

EFFECT OF Li^+ ION ON THE GROWTH AND CHARACTERIZATION L-ASPARAGINE MONOHYDRATE SINGLE CRYSTALS

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Abstract

Single crystals of pure and Li^+ doped L-Asparagine monohydrate (LAM) was successfully grown by slow evaporation method at room temperature. Grown crystals were characterized by powder X-ray diffraction analysis. The presence of various functional groups was identified from FTIR spectral analysis. The incorporation of Li^+ into the crystal was confirmed from ICP (Inductively Coupled Plasma) elemental analysis. Optical properties such as optical transmittance and second harmonic generation were also studied on the grown pure and doped crystals.

Key words: Amino acid, X-ray Diffraction, UV –Vis spectrum, second harmonic generation

I. 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. L-Asparagine monohydrate (LAM) is an interesting material from amino acid family to investigate because it crystallizes in a structure exhibiting a complex network of hydrogen bonds among asparagine molecules and between asparagine and water molecules [1]. Verbist et al., have reported that LAM crystallizes in orthorhombic structure [2] and it belongs to space group $P2_12_12_1$ with four molecules per unit cell. Being a

noncentrosymmetric material, L - Asparagine can be a second harmonic generator and it is attracting great deal of attention due to their practical applications in optical devices, advanced laser imaging, communication, data storage and counter design. Several researchers have carried out organic and metal ion doped crystal growth and characterization of L- Asparagine monohydrate crystals. In this growth process lithium is used as the dopant. The lithium ion which exists at the upper left of the periodic table has the strongest polarity among the metal cations [3] and acts as a structure maker [4].

1. EXPERIMENTAL

Saturated solution of LAM and 5% lithium ion doped LAM was prepared separately using commercially available AR grade L-Asparagine monohydrate ($C_4H_8O_3N_2 \cdot H_2O$). Both the solutions were stirred continuously for about three hours using the magnetic stirrer and filtered using Whatmann filter paper. Filtered solution was covered with perforated polythene sheet and kept for crystallization in a constant temperature bath in order to avoid thermal fluctuations. Good quality LAM single crystal of size 6 mm × 2 mm × 2 mm was harvested after a growth period of 20 days as shown in fig.1 (a). Li^+ doped LAM single crystal of size 15 mm × 5 mm × 4 mm harvested after a growth period of 20 days is shown in fig.1 (b).



Fig: 1(a)

Grown pure LAM and Li^+ -doped LAM crystals



Fig: 1(b)

II. RESULTS AND DISCUSSIONS

1.1. Powder X-ray Diffraction Analysis

As grown pure and Li^+ -doped LAM crystals were finely powdered and subjected to powder XRD analysis using the Bruker AXS D8 Advance Model, X-ray diffractometer, Nickel filtered $CuK\alpha$ radiation with $\lambda = 1.54056 \text{ \AA}$. The 2θ range was from 10° to 90° . The powder

XRD patterns of Li^+ -doped samples are compared with that of undoped one. However a slight variation in intensity is observed as a result of doping. The well-defined peaks at specific 2θ values show high crystallinity of the grown crystals. Experimental 'd' values of pure sample are in well agreement with standard JCPDS values. The XRD pattern of pure and Li^+ - doped crystals are shown in fig.2 (a) and fig.2 (b) respectively.

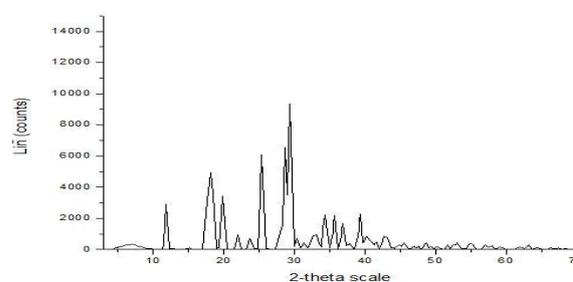


Fig: 2(a) Powder XRD pattern of pure LAM crystal

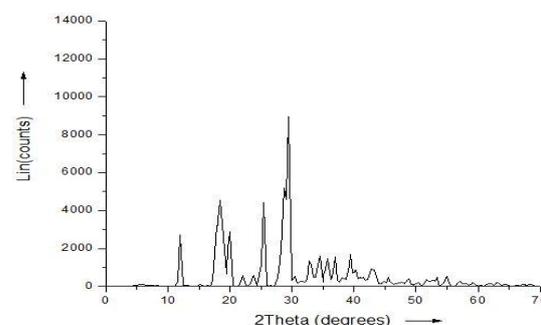


Fig: 2(b) Powder XRD pattern of Li^+ -doped LAM crystal

1.2. FT-IR Analysis

The infrared spectral analysis (FTIR) has been carried out to understand the chemical bonding and it provides useful information regarding the molecular structure of the compound. The recorded FT-IR spectrum of pure and Li^+ -doped LAM was recorded on Thermo Nicolet

Avatar 370 FT-IR spectrometer using KBr pellet in the range 4000 - 400 cm^{-1} . The FTIR spectra of both pure and doped LAM crystals are shown in fig.3 (a) and fig.3 (b) respectively. A peak appeared at 3383.53 cm^{-1} for pure and 3383.98 cm^{-1} for doped LAM, indicating the presence of O-H stretching vibration. The intense and fairly sharp band at 3113.13 cm^{-1} for pure and 3112.25 cm^{-1} for doped crystal, should be assigned to the NH_2 stretching vibration [5]. The appearance of the broad band at 2952.12 cm^{-1} can only be due to the NH_3^+ stretching vibration confirming the zwitter ion structure of the molecule [6]. Other characteristic vibrations establishing the identity of the functional groups present in the compounds are listed in table 1. The FT-IR spectra of both the pure and doped LAM confirm the structural aspects of pure compounds. Although the spectrum of lithium doped LAM crystals provides similar features as that of pure LAM, there is slight shifting observed suggesting that it may be due to the incorporation of Li^+ ions in the lattice of LAM.

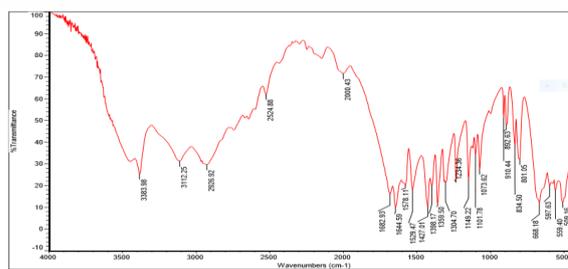


Fig: 3(b)

Table 1: FTIR spectral assignments of pure and Li^+ -doped LAM crystals

Pure LAM(cm^{-1})	Li^+ -doped LAM(cm^{-1})	Band assignments
3383.53	3383.98	O-H stretching
3113.13	3112.25	NH_2 stretching
2953.12	2926.92	NH_3 stretching
2525.42	2524.43	C-H stretching
2001.95	2000.30	N-H stretching
1645.20	1644.59	NH_3^+ deformation
1528.89	1529.47	NH_2 bending
1427.42	1427.01	COO^- bending
1360.01	1359.50	CH bending
1314.17	1304.70	CH_2 wagging
1234.58	1234.36	NH_2 rocking
1149.32	1149.22	NH_3^+ rocking
806.44	801.05	C-C stretching
508.44	509.16	COO^- rocking

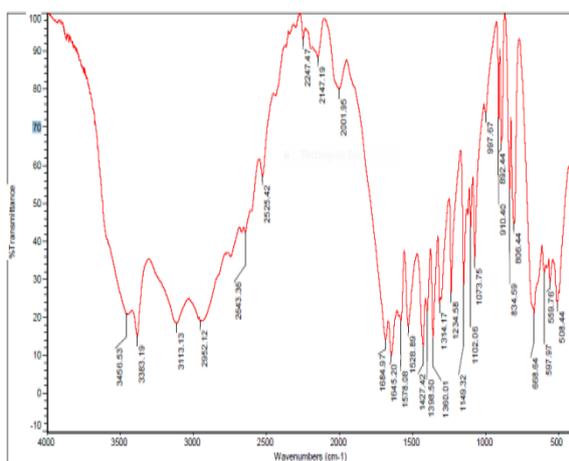


Fig:3(a)

1.3. UV-Visible spectral studies

The UV-Visible absorption spectra of the crystals were recorded in range 200 to 800 nm using Perkin Elmer double beam UV-Vis- NIR spectrometer. A non linear optical material can be of practical use only if it has a wide transparency window. Fig.4 (a) & 4(b) shows the absorbance spectrum of pure and doped LAM crystal. It is seen from the spectra that both samples are colourless, absorption is not observed between 224 nm to 700 nm (visible

region). The lower cut-off wavelength is found to be at 225 nm and 224 nm for pure and Li^+ -doped LAM respectively. It is clear that both pure and Li^+ -doped LAM crystal has good optical transparency in the complete UV-Vis region. But Li^+ -doped LAM crystal has a small shift in its absorbance spectrum. This confirms the incorporation of the metal dopant. In the visible region, the crystal is highly transparent and it could be used for optoelectronic application. Using the formula Band gap energy, $E_g = 1240 / \lambda$ (here λ is in nm), band gap energy (E_g) for pure LAM, is 5.53eV and that of Li^+ -doped LAM is 5.51eV.

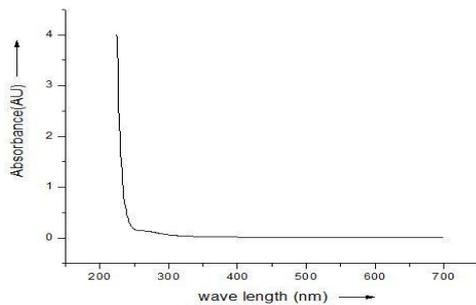


Fig: 4(a)

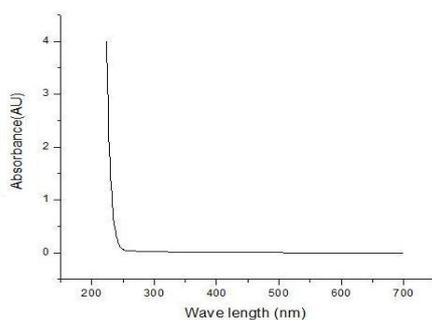


Fig: 4(b)

UV-Visible absorbance spectrum of pure and Li^+ -doped LAM crystals

1.4. Second Harmonic Generation

Studies

The NLO conversion efficiency test was carried out for the samples using Kurtz powder technique. The sample was illuminated using a 1064 nm Nd: YAG laser with input pulse of energy 5.7 mJ. The second harmonic generation signal generated in the sample was confirmed from emission of green radiation (532 nm). The SHG output for all the specimens of grown crystals is given in table 2. From the table, one can see that the SHG efficiency of LAM crystal was enhanced considerably when it was doped with lithium.

Table 2: SHG output of grown crystals

Sample	SHG signal(mV)
LAM	521
Li^+ -doped LAM	662

1.5. ICP Elemental Analysis

ICP (Inductively Coupled Plasma) is an emission spectrophotometric technique, based on the fact that excited electrons emit energy at a given wavelength as they return to ground state. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its chemical character. This technique is used to find qualitative and quantitative determination of

lithium present in the LAM crystal. The result shows that 67 ppm amount of lithium is present in the sample.

2. CONCLUSIONS

The single crystals of pure and Li^+ -doped L-Asparagine monohydrate was grown from aqueous solution by slow evaporation technique under room temperature. The grown crystals are transparent and have well defined external appearance. The size of the doped crystal is larger than pure, due to the presence of lithium dopant. Powder XRD studies confirm the high crystallinity of grown crystals. The UV-Visible study identified the UV cut-off wavelength of pure and Li^+ -doped LAM crystals as 225 nm and 224 nm respectively. The functional groups present in the grown crystals were identified by the FT-IR spectrum analysis. ICP elemental analysis confirms the presence of lithium in the grown crystal. The NLO activity of both pure and Li^+ -doped LAM was confirmed by measuring SHG efficiency. The Second Harmonic Generation in the grown crystals makes it a good material for frequency conversion in laser systems. Hence it can be concluded that the pure and Li^+ ion doped L-Asparagine crystals are efficient candidates for SHG and device applications.

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