


# Growth and characterization of L-Glycine thiourea nonlinear optical single crystal for optoelectronic applications

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**Abstract** L-Glycine thiourea single crystals have been grown by slow evaporation solution growth technique (SEST). The cell parameters were estimated from single crystal X-ray diffraction analysis and it was found that the material crystallized in the orthorhombic symmetry with space group  $P2_12_12_1$  and the theoretical data were estimated. The powder X-ray analysis proved its crystalline nature without the formation of secondary phases. The presence of functional groups and the nature of bonds appearing in the material were identified by FTIR spectroscopy. Optical constants were estimated by UV–Visible spectrum and the lower cut off wavelength was observed at 200 nm. The scanning electron microscope analysis has been carried out to determine the surface morphology of the grown crystal. Energy dispersive spectrum was done to confirm the composition of elements present in the title material. The second harmonic generation (SHG) efficiency was done by Kurtz powder technique and the conversion efficiency was compared with KDP crystal of the title compound. Third order nonlinear optical susceptibility was measured using z-scan technique and it was found that the crystal has a positive refractive index which is self focusing in nature. The obtained results showed that L-glycine thiourea crystals are potential materials for NLO device fabrication.

## 1 Introduction

The field of non-linear optics is based on the development of new materials, which have strong interaction with the light beam [1]. Semiorganic compounds have been recently recognized as potential candidates for such second harmonic generation (SHG) [2, 3]. Nonlinear optical materials find a number of applications like frequency conversion, optical switching, light modulation, optical memory storage, dynamic holography, harmonic generators and optical limiting [4, 5]. Amino acid family crystals are promising materials for these applications and it depends on the properties such as transparency, birefringence, refractive index, dielectric constant, thermal, photochemical and chemical stability [6]. Amino acids are considered to be interesting organic materials for NLO devices as they contain donor carboxylic (COOH) group and the proton acceptor amino acid ( $\text{NH}_2$ ) group known as zwitterions which create hydrogen bonds. Complexes of amino acids with inorganic acids are promising materials for optical second harmonic generation (SHG), as they tend to combine the advantages of the organic amino acid with that of the inorganic acids [7]. Considerable efforts have been made by many researchers on amino acid mixed complex crystals in order to make them suitable for device fabrications [8–11]. Glycine is the simplest amino acid with three polymeric crystalline forms  $\alpha$ ,  $\beta$ , and  $\gamma$ . Unlike other amino acids, it has no asymmetric carbon atom and is optically inactive. Since the glycine molecule can exist in zwitterionic form, it is capable of forming compounds with anionic, cationic and neutral chemical compounds. Thus a large variety of glycine coordinated compounds can be formed. However, only those complexes of glycine, which crystallizes in non centrosymmetric structure, are expected to exhibit nonlinear optical second harmonic generation [12].

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Most of the organic NLO crystals usually have poor mechanical and thermal properties whereas the inorganic NLO materials have excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity. Therefore semi organic crystals combine the positive aspects of organic and inorganic materials resulting in desired nonlinear optical properties [13]. The properties of large nonlinearity, high resistance, low angular sensitivity, good mechanical hardness and the further significance are centred on semi organic crystals. Hence, investigations are done to develop various semi-organic crystals which are more suitable for device fabrication [14, 15]. A series of amino acid based semi-organic compound such as L-Alanine potassium chloride [16], L-Alanine sodium nitrate [17], L-Histidine tetrafluoroborate [18] have been reported earlier. The earlier works on L-GT were restricted to optical, thermal and second harmonic generation studies [19].

The present manuscript reports on the crystal growth of L-glycine thiourea crystals from aqueous solution followed by the characterizations single crystal X-ray diffraction, fourier transform infrared spectroscopy, optical absorption, scanning electron microscopy, elemental analysis, second harmonic generation efficiency and z-scan studies are carried out and the results are discussed. Estimation of optical constants, theoretical data on SXRD, third order NLO susceptibility and second harmonic generation efficiency studies are the highlights of the present work.

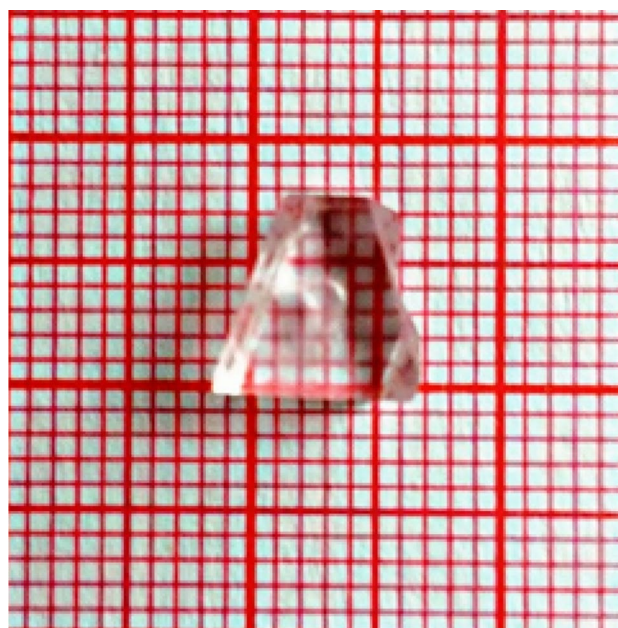
## 2 Experimental

### 2.1 Materials and method

L-glycine thiourea (L-GT) single crystals were synthesized from AR grade L-glycine and thiourea with equimolar ratio. The calculated amount of the reactants was thoroughly dissolved in deionised water. Slow evaporation solution growth technique was adopted for the growth of single crystals [20–22]. To obtain a homogeneous mixture the prepared solution was stirred well for about 5 h using a magnetic stirrer and then the solution was filtered and allowed to evaporate in the dust free atmosphere. Using successive recrystallization, good quality single crystals with the dimensions of  $8 \times 7 \times 3$  mm<sup>3</sup> were grown in a period of 30 days and the photograph of the as grown L-glycine thiourea crystal is shown in Fig. 1.

### 2.2 Characterization techniques

The grown crystals were subjected to various characterization analyses to test their suitability for optical device applications. Single crystal X-ray diffraction analysis was carried out using Four-circle Enraf Nonius CAD4/MACH3 single



**Fig. 1** As grown L-GT single crystal

crystal diffractometer to determine the lattice parameters and space group. Powder X-ray diffraction studies were carried out using XPERT-PRO X-ray diffractometer with CuK<sub>α</sub> ( $\lambda = 1.5418$  Å) radiation. The presence of functional groups in the grown crystal was identified using fourier transform infrared spectral analysis using a PERKIN ELMER SPECTROMETER by KBr pellet technique within the range of 400–4000 cm<sup>-1</sup>. In order to examine the optical properties of the grown crystal in the UV–Vis–NIR regions of electromagnetic spectrum, the linear optical study was carried out using PERKIN ELMER LAMBDA 35 UV–Visible spectrophotometer within the range of 200–1100 nm. SEM analysis was carried out by using CARL ZEISS SIGMA VP scanning electron microscope equipped with EDAX to analyse the crystal surface morphology and the elements present in the L-glycine thiourea crystal. Second harmonic generation efficiency test for the grown samples was performed by Kurtz and Perry powder technique using a Q-switched high energy Nd:YAG Laser (QUANTA RAY Model LAB-170-10) Model HG-4B- High efficiency with repetition rate at 10 Hz. Third order nonlinear optical susceptibility was identified using a He-Ne laser of wavelength 632.8 nm.

## 3 Results and discussion

### 3.1 Single crystal XRD analysis

Single crystal XRD is a non-destructive technique which provides detailed information about the internal lattice of

the crystalline substances including unit cell dimension. The title compound L-glycine thiourea crystallizes into orthorhombic system with non-centrosymmetric space group  $P2_12_12_1$ . From the XRD data, the calculated lattice parameter values are found to be  $a=5.52 \text{ \AA}$ ,  $b=7.72 \text{ \AA}$ ,  $c=8.63 \text{ \AA}$ ,  $\alpha=\beta=\gamma=90^\circ$  and cell volume  $V=368 \text{ \AA}^3$  and are tabulated in Table 1. The valence electron plasma energy,  $\hbar\omega_p = 28.8(Z\rho/M)^{1/2}$  is given by [23–25].

$$\hbar\omega_p = 28.8(Z\rho/M)^{1/2}$$

where  $Z=((3 \times Z_K) + (9 \times Z_B) + (3 \times Z_C) + (2 \times Z_H) + (1 \times Z_O))=54$  is the total number of valence electrons,  $\rho$  is the density and  $M$  is the molecular weight of the crystal. The calculated value of plasma energy is given by 29.862 eV. The Penn gap and the Fermi energy are explicitly dependent on the  $\hbar\omega_p$ , which are given by

$$E_p = \frac{\hbar\omega_p}{(\epsilon_\infty - 1)^{1/2}}$$

and

$$E_F = 0.2948(\hbar\omega_p)^{4/3}$$

Therefore the Penn gap and Fermi energy is calculated as 31.278 and 27.311 eV respectively. The Polarizability  $\alpha$  is obtained using the relation

$$\alpha = \left( \frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2} \right) \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3$$

where  $S_0$  is a constant for the material which is given by

$$S_0 = 1 - \left( \frac{E_p}{4E_p} \right) + \left( \frac{1}{3} \frac{E_p}{4E_F} \right)^2$$

and the value of Polarizability is estimated as  $4.84729 \times 10^{-23} \text{ cm}^3$ .

All these calculated data for the grown crystal are given in the Table 2.

**Table 1** Single crystal XRD analysis data of L-GT

	Crystal data
L-Glycine thiourea	Orthorhombic
Crystal system	$P2_12_12_1$
Space group	$a=5.52 \text{ \AA}$
Unit cell dimensions	$b=7.72 \text{ \AA}$
	$c=8.63 \text{ \AA}$
	$\alpha=\beta=\gamma=90^\circ$
Volume	$368 \text{ \AA}^3$

### 3.2 Powder X-ray diffraction analysis

The crystallinity and phase of the grown crystal is studied by powder X-ray diffraction. The crystalline nature of the synthesized material is well revealed by the prominent peak at specific  $2\theta$  angle. The pattern is obtained within the  $2\theta$  range of  $10^\circ$ – $70^\circ$ . The material obeys the Bragg's condition for diffraction resulting in the formation of the powder XRD pattern. The powder XRD pattern of L-glycine thiourea is shown in Fig. 2. The changes in lattice parameters are responsible for the shifting of prominent peaks and in addition to that small variations in the intensities are also observed.

### 3.3 Calculation of crystallite size, micro strain and bond length

The average crystallite size of the samples is calculated using Debye Scherrer formula [26]

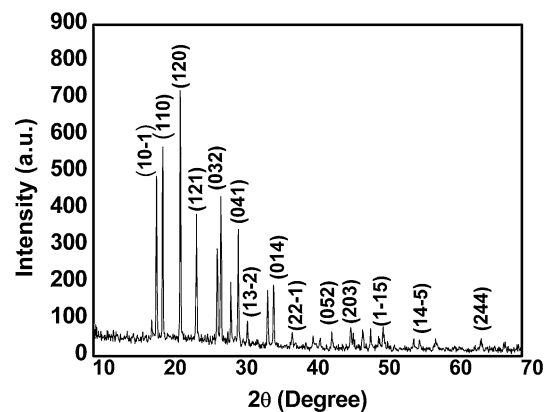
$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where,

$\lambda$  is the wavelength of the radiation used,  $\beta$  is the full width half maximum,  $\theta$  is the angle of diffraction. The calculated value of crystallite size of the sample is given by 54.87 nm.

**Table 2** Some theoretical datas on L-GT single crystals

Parameters	Values
Plasma energy (eV)	29.862
Penn gap (eV)	31.278
Fermi energy (eV)	27.311
Polarizability (cm <sup>3</sup> )	$4.84729 \times 10^{-23}$



**Fig. 2** Powder XRD pattern of L-GT

Micro strain ( $\epsilon$ ) is calculated using the expression

$$\epsilon = \frac{\beta \cos \theta}{4}$$

and the value of micro strain is estimated as  $6.316 \times 10^{-4}$ .

The bond length of the L-glycine thiourea crystal was given by.

$$l = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2}$$

$$u = \frac{a^2}{3c^2} + 0.25$$

Therefore the value of bond length is given 3.3011. The calculated values are presented in Table 3 and it is evident from the table that the material has retained its orthorhombic structure.

### 3.4 Fourier transform infrared spectral analysis

The Fourier transform infrared spectroscopy is effectively used to identify the functional groups of the samples. The crystals are finely powdered and mixed with potassium bromide. The mixture is made into pellets using a pelletizer and placed on the sample holder and the presence of functional groups in the compound L-glycine and thiourea is identified [27] and is shown in Fig. 3. The vibration peak at  $3269 \text{ cm}^{-1}$  represents  $\text{NH}_2$  asymmetric stretching vibration. The absorption peak at  $3172 \text{ cm}^{-1}$  shows  $\text{NH}_2$  symmetric stretching vibration. The absorption band at  $1592 \text{ cm}^{-1}$  represents  $\text{NH}_2$  bending vibration. The sharp peak at  $1464 \text{ cm}^{-1}$  denotes C–N asymmetric stretching vibration. The absorption peak at  $1415 \text{ cm}^{-1}$  refers to C=S asymmetric stretching vibration. The absorption band at  $1091 \text{ cm}^{-1}$  corresponds to C–N asymmetric stretching vibration. The sharp peak at  $738 \text{ cm}^{-1}$  denotes C=S symmetric stretching vibration. The peak at  $630 \text{ cm}^{-1}$  corresponds to N–C=S asymmetric stretching vibration. The sharp peak at  $494 \text{ cm}^{-1}$  assigned to N–C=S symmetric stretching vibration. The observed bands along with their vibration assignment are presented in Table 4.

### 3.5 UV–Visible NIR spectral analysis

Optical transparency in the entire visible region with a good percentage of transmission is the key properties of an NLO

**Table 3** Powder XRD analysis data of L-GT

Crystallite size (D)	54.87 nm
Micro-strain ( $\epsilon$ )	$6.316 \times 10^{-4}$
Bond length (l)	3.3011

**Table 4** Vibrational assignments of L-GT

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
3269	$\text{NH}_2$ asymmetric stretching
3172	$\text{NH}_2$ symmetric stretching
1592	$\text{NH}_2$ bending
1464	C–N asymmetric stretching
1415	C=S asymmetric stretching
1091	C–N asymmetric stretching
738	C=S symmetric stretching
630	N–C=S asymmetric stretching
494	N–C=S symmetric stretching

material. The optical properties such as the lower cut off, transmission range are examined by subjecting the samples to UV–Visible spectroscopy analysis. The transmission spectrum of L-glycine thiourea is shown in Fig. 4. From the figure it is observed that the lower UV cut off wavelength is below 200 nm and the crystal is transparent in the range 300–1100 nm. This is one of the most desirable properties of the NLO material for device fabrication.

### 3.6 Calculation of optical constants

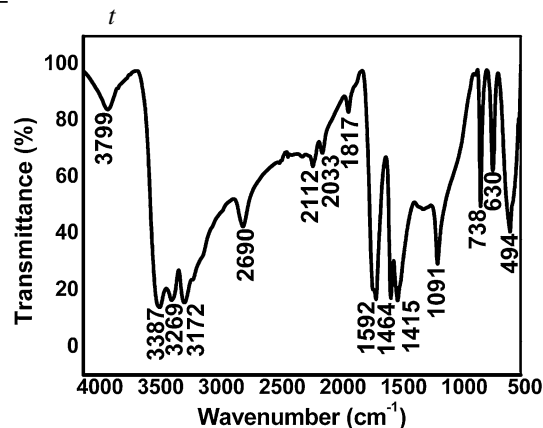
Optical constants such as the optical band gap, extinction coefficient and refractive index of L-glycine thiourea crystals are estimated from the following relations.

The optical band gap ( $E_g$ ) of L-glycine thiourea crystals is estimated from the relation

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

where A is the constant, h is the planck's constant,  $\nu$  is the frequency of the incident photons,  $\alpha$  is the extinction coefficient which is obtained from the transmittance value

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t}$$



**Fig. 3** FTIR spectrum of L-GT



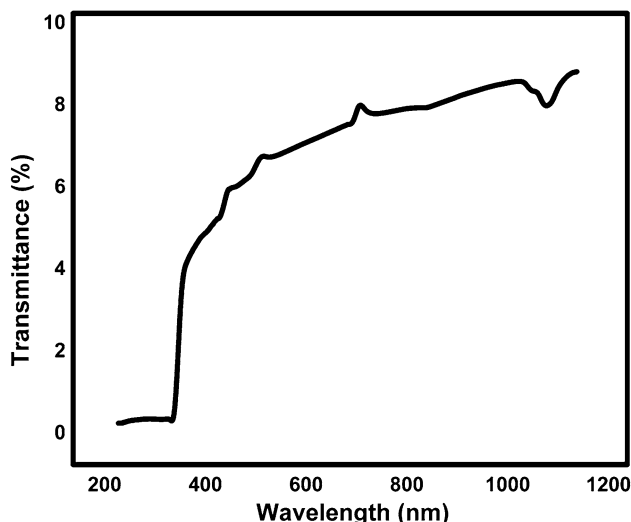


Fig. 4 UV-Visible-NIR transmission spectrum of L-GT

Extinction coefficient (K) can be obtained from the relation

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

The reflectance (R) and refractive index (n) are derived from the relations

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

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

The refractive index is calculated from the plot of refractive index versus wavelength and it is found to be n=1.24 and is shown in Fig. 5. Here the refractive index as function of wavelength was extracted from the transmittance data of UV-Vis studies which uses conventional white light as source of excitation. Hence the estimated value represent the linear refractive index of the material.

### 3.7 Morphological studies

Scanning electron microscopy (SEM) analysis has been carried out for the grown crystal to study the nature, surface morphology and the presence of imperfections in the grown crystals. The transparent regions of the crystals are cut into few mm for examining the surface morphology. Gold carbon coating is given before subjecting the crystal surface to electron beam. The maximum magnification possible in the equipment is 3,00,000 times with a resolution of 10 nm. From the SEM micrograph it can be observed that the grown crystal is having cloud like

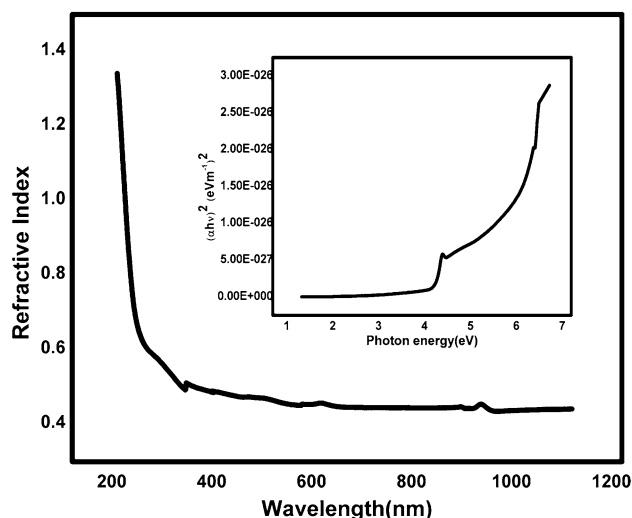


Fig. 5 Plot of refractive index versus wavelength of L-GT (Inset shows plot of bandgap vs. photon energy of L-GT)

appearance due to the agglomeration of the particles in the crystals and observed to be cracks and few inclusions which may be due to the impact of growth conditions and is shown in Fig. 6.

Energy dispersive X-ray analysis (EDX) is a micro-analytical technique which is used to obtain information regarding the chemical composition of the grown crystal. A fine beam of X-rays was made to fall into the sample. The energy of the X-rays emitted by the sample is measured by an energy-dispersive spectrometer. Since the energy of the X-rays emitted from the sample is attributed to the energy difference between the two shells and of the atomic structure of the compound, the elemental composition of the specimen can be measured and the percentage of inclusions in the sample are presented in Table 5.

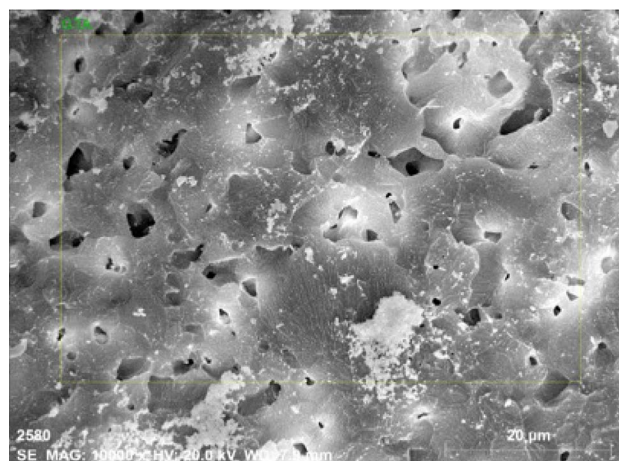


Fig. 6 SEM image of L-GT

From the EDX analysis, the presence of elements such as Carbon (C), Nitrogen (N), Oxygen (O), Sulphur (S) percentage composition is confirmed in the grown specimen and is shown in Fig. 7.

### 3.8 Second harmonic generation

The first and the most widely used technique for confirming the SHG from prospective second order NLO materials is the Kurtz powder technique [28]. A preliminary study of the powder SHG measurements are performed using a modified Kurtz technique with 1064 nm laser radiations. A Q-switched Nd:YAG laser producing pulses with a pulse width of 8 ns and a repetition rate of 10 Hz is used. The crystalline sample is powdered to particle sizes in the range 125–150  $\mu\text{m}$ . To make relevant comparisons with known SHG materials, KDP is also ground and sieved into the same particle size range. The powdered samples were filled air-tight in separate micro-capillary tubes of uniform bore of about 1.5 mm diameter. The SHG output (532 nm) is emitted and collected by a photomultiplier tube after being monochromated to collect only the 532 nm radiation. The

optical signal incident on the PMT is converted into voltage output at the CRO. The SHG output in each case is measured as the average of a few pulses to eliminate light variations of input power. The input laser energy incident on the capillary tube is chosen to be 3 mJ, an energy level optimized not to cause any chemical decomposition of the sample. The SHG efficiency of L-glycine thiourea crystal is found to be 0.6 times that of KDP and it confirms the suitability of L-glycine thiourea crystals for NLO applications.

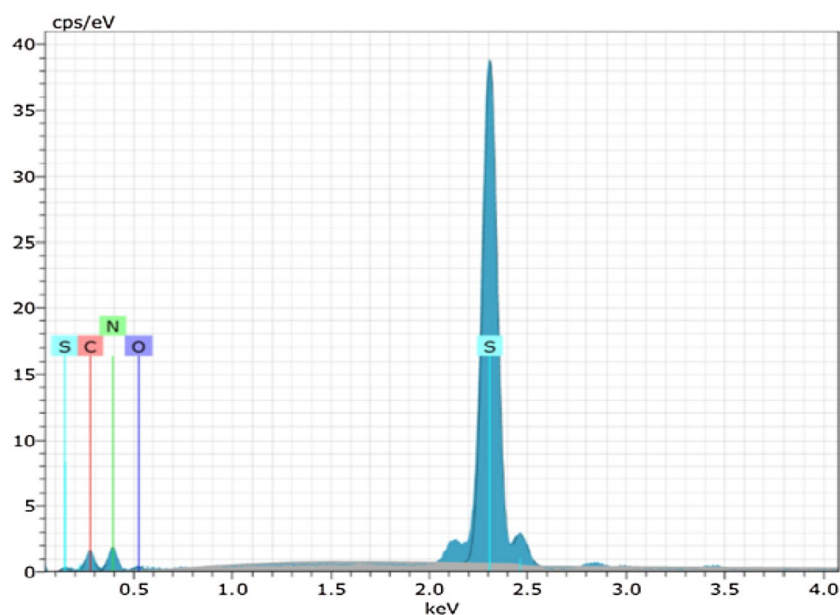
### 3.9 Z-scan technique

Z-scan technique was originally introduced by Sheik Bahae et al. [29, 30]. This is a simple and sensitive single beam technique to measure the sign and magnitude of both real and imaginary part of third order nonlinear susceptibility,  $\chi^{(3)}$ . In the original single beam configuration, the transmittance of the sample is measured, as the sample is moved, along the propagation direction of a focussed Gaussian laser beam. A laser beam propagating through a nonlinear medium will experience both amplitude and phase variations. If transmitted light is measured through an aperture placed in the far field with respect to focal region, the technique is called closed aperture Z-scan experiment. In this case, the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction. In a closed aperture Z-scan experiment, phase distortion suffered by the beam while propagating through the nonlinear medium is converted into corresponding amplitude variations. On the other hand, if transmitted light is measured without an aperture (in this case the entire light is collected), the mode of measurement is referred to as open aperture Z-scan. In this case, the throughput is sensitive only to the nonlinear

**Table 5** EDAX Quantification table of L-GT

Element	Weight%	Atomic%
Carbon	26.04	37.08
Nitrogen	31.74	38.76
Oxygen	3.05	3.26
Sulfur	39.17	20.89
Hydrogen	0.00	0.00
Total	100.00	100.00

**Fig. 7** EDAX spectrum of L-GT



absorption. Closed and open aperture Z-scan graphs are always normalized to linear transmittance i.e. transmittance at large values of  $|z|$ . Closed aperture Z-scan and open aperture Z-scan experiments respectively yield the real and imaginary parts  $\chi^{(3)}$ . Usually closed aperture Z-scan data is divided by open aperture data both measured simultaneously, to cancel the effect of nonlinear absorption contained in the closed aperture measurement. The new graph, called divided Z-scan graph, contains information on nonlinear refraction alone. In a Z-scan measurement, it is assumed that sample is thin, i.e. the sample length is much less than Rayleigh's range  $Z_0$ . [ $Z_0 = k\omega_0^2/2$  where  $k$  is the wave vector and  $\omega_0$  is the beam waist]. This is essential to ensure that beam profile does not vary appreciably inside the sample. Photodetector (PDI) monitors the input laser energy. PD2 and PD3 give open and closed aperture measurements respectively. Different variants of this technique such as eclipsing Z-scan and two colour Z-scan have also been introduced [31–33].

In non degenerate (two colour) Z-scan, the effect of nonlinear refraction and absorption induced by a strong excitation beam at a frequency  $\omega_e$  on a weak probe beam at a different frequency  $\omega_p$  i.e.  $\Delta n(\omega_e, \omega_p)$  and  $\Delta\alpha(\omega_e, \omega_p)$  are measured. [ $\Delta n$  refers to the change in refractive index and  $\Delta\alpha$  refers to the change in absorption coefficient]. Non degenerate Z-scan technique has some advantages over conventional single beam technique. The frequency difference ( $\omega_p - \omega_e$ ) can be exploited to get information about the dynamics of the nonlinear response with time resolution much less than the laser pulse width. With two colour Z-scan technique, it is possible to make time resolved measurements by suitably delaying the probe pulse with respect to pump beam. Investigation of non-degenerate nonlinearity has technological importance in the area of dual wavelength all optical switching applications, where cross phase modulation is very important. In eclipsing Z-scan technique, the far field aperture is replaced with an obscuration disk, which blocks most of the beam. This modification of the Z-scan technique enhances sensitivity to induced wave front distortion to an order of  $\lambda/10^4$ . Two colour eclipsing Z-scan technique has also been suggested [34].

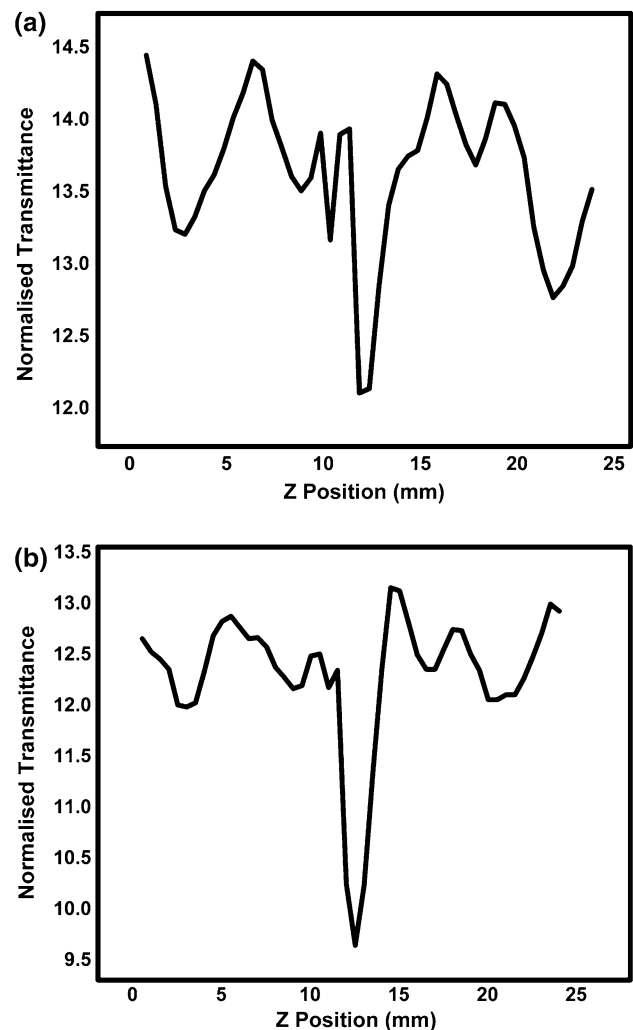
The third order nonlinear refractive index  $n_2$  and the nonlinear absorption coefficient  $\beta$  of L-glycine thiourea crystal are evaluated by the measurements of Z-scan. The technique is performed using a He–Ne laser of wavelength 632.8 nm. The sample is translated in the z-direction along the axis of the focussed Gaussian beam from He–Ne laser source, and the variation in the far field intensity of the beam from the laser source with the sample position is measured. The amplitude of the phase shift determined thoroughly by monitoring the change in the resistance through a small aperture at the far field position (closed aperture). Intensity dependent absorption of the sample

is measured by moving the sample through the focus and without placing the aperture at the detector (open aperture) Fig. 8a, b. By focusing a beam of laser through the crystal, a spatial distribution of the temperature in the crystal surface is produced. Hence a spatial variation in refractive index was created, which acts as a thermal lens, resulting in the phase distortion of the propagating beam.

The difference between the peak and the valley transmission ( $\Delta T_{P-V}$ ) was given in terms of the on-axis phase shift at the focus as,

$$\Delta T_{P-V} = 0.406(1 - S)^{0.25} |\Delta\Phi|$$

where  $S$  is the aperture linear transmittance and is calculated by using the relation  $S = 1 - \exp\left(\frac{-2r_a^2}{w_a^2}\right)$ , where  $r_a$  is the aperture radius and  $w_a$  is the beam radius at the aperture. The nonlinear refractive index ( $n_2$ ) is given by the expression [35, 36],



**Fig. 8** a Z scan open aperture of L-GT. b Z scan closed aperture of L-GT

$$n_2 = \frac{\Delta\Phi}{KI_oL_{eff}}$$

where  $K = \frac{2\pi}{\lambda}$  in which,  $\lambda$  is the wavelength of the laser light,  $I_o$  is the intensity of the laser beam at the focus ( $Z=0$ ),  $L_{eff}$  is the effective thickness of the crystal,  $L$  is the thickness of the crystal which is calculated using the expression,

$$L_{eff} = \frac{1 - e^{(-\alpha L)}}{\alpha}$$

From the open aperture z-scan data, the nonlinear absorption coefficient ( $\beta$ ) is determined by using the relation,

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

where  $\Delta T$  is the one valley value at the open aperture z-scan curve. From the  $n_2$  and  $\beta$  values the real and imaginary part of the third order nonlinear optical susceptibility are determined. These are obtained by using the relations,

$$\text{Re } \chi^{(3)}(esu) = 10^{-4} (\epsilon_o C^2 n_o^2 n_2) / \pi \text{ in cm}^2/\text{W}$$

$$\text{Im } \chi^{(3)}(esu) = 10^{-2} (\epsilon_o C^2 n_o^2 \lambda \beta) / (4\pi^2) \text{ in cm}^2/\text{W}$$

where  $\epsilon_o$  is the permittivity of free space,  $n_o$  is the linear refractive index of the crystal, and  $C$  is the velocity of light in vacuum.

$$|\chi^{(3)}| = \left[ (\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2 \right]^{1/2}$$

The third order nonlinear refractive index and the nonlinear absorption coefficient are evaluated from the z-scan measurements [37] and the results of z-scan technique for L-glycine thiourea is given in Table 6. The calculated value of nonlinear refractive index ( $n_2$ ) is  $9.41 \times 10^{-12} \text{ cm}^2/\text{W}$ . The crystal has a positive refractive index (i.e. self focusing) [38]. The self focusing nature of the sample is due to the thermal nonlinearity resulting from the absorption of radiation at 632.8 nm. From the open aperture z-scan curve, the nonlinear absorption coefficient ( $\beta$ ) is found to be  $0.57 \times 10^{-4} \text{ cm/W}$ . The real and imaginary part of the third order susceptibility ( $\chi^3$ ) is found to be  $3.18 \times 10^{-10} \text{ esu}$  and  $1.6 \times 10^{-7} \text{ esu}$ . Third-order nonlinear optical susceptibility ( $\chi^3$ ) is given by  $4.68 \times 10^{-4} \text{ esu}$ .

## 4 Conclusion

A semi-organic NLO material L-glycine thiourea has been grown by slow evaporation solution growth technique. The harvested crystals of size  $8 \times 7 \times 3 \text{ mm}^3$  were obtained after a period of 30 days. Unit cell parameters were evaluated by single crystal X-ray diffraction analysis, which confirmed that the grown crystal belongs to orthorhombic

**Table 6** Measurement details and the results of the z-scan technique

Laser beam wavelength ( $\lambda$ )	632.8 nm
Lens focal length (f)	8.5 cm
Optical path distance (Z)	115 cm
Spot-size diameter in front of the aperture ( $\omega_a$ )	1 cm
Aperture radius ( $r_a$ )	2 mm
Incident intensity at the focus (Z=0)	3.13 MW/cm <sup>2</sup>
Effective thickness (L <sub>eff</sub> )	2.09 mm
Linear absorption coefficient ( $\alpha$ )	0.0118
Nonlinear refractive index ( $n_2$ )	$9.41 \times 10^{-12} \text{ cm}^2/\text{W}$
Nonlinear absorption coefficient ( $\beta$ )	$0.57 \times 10^{-4} \text{ cm/W}$
Real part of the third-order susceptibility	$3.18 \times 10^{-10} \text{ esu}$
Imaginary part of the third-order susceptibility	$1.26 \times 10^{-7} \text{ esu}$
Third-order nonlinear optical susceptibility ( $\chi^3$ )	$4.68 \times 10^{-4} \text{ esu}$

system with space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. The intensified peaks that were observed in the powder XRD pattern showed good crystalline nature of the compound. The various functional groups and their vibrational interactions of the grown crystal were confirmed by Fourier transform infrared analysis. The optical study showed that the lower cut off wavelength was below 200 nm and possessed good transparency in the entire visible region. The crystal morphology showed that the surface of the grown crystal appeared to have cracks and few inclusions and the percentage of elements of the grown crystal was confirmed by elemental analysis. The estimated SHG efficiency of L-glycine thiourea crystal was found to be 0.6 times that of KDP crystal. The crystal has a positive refractive index (i.e. self focusing) and the third-order nonlinear optical susceptibility ( $\chi^3$ ) was calculated as  $4.68 \times 10^{-4} \text{ esu}$ . Thus L-glycine thiourea crystal can be exploited as a potential material for photonics, electro-optic and SHG device applications.

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