# SYNTHESIS AND CHARACTERIZATION OF L-ASPARAGINE MONOHYDRATE HYDROCHLORIDE CRYSTALS

C.PRASANNA DEVI [1], DR.G.V.ANURADHA[2*], DR.V.SHIVASHANKAR[3*]

[1]Research Scholar, St.Xavier's College (Autonomous), Palayamkottai-627003.
[2]Assistant Professor of Physics, Sri Parasakthi College for Women (Autonomous), Courtallam-627802.
[3]Assistant Professor of Physics, St.Xavier's College (Autonomous), Palayamkottai-627003.

## Abstract

Single crystals of L-Asparagine monohydrate hydrochloride crystals have been grown by slow evaporation solution growth technique. Crystal structure and cell parameters of grown crystals were determined by Single Crystal X-ray diffraction. The occurrence of prospective functional groups was initially identified by Fourier transform infrared spectroscopic analysis .The UV-Visible transmittance spectrum shows that the material has wide optical transparency in the entire visible region .The mechanical properties have been studied using Micro hardness test. The optical behavior was analyzed by Photoluminescence methods.

**Keywords: Slow evaporation, Crystal growth, SXRD, FT-IR, UV-Visible spectroscopy, Vickers Micro hardness test, Photoluminescence Studies.**

## 1. Introduction

Nonlinear optics is a very useful technology because it extends the usefulness of lasers by increasing the number of wavelengths available. Non linear optics has emerged as one of the most attractive field of current research in view of its vital applications in the area of optical modulation, optical switching, optical logic, frequency shifting, high speed information processing, optical communications and optical data storage for developing technologies in telecommunication and Signal Processing and different optoelectronics applications [1-3]. Organic nonlinear materials for attracting a great deal of attention as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power compared with in organic materials[4,5]. Organic molecules with significant not linear optical activity generally consist of a ∏-electron conjugated structure. L-asparagine with 20 amino acids, is one such promising organic NLO material, with space group $P2_12_12_1$[6] and processing 4 molecules in the unit cell .L-asparagine monohydrate is an interesting material to investigate because it crystallizes in a structure exhibiting a complex network of hydrogen bonds among Asparagines molecules and between asparagines water molecules. The present investigation deals with the growth of LAMHCL single crystals by slow evaporation technique. The grown crystal has been subjected to different analyses in order to know its suitability for device fabrication.

## 2. Experimental Synthesis and Crystal Growth

L-asparagine monohydrate hydrochloride crystals are grown from aqueous solution by slow evaporation technique. The L-asparagine monohydrate is first dissolved in double distilled water, and then the same molecular amount of HCL was slowly dissolved in the solution. The solution was stirred for 6 hours constantly using magnetic stirrer and heated slightly above the room temperature, then solution was filtered using whatmann filter paper and the prepared solution was allowed to evaporate at room temperature. The following chemical reaction was expected to occur between L- aspragine Monohydrate and HCL.

$$C_4H_{10}N_2O_4+HCL\rightarrow C_4H_{11}ClN_2O_4$$

After a growth period of three weeks a transparent and colorless crystals harvested. Figure 1 shows the photograph of the Crystal

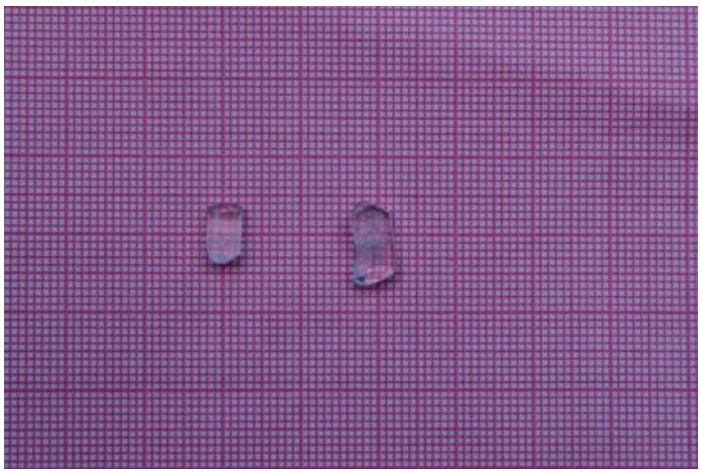

**Fig.1: Harvested crystals of LAMHCL**

## 3. Results and Discussion

### 3.1 Single crystal X-ray diffraction studies

One of the good quality harvested crystal was selected for single crystal X-ray diffraction. The single crystal XRD data of LAM HCL crystal is presented in Table 1. Single Crystal X-ray diffraction studies confirmed that, the LAMHCL crystallizes in orthorhombic crystallographic system with space group $P2_12_12_1$. The lattice parameters are obtained as a=11.1622 $A^{\circ}$, b=19.6492 $A^{\circ}$, c=23.5972$A^{\circ}$, $\alpha=90^{\circ},\beta=90^{\circ},\gamma=90^{\circ}$ and unit cell volume is 5175.5 $A^{\circ 3}$.

**Table 1: SXRD data for LAMHCL crystal**

| Crystal parameters | Values |
|---|---|
| a | 11.1622 A° |
| b | 19.6492 A° |
| c | 23.5972 A° |
| α | 90° |
| β | 90° |
| γ | 90° |
| Crystal system | Orthorhombic |
| space group | $P2_12_12_1$ |
| Volume($A^{o3}$) | 5175.5 |
| Z | 24 |

### 3.2 FT-IR Analysis

The FT-IR spectrum of LAMHCL crystal is shown in figure 2.The spectrum was recorded on FT-IR NICOLET IS5R FTIR, Kbr Windows with AR Diamond crystal plate within the wave number range 400$cm^{-1}$ to 4000 $cm^{-1}$ .The presence of functional groups were confirmed by identifying absorption speak in their characteristics regions. A broad peak at 3377 $cm^{-1}$ indicates the presence of O-H stretching vibrations. The appearance of the band at 2929 $cm^{-1}$can is due to the $NH_3^+$ stretching vibration. The CH symmetric stretching vibration is observed in 2518 $cm^{-1}$.The band at 1644 $cm^{-1}$ is attributed to $NH_3^+$ bending vibration. The peaks obtained at 1428 $cm^{-1}$ is due to symmetric vibration of $COO^-$ group .The various absorption peaks/ bands of FT-IR spectrum of LAMHCL crystals are provided in the table 3.

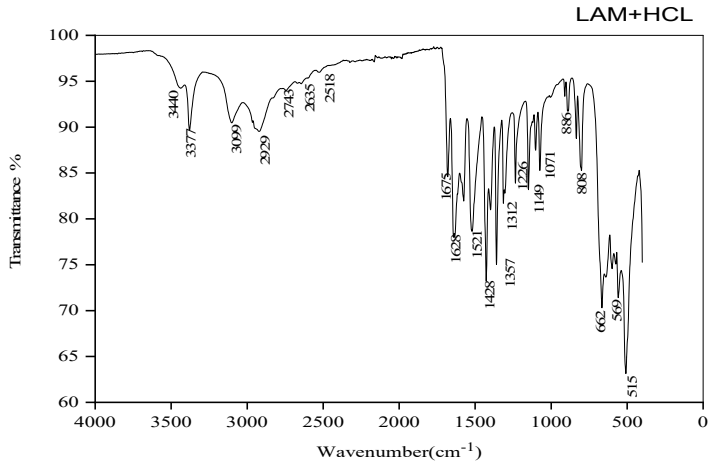


**Fig.2: FTIR spectrum for LAMHCL**

**Table 2: FTIR assignments for LAMHCL**

| Bands/Peaks | FT-IR assignments |
|---|---|
| 3440 | OH Stretching |
| 3377 | OH Stretching |
| 2929 | $NH_3^+$ stretching |
| 2518 | CH Symmetric stretching |
| 1644 | $NH_3^+$ bending |
| 1521 | $NH_2$ bending |
| 1428 | $COO^-$ stretching |
| 1357 | CH bending |
| 1226 | $NH_2$ rocking |
| 1071 | C-N Stretching |
| 808 | C-C Stretching |
| 507 | $COO^-$ rocking |

### 3.3 UV- Visible spectral studies

The UV- Visible spectral studies are used to find transmittance, absorbance, band gap, reflectance; linear refractive index of crystalline materials. The corresponding spectrum of the LAMHCL has been recorded for the wavelength range between 200 and 800nm. The absorption spectrum of LAMHCL is shown in figure 3(a) .The Crystal has low UV cutoff wavelength of 248nm. The optical absorption Coefficient (α) was evaluated from Tauc's relation. [7]

$$\alpha h\nu = A(E\nu - E_g)^n$$

where A, $E_g$, h, ν refers to a constant, band gap, Planck constant($6.63X10^{-3}$Js), frequency of incident photons and n is theoretical equal to 1/2 and 2 for direct and indirect transitions, respectively.

The measured absorption value (A) was used to calculate the absorption Coefficient (α) by using the equation.

$$\alpha = \frac{2.3026 \log(\frac{1}{T})}{d}$$

where d is the thickness of the Crystal, T is the transmittance (%).The graph between $(\alpha h\nu)^2$ versus Photon energy(hν) is shown in figure 3(b) .The band gap energy value was found to be 5.04eV.Theoretically, the optical energy band gap value can be calculated by using the equation.

$$E_g = 1240/\lambda_{max}$$

where $\lambda_{max}$ is cutoff wavelength [8](248nm). From the equation the obtained energy band value is measured 5.1eV which is close to our experimental value.

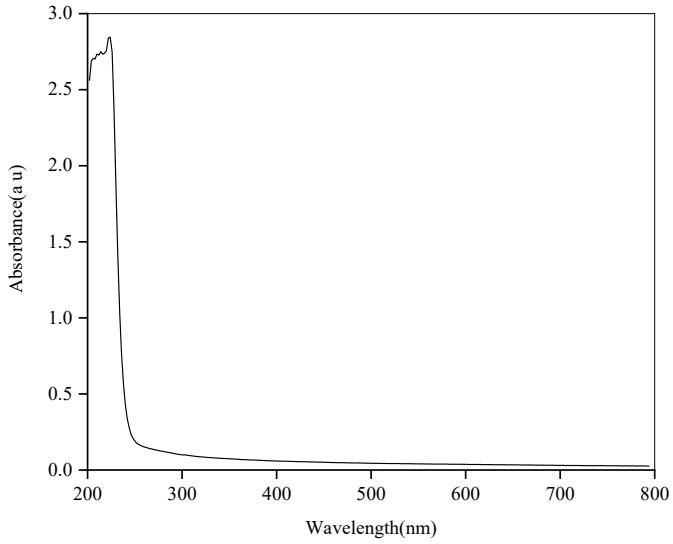


**Fig.3 (a): UV-Visible absorbance spectrum of LAMHCL**

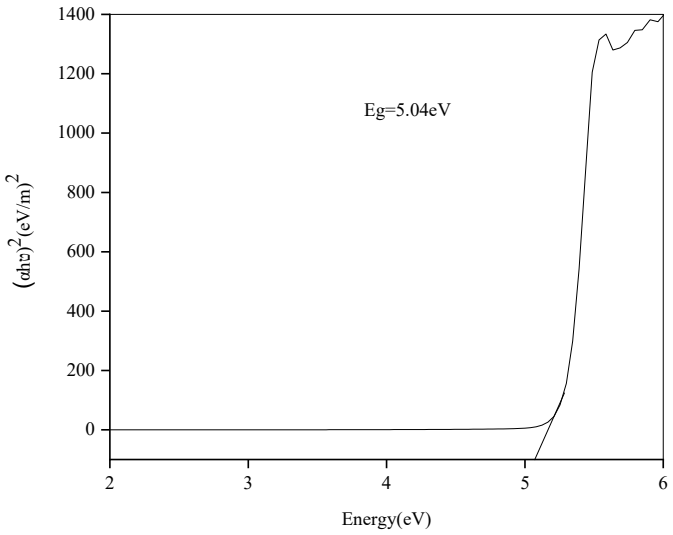


**Fig.3 (b):Tauc's plot of LAMHCL**

### 3.4 Microhardness test

Hardness is one of the important properties to determine the plastic nature and strength of a material. Vickers microhardness indentation test is used to characterize the hardness of the material. It is a non-destructive method to study the mechanical behavior of the material. It is a resistance against plastic deformation [9] .Vickers microhardness number was evaluated from the relation $H_V=\frac{1.8544P}{d^2}$ ($Kg/mm^{2)}$ where p is the applied load and d is the mean diagonal length of the indenter impression. A plot between the load and hardness $H_V$ is shown in figure 4(a). The hardness number was found to increase with increase in applied load up to 50g. After 50 g the hardness decreases with increasing load. The maximum hardness value obtained as 257.9 $Kg/mm^2$ at 50g. The relation between load (P) and the size of the indentation (d) is given by well known Meyer's law $P=ad^n$ and this relation is plotted in figure 4(b) .Here a and n are constants depending upon the material. From the slope of the calculated value for n value is 1.294 .According to Onitsch, $1.0\leq n\geq 1.6$ for hard material and $n>1.6$ for soft materials.[10,11]. Since, the calculated value of 'n' is less that 1.6; therefore the grown crystal comes under the category of hard material.

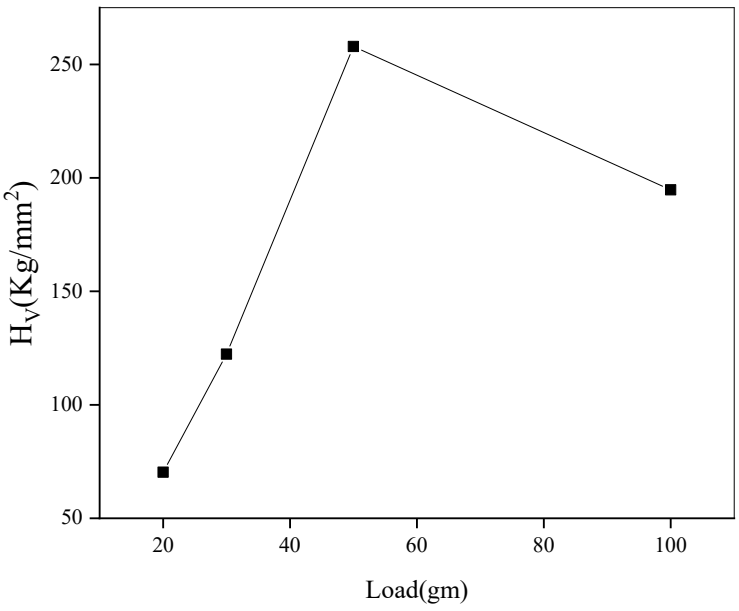


**Fig.4 (a): Hardness Vs load graph of LAMHCL**

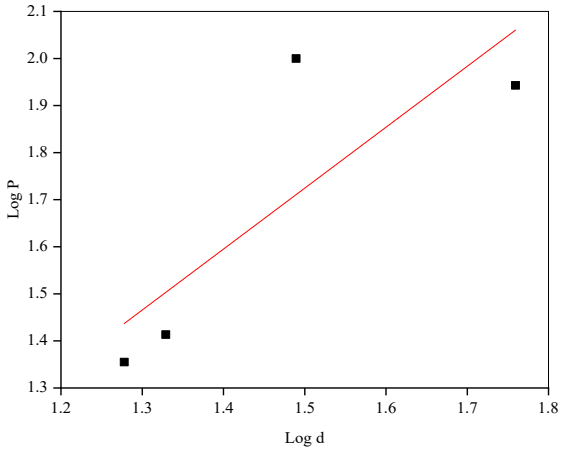


**Fig.4 (b): log d Vs log P graph of LAMHCL**

### 3.5 Photoluminescence Studies

Photoluminescence in solids is the occurrence in which electronic states of solids are excited by light energy [12]. Photoluminescence emission spectrum of L-Asparagine Monohydrate Hydrochloride crystals were recorded at room temperature and a graph was plotted between intensity and wavelength which is shown in figure 5 .The emissions in the region between 200 nm and 800 nm. In the spectrum of L-Asparagine Monohydrate Hydrochloride crystals, five peaks were observed at 241nm, 301 nm, 466nm, 538 nm and 622 nm.The sharp high intense emissions peak is obtained at 466 nm. L-Asparagine Monohydrate Hydrochloride crystals emits UV light, blue and red fluorescence light. The LAMHCL sample emitting the strong blue light.

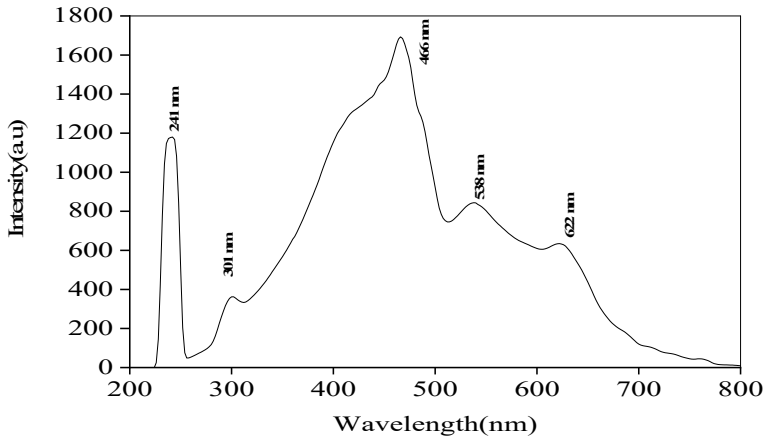


**Fig.5: PL emission of LAMHCL Crystal**

## 4. Conclusion

Colorless and transparent crystals of L-asparagine monohydrate hydrochloride crystals were conveniently grown by slow evaporation technique. The single crystal XRD studies confirmed that LAMHCL crystallizes in Orthorhombic Crystal system with non-centrosymmetric space group $P2_12_12_1$.From SXRD study, good crystallinity and lattice parameters were confirmed of the grown LAMHCL crystal. The presence of various functional groups was confirmed by FTIR analysis. The grown crystals were good optical transmittance in UV-Visible region and the cutoff wavelength was 248nm and the optical band gap value was found to be 5.04eV using Tauc's plot. The Vicker's microhardness study lead to the evaluation of the hardness number ($H_V$) and Meyer's plot proves LAMHCL as the hard material category.The optical properties are studied by using Photoluminescence.

## References:

1. S.S.Hussaini,N.R.Dhumane,V.G.Dongre,P.Ghughare,andM.D.Shirsat,J.Optoelectron.Adv.Mater.Rapid comm..1,707 (2007).
2. N.Vijayan,S.Rajasekaran. G.Bhagavannarayana ,R.Ramesh Babu, R. Gopalakrishnan,M. palanichamy, and P.Ramasamy, cryst. Growth Des. 6, 2441 (2006).
3. S.Ariponnammal, S.Radhika,R.Selva and N.Victor Jeya,Cryst.Res.Technol.40,786(2005).
4. L.Jothi, K.Ramamurthi,Indian Journal of science and technology, June 2011, Volume 4.
5. M.Suresh, S.Azathbhahadur and S.Athimoolam, Advances in applied Science Research, 2013,4(4) 160-164.
6. Kathiravan P and Balakrishnan T, 2015 and Characterization of pure and Cesium-doped L-Asparagine monohydrate single crystals struct chem. Crystallogr commun 1,19 ISSN 24709905.
7. N.D.Desai, S.S.Mal, R.M.Mane, V.B.Ghanwat,C.K.Hong, P.N.Bhosale,J.Mater.Sci.**27**,11379-11750(2016).
8. D.Shanthi, P.Selvarajan,S.Perumal,Physica Scripta.,89(2014) 125805.
9. Sangwal.K(2000) on the Reverse Indentation Size effect and Micro hardness measurements of solids,Materials Chemistry and Physics, 63,145-152,http://dx.doi.org/10.1016/so254-0584(99)00216-3.
10. Soft material E.M.Onitsch, mikroscopie 2(1947)131.
11. Hard material E.M.Onitsch,The present status of testing the hardness of materials mikroscopie 95,12-14(1956).
12. R.K.Balachander, S.Kalainathan, Spectrochim.Acta A **126**,324(2014).