

Studies on growth and characterization of Triglycine acetate (TGAc) NLO single crystals

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Triglycine acetate belongs to amino acid group revealing non-linear optical property. Single crystals of Triglycine acetate (TGAc) have been grown by slow evaporation of solution at 30 °C. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system. The optical absorption studies show that the crystal is transparent in the entire visible region with a cut off wavelength of 250 nm. The optical band gap is found to be 4.60 eV. The dependence of extinction coefficient (K) and refractive index (n) on wavelength has also been reported. Mechanical studies were carried out on the as grown crystal. The dielectric studies show that the dielectric constant and dielectric loss decrease exponentially with frequency at room temperature. Photoconductivity study confirms the negative photoconducting nature of the crystal which confirms the high degree of transparency of the material.

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1. Introduction

Over the past two decades much attention has been paid to the search of novel good quality NLO materials that can generate large second order optical non-linearities, significant for potential applications including telecommunication, optical computing, and optical data storage and processing [1 – 6]. In many of the organic NLO materials there is a solid framework of conjugated π electrons along with weak Vander Waals and hydrogen bonds which are responsible for most of their NLO properties. Organic NLO materials are superior to their inorganic counterparts due to high conversion efficiency for second harmonic generation and good transparency in the visible region, high resistance to optical damage and so on. The complexes of amino acids and salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of organic amino acids with those of the inorganic acids/salts. Glycine is a simple amino acid which has three polymeric crystalline forms α , β and γ . There are two types of glycine groups such as glycinium ions and zwitter ion. The zwitterionic structure of glycine is useful for its optical activity [7]. Many NLO crystals grown by mixing amino acids with various organic and inorganic acids have been reported in the literature [8–10]. The growth and characterization of TGAc has been reported [11]. In the present work, the band gap energy calculation based on optical absorption spectrum has been done for the grown crystals. Mechanical studies have been carried out and the results are presented. The dielectric property was also studied at different frequencies and temperatures to find out the different kinds of polarization mechanism.

2. Experimental

Triglycine acetate (TGAc) was synthesized by the reaction between glycine and glacial acetic acid taken in 3:1 molar ratio. The reactants were thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then the solution was allowed to evaporate at room temperature, which yield colorless crystalline salt of TGAc due to supersaturation. The seed crystals were harvested from the solution after eight days and a suitable seed was selected. The selected seed was suspended in the freshly prepared solution. After a period of three weeks, optically transparent defect free crystals were obtained from the mother solution. Fig.1 shown as grown crystal of TGAc.

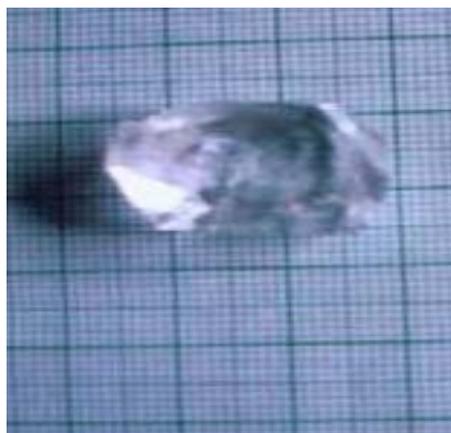


Fig. 1. Photograph of a TGAc crystal.

3. Single-crystal X-ray diffraction

The lattice parameter values of the TGAc crystal were calculated as $a = 5.1021 \text{ \AA}$, $b = 11.9704 \text{ \AA}$ and $c = 5.4617 \text{ \AA}$, $\alpha = \gamma = 90$, and $\beta = 111.7665^\circ$, from the single crystal X-ray analysis. The volume of the unit cell of the crystal is 309.7863 \AA^3 . XRD data prove that the crystal has monoclinic structure. The findings are very much similar to that of S. S. Hussaini et al [11].

4. Optical absorption

The optical absorption spectrum of TGAc (Fig. 2) was recorded in the range 200–800 nm using VARIAN CARY 5E spectrophotometer. The transparency is around 90% within the range of 230–800 nm. This is the most desirable property of the materials possessing NLO activity [12].

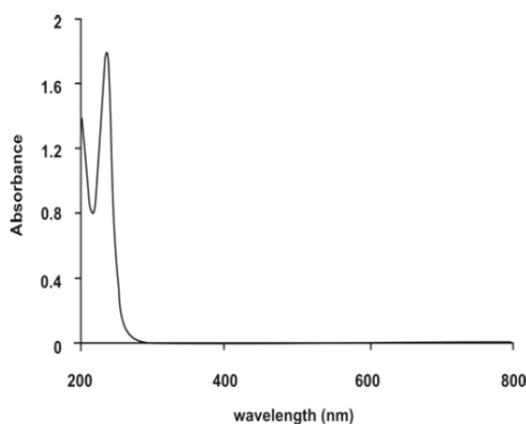


Fig. 2. UV-visible absorption spectra.

5. Determination of optical band gap and optical constants

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of the electron. The absorption coefficient (α) and the optical constants (n , K) are determined from the transmission (T) and reflection (R) spectrum based on the following relations [13].

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

where t is the thickness and α is related to extinction coefficient K by

$$K = \frac{\alpha \lambda}{4\pi} \quad (2)$$

The reflectance (R) in terms of the absorption coefficient and refractive index (n) can be expressed as follows as

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t))}}{1 + \exp(-\alpha t)} \quad (3)$$

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \quad (4)$$

In the high photon energy region, the energy dependence of absorption coefficient suggests the occurrence of direct band gap of the crystal obeying the following equation for high photon energies ($h\nu$)

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (5)$$

where E_g is the optical band gap of the crystal and A is a constant. The plot of $(\alpha h\nu)^2$ against $h\nu$ is shown in Fig 3. E_g was evaluated by extrapolation of the linear part [14]. The band gap is found to be 4.60 eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [15]. Figs. 4–6 represent the dependence of reflectance, the extinction coefficient and refractive index on the wave length [16].

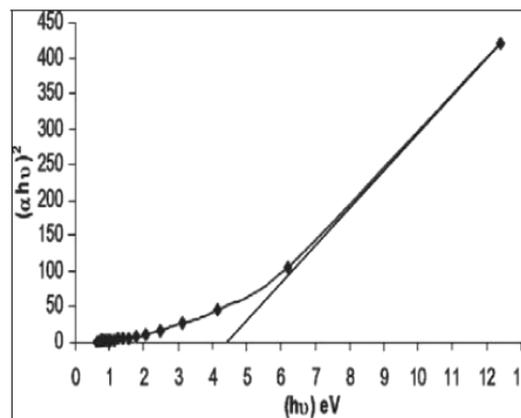


Fig. 3. Spectral dependence $h\nu$ vs $(\alpha h\nu)^2$.

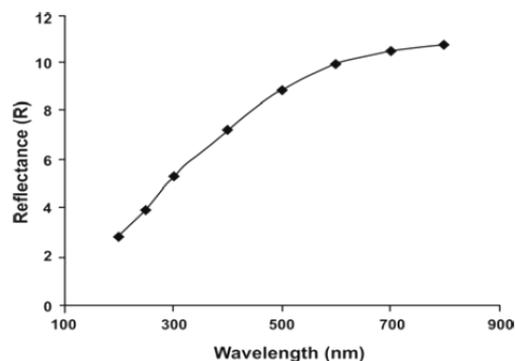


Fig. 4. Reflectance (R) vs Wavelength.

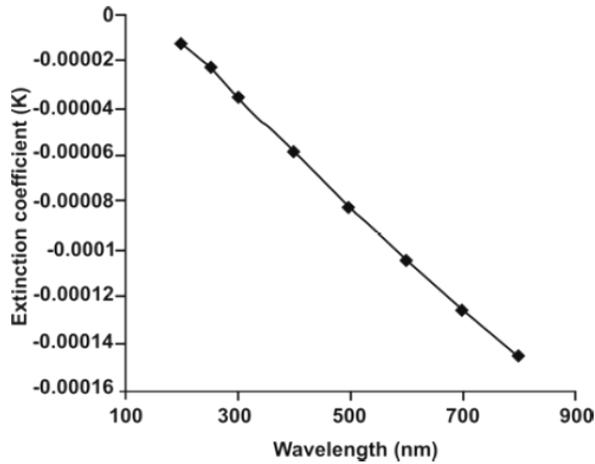


Fig. 5. Extinction coefficient (K) vs Wavelength.

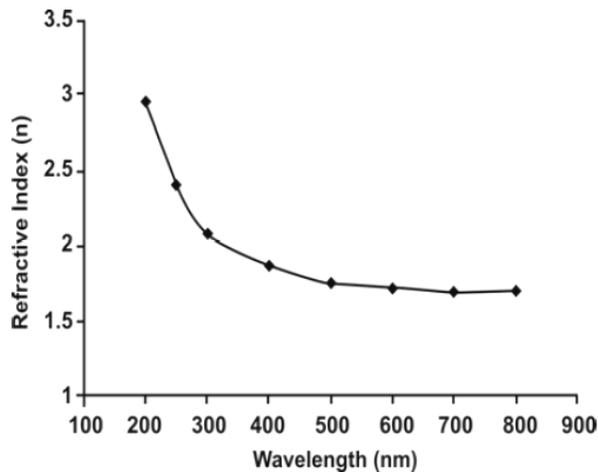


Fig. 6. Refractive index (n) vs Wavelength.

6. Mechanical property

To find surface hardness of the as grown TGAc crystal, microhardness was measured from a 25 to 100 gram load using HMV Microhardness tester. The hardness values were calculated from the formula $H_v = 1.8544P/d^2$ kg/mm² where P is the applied load and d is the mean diagonal length of the indentation. The trace is shown in Fig. 7, which shows that the hardness increases with the increase of load. From Meyer's law $P = ad^n$ connecting the applied load (P) and diagonal length (d) of the indentation, work hardening coefficient 'n' was calculated. Here, a is the constant for a given material. The work hardening coefficient was found to be 3.20 by taking a slope in the straight line of the graph drawn between log P and log d. According to Onitsch [17] 'n' lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials [18, 19]. The 'n' value observed in the present studies is around 3.20 suggesting that the grown TGAc crystal is a relatively softer material. Yield strength can also be

calculated using the relation [18] $\sigma_y = (H_v/3)(0.1)^{n-2}$, where σ_y is the yield strength, H_v is the hardness of the material and n is the logarithmic exponent. According to the relation, the yield strength is found to be 3.11 MPa and hence the grown TGAc crystal has relatively low mechanical strength. Since the material is soft optical damage will be high. Therefore, the material requires more attraction during the application.

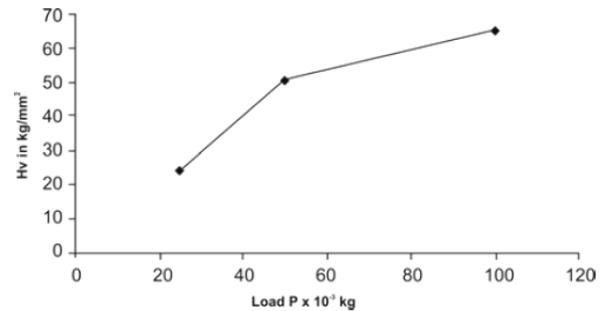


Fig. 7. Hardness vs. load.

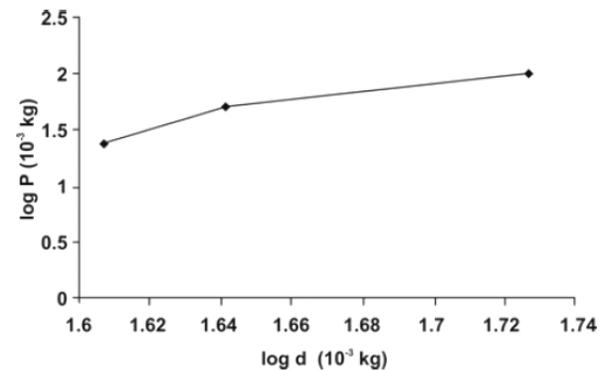


Fig. 8. log P vs log d.

7. Photoconductivity

Photoconductivity measurements were carried out on a polished portion of the grown single crystal by fixing it onto a microscopic slide. Two electrodes of thin copper wire of 0.3 mm thickness were fixed using silver paint and the sample was connected in series with a DC power supply and KEITHLEY 485 picoammeter. The sample was covered with a black cloth and the dark current (I_d) of the crystal was recorded with respect to different applied voltages. Then the sample was illuminated by the radiation from 100 W halogen lamp containing iodine vapour and tungsten filament and the corresponding photocurrent (I_p) was recorded for the same values of the applied voltage. The field dependent photoconductivity of the crystal is shown in Fig. 9. From the figure, photocurrent is found to be less than that of the dark current for all ranges of applied field which enunciates negative photoconductivity. The negative photoconductivity in this case may be due to the reduction in the number of charge carriers or their

lifetime in the presence of radiation. Decrease in lifetime with illumination, could be due to the trapping process and increase in carrier velocity [20].the relaxation time is given by

$$\tau = (vsN)^{-1} \quad (6)$$

where v is the thermal velocity of the carriers, s is the capture cross-section of the recombination centers and N is the carrier concentration. As intense light falls on the sample, the lifetime decreases. In Stockmann's model, a two level scheme is proposed to explain negative photoconductivity [21].The upper energy level is situated between the Fermi level and the conduction band, whereas the other one is located in the neighborhood of the valence band. The lower level has high capture cross section for electrons from the conduction band and holes from the valence band. As a result, when the sample is kept under exposed light, the recombination of electrons and holes take place, resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity.

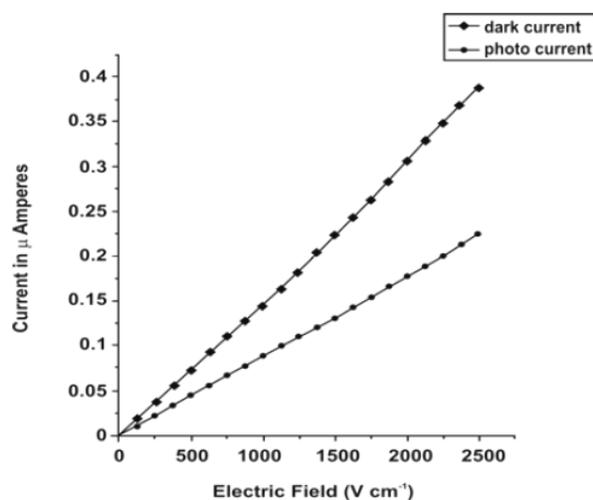


Fig. 9. Plot of field dependent photoconductivity of the title crystal.

8. Dielectric constant and dielectric loss

Dielectric studies of TGAc crystal were carried out at various frequencies and temperatures using HIOKI 3532-50 LCR HITESTER model. The sample was prepared from the transparent part of the crystal and both its surfaces were coated by graphite paste to make a contact with the electrodes. Then the prepared sample was mounted between the two electrodes and heated from ambient temperature to 150 °C within the frequency range of 100 Hz to 1 MHz. Capacitance and dielectric loss were measured at this frequency range and hence dielectric constant was calculated from the value of capacitance. Fig.10 and 11 represent the plots of dielectric constant and

dielectric loss against frequency. From the graph it is observed that dielectric constant is maximum at 100 Hz since all types of polarization such as electronic, ionic, orientation and space charge polarizations occur at lower frequency. Dielectric loss was also found to increase with the increase of temperature and decreases with the increase of frequencies. Because of the inertia of the molecules and ions at high frequencies, the orientation and ionic contributions of polarization are small [22]. So, the magnitude of polarization increases with the decrease of frequencies.

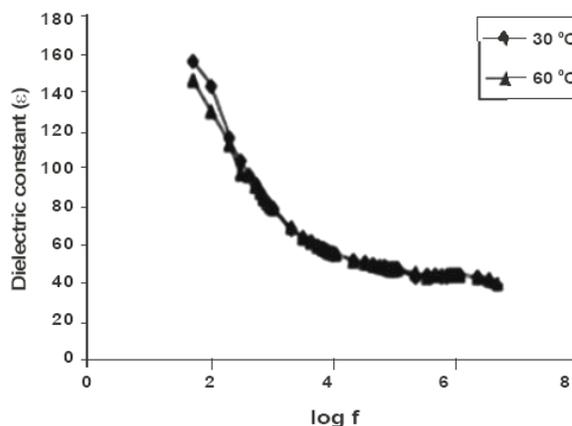


Fig. 10. Frequency vs dielectric constant.

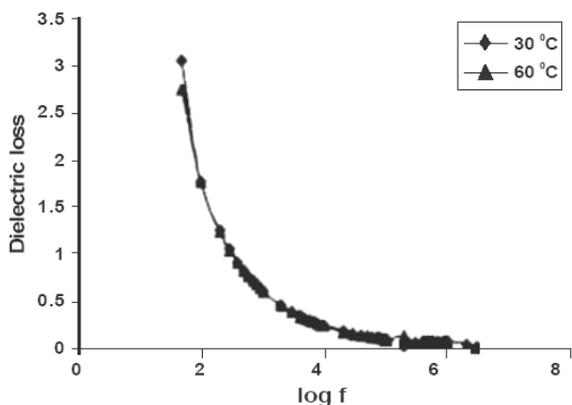


Fig. 11. Frequency vs dielectric loss.

9. Conclusion

Single crystals of Triglycine acetate (TGAc) were grown from aqueous solution by slow evaporation technique at room temperature. The grown crystals were characterized by single crystal XRD and it was confirmed that the crystal belongs to the monoclinic system. The band gap energy for the grown crystal is found to be 4.60 eV which is found to be in good agreement with the theoretical predicted value 4.96 eV. The optical investigations show a high value of both extinction coefficient (K) and refractive index (n) indicating high transparency of the crystal which confirms its suitability

for optical switch device fabrications. The grown TGAC crystal is a relatively soft material and having low yield strength from the investigations of microhardness. The frequency dependence of dielectric constant and dielectric loss reveals the nature of polarization mechanism. Photoconductivity study reveals negative photoconductive nature of the crystal.

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