs around the endotherm, 40.7 °C

[27]. At 750 °C, 13.5 % of the sample remains as a residue. It is observed that the thermal stability of P-Chlorobenzophenone is reduced due to the inclusion of α-Glycine [28].

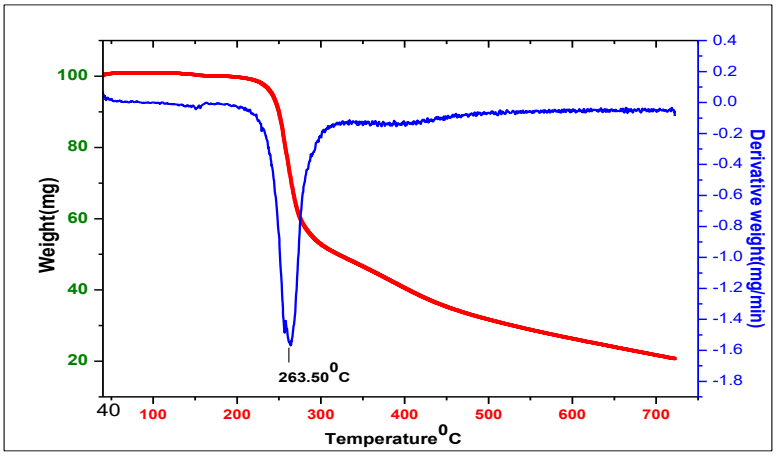

Figure 13. TGA, DTA thermo gram of GGLY

4.9 Impedance analysis

The frequency dependent properties of a material are often represented as complex impedance Z* and which is related as Z*(ω) = Z' –jZ'' where Z' and Z'' are the real and imaginary components of impedance. The variations of real part of impedance (Z') and imaginary part of impedance (Z'') with different frequencies at different temperatures are shown in the figures 14 and 15. From the result it is observed that the real and imaginary part of impedance decreases with the increase in temperature and frequency. This decrease of the impedance shows an indication of negative temperature coefficient of resistance behaviour like that of an insulator. The high value of impedance at low frequency shows low ionic mobility in the grown GGLY crystal. The shift in the position of peak with temperature shows a temperature dependent relaxation process, possibly a Debye type relaxation in the crystal [29]. The Nyquist plots for the grown GGLY crystal has been drawn between real part and imaginary part of impedance at different temperatures. The Z'- Z'' graph of GGLY at 140 °C is shown in figure 16. The Z'-Z'' graph drawn at various temperatures, produce a single Debye semicircle indicating single relaxation time. Thus GGLY behaves like a Debye type material.

This small semicircle near high frequency is due to grains. Also the single semicircular arc was obtained and this semicircle indicates that the electrical properties of the material arising mainly due to the bulk effects [30-31].

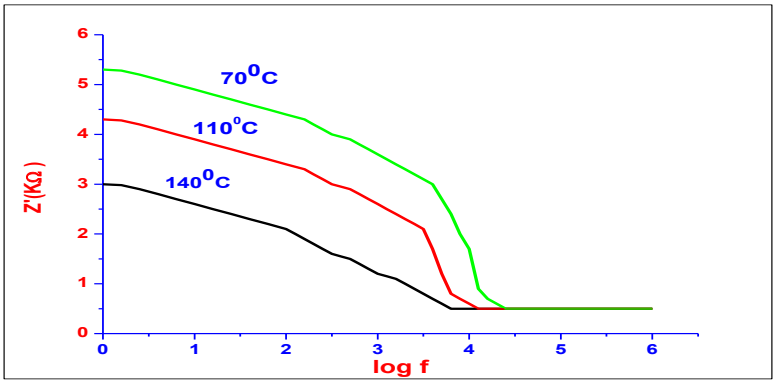

Figure 14. Plot of real of impedance verses log frequency for GGLY

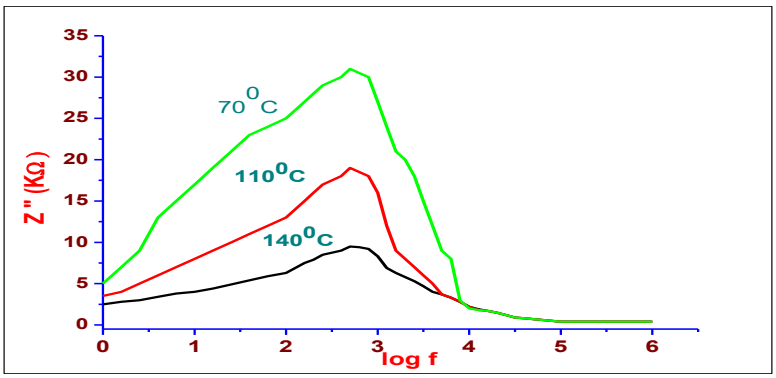

Figure 15.plot of imaginary impedance verses log frequency for GGLY

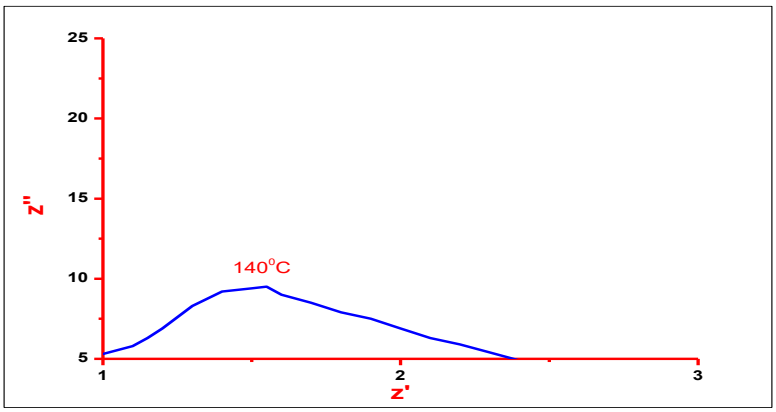

Figure16. Z' versus Z'' plot of GGLY at 140 °C

Conclusion

The Glycine with P-Chlorobenzophenone compound of GGLY was successfully Synthesized and the single crystals have been grown by solution growth technique. Its cell parameters have been determined by the single crystal XRD and powder XRD analysis. The presence of functional groups in gamma glycine has been identified from the FTIR analysis. Optical absorption study reveals the absorption edge at 220 nm. The phase matching natures of the grown crystals have been confirmed by Kurtz and Perry powder method. The micro hardness measurements prove that gamma glycine belongs to the soft category of materials.

The thermo characteristic study confirms the crystal is stable and is suitable for device applications. The SHG efficiency shows the GGLY has high NLO property.

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