International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.08, pp 363-370, 2014-2015

Growth, XRD, Optical absorption spectrum, FTIR Spectroscopy and Z – scan study of L- Serine

B. Thirumalaiselvam[1, 2], R. Kanagadurai[1], D. Jayaraman[1], V. Natarajan[3]

[1]Department of Physics, Presidency College, Chennai, India.
[2]Department of Physics, Maamallan Institute of Technology, Chennai, India.
[3]Department of Physics, Rajalakshmi Institute of Technology, Chennai, India.

Abstract: L-serine is an organic nonlinear optical material. It was grown as single crystal by low temperature solution growth technique. The grown crystal was characterized by single crystal XRD and powder XRD methods to obtain the lattice parameters and the diffraction planes of the crystal. UV - vis – NIR absorption spectrum was used to measure the range of optical transmittance and optical bandgap. The optical transmission range was measured as 250- 1200 nm and optical bandgap was calculated as 3.99 eV. FTIR spectroscopy study was carried out to identify the presence of functional groups in the grown crystal. The third order nonlinear property of the material was analysed using Z – scan technique. It is found that the crystal is capable of exhibiting saturation absorption and self- defocusing performance.
Keywords: Solution growth method, single crystal and powder XRD, UV-vis-NIR absorption, FTIR spectrum, Z-scan technique, Third order non-linear property.

1. Introduction

The compound L-serine ($C_3H_7NO_3$) is one of the amino acid materials capable of exhibiting NLO property. Though it is an NLO material, it has also pharmaceutical [1-6] and electrochemical properties [7,8]. The second order non-linearity of the grown crystal has been already reported [9].It can also generate third order harmonics due to non-centro symmetric nature. Hence, we report in this paper, the growth and important characterizations including third order nonlinear optical property of the grown crystal. The grown material was first crystallized under ambient conditions using solution growth technique. The crystal was then characterised using single crystal and powder XRD methods, UV-vis-NIR and FTIR spectral analyses, dielectric and thermal studies. Z –scan technique was finally employed to analyze the third order nonlinear coefficients like nonlinear absorption coefficient, nonlinear refractive index and susceptibility for certain NLO applications. Generally, third order NLO materials are used as optical emitter, broadband optical windows, all optical switching devices, photonic devices and holography applications.

2. Experimental Procedure

2.1 Growth of L-serine

Pure L-serine single crystal was grown by slow evaporation solution growth technique. A saturated solution was prepared by dissolving analar grade (AR) L-serine in methanol at room temperature (30˚C) using the solubility data. The prepared solution was filtered out using a borozil filter paper. The filtered saturated solution was transferred to petri disc covered with tissue paper having suitable number of pin holes and allowed for slow and steady evaporation of the solution. The solution was then placed in a constant temperature bath to maintain the solution at a constant temperature (30ºC) with an accuracy of ±0.01˚C. When the solution begins to evaporate, the saturation gradually attains supersaturated level leading to nucleation to form tiny crystals. After a period of two weeks, optically transparent and good quality of single crystals of L-serine was obtained. The size and purity of crystal were improved by successive crystallization processes. The as-grown single crystal of L-serine with dimensions of 40×13×2 mm^3 is shown in Fig. 1.

Fig. 1 Photograph of as –grown crystal of L-serine

2.2 Characterization studies

The grown crystal was subjected to various characterization techniques like UV-vis-NIR and FTIR spectral studies, single crystal XRD, powder XRD and nonlinear optical studies. Single crystal X-ray diffraction analysis of L-serine was carried using an automatic X-ray diffractometer (MESSERS ENRAF NONIUS CAD-4, Netherlands) with Cu Kα radiation (λ = 1.5406 Å). Powder X-ray diffraction spectrum was recorded using a rich seifert diffractometer. The optical absorption spectrum of L-serine crystal was recoeded in the wavelength region of 200 nm - 2000 nm using VARIAN CARY 5E model spectrometer. FTIR spectrum of L-serine was recorded in the range of 450 - 4000 cm-1 using IFS 66V, FTIR spectrometer. Z-scan technique was employed for analysing the third order non-linear optical behaviour of the material.

3. Results and Discussion

3.1 XRD analysis

3.1.1 Single crystal XRD

The grown L-serine crystal was subjected to single crystal X –ray diffraction analysis to confirm the crystallinity and also to estimate the lattice parameters using ENRAF NONIUS CAD-4 X-RAY diffractometer. From the single XRD data obtained, it is observed that the grown single crystal belongs to orthorombic system with space group P212121. , Z = 4. The unit cell lattice parameters determined from single crystal X-ray diffraction analysis data are a = 5.634 Å, b = 9.163 Å and c = 8.542 Å and α = β= γ = 90º with V = 440.9751 $Å^3$. From the space group of L – serine, it is understood that it is non-centro symmetric in nature. The basic requirement for exhibiting nonlinear behaviour is thus fulfilled.

3.1.2 Powder XRD

Powder X-ray diffraction analysis was carried out using a rich seifert diffractometer with CuKα(λ =1.540598Aº) radiation to confirm the crystal system of the grown L-serine material. The powder sample was scanned over the range of 10-70º at a scan rate of 1º per minute. The powder XRD spectrum is shown in Fig.2. Using the data obtained from powder XRD spectrum, the'd' values for different 2θ corresponding to the reflecting planes (h k l) of the crystal were calculated and the lattice parameters were determined using TERROR program. The lattice parameters are found to be a=5.615Å, b= 9.34Å, and c= 8.596 Å and α = β= γ =90˚. The results of powder XRD and single crystal XRD studies are found to be in good agreement with the reported values [JCPDS NO. 27-1989]. The powder XRD pattern with the sharp peaks reflects the good crystalline nature of the grown material L-serine.

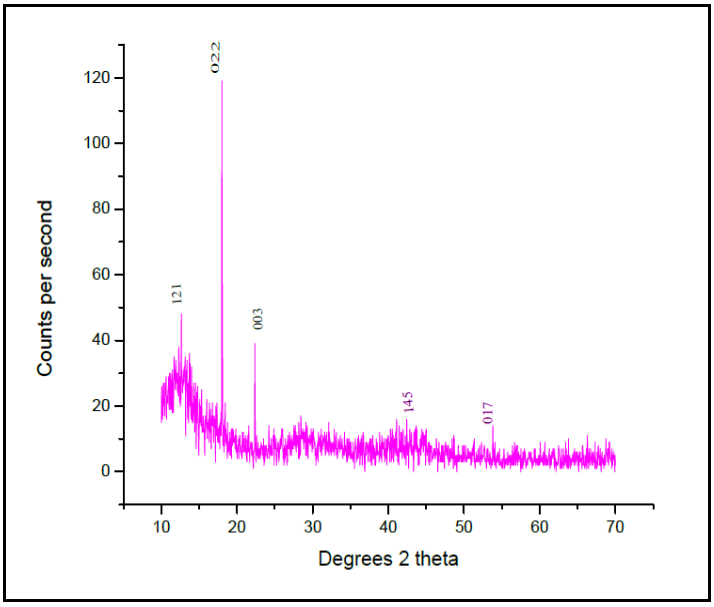

Fig. 2 Powder X-ray diffraction pattern of L-serine crystal

3.2 Optical studies

3.2.1 UV-vis-NIR study

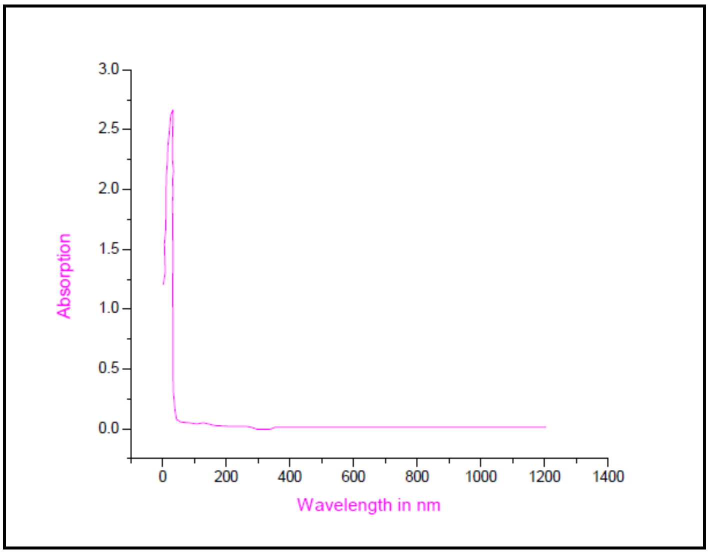

Fig .3 UV-vis-NIR spectrums of L-serine crystal

A good optical transmittance is very desirable for any crystal to find applications in photonics and optoelectronics. UV –vis – NIR absorption spectrum is very important for any NLO material to find the transmission range over a considerable region of wavelength [10]. Fig .3 shows the optical absorption spectrum of the crystal recorded in the range of 180 – 1400 nm. From the spectrum, it is noticed that the absorption of the crystal is considerably low in the wavelength region 225 -1400 nm with cutoff wavelength 225 nm. The prominent peaks observed in the spectrum may be due to overtones or the combination bands of either stretching or bending vibration in the UV region. From the UV-vis-NIR spectrum, it is observed that the crystal shows good transparency in the region 225 – 1400 nm which includes visible and NIR region. The transparency in the visible and NIR regions for this crystal makes the material suitable to transmit the laser light of wavelength 1060nm for exhibiting NLO behaviour.

3.2.2 Optical band gap

The optical absorption coefficient (α) was calculated using the relation,

$\alpha = (1/d) \log (1/T)$ ----------- (1)

where T is the transmittance and d is the thickness of the crystal. The absorption coefficient (α) is related to band gap energy (E_g) obeying the following relation for high photon energies (hν) [11] as,

$\alpha = A (h\nu - E_g) / h\nu$ -------------- (2)

where Eg is the optical band gap of the crystal and A is a constant. Tauc's plot of $(\alpha h\nu)^2$ against photon energy (hν) at room temperature is shown in Fig. 4. The linear behavior of the plot is the evidence of indirect transition between valence band and conduction band. Hence, optical band gap (E_g) was estimated by the extrapolation of the linear part of the plot. The band gap energy of the material was calculated as 3.99 eV. As a consequence of wide band gap [12], the grown crystal is confirmed to possess dielectric nature. Only the dielectric materials can possess the wide transmittance.

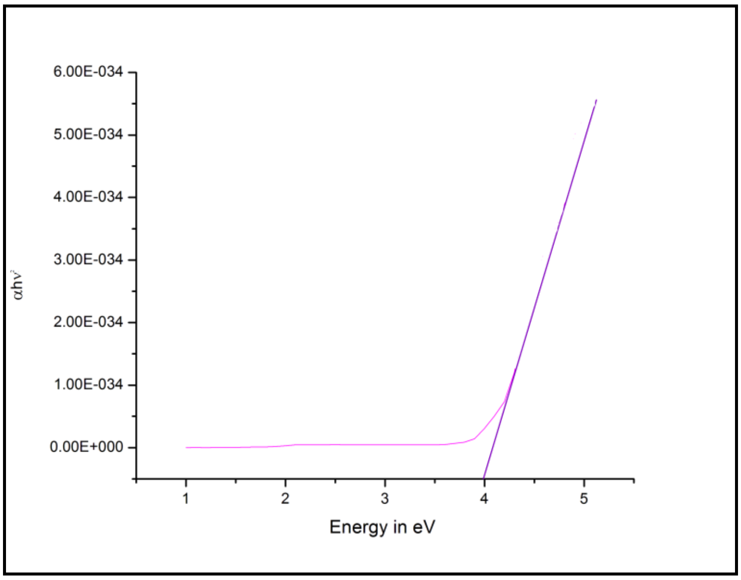

Fig. 4 Plot of $(\alpha h\nu)^2$ vs hν for L-serine crystal

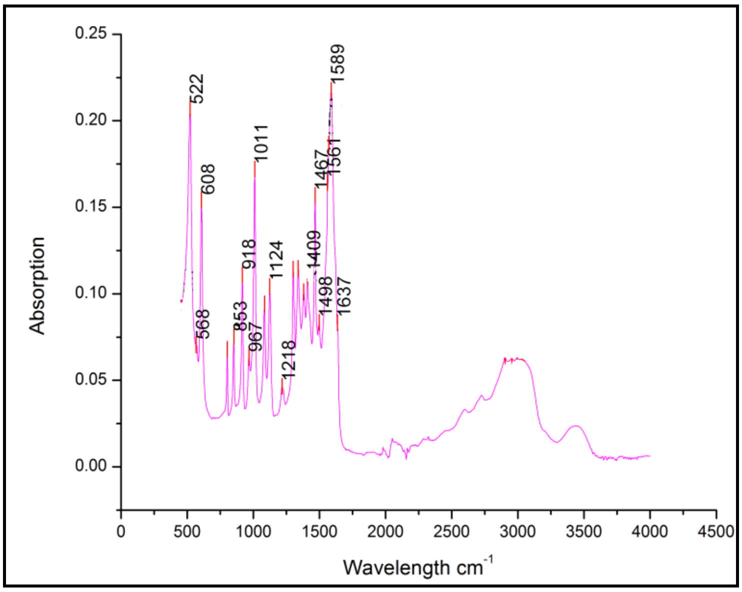

Fig .4 FTIR spectrum of L-serine crystal

3.3 FTIR analysis

Fig. 5 presents the FTIR spectrum of L-serine single crystal recorded in the range of 450 – 4000 cm^{-1}.The peaks corresponding to 522 cm^{-1} and 608 cm^{-1} show the presence of CH_2-CH-N bend and CH-CO_2 stretch vibrations respectively. The peaks at 804 cm^{-1} and 853 cm^{-1} are due to CO_2 scissors and wag modes. The peak at 967 cm^{-1} is due to $CC_{stretch}$ mode. NH3 rock modes are observed at 1011 cm^{-1} and 1024 cm^{-1}.The peak against 1218 cm^{-1} corresponds to CH_2 twist. The peak at 1467 cm^{-1} is due to CH_2 bend. The peaks at 1589 cm^{-1} and 1637 cm^{-1} indicates NH_3 symmetric bending vibrations. FTIR spectrum thus clearly reveals the presence of functional groups present in the grown material.

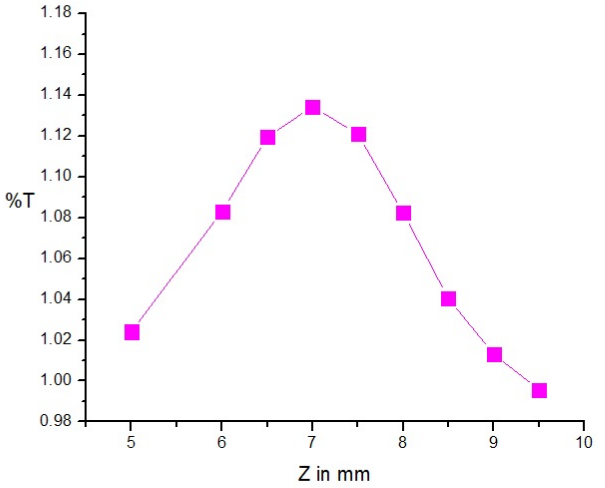

Fig. 5 Normalized Transmission for Open aperture (OA) for L-serine crystal

3.4 Non Linear Optical Study

Z-scan method:

Since the grown material L-serine is non-centrosymmetric in nature, the material can exhibit both second order and third order nonlinear properties. In the present study, third order nonlinear property is analyzed. Z- Scan technique was employed to determine the third order nonlinear coefficients: nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and the third order susceptibility ($\chi^{(3)}$).

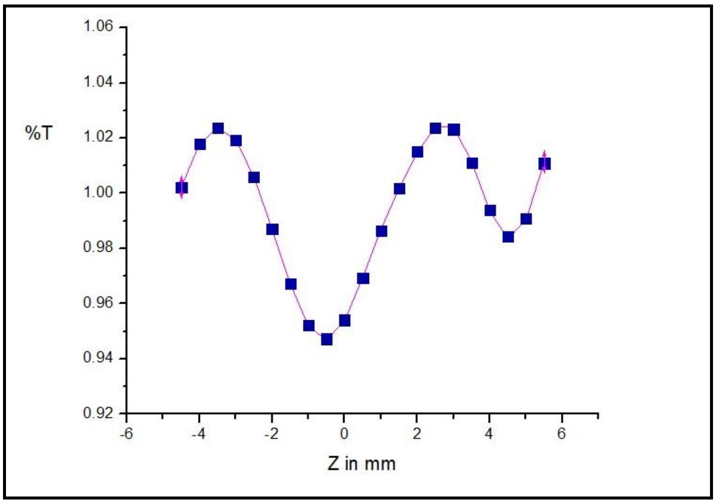

Fig. 6 Normalized Transmission for Closed aperture (CA) for L-serine crystal

Fig. 6 shows the normalized transmission for open aperture and closed aperture curves of the grown crystal. The asymmetric nature of Z-scan open aperture curve in Fig. 6 confirms the high nonlinear behavior of the material. In the closed aperture curve shown in Fig.7, the peak is followed by valley. Hence, the nonlinear refractive index and nonlinear susceptibilities are negative exhibiting saturation absorption and self-defocussing effect.

The values of β, n_2, and $\chi^{(3)}$ were calculated as follows.

$\beta = 2\sqrt{2}\Delta T_p / I_0 L_{eff}$ -------------- (3)

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

where I_0 is the intensity of the beam at focus, ΔT_p is the value obtained from open aperture of the Z-scan curve, α is the linear absorption co-efficient at 632.8 nm and d is the thickness of the sample.

The non-linear refractive index of the grown crystal was calculated using the relation,

$n_2 = \Delta\Phi_0 / K I_0 L_{eff}$ ---------------- (5)

The phase shift at the focus (Z = 0) was calculated using the relation,

$\Delta\Phi = \beta I_0 L_{eff}/Z$ ---------------- (6)

where K is the vector and Z is the propagation depth corresponding to Z=0

The absolute third order susceptibility $|\chi^{(3)}|$ is written as,

$|\chi^{(3)}| = \{[\chi_I^{(3)}]^2 + [\chi_R^{(3)}]^2\}^{1/2}$ -------------(7)

where $\chi_I^{(3)}$ and $\chi_R^{(3)}$ are the imaginary and real part of the third order nonlinear susceptibility respectively,

$\chi_I^{(3)} = 10^{-2}\varepsilon_0 c^2 n_0^2 \lambda\beta/4\pi^2$ ---------------- (8)

$\chi_R^{(3)} = 10^{-4}\varepsilon_0 c^2 n_0^2 n_2/\pi$ ---------------- (9)

Here ε_0 is the vacuum permittivity, n_0 is the refractive index of the sample and c is the velocity of light in vacuum.

Sample	$n_2 \times 10^{-12}$ cm^2/W	$\beta \times 10^{-07}$ cm/W	$\chi_R^{(3} \times 10^{-08}$esu	$\chi_I^{(3)} \times 10^{-08}$ esu	$\chi^{(3))} \times 10^{-08}$ esu
L-serine	9.10759	1.6288	5.6511	9.4858	11.0415

The above table presents the third order NLO parameters of the grown crystal.These values are copmparable with reported values of Third order non-linearity arises generally due to (i) non-linear absorption,(ii) two photon absorption,(iii) saturable absorption,(iv) reverse saturable absorption and (v) non-linear refraction. It is observed that $\chi_I^{(3)} > \chi_R^{(3)}$ which means that contribution of nonlinear absorption change is more dominant than the nonlinear refraction for the nonlinearity. This is confirmed from Fig.7 where valley is larger than the peak. Nonlinear index of refraction is the change in refractive index or the spatial distribution of the refractive index of a medium due to presence of optical waves and has generated significant and technological impact.

3.5 Conclusion

Good quality single crystals of L-serine was successfully grown using slow evaporation technique at ambient conditions. Single XRD analysis was used to identify the crystal systems and space group which was confirmed by powder XRD analysis. The optical absorption studies from UV-vis-NIR spectrum show that the grown crystals are optically transparent in the region 180- 1100 nm with 225 nm as the lower cutoff wavelength. FTIR spectral study was carried out to identify the molecular vibrations of various functional groups present in the crystal. The third order non liner coefficients were estimated using Z scan technique and these coefficients are found to exhibit self-defocussing effect. Hence, L-serine is an excellent third order NLO material which can find applications in optoelectronic, photonics and holographic applications.

References

1. de Koning TJ, Snell K, Duran M, Berger R, Poll-The BT, Surtees R, Biochem J,371(2003),653-661.
2. Hai-Hui Xue,Takanori Sakaguchi, Michio Fujie‖, Hirofumi Ogawa and Arata Ichiyama,23,274(1999), 16028 –16033.
3. Reto Savoca, Urs Ziegler,Peter Sonderegger, Journal of Neuroscience Methods,61(1995),159-167.
4. L Gluck , M Sribney and Marie V Kulovich, Pediatric Research,1(1967),247-265.
5. Yaakov Lavie, Hui-ting Cao, Stuart L. Bursten, Armando E. Giuliano and Myles C. Cabot,The journal of biological chemistry,271(1996),19530-19536.
6. Shuting Li, Qinglei Yu, Xin Lu and Shulin Zhao, Journal of Separation Science,32(2009),282-287.
7. Jinchun Song, Ji Yang, Xianming Hu, Journal of Applied Electrochemistry 6,38(2008),833-836.
8. M. A. Deyab, RSC Adv., 5(2015), 41365-41371.
9. K. Rajesh and P. Praveen Kumar, Journal of Materials, 2014(2014),790957-790961.
10. V. Krishnakumar and R.Nagalakshmi, Acta A, 61(2005), 499-507.
11. J Tauc, Amorphous and liquid semiconductor, Plenum press, New york, 1974, p .159.
12. D.D.O Eya, A.J.Ekpunobi and C.E.Okeke, Acad. Open Interet J. 17(2006).

***** *****

*****