

GROWTH AND CHARACTERIZATION OF L-ALANINE AMMONIUM ACETATE NONLINEAR OPTICAL (NLO) SINGLE CRYSTALS

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Abstract: The homogeneous solution of L-Alanine Ammonium Acetate (L-AAA) was prepared for equal molar ratio and good optical crystals were grown by slow evaporation method. The grown crystal was subjected to various characterizations such as single, powder X-ray diffraction (XRD), Fourier Transform Infra-red (FTIR) spectroscopy, UV-Vis Absorption spectroscopy. The presence of elements in the compound was identified by EDAX analysis. Thermo Gravimetric Analysis (TGA) and Second harmonic Generation (SHG). The cell parameters were determined by single crystal X-ray diffraction such as $a = 5.80 \text{ \AA}$, $b = 6.05 \text{ \AA}$, $c = 12.32 \text{ \AA}$, $V = 432 \text{ \AA}^3$; $\alpha = \beta = \gamma = 90^\circ$ and confirmed that it belongs to orthorhombic crystal system. The characteristics of the grown crystal were discussed in detail i.e., Cell parameters, optical, functional group analysis and Thermal studies result.

Key Words: NLO, solution growth, thermo gravimetric (TG), UV-VIS-NIR, SHG, DSC and FT-Raman.

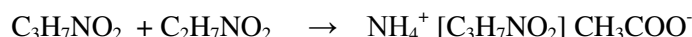
1. INTRODUCTION:

Recent developments in the field of nonlinear optics (NLO) have pushed organic second order nonlinear optical material into practical applications such as high-speed information processing, optical communication and optical data storage [1]. Among organic crystals, α -amino acids exhibit favourable features of molecular chirality and also possess wide transparency in the whole visible spectrum [2]. In NLO applications the amino acid crystals have greater importance due their chiral symmetry and crystallize in noncentrosymmetric space groups. Amino acid crystals have very good structure for the NLO applications such as proton donating and proton accepting group [3]. Many amino acid crystals were reported with good NLO property i.e., L-alanine cadmium chloride, L-valine cadmium chloride. This manuscript defines the crystal structure of L-Alanine Ammonium Acetate and the crystalline nature is studied by the powder X-ray diffraction. Functional groups have been identified by the FTIR studies [4]. The optical absorption is studied by the UV-Vis spectrophotometer and also SEM and EDAX analyses were discussed in this manuscript.

2. EXPERIMENTAL PROCEDURE:

2.1. SYNTHESIS AND CRYSTAL GROWTH

The L – Alanine doped Ammonium acetate materials were taken in equal molar ratio. In adduct is formed according to the following reaction [5].



The double distilled water and stirred at room temperature for 4 hours to achieve the homogenous condition. The L-Alanine doped ammonium acetate material was synthesized by slow evaporation method (L-AAA) tiny crystals also grown. The L- AAA material was purified by repeated recrystallization [6]. After purification the solution was prepared for super saturation condition and filtered with whatmann filter paper. The crystal clear solution carefully transferred to 50 ml beaker and closed with pinholes plastic sheet for natural evaporation [7]. After 4 weeks, optically clear crystal was harvested with good dimension 6mm x 5mm x 3mm. Good dimension crystals are very essential for device fabrications and optical applications. The grown crystal is shown in Fig.1.



Fig.1. Photograph of L-AAA crystal grown

3. RESULTS AND DISCUSSIONS

3.1. POWDER X-RAY DIFFRACTION

The good optical L-AAA crystal was powdered finely and subjected powder X-ray diffraction characteristics using the Bruker D8 Advanced powder X-ray diffractometer with Cu K α ($\lambda = 1.5418\text{\AA}$) [8]. The study was carried in the range of 10° to 80° . The recorded X-ray pattern is shown in Fig.2. The good crystalline nature was confirmed from the single sharp peak.

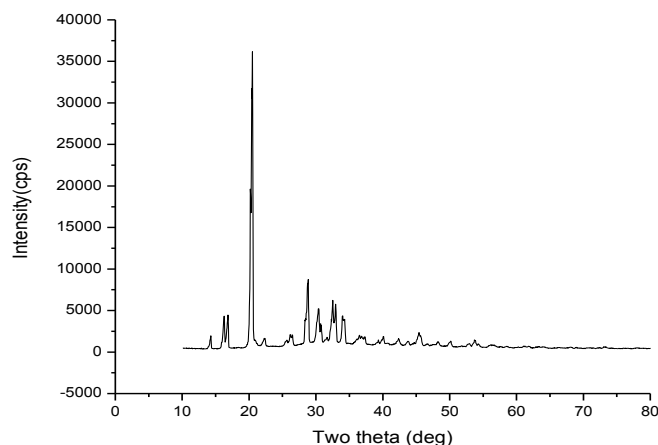


Fig.2.X-ray pattern of L-AAA crystal

3.2. SINGLE X-RAY DIFFRACTION

The good quality grown of L-AAA crystal were subjected to single crystal X-ray diffraction analysis using the Bruker instrument the cell parameter and space group were found. The cell parameter of L- L-Alanine doped ammonium acetate crystal are $a = 5.80\text{ \AA}$, $b = 6.05\text{ \AA}$, $c = 12.32\text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and orthorhombic system with the space group $P2_12_12_1$, the crystallographic data as good agreement with the reported values [9].

3.3. FOURIER TRANSFORM INFRARED SPECTRASCOPIY

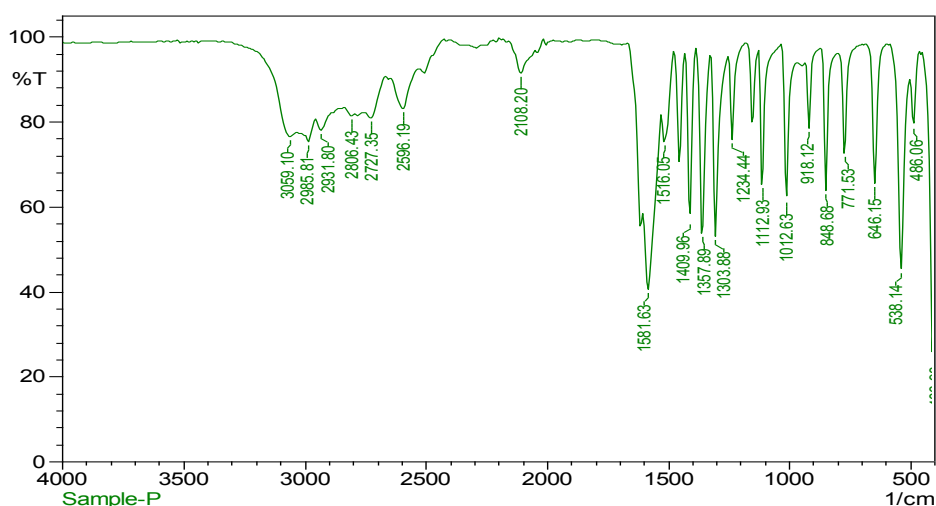


Fig.3.FTIR spectrum of L-AAA crystal

FTIR spectroscopic analysis the recorded FTIR spectrum of L-AAA is as shown in figure 3. The stretching frequency around 3059 cm^{-1} clearly indicates $=\text{C-H}$ stretching of alkane group and the presence of hydrogen bonding [10]. In addition, stretching frequency at 2985 cm^{-1} shows the presence of CH group in alkane functionality. The presence of dimer OH indicates carboxylic group gives its stretching frequency around 2806 cm^{-1} [11]. The stretching vibration NH_3^+ and frequency around 2596 cm^{-1} and it also clearly seen in the crystal. The peaks at 1581 cm^{-1} are assigned to stretching modes of C-O stretching of carboxyl group. The $=\text{C-H}$ bending indicates the alkynes groups and its particular frequency around 646 cm^{-1} [12].

S. No	Wave number (cm ⁻¹)	Assignments
1	3059	=C - H stretching
2	2985	CH stretch
3	2806	Dimer OH
4	2596	NH ₃ ⁺ stretching vibration
5	1581	C-O stretching
6	646	=C-H bend

Table.1. Vibrational band assignments of L-AAA crystal

3.4. Raman Spectrum

For the purpose of identification of compounds and qualitative analysis the FT-Raman spectral analysis the FT-Raman spectral analysis method has been adopted also using the instrument Bruker RFS 27 FT-Raman spectrometer [13]. An Nd:YAG air cooled diode pumped laser beam of powder 100mW was focused on the sample. The scattered light was collected at the angle of 180° in the region 200-3500 cm⁻¹ resolution 2 cm⁻¹, 200 scans [14]. The observed spectrum is shown in Fig 4. The C-H stretching is identified at 3127cm⁻¹ [15]. The peak at 1404 cm⁻¹ is seen because of COO⁻ symmetric stretching [16]. The wave number at 1684 cm⁻¹ is C=O stretching. Raman assignment of L-AAA is presented in Table 2.

FT-IR wave number cm ⁻¹	FT-Raman wave number cm ⁻¹	Assignment
3059	3127	=C-H stretch
2596	-	NH ₃ ⁺ Stretching Vibration
1581	1567	Amino acid group primary
1516	1495	NH ₃ ⁺ symmetric stretch
1409	1404	COO ⁻ symmetric stretch
1357	1343	CH ₂ wagging, CH ₃ Assymmetric bend
1303-1112	1315-1109	COO ⁻ symmetric stretch
1012	1058	C-N Stretch
918	924	C-H Bending
848	851	C-C-N Symmetric Stretching
646	654	=C-H bend

Table.2. FT-IR and Raman Assignment of L-AAA Crystal

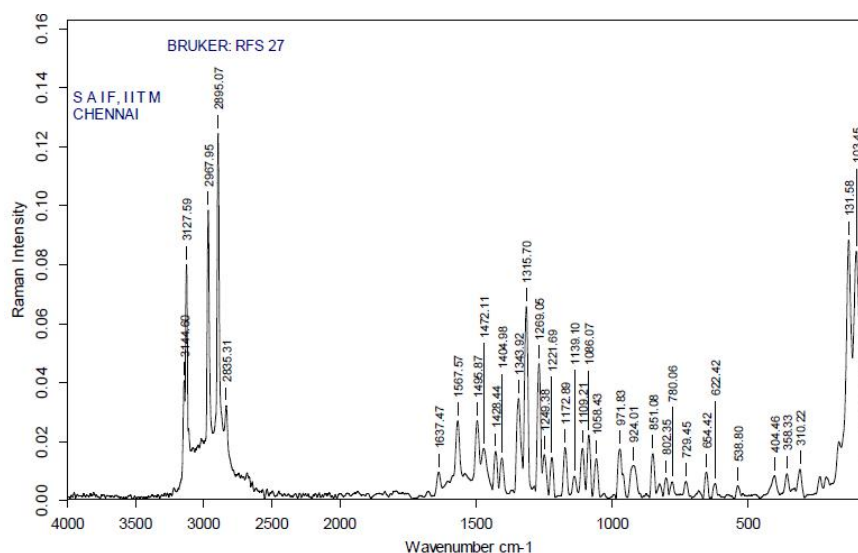


Fig.4. The FT-Raman Spectrum of L-AAA

3.5. SEM and EADX analysis

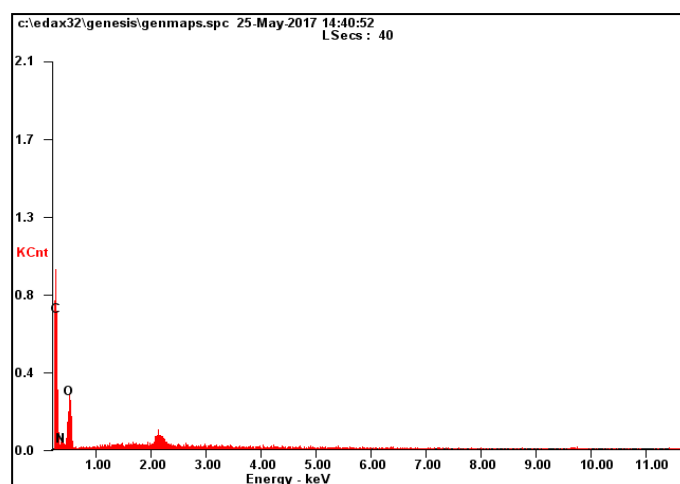


Fig .5. EDAX pattern of L-AAA

Energy dispersive X-ray spectrometry (EDX) providing the crystal line information from the few nanometer depth of the material surface [17]. Spectrum energy vs. relative counts of the detected X-ray is obtained and evaluated for qualitative and quantitative determination of the elements present in the sample volume. The EDAX spectrum of LAAA crystal is shown in Fig, 5

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>CK</i>	55.74	61.56
<i>NK</i>	14.73	13.95
<i>OK</i>	29.53	24.48
<i>Matrix</i>	Correction	ZAF

The external morphology of the sample is derived from signal received from electron interaction. A two dimensional image is generated over a selected area of the surface of the sample for analysis [18]. The recorded SEM image is shown fig. 6. From the figure it is observed that surface is smooth and free from cracks, however very few micro crystals are seen on the surface [19].

3.6. UV-VIS-NIR SPECTRAL STUDIES OF L-AAA CRYSTAL

The grown crystal of L-AAA was subjected to UV- absorption spectra. The peak was absorbed in the range of 200 - 800 nm [20] and shown in Fig.7. The grown crystal has highly transparent above the 201 nm also it is potential candidate for the optical applications.

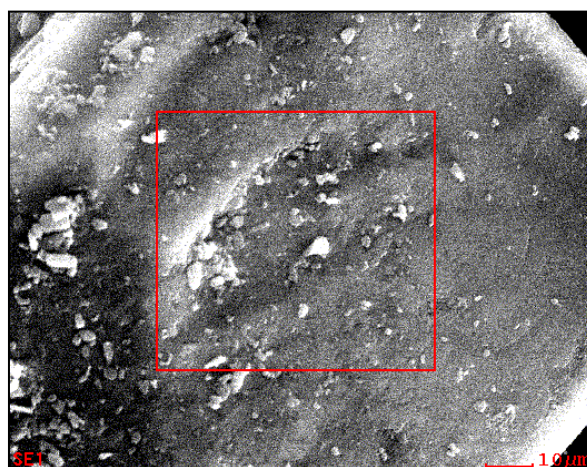


Fig .6. SEM image of LAAA Crystal

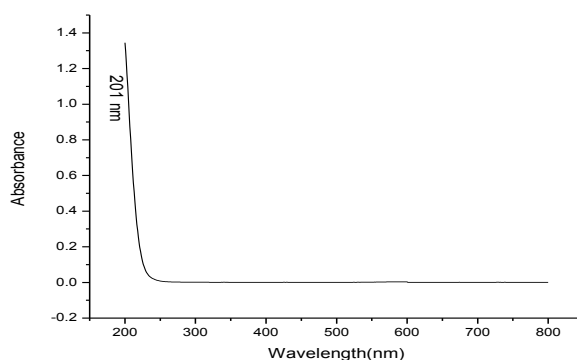


Fig.7. UV-Vis -NIR Spectrum of L-AAA Crystals

3.7. BAND GAP ENERGY

The energy band gap for a grown crystal was calculated using the Tauc equation $(\alpha h\nu) = A (h\nu - E_g)^n$. Where α is the absorption coefficient, h is the Plank's constant and ν is the frequency of incident photon, A is a constant [21]. The linear portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$ when extrapolated to the energy axis, gives the band gap. A plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 8. from the intercept of straight line on the energy axis, the band gap was found to be 5.6 eV. Large value of band gap indicates that the material is a good insulator and can provide large transmission in visible region [22].

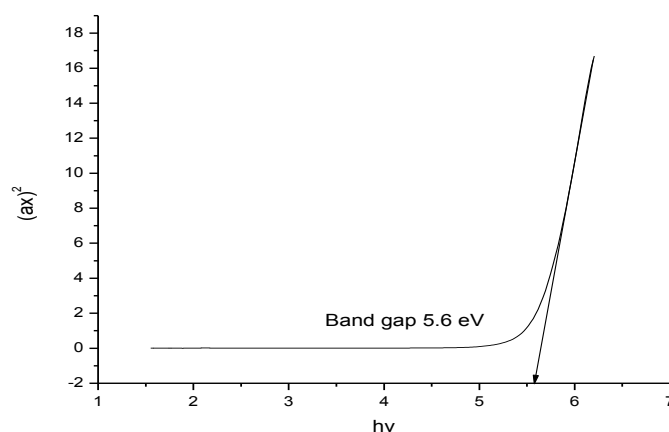


Fig.8. Band gap of L-AAA crystals

3.8. THERMO GRAVIMETRIC ANALYSIS

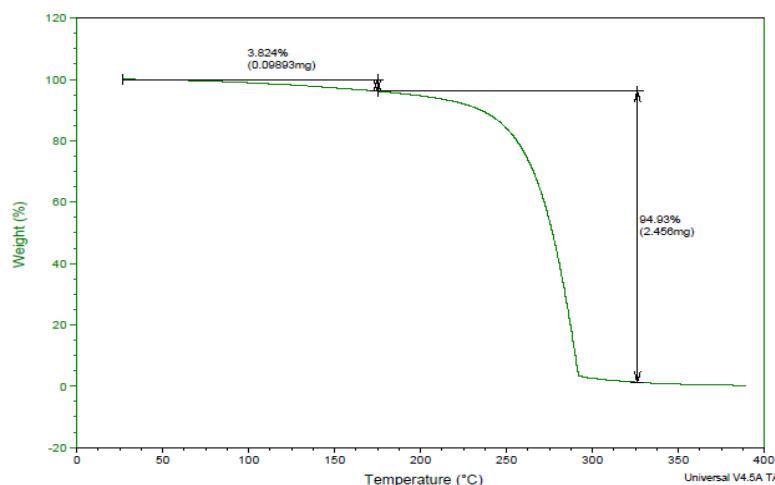


Fig.9. TGA curve for L-AAA crystals

In order to study the thermal stability of the grown crystal, Thermo Gravimetric Analysis (TGA) have been carried out using a SDT Q600 V20.9 Build 20 model thermal analyzer in an inert nitrogen atmosphere [23]. The thermal studies such as TGA studies were carried out for L– Alanine doped ammonium acetate crystal in the temperature range 28 to 800°C at the heating rate of 20°C per min. The recorded TGA thermal curves for L–Alanine doped ammonium acetate crystal are shown in the figure 9. From the TGA curves, there is a weight loss occurs at 290°C (94.95%) [24]. This weight loss may be attributed to the dissociation of L–Alanine decomposition.

The DSC analysis of the grown crystal was carried out between 28 °C to 800 °C. There is a sharp endothermic peak starting at 269.86 °C to 289.19 °C, which corresponds to the decomposition as observed in TGA analysis [25]. Again it also confirms absence of melting and any entrapped solvent in the lattice. DSC curve shows the sharp endothermic peak indicates the crystal has good crystal and decomposition point of as grown L-AAA crystal is 289.19 °C [26].

The TGA-DSC result shows that the grown crystal is thermally stable up to 269.86 °C and establishes its suitability to with stand the high temperature for laser experiments [27].

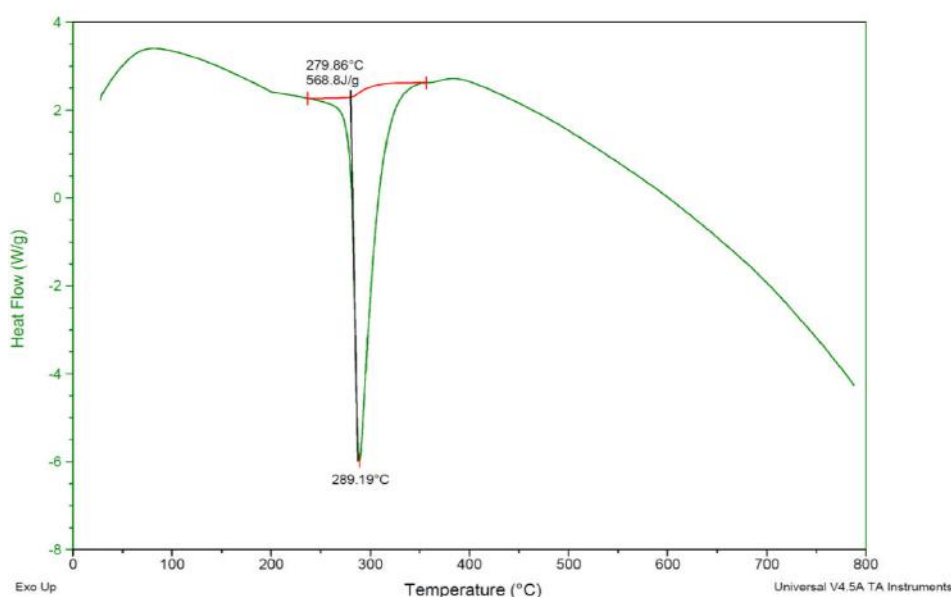


Fig.10. DSC curve for L-AAA crystal

3.9. SECOND HARMONIC GENERATION EFFICIENCY

The relative second harmonic generation (SHG) efficiency was determined by modified Kurtz powder technique [28]. It is an important and well accepted tool to evaluate the conversion efficiency of a nonlinear optical material. A Q-switched Nd:YAG laser operating at the fundamental wavelength of 1064 nm, generating about 0.701 J and pulse of width 8 ns with a repetition rate of 10Hz was used for the present experimentl study [29]. The input laser beam was passed through an IR reflector and then incident on the powdered form of the L-AAA specimen, which was packed in a glass capillary tube. The output energy was detected by a photodiode detector integrated with oscilloscope assembly. Second harmonic signal was confirmed when the laser beam was passed through L-AAA specimen. From this measurement the second harmonic signal of 0.01638 J were obtained from L-AAA resepectively. It is observed that the SHG efficiency of the grown L-AAA single crystal is 0.581 time less of the standard KDP crystal.

4. CONCLUSION:

Optically good quality single crystals of L-AAA with dimensions upto 6×5×3 mm³ have been grown by slow evaporation solution growth technique. The sharp and well defined Bragg's peaks of powder XRD pattern at specified 2θ angles shows the crystalline nature and purity of the crystal. The lattice parameters of L-AAA are determined by single crystal XRD. It belongs to orthorhombic crystal system with space group P2₁2₁2₁. The presence of functional groups was confirms by FT-IR and FT-Raman analysis. The presence of elements in the sample is confirmed by EDAX. UV-Vis-NIR spectrum of L-AAA shows that it has minimum absorption in the entire visible region. The band gap is found to be 5.6 eV [30]. Kurtz powder technique shows that the SHG efficiency of L-AAA crystal is 0.581 times less of the standard KDP crystal. The TGA and DSC measurement reveals that the crystal is thermally stable up to 269.86°C and there is no structural phase transition in the low temperature region. It is concluded that the L-AAA crystal can be used as an efficient material for NLO applications and further it can utilized for fabrication of devices.

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