

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Growth and Characterization of L - Aspararginium Tartrate Single Crystal.

E Kavitha^a, J Madhavan^b and G Prabakaran^{c*}.

^aDepartment of Physics, Dr. M. G. R Educational and Research Institute, Chennai – 95, Tamil Nadu, India.

^bDepartment of Physics, Loyola College, Chennai - 34, Tamil Nadu, India.

^cDepartment of Physics, Govt. Arts College for men Nandanam, Chennai – 35, Tamil Nadu, India.

ABSTRACT

L - Aspararginium Tartrate (LAsT) acid single crystals of size 5 x 4 x 8 mm³ were grown. Structural confirmation of grown crystals was done by powder X-ray diffraction that the crystal belongs to monoclinic system with space group P12₁1. The lattice parameters of the titled compound was found to be a = 9.9680 Å, b = 7.9837 Å, c = 4.8826 Å. The functional groups have been identified from FT-IR and Raman spectra. The grown crystals are optically transparent. Optical study shows that the grown crystals are highly transparent (~ 80%) in entire testing range. Optical band gap was calculated and found to be 5.3 eV. The high thermal stability of grown crystal was ascertained by TG/DTA analysis. The second harmonic generation (SHG) efficiency measured using Nd-YAG laser is 3 times that of KDP.

Keywords: LAsT, FT-IR and Raman, TG/DTA, KDP.

**Corresponding author*

INTRODUCTION

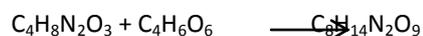
In the last few years, much progress has been made in the development of nonlinear optical (NLO) organic materials for second harmonic generation (SHG). However, most of the organic NLO crystals are constituted by weak van der Waals and hydrogen bonds with conjugated π electrons [1]. In this respect, amino acids are interesting materials for NLO applications [2,3]. The presence of Zwitter ions influences the physical and chemical properties of amino acids. The proton donor carboxyl acid ($-\text{COO}$) group donates its proton to acceptor amino ($-\text{NH}_2$) group. Thus, an amino acid exists as a dipolar ion in which carboxyl group is present as carboxylate ion and amino group is present as ammonium ion. Due to this dipolar nature, they possess good mechanical and physical properties, viz. crystal hardness and high melting point, which make them ideal candidates for NLO applications. Among the synthetic materials that have been suggested as sources of piezoelectric elements, some tartrates, e.g. Rochelle salt (sodium potassium tartrate tetrahydrate) and ethylene diamine tartrate (EDT) are strongly piezoelectric. It therefore seemed likely that the examination of other organic tartrates might be fruitful [4]. Crystal and molecular structure of Urea-(+) tartaric acid was reported [5]. The present work deals with the growth and characterization of L - Aspararginium Tartrate.

EXPERIMENTAL

SYNTHESIS AND SOLUBILITY OF LAST

L-Asparagine-L-tartaric acid (LAST) was synthesized by dissolving one mole of L-Asparagine (Merck 99%) in double distilled water containing one mole of L-tartaric acid.

The reaction is as follows



The synthesized salt was further purified by repeating the crystallization process at least thrice. The solution growth technique is widely employed to grow single crystals of organic compounds. The solubility of LAST in deionized water (solvent) was determined by adding a solute in solvent till it is completely dissolved. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. Using this technique, the solubility of LAST at five different temperatures (30, 35, 40, 45 and 50°C) has been evaluated. The temperature dependence of solubility of LAST is shown in Figure 1. From the graph it is found that the solubility of LAST increases with temperature.

The synthesized salt of LAST was purified by repeated crystallization and saturated solution was prepared in accordance with the solubility data. In order to achieve single crystals of good optical quality and relatively large size, many growth attempts have been made. The easiest method was to form tiny crystals by spontaneous nucleation; among them seed crystals with perfect shape and free from defects were chosen for growth experiments. The seeds were suspended in the mother solution with nylon thread. Crystals of dimension up to $5 \times 4 \times 8 \text{ mm}^3$ were harvested after a period of 25-30 days. Figure 2 shows the photograph of as grown crystal of LAST. The grown crystals are stable, do not decompose in air and non-hygroscopic in nature. An important observation during the growth of LAST is the absence of any kind of microbial contamination during the growth period.

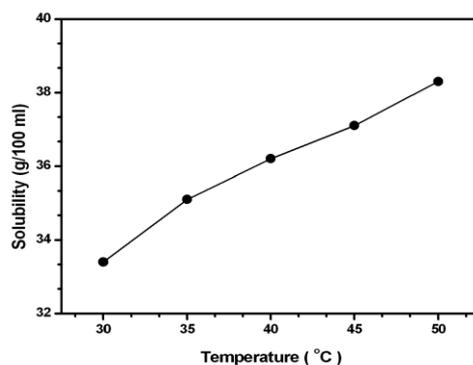


Figure 1: The solubility curve of LAST



Figure 2: Photograph of as grown LASrT single crystal

RESULTS AND DISCUSSION

XRD – Analysis

The grown crystals were subjected to powder X-ray diffraction analysis. A Rich-Seifert powder X-ray diffractometer with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) was used at a scan speed of $0.02^\circ/\text{s}$. From the single crystal analysis it was observed that the crystal belongs to monoclinic crystal system. Lattice parameters values are found to be $a = 9.9680 \text{ \AA}$, $b = 7.9837 \text{ \AA}$, $c = 4.8826 \text{ \AA}$ and $\alpha = \gamma = 90^\circ$, $\beta = 83.140^\circ$ having non-centrosymmetry with $P12_11$ space group.

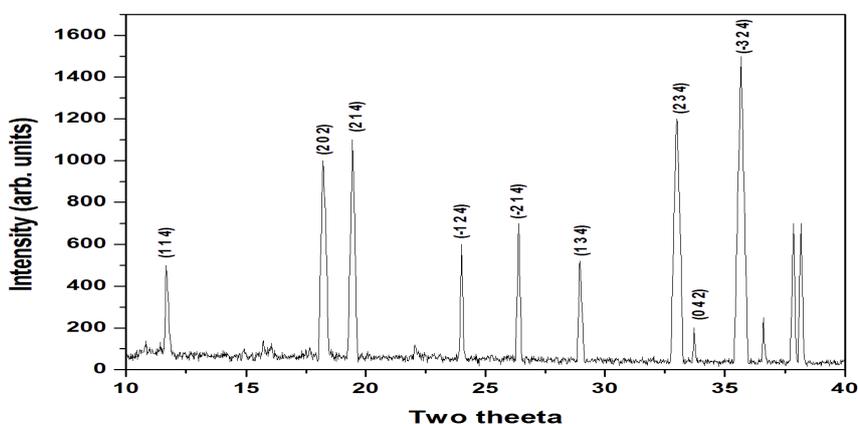


Figure 3: Powder XRD spectrum of LASrT crystal

FT-IR and FT-Raman Analysis

FT-IR spectrum of the grown crystal was recorded in the range 500 cm^{-1} to 4000 cm^{-1} , using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. FT-Raman was recorded in the range of 0 to 4000 cm^{-1} . The experimental FT-IR and FT-Raman spectra were shown in the Figures 4 and 5 respectively.

NH₂ Vibrations

The NH₂ asymmetric stretching vibrations [6] give rise to a strong band in the region $3390 \pm 60 \text{ cm}^{-1}$ and the symmetric NH₂ stretching is observed as weak band in the region $3210 \pm 60 \text{ cm}^{-1}$. In the present work, NH₂ symmetric stretching is assigned at 3320 cm^{-1} in IR region and also in 3280 cm^{-1} .

C-H Vibrations

Presence of band in the region $2700\text{--}3000 \text{ cm}^{-1}$ is the characteristic region for the identification of C–H stretching vibrations [7]. In this region the bands are slightly affected by the nature of the substituent. The IR vibrations are around 2900 cm^{-1} . For LASrT molecule prominent numbers of CH symmetric vibrations are

obtained at frequencies 3092, 2977 in IR and 2960 and 2932 in Raman respectively.

COO⁻ Vibrations

Carboxyl group vibrations give rise to intense characteristic bands due to conjugation or formation of hydrogen bonds. These stretching and bending vibrations of acid group are generally expected in the region 1400–1200 cm⁻¹ [6]. In the present work COO symmetric stretching is at 1420 cm⁻¹ in IR and 1425cm⁻¹ in the Raman respectively. Similarly 1553 cm⁻¹ have asymmetric stretching in IR region and 1591 cm⁻¹ in Raman.

O–H Vibrations

The O–H group gives rise to three vibrations (stretching, in-plane bending and out-of-plane bending vibrations). The O–H group vibrations are likely to be the most sensitive to the environment, so they show pronounced shifts in the spectra of the hydrogen bonded species. The hydroxyl stretching vibrations are generally [8] observed in the region around 3500cm⁻¹. In the title compound the O-H vibrations is present at 3450 cm⁻¹ in IR region.

Optical absorption spectrum

To determine the transmission range and hence to know the suitability of LASt single crystals for optical applications, the UV–Vis–NIR spectrum were recorded in the range of 200 – 1300 nm. The UV-Vis-NIR spectrum gives information about the structure of molecule because the absorption of UV and visible light involves the promotion of the electrons in the σ and π orbitals from the ground state to higher energy states. The large transmission in the entire visible region enables it to be a good candidate for optoelectronic applications. Figure 6 shows the optical

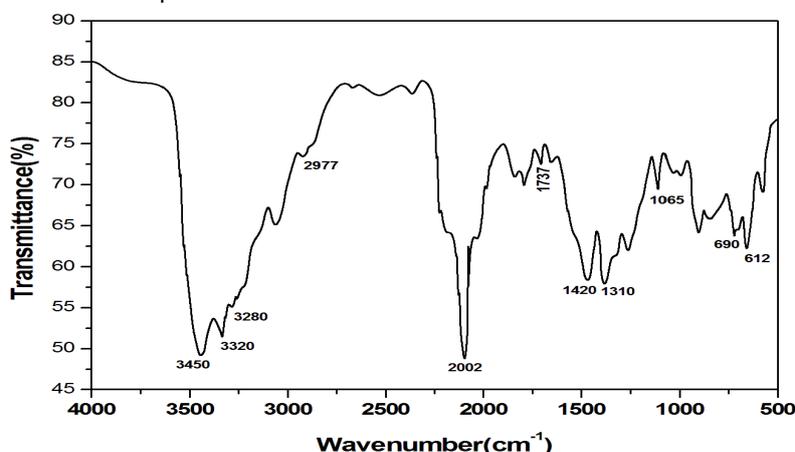


Figure 4: Experimental FT-IR Spectrum of LASt

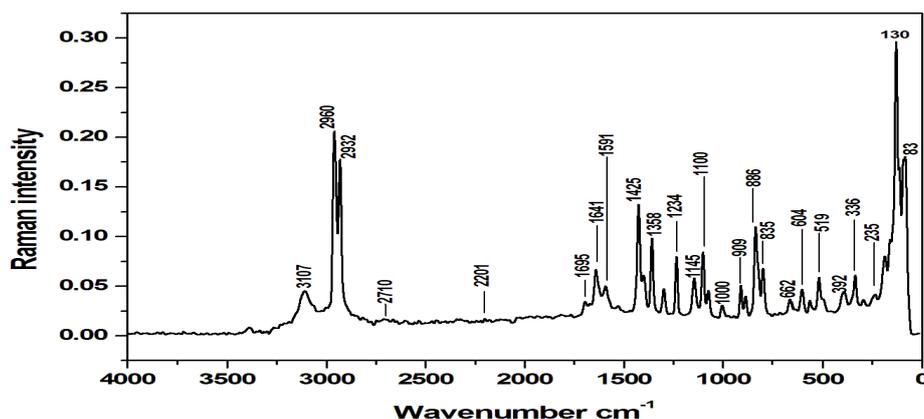


Figure 5: Experimental FT-Raman Spectrum of LASt

absorption spectrum of LAsT. From the spectrum, it is observed that there is very low absorption in the visible and NIR region. The UV cut-off wavelength of LAsT is seen around 255nm. There is no absorption in this range, thus enabling the use of this material for secondharmonic generation (SHG) applications. Figure 7 shows the Tauc's plot of LAsT. The direct band gap energy of LAsT was calculated from the graph between $h\nu$ and $(\alpha h\nu)^2$ by extrapolating the linear portion of the curve to zero absorption. The direct band gap is found to be 5.3 eV. This indicates that LAsT is a higher energy band gap energy material.

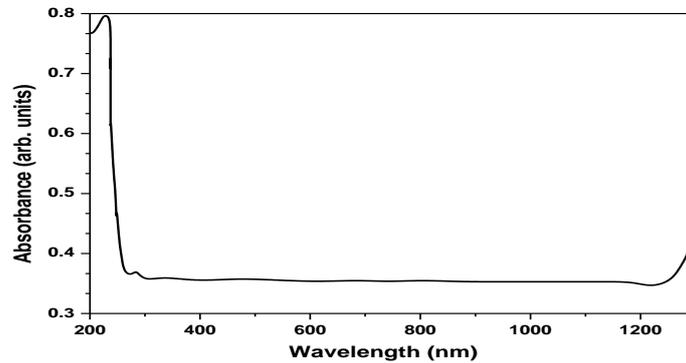


Figure 6: Optical absorption spectrum of LAsT crystal

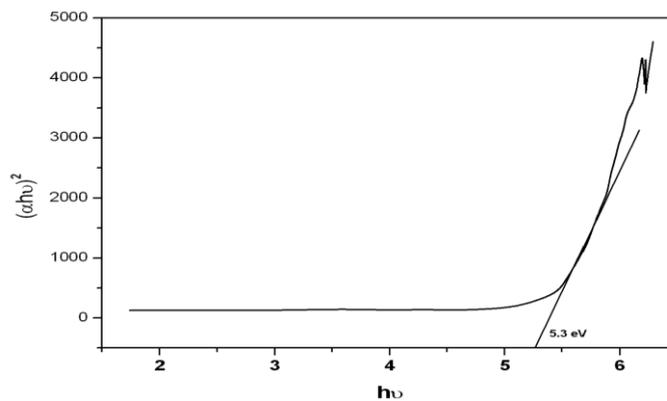


Figure 7: Optical band gap of LAsT crystal

Thermogravimetric analysis

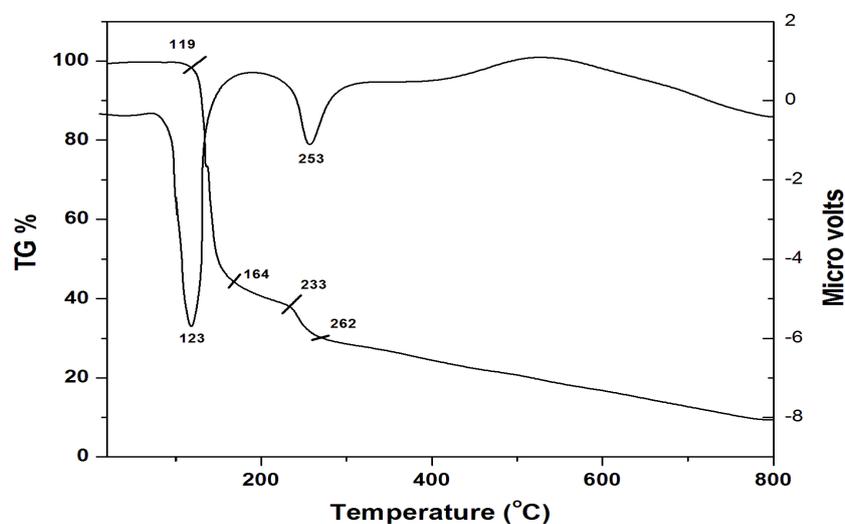


Figure 8: TGA and DTA curve of LAsT crystal

TG-DTA was carried out on the grown LAsT sample for qualitative analysis and the respective curves

are shown in Figure 8. From the DTA curve it has been observed that endothermic peak at about 123 °C corresponds to the melting point of the compound which is coinciding with the stability of the material shown by TGA trace. This is attributed to utilization of the thermal energy to overcome the valence bonding between the L-asparagine cation and tartrate anion, which happens in the initial stage of decomposition. The two broad endothermic peaks at 123 and 253 °C represent the decomposition of molecular fragments in two stages. The reactions of simplest amino acids induced by heating include the condensation reactions of carboxyl and amino groups leading to the formation of peptide bonds. The total weight loss nearly equals to 90% and the resulting residue (10 %) is stable upto 800 °C. From this study it is concluded that the melting and decomposition occur in successive steps but the process appear to occur closely. This analysis indicates the possible NLO application of the material up to 119 °C.

SHG efficiency studies

The second harmonic generation efficiency of the powdered material is measured using Kurtz and Perry method. For the SHG efficiency measurements, microcrystalline material of KDP is used for comparison. The sample was ground into fine powder and tightly packed in a micro capillary tube. It is mounted in the path of the laser beam of pulse energy 10.8 mJ obtained by splitting the original laser beam. The transmitted light is passed through 532 nm monochromator. The green light at double the incident frequency was collected by photo multiplier tube and converted into electrical signal. The sample is illuminated using Q-switched mode locked Nd:YAG laser with input pulse of 10.8 mJ. This signal was displayed on the oscilloscope. Signal amplitude in milli volts on the oscilloscope indicates the SHG efficiency of the sample. The emission of green radiation from the crystal is confirmed the second harmonic signal generation in the crystal. A second harmonic signal of 161 mV is obtained for LAsT with reference to KDP (53 mV). Thus the SHG efficiency of LAsT is 3 times that of KDP.

CONCLUSION

Single Crystals of L-Asparagine–L-tartaric acid (LAsT) of dimension 5 x 4 x 8 mm³ are conveniently grown by slow evaporation technique at room temperature. A solvent of deionized water is used for the growth process. The powder XRD analysis proves that LAsT crystal belongs to monoclinic in structure with a noncentrosymmetric space group P12₁1. Optical absorption studies confirm the UV cut-off wavelength of LAsT at 255 nm. The band gap energy of the sample is calculated and it is found to be 5.3 eV. The sample is thermally stable up to 119 °C. The second harmonic generation (SHG) efficiency measured using Nd-YAG laser is 3 times that of KDP.

REFERENCES

- [1] Madhavan J, S Aruna, K Prabha, J Packium Julius, Ginson P Joseph, S Selvakumar, P Sagayaraj. *J Crystal Growth* 2006;293:409–414.
- [2] Madhavan J, Aruna S, Anuradha A, Prem Anand D, Vetha Potheher I, Thamizharasan K, Sagayaraj P. *Optical Mater* 2007;29:1211-1216.
- [3] P Praveen Kumar, V Manivannan, S Tamilselvan, S Senthil, Victor Antony Raj, P Sagayaraj, J Madhavan. *Opt Comm* 2008;281:2989–2995.
- [4] Vimalan M, Rajesh Kumar T, Tamilselvan S, Sagayaraj P, Mahadevan CK. *Physica B* 2010;405:3907–3913.
- [5] Yu Wentao, Lu Mengkai and Meng Fanqing. *Mater Res Bull* 1996;31:1127-1131.
- [6] Roeges NGP. *A Guide to the Complete Interpretation of the Infrared Spectra of Organic Structures*. Wiley, NY, 1994.
- [7] Shanmugam, Sathyanarayana. *Spectrochim Acta* 1984;40A:757.
- [8] Sajan D, I Hubert Joe, Jayakumar VS, Zaleski J. *J Mol Struct* 2006;785:43.