

Non-linear optical properties of α -glycine single crystals by Z-scan technique

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Abstract

Single crystals of α -Glycine up to the size of $4 \times 4 \times 1 \text{ mm}^3$ were grown for optical characterization by the solution growth method using methanol as a solvent. The crystal structure was studied by X-ray diffraction. The UV-visual absorption spectra indicate a good transparency between 200 and 1400 nm. The non-linear refractive index n_2 and susceptibility $\chi^{(3)}$ have been measured through the Z-scan technique. α -Glycine exhibits saturation absorption and self-focusing performance. Non-linear absorption co-efficient β is determined as $2.4763 \times 10^{-5} \text{ cm/W}$. Non-linear refractive index n_2 measured at the wavelength of 632.8 nm is calculated as $2.14435 \times 10^{-8} \text{ cm}^2/\text{W}$. The real and imaginary parts of $\chi^{(3)}$ have been measured at 632.8 nm and found to be $7.9732 \times 10^{-07} \text{ esu}$ and $8.0018 \times 10^{-07} \text{ esu}$, respectively. The measured 3rd order non-linear properties confirm its suitability for non-linear optical devices such as optical switching device.

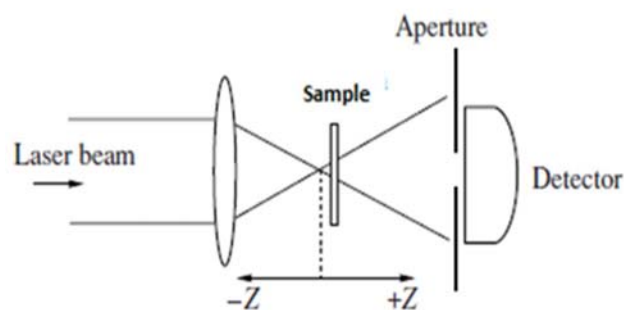
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Introduction

α -Glycine [$\text{NH}_2\text{CH}_2\text{COOH}$ amino acetic acid] is the simplest amino acid. Unlike other amino acids, it has no centre of chirality and is optically inactive. While glycine can exist as a neutral molecule in the gas phase, it exists as zwitterions in solution and in the solid state. The form consists of hydrogen bonded double layers of molecules, which are packed by van der Waals forces. In this paper we present the third order non-linear optical properties of α -Glycine single crystals by Z-Scan technique. The Z-Scan technique (Sheik - Bahe M *et al.* 1990, Zhao W *et al.* 1994 ; Yin M *et al.* 2006) is a popular method for the measurement of optical non-linearity of the material. It has the advantage of high sensitivity, accuracy and simplicity. In the Z-scan technique the transmittance of a tightly focused Gaussian beam through a finite aperture in the far field is measured as a function of the sample position "Z" with respect to the focal plane. At each position, the sample experiences a different light intensity. The nonlinear refraction of the sample causes a spatial beam broadening or narrowing in the far field and thus modifies the fraction of light that passes through the aperture as the sample position is changed. A typical peak-valley transmittance curve is obtained when the nonlinear refractive index of the medium is negative. For thin samples whose thickness is less when compared to the Rayleigh length ($L < z_0$), it is possible from the peak to valley variation of the

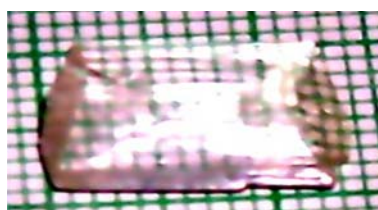
measured transmittance curve to evaluate the maximum nonlinear phase-shift and hence, knowing the incident laser power, to obtain the nonlinear refractive index n_2 . Removing the aperture in the far field it is possible to perform nonlinear absorption measurements. For media exhibiting both nonlinear refraction and absorption properties, a closed aperture Z-scan measurement is sensitive to both effects. Dividing the closed aperture data by the open aperture one yields a Z-scan trace typical of a purely refractive nonlinearity. The experimental setup used to measure the nonlinear

Fig. 1. Schematic diagram of Z-scan setup



refractive index and absorption of our crystal sample in this work is depicted in Figure 1.

Fig.2. α -Glycine single crystal



Crystal growth

α -Glycine single crystals were grown using AR grade chemical and de-ionised water as a solvent by slow evaporation technique. By repeated recrystallization, water-clear crystals of $14 \times 10 \times 4 \text{ mm}^3$ are obtained within 25

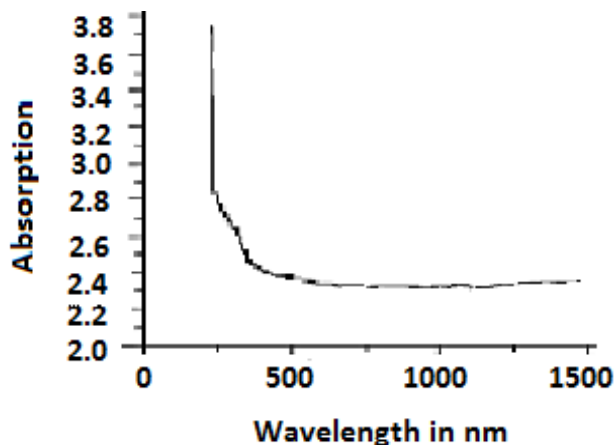
days. The grown crystals present good optical transparency. Grown crystals were as shown in Fig. 2.

Results and discussion

Single crystal X-ray diffraction analysis for the grown crystals has been carried out using ENRAF NONIUS CAD4 X-Ray diffractometer to confirm the lattice parameters of α -Glycine. The values are $a=5.107(2)$ Å, $b=12.040(2)$ Å, $c=5.460(2)$ Å, unit cell Volume $V=947$ Å³, $\beta =111.82(2)^\circ$, $\alpha = \gamma = 90^\circ$. The crystal belongs to the monoclinic system with the crystal symmetry of $P2_1/n$ a centro symmetric space group.

The optical absorption spectrum analysis of the grown crystal was carried out between 250 nm to 1500 nm using Perkin Elmer UV visual spectrophotometer. The recorded spectrum is as shown in Fig. 3. The crystal is transparent in the entire visible region and shows least UV absorption.

Fig. 3. UV absorption spectra of α -Glycine.



The refractive index of α -Glycine single crystal was determined by Brewster's angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal is mounted on a rotating mount at an angle varied from 0 to 90 degrees. The angular reading on the rotary stage was observed, when the crystal was perfectly perpendicular to the intra-cavity beam. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output. Brewster's angle (θ_p) for α -Glycine single crystal is measured to be 55.59 degrees. The refractive index has been calculated using the equation $n = \tan \theta_p$; where θ_p is the polarizing angle and it is found to be 1.460

Powder SHG studies for α -Glycine single crystal has been carried out in accordance with the powder method developed by Kurtz and Perry (1968). A Q-switched Nd:YAG laser beam of wavelength 1064 nm and pulse width of 8ns with a repetition rate of 10 Hz was used. The α -Glycine single crystals were powdered with a particle size of around 150 μm and placed in a micro capillary

tube and exposed to laser radiation. The absence of second harmonic signal confirms the centro symmetry nature of this crystal.

Third order non-linear optical measurement

A spatial distribution of the temperature in the crystal surface is produced due to the localized absorption of a tightly focused beam propagating through the absorbing sample. Hence a spatial variation of the refractive index is produced which acts as a thermal lens resulting in the phase distortion of the propagating beam. The difference between the peak and valley transmission (ΔT_{p-v}) is written in terms of the on axis phase shift at the focus as

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} |\Delta\Phi|, \quad (1)$$

$\Delta\Phi_0$ is the Phase shift at the focus and S is the aperture linear transmittance. It is calculated using the relation

$$S = 1 - \exp\left(-2 r_a^2 / \omega_a^2\right), \quad (2)$$

Where, r_a is the aperture and ω_a is the beam radius at the aperture. The non-linear refractive index is given by

$$n_2 = \frac{\Delta\Phi}{KI_0 L_{\text{eff}}}. \quad (3)$$

Where $K = 2\pi / \lambda$ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus ($Z=0$),

$$L_{\text{eff}} = [1 - \exp(-\alpha L)] / \alpha \quad (4)$$

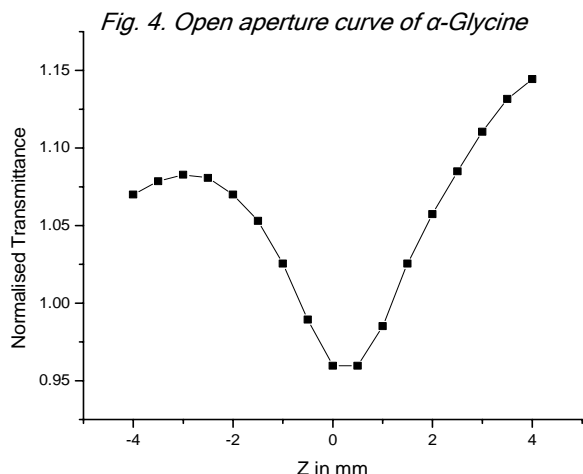
L_{eff} is the effective thickness of the sample, α is the linear absorption and L is the thickness of the sample (grounded to 2 mm). From the open aperture Z-scan data, the non-linear absorption coefficient is estimated as

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{\text{eff}}}, \quad (5)$$

Where, ΔT is the one valley value at the open aperture Z-scan curve. The value of β will be positive for saturable absorption and negative for two photon absorption. The real and imaginary parts of the third order Non-linear optical susceptibility $\chi^{(3)}$ are defined as

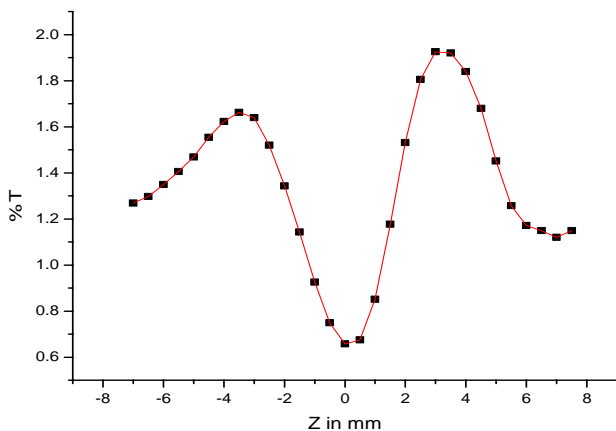
$$\begin{aligned} \text{Re } \chi^{(3)} (\text{esu}) &= 10^{-4} (\epsilon_0 C^2 n_0^2 n_2) / \pi (\text{cm}^2 / \text{W}), \\ \text{Im } \chi^{(3)} (\text{esu}) &= 10^{-2} (\epsilon_0 C^2 n_0^2 \lambda \beta) / 4\pi^2 (\text{cm} / \text{W}), \end{aligned} \quad (6)$$

Where, ϵ_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. Fig. 4 shows the normalized transmission for



the open aperture (OA). The transmission is symmetric with respect to the focus ($Z=0$), where it has a minimum transmission. This indicates that the sample exhibits saturation absorption (SA). The normalized transmittance

Fig. 5. Closed aperture curve of α -Glycine single crystals



for closed aperture (CA) is observed in Fig. 5. The peak to valley configuration of the curve (Fig. 5) suggests that the refractive index change is negative, exhibiting a self de-focusing effect. This may be an advantage for the application in protection of optical sensors. As seen from the closed aperture Z-scan curve, the prefocal transmittance peak is followed by the post focal valley which is the signature of negative nonlinearity (Wei *et al.*, 1992). The calculated value of the non-linear refractive index n_2 is found to be $2.14435 \times 10^{-8} \text{ cm}^2/\text{W}$. As the material has a negative refractive index, it results in self de-focusing nature of the material. From the open aperture Z-scan curve, it can be concluded that the non-linear absorption is regarded as saturation absorption. The non-linear absorption coefficient is found to be $2.4763 \times 10^{-5} \text{ cm/W}$. The third order susceptibility of α -Glycine is $8.018 \times 10^{-8} \text{ esu}$. The value of $\chi^{(3)}$ is found to

be larger than the other well known compounds (Gu *et al.*, 1993).

Conclusion

We have reported here the optical properties of α -Glycine single crystal. The Z-scan measurement with 632.8 nm laser revealed that non-linear refractive index of the crystal is in the range of $10^{-8} \text{ cm}^2/\text{W}$. The measured 3rd order non-linear properties confirm its suitability for non-linear optical devices such as optical switching device (Henari *et al.*, 1993).

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