International Journal of Innovative Research and Advanced Studies (IJIRAS)
Volume 3 Issue 12, November 2016

ISSN: 2394-4404

Growth And Characterization Of A Semi-Organic Nonlinear Optical Crystal: L-Alanine Sodium Sulphate Anhydrous

D. Abila Darling

S. Ajitha

Department of Physics,
Nanjil Catholic College of Arts and Science

Abstract: ***Single crystal of L-Alanine Sodium Sulphate Anhydrous (LASS), a semi organic nonlinear optical material has been grown using the simple chiral amino acid L-alanine and sodium sulphate anhydrous by slow evaporation method. Crystal structure has been studied by XRD, L-alanine sodium sulphate anhydrous possessed orthorhombic structure. The incorporation of L-alanine in sodium sulphate anhydrous was estimated qualitatively by FTIR spectra. Thermal analysis carried out for the L-alanine sodium sulphate anhydrous exhibits a single sharp melting point at 258℃.The Vickers microhardness values were measured for the grown crystal. Its optical properties were examined by UV-Vis spectroscopic analysis, which shows that the crystal is transparent been the wavelengths 400 and 1000nm. The dielectric behavior of samples has been studied. The variation of dielectric constant, dielectric losses and a.c.conductivity with frequency of applied field in the range from 20Hz to 1MHz was studied. The dielectric constant and dielectric loss decreased with increase the value of frequency of applied field.***

I. INTRODUCTION

Nonlinear optical processes provide the key functions of frequency conversion and optical switching. These applications depend upon the various properties of the materials, such as transparency, birefringence, laser damage threshold, hardness, dielectric constant, thermal, photochemical and chemical stability.[1]. In addition, the organic crystals have large optical susceptibility, inherent ultra fast response times and high optical threshold for laser power as compared with inorganic materials [2]. Semi organic nonlinear optical crystals combine good thermal and mechanical properties of inorganic with high optical nonlinearity of purely organic compound [3]. Amino acids are interesting materials for NLO application as they contain proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group in them [4]. Especially some amino acids like arginine, lysine, L-alanine and γ-glycine are evidently showing NLO activity because they have a donar NH_2 group and acceptor COOH group and also intermediate charge transfer was possible. In the present study, single crystals of L-alanine sodium sulphate anhydrous have been successfully grown by slow evaporation technique at room temperature.

II. EXPERIMENTAL STUDIES

A. CRYSTAL GROWTH

Growth of L-Alanine Sodium Sulphate Anhydrous (LASS) crystals were carried out by slow evaporation technique. In the present study, analar grade samples L–alanine and sodium sulphate anhydrous were used. Double distilled water was used as the solvent. L-alanine sodium sulphate anhydrous was synthesized by the reaction between equimolar sodium sulphate anhydrous and amino acid, L-alanine. The reactants were thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer at 45˚C to yield a homogeneous mixture of solution. The solution was filtered using the wattman filter paper. Within a period of 6 days the crystal nucleates on the bottom surface of the crystallizer. During this period, the observation was made daily. Within a period of 15 to 20 days, well defined highly transparent L-alanine sodium sulphate anhydrous single crystals could be grown by slow evaporation technique. The process of recrystallization was carried out to purify the synthesized salt of LASS. The dimension of the grown crystal is about 0.8× 0.5 × 0.5 cm^3.

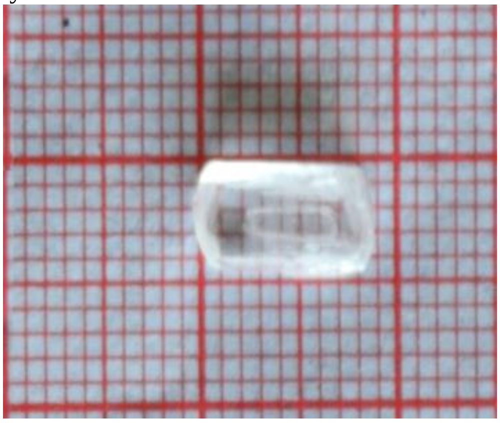

Figure 1: The grown L-alanine sodium sulphate Anhydrous single crystal

III. CHARACTERIZATION

A. STRUCTURAL ANALYSIS (XRD)

The X-ray diffraction studies are a finger print by which crystalline substances are identified [5]. The technique employed in the XRD method is the powder diffraction method. X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials. The powder XRD study was conducted to verify the single phase nature of the samples [6].

The crystals grown in the present investigations have been characterized for their structural properties by using XRD technique. The crystallographic parameters of L-alanine sodium sulphate anhydrous crystal in the present case have been evaluated using CuK_α radiation in XRD technique. For X-ray diffraction the samples were ground at room temperature and were passed through a 106 mesh sieve. The X-ray diffractograms (XRD) of this compound was recorded on Philips PW1710 Diffractometer using CuK_α radiation of wavelength 1.5405Å. The samples were scanned for 2θ values from 10°C to 90°C at a rate of 2°/min. Figure.5.1 shows the X-ray diffractograms of L-alanine sodium sulphate anhydrous (LASS) crystals. The sharp peaks indicate the good crystalline nature of the LASS crystals. The "X" PERT HIGHSCORE X-ray software was used for analysis of powder XRD patterns. Well defined Bragg peaks are obtained at specific 2θ angles indicating that crystals are ordered. Using orthorhombic crystallographic equation, lattice parameter values are calculated and listed in table.

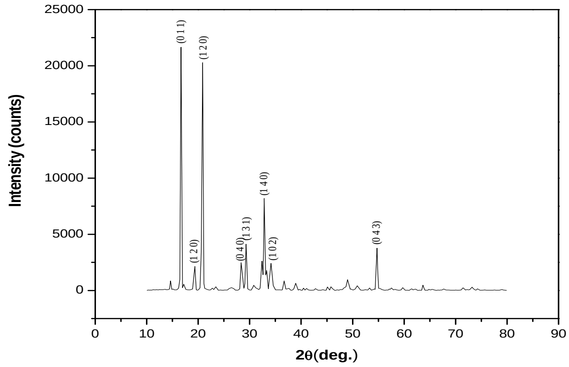

Figure 2: PXRD spectrum of L-alanine sodium sulphate anhydrous single crystals

Crystal	**L-alanine sodium sulphate anhydrous**
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a(Å)	6.720
b(Å)	12.425
c(Å)	5.880
α=β=γ	90°
Unit cell volume $(Å)^3$	493

Table 1

B. FTIR ANALYSIS

Infrared spectroscopy is an extremely effective method for determining the presence or absence of a wide variety of functional groups in a molecule [7]. In the present study, FT-IR spectrum was recorded in order to qualitatively analyse the presence of functional groups in L-alanine sodium sulphate anhydrous single crystals in the range $400cm^{-1}$ to $4000cm^{-1}$ using the Perkin Elmer grating infrared spectrophotometer.

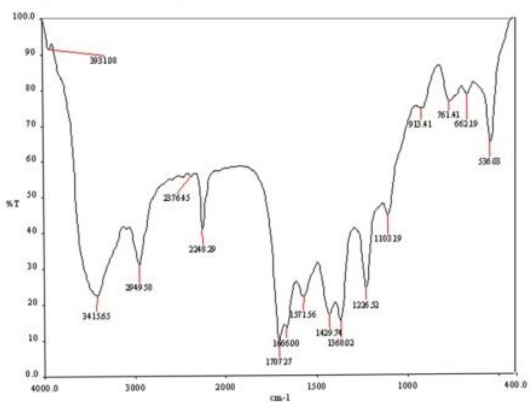

Figure 3: The FTIR spectrum of L-alanine sodium sulphate anhydrous single crystals

The table 2 shows the functional groups assignments for L-alanine sodium sulphate anhydrous crystals.

Absorption wave numbers cm^{-1}	**Assignment**
3415.05	O – H stretching
2949.58	CH_3 asymmetric stretching
1707.27	saturated C=O stretching

International Journal of Innovative Research and Advanced Studies (IJIRAS)
Volume 3 Issue 12, November 2016

ISSN: 2394-4404

1666.00	N-H stretching (strong)
1571.56	N-H inplane bending
1429.7	C=H bending
1368.02	O-H inplane bending
1226.52	C-N stretching
1103.19	S –O stretching
913.41	O-H out of plane bending
761.41	NH_2 out of plane bending
662.19	NH_2 Wag (broad)
536.03	S-S stretching

Table 2

IV. THERMAL ANALYSIS

The thermal analysis of grown crystal was carried out by Perkin Elmer thermal Analyzer in the temperature range 40°C - 900°C at a heating rate of 15°C/min, the thermogram is shown in the figure 5.3. The curve shows that there is a single major weight loss of 75% at about 250°C. It is confirmed by the presence of sharp endotherm of the DTA curve. Hence, the material is thermally stable up to 258°C. The sharp weight loss around 75% between 258°C and 269°C indicates the complete elimination of CO_2, SO_2, NH_2 gases from the substance. The sharpness of the endothermic peak shows good degree of crystallinity of the sample. Based on this result it is said that the compound can be used for NLO applications up to this temperature (291.72°C) [8].

Sample	Decomposition point °C	Reference
LASS	258	[Present work]
L-alaninium oxalate	196	[33]
L-alanine sodium nitrate	220	[26]

Table 3: Comparative thermal stability of semiorganic NLO materials

Table.3. shows the comparative thermal stability between the present work and some semiorganic NLO materials. Hence LASS compound has a good thermal stability up to 258°C and we can conclude that LASS crystal is suitable for many applications up to 258°C and it has a good thermal stability compared to other semiorganic NLO crystals such as L-alaninium oxalate and L-alanine sodium nitrate.

V. UV- VISIBLE SPECTRAL ANALYSIS

The optical transmittance range and transparency cut-off wavelength are the main requirements for device applications. The UV- Visible study of the grown crystal was carried out by Lambda - 35 UV- Visible spectrometer in a range 190 – 1100 nm. Optically clear single crystal L-alanine sodium sulphate anhydrous was used for this study. There is no appreciable absorption of light in the entire visible region. Good optical transmittance and lower cut off wavelength are very important properties for nonlinear optical (NLO) crystals [9]. The optical transmission range shows that L-alanine sodium sulphate anhydrous is a suitable candidate for second harmonic generation. The optical transmittance spectrum of LASS is shown in the figure 5.11.

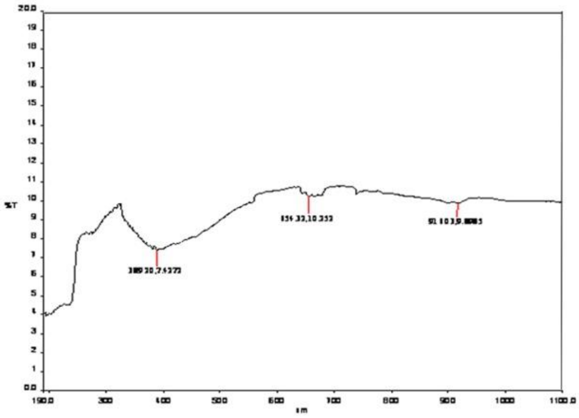

Figure 4: UV-Visible spectrum of L-alanine sodium sulphate anhydrous single crystals

VI. VICKERS HARDNESS STUDY

The mechanical strength of the grown crystal was measured using Vickers hardness study. In the present study, L-alanine sodium sulphate anhydrous was subjected to Vickers microhardness test with the load varying from 25 to 100g [10]

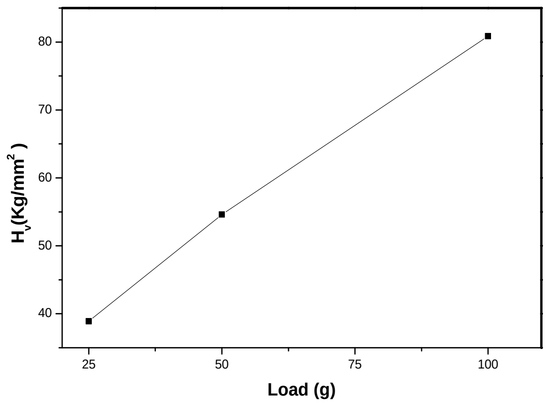

Figure 5: Vickers Microhardness values of L-alanine sodium sulphate anhydrous single crystals

VII. DIELECTRIC STUDIES

An important property of a dielectric is its ability to support an electrostatic field while dissipating minimal energy in the form of heat. The lower the dielectric loss (the proportion of energy lost by heat), the more effective is a dielectric material and the crystals with high dielectric constant lead to power dissipation. The plots of dielectric constant, dielectric loss, a.c. conductivity of LASS crystal is shown in figures 6, 7, 8 respectively.

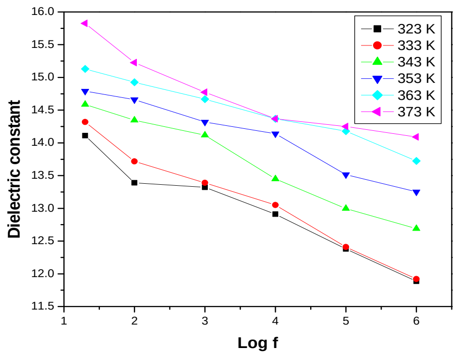

Fig.6.Plot of dielectric constant Vs log f

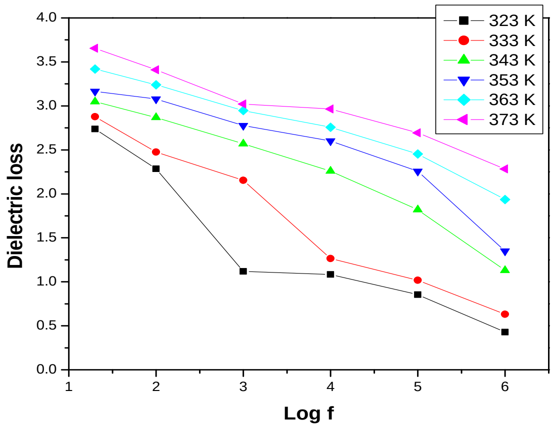

Figure 7: Plot of dielectric loss Vs log f

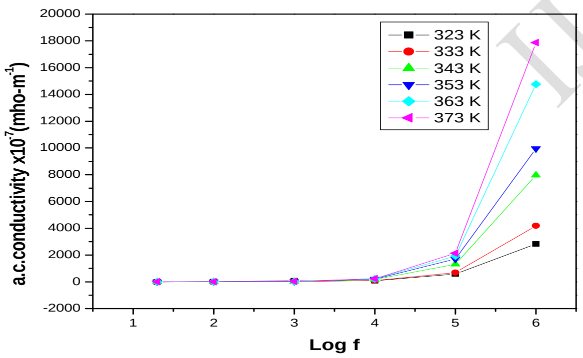

Figure 8: Plot of A.C conductivity vs log f

The dielectric studies of L-alanine sodium sulphate anhydrous crystals were carried out at different frequencies. The dielectric constant(ε_r) and dielectric loss (tanδ) depend on frequency of applied field. Figure 5.8, 5.9 shows that the dielectric constant and dielectric loss are both inversely proportional to frequency. This is a normal dielectric behavior [16]. The value of dielectric constant and dielectric loss decreases as the frequency increases (5.8, 5.9). This can be understood on the basis that the mechanism of polarization similar to that of the conduction process. The high value of dielectric constant in the low frequency region may be due to the contributions from all four polarizations namely, electronic, ionic, orientational and space charge polarizations[11]. The electronic exchanges of the number of ions in the crystals give local displacement of electron in the direction of the applied field, which inurn give rise to polarization. As the frequency increases a point will be reached where the space charge cannot sustain and comply with the external varying field and hence the decrease by exhibiting the diminishing values of dielectric constant. Continuous and gradual decrease in dielectric constant suggests that L-alanine sodium sulphate anhydrous crystals like any normal dielectric may possess domains of different size varying relaxation times. Figure 5.9 shows the variation of dielectric loss with frequency. This is the normal behavior of observed earlier [12, 13]. The dielectric loss is a measure of the energy absorbed by the dielectric. AC conductivity ($\sigma_{a.c}$) of the sample has been determined using the relation, $\sigma_{a.c}=\varepsilon_0\varepsilon_r 2\pi f \tan\delta$, where f is the frequency of a.c. supply, ε_r is the dielectric constant, ε_0 is the permittivity of free space, tanδ is the dielectric loss. The variation of a.c.conductivity ($\sigma_{a.c.}$) with the frequency of applied field is shown in figure 6.0. The a.c.conductivity increases as the frequency increases [14]. Generally, the low value of dielectric loss indicates that the sample possess good crystalline quality with fewer defects. The lower value of dielectric constant is a suitable parameter for the enhancement of second harmonic generation (SHG) signals [15].

VIII. CONCLUSION

Single crystals of L – alanine sodium sulphate anhydrous (LASS) which is grown by slow evaporation technique. Powder X-ray diffraction studies were carried out for the L-alanine sodium sulphate anhydrous crystals and the lattice parameters were calculated. LASS crystal belongs to orthorhombic crystal system with the space group $P2_12_12_1$. From the FTIR spectrum we can confirm the structure of the L– alanine sodium sulphate anhydrous to have both the alanine and sodium sulphate anhydrous molecules. The crystals were subjected to thermo gravimetric analysis. From the TG curves the thermal stability of the crystals was determined. The grown material is thermally stable up to 258°C. The sharp endothermic peak at 291.72°C is due to the decomposition of the sample desired by its DTA analysis. Based on this result it is said that the compound can be used for NLO applications up to this temperature (291.72°C).

Vickers hardness test was performed on grown crystals to test the hardness of the sample. From this test we find the micro hardness number increases with load. Further the value of the work hardening coefficient is found to be 4.55. From this result we conclude that the crystal is soft. The optical transmittance range of L–alanine sodium sulphate anhydrous was recorded using Lambda – 35 spectrometer in the range 190 – 1100nm. From the UV visible spectrum we find that the crystal is transparent in the range 550 – 1100nm and the optical band gap is found to be 5.15 eV. The dielectric study on L–alanine sodium sulphate anhydrous single crystal was carried out using a digital LCR meter. The capacitance of the sample was noted in the temperature range 50°C to 100°C at multiple frequencies. Dielectric constant and dielectric loss of L–alanine sodium sulphate anhydrous decreases with increasing frequency. The value of dielectric constant (ε_r) mainly depends on the presence of space charge polarization

 ISSN: 2394-4404

which in turn depends on the purity and perfection of the sample. Two probe method is used to find a.c. conductivity of L–alanine sodium sulphate anhydrous single crystal. It can be seen that a.c. conductivity increases with increase in frequency.

REFERENCES

[1] Dalton LR. (2003) Matter, Rational design of organic electro-optic materials. J Phys Condens Matter; 15: R897-R934.
[2] P. Praveen Kumar, (2011), Arch. Appl. Sci. Res., 3 290
[3] V. Kannan, R. Bairava Ganesh and .Ramaswamy, (2006) J. Cryst Growth and Design 6, 1876.
[4] Tapati Mallik, Tanusree kar, (2005) J Crystal Growth 285**,** 178.
[5] A. M. Petroyan, R. P. Sukiyasan, H. A. Karpefyan, S. S. Tenzyan, R. S. Feigefron, (2003) J. Cryst.Growth 213, 103.
[6] Ferdousi Akhtar and Jiban Podder, J. Cryst. Pro and Technol(2011), 155.
[7] Brian Smith Infrared spectral interpretation systematic Approach, CRC press LLC, America, 1999.
[8] M. D. Aggarwal, J. Stephans, A. K. Batra, R. B. Lal, (2003) Journal Optoelectronic Advanced Materials, 5, 555.
[9] Ferdousi Akhtar and Jiban Podder, (2011) Journal Crystal Pro and Technol, 1, 55.
[10] K. J. Arun and S. Jayalekshmi, (2009) Journal of Minerals & Materials Characterization & Engineering, 8, 635
[11] E. M. Onitsch (1947), Mikroskopie, 2, 131.
[12] N. V. Prasad, G. Prasad, T. Bhimasankaran, suryanarayana, and G. S. Kumar (1996), Indian Journal of Pure Applied Physics.34,639.
[13] Anderson JC1965, Dielectrics. Champman and Hall,
[14] K. D. Parikh, D. J. Dave, and M. J. Joshi, (2003) Modern Phys.118, 2349.
[15] M. Meena and C. K. Mahadevan, (2008) Crystal. Res. Technol.43, 166
[16] Brahadeeswaran S, Bhat HL, Kini NS, Umarji AM, Balaya P and Goyal PS. (2000) Dielectric, thermal, and mechanical properties of the semiorganic nonlinear optical crystal sodium p-nitrophenolate dihydrate. J Applied Physics; 88: 5935-5940.