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# STUDIES OF GAMMA GLYCINE CRYSTLAS GROWN IN THE AQUEOUS SOLUTION OF ZINC CHLORIDE

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**Abstract:**

Solution method was adopted to grow single crystals of gamma glycine from the aqueous solution of zinc chloride (GGZC). The harvested crystals were observed to be colourless, transparent and non-hygroscopic. The solubility studies were carried out by gravimetrical method at different temperatures and nucleation kinetic studies were done on the sample to understand the nucleation phenomena. The grown crystals were characterized by various studies like XRD studies, optical studies, dielectric studies, microhardness studies, LDT studies, SHG studies and measurement of density etc and the obtained results were analyzed and discussed. The results show that the grown GGZC crystal emits green laser light when the infrared laser light from Nd:YAG laser is passed onto the crystal. The grown GGZC crystal is found to be transparent in the visible region and it has high optical band gap.

## 1. Introduction:

Glycine is the simplest amino acid and it has many polymeric forms like alpha glycine, beta glycine, gamma glycine (γ-glycine), delta glycine etc. Gamma glycine is thermodynamically the most stable form at room temperature but transforms into the α-form at high temperatures. The growth of γ-form of glycine crystals can be carried out from aqueous solution or gel in the presence of additives [1-3]. Structural and NLO properties of γ-glycine were reported in the literature [4, 5]. Khanna *et al*. investigated the spectral studies of γ-glycine [6]. Selvarajan *et al*. have reported that when glycine is mixed with ammonium chloride in 3:1 ratio, it becomes γ-glycine. The comparative study of pure and urea doped γ-glycine crystals resulted in the fact that urea has marginally increased the solubility, optical transparency window and NLO efficiency [7]. Renuka Devi *et al.* have grown large dimensional single crystals of γ-glycine with additives such as sodium acetate, sodium nitrate, sodium hydroxide and malonic acid by the top seeded slow cooling method [8]. In this work, gamma glycine crystals have been grown by solution method using zinc chloride as an additive and let it be called as GGZC. The grown gamma glycine crystals have been characterized by various studies. The results obtained from the various studies are presented and discussed in this paper.

## 2. Growth of Sample Crystals:

Single crystals of gamma glycine were grown by taking AR grade glycine and zinc chloride in 1: 0.5 molar ratios. Since it is grown using zinc chloride as an additive, let us call this crystal as GGZC crystal. The calculated quantities of reactants were dissolved double distilled water and the saturated solution was prepared and this solution was stirred for about 3 hr using a hot plate magnetic stirrer and it was filtered using high a quality filter paper to remove the unwanted dusts and other particles. Then the filtered solution was allowed for slow evaporation to obtain the crystals. It took about 30 days to get single crystals of GGZC. The sample was re-crystallized again to improve the purity. The grown crystal of GGZC is shown in the figure 1. It is observed that the grown crystal is transparent, colourless and non-hygroscopic.

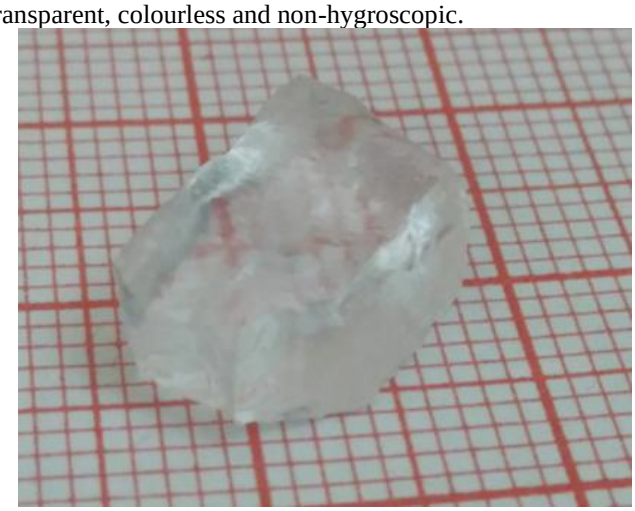

Figure 1: A harvested crystal of gamma glycine using zinc chloride as an additive (GGZC)

**3. Measurement of Solubility and Nucleation Parameters:**

Solubility study was carried out by gravimetric method using a hot-plate magnetic stirrer and a digital thermometer. A voltage regulator was attached with hot-plate magnetic stirrer in order to maintain the temperature constant. Also a constant temperature was used for maintaining the temperature the solution constant [9]. And then it was determined for the solution at different temperatures and the variation of solubility with temperature for GGZC crystal is shown in the figure 2. The obtained result shows that the solubility of GGZC crystal increases with increase of temperature and hence this sample has positive temperature coefficient of solubility.

Nucleation kinetic studies were performed for the grown crystals of undoped and doped gamma-glycine using a constant temperature bath (CTB). From these studies, the data of critical nucleation parameters were obtained and these data will be useful to understand the nucleation phenomena that are taking place in the supersaturated solutions of sample. The induction period ($\tau$) was measured by isothermal method at the selected supersaturation ratios viz., 1.2, 1.24, 1.28, 1.32 and 1.36. The plot of induction period versus supersaturation ratio for GGZC crystal was shown in the figure 3. The induction period for GGZC sample is noticed to be decreasing with increase of the supersaturation value. According classical theory of nucleation, the expression of the induction time ($\tau$) can be written for critical nucleus in terms of interfacial tension as $\ln \tau = -B + (16\pi\sigma^3 v^2 N^3 / [3R^3 T^3 (\ln S)^2]$ where B is a constant, R is the universal gas constant, S is the supersaturation ratio, v is the volume of unit cell, T is absolute temperature of the solution, $\sigma$ is the interfacial tension and N is the Avogadro's number. The Gibbs free energy change for critical nucleus is $\triangle G^* = mRT / [N (\ln S)^2]$ and the interfacial tension can be determined using the formula $\sigma^3 = [3 \ln\tau R^3 T^3 (\ln S)^2] / (16 \pi v^2 N)$. The critical radius is calculated using the relation $r^* = 2 \sigma v N / RT \ln S$ where where R is the universal gas constant and N is the Avagadro'snumber. The number of molecules in a critical nucleus is found using the equation $n = (4/3) (\pi/v) r^{*3}$. The nucleation rate (J) can be calculated using the equation $J = A \exp[-\Delta G^* / (kT)]$ where A is the pre-exponential factor and k is the Boltzmann's constant. Using these formulae, the values of critical nucleation parameters were calculated and these data are provided in the table 1. From the results it is observed that the nucleation parameters such as radius of critical nucleus, Gibbs free energy change, and number of molecules in the critical nucleus decrease with supersaturation ratio and the nucleation rate is observed to be increasing with the increase of supersaturation ratio. The calculated value of interfacial tension for GGZC crystal is $2.937 \times 10^{-3}$ J / $m^2$. The variables that affect the nucleation rate and nucleation parameters are pH, supersaturation, temperature and presenceof dopants and interfacial tension of the solution. Decrease in induction period is expected to increase the nucleation rate. With the optimized values of nucleation kinetic data, the growth of good quality crystals could be grown by solution method [10-12].

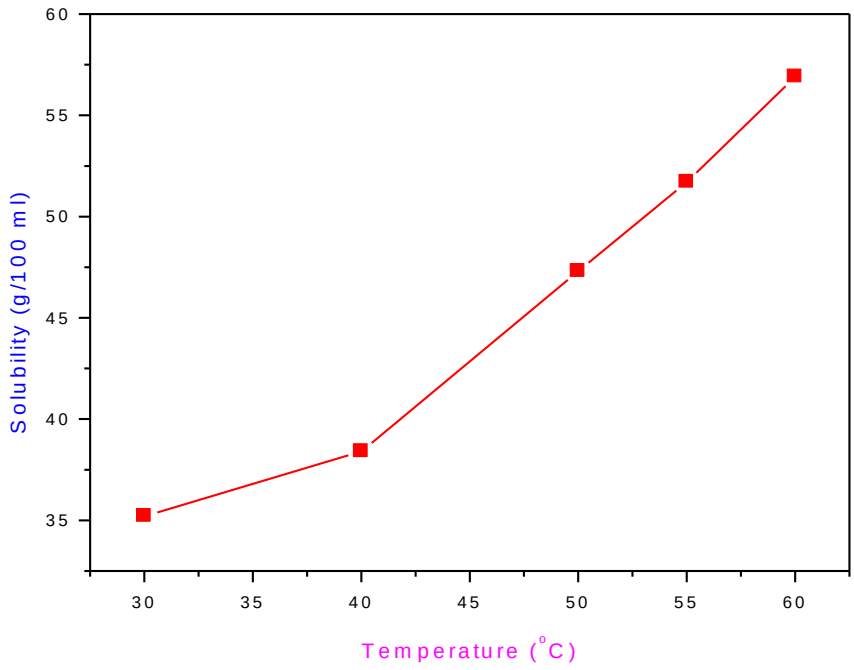


Figure 2: Solubility curve of GGZC crystal

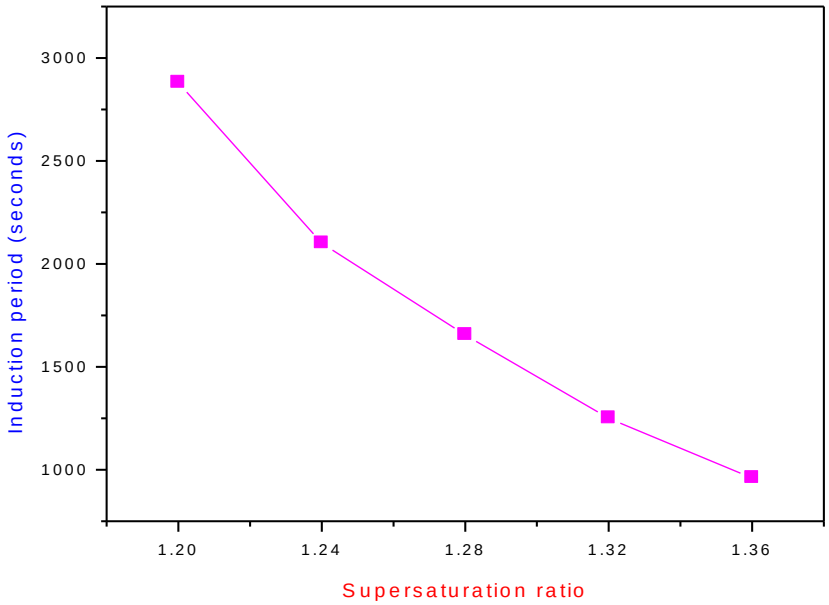


Figure 3: Plot of induction period versus supersaturation ratio for GGZC crystal

Table 1: Values of critical nucleation parameters for GGZC crystal

| Sample | S | $\Delta G^{*} \times 10^{-20}$ (joules) | $J \times 10^{24}$ nuclei/s/volume | $r^{*} \times 10^{-10}$ (m) | n | $\sigma \times 10^{-3}$ J/m$^2$ |
|---|---|---|---|---|---|---|
| GGZC | 1.2 | 16.349 | 1.036 | 10.237 | 19 | 2.937 |
| | 1.24 | 12.450 | 3.652 | 8.021 | 15 | |
| | 1.28 | 9.154 | 6.438 | 6.454 | 12 | |
| | 1.32 | 5.237 | 8.329 | 5.023 | 7 | |
| | 1.38 | 3.271 | 9.850 | 4.295 | 5 | |

**4. Single Crystal XRD Studies:**

A single crystal of GGZC was subjected to single crystal XRD studies using on ENRAF NONIUS CAD4 diffractometer with $MoK_{\alpha}$ radiation ($\lambda$ = 0.71073 Å) to identify the crystals structure. This instrument has a high versatility of the 4-circle goniometer combined with the sensitive and fastest CCD detector. It is a fine ultimate instrument for structure determination. The system comes with a Molybdenum fine focus sealed tube combined with a flat graphite monochromator. The obtained unit cell parameters for GGZC crystal are provided in the table 2. From the data, it is noticed that the grown crystal of GGZC crystallizes in hexagonal crystal structure. The number of molecules per unit cell is found to be 3. Refinement method here used was full matrix least square method.

Table 2: Single crystal XRD data for GGZC crystal

| Sample | Axial Lattice Parameters | Angular Lattice Parameters | Volume of the Unit Cell |
|---|---|---|---|
| GGZC crystal | a = 7.092 (4) Å<br>b = 7.092(4) Å<br>c = 5.501(3) Å | $\alpha = 90^{o}$<br>$\beta = 90^{o}$,<br>$\gamma = 120^{o}$ | 236.84 (2) Å$^3$ |

**5. Dielectric Measurement:**

The grown crystal of GGZC was cut, polished and subjected to the measurement of dielectric constant and loss factor and these values of crystalline samples were measured using a two probe arrangement and an LCR meter. It is known that if a dielectric like GGZC crystal is placed between the parallel plates of a capacitor, the capacitance increases and this increase of capacitance provides the basic experimental method for dielectric measurement [13, 14]. All the polarization mechanisms depend upon the variation of frequency. When an electric field acts on any matter the latter dissipates a certain quantity of electrical energy that transforms into heat energy. This phenomenon is commonly known as loss of power or energy loss. The amount of power loss in a dielectric under the action of the voltage applied to it is commonly known as dielectric loss. When considering dielectric loss we usually mean the loss precisely under an alternating voltage. The lower the dielectric loss the more effective is a dielectric material. The dielectric parameters like dielectric constant ($\varepsilon_r$) and dielectric loss factor (tan $\delta$) were measured at different frequencies and temperatures and these values are

given in the figures 4 and 5. The results show that both the dielectric constant and loss factor are more in the low frequency region and these values decrease with increase of frequency. Space charge polarization is responsible for more values of dielectric parameters in the low frequency region. The space charge contribution will depend on the purity and perfection of the material and it has noticeable influence in the low frequency region. Beyond $10^3$ Hz, the low value of dielectric constant at higher frequencies may be due to the loss of significance of the polarization gradually. The dielectric parameters are observed to be more when the temperature of the sample increases and this is due to increase of polarization phenomena, thermally generated charge carriers, expansion of crystal and hence increase of dipole moment. The values of AC conductivity of GGZC crystal were determined using the dielectric constant and loss factor and the variations of AC conductivity with frequency at temperatures 30 $^{o}$C and 50 $^{o}$C are shown in the figure 6. The AC conductivity of the grown crystal increases with increase in temperature and also it increases with increase of frequency. When the temperature of the crystal is increased, there is a possibility of weakening of bonds and this result in production of free charge carriers and this leads to an enhanced conductivity in the sample.

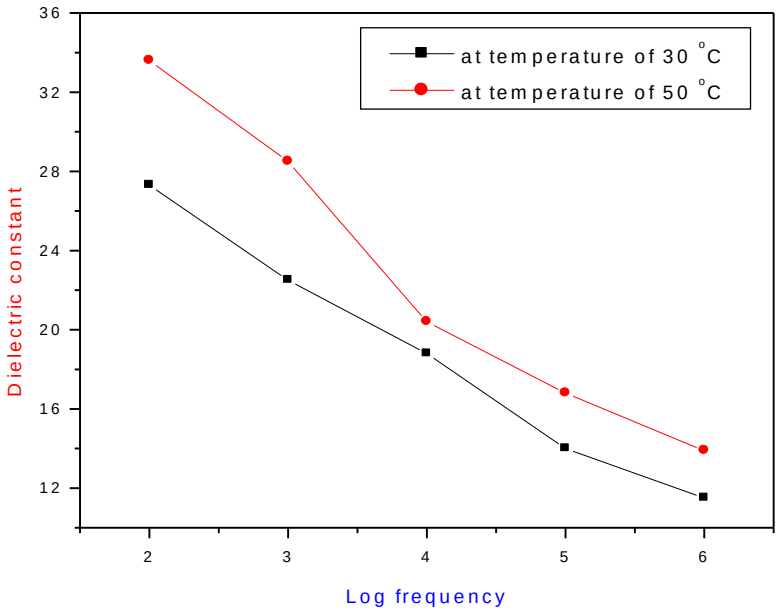


Figure 4: Variation of dielectric constant with frequency for GGZC crystal at different temperatures

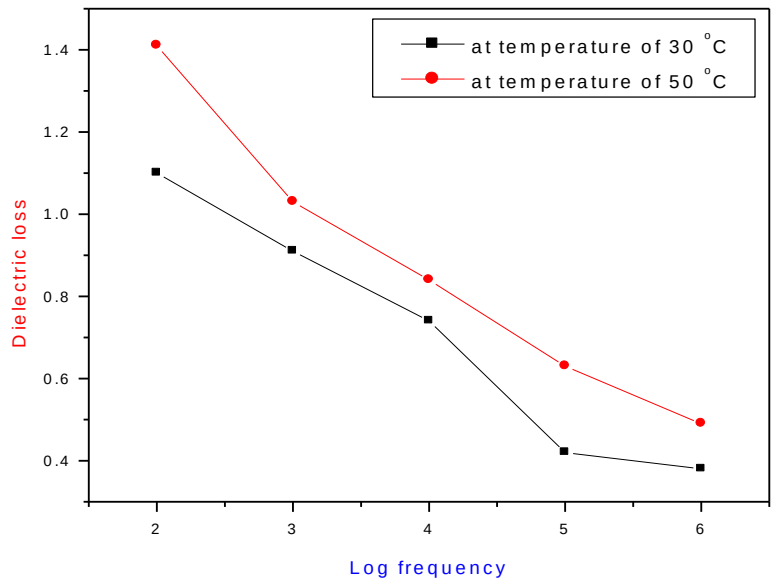


Figure 5: Variation of dielectric loss with frequency for GGZC crystal at different temperatures

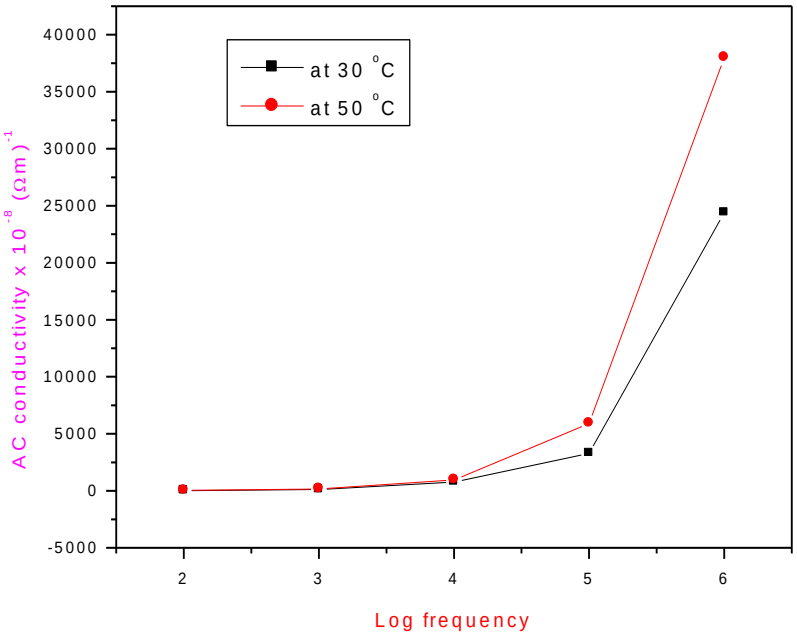


Figure 6: Plots of AC conductivity with frequency for GGZC crystal at different temperatures

**6. Micro Hardness and Work Hardening Coefficient:**

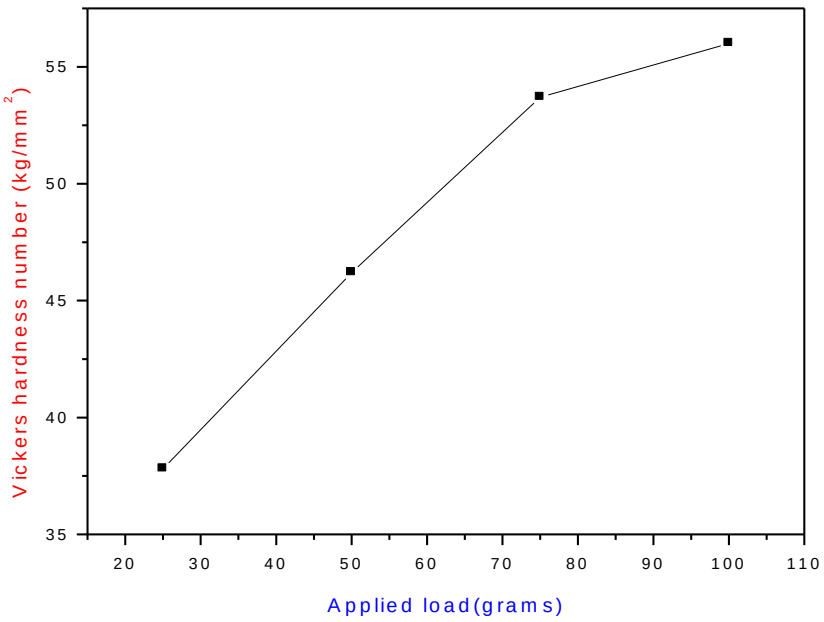


Fig.7: Plot of Vickers hardness number versus applied loaf for GGZC crystal

The important mechanical parameters are hardness, stiffness constant and yield strength etc. The mechanical strength of crystals was tested by carrying out micro hardness studies by applying different low loads. The hardness of a solid is defined as its resistance to local plastic/permanent deformation and the simplest way to obtain it is to press a hard indenter of known geometry and to divide the applied load (P) by the area (A) of the indentation produced. The hardness of a material is usually calculated from the measured value of indentation diagonal length (d) produced by an applied load [15, 16]. The mean diagonal length of the indentation or impression was measured using a LEITZ micro hardness tester, fitted with a Vickers diamond pyramidal indenter. The well polished crystal was placed on the platform of Vickers micro hardness tester and the loads of different magnitudes were applied in a fixed interval of time. Vickers micro hardness values were calculated by using the formula $H_v = 1.8544\ P/d^2$ kg/mm$^2$ where P is the applied load in kg, d is the mean

diagonal length of the indentation in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. The variation of Vickers hardness number with a load for GGZC crystal is shown in the diagram 7. For this sample, hardness is observed to be increasing with the increase of load and this is due to reverse indentation size effect and this can be explained qualitatively on the basis of depth of penetration of the indenter. In order to analyze the indentation size effect (ISE) in the hardness testing it needs to fit the experimental data according to the Meyer's law which correlates the applied load to the resulting indentation size (d) and is given by $P= a d^n$ where A is a constant parameter for a given material and n is the Meyer's index or work hardening coefficient. These parameters were derived from the curve fitting of experimental results of indentation. The plot of log P versus log d GGZC crystal is shown in the figure 8. From this plot, the value of the slope is obtained as 2.895 and this is equal to the work hardening coefficient.

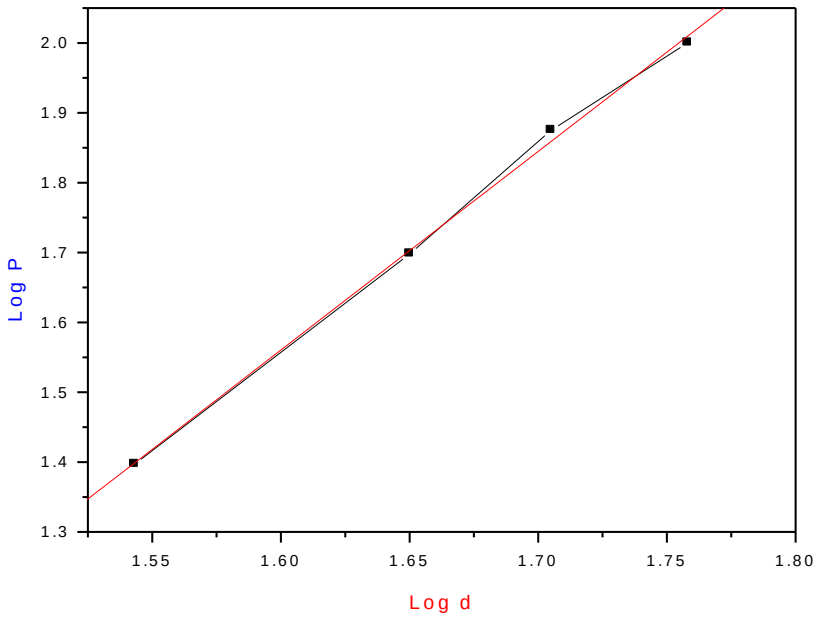


Figure 8: Plot of log P versus log d GGZC crystal

**7. SHG Measurement:**

The second harmonic generation (SHG) behavior of the powdered material was tested using the Kurtz and Perry method [17]. The grown crystals were ground into a homogenous powder and a Q-switched Nd:YAG laser beam of wavelength 1064 nm with an input energy of 0.68 J/pulse, pulse width of 6 ns and repetition rate of 10 Hz was directed on the sample. The SHG output of wavelength 532 nm (green light) was detected by the photomultiplier tube (PMT). The powdered material of potassium dihydrogen phosphate (KDP) was used in the same experiment as a reference material. It is to be mentioned here that the grain size of KDP is almost kept as same as that of the grown sample. The value of relative SHG efficiency of GGZC crystal is found to be 1.58 times that of KDP.

**8. Linear Optical Parameters:**

The grown crystal of GGZC was cut and polished and the specimen of 1.5 mm thick was subjected to transmission measurement using a spectrophotometer in the spectral region of 200–1100 nm. The recorded transmittance spectrum of the sample is shown in the figure 9. From the transmittance spectrum it is evident that the crystal of GGZC has the UV lower cut-off wavelength at 226 nm and the crystal is transparent in the entire visible region and it suggests that the crystal is suitable for second harmonic generation. The absorbance was determined using the relation A= log (1/T) where T is the transmittance. Using the values of absorbance, the absorption coefficient ($\alpha$) was calculated. The reflectance values were determined using the following formula

$$R = \frac{1 \pm \sqrt{1 - e^{(-\alpha d)} + e^{(\alpha d)}}}{1 + e^{(-\alpha d)}}$$

Where d is the thickness of the crystal [17-19]. The absorbance and reflectance spectra of GGZC crystal are shown in the figures 10 and 11. The results indicate that the values of absorbance and reflectance are low in visible region and these values are high at band gap value. The low absorption and low reflectance make the sample as the prominent material for antireflection coating in solar thermal devices and nonlinear optical

applications. The energy dependence of absorption coefficient (α) suggests the occurrence of direct band gap of the crystal obeying the following relation

$$\propto h\nu = A\sqrt{(h\nu - E_g)}$$

where $E_g$ is the optical band gap energy of the crystal, h is the Planck's constant and A is a constant. The plot of variation of $(\alpha h\upsilon)^2$ versus $h\upsilon$ is is shown in the figure 12. From this Tauc's plot, the optical band gap is obtained to be 5.5 eV.

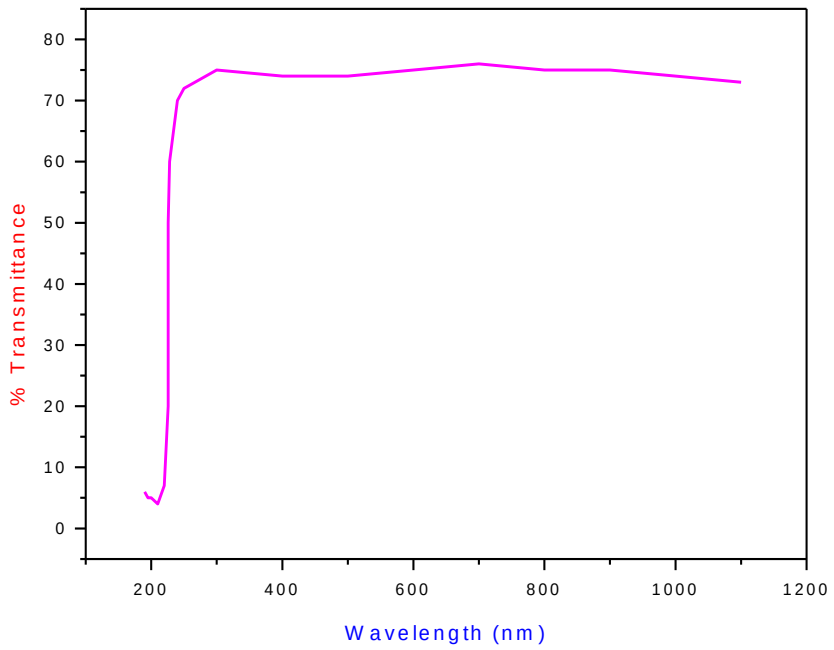


Figure 9: Transmittance spectrum of GGZC crystal

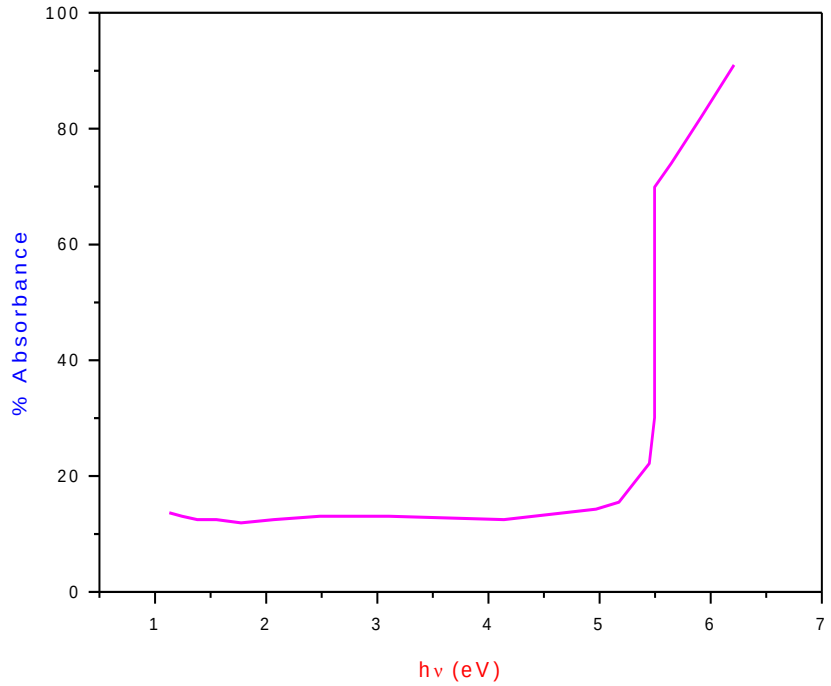


Figure 10: The absorbance spectrum of GGZC crystal.

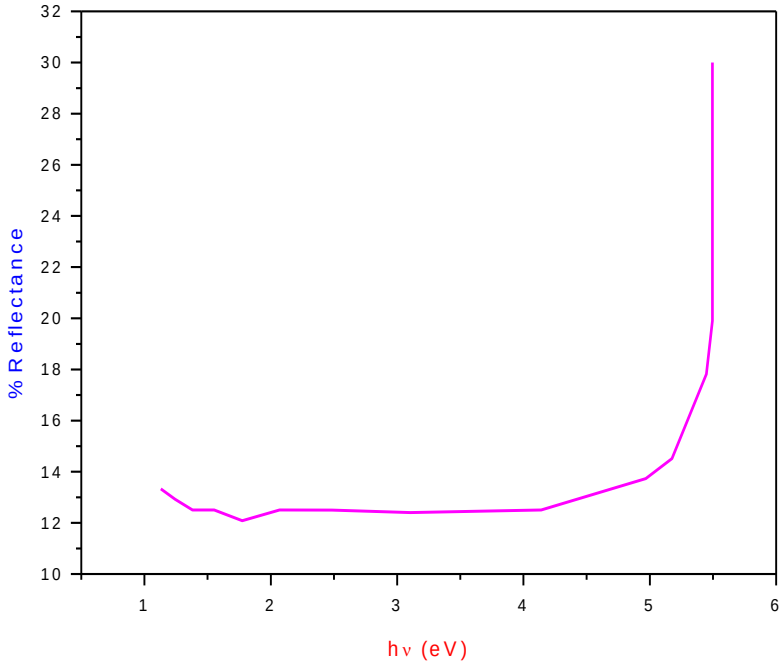


Figure 11: The reflectance spectrum of GGZC crystal.

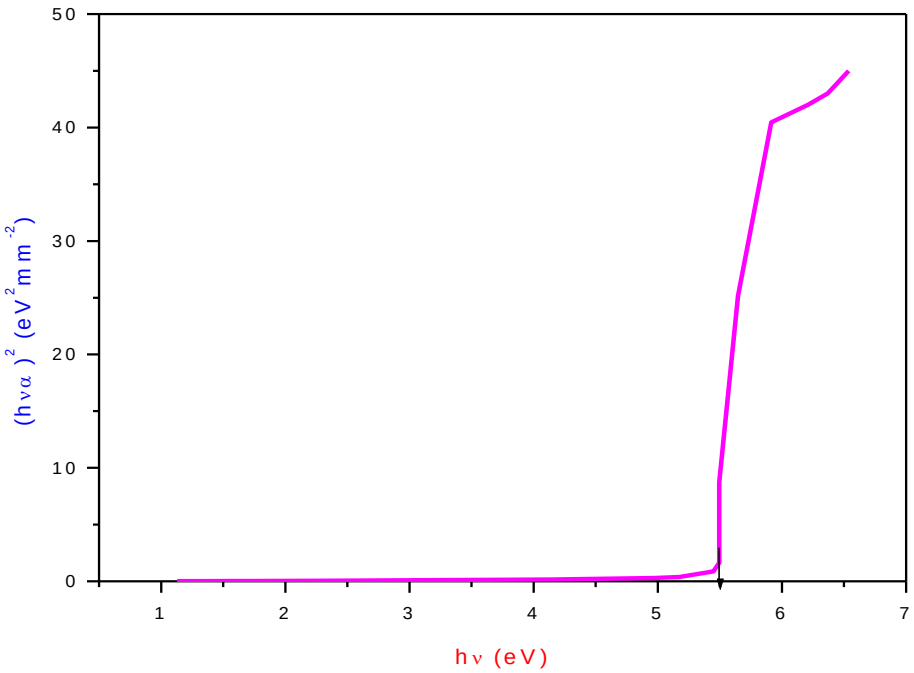


Figure 12: Tauc's plot for GGZC crystal

**9. LDT Studies:**

Laser damage threshold is an important material parameter, the knowledge of which is essential for using the crystal as an NLO element in various applications involving large laser input power like frequency doubling, optical parametric processes, etc. In fact, laser induced damage in optical materials remains the limiting factor in the development of high power laser systems and optoelectronic devices. The damage in NLO materials like KDP and Deuterated Potassium Phosphate (DKDP), manifests itself as micro-cavity whose sizes are insensitive to the wavelength of the laser beam, suggesting a wavelength independent absorption mechanism

[20]. Laser damage measurement was carried out on the crystal at 1064 nm. The laser damage threshold depends on pulse duration, focal spot geometry, sample quality, previous history of the sample, experimental technique employed etc. Using a Q-switched Nd:YAG laser of wavelength 1064 nm and pulse width 10 ns was used for the measurement of LDT value. The energy of the laser beam was measured by Coherent energy/power meter (Model No. EPM 200). LDT value is determined using the formula $P= E/ \tau\pi r^2$ where $\tau$ is the pulse width in ns, E is the input energy in mJ, r is radius of the spot in mm. The obtained value of LDT of the grown GGZC crystal is 0.528 GW/cm$^2$.

**10. Density Measurement:**

The density of crystals was determined by floatation method. In this experiment, carbon tetrachloride and bromoform were used. After mixing the carbon tetrachloride and bromoform in a suitable proportion in a specific gravity bottle, a small piece of crystal was immersed in a mixture of the liquids. When the sample was attained in a state of mechanical equilibrium, the density of the crystal would be equal to the density of mixture of liquids. The density was calculated using the relation $\rho= w_3 – w_1 / w_2 – w_1$ where $w_1$ is the weight of empty specific gravity bottle, $w_2$ is the weight of the specific gravity bottle with full of water, and $w_3$ is the weight of the specific gravity bottle full of the mixture of carbon tetrachloride and bromoform. The measured value of density of GGZC crystal is 1.657 g/cc.

**11. Conclusions:**

Gamma glycine crystals were grown from the aqueous solutions of zinc chloride and the grown crystals were characterized by various studies. From XRD studies, gamma glycine crystal crystallizes in hexagonal crystal structure. The grown crystal has positive temperature coefficients of solubility ad critical nucleation parameters were evaluated. The dielectric parameters of the GGZC crystal are found to be decreasing with increase of frequency. The work hardening coefficient of GGZC crystal was found to be and the optical band gap of the crystal is obtained to be 5.5 eV from the Tauc's plot. The LDT value of GGZC crystal was estimated to be 0.528 GW/cm$^2$ and the density of the sample was found to be 1.657 g/cc. GGZC crystal is second harmonic generator and hence it can generate visible laser light.

**12. Acknowledgement:**

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