Structural, Optical and Mechanical Studies on L-Asparaginium Bromide Monohydrate Crystal

C. Prasanna Devi[1*], P. Sumithraj Premkumar[2], V. Sivashankar[3], G.V.Anuradha[4*]

1. Department of Physics, CSI Jeyaraj Annapackiam College of Arts and Science, Alangulam, Tenkasi – 627853
2. Research Department of Physics, St. John's College, Palayamkottai, Tirunelveli-627002, Tamilandu.
3. Department of Physics, St. Xavier's College (Autonomous), (Affiliated to Manonmaniam Sundaranar University, Tirunelveli - 627012), Palayamkottai-627002
4. Department of Physics, Sriparasakthi College for Women (Autonomous), Courtallam-627802

ABSTRACT

Single crystal of L-Asparaginium bromide Monohydrate (LABMH) was grown by slow evaporation solution growth technique. Single Crystal X-ray diffraction analysis was employed to identify the cell parameter. The powder X-ray diffraction showed a high degree of crystallinity of the grown crystal. The EDAX gave the elemental composition of grown crystal. The presence of various functional groups was identified from FTIR spectral analysis. UV -visible spectrum study was assessed the optical quality and also the band gap energy of the grown crystal was evaluated. The optical and mechanical behavior of the grown crystal was studied by involving photoluminescence and Vicker's Micro hardness study.

Keywords: Crystal Growth; structural; optical; electrical; non-linear optical

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I. Introduction

Nonlinear optical materials are reputed candidate due to its interesting and variety of application of device fabrication for good mechanical strength, better nonlinearity high thermal stability and large laser damage threshold. In the beginning of research work, the researchers have concentrated on inorganic materials compared to the organic materials. However, organic non-linear optical (NLO) materials that exhibit highly non-linear optical responses which have received extensive scientific and technological interest due to their potential applications towards optical frequency doublers, high-speed information processing, telecommunication, photonics, high-density optical disk data storage, and optoelectronics [1,2]. Generally, the organic materials have attracted more attention over inorganic materials due to the conjugated π electron system as well as the presence of the asymmetric charge transfer which have a high order of nonlinearity. So the considerable effort to develop new organic materials with large second-order nonlinear optical susceptibilities with reasonable thermal stability and good transparency would be the choice of optoelectronic applications [3].

Amino acids are organic crystalline compounds and have demonstrated their strength in many different applications and one among them includes the NLO sector. The observation of such NLO property by the amino acids is the existence of asymmetry in the structure and high order of conjugate molecules. [4-5]. These molecules exhibit

double ions such as anion and cation in the same molecule [6]. This happens when the amino group got protonated and the carboxylic acid group is deprotonated at the same time [7]. Such double ions are called Zwitterions which enhancing the nonlinear optical (NLO) response [8]. Though the organic materials exhibit the nonlinear optical property, these are having poor physical properties such as mechanical, thermal and electrical. Therefore, recently, there have been much effort focused on designing and synthesizing new materials with superior NLO properties for practical applications [9-10]. Usually, the single crystal with a wide optical window and high transmittance are the essential parameters for the transmission of second and third harmonic generation [11]. With this aim, the single crystal of L-Asparaginium bromide monohydrate was synthesized and grown. The physical and nonlinear optical property were studied.

2. Materials and Method

AR grade L-Asparagine Monohydrate, Hydro bromic acid and deionized water were used for the growth of L-Asparaginium bromide Monohydrate single crystals.

L-Asparagine Monohydrate and Hydro bromic acid were taken as 1:1 ratio and dissolved in the deionized water. The solution was continuously stirred with heated slightly above the room temperature to reach the homogeneity. Then the solution was filtered using Whatman filter paper and transferred to growth vessel. The growth vessel was completely covered with aluminum sheet and kept in the constant temperature bath for crystallization. The general equation for the synthesis of L-Asparaginium bromide Monohydrate is as follows,

$$C_4H_{10}N_2O_4 + Hbr \rightarrow C_4H_{11}BrN_2O_4 \quad (1)$$

After a week, the crystals of L-Asparaginium bromide Monohydrate were appeared at the bottom of the container and collected to grow the single crystals. The saturated solution of the L-Asparaginium bromide Monohydrate was prepared using deionized water and stirred for two hours to reach the homogeneous solution. Then, it was transferred and placed in the constant temperature bath at 40˚C. Good quality of pure L-Asparaginium bromide Monohydrate (LABMH) crystal was harvested after the growth period of 15 days and it is shown in figure 1.

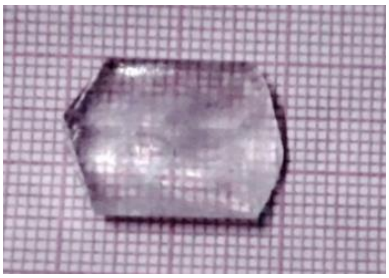

Figure1. The photograph of the as-grown LABMH Crystal

3. Results and discussion

3.1 Single Crystal X-ray Diffraction (SCXRD) analysis

In order to identify the lattice parameters of the grown crystal, single-crystal x-ray diffraction study was performed using the Bruker SHELXTL (λ=0.71073Å). The obtained lattice parameters of grown LABMH Crystal are shown in table1. The result of the presented work is in good agreement with the reported values [12].

* c.prasannadevi@gmail.com, anuayappan@gmail.com

Table 1 Single Crystal XRD data of grown LABMH

Parameter	Data
a	5.5833Å
b	9.8151 Å
c	11.7957 Å
α	90°
β	90°
γ	90°
volume	646.41Å^3
Crystal System	Orthorhombic
Space group	$P2_12_12_1$
Z	4

3.2 Powder X-ray diffraction analyses

As grown LABMH crystals were finely powdered and subjected to powder XRD analysis. PXRD of the grown LABMH crystal was recorded using Shimadzu XRD 6000 X-Ray Diffractometer in the range between 5º and 80º through Cuk alpha with the wavelength 1.540 Å. The recorded PXRD pattern of the grown LABMH crystal is shown in figure 2. The obtained PXRD pattern were indexed using powder x software [13-14]. The well-defined peaks at specific 2θ values showed a high crystallinity of the grown crystals.

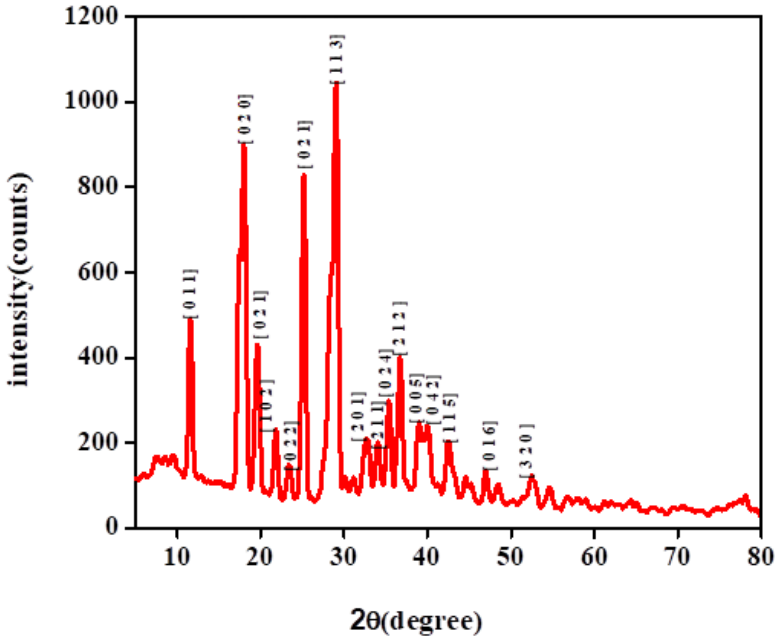

Figure 2: Powder X-ray Diffraction pattern of grown LABMH crystal

By considering the high reflections, the unit cell parameters for LABMH crystal was calculated and found be a = 5.5833 Å, b = 9.8161 Å, c = 11.7892 Å. The lattice parameters obtained from powder XRD method are found to be almost the same to the lattice parameters obtained from single crystal XRD method. Crystallite size, Dislocation density, and micro strain are calculated from the recorded PXRD data of LABMH crystal. The average Crystallite size was calculated using Debye-Scherrer's formula

$D=K\lambda/(\beta \cos\theta)$ nm (2)

Where D-Crystallite size, K-shape factor, λ-wavelength. From the calculations, the average crystallite size of the LABMH is 21.59nm.

The strain was calculated using Williamson-Hall relation (23)

$\beta \cos \theta = (K\lambda)/D + \epsilon 4\sin\theta$ (3)

Where β, D, ϵ and k are full width half-maxima(FWHM), crystallite size, strain and the shape factor, respectively. A graph between βcos θ and 4sinθ was plotted and it is shown in figure 3. The crystallite size and lattice strain was calculated from the intercept and slope of straight line fitting of such plot respectively. The strain in the crystal is found to be 0.00077 and the crystallite size is measured as 22.4 nm.

3.3 Energy Dispersive Analysis

An elemental analysis was carried out for the grown LABMH crystal by employing JEOL-6360 Scanning Electron Microscope energy dispersive X-Ray analysis. Figure 4 shows the EDAX spectrum of the grown LABMH crystal. All the elements such as carbon, oxygen, Nitrogen and bromine except hydrogen in the grown crystals were identified from the characteristic peaks of 0.277keV, 0.525keV and 1.480keV,0.392keV respectively. The peak height or areas in the EDAX spectrum give a measure of the quantity of concerned element in the spectrum [15]. The composition of all the elements and the percentage of atoms present in the grown crystal was calculated and tabulated in table 2.

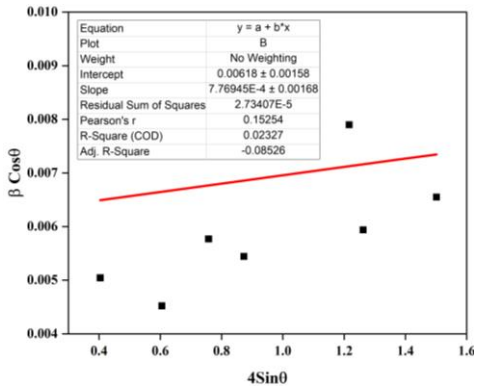

Figure 3: W-H Plot of Grown LABMH Crystal

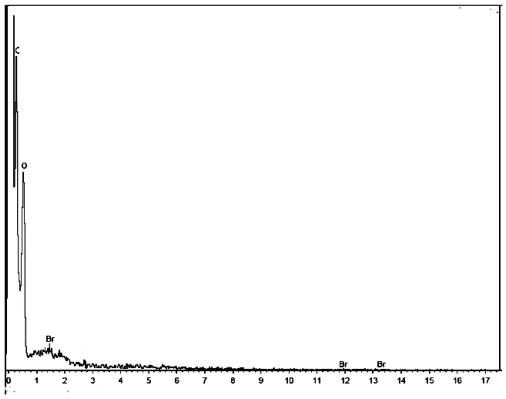

Figure 4: EDAX Spectrum of the Grown LABMH Crystal

Table 2: Elemental composition of the grown crystal

Elements	Energy (keV)	Atomic Weight %	
		Theoretical	Experimental
Br	1.480	9.09	9.99
C	0.277	36.36	37.76
O	0.525	36.36	38.22
N	0.392	18.18	14.03

3.4 FT-IR Analysis

The functional groups of the grown LABMH crystal were confirmed using Nicolet TM 5 with KBr windows FTIR spectrometer by KBr pellet technique with a scan range 4000-400 cm^{-1}. The FTIR Spectrum and the band assignments of the grown LABMH crystal is shown in figure 5 and Table 3 respectively. The broad peak appeared at 3373 cm^{-1} is due to O-H stretching vibration and the 2915 cm^{-1} peak assigned for C-H stretching vibration. The Sharp peak observed at 1677 cm^{-1} is due to the weak asymmetric NH_3^+ bending. The broad top peak discovered at 1516 cm^{-1} is strong for COO^- symmetrical stretching band. A peak observed at 1142 cm^{-1} is due to NH_3^+ rocking. The C-C stretching band was observed at 804 cm^{-1}

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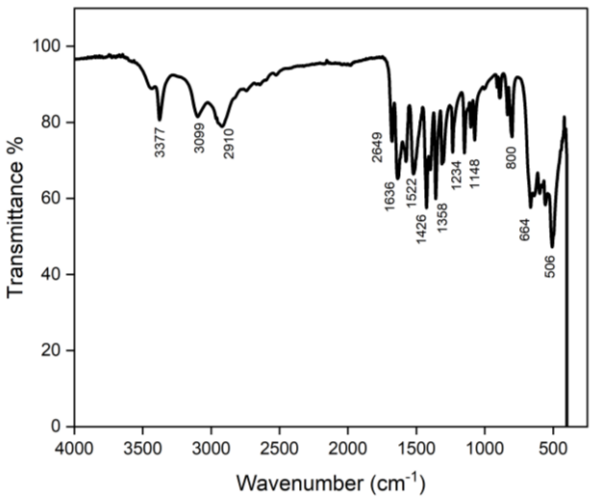

Figure 5.FTIR Spectrum of LABMH Crystal

Table 3: FT-IR Spectral assignment of LABMH Crystal

Wave number cm^{-1}	Vibrational assignment
3377	O-H Stretching
3099	NH_3Stretching
2910	C-H Stretching
1522	COO^- symmetric stretching
1358	CH bending
1148	NH_3rocking
800	C-C Stretching
506	NH_3^+ torsion

3.5 Optical Studies

The linear optical properties of L-Asparaginium bromide Monohydrate crystal were studied by recording the UV-Visible optical absorption using the instrument HITACHI UH 5300 for the wavelength range between 200 and 700 nm and the corresponding spectrum of the L-Asparaginium bromide Monohydrate Crystal is presented in figure 6.

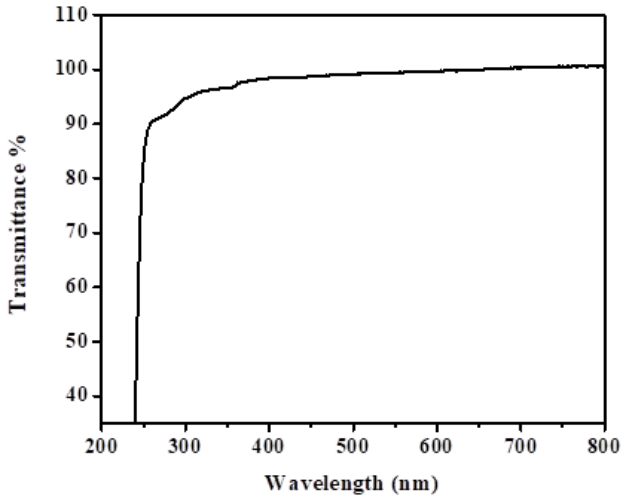

Figure 6. UV-Visible transmittance for LABMH Crystal

The lower cut-off wavelength of the grown crystal is found to be 245 nm and the crystal demonstrates good transmittance in the visible region which is an indication of the function of the crystals for nonlinear optical applications [16].

The optical absorption Coefficient (α) was evaluated from Tauc's relation, [17]

$$\alpha h\nu = A(E\nu - Eg)^n \quad (4)$$

where A, Eg, h, ν refers to a constant, band gap, Planck constant ($6.63X10^{-34}$Js), frequency of incident photons and n is theoretical equal to 1/2 and 2 for direct and indirect transitions, respectively.

The optical band gap of L-Asparaginium bromide Monohydrate Crystal was evaluated from extrapolation of the linear curve of the Tauc's plot figure 7 and the value of the band gap of grown crystal was found to be 5.2eV. The wide band gap of the grown crystal confirms that it could be suitable for optoelectronic devices like laser diode [18].

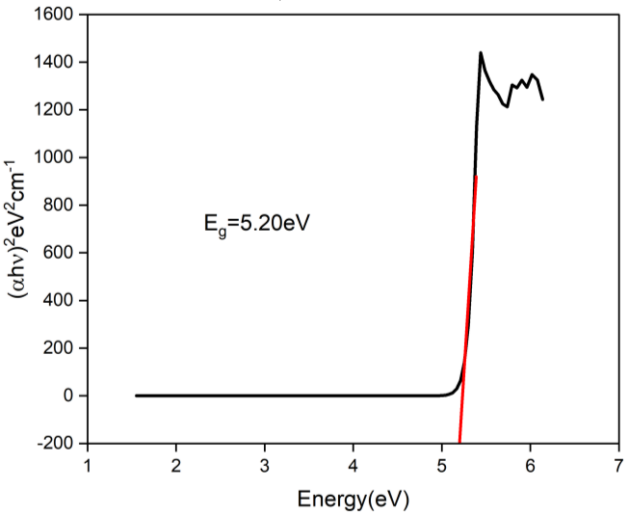

Figure 7.Tauc's plot of LABMH Crystal

3.6 Photoluminescence study

Photoluminescence (PL) measurements are used to investigate the electronic structure of materials and to identify defects, including deep and shallow level defects and imperfections [19-20]. Photoluminescence occurs when ultraviolet light falls on a sample and it can be expected in molecules that are aromatic or contain multiple conjugated double bonds with a high degree of stability. It finds wide applications in the branches of biological, Medical and chemical fields. PL emission spectrum of grown LABMH crystal was recorded using JASCO Spectrofluorometer FP-8300 and a graph was plotted between PL intensity and wavelength. Figure 8 shows a sharp high intense emission peak at 465nm with blue emission. This emission peaks are broad and asymmetric. The intensity of the peak depends upon the crystallinity. The result also shows weak emissions at 533 nm and 623 nm with green and red shift respectively. Therefore the grown LABMH Crystal is suitable for photonic device applications [13].

3.7 Microhardness test

Micro hardness testing is one of the best methods of understanding the mechanical properties of materials such as fracture behavior, yield strength, brittleness index and temperature of cracking. HM-200A was used to measure the mechanical characterization of the grown LABMH crystal. The Vicker's micro hardness number was calculated using the relation [21]

$$HV=1.8544P/d^2 \quad (Kg/mm^2) \qquad (5)$$

P is the indenter load and d is the average diagonal length of impression. Each data point represents an average value obtained from several indentations. The selected face of Crystal was indented gently by loads varying from 10 to 100 gm. The hardness number with applied load is plotted and represented in figure 9. From figure 9, it is observed that the hardness value starts increasing with increase in the load which depends on the bonding structure of the crystal. The material withstands the strength up to 100 g. Beyond the 100 g load, cracks were formed on the surface of the crystal. The maximum hardness value is 28.1 Kg/mm2. From the graph, it is understood that Hv increases with the increase of load which indicates the reverse indentation size effect (RISE) [22].

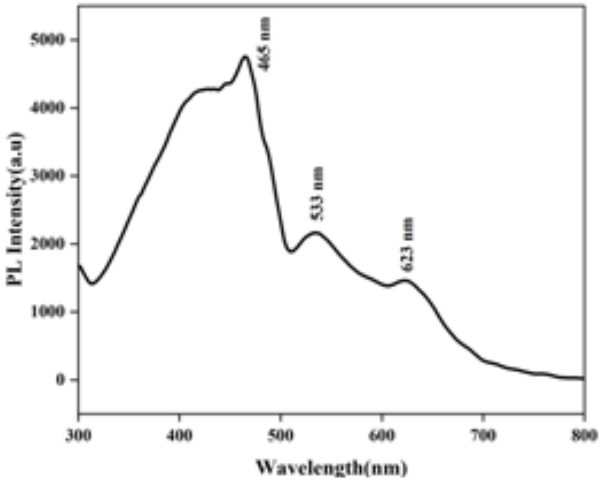

Figure 8: Photoluminescence spectrum of LABMH crystal

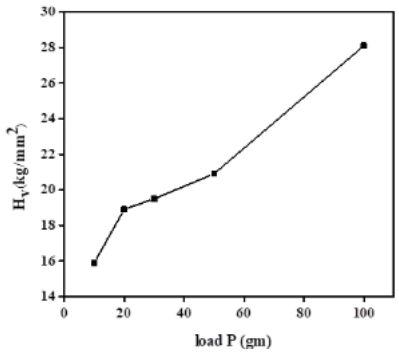

Figure 9.Variation of Load P Vs HV of LABMH Crystal

The Mayer's law relates the load and the size of the indentation as P=adn 'n ' is known to be Mayer's index or work hardening Coefficient [23]. 'n' can be calculated from the slope by the plot between log d and log p which is shown in figure 10. From the slope, Mayer's index was found to be 1.96. According to Onitsch, 'n ' should be lie between 1.0 and 1.6 for hard material and above 1.6 for soft material. Thus from the observation, single crystal of LABMH belongs to soft materials category.

3.8. Nonlinear Optical Property (NLO)

Non-linear optics involves the interaction of light and matter. The non-linear optical property of the LABMH was determined through computational method using Firefly [24]. The general structure of the LABMH was found and is displayed in figure 11.

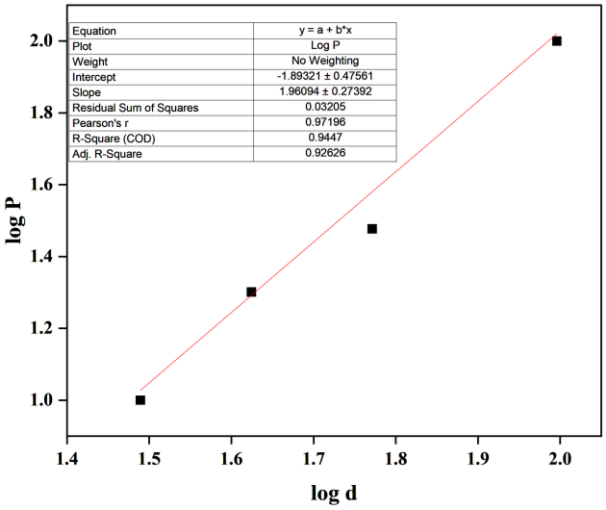

Figure 10. Plot of Log d Vs log P of LABMH Crystal

Figure 11. Crystal structure of LABMH

The relation between mass-dielectric polarization vector P and the incident wave field E is given as, P=χ E,the coefficient χ is the electromagnetism of the medium. The optical higher harmonics are derived by P= χ(1)E + χ(2)EE + χ(3)EEE +…..where χ(1),χ(2) ,χ(3) are the primary, quadratic and cubic polarizability tensors. Results obtained for the NLO activity of LABMH are given in Table 4 with the field of 0.01 applied through the z-axis of the molecule. The cubic non-linear polarisation is higher than the quadratic non-linear polarisability.

Table 4. Nonlinear optical property of LABMH.

Components	Axis	Dipole based (au)
DIPOLE	z	-3.2762221E-01
Alpha	xz	-1.95E+00
Alpha	yz	2.00E+00
Alpha	zz	4.76E+01
Beta	xzz	-1.06E+02
Beta	yzz	5.81E+01
Beta	zzz	2.60E+01
Gamma	zzzz	4.35E+03

4. Conclusion

The single crystal of pure L-Asparaginium bromide Monohydrate crystals were grown from aqueous solution by slow evaporation technique at 40°C temperature. Single crystal-ray diffraction and powder X ray diffraction studies confirmed the LABMH crystal in Orthorhombic crystal system. EDAX analysis showed the presence of Carbon, Oxygen, Nitrogen and Bromine in the sample with the appropriate atomic percentage. The FT-IR spectrum confirmed the presence of functional groups of the grown crystals. The grown crystal has high transmission in the entire visible region and suggested that the potential candidate for the optical applications. The band gap energy of the grown LABMH was found to be 5.2eV. Photoluminescence study confirmed the suitability of the material for the generation of blue radiation. Vicker's hardness test was used to determine the mechanical strength of the grown crystals and the value of Mayer's index suggested soft nature of crystals. The grown crystal exhibited third order non-linear property.

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