Structural and Optical Studies of Solution Grown L-Alanine Acetate Single Crystals

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Abstract

L-Alanine acetate (LAA) single crystals were prepared by using solution growth technique for which saturated solution prepared by dissolving equimolar ration of L-Alanine and acetic acid powder in water (distilled) was allowed to undergo slow evaporation. Single crystals of good transparency & optical quality (confirmed after employing below detailed characterization techniques) were extracted having sizes 11×7×1 mm^3, 10×4×1.5 mm^3 and 6×6×1 mm^3 after an interval of 42 days. Structural properties of the LAA crystals like crystallinity and presence of various functional groups were confirmed by using powder X-ray diffraction technique and FTIR spectroscopic technique. Optical properties like UV cutoff wavelength value (observed at 232 nm) and optical energy bandgap value of 5.16 eV were determined using UV-Visible spectroscopic technique.

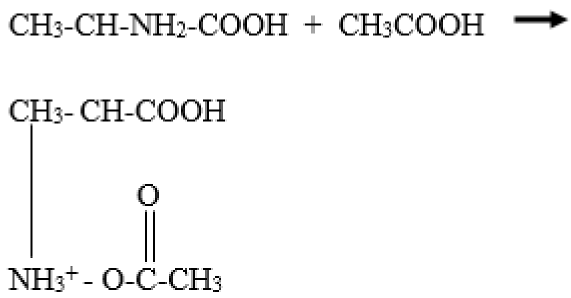
Keywords: Amino Acids, L-Alanine, Acetic Acid, Uv Cutoff Wavelength, Slow Evaporation.

Introduction

In recent times, researches on the growth of organic materials like amino acids and their organic-inorganic complex form by several experimental methods have significantly increased due to their potential applications in almost every technological and industrial fields [1]. Molecules belonging to amino acids based organic materials or semi-organic complexes possess proton donor carboxylic group (COO^-) and proton acceptor amine group (NH_3^+) making these materials a suitable candidates for the NLO applications [2]. Many researchers have reported their studies on the crystals formed by these materials and showed their capability to be engaged as promising materials for applications related to the concept of optical second harmonic generation [3]. These NLO materials are very much popularized now-a-days in the fields of optical communication, data storage, photolithography etc. being having state-of-art characteristics like high laser damage threshold, high SHG efficiency coefficient, easy growth, low cutoff wavelengths, short response time etc. [4-6]. Extensive investigations are reported by various researchers on the growth of pure L-alanine [7], L-Alanine alaninium nitrate (LAAN) [8], L-Alanine cadmium bromide [9], L-Alanine Cadmium chloride (LACC) [10], L-Alanine alaninuim picrate monohydrate [11], Lithium, HCl added L-Alanine [12] etc. L-alanine acetate crystals also have been reported as suitable in NLO applications in preface of its high SHG efficiency, lower cutoff wavelength and other related parameters [13]. In this research paper, we have prepared L-alanine acetate single crystals using solution grown methodology and further its structural and optical properties were analyzed using XRD, FTIR and UV-Vis characterization techniques.

Experimental Methodology

Slow evaporation solution grown methodology was employed for the growth of L-alanine acetate crystals. For this purpose, initially CDH made L-alanine powder (> 98 % purity) and Acetic acid (powdered form) having > 99.5% purity was mixed together by taking in equimolar amounts. In our case, 65.6 gm of L-alanine powder was mixed with 44.2 gm of acetic acid (in powder form). The mixture was then dissolved in 400 ml water which was pre-distilled thrice a time before use. The solution thus obtained as shown in below chemical reaction [14] was placed over magnetic stirrer and a magnetic bit was dipped into the solution. The solution was stirred continuously for approximately 3.5 hours with temperature of the solution maintained at 25° C in order to obtain saturated solution as well as to achieve its complete homogeneity.



The saturated solution was then filtered twice using Whatmann filter paper (Grade-1001) in order to eliminate microscopic contaminants. The filtered saturated solution was then covered by perforated sheets with pinning a single hole at the centre for desired gradual evaporation of the solvent. During this phenomenon, the temperature of the solution was lowered at a constant rate of 0.05°C/day with the help of thermostat assembly. Both slow cooling & slow evaporation of the solution caused super-saturation of the solution forming tiny crystals at the bottom of the beaker in a few days. The solution was kept isolated in such a way that no vibration/ motion can occur within as it can affect & disrupt the process of crystallization which may have a direct influence on the quality of the crystals. The solution was checked at regular intervals & finally after 42 days, L-alanine acetate single crystals (confirmed after employing below detailed characterization techniques) were extracted having sizes 11×7×1 mm^3, 10×4×1.5 mm^3 and 6×6×1 mm^3 as shown in below figure 1.

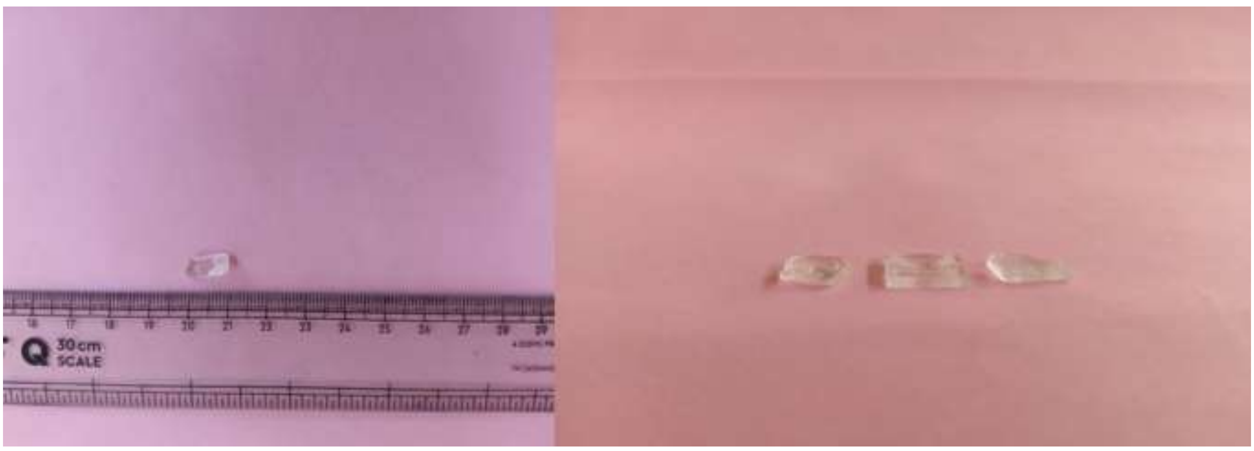


Figure 1 Solution grown L-alanine acetate (LAA) crystals.

X-ray diffraction analysis

Crystallinity and other crucial parameters like diffraction angles showing intensity peaks about solution grown L-Alanine acetate (LAA) crystals were confirmed and measured using X-ray diffraction analysis for which sample was first converted into powdered form and then exposed to X-rays using Miniflex 600 model of the X-ray diffractometer. As per reported data, LAA crystals belong to orthorhombic lattice type and bears $P2_12_12_1$ space group **[15]**. The LAA sample was scanned for diffraction angle (2θ) ranging from 0° to 90° with sample scan speed maintained at 10°/minute through the complete scan. During the characterization process, X-rays originated from Copper made target attributed to K_α spectral line with wavelength 1.540 Å were incident on the LAA crystals.

High intensity sharp diffraction peaks are observed at diffraction angles (2θ) 16.45°, 20.81°, 32.88°, 41.91°. Observation of these sharp intensity peaks confirmed the high crystallinity of the crystals grown.

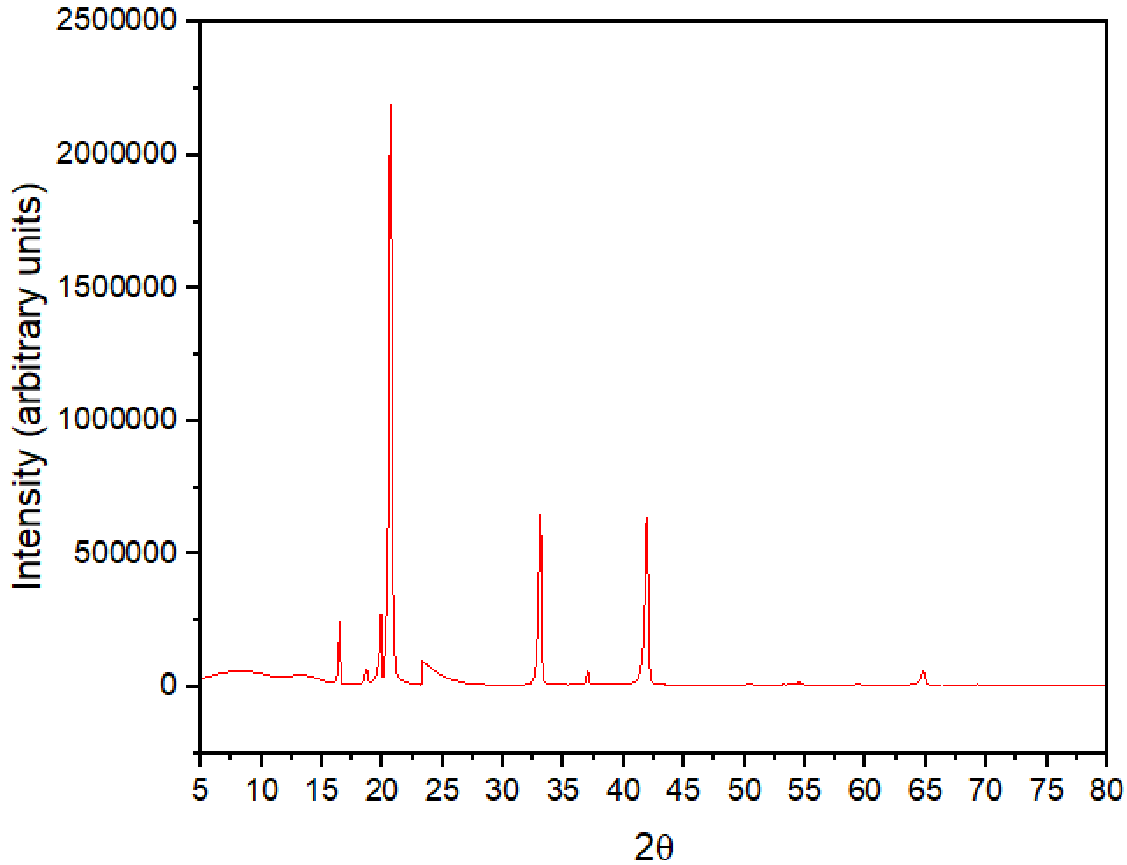


Figure 2 XRD pattern of LAA crystals

FTIR spectroscopic study

Qualitative analysis of the LAA crystals for the purpose of identification of various functional groups present in it was carried using this spectroscopic technique. Shimdzu ATR model FTIR spectrophotometer was employed in this study and infrared rays in the wavelength range 500 to 4500 cm^{-1} were incident on the sample. Using origin software, absorption peaks were identified in the Transmittance (%) vs Wavenumber (cm^{-1}) spectrum as shown in below figure 3 at various value of wavenumber. In the FTIR spectrum, sharp and broader absorption peaks of different strength were observed at different wavenumber values. For example wavenumber values corresponding to 3706, 3781, 2983, 2320, 2137, 1844, 1679 cm^{-1} refers to broader absorption peaks while wavenumber values corresponding to 1517, 898, 798 cm^{-1} correspond to relatively sharper absorption peaks.

Intensity peak observed at 2983 cm^{-1} was probably attributed to CH_3 stretching and peak corresponding to 2137 cm^{-1} is due to NH_3^+ asymmetric deformation. Intensity peak observed at 1517 cm^{-1} was due to NH_3^+ symmetric deformation. Intensity peak corresponding to 1382 cm^{-1} is observed as a result of CO_2 symmetric stretching vibrations. Vibrations occurring due to CH group deformation resulted into formation of intensity peak at 1326 cm^{-1}.

Asymmetric type vibrations occurring while coupling of alanine (LA) and acetate ions were confirmed from the intensity peaks observed at 898 & 1186 cm^{-1}.

Intensity peak observed at 654 cm^{-1} was due to wagging vibrations of NH_2 functional group.

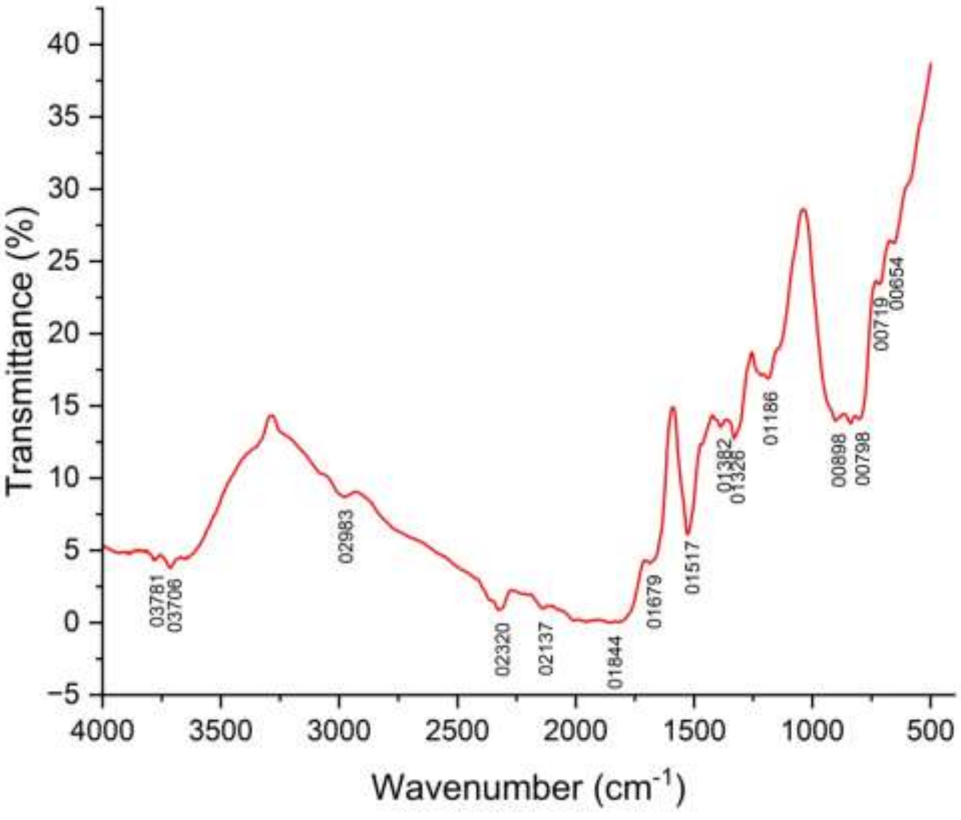


Figure 3 Fourier transform Infrared spectra of LAA crystals.

Uv-Visible spectroscopic study

This method is employed to study the optical characteristics of a material by analyzing its response to ultraviolet-visible (UV-Vis) radiation. Specifically, it involves recording data on transmittance, reflectance, and absorption, which result from the interaction between the material and incident radiation within the UV-Vis spectrum. These interactions lead to electronic excitations—such as π to π*, n to π*, and σ to σ* transitions—from the valence shell electrons of the material's atoms [16]. Shimdzu 1800 UV-Vis Spectrophotometer model was employed to carry out UV-Vis analysis of sample. This spectroscopic study exhibits that LAA crystals have a wide transparency window in the wavelength range 232 to 800 nm. UV rays transmittance decreases drastically near below 250 nm with UV cutoff estimated at 232 nm as shown in below figure 4. Optical energy bandgap value of LAA single crystals was measured by employing Tauc's theoretical formula in the UV-Vis spectrum plotted using origin software and thereby applying Beer-Lambert's law. Its value was measured to be 5.16 eV as shown in below figure 5. Wide transparency window over 232 nm and high value of optical energy bandgap suggest high possibility of LAA single crystals to be sought advantages in NLO (Non-linear optical) related technological & industrial applications.

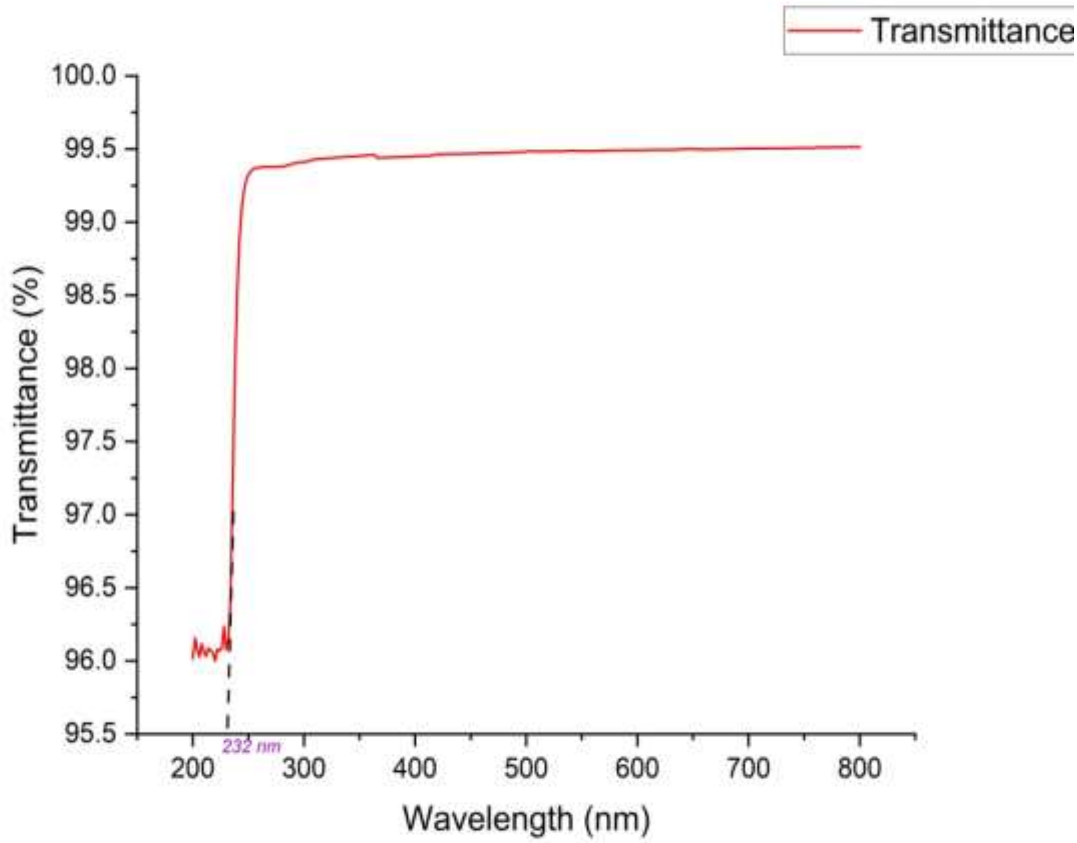


Figure 3 UV-Vis spectra of LAA crystals showing UV cutoff wavelength.

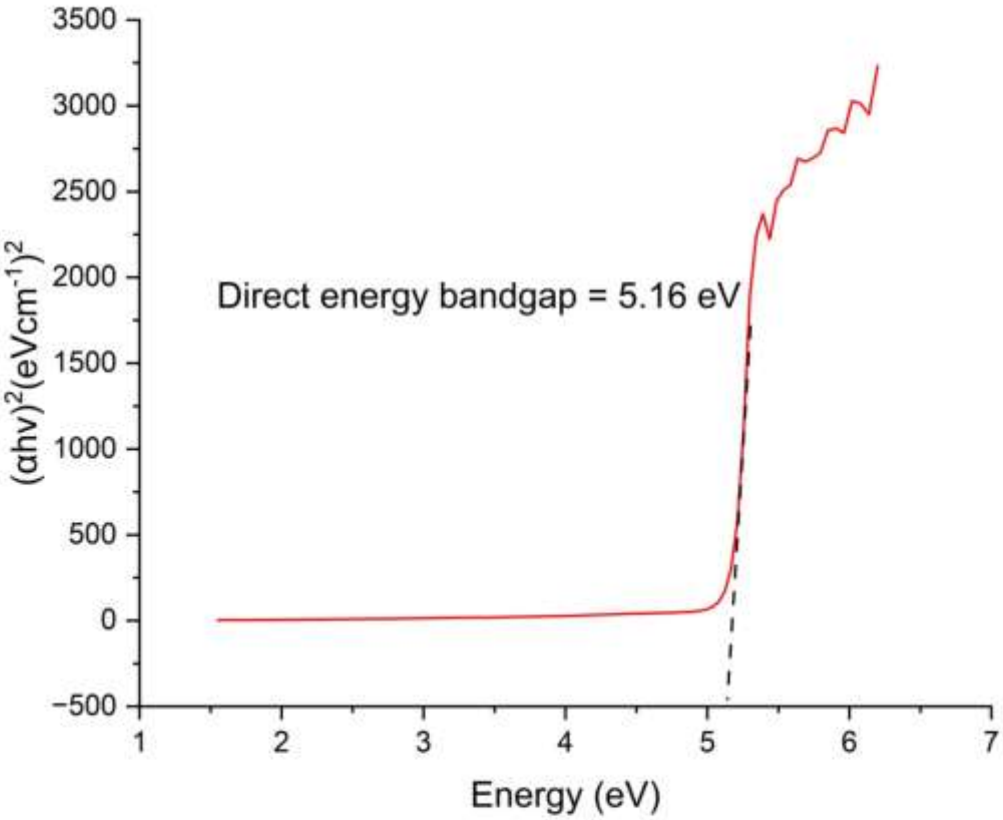


Figure 3 UV-Vis spectra of LAA crystals showing its optical bandgap.

Conclusion

Good quality L-alanine acetate single crystals were grown by slow evaporation solution growth methodology. Sharp intensity peaks observed in the XRD spectrum at different diffraction angles confirmed the high degree of crystallinity and purity of the crystals grown. FTIR spectroscopy detected the presence of various incorporated functional groups and the respective wavenumber values are in well agreement with previously reported data. Wide transparency window over 232 nm and large optical energy bandgap value 5.16 eV of LAA single crystals confirmed its suitability in NLO applications in view of its optical prepoerites.

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