STUDIES ON L-ALANINE SULPHANILATE CRYSTAL AND ITS CHARACTERISATIONS

G.Rajeswari[1], M.K.Sangeetha[2], G.Thanapathy[3]

1Assistant Professor, Department of Physics, A.V.C College of Engineering, Mayiladuthurai, India

2Assistant Professor, Department of Chemistry, A.V.C College of Engineering, Mayiladuthurai, India

3Associate Professor, Department of Physics, Poombuhar College, Melaiyur-638316, India

Abstract:

L-Alanine sulphanilate crystals (LASA) was synthesized and successfully grown as bulk single crystal by the slow evaporation solution growth method using double distilled water as a solvent. The grown crystals were studied for the structural, optical and thermal properties. The crystalline nature and its various planes of reflections were observed by the powder XRD. The presence of functional groups in the grown crystal was identified from FT-IR. The TG - DTA evaluates the thermal properties of the grown crystal. The transparency of the grown crystal was investigated by recording UV- Vis analysis.SEM analysis indicates the smoothness of the crystal and SHG measurements its NLO applications. Minimum inhibitory concentration (MIC) of LASA for antibacterial activity was determined using the microdilution bioassay as described by ELOFF.

Keywords: Slow evaporation, Powdered X-ray diffraction, FT-IR, TGA-DTA, SEM, SHG, MIC

1. Introduction

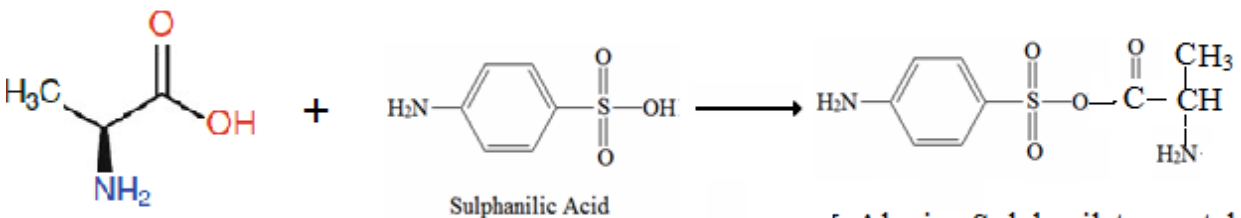
Materials with nonlinear optical properties have wide applications in modern optical and optoelectronic devices. Several important technologies like microelectronics, optoelectronics, computers, photonics, lasers, information science, etc., need well characterized bulk single crystals. In recent years the amino acid group materials were mixed with organic or inorganic salts in order to improve their chemical stability, laser damage threshold, thermal and physical properties and linear and non-linear optical properties. Amino acids are interesting organic materials for NLO applications. They contain proton donor carboxylic acid (COOH) and the proton acceptor amino (NH_2) groups which provide the ground state charge asymmetry of the molecule required for second order non linearity [1-10]. Among NLO materials, organic NLO materials are generally believed to be more versatile than their inorganic counterparts due to their more favorable nonlinear response. In the organic class, R-amino acids exhibit some specific features such as molecular chirality, weak Vander Waals and hydrogen bonds, the absence of strongly conjugated bonds, wide transparency ranges in the visible and UV spectral regions, and zwitter ionic nature of the molecule which favors crystal hardness. L-Alanine is an essential amino acid with the chemical formula $C_3H_7NO_2$ and it is an important source of energy for muscle tissue, the brain and central nervous system and also it strengthens the immune system by producing antibodies, helps in the metabolism of organic acids and sugars L-Alanine can be considered as the fundamental building block of more complex amino acid which shows strong nonlinear behavior.(11-18). In the recent years, efforts have been made on organic-materials mixed amino acid crystals, in order to improve the chemical stability, laser damage threshold and

nonlinear optical properties. Several researchers have carried out a lot of studies on pure and organic, and metal ions-doped crystals. Sulphanilic acid (SA) ($C_6H_7NO_3S$) is a promising and interesting compound, which finds a number of applications including nonlinear optics. Sulphanilic acid possesses several good features of good dosimeter and is characterized by its simple spectrum. Sulphanilic acid is nearly tissue equivalent which enables its use in radiation therapy dosimetry, also it is isotropic and its detection limit is about 100 ± 30 mGy. Among many investigated dosimeters, the SO^{3-} anion was used by several authors and it has been proved to have quiet consistent dosimetric properties. Sulphanilic acid was already reported to possess dosimetric properties.(19,20) The Sulphanilic acid compound displays an anionic part and a cationic part, indicative of the Zwitterionic structure. Sulphanilic acid crystallizes in the orthorhombic structure with space group of Pbca.

In the present investigation L-Alanine sulphanilate crystals was synthesized by slowly evaporating the solvent. L-Alanine and Sulphanilic acid in stoichiometric ratio of (1:1) were taken and grown as a single crystal.

II. EXPERIMENTAL

The starting material was synthesized by taking L-Alanine (AR grade) and Sulphanilic acid (AR grade) in a 1:1 stoichiometric ratio. The required amount of starting materials for the synthesis of L Alanine Sulphanilate crystal was calculated according to the following reaction:



The calculated amount of Sulphanilic Acid was first dissolved in water. L-Alanine was then added to the solution. The solution was stirred continuously with magnetic stirrer for 2 hours till complete dissolution of the starting materials. The prepared solution was filtered and allowed to dry at room temperature. The crystals were obtained by slow evaporation technique. The purity of the synthesized crystal was further improved by successive recrystallization process; thereby good optical qualities of single crystals were obtained in 25 days. The photograph of the grown crystal is shown below.

III CHARACTERISATION

3.1. POWDERED XRAY DIFFRACTION

Powder X-ray diffraction studies of L-Alanine and LASA crystal was carried on a Bruker D500 Xray diffractometer with CuK(k=1.15418A) radiation. The samples were Scanned for 2θ values from 10-90 at a rate of 2 min. The X-ray powder diffraction method used to study the structural property of the LASA. The powder XRD pattern of L-Alanine and LASA crystal is shown in figure.1and 2. By least square fit method, the diffraction patterns of LASA crystal have been indexed. The observed values for different 2θ values of the corresponding reflective planes for the L-Alanine and LASA are given in the table 1.

Table 1 X-ray powder diffraction data of L-alanine crystal

L-Alanine		**LASA**	
Pos./°2θ	d-spacing/A°	Pos./°2θ	d-spacing/A°
16.5024	5.36745	16.5562	5.3501
17.0380	5.19988	17.719	5.0014
20.8409	4.25884	20.965	4.2339
22.6595	3.92098	22.76	3.9035
26.7316	3.33221	26.482	3.3631
28.8869	3.08831	28.8445	3.0927
30.5910	2.92004	30.269	2.9504
32.7803	2.72985	32.884	2.7215
33.2133	2.69524	33.362	2.6835
34.5685	2.59262	34.907	2.5682

Figure.1 Powder XRD analysis of L-Alanine

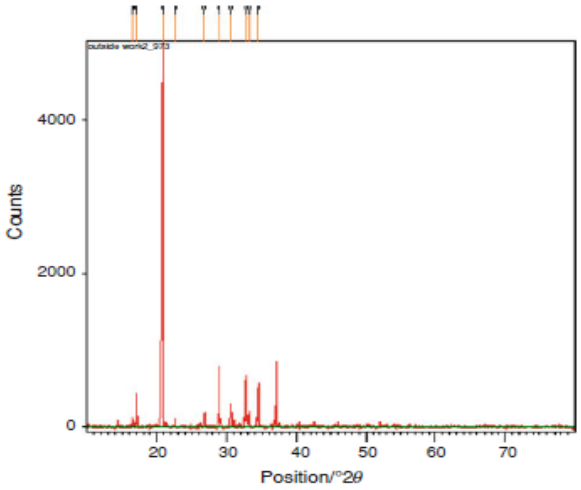
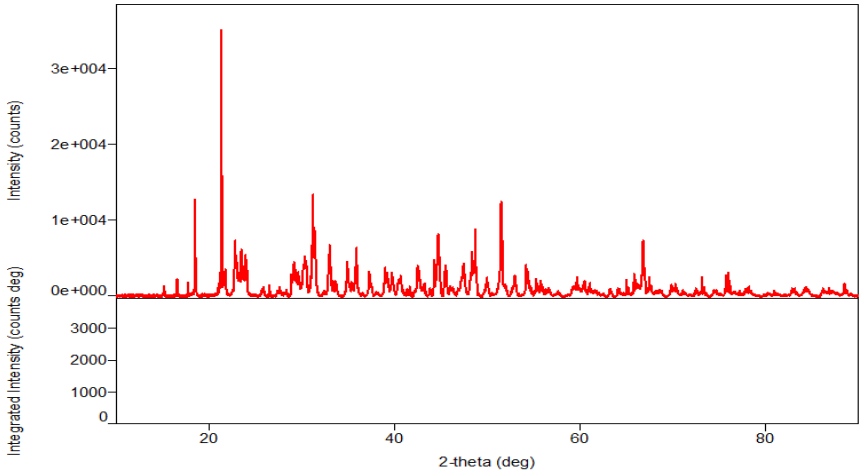


Figure.2 Powder XRD analysis of LASA



3.2 FTIR spectral studies

From potassium bromide pellets technique the infrared spectra of L-Alanine and LASA were obtained by using Make- Bruker Optic GmbH Model No-TENSOR27 SOFTWARE-OPUS Version 6.5, Spectrophotometer in the range of 4,000-400cm cm^{-1}. In figure 3 and 4 the infrared spectrum of L-Alanine and LASA are shown, The IR spectra of LASA mainly arise because of internal vibration of functional groups NH_3, CH, CH_3 and COOH. S-O, SO_3. The absorptions of LASA have been compared with those of the parent compound (L-Alanine) in Table 3. From the fig. the bands of SO_3 group characteristic vibration of 4-di substitute aromatic rings as well as those of amino groups are identified within the range of 3600-3100 cm^{-1} and overlap of the stretching vibration of O-H with those of amino group is visible.

Table.3 Comparison of FTIR Spectra of L-Alanine and LASA

Wave number/cm^{-1}		**Assignments**
L-Alanine	LASA	
3381	3486.75	O-H stretching vibration
2604.00	2603.65	O-H stretching vibration
2110	2111.38	NH_2 stretching
1200.49	1232.26	Stretching mode of C-H
1109.00	1113.06	Stretching vibration of SO_2 from SO_4
1011.50	1014.34	C-O stretching vibration
958.33	919.16	C-H Bending vibration
648.19	647.87	C-H Bending vibration

Fig.3 FTIR Spectrum of L-Alanine

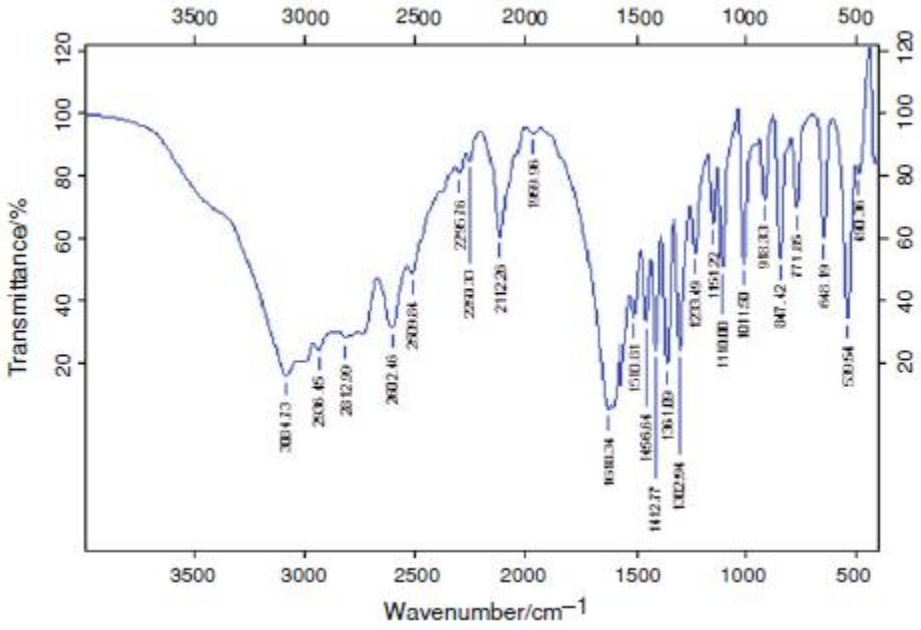
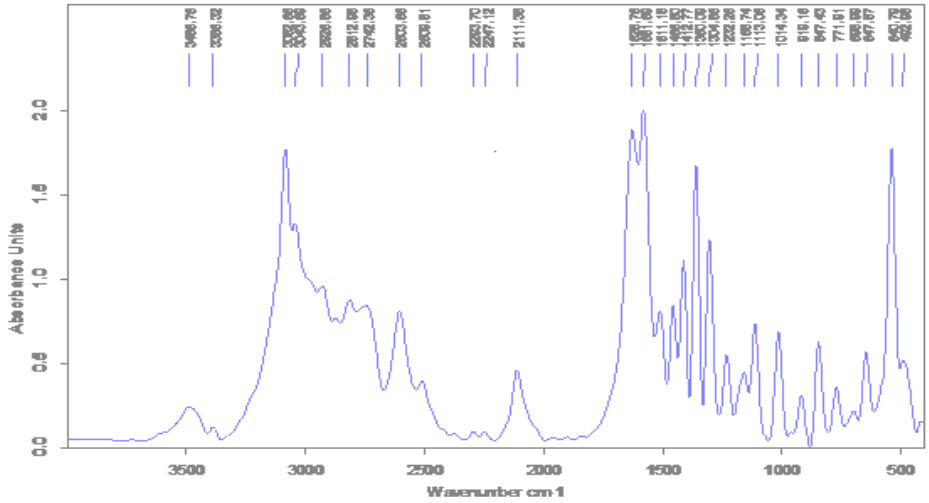


Figure 4 FTIR Spectrum of LASA



3.3 UV–Vis–NIR spectral analysis

The UV-Vis-NIR spectra were recorded on Jasco V-630 spectrophotometer in the range of 200-1,100 nm with scanning speed of 400 nm min. These UV-Vis-NIR spectra are used to compare the optical absorption range of L-Alanine and **of LASA** crystals. (Fig.5,6) .A sharp fall in the transmittance at 310 nm corresponds to the fundamental absorption (UV cut-off wavelength) of LAS. Absorption in the near- ultra violet region arises from electronic transitions associated within the samples. The absence of absorption of light in the visible region is an intrinsic property of all amino acids. From the transmittance spectra, it is noticed that LAS crystal has high transmittance in the entire visible–NIR region of the spectra and this property enables the materials for optoelectronic applications.

Figure 5 UV-VIS-NIR Spectrum of L-Alanine

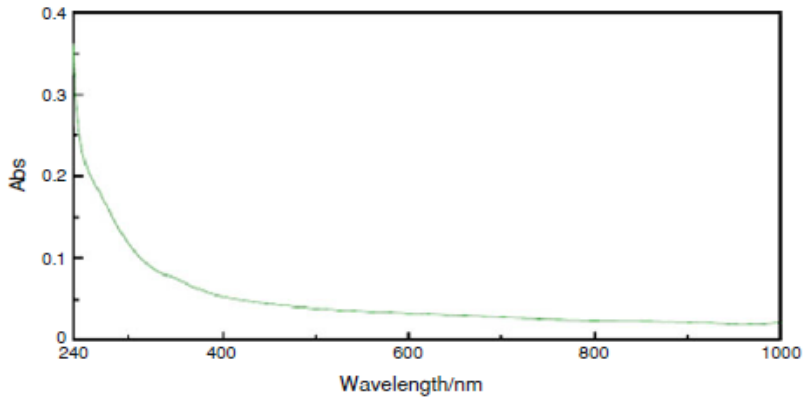
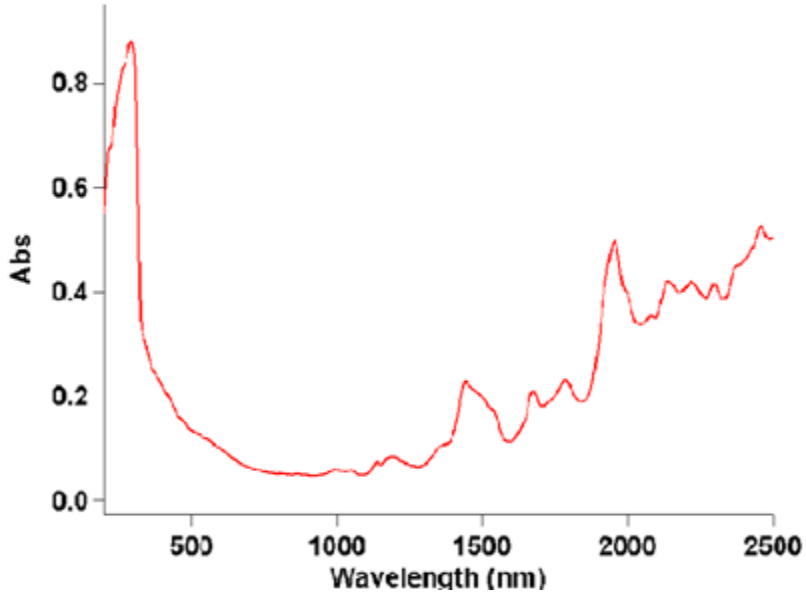


Figure 6 UV-VIS-NIR Spectrum of LASA



3.4 TGA- DTA studies

Thermograms provide information about decomposition patterns of materials and weight loss also. The thermogravimetric analysis (TGA) of LASA was carried out between 150 - 1000 ºC in nitrogen atmosphere at a heating rate of 10 ºC / min (Model: NETZSCH STA 409). There is no weight loss upto198.42ºC, which clearly illustrates the absence of physical absorption. A single intense weight loss starts at about 288.86 ºC and it is assigned to the water molecules of LASA. Based on this observation it can be said that the compound is completely volatilized up to 907.73 ºC. The resulting LASA thermal spectrum is as shown in Fig.8.In the trace of Differential Thermal Analysis (DTA), there is a sharp endothermic peak at about 276.87 ºC, which is assigned to melting point of the grown crystal. This is followed by a broad exothermic peak at 793.83 ºC shows that LAS starts to decompose. In the DTA trace no other endothermic or exothermic peaks are observed which suggest the absence of any isomorphic transformation below its melting. The sharpness of the endothermic peak shows good degree of crystallinity of the grown ingot.

Figure7 TGA curves L-Alanine

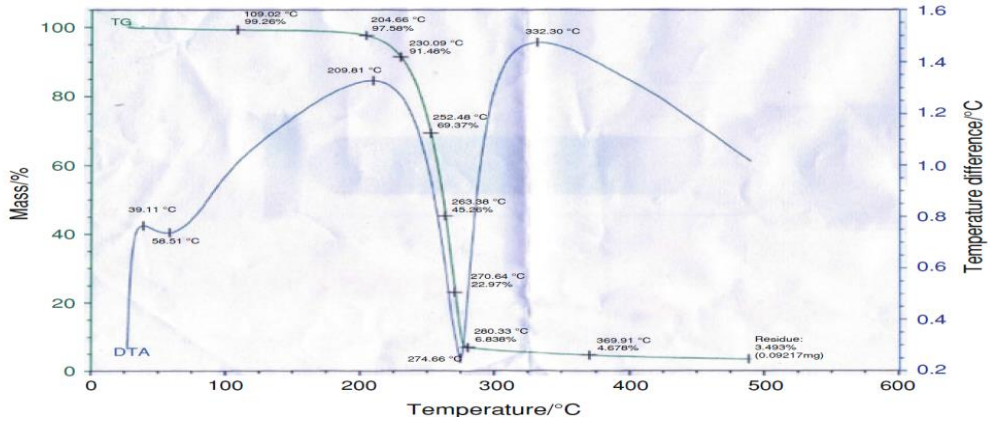


Figure 8 DTA-TGA curves of LASA

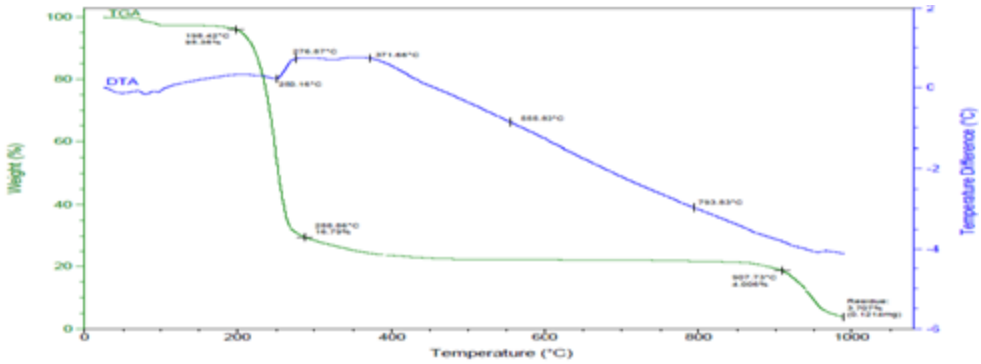
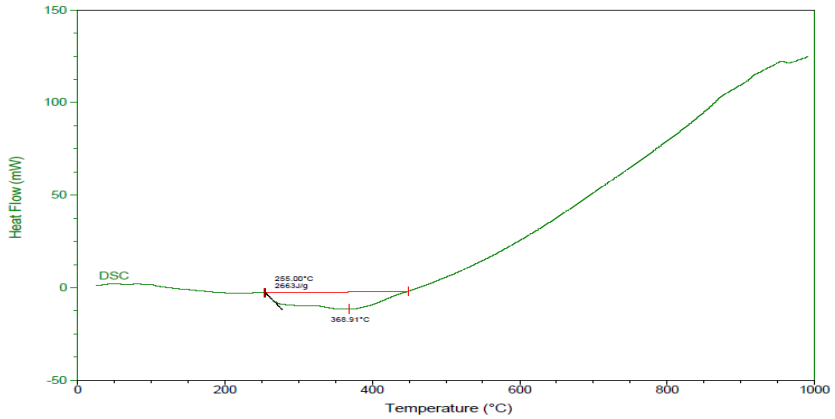


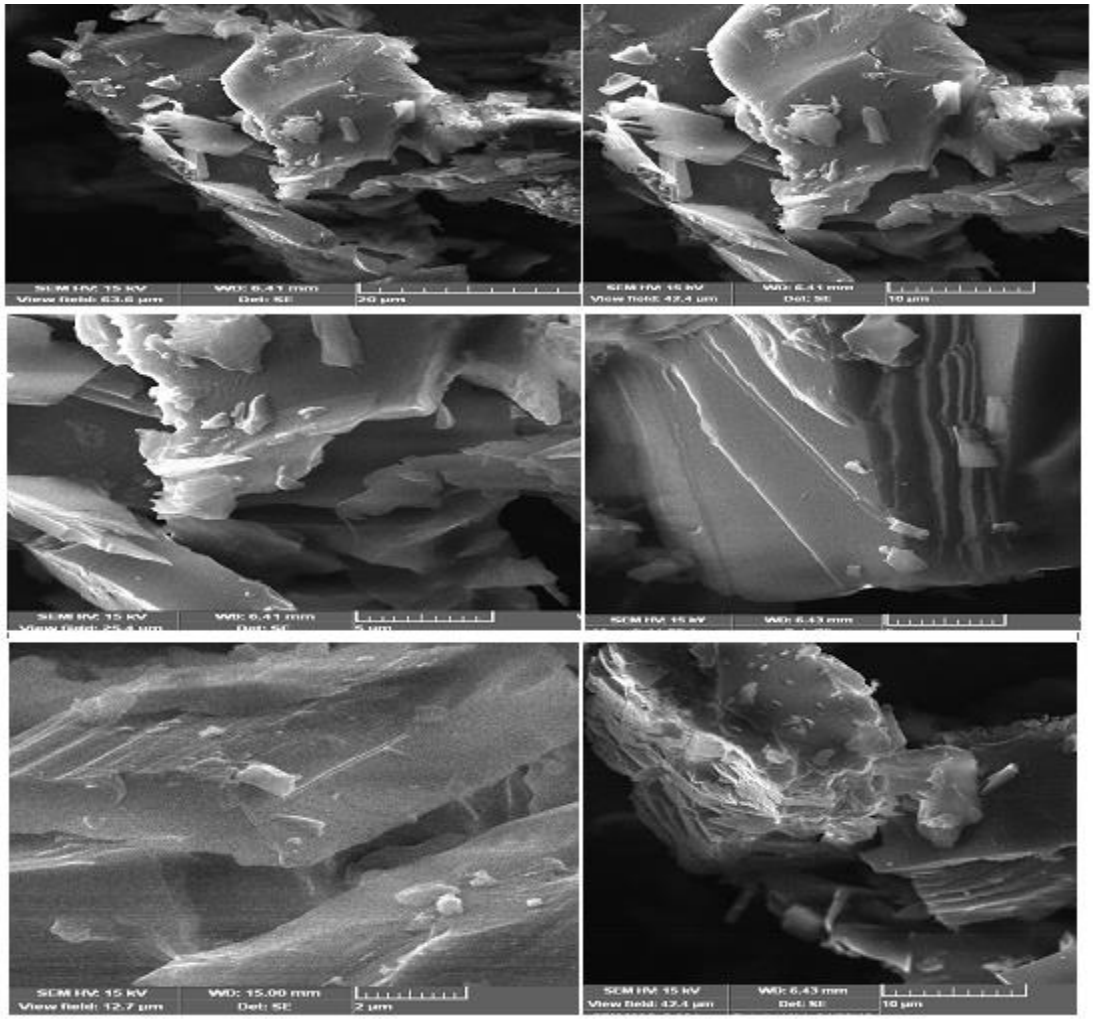
Fig.9 DSC curves of LASA



3.5Crystal surface analysis by SEM

SEM analysis was used to study the morphology of **LASA** and is given in Fig.10 From the Fig. 10 the following observations are evident.

Fig.10 a SEM images of LASA



(1) At a magnifications of 15kv and at a scale of 20μm, we observe the crystals have smoothed surfaces. We can also see the significant differences in the following magnification and scales.

(2) At a magnifications of 15kv and10μm.
(3) At a magnifications of 15kv and at a scale of 5μm.
(4) At a magnifications of 15kv and at a scale of 5μm.
(5) At a magnifications of 15kv and at a scale of 2μm.
(6) At a magnifications of 15kv and at a scale of 10μm.

3.6 SHG Efficiency measurement

The study of NLO conversion efficiency of grown crystal has been carried out with the classical powder method developed by Kurtz and Perry. It is an important popular to evaluate the conversion efficiency of NLO materials. The crystal was ground into fine powder and packed in the micro capillary tube. A Q-Switched Nd; YAG laser (1064nm) has been used. The input pulsed energy of 1.2mJ/pulse was incident on the crystalline powder. The generation of second harmonic was confirmed by the emission green radiation. The present result shows that SHG conversion efficiency of KDP is 50mv and for LASA 80mV.

The enhancement in SHG efficiency of L-Alanine doped Sulphanilic Acid is due to the optically active amino group which may get added in the structure and increases its SHG efficiency.

3.7 Antimicrobial activity

Minimum inhibitory concentration(MIC) of compounds for antibacterial activity were determined using the microdilution bioassay as described by ELOFF. Over night cultures (incubated at 37ºC in a water bath with an orbital shaker) of 1gm positive (Staphylococcus aureus,bacillus subtilis and streptococcus pyogens) and 2gm negative(Escherichia coli pseudomonas aeruginosa and salmonella typhii)bacterial strains were diluted with sterile Mueller-Hinton(MH) broth to give final inocula of approximately 106 CFU/ml(colony forming units). The compound LASA was dissolved in water to known concentration 50mg/ml. 100micro litres of this sample was diluted two-fold with sterile distilled water in a 96Well micro litre plate for each of the five bacterial strain. One hundred micro litres of each bacterial culture were added to each well. The plates were covered with parafilm and incubated at 37ºC for 24hrs. Bacterial growth was indicated by adding 50µl of 0.2mg/ml p-iodonitrotetrazoliu chloride(INT) with further incubation at 37ºC for 2hrs. since the colourless tetrazolium salt is biologically reduced to a red product due to the presence of active organism, the MIC values were recorded as the concentration in the last well in which no colour change was observed after adding the INT indicator. Bacterial growth in the well was indicated by a redish pink colour. The assay was repeated twice with two replicates per assay(21).

The results of this study revealed that the compound LASA exhibite antibacterial activity which might be helpful in preventing the progress of various diseases and can be used in alternative system of medicine. The table below shows the MIC values of the pathogens against LASA.

Compound	Bacillus subtilis	***Vibrio cholerae***	Escherichia coli
LASA	6.25	6.25	0.0975

CONCLUSION

A Semi Organic single crystal LASA was successfully grown employing slow evaporation solution growth technique. The crystallographic planes were identified for the crystal by performing powder XRD studies and the sharp and intense peaks reveal that the grown crystal has good crystalline perfection. The FTIR spectral analysis verifies the presence of functional groups of crystal LASA. Optical study carried out confirms that LASA crystal can be utilized for the applications of optical window by utilizing the wavelength region ranging from 310 to 2500 nm. TGA/DTA analysis asserts that the crystal melts around 198.46°C and dehydrates and the dehydrated LASA is chemically stable at the melted state up to 793.63°C.

The crystal surface is very smooth at the micro level which shows that can add more molecules to grow into a large crystal. The Kurtz powder second harmonic generation test shows that the crystal LASA (80mV) is a promising candidate for optical second harmonic generation application. The antimicrobial activity of LASA was confirmed by Micro dilution bioassay as described by ELOFF.

REFERENCE

1. A.Ashour, N.El-kadry, S.A.Mahmoud, Thin Solid Films. 269. 117–120, (1995)
2. A.P.Voronov, Yu.T.Vyday, V.I.Salo, V.M.Puzikov, S.I.Bonderenko, Radiat. Measurem.,42. 553 – 556, (2007)
3. P. N. Kizer, J. R. Morton, and K. F. Preston, J. Chem. Soc. Faraday Trans., 87.3147–3149(1991).
4. K.B.R. Varma, K.V. Ramanaiah, K.V. Rao, Bulletin of Material Science. 5.39–48 (1983).
5. D.S. Chemla, J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, vol. 1.(Academic Press, Orlando, 1987)
6. P. Mythili, T. Kanagasekaran, S.N. Sharma, R. Gopalakrishnan,J. Cryst. Growth **306.**344–350 (2007)
7. S. Sohma, H. Takashashi, T. Taniuchi, H. Ito, Chem. Phys. **245**,359 (1999)
8. K.V. Rao, A. Smakula, J. Appl. Phys. **37**, 319 (1966)
9. D.K. Pradhan, B.K. Samantary, R.N.P. Chaudhary, A.K. Thakur,Mater. Sci. Eng. B **11.**7 (2005)
10. J. Suchanicz, Mater. Sci. Eng. B **55**,114 (1998)
11. D. Vladikova, J.A. Kilner, S.J. Skinner, G. Raikova, Z. Stoynov,Electrochim. Acta **51**.1611–1621 (2006)
12. B.T. Hatton, K. Landskron, W.J. Hunks, Mater. Today **9**(3), 22–31(2006)
13. C. Balarew, R. Dehlew, J. Solid State Chem. **55**(1), 1–6 (1984)
14. A.W. Coats, J.P. Redfern, Nature **201**, 68–69 (1964)
15. N. Tigau, V. Ciupinaa, G. Prodana, G.I. Rusub, C. Gheorghies, E.Vasilec, J. Optoelectron. Adv. Mater. **6**, 211–217 (2004)
16. A.K. Chawla, D. Kaur, R. Chandra, Opt. Mater. **29**, 995–998(2007)
17. D.D.O. Eya, A.J. Ekpunobi, C.E. Okeke, Acad. Open Internet J.**17**, 1311–4360 (2006)
18. R.C. Dhas, J. Charles Bennet, F.D. Gnanam, J. Cryst. Growth **137**,295–298 (1994)
19. Sangeetha MK, Mariappan M, Madhurambal G, Mojumdar SC , J Therm. analysis Calorim.108:887–94(2012)
20. M. Anantharaja and R. Gopalakrishnan* International Journal of ChemTech Research Vol.6, No.1,pp 222-235, Jan-March 2014
21. M.S. Kajamuhideena, K. Sethuramana,∗, P. Sasikumarb, H. Shakila, Materials Science & Engineering B,240.106-115,2019