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SECOND ORDER NLO, THIRD ORDER NLO AND OTHER STUDIES OF GAMMA GLYCINE CRYSTALS GROWN USING ZINC ACETATE AS AN ADDITIVE

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Abstract:

Single crystals of gamma glycine were grown by slow evaporation method using zinc acetate as an additive. The grown crystals were subjected to X-ray diffraction technique to determine the lattice parameters. Linear optical constants such as linear absorption coefficient, transmittance, reflectance, optical band gap etc have been determined for grown sample. Second order and third order nonlinear optical (NLO) studies have been carried out to find SHG efficiency, nonlinear absorption coefficient, nonlinear refractive index and nonlinear optical susceptibility of the grown crystal. Photoconductivity was measured for the sample at different applied electric fields. Density of the sample was measured by floatation method and the results are discussed.

Key Words: Gamma Glycine, Single Crystal, Solution Method, XRD, NLO; SHG, Third Order NLO & Photoconductivity

1. Introduction:

Amino acids are the promising materials for variety of applications as they contain proton donor carboxylic acid group and the proton acceptor amine group in them. Among the amino acids, glycine is the simplest molecule and it has a lot of potential applications. If glycine is mixed with different organic and inorganic materials, it forms novel materials for nonlinear optical (NLO) applications [1-5]. Glycine (NH_2CH_2COOH) is the simplest amino acid that crystallizes in six different forms viz. α, β, γ, δ, ε and β'-forms. Among the six forms of glycine, γ-glycine (gamma-glycine) exhibits strong piezoelectric and NLO effect [6]. Since γ-glycine crystallizes in a non-centrosymmetric space group $P3_2$, it possesses excellent NLO properties [7]. The first report on the details of γ-glycine was published in the literature in 1958 [8]. Recently, growth and various studies of γ-glycine crystals have been reported by many researchers [9-11] and it is observed that γ-glycine single crystals have been grown using additives such as potassium chloride, sodium chloride, lithium chloride, potassium bromide etc. In this work, γ-glycine crystal (gamma glycine) is formed using zinc acetate as an additive and let this sample be called as GGZA crystal. GGZA crystals were grown by low temperature solution method with slow evaporation technique. The grown crystals have been characterized by various studies like XRD, linear optical studies, nonlinear optical studies, density measurement, solubility measurement and photoconductivity measurement etc.

2. Crystal Growth and Solubility:

Gamma glycine crystals were grown using alpha-glycine and zinc acetate in 1:1 molar ratio in water as the solvent. Slow evaporation method was followed to grow the crystals of gamma glycine. The calculated amounts reactants were dissolved in water and the solution was stirred well using a magnetic stirrer. The saturated solution was kept in a growth vessel and after 4 or 5 days and super saturation stage was reached. Initially, small crystal nuclei were formed in the supersaturated solution and they grew into big-sized crystals. After 30 days, transparent and colourless crystals of gamma glycine have been formed. Re-crystallization was also carried out to get better quality crystals. The harvested crystals of gamma glycine are shown in the figure 1.

Figure 1: A grown crystal of GGZA

The solubility of the crystal of GGZA was measured in the temperature range 30-60 ^{o}C. A volume of 100 ml of water was taken in a container and the grown crystal was added. The temperature of the solution was maintained above the chosen constant temperature and continuously stirred using a magnetic stirrer to ensure homogeneous temperature and concentration throughout the entire region of the solution. Once the saturation was reached, the equilibrium concentration of the solute was analyzed gravimetrically. The experiment was carried out for various temperatures from room temperature to 60 °C in steps of 10 °C and the solubility curve was drawn and it is presented in the Fig.2. The solubility curve indicates the GGZA crystal has positive temperature coefficient of solubility and it shows three regions viz. saturation region is along the solubility curve, super saturation region is above the solubility curve and under saturation region is below the solubility curve. Using these results, the saturated and supersaturated solutions of the sample could be prepared at a particular temperature and nucleation kinetic studies and growth of crystals could be carried out [12].

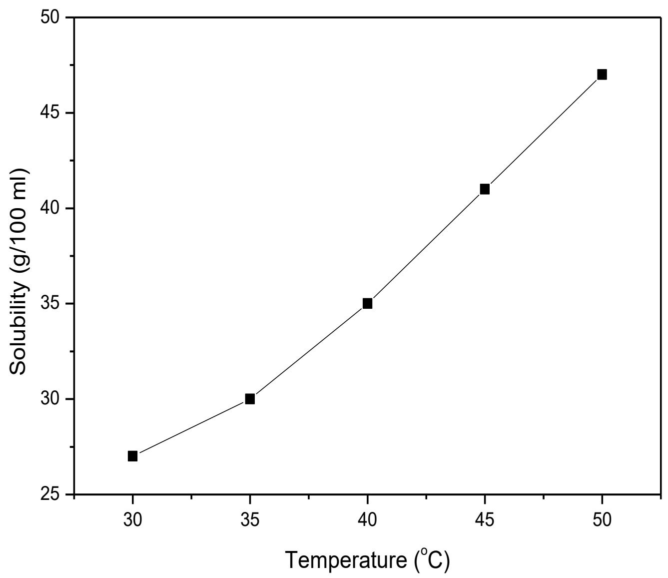

Figure 2: Solubility curve of GGZA crystal

3. Crystal Structure:

A good quality and small crystal of gamma glycine was used for the single crystal XRD study. The obtained crystallographic data for the grown GGZA crystal are a=7.097(2) Å, b=7.097(2) Å , c= 5.481(2) Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$ and V=239.06(4) $Å^3$. From the results, it is observed that the grown crystal crystallizes in hexagonal crystal system [13].

4. Linear Optical Properties:

To determine the transparency range of the grown GGZA crystal, UV-vis transmittance spectrum was recorded and it is shown in Fig.3. Optically clear single crystal of thickness 2 mm was used for this study. The cut- off wavelength of the crystal occurs at 225 nm. From the figure, it shows that the crystal was optically transparent in the wavelength range from 300 to 1100 nm and it is a feature that promotes possible optical applications in NLO devices. The crystal has sufficient transmission in the visible and IR region. The optical absorption coefficient (α) was determined using following formula $\alpha = (2.303 \log (1/T)) / t$ where T is the transmittance and t is the thickness of the crystal. The variation of absorption coefficient with wavelength for GGZA crystal is shown in the figure 4. The values of absorption coefficient for the sample are observed to be low in UV-visible region and hence it is good sample for NLO applications. The reflectance of the sample can be determined using the following formula [14]. Here d is the thickness of the sample. The reflectance spectrum of the sample is presented in the figure 5. The result shows that the reflectance is low in the entire visible region and it is high at the cut-off wavelength.

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

The relation between the optical band gap, absorption coefficient and energy of the incident photon is given by $\alpha h\nu = B(h\nu - E_g)^r$ where E_g is the optical energy gap, B is a constant and r is an index which can be assumed to have values of ½,3/2, 2,and 3 depending on the nature of the electronic transition responsible for the absorption. r =1/2 for allowed direct transition, r=3/2 for forbidden direct transition, with r=2 refers to indirect allowed transitions and r=3 refer to indirect forbidden transition. Tauc's plot [15] is drawn and is shown in the figure 6. From the Tauc's plot, the optical band gap of GGZA crystal is obtained to be 5.48 eV.

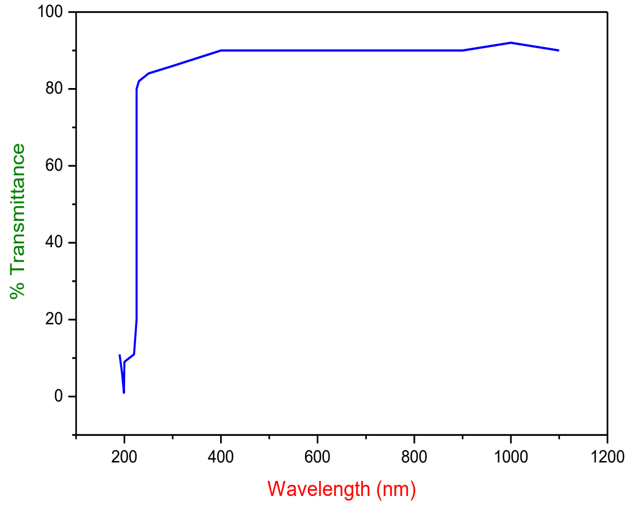

Figure 3: Optical transmittance spectrum of GGZA crystal

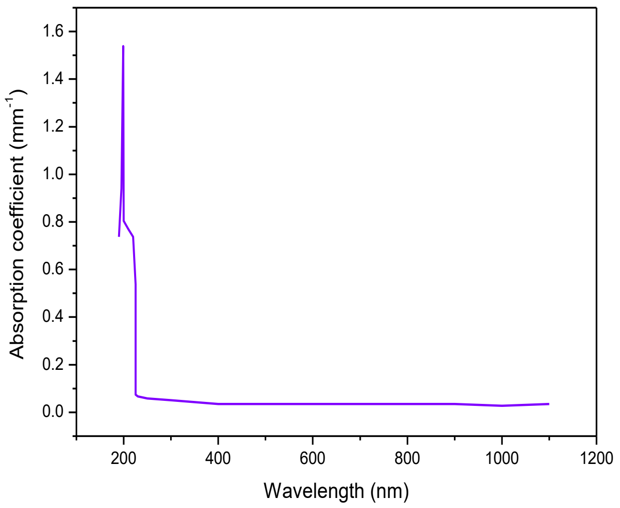

Figure 4: Variation of absorption coefficient with wavelength for GGZA crystal

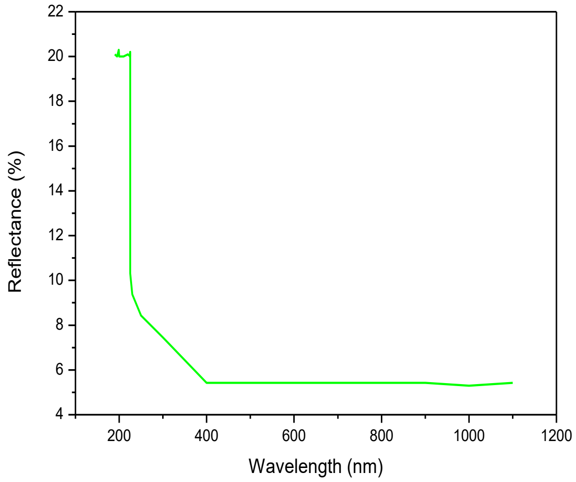

Figure 5: Reflectance spectrum of GGZA crystal

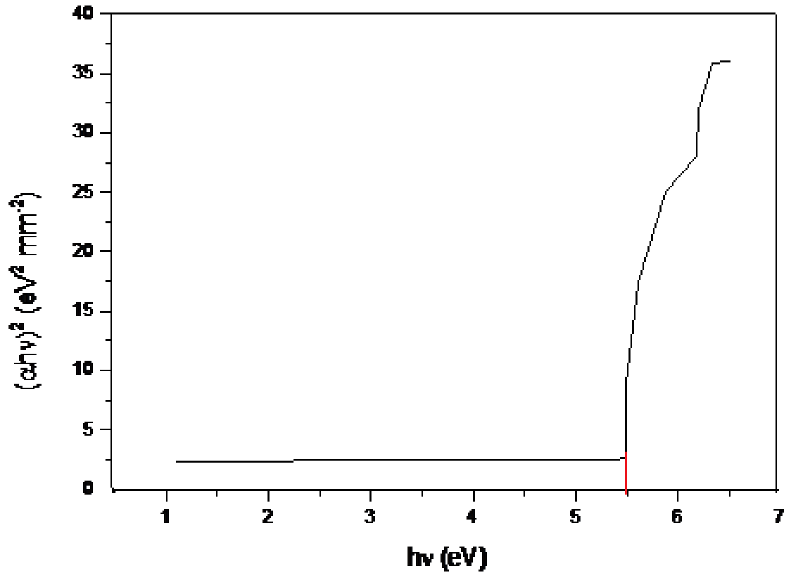

Figure 6: Tauc's plot for GGZA crystal

5. Second Order NLO Properties:

Second harmonic generation (SHG) is also called a frequency doubling in which photons interacting with a nonlinear material are combined to form new photons with twice the frequency of the initial photons. The study of NLO efficiency has been carried out by modified experimental set up of Kurtz and Perry [16]. The grown crystal GGZA was ground into a homogenous powder and this was used in this experiment. An intensity of Nd:YAG laser (λ=1064 nm) with input pulse of 1.9 mJ was passed through an IR reflector and then directed on the micro crystalline powdered sample packed in a capillary tube. The SHG behavior was confirmed from the output of the laser beam having green light emission. The measured SHG efficiency of GGZA crystal is 3.66 times greater than that of KDP crystal.

6. Photoconductivity Measurement:

Dark conductivity and photoconductivity of the sample have been measured using a photoconductivity set-up with a Keithley 485 picoammeter. By connecting the sample in series to a DC power supply and a picoammeter, the dark conductivity of the sample was measured at different applied voltages. In order to measure the photo current, the sample was illuminated with a halogen lamp (100 W) by focusing a spot of light on the sample with the help of a convex lens. The DC input was increased in the same range as done in the previous case and the corresponding photocurrents were measured. The variations of dark and photo currents for GGZA crystal are shown in the figure 7. It is noticed that the values of dark current and photo current increase with increase of applied electric field. It is observed that the photo current is more than dark current and hence the sample has positive photoconductivity. The positive photoconductivity of the sample is due to increase of charge carriers when light is passed onto the sample.

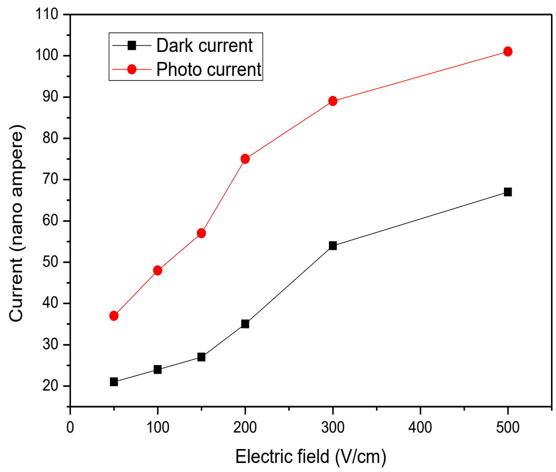

Figure 7: Variation of photocurrent and dark current with the applied field for GGZA crystal

7. Measurement of Density of Crystal:

Flotation method was used to find the density of crystals. A high density liquid like bromoform (density: 2.89 g/cc) and a low density liquid like xylene (density: 0.99 g/cc) were used for this experiment. After mixing the liquids bromoform and xylene in suitable proportion in a specific gravity bottle, small piece of crystal was immersed in the mixture of liquids. When the sample attains 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 $\rho = (W_3 - W_1) / (W_1 - W_2)$ where W_1 is the weight of the 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 specific gravity bottle with full of mixture of bromoform and xylene. The obtained value of density of GGZA crystal is 1.683 g/cc.

8. Third order NLO Studies:

Z-scan technique is used to carry out the third order nonlinear optical (NLO) studies for crystalline materials. It is a simple and sensitive single beam technique for measuring the change in phase induced on a laser beam upon propagation through a nonlinear material. There are two modes in the Z-scan analysis namely, open and closed aperture modes. In the closed aperture method, an aperture is placed in front of the detector to prevent some of the light from reaching the detector. Hence, only the central region of the cone of light reaches the detector. The detector is now sensitive to any focusing or defocusing that a sample may induce. In the open aperture method, the aperture is removed to allow all the light to reach the detector and hence sets the normalized transmittance. This method is used in order to measure the nonlinear absorption which arises due to absorption of two photons [17,18]. A crystal of thickness of 1.2 mm and He-Ne laser of wavelength 632.8 nm were used in this technique. Measurements of the normalized transmittance by varying the sample position (Z) have been made for the grown crystals in open and closed aperture modes. The obtained open and closed aperture Z-scan curves for GGZA sample are presented in the figures 8 and 9. In the closed Z-scan curve, it is noticed that there is a transmittance peak followed by a transmittance valley. The transmission difference between peak and valley ($\Delta T_{p\text{-}v}$) is determined from closed aperture curves. The phase shift ($\Delta\phi$) and the linear transmittance aperture (S) and the third-order nonlinear refractive index (n_2) can be found using the following equations. Using the open aperture curves, the nonlinear absorption coefficient (β) can be calculated.

The transmission difference between peak and valley ($\Delta T_{p\text{-}v}$) is written in terms of phase shift.

$$\Delta T_{p-v} = 0.406\,(1-s)^{0.25}|\Delta\phi|$$

Linear transmittance aperture (S) is calculated using the relation

$$S = 1 - \exp\left(\frac{-2r_a^2}{\omega_a^2}\right)$$

where r_a is the radius of the aperture and ω_a is the beam radius at the aperture. The third-order nonlinear refractive index (n_2) of the crystal was calculated by following the relation.

$$n_2 = \Delta\phi / (k\, I_o\, L_{eff})$$

where I_o is the intensity of the laser beam at the focus (Z = 0) and $k = 2\pi/\lambda$ (λ is the wavelength of laser beam).

The effective thickness can be calculated using the relation

$$L_{eff} = [1-\exp(-\alpha L)] / \alpha$$

where α is the linear absorption coefficient and L is the thickness of the sample. The nonlinear absorption coefficient (β) can be calculated using the following relation

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}$$

where ΔT is the one peak value in the open aperture Z-scan curve. The equations for real and imaginary parts of the third order nonlinear optical suceptibility ($\chi^{(3)}$) are given below.

Real part of $\chi^{(3)} = (10^{-4}\varepsilon_o c^2 n_o^2 n_2) / \pi$ (esu)

Imaginary part of $\chi^{(3)} = (10^{-2}\varepsilon_o c^2 n_o^2 \lambda \beta) / 4\pi^2$ (esu)

Absolute value of $\chi^{(3)} = [\{\text{Real part of } \chi^{(3)}\}^2 + \{\text{Imaginary part of } \chi^{(3)}\}^2]^{1/2}$ (esu).

Here ε_o is the vacuum permitivity, n_o is the linear refractive index of the sample and c is the velocity of the light in vacuum. Using the above equations, nonlinear refractive index, third order susceptibility and the nonlinear absorption coefficient of the crystals could be determined [19,20]. It is reported that the negative nonlinear refractive index of the sample shows transmittance peak followed by transmittance valley, but the positive nonlinear refractive index shows the transmittance valley followed by transmittance peak. It is observed from the results that the have negative nonlinear refractive index because the sample shows transmittance peak followed by transmittance valley and therefore the sample shows the self-defocusing behaviour. The obtained Z-scan data for GGZA crystal are given in the table 1.

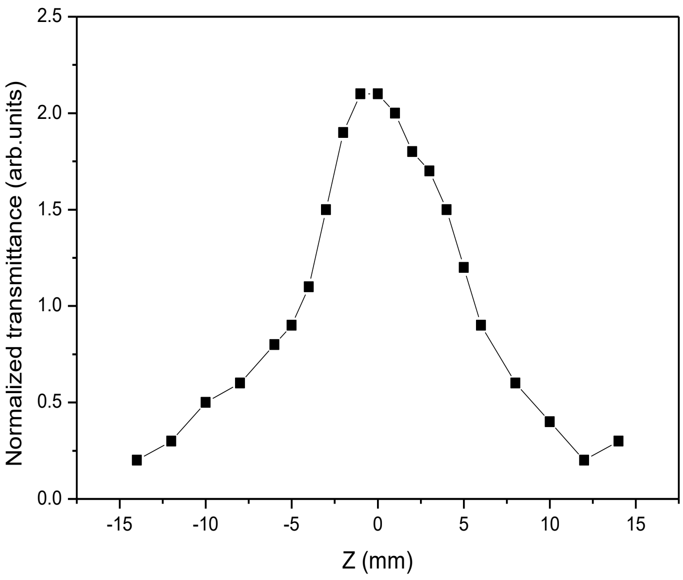

Figure 8: Z-scan open aperture curve for GGZA crystal

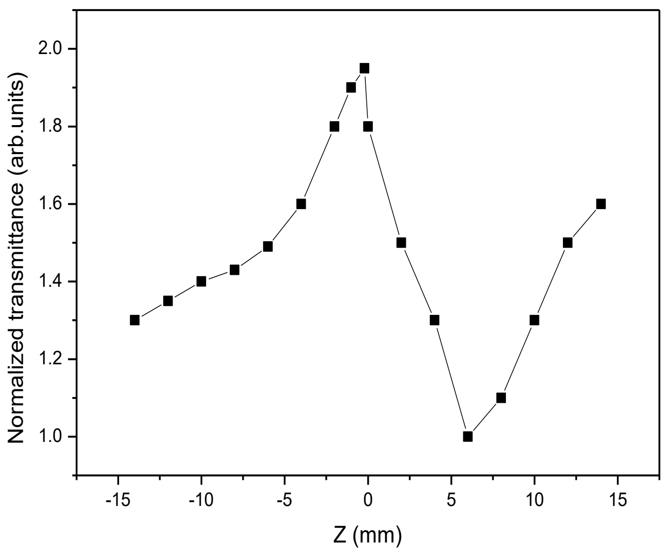

Figure 9: Z-scan closed aperture curve for GGZA crystal

Table 1: Z-scan data for GGZA crystal

Wave length of the laser used (λ)	632.8 nm
Focal length of the lens	22.5 cm
Incident intensity at the focus (Z = 0)	2 MW/cm^2
Nonlinear refractive index (n_2)	-2.468× 10^{-11} m^{2}/W
Nonlinear absorption coefficient (β)	3.260 ×10^{-4} m/W
The third order nonlinear susceptibility	4.785×10^{-7} esu

9. Conclusions:

Solution method was adopted to carry out the single crystals of gamma glycine using zinc acetate as an additive. XRD study reveals that the grown crystal of GGZA crystallizes in hexagonal crystal system. Transmittance spectrum, reflectance spectrum, absorption spectrum of the sample have been obtained to obtain linear optical properties. SHG efficiency of the sample is 3.66 times that of KDP. Density of the grown crystal was found to be 1.683 g/cc. The grown crystal of GGZA has the positive conductivity properties. Z-scan studies were done to find the third order NLO properties.

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