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GROWTH AND CHARACTERIZATION OF L-ALANINE SODIUM NITRATE SINGLE CRYSTAL FOR SECOND AND THIRD ORDER NLO APPLICATIONS

[1] S. Arockia Avila, [1] A. Leo Rajesh
[1] Department of Physics, St. Joseph's college,
[1] Tiruchirappalli - 620 002, India.

ABSTRACT- Single crystals of semiorganic nonlinear optical material of L-Alanine sodium nitrate (LASN) have been successfully grown by Slow Evaporation solution growth Technique. Cell parameters of the grown crystal was identified using single crystal X-ray diffraction analysis and found that the material crystallizes in orthorhombic crystal system with space group of $P2_12_12_1$.The presence of functional groups and the spectral properties were assessed by FTIR analysis. Optical transparency of the grown crystals was investigated by UV-Vis-NIR spectrum. Second harmonic generation efficiency of the grown crystal have been measured by Kurtz and Perry technique and it was found to be 2.8 times greater than that of KDP. Third order nonlinear optical susceptibility was identified using z-scan technique. The encouraging results show that the L-Alanine sodium nitrate crystals have potential application in optical devices.

Keywords- [Solution Growth technique, UV-Vis-NIR, Kurtz SHG test, Z-Scan]

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 nonlinear behaviour and anomalous phonon coupling and is a system exhibiting vibrational solitons [10]. Investigations were done to develop various semiorganic crystals which are more suitable for device fabrication by Selvakumar et al., [11-13]. The earlier works on LASN were restricted to high resolution X-ray diffraction, thermal, optical and dielectric studies sethuraman et al [14]. Hence an attempt is made to grow an semiorganic NLO material L-alanine sodium nitrate (LASN) using L-alanine and sodium nitrate by using slow evaporation technique and the grown crystal was subjected to SXRD, FTIR, UV-Vis-NIR, Second order and third order nonlinear optical studies and the results were discussed[15,16].

2. EXPERIMENTAL

2.1. SYNTHESIS OF L-ALANINE SODIUM.M NITRATE CRYSTALS

L-Alanine sodium nitrate (LASN) single crystals were synthesized from AR grade L-alanine and sodium nitrate 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 with the dimensions of 19x8x5 mm^3 and the photograph of the as grown L-alanine sodium nitrate crystal is shown in Fig.1.

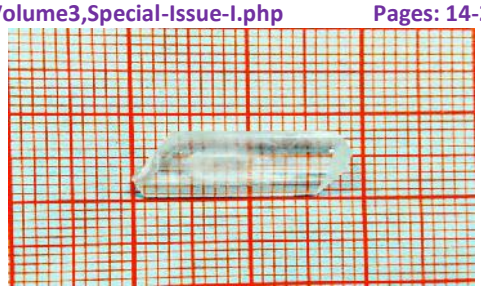


Figure. 1. As grown L-Alanine sodium nitrate single crystal

3. RESULTS AND DISCUSSION

3.1. Single crystal X-ray Diffraction analysis

Single crystal X-ray diffraction pattern is recorded for the grown crystal using Enraf Nonius CAD4 X-ray Diffractometer with MoKα radiation (λ = 0.7107Å) to obtain the lattice parameters and space group. The single crystal XRD data reveals that the grown LASN crystal belongs to orthorhombic system with space group $P2_12_12_1$. From the XRD data, the calculated lattice parameter values are found to be a = 6.109Å, b = 12.412 Å, c = 5.718 Å the cell volume, V = 433.56 $Å^3$ and are tabulated in table 1(a) .

L-Alanine SN	**Crystal Data**
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 6.109Å b = 12.412Å c = 5.718Å α = β = γ = 90°
Volume	433.56 Å

Table 1- (a) Single Crystal XRD data of L-ASN crystals

Some thereotical data is calculated and estimated as below that the valence electron plasma energy, $\hbar\mu_p$ is given by

$$\hbar\mu_p = 28.8(Z^\circ / M)^{1/2}$$

where Z = ((3 × Z_K) + (7 × Z_B) + (2 × Z_C) + (4 × Z_H) + (1 × Z_O)) = 54 is the total number of valence electrons, ρ is the density and M is the molecular weight of the crystal. The Penn gap and the Fermi energy are explicitly dependent on the $\hbar\mu_p$ [17] which are given by

$$E_p = \frac{\hbar\mu_p}{(\text{£}_\infty - 1)^{1/2}} \quad \text{and} \quad E_F = 0.2948(\hbar\mu_p)^{4/3}$$

polarizability α is obtained using the relation [18]

$$\sim = \left(\frac{(\hbar \mu_p)^2 S_0}{(\hbar \mu_p)^2 S_0 + 3E_p^2} \right) \times \frac{M}{\circ} \times 0.396 \times 10^{-24} cm^3$$

where S_o is a constant for the material which is given by

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

All these calculated data for the grown crystal are shown in the table 1(b).

Parameters	Values
Plasma energy (eV)	31.88
Penn gap (eV)	1.539
Fermi energy (eV)	35.65
Polarizability (cm^3)	1.66×10^{-23}

Table.1.(b) Some theoretical datas on L-GT single crystals.

3.2. Fourier Transform Infrared Spectroscopic Studies

The FTIR spectra of the grown crystal is 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 sodium nitrate is identified by Fourier Transform Infrared (FTIR) spectrum. The vibration peak at 3085cm^{-1} is due to asymmetric NH_3^+ stretching and that at 2293cm^{-1} corresponds to CH_3 stretching. The peaks at 1455, 1592, 1511cm^{-1} are assigned to NH_3^+ bending. The absorption peak at 1455 cm^{-1} is due to asymmetric CH_3^+ bending. The peak at 1411 cm^{-1} is due to symmetric stretching of C-COO. The NO_3 stretching is observed at 1360 cm^{-1} and C-H and N-H bending at 1304 cm^{-1}. The absorption band at 1234, 1150 cm^{-1} corresponds to NH_3^+ rocking. The NO_3 stretching is attributed to 1111 cm^{-1}. The vibration peaks at 1012, 918 cm^{-1} is due to overtone of torsional oscillation of NH_3^+ . The sharp peaks at 848, 772 cm^{-1} is due to NO_3 stretching. The COO- in plane deformation is due to the peak 648 cm^{-1} . The vibration peak at 538 cm^{-1} corresponds to torsional oscillation of NH_3^+. The observed wavenumbers and the proposed assignment of the spectrum are shown in Table 2. The absorption peak at 488 cm^{-1} is due to NH_3^+ in plane rocking. The presence of nitro groups in the spectrum confirms the grown LASN compound.

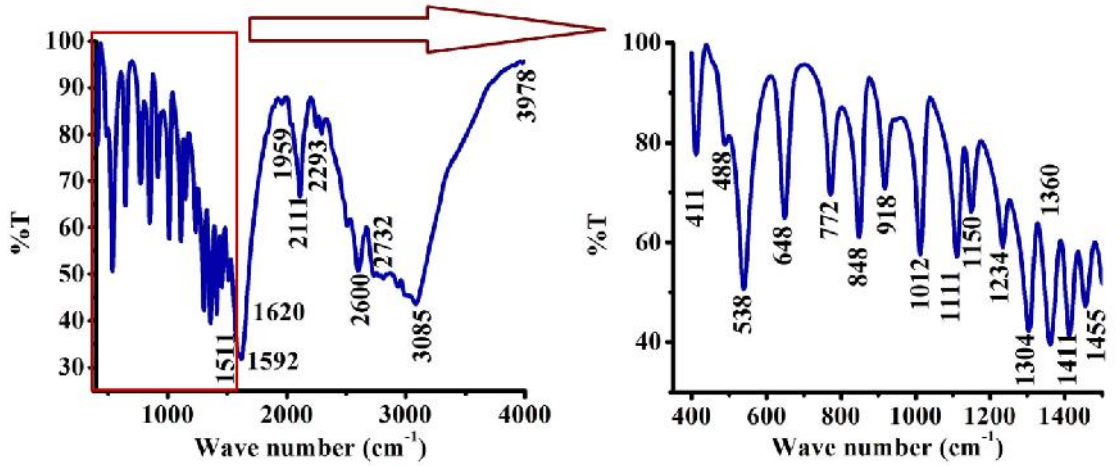


Figure 2- FTIR spectrum of L-ASN

Wavenumber (cm^{-1})	Assignment
3085	asymmetric NH_3^+ stretching
2293	CH_3 stretching
1592,1511	NH_3^+ bending
1455	asymmetric CH_3^+ bending
1411	symmetric stretching of C-COO
1360	NO_3 stretching
1304	C-H and N-H bending
1234, 1150	NH_3^+ rocking
1111	NO_3 stretching
1012, 918	overtone of torsional oscillation of NH_3^+
848, 772	NO_3 stretching
648	COO- in plane deformation
538	torsional oscillation of NH_3^+
488	NH_3^+ in plane rocking

Table 2- Vibrational assignments of L-ASN

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 is carried out using PERKIN ELMER LAMBDA 35 UV-Visible spectrophotometer.

Calculation of optical constants

Optical constants such as the optical band gap, extinction coefficient and refractive index of L-Alanine sodium nitrate crystals are estimated from the following relations [19].

The optical band gap (E_g) of L-Alanine SN crystal is estimated from the relation

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

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

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

Extinction coefficient (K) can be obtained from the relation

$$K = \frac{\sim^{a}}{4®}$$

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

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

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

Fig.3 Shows the UV-Visible-NIR transmission spectrum of L-ASN{Inset shows Plot of bandgap vs photon energy of L-ASN}. Fig.4 Shows the refractive index is calculated from the plot of wavelength vs refractive index and it is found to be n=1.87 and {Inset shows Plot of optical conductivity vs photon energy of L-ASN}

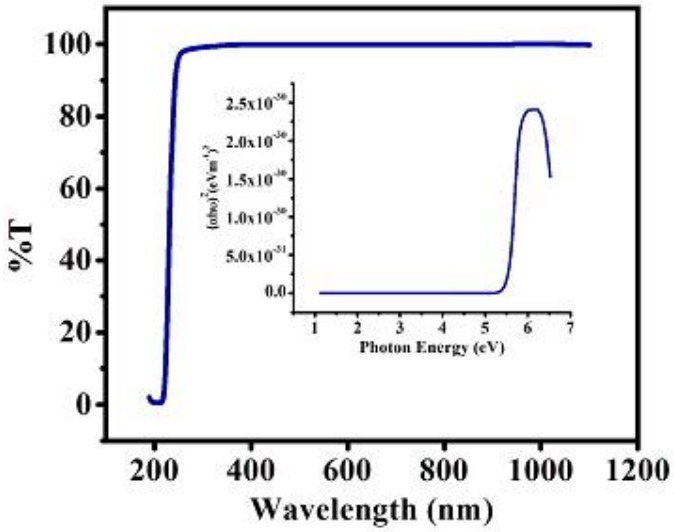


Figure 3- UV-Visible-NIR transmission spectrum of L-ASN {Inset shows Plot of bandgap vs photon energy of L-ASN }

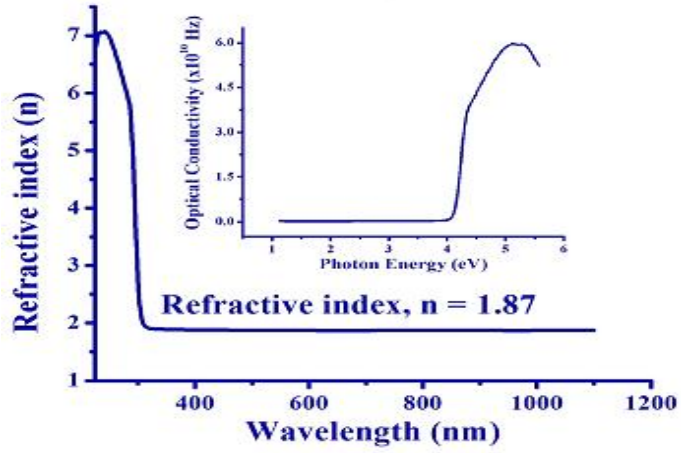


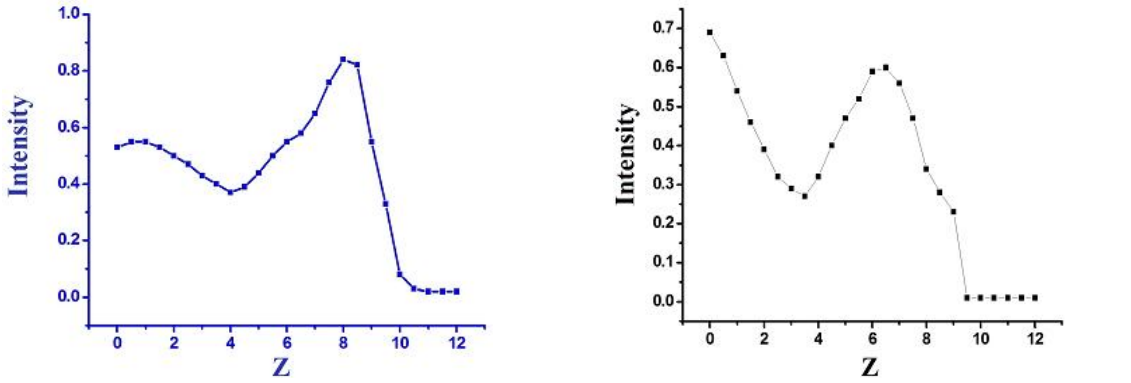
Figure 4- Plot of Refractive index vs Wavelength of L-ASN {Inset shows Plot of optical conductivity vs photon energy of L-ASN}

3.4. Second harmonic Generation efficiency

Second Harmonic Generation test for the grown samples are 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 is at10 Hz. Finely powdered crystal is packed tightly in a micro capillary tube. The SHG efficiency of the title material is measured with respect to the efficiency of the KDP crystals. A photomultiplier tube is 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 is allowed to strike on the powdered sample. The experiment is carried out at room temperature [20]. The input energy used is 3.2mJ/pulse with a pulse width of 8ns with a repetition rate of 10Hz are used. The estimated SHG efficiency of L-Alanine sodium nitrate crystal is found to be 2.8 times greater than that of KDP crystal. Thus the SHG efficiency test confirms the suitability of L-Alanine sodium nitrate crystals for NLO applications.

3.5. Z-Scan studies

The third order nonlinear refractive index n_2 and the nonlinear absorption coefficient β of L-alanine sodium nitrate crystal is 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. 5(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.



(a) Z position (nm) (b) Z position (mm)

Figure 5- (a) Z-scan open aperture of L-ASN (b) Z-scan closed aperture of L-ASN

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 (n_2) is given by the expression [21,22]

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

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, 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 (β) is determined by using the relation,

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

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,

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

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

where ε_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.

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

The third order nonlinear refractive index and the nonlinear absorption coefficient are evaluated from the z-scan measurements. Table.5. shows the experimental details and the results of z-scan technique for L-Alanine sodium nitrate. As seen from the closed aperture Z-scan curve, pre focal transmittance peak is followed by the post focal valley on both the sides of the focus, which shows the nonlinearity [23]. The calculated value of nonlinear refractive index (n_2) is -5.22x10^{-8} cm^2/W. The crystal has a negative refractive index (i.e. self defocusing). The self defocusing is due to local variation of the refractive index with temperature [24]. This is an essential property for the application of the crystal in the protection of optical sensors like night vision devices [25]. From the open aperture z-scan curve, the nonlinear absorption coefficient (β) is found to be -6.68x10^{-3} cm/W. This concludes that the nonlinear absorption coefficient is regarded as two-photon absorption [26]. The real and imaginary part of the third order susceptibility (χ^3) is found to be 3.10x10^{-6} esu and 1.68x 10^{-6} esu. Third order nonlinear optical susceptibility (χ^3) is found to be 3.5 x10^{-6} esu.

Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	12cm
Optical path distance (Z)	115cm
Spot-size diameter in front of the aperture (ω_a)	1cm
Aperture radius (r_a)	4mm
Incident intensity at the focus (Z=0)	20μW/cm^2
Effective thickness (L_{eff})	0.9980mm
Linear absorption coefficient (α)	2
Nonlinear refractive index (n_2)	-5.22x10^{-8} cm^2/W
Nonlinear absorption coefficient (β)	-6.68x10^{-3} cm/W
Real part of the third-order susceptibility	3.10x10^{-6} esu
Imaginary part of the third-order susceptibility	1.68x 10^{-6}esu
Third order nonlinear optical susceptibility (χ^3)	3.5 x10^{-6} esu

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

CONCLUSION

A semiorganic NLO material of L-Alanine sodium nitrate was grown by slow evaporation solution growth technique. Unit cell parameters were evaluated by single crystal X-ray diffraction analysis, which confirmed the grown crystal belongs to orthorhombic system with space group $P2_12_12_1$. 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 200 nm. SHG efficiency of L-Alanine sodium nitrate crystal is nearly 2.8 times greater than that of KDP crystal. Z-scan analysis explains that the crystal has a negative refractive index (i.e. self defocusing). The self defocusing is due to local variation of the refractive index with temperature and is an essential property for the application of the crystal in the protection of optical sensors like night vision devices. Thus L-Alanine sodium nitrate crystal can be used as a potential material for photonics, electro-optic and SHG device applications.

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