Growth, XRD, Spectroscopic, Hardness and SHG studies of L-asparagine monohydrate single crystals

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ABSTRACT

Single crystals of L-asparagine monohydrate (LAM) have been grown by slow evaporation solution growth technique. Single crystal X-ray diffraction analysis was employed to identify the cell parameters. The reflection planes of LAM crystal were confirmed by the powder X-ray diffraction study and diffraction peaks were indexed. Functional groups of the sample were identified by FTIR analysis. Optical properties such as optical transmittance and second harmonic generation were also studied on the grown LAM crystals. The soft nature of LAM crystal was checked by measuring the microhardness test.

1. Introduction

Amino acids are the building blocks for proteins and other essential substances such as neurotransmitters, hormones and nucleic acids and they play a major role in the areas of nutrition, medicine and plant protection [1, 2]. L-Asparagine organic compound, one of the 20 amino acids commonly found in animal proteins. Only the L-stereoisomer participates in the biosynthesis of mammalian proteins and it plays an imperative role in the metabolic control of some cell functions in nerve and in brain tissues [3]. L-Asparagine monohydrate (LAM) 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. Being a non-Centro symmetric material, L-asparagine can be a second harmonic generator and is attracting great deal of attention due to their applications in optical devices, advanced laser-based imaging, communication, data storage and counter measure system design [4, 5]. A series of L-asparagine based crystals have been grown and studied by many researchers and these materials are proved to be good NLO materials [6-8]. In this work, the growth, structural, spectroscopic, mechanical and SHG studies of L-asparagine monohydrate (LAM) crystals are reported.

2. Materials and Methods

2.1. Solubility

High quality sample of L-Asparagine monohydrate (LAM) (99% purity) was purchased from Highmedia, India and its purity was further improved by re-crystallization process. Solubility of the material in a solvent decides the amount of the material which is available for growth and hence defines the total size limit. Solubility gradient is another important parameter which dictates the growth procedure. Solubility was determined using a constant temperature bath (CTB) by gravimetrical method. Initially, the temperature was set at 30 oC in the CTB. The salt of LAM was added step by step to 50 ml of double distilled water in an air-tight container loaded in the constant temperature bath and solution was stirred well. Stirring was continued and the sample was added till a small precipitate was formed in the solution. This gave confirmation of saturated condition of the solution. Then, 25 ml of the solution was pipetted out and taken in a petri dish and it was warmed up till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of the sample in water was determined. The same procedure was followed to find solubility of the sample at various other temperatures. The variation of solubility with temperature for LAM sample is shown in the figure 1. From the solubility curve, it is evident that the solubility increases with temperature and this sample has positive temperature coefficient of solubility. Solubility measurement provides information about the amount of solute available in the solution for the growth, and helps to select suitable solvent for the growth and to select suitable method for the growth. Since the sample has positive temperature coefficient of solubility in water, both slow cooling and slow evaporation methods can be adopted to grow bulk crystals [9].

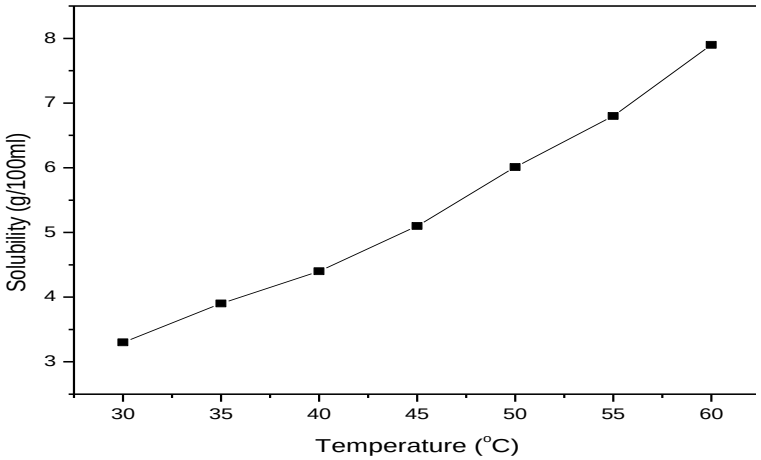

Fig.1: Solubility curve for LAM sample

2.2 Growth

In accordance with the solubility data, the saturated solution of LAM was prepared at 30 ^{o}C in a 500 ml beaker and stirred well using a magnetic stirrer for about 2 hours. Then the solution was filtered using a Whatmann filter paper. After filtering, the beaker was loaded in the constant temperature bath and temperature was maintained at 30 ^{o}C. Seed crystals obtained by slow evaporation were immersed in the beaker to harvest crystals after a growth period of 30 days. The grown crystal of LAM is displayed in the figure 2. The grown LAM crystals are observed to be stable and they do not decompose in air and are non-hygroscopic at ambient temperature. The grown crystals are found to be transparent, colourless, and the crystal faces and edges are well formed.

Fig.2: Harvested crystals of LAM

2.3 Instrumentation

A grown LAM crystal was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_α (λ=0.71069 Å) radiation to evaluate the lattice parameter values. Powder X-ray Diffraction (PXRD) pattern of the powdered sample of LAM was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K_α radiations with λ= 1.54056 Å at 35 kV, 10 mA). UV-visible transmission spectrum of LAM was obtained using a Lambda 35 model Perkin Elmer double beam UV-vis-NIR spectrometer in the range from 190 nm to 1100 nm. The Fourier transform infrared spectrum was recorded in the region 400-4000 cm^{-1} with Perkin Elmer Fourier transform infrared spectrometer (Model : Spectrum RXI) using KBr pellet containing LAM powder obtained from the grown single crystal. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm [10]. Mechanical property was studied by measuring microhardness of the grown LAM crystal and this was carried out using Vickers microhardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study. Indentations were made for various loads from 25 g to 75 g. Several trials of indentation were carried out on the (001) plane and the average diagonal lengths were measured for an indentation time of 5 seconds.

3. Results and Discussion

3.1 Single crystal X-ray diffraction data

Single crystal X-ray diffraction (XRD) study of a LAM single crystal was carried out using a single crystal CCD diffractometer and the intensity data was collected and accurate unit cell parameters were determined from the reflections. The obtained single crystal XRD data are provided in the table 1. It is observed from the results that the grown crystal of LAM crystallizes in orthorhombic crystal system with space group $P2_12_12_1$. The number of molecules per unit cell is found to be 4.

Table 1: XRD data for LAM crystal

Crystal parameters	Values
a (Å)	5.589
b (Å)	9.831
c (Å)	11.810
α	90°
β	90°
γ	90°
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Volume ($Å^3$)	648.905
Z	4

3.2 Powder XRD studies

To confirm the values of lattice parameters obtained from single crystal XRD studies, the powder XRD studies were also carried out and the XRD pattern for LAM sample is presented in figure 3. The well-defined peaks at specific 2Θ values show high crystallinity of the grown crystals. All the reflections of the powder XRD pattern were indexed using the INDEXING and TREOR software packages. The powder XRD data for LAM sample are given in the table 2. The lattice parameters obtained from the indexed XRD patterns using UNITCELL software package are observed to be in comparable with the values obtained from single crystal XRD studies.

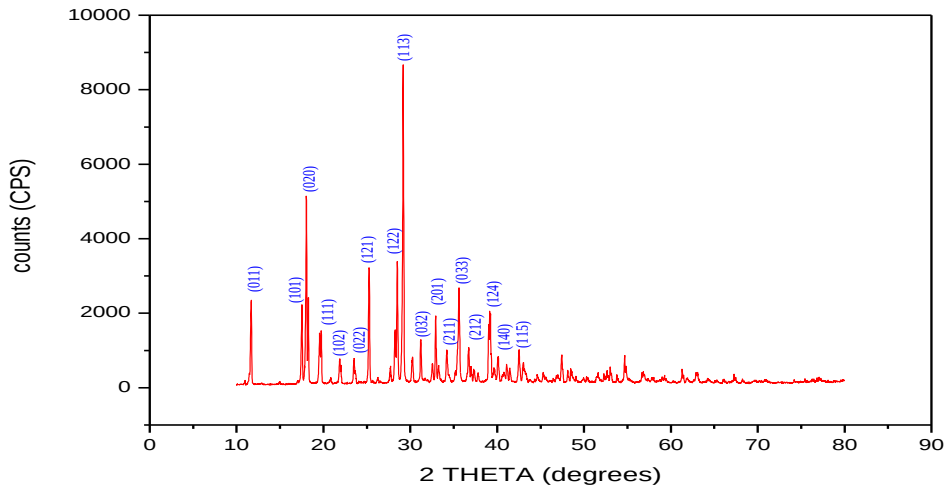

Fig.3: Powder XRD pattern for LAM sample

Table 2: Powder XRD data for LAM sample

Peak. No.	h	k	l	d_{obs} (Å)	d_{cal} (Å)	2-theta(deg)	Rel.density(%)
1	0	1	1	7.55342	7.55431	11.712	24.51
2	1	0	1	5.05317	5.05036	17.536	24.84
3	0	2	0	4.91115	4.91622	18.047	56.95
4	1	1	1	4.48996	4.49240	19.756	16.35
5	1	0	2	4.05955	4.05853	21.876	7.88
6	0	2	2	3.77490	3.77838	23.548	7.99
7	1	2	1	3.52158	3.52276	25.269	35.95
8	1	2	2	3.12981	3.12981	28.495	38.48
9	1	1	3	3.05788	3.05860	29.180	100
10	0	3	2	2.86411	2.86575	31.202	13.65
11	2	0	1	2.71937	2.71842	32.909	20.50
12	2	1	1	2.61795	2.62013	34.223	10.59
13	0	3	3	2.52017	2.51892	35.594	29.19
14	2	1	2	2.44459	2.44581	36.733	11.43
15	1	2	4	2.30676	2.30570	39.014	17.74
16	1	4	0	2.24911	2.24996	40.056	7.83
17	1	1	5	2.12399	2.12438	42.527	10.61

3.3 Fourier Transform Infrared (FTIR) studies

The FTIR spectrum of LAM sample is shown in Fig.4. A broad peak appeared at 3384 cm^{-1} is due to O-H stretching vibration. The band at 3114 cm^{-1} is assigned to the NH_2 stretching vibration. The appearance of the broad band at 2939 cm^{-1} is corresponding to NH3 stretching vibration confirming the zwitterion structure of the molecule. The CH symmetric stretching vibration is observed in 2528 cm^{-1}. The band at 1642 cm^{-1} is attributed to NH_3 deformation vibration [11]. The peak obtained at 1428 cm^{-1} is due to symmetric vibrations of COO^-. The characteristic frequencies and the assignments are provided in the table 3.

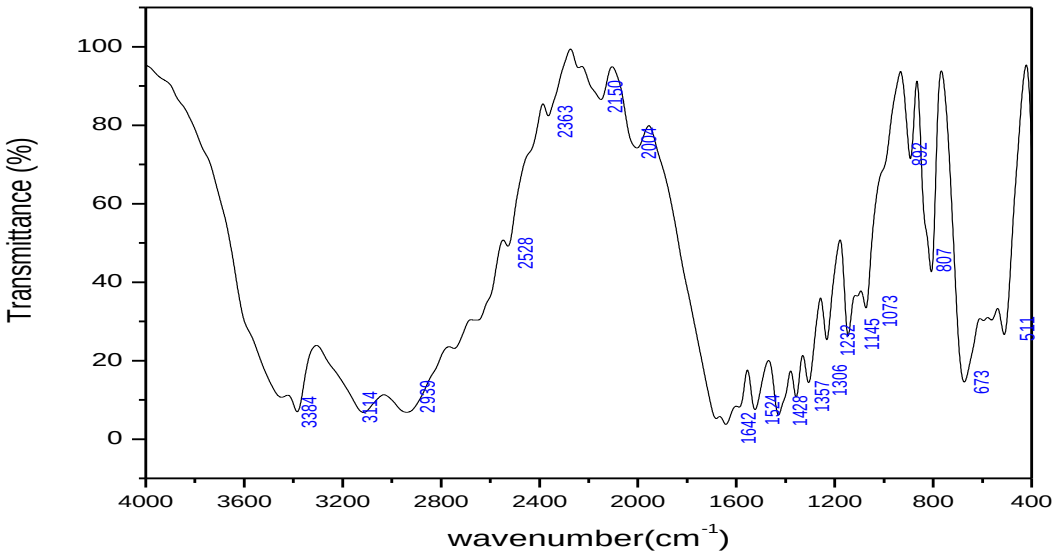

Fig.4: FTIR spectrum for LAM sample

Table 3: FTIR spectral assignments for LAM sample

Peaks/bands (cm^{-1})	Spectral assignments
3384	O-H stretching
3114	NH_2 stretching
2939	NH_3^+ stretching
2528	C-H stretching
2004	N-H stretching
1642	NH_3^+ deformation; COO^- stretching
1524	NH_2 bending
1428	COO^- bending
1357	CH bending
1306	CH_2 wagging
1232	NH_2 rocking
1145	NH_3^+ rocking
1073	C-N stretching
892	CH_2 rocking
807	C-C stretching
673	H_2 O rocking
511	COO^- rocking

3.4 UV-Visible spectral studies

A nonlinear optical material can be of practical use only if it has a wide transparency window. To check the transparency, UV-visible transmittance spectrum was recorded and the Fig.5 shows the transmittance spectrum of LAM crystal. The lower cut-off wavelength is found to be at 227 nm for LAM sample. From the results, it is clear that LAM crystal has good optical transparency in the complete visible region and it could be used for optoelectronic applications [9]. Using the formula

$E_g = 1240 / \lambda$ (here λ is in nanometre), the band gap energy is calculated to be 5.46 eV.

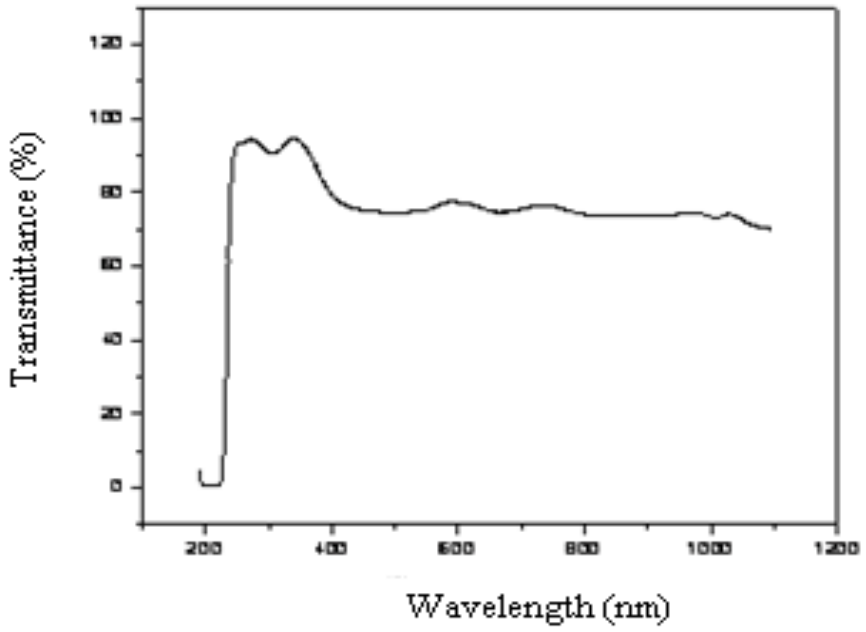

Fig.5: UV-Visible transmittance spectrum of LAM crystal

3.5 Density and microhardness

The density value of LAM crystal was measured by floatation method and the density was found to be 1.542 g/cc. The density was also calculated from the crystallographic XRD data using the relation $\rho = (MZ)/(NV)$ where M is the molecular weight of LAM crystal, Z is the number of molecules per unit cell, N is Avogadro's number and V is volume of the unit cell and it was found to be 1.535 g/cc .

Mechanical property of the sample was studied by measuring microhardness number with various loads. The hardness of a material is a measure of its resistance to plastic deformation. Vickers microhardness number was evaluated from the relation $H_v = 1.8544\ P / d^2$ (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 P and hardness number H_v is shown Fig.6. The hardness number was found to increase with increase in applied load and hence the grown LAM crystal exhibits the reverse indentation size effect, in which the hardness value increases with the increasing load. The relation between load (P) and size of the indentation (d) is given by well known Meyer's law $P = a\, d^n$ and this relation is plotted in figure 7. Here a and n are constants depending upon the material. The value of the work hardening coefficient n was found to be 2.265. According to Onitsch, $1.0 \leq n \geq 1.6$ for hard materials and $n > 1.6$ for soft materials [12]. Hence, it is concluded that LAM belongs to the soft category materials.

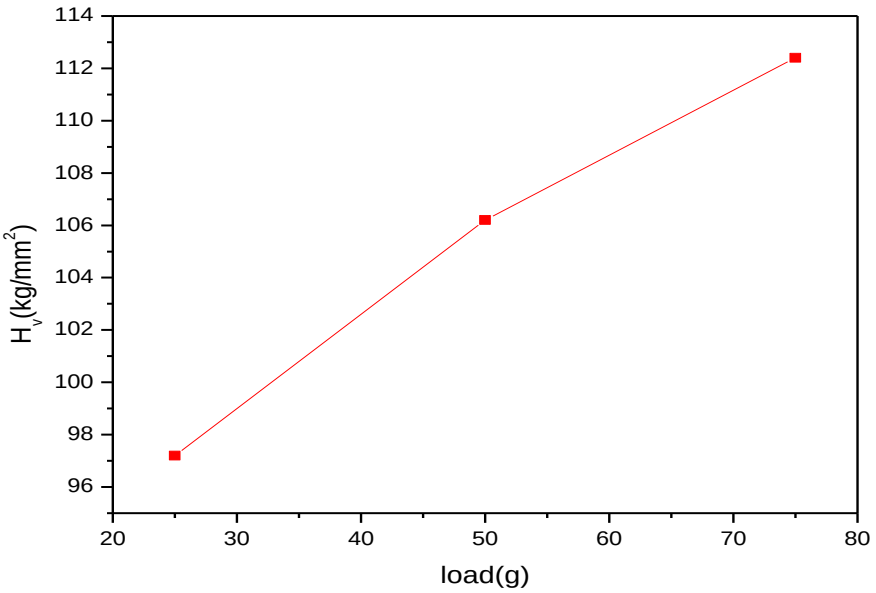

Fig.6: Variation of hardness number with the applied load for LAM crystal

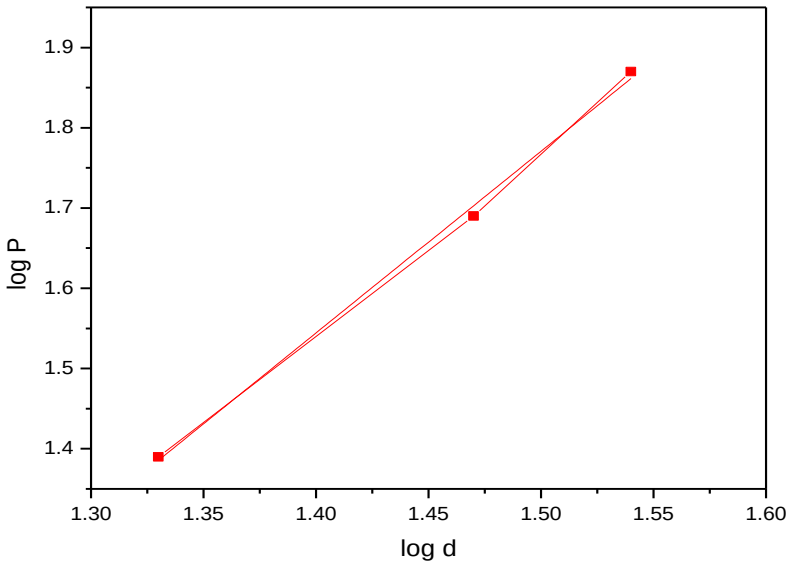

Fig.7: Plot for proving Meyer's relation

3.6 Second Harmonic Generation (SHG) studies

The second harmonic generation (SHG) behavior of the powdered material of LAM was tested using the Kurtz and Perry method. A Q switched Nd:YAG laser beam of wavelength 1064 nm with an input power of 0.68 J/pulse, pulse width of 6 ns and repetition rate of 10 Hz was directed on the sample. The SHG output of wavelength 532 nm (green light) was finally detected by the photomultiplier tube (PMT) and hence LAM crystal is a second harmonic generator. Thus, LAM generates visible laser light which will be useful in the optical communication and optical computing.

4. Conclusion

Solubility study shows that LAM crystal has positive temperature coefficient of solubility. Single crystals of LAM were grown by slow evaporation in a controlled manner. Single crystal XRD and powder XRD studies reveal that LAM crystal crystallizes in orthorhombic structure. The molecular groups were identified and the NLO activity of LAM crystals was confirmed by measuring SHG efficiency. The cut-off wavelength for LAM sample was found to be 227 nm and it is observed that LAM crystal has good transparency in the visible region. The mechanical strength of LAM crystal was checked by measuring microhardness values.

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