Investigation on Growth and Characterization of γ-Glycine Single Crystal from Lithium Sulphate

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Abstract: **A nonlinear semi-organic single crystal of γ-Glycine has been grown by slow-evaporation method. Well developed good quality crystal of size13X11X10mm^3 was harvested. The cell parameters of the grown crystal were estimated by single crystal X-ray diffraction analysis. The presence of functional group was identified from FT-IR spectrum. The UV absorption spectra of this crystal show the cut off wavelength. Thermal analysis (TGA/DTA) was performed to study the thermal stability of the grown crystal. Vickers micro hardness and photo conductivity were carried on the well-developed crystal to study its mechanical strength and field dependent current. The dielectric response of the sample is studied as a function of frequency and temperature.**

Keywords: **NLO materials; Slowevaporation; Thermal studies; Mechanical property; Photoconductivity; Dielectric measurements.**

I. INTRODUCTION

Organic Material possesses good optical non-linearity but they are thermally unstable. Inorganic materials possess excellent mechanical and thermal properties with moderate non-linearity. Organic materials are soft and difficult to polish, as they are constituted by weak Vander walls and hydrogen bond with conjugated π electrons. Further these materials have more absorption in UV region. In view of these problems, semi organics are formed by combining organic molecules of high polarization with mechanically strong and thermally stable Inorganic molecules. These materials combine the chemical flexibility and non-linearity of organics and favorable physical properties of inorganics.

Glycine is one of the twenty biologically naturally occurring amino acid that can be found in protein. It has been reported that some complexes of amino acids with Inorganic salt may exhibit ferroelectric properties[1-3].Some complexes of glycine with Li NO [4],CaNo3[5],H_2SO_4[6],srcl$_2$[7]form single crystals but none of them were reported to have nonlinear optical property. Glycinecrystallizes in 3 kinds of polymorphs with different thermal stability[8].Since α and β forms has Centro symmetric and space group p2$_1$/c, it is not feasible for optical second harmonic generation[9-10].But γ-glycinecrystallizes in non-Centro symmetric space group p3$_1$,enabling itself ideal for piezo electric and NLO applications. Many researchers has reported the growth of γ-glycine. Ambujam et al [11]and Ramachandran[12] have successfully crystallized γ-glycine through gel technique. In this work an attempt was made successful to grow γ-glycine from lithium sulphate. The grown crystal were characterized by single crystal XRD and powder XRD, FT-IR,UV Optical studies TGA-DTA analysis, Micro hardness, photo conductivity and dielectric measurements.

II. EXPERIMENT PROCEDURES

Crystal Growth:

Single crystal of γ-glycine was grown by slow evaporation method at room temperature .The commercially available glycine (ARgrade) and Lithium sulphate were taken in the ratio 3:1 dissolved in double distilled deionized water and stirred well using a temperature controlled magnetic stirrer at 40^0 C to get a homogeneous mixture of solution. Saturated γ-glycine solution was prepared finally and this fully reacted solution was allowed for slow evaporation to get crystalline

salt. Highly purified crystalline salt was obtained by repeated recrystallization process. The supersaturated solution of synthesized γ -glycine was kept undisturbed at room temperature. Optically good quality seed crystals were grown from this solution.γ-glycine crystal was grown up to the dimension of 13x 11x10 mm^3 in a period of 45 days.
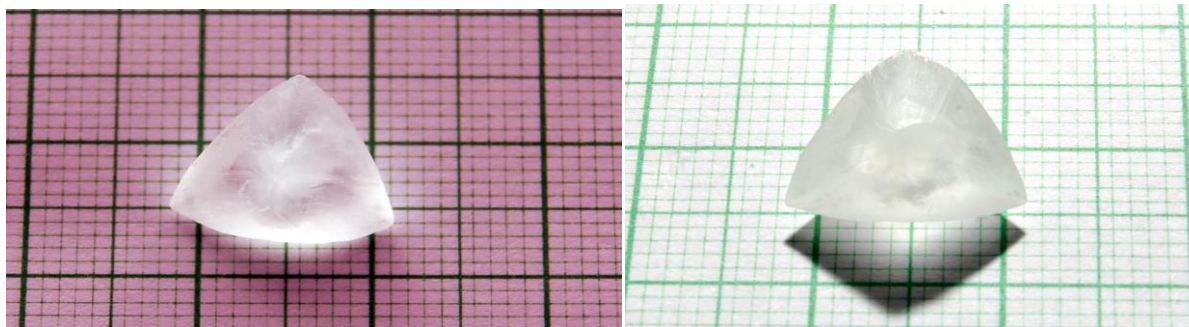

Fig.1 Photographs of as grown γ-glycine crystal

III.   RESULTS& DISCUSSION

3.1. Single Crystal XRD

The single crystal XRDanalysis for the grown crystal has been carried out by ENRAFNONIUSCAD4diffractometer.Least square refinement of 25 reflections was done in the range of 20^0-30^0. The unit cell parameters obtained for γ-glycine is given in the table 1 and it is compared with literature value reported by litaka [13], which confirms that the grown crystal is in the γ phase and belongs to the hexagonal system. It is also evident that lithium sulphate is not incorporated in to the grown crystal but its presence in the solution inhibit the growth of γ-glycine

Table.1

Parameter	γ-glycine (Reported value)	γ-glycine (Present study)
a	7.037Å	7.01Å
b	7.037Å	7.01Å
c	5.483Å	5.45Å
Structure	Hexagonal	Hexagonal
Volume	$235Å^3$	$232Å^3$

3.2. Powder XRD Analysis

The powder XRD patterns of the grown crystals were recorded using D8AdvancedBruker powder X-ray diffractometer. The sample was scanned in the range 10^0to70^0at a scan rate of 1^0min-1. The powder XRD pattern is shown in the fig1.The powder X-ray diffraction experiment shows that the synthesized material and grown crystal were the single phase of γ-glycine.
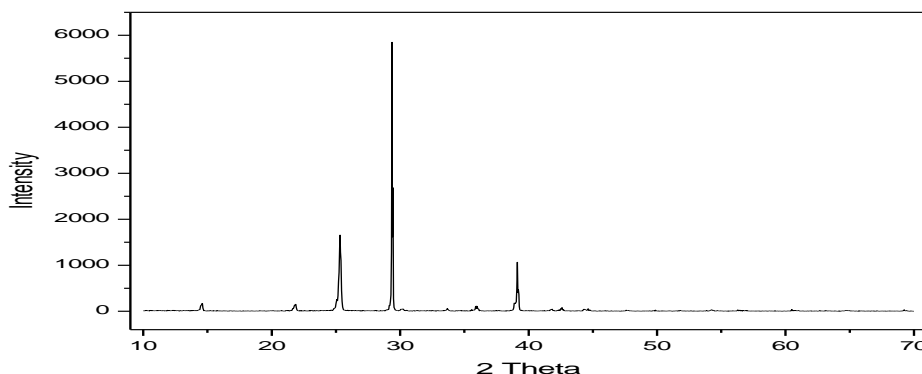

Fig.2 Powder X-ray diffraction pattern of GG

IV.   FT-IR ANALYSIS

The FT-IR spectrum of γ-glycine was shown in the Fig 2. The spectrum was recorded in the frequency region of 4000-400 cm^{-1} to identify the functional group present in the grown crystal of γ-glycine using BRUKER IFS 66vFT-IR spectrometer with KBr pellet technique. The band absorbed at 530,648 cm^{-1} are attributed to carboxylate groups, while the bands absorbed at 1119, 1452, 2600cm^{-1} are attributed to $NH3^+$ group.Thus carboxyl group is present as carboxylate ion and amino group exists as ammonium ion in γ-glycine. The peak at 1423cm^{-1} is attributed to CH_2 bending and wagging. Further the peaks at 1629 cm^{-1} corresponds to COO-symmetric stretch. The prominent band at 2933 and 3080 cm^{-1} are attributed to the combination of symmetric and asymmetric vibration of $NH3^+$ group.The absorption peak of γ-glycine single crystals are in line with the literature value (13,14 and 15).
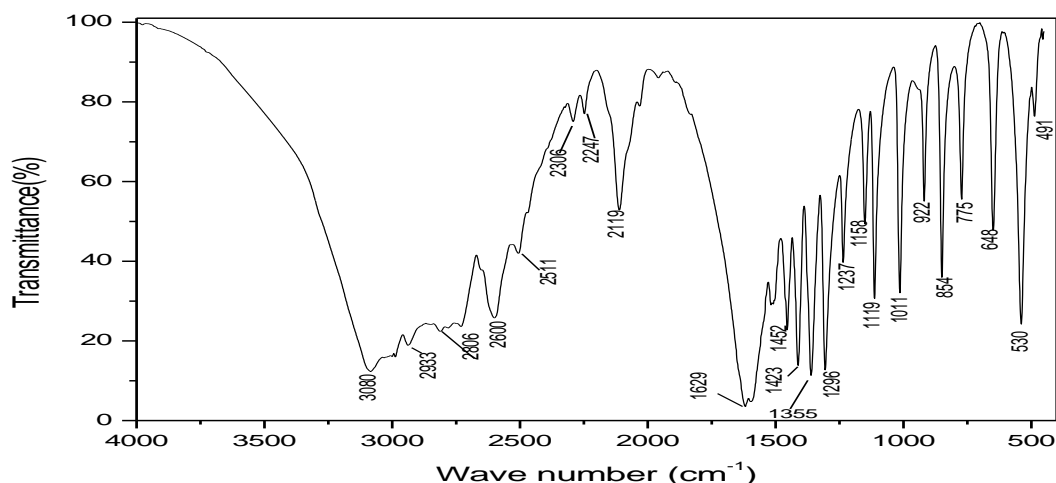

Fig.3 FT-IR spectrum of GG

Wave number	Assignments
2933,3080	NH_3^+ Symmetric and asymmetric stretch
1629	COO^- asymmetric stretch
1423	CH_2 bending and wagging
1355	CH_2 wagging
1119,1452	NH_3^+ rock
922	CH_2 rock
854	CCN symmetric and asymmetricstretch
648	COO^- Stretch
530	COO^- Stretch

V.   OPTICAL STUDIES (UV-VIS-NIR)

The optical property of γ-glycine was characterized by using Perkin Elmer Lamda spectrophotometer. The grown crystal is transparent in the UV and visible region as the absorbance is less than 1.3 units. The lower cut off wavelength was around 230nm and there was no absorption from 250nm to 1100nm which clearly shows that the crystal possess good optical transparency for the second harmonic generation. Fig3.represents the optical absorption spectrum.
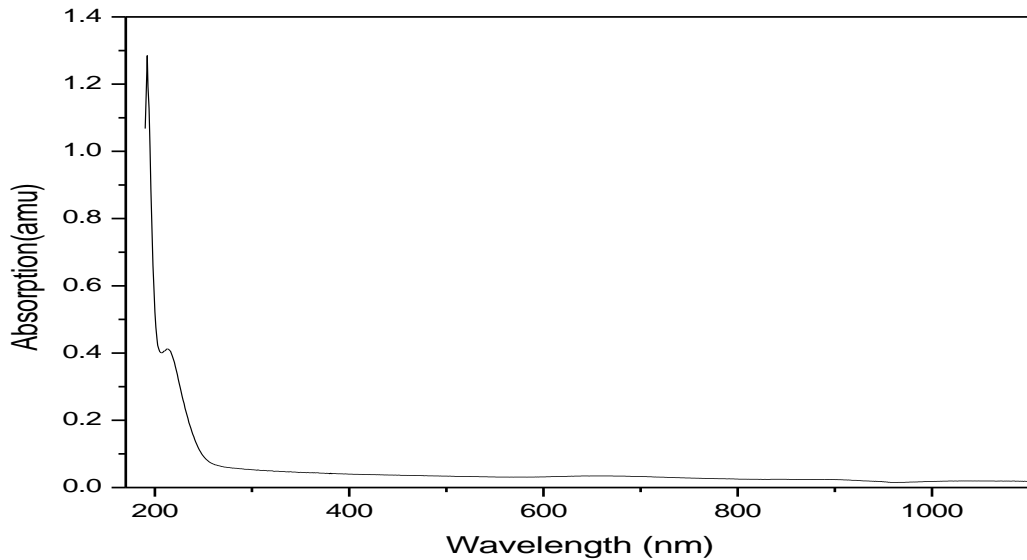

Fig.4 Optical absorption spectrum of GG

To estimate the direct band gap value a graph has been plotted betweenev and $(\alpha h v^2)$ where α is the absorption coefficient and h is the energy of the incident photon. From the Fig 4, the band gap energy is found to be5.428evwhich is very useful for analyzing induced polarisation
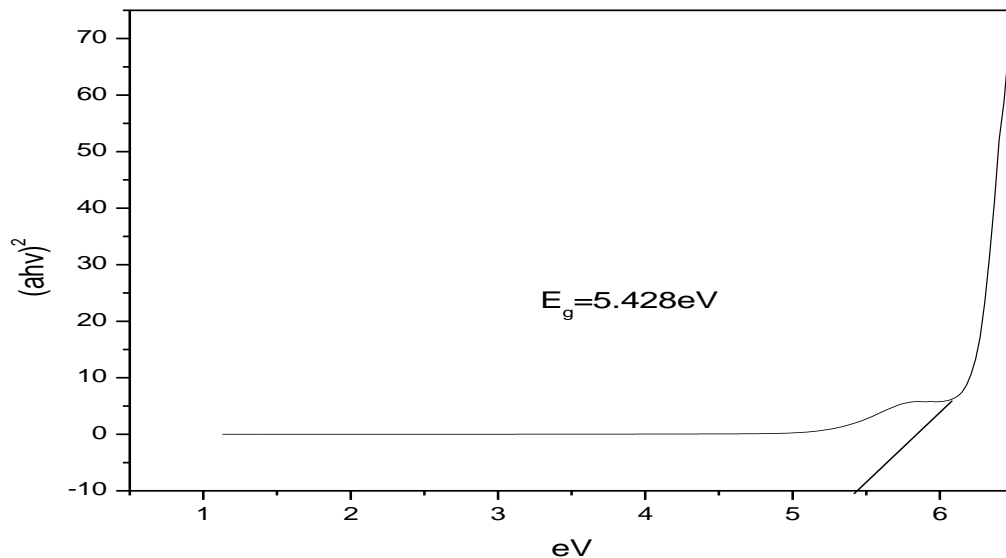

Fig.5 Taucs plot of GG

VI.   THERMAL ANALYSIS

The thermo gravimetric analysis was carried out using TGAQ500V 6.6 thermal analyzer at a heating rate 10k/min in nitrogen inert atmosphere at temperature range from R.T – 750°C. The sample was placed in an alumina crucible. The TGA curve shows the compound is thermally stable upto233.6^{o}C. There is no weight loss up to 233.6^{o}C, the mass change at 285°C is about 42.03% The gradual mass change occurs at 350°C, 470°Crespectively are in the order of 9.27 % and 11.67%. The residual mass at 749.5^{o}C is 21.04%
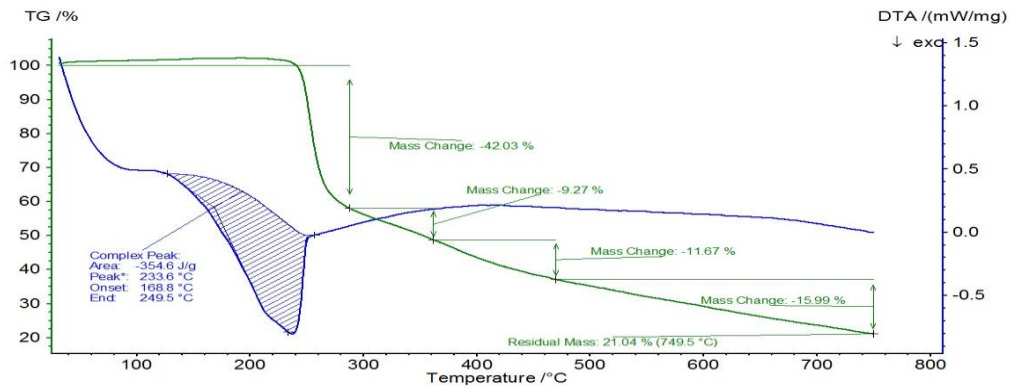

Fig.6 TG-DTA Traces of GG Crystal

VII.   NLO PROPERTY

The study of non linear optical conversion efficiency was carried out by using the experimental set up of Kurtz and perry [17]. A Q-switched Nd:YAG laser beam of wavelength 1064nm with an input power of 68j with repetition rate of 10 H Z were used. The as grown crystal of GG was powdered with a uniform particle size and then packed in a micro capillary of uniform bore exposed to laser radiation. The generation of second harmonics was confirmed by the emission of green light.

VIII.   VICKER'S MICRO HARDNESS STUDY

Vickers micro hardness study for GG is performed on the smooth surface of the crystal with different loads(25-200gm).The variation of vicker's hardness number against applied load indicates that the hardness number of crystal increases with the increase in load.

The fig7.shows the variation of logdvslogp. The slope of the straight line obtained is known as work hardening co-efficient (n). The value of n for γ-glycine is 3.38743 which is shown in the graph. According to onitsch if n>1.6, then those materials are soft materials [18].
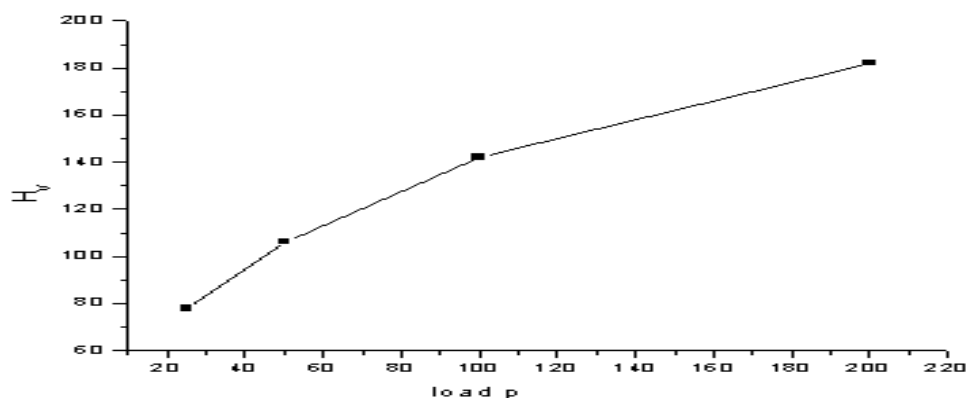

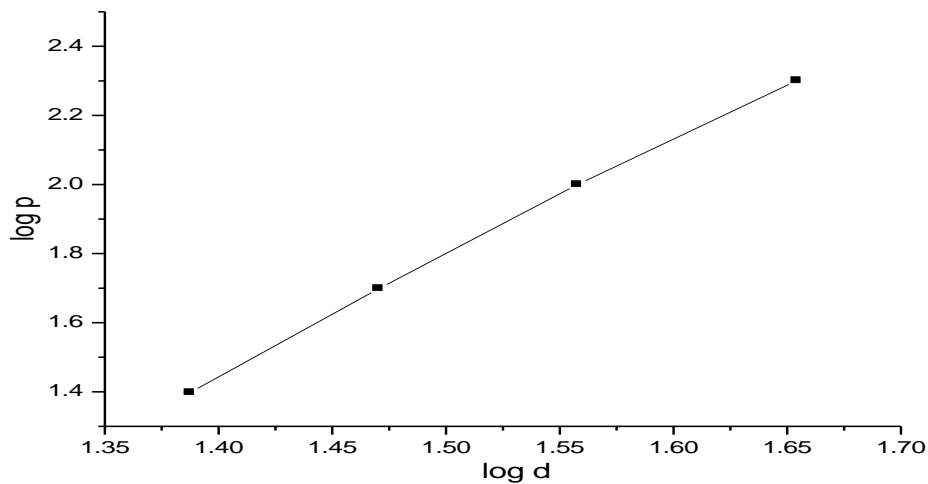**Fig.7 Variation of Vickers hardness number Vs applied load**

Fig.8 Plot of log d versus log p

IX.   PHOTO CONDUCTVITY STUDIES

The field dependent dark and photo current of GG is shown in the fig 8. The dark current is found to be less than that of photo current at every applied electric field. This phenomenon is known as positive photoconductivity. This is attributed to the reason that it may be due to large number of mobile charge carriers generated by absorption of photons.
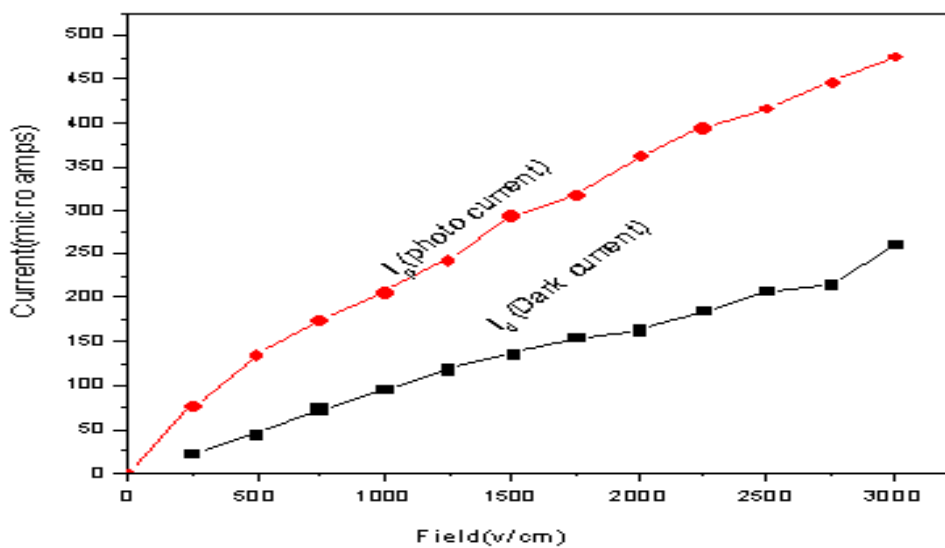

Fig.9 Field dependent photoconductivity

X.   DIELECTRIC STUDIES

The dielectric studies on γ-glycine single crystal has been carried out using H10K13532-50 LCR HITESTER. Fig shows the variation of dielectric constant and dielectric loss with applied frequency. The dielectric constant is found to be high in the lower frequency region and decrease continuously with increase in the frequency. In the lower frequency region the dielectric constant is high due to the combination of all the polarization such as electronic, ionic, dipole and space charge[19].At high frequency region, both the dielectric constant and dielectric loss is minimum,which confirms that the grown crystal has minimum defects and hence posses good optical quality crystal[20].
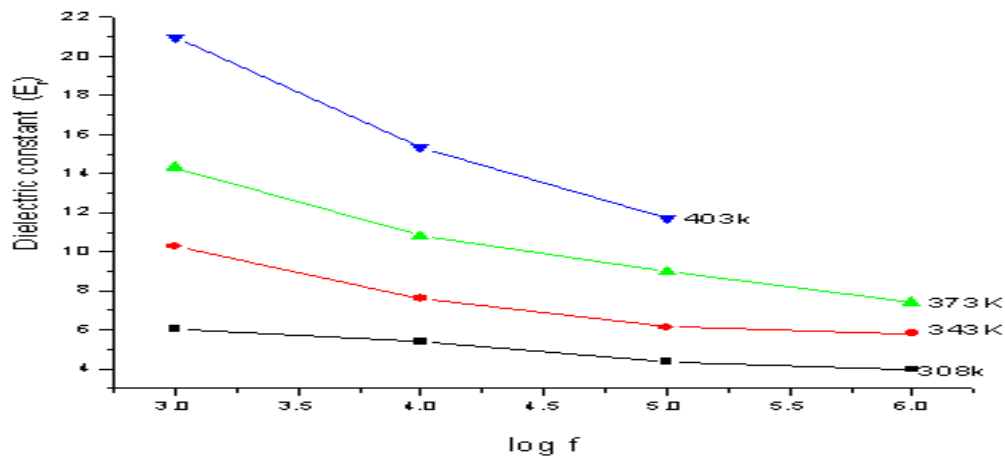
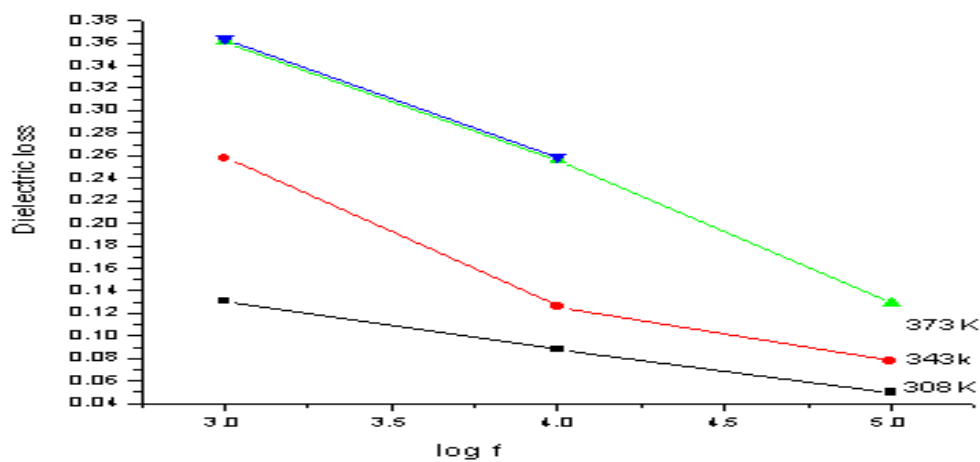**Fig.10 Temparature dependence of dielectric constant for GG**

Fig.11 Variation of dielectric loss with log frequency for GG

XI.   CONCLUSION

Single crystal of γ-glycine was successfully grown by slow evaporation technique at room temperature. The structure of grown crystal was observed to be hexagonal. FT-IR analysis confirms the presence of various functional groups. The UV-Vis cut off wave length is around 230nm and the absorbance is less than 1.3 units. NLO property is confirmed by Kurtz powder SHG test. The band gap energy of the sample is found to be the 5.428 eV. TGA/DTA confirms thermal stability. Photo conductivity study reveals positive photoconductivity nature. Vickers hardness test show the crystal is of soft nature. This study of crystal shows that this can be used for photonics device fabrication.

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