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Growth, optical, thermal and electrical properties of nonlinear optical γ-glycine single crystal

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Single crystal growth of γ-glycine has been grown by solution growth technique. The lattice parameters and crystal system of the grown crystals were confirmed by single crystal X-ray diffraction analysis. The functional groups present in the grown crystal were identified by FT-IR spectral analysis. The optical property of the γ-glycine crystal is studied by UV-Visible spectrum. Optical constants such as band gap, refractive index, extinction coefficient and electrical susceptibility were calculated to analyze the optical property from UV-Visible spectrum. The thermal analyses revealed good thermal stability of the material thus proving its suitability for NLO applications. The second harmonic generation (SHG) test has been confirmed by the Kurtz powder test. The dielectric studies of γ-glycine crystal were studied in the different frequency and different temperatures. Photoconductivity measurements were carried out in order to reveal the negative photoconductivity of the γ-glycine crystal.

Key words: Nonlinear optical (NLO), single x-ray diffraction, UV-visible spectrum, second-harmonic generation (SHG), dielectric constant, dielectric loss.

INTRODUCTION

Single crystal growth has a prominent role in the present era of rapid scientific and technical advancement, whereas the application of crystals has unbounded limits. Single crystal may be briefed out as the ordered array of atoms in repeated groups that shows characteristic symmetry elements by which the entire block of the material is built. Lots of basic science focuses the property of the crystal which depends on the production of high quality crystals with reasonable size. Nonlinear optical (NLO) materials have come upon the materials science scene and are being studied by many research groups around the world. These materials operate on light in a way very analogous to the way of semiconductors which operate on electrons to produce very fast electronic switching and computing circuits. Amino acids have proton donor carboxylic acid (COO⁻) groups and proton acceptor amino (NH_2) groups. The importance of amino acids in NLO applications is due to the fact that all amino acids have a chiral symmetry and crystallize in noncentro-symmetric space groups. Amino acids and their complexes belong to a family of organic materials that have NLO applications (Prasad and

Williams, 1991; Chemla and Zyss, 1987; Sagadevan,2014; Sagadevan, 2014).

Aminoacid family crystals are gaining importance as highly feasible second order NLO materials. The α-aminoacid, glycine forms addition compounds with a number of inorganic materials, especially inorganic acids. Complexes of glycine with inorganic acid /salts are promising materials for optical second harmonic generation as they tend to combine advantages of the organic aminoacid with that of the inorganic salt. These materials exhibit promising structural background in view of their zwitterionic, protonated forms and structural stabilization with hydrogen bonding. These factors account for the delocalization and corresponding enhancement in second order NLO activity. The carboxylic acid group present in the γ-glycine donates its proton to the amino group to form a salt of structure $CH_3CH\ COO^-\ NH_3^+$. Thus in the solid state, γ-glycine exist as a dipolar ion in which carboxyl group is presented as carboxylate ion and amino group is presented as ammonium ion. Due to this dipolar nature, it has a high melting point. The growth mechanism of γ-glycine is not a standard one and it depends on parameters such as impurities, solvent and pH of the growth medium. The γ-glycine, because its non-centrosymmetry structure makes it a suitable candidate for piezoelectric and nonlinear optical applications. The present investigation deals with the growth of γ-glycine single crystal that was grown by slow evaporation technique. The grown crystals were characterized by single crystal X-ray analysis, FTIR, UV spectral analysis, thermal, dielectric, SHG, and photoconductivity measurements. The results of these studies have been discussed in this paper in detail.

Crystal growth of γ-glycine

Glycine (grade AR) and hydrogen fluoride (grade AR) were used as such without further purification. Glycine and hydrogen fluoride were mixed in an equimolar ratio (1:1). The solutions of glycine and hydrogen fluoride were mixed together and the resulting solution was stirred for 5 h, to get a homogenous mixture. The solution was filtered to remove the solid impurities in the mother solution using an ultrapore filter and kept undisturbed in room temperature. Due to slow evaporation of the solution, spontaneous nucleation occurs and these are grown into crystals of comparable size. The synthesized salt was then purified by repeated crystallization. Transparent colourless crystals were harvested in a period of 2 weeks. Figure 1 shows as-grown crystals of γ-glycine.

RESULTS AND DISCUSSION

Single-crystal x-ray diffraction

The single-crystal X-ray diffraction analysis of the grown crystals was carried out to identify the cell parameters. From the single crystal X-ray diffraction analysis, we found that the lattice parameters were calculated to be a = 7.023 Å, b = 7.024 Å, c = 5.412 Å. It exhibits hexagonal crystal system with the space group of $P3_1$.The ORTEP representation of the molecule with atom numbering scheme is shown in Figure 2 and the packing diagram is shown in Figure 3. From the structural point of view, in γ-glycine, the carboxylate oxygen is electrostatically bonded by the hydrogen atom of NH_3 and forms strong H-bond along the c-axis. The crystal structure packing diagram shows that there are three molecules present per unit cell.

FTIR spectral analysis

In order to analyze qualitatively, the presence of functional groups in γ-glycine, Fourier transform infrared (FTIR) spectrum was recorded in the range 450 and 4000 cm^{-1} using Bruker IFS 66V. The sample used was in pellet form embedded with KBr phase. The middle infrared FTIR spectrum of γ-glycine is shown in Figure 4. There is a broad envelope between 2200 and 3600 cm^{-1}, and this includes NH vibrations at 3113 cm^{-1}, CH vibrations at 2892 cm^{-1} and NH vibrations at 2602 cm^{-1}. The OH vibrations are not clearly seen and hence the amino acid is zwitterionic. The sharp peak at 2168 cm^{-1} is due to the asymmetrical NH bend and torsional oscillation of NH_3^+ is seen at 503 cm^{-1}. The peak at 1594 cm^{-1} is broad and it is due to COO^- stretch and asymmetric NH_3^+ bend is seen at 1488 cm^{-1}. The symmetrical COO^- stretch occurs at 1393 cm^{-1}. The peak at 1335 cm^{-1} is due to CH bend.

UV-Vis-NIR spectral analysis

The UV-Visible spectrum of γ-glycine single crystal was recorded in the wavelength region 200 to 1000 nm and it is shown in Figure 5. For optical fabrications, the crystal should be highly transparent in the considered region of wavelength (Suresh and Arivuoli, 2011; Koteeswari and Sagadevan, 2014). The favorable transmittance of the crystal in the entire visible region suggests its suitability for second harmonic generation (Suresh and Anand, 2012). The UV absorption edge for the grown crystal was observed to be around 315 nm. The dependence of optical absorption coefficient on photon energy helps to study the band structure and type of transition of electrons (Sagadevan, 2014) (Figure 6). There is no absorption of light to an appreciable extent in the visible range of the electromagnetic spectrum, which is the intrinsic property of all the amino acids. It should be pointed out that γ-glycine presents a good optical transparency at the wavelength of source commonly used in SHG devices such as Nd: YAG laser. The optical absorption coefficient (α) was calculated from
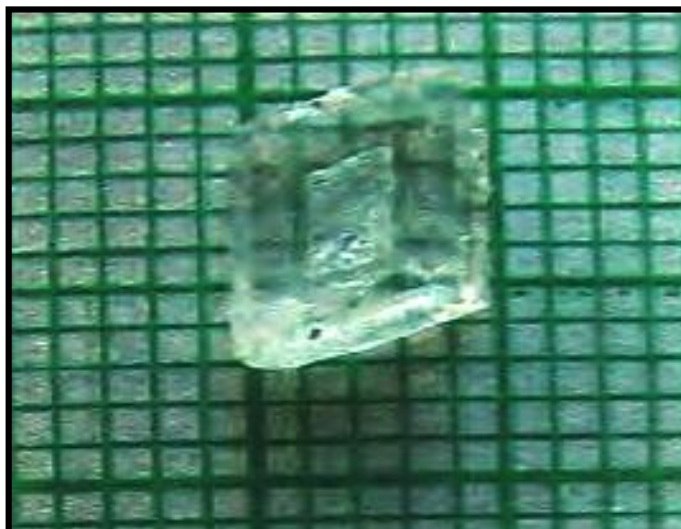
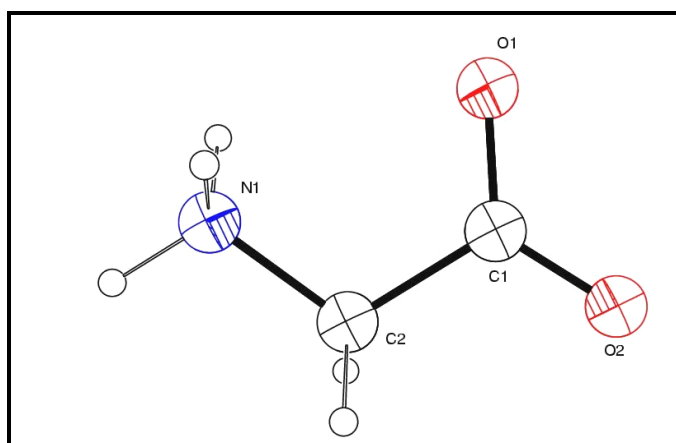**Figure 1.** Photograph of grown γ-glycine single crystal.

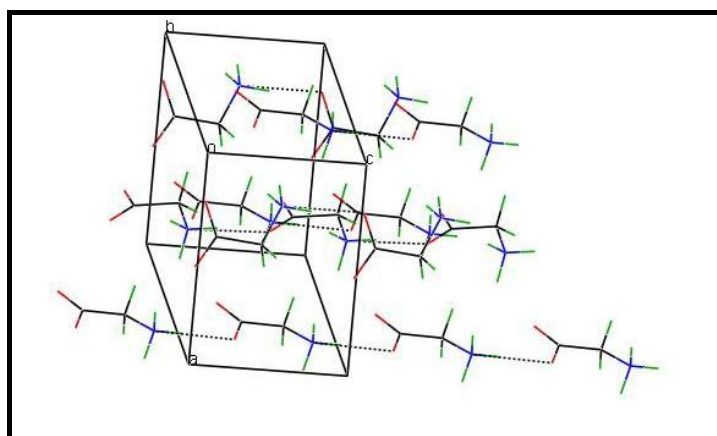**Figure 2.** ORTEP representation of γ-glycine crystals.

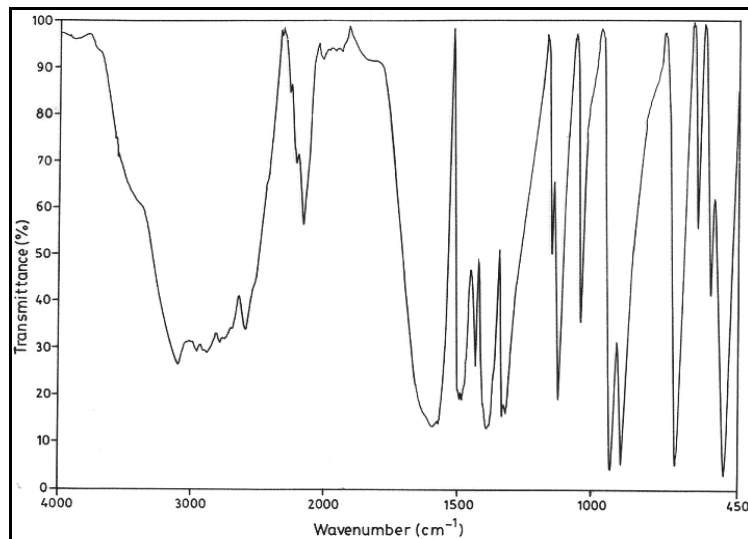**Figure 3.** Packing of molecules in γ-glycine single crystal.

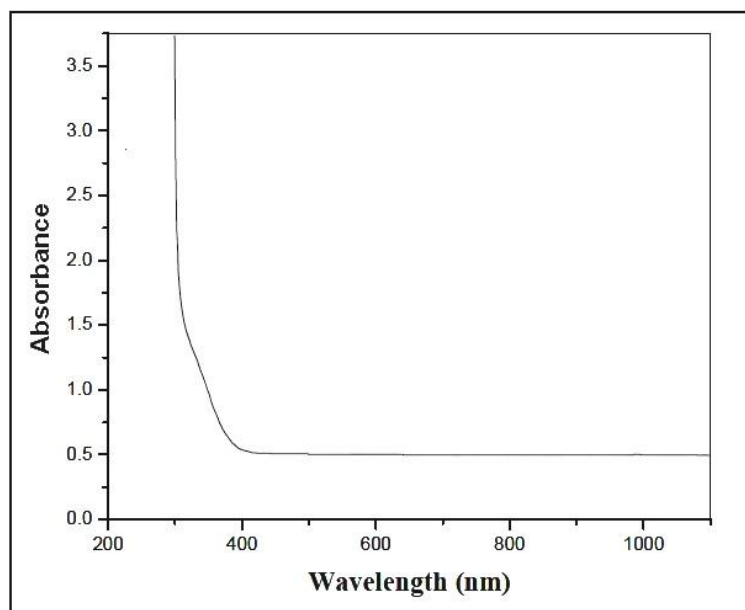**Figure 4.** FTIR spectrum of γ-glycine single crystal.

Figure 5. UV- Visible spectrum of γ-glycine crystal.

transmittance using the following relation:

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right)$$

(1)

Where T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hv)

$$\alpha = \frac{A(hv - E_g)^{1/2}}{hv}$$

(2)

Where E_g is the optical band gap of the crystal and A is a constant. A plot of variation of $(\alpha hv)^2$ versus hv is shown in Fig.4. E_g is evaluated using the extrapolation of the linear part. Using Tauc's plot, the energy gap (E_g) was calculated as 3.7 eV and the large band gap clearly indicates the wide transparency of the crystal.
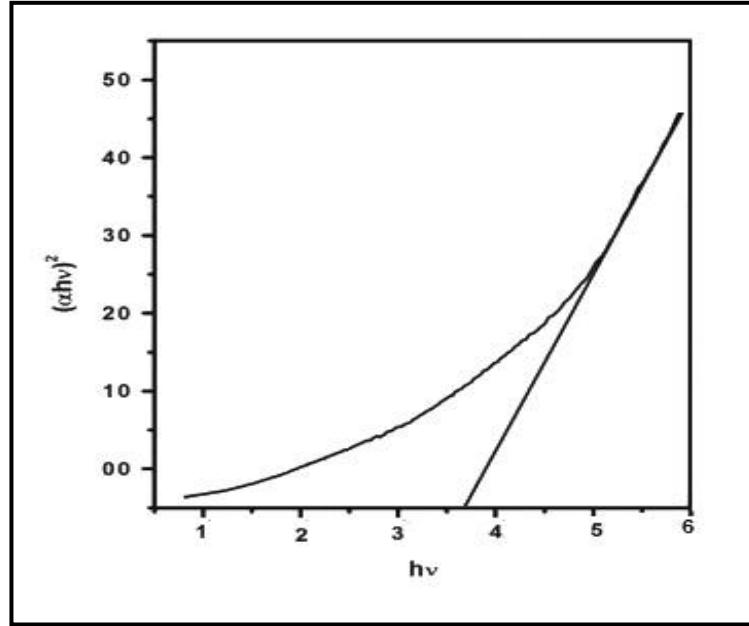
Figure 6. Plot of $(\alpha h\nu)^2$ vs photon energy.

This high band gap value indicates that the grown crystal possesses dielectric behaviour to induce polarization when powerful radiation is incident on the material.

Determination of optical constants

Two of the most important optical properties: the refractive index and the extinction coefficient which are generally called optical constants. The amount of light that transmits through material depends on the amount of the reflection and absorption that takes place along the light path. The optical constants such as the refractive index (n), the real dielectric constant (ε_r) and the imaginary part of dielectric constant (ε_i) were calculated using UV- Visible spectrum.The extinction coefficient (K) can be obtained from the following equation:

$$K = \frac{\lambda \alpha}{4\pi}$$

(3)

The extinction coefficient (K) was found to be 4.2×10^{-6} at λ = 1000 nm. The transmittance (T) is given by Sagadevan and Murugasen (2014):

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)}$$

(4)

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence:

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t)}}{1 + \exp(-\alpha t)}$$

(5)

Refractive index (n) can be determined from reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)}$$

(6)

The refractive index (n) was found to be 1.625 at λ = 1000 nm. From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation:

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2$$

(7)

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi}$$

(8)

where ε_0 is the permittivity of free space. The value of electric susceptibility χ_C is 0.152 at λ =1000 nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the
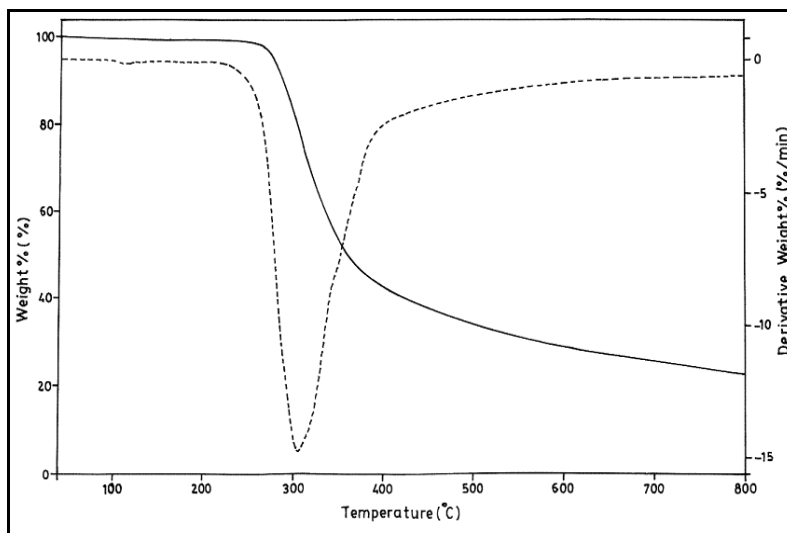
Figure 7. The TG-DTA curve of γ-glycine.

following relations:

$$\varepsilon_r = n^2 - k^2 \tag{9}$$

$$\varepsilon_i = 2nk \tag{10}$$

The value of real ε_r and ε_i imaginary dielectric constants at λ = 1000 nm were estimated as 1.752 and 6.302 x 10^{-5}, respectively. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation (Sagadevan and Murugasen, 2014).

NLO test – Kurtz powder SHG method

In this technique, the powdered sample with an average particle sizes range 125 to 150 μm is filled in a microcapillary tube about 1.5 mm diameter. Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm with an input power of 6.2 mJ/pulse and a pulse width of 8 ns with a repetition rate of 10 Hz was made to fall normally on the sample. The output from the sample was monochromated to collect the intensity of 532 nm component and to eliminate the fundamental wavelength. The second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected and a photo multiplier tube. The generation of the second harmonic was confirmed by a strong bright green emission emerging from the powdered sample. A potassium dihydrogen phosphate (KDP) crystal was used as a reference material in the SHG measurement. The

results indicate that the efficiency is found to be 1.5 times greater than that of pure KDP.

Thermal analysis

The thermal analysis of γ-glycine crystal was carried out using Perkin Elmer thermal analyzer. The sample of weight 4.178 mg was taken in a crucible and subjected to a heating rate of 20°C per min in nitrogen atmosphere. The obtained thermo gram is shown in Figure 7. γ-glycine transforms irreversibly into α-glycine at a temperature of 168°C. The peak at 280°C is due to the decomposition of glycine. The thermo gram shows only one step of decomposition at 305°C, which is assigned to the melting point of the crystal. The single step decomposition at 303°C confirms the purity of the crystal without any incorporation of impurities and water of hydration in the lattice of the crystal. At 800°C about 78.398% of the sample decomposes leaving only 22.712% as an end residue. The DTA curve shows a sharp irreversible endothermic peak at 305°C which agree with the TG curve and confirms the melting point of the crystal. From the thermal analysis (TG-DTA), it is confirmed that the crystal is thermally stable up to 305°C without any thermal strain.

Dielectric studies

Dielectric properties are related with the electric field distribution within solid materials. γ-glycine crystals were selected and polished by soft polishing pad with fine grade alumina powder. The face of single crystal was cut in to rectangular shape and well-polished, so that it
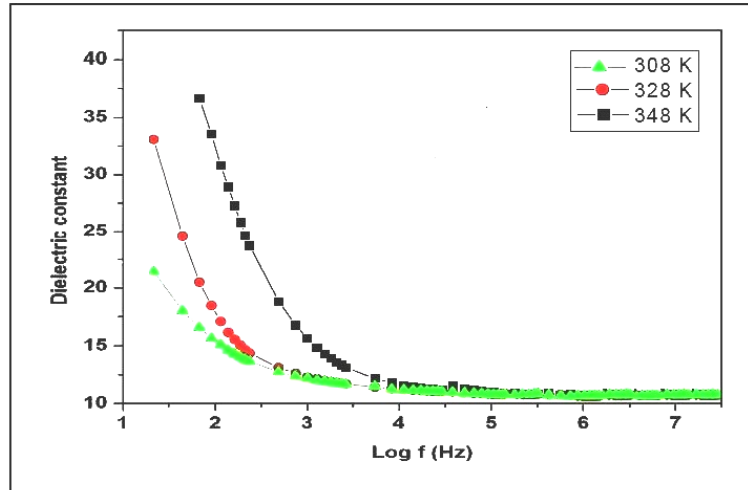
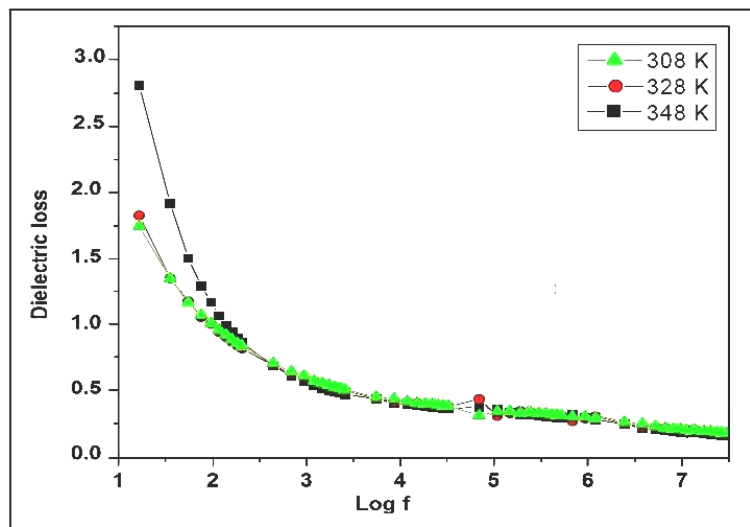**Figure 8.** Variation of dielectric constant with log frequency.

Figure 9. Variation of dielectric loss with log frequency.

behaves as a parallel plate capacitor. Silver paste was used for making the electrode plates on these surfaces of the crystal. The plots of dielectric constant and dielectric loss with frequency for various temperatures are shown in Figures 8 and 9. The dielectric constant is high in the lower frequency region and variation of dielectric constant with log f decreases with an increase in frequency. The high value of dielectric constant at low frequency may be due to presence of all polarizations and its low value at higher frequencies may be due to the significant loss of all polarizations gradually (Sagadevan, 2014). The dielectric loss was also studied as a function of frequency for different temperatures and is shown in Figure 9. The low dielectric loss at high frequencies for the given sample indicates very high purity of the material. This parameter is of vital importance for nonlinear optical materials in their applications. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field. The higher values of dielectric loss at low frequencies originate from space charge polarization mechanism and the characteristic of low dielectric loss at high frequencies reveals that the grown crystal possesses relatively high optical quality with low defect density. The behaviour of low dielectric loss with high frequency for the crystal suggests that the crystal possess enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices (Suresh and Arivuoli, 2011;
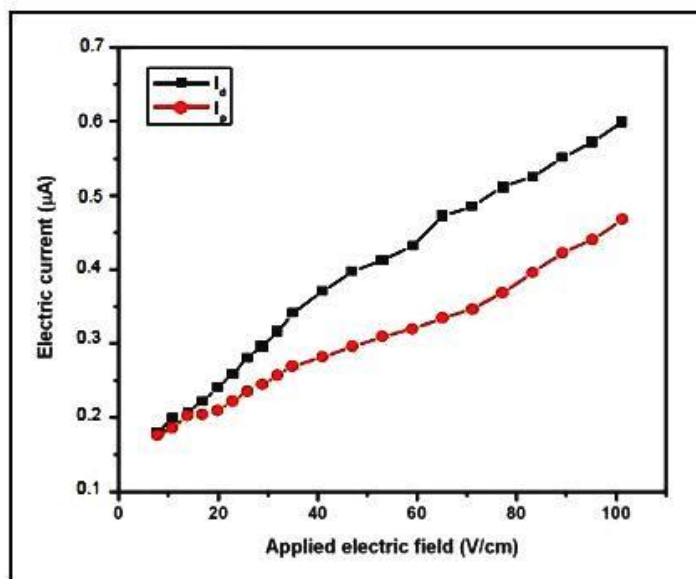
Figure 10. Field dependent photoconductivity of γ- glycine single crystal.

Photoconductivity studies

The crystal is well-polished and surfaces are cleaned with acetone. This is attached to a microscope slide and two electrodes of thin copper wire (0.14 cm diameter) are fixed onto the specimen at some distance apart using silver paint. After this, it is annealed at a temperature of 100°C to perfect dryness. A D.C. power supply, a Keithley 485 picoammeter and the prepared crystal was connected in series. The crystal is covered with a black cloth to avoid exposure to any radiation. The current (dark) is measured. To measure the photoconductivity, light from a 100 W halogen lamp is focused onto the crystal. The dark current was recorded by keeping the sample unexposed to any radiation. The Figure 10 shows the variation of both dark current (I_d) and photocurrent (I_p) with the applied electrical field. It is seen from the plots that both I_d and I_p of the sample increase linearly with the applied electrical field.

According to Stockmann model, the forbidden band gap contains two types of centres with energies E_1 and E_2. One type is located between the Fermi level and the conduction band, while the other is situated close to the valence band or between the Fermi level and the valence band. It is also assumed that the first type of centres have a high capture cross section for electrons and the probability of electrons being ejected to the conduction band is very low. In short, the function of these types of centers in the presence of radiation is to create holes (by accepting electrons from the valence band) but at the same time not to increase the number of free electrons. The second type of centres has a high cross-section for electrons and holes and consequently they capture electrons from the conduction band and holes from the valence band and recombine them. Thus, the net number of mobile charge carriers is reduced due to incident radiation giving rise to negative photoconductivity. It is observed from the plot that the dark current is always greater than the photo current, thus confirming the negative photoconductivity (Suresh, 2014).

Conclusion

A single crystal of γ-glycine has been grown by slow evaporation method. The lattice parameters of the grown crystals were determined by single crystal XRD. The different functional groups in the γ- glycine crystal were identified by FTIR spectral analysis. The UV cut-off of γ-glycine crystal is found to be 315 nm. Optical constants such as band gap, refractive index, extinction coefficient and electric susceptibility were calculated from UV-Visible spectrum. TG and DTA reveals that the γ-glycine single crystals are stable upto 305°C. The NLO property of the crystal was examined by performing Kurtz powder test using Nd: YAG laser. The SHG efficiency is found to be 1.5 times than that of KDP. The dielectric constant and dielectric loss of the γ-glycine crystal were calculated for different frequencies and temperatures. The low value of dielectric constant at high frequencies is important for the

device applications. The photoconductivity studies confirm that γ-glycine crystal has negative photoconductivity nature.

Conflict of Interest

The authors have not declared any conflict of interest.

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