Linear and Nonlinear Optical Properties of L-Alanine Oxalate Single Crystals

S. Arockia Avila and A. Leo Rajesh
Department of Physics, St. Joseph’s College (Autonomous), Tiruchirappalli

1. Introduction

Nonlinear optical processes provide the key functions of frequency of the system and their applications depends upon the various properties of the materials, such as transparency, birefringence, laser damage threshold, refractive index, dielectric constant, second order nonlinearity and large third order susceptibilities etc. [1]. Nonlinear optical materials with large third order nonlinear susceptibilities are essential for all optical switching, modulating, and computing devices because the magnitude of the quantity dominates the device performance [2,3]. New molecular organic compounds with one or more aromatic systems in conjugated positions, leading to highly efficient charge transfer systems have been actively studied [4-6]. Most of the organic crystals are composed of aromatic molecules that are substituted with π-electron donors and acceptors which exhibit intermolecular charge transfer resulting in high SHG efficiency. These compounds must crystallize in a non-centrosymmetric class in view of applications making use of quadratic optically nonlinear effects. Organic compounds are formed by weak Vander Waal’s and hydrogen bonds and it possess high degree of delocalization and hence they are optically more nonlinear than inorganic materials [7]. Some of the advantages of organic materials include flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity, high damage resistance etc [8]. Organic materials with delocalized π-electrons usually display a large NLO response which makes it most resourceful for various application including optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions and laser remote sensing [9]. Further investigations on organic NLO materials have subsequently produced very good materials with highly attractive characteristics. Amino-acid family single crystals are gaining importance as highly feasible second-order NLO materials. The amino acid L-alanine can be considered as the fundamental building block of more complex amino acids which shows strong non linear behaviour and anomalous phonon coupling and is a system exhibiting vibrational solitons [10]. The earlier works on LAO were restricted to structure solving, thermal, optical and photoacoustic studies [11-12]. Hence an attempt is made to grow an organic NLO material L-alaninium oxalate (LAO) using L-alanine and oxalic acid by using slow evaporation technique and the grown crystal was subjected to powder XRD, FT-IR, UV-Vis-NIR, Second order and third order nonlinear optical studies and the results were discussed.

2. Experimental

2.1 Synthesis of L-alanine oxalate crystals

L-Alanine oxalate (LAO) single crystals were synthesized from AR grade L-alanine and oxalic acid with equimolar ratio. The calculated amount of the reactants was thoroughly dissolved in deionised water. To obtain a homogeneous mixture the prepared solution was stirred well for about 5 hours using a magnetic stirrer and then the solution was filtered and allowed to evaporate in the dust free atmosphere. Using successive recrystallization, good quality large size single crystals were obtained in a period of 30 days of the dimensions 23x6x5 mm^3 and the photograph of the as grown L-alanine oxalate crystals are shown in Fig.1.

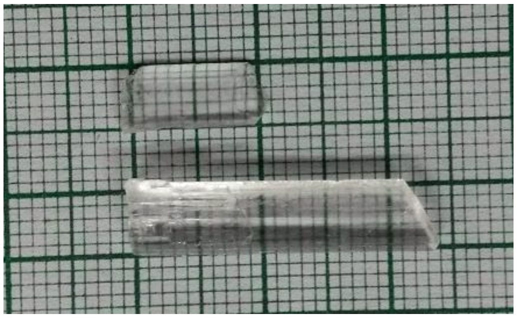


Fig. 1. As grown L-Alanine oxalate single crystal

3. Results and Discussion

3.1 Single crystal X-ray Diffraction analysis

Single crystal X-ray diffraction pattern was recorded for the grown crystal using Enraf Nonius CAD4 X-ray Diffractometer with Mo Kα radiation (λ = 0.7107Å) to obtain the lattice parameters and space group. The single crystal XRD data reveals that the grown LAO crystals belongs to orthorhombic system with space group $P2_12_12_1$ and the calculated lattice parameter values are found to be a = 5.591 Å, b = 7.276 Å, c = 19.569 Å and the cell volume, V = 796.06 $Å^3$ [13].

Table 1. Single Crystal XRD data of L-Alanine oxalate crystals

LAOX (Reported)	LAOX (Obtained)
a = 5.6302 Å	a = 5.591 Å
b = 7.235 Å	b = 7.276 Å
c = 19.5973 Å	c = 19.569 Å
V = 803.146 $Å^3$	V = 796.06 $Å^3$
orthorhombic	orthorhombic
$P2_12_12_1$	$P2_12_12_1$

3.2 Fourier Transform Infrared Spectroscopic Studies

The FTIR spectra of the grown crystal were analysed by Fourier Transform Infrared spectral analysis using a Perkin Elmer Spectrometer by KBr pellet technique within the range of 400-4000 cm^{-1} and the resulting spectrum is shown in Fig.2. The presence of the functional groups of L-Alanine oxalate was identified by Fourier Transform Infrared (FTIR) spectrum. The characteristic vibrations of the carboxylate ions and the zwitter ionic group NH_3^+ of LAOX are depicted in the spectrum. Observed frequencies are compared with those of similar functional groups including carboxylate ions. During the synthesis NH_2 group in the free acid is converted into NH_3^+ ions. In the spectrum, the peak at 3244 cm^{-1} corresponds to OH stretching of COOH group of amino acid the peak at 2905 cm^{-1} is due to NH_3^+ symmetric stretching in plane and the peak at 2517 cm^{-1} is attributed to NH_3^+ symmetric stretch out of plane vibrations. The C-C overtone vibration is observed at 1919 cm^{-1}, and C=C stretching at 1720 cm^{-1}.The vibration peak at 1580 cm^{-1} is due to NH_3^+ asymmetric bending and that at 713 cm^{-1} corresponds to C=O bending. The FTIR vibrational spectrum establishes the presence of NH_3^+ group in the crystal confirming the protonation of amino acid group leading to the formation of LAOX molecule.

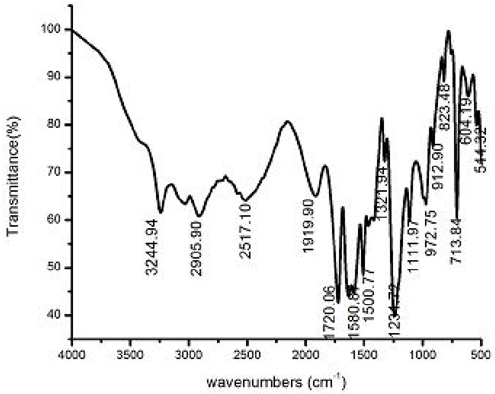


Fig.2. FTIR spectrum of L-Alanine oxalate

Table 2. Vibrational assignments of L-Alanine Oxalate

Wavenumber (cm^{-1})	Assignment
3245	OH stretching of COOH group of amino acid
2906	NH3+ symmetric stretching in plane vibration
2517	NH3+ symmetric stretch out of plane vibrations
11919	C-C overtone vibration
11720	C=C stretching vibration
1580	NH3+ asymmetric bending vibration
7713	C=O bending vibration

3.3 UV-Visible NIR spectral analysis

The optical transmission spectrum gives valuable information about the atomic structure of the molecules because the absorption of UV and visible light involves the promotion of σ and π orbital electrons from the ground state to higher energy state. To measure the optical transparency of the grown crystal within the range of 190-1100 nm region of electromagnetic spectrum, the linear optical study was carried out using Perkin Elmer Lambda 35 UV-Visible spectrophotometer.

Estimation of Optical Constants

Optical constants such as the optical band gap, extinction coefficient and refractive index were estimated in order to know the optical property of the title materials [14]. The optical band gap (E_g) of L-Alanine oxalate crystals was estimated from the relation

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

where A is the constant, h is the planck's constant, ν is the frequency of the incident photons, α is the extinction coefficient which is obtained from the transmittance value

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

The optical band gap was obtained by extrapolating the linear part of the plot between hν vs $(\alpha h\nu)^2$ which is shown in Fig. (3).

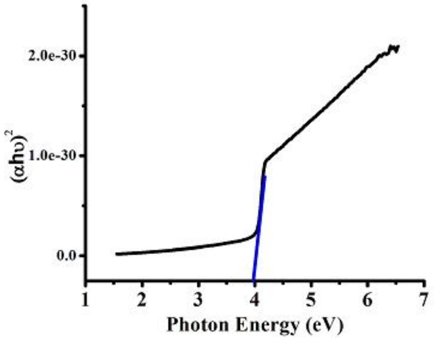


Fig. 3: hν Vs $(\alpha h\nu)^2$

Extinction coefficient (K) can be obtained from the relation $K = \frac{\alpha\lambda}{4\pi}$

The plot of extinction coefficient as a function of photon energy is shown in Fig. (4).

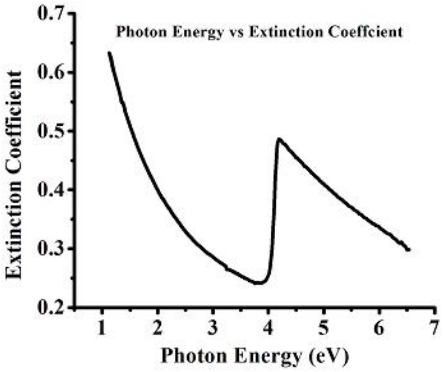


Fig. 4: Photon energy Vs Extinction coefficient

The reflectance (R) and refractive index (n) can be 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 reflectance was also plotted as a function of photon energy and is shown in Fig. (5).

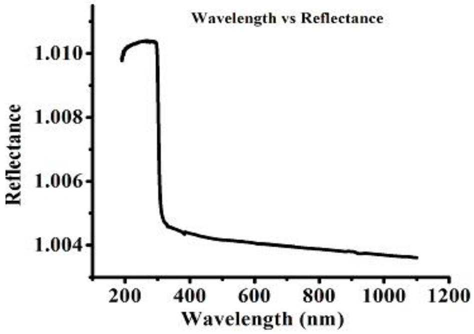


Fig. 5: Reflectance Vs Wavelength

The refractive index was calculated from the plot of refractive index vs wavelength and is shown in Fig. (6). The value of refractive index was found to be n=1.64.

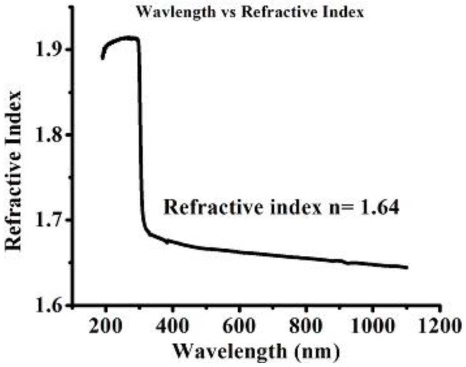


Fig. 6: Refractive index Vs Wavelength

3.4 Second harmonic Generation efficiency

Second Harmonic Generation test for the grown samples were 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, and the Repetition rate was at10 Hz. Finely powdered were packed tightly in a micro capillary tube. The SHG efficiency of the title material was measured with respect to the efficiency of the urea crystals. A photomultiplier tube was used to detect the frequency conversion process which results in the emission of green emission. A Q-switched Nd:YAG laser emitting fundamental wavelength of 1064nm was allowed to strike on the powdered sample. The experiment was carried out at room temperature. The input energy used was 3.2mJ/pulse with a pulse width of 8ns with a repetition rate of 10Hz were used. The estimated SHG efficiency of L-Alanine oxalate crystal was found to be 1.1 times that of urea crystal. The SHG efficiency test result confirms the suitability of L-Alanine oxalate crystals in NLO applications.

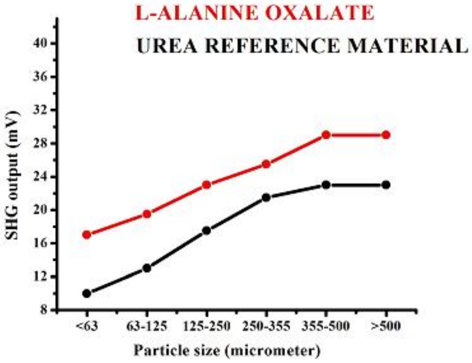
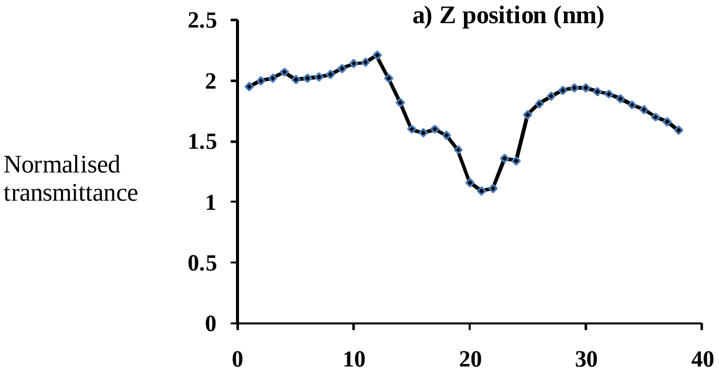


Fig. 7: Particle size dependency of L-Alanine oxalate crystal

3.5 Z-Scan studies

The third order nonlinear refractive index n_2 and the nonlinear absorption coefficient β of L-alanine oxalate crystal were 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. 8(a) and (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 is created, which acts as a thermal lens, resulting in the phase distortion of the propagating beam.



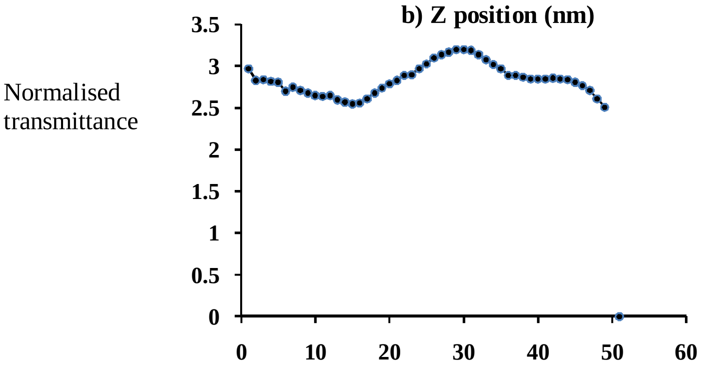


Fig.8. (a) z scan open aperture (b) z scan closed aperture

The difference between the peak and the valley transmission (ΔT_{P-V}) is 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 is given by the expression,

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

where $K = \frac{2\pi}{\lambda}$ in which, λ 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, which is calculated using the expression,

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

where, L is the thickness of the crystal and α is the linear absorption,

$$\left(\alpha = \frac{2.303\log\left(\frac{1}{T}\right)}{d}\right)$$

where d is the thickness of the crystal and T is the transmittance of the crystal. From the open aperture z-scan data, the nonlinear absorption coefficient is determined by using the relation,

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

where ΔT is the one valley value at the open aperture z-scan curve,

From the n_2 and β values the real and imaginary part of the third order nonlinear optical susceptibility are determined.

These are obtained by using the relations,

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

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

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

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

The value of β is for saturable absorption and for two-photon absorption. The third order nonlinear refractive index and the nonlinear absorption coefficient were evaluated from the z-scan measurements. Table (3) presents the experimental details and the results of z-scan technique for L-alanine oxalate.

Table 3: Measurement details and the results of the z-scan technique

Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	12 cm
Optical path distance (Z)	115 cm
Spot-size diameter in front of the aperture (ω_a)	1 cm
Aperture radius (r_a)	4 mm
Incident intensity at the focus (Z=0)	20 μW/cm^2
Effective thickness (L_{eff})	0.9980 mm
Linear absorption coefficient (α)	2
Nonlinear refractive index (n_2)	2.9787×10^{-1} cm^2/W
Nonlinear absorption coefficient (β)	3.133×10^5 cm/W
Real part of the third-order susceptibility	1.2975×10^{-3} esu
Imaginary part of the third-order susceptibility	1.077×10^{-4} esu

The calculated value of nonlinear refractive index (n_2) is 2.9787×10^{-1} cm^2 /W. The crystal has a positive refractive index (i.e. self focusing). The self focusing nature of the sample is due to the thermal nonlinearity resulting from the absorption of radiation at 632.8nm. From the open aperture z-scan curve, the nonlinear absorption coefficient (β) is found to be 3.133×10^5 cm /W. This concludes that the nonlinear absorption coefficient is regarded as two-photon absorption.

The real part of the third order susceptibility is found to be 1.2975×10^{-3} esu and the imaginary part of the third order susceptibility is found to be 1.077×10^{-4} esu.

4. Conclusion

A semiorganic NLO material of L-Alanine oxalate has been grown by slow evaporation solution growth technique. FTIR studies confirm the various functional groups and their vibrational interactions. The optical study shows that the crystal was optically transparent in the entire visible and near infrared region with lower cut-off wavelength of 330 nm. SHG efficiency of L-Alanine oxalate crystal is nearly 1.1 times that of urea crystal. It is concluded that the L-Alanine oxalate crystal can be used as an efficient material for NLO applications and further it can utilized for fabrication of devices. The nonlinear absorption is regarded as a two photon absorption process due to self-focusing nature of the L-Alanine oxalate crystal. As many attracting linear and nonlinear optical properties are observed in LAOX crystal, thus become a suitable candidate for optoelectronic applications.

References

1. M. D. Aggarwal, J. Stephens, *J. optoelectron. Adv. Mater*, 5, 3 (2003).
2. C. Razzetti, M. Ardoino, Zanotti, M. L. Zha, C. Paorici, *Cryst.Res.Technol*, 37, 456 (2002).
3. B. J. McArdle, J.N. Sherwood, A.C.Damask, *J. Cryst. Growth*, 22, 193 (1974).
4. E. M. Hampton, B. S. Shah, J. N. Sherwood, *J. Cryst. Growth*, 22, 22 (1974).
5. S. Dhaushkodi, K. Vasantha, *Cryst. Res. Technol*, 39, 3 (2004).
6. H. L. Bhat, *Bull. Mater. Sci*, 17, 123 (1994).
7. M. Narayanan Bhat, S.M, Dharma-prakash, *J. Cryst. Growth*, 235, 511-516 (2002).
8. B. Narayana Moolya, S. M. Dharmaprakash, *J. Cryst. Growth*, 290, 498-503 (2006).
9. Tanusri Pal, Tanusree Kar, Gabriele Bocelli, Lara Rigi, *Crystal Growth & Design*, 3, 13-16 (2003).
10. S. R. Marder, J. E. Sohn, G.D. Stucky, Materials for Non-Linear Optics; American Chemical Society: Washington, DC, (1991).
11. S. Alfred Devaprasad and J. Madhavan, *J. Arch, Appl. Sci. Res.*, 2,4, 26-32 (2010).
12. S. Dhanuskodi and K. Vasantha, *Cryst. Res. Technol*. 39(3), 259-265 (2004).
13. K.J. Arun and S. Jayalekshmi, Journal of Minerals, *Materials Characterization & Engineering*, 8(8), 635-646 (2009).
14. J. Thomas Joseph Prakash, J. Martin Sam Gnanaraj, S. Shek Dhavud, *Journal of Opt. Laser Technol*, 72, 108-115 (2015).