

Growth and Characterization of Pure and Cesium - Doped L - Asparagine Monohydrate Single Crystals

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Abstract

Single crystal of pure and doped L – Asparagine monohydrate (LAM) was successfully grown by slow evaporation method at room temperature. Transparent, bulk single crystals of size of $10 \times 4 \times 4 \text{ mm}^3$ were harvested in ten days. The lattice parameters were calculated by single crystal X – ray diffraction. The effect of Cs - doping on the growth, optical and microhardness properties has been investigated. The presence of functional groups have been assigned by FTIR spectral analysis. UV – Vis – NIR spectrum was recorded to study the optical transmittance and absorbance of grown crystal. The dielectric behaviour of the crystals was also studied. The thermal properties of pure and Cs – doped LAM crystals were investigated by thermo gravimetric, differential thermal analysis and differential scanning calorimetry analyses. Chemical etch study was carried out using optical microscopy to study the dislocation, surface defects and morphology.

Keywords: Crystal growth; X -ray diffraction; Micro hardness; Dielectric studies; Thermal analysis

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Introduction

The search and design of highly efficient nonlinear optical (NLO) crystals for visible and ultraviolet (UV) region are extremely important for laser processing. In view of this, it is desired to find new NLO crystals which have a shorter cut-off wavelength. High quality organic NLO crystals must possess sufficiently large NLO coefficient, transparent in UV region and high laser damage threshold power and easily grown with large dimensions [1]. Among the biological molecules, asparagine is a very important amino acid because it plays a role in the metabolic control of some cell functions in nerve and brain tissue and is also used by many plants as a nitrogen reserve source [2]. Amino acid family of crystals are under extensive investigations in recent times owing to their favourable nonlinear optical properties [3,4]. The structure of L – asparagine monohydrate has been discussed several times [5]. Verbist have reported that L - Asparagine monohydrate (LAM) single crystal crystallizes in orthorhombic structure [6] and belong to $P2_12_12_1$ space group with four molecules per unit cell. Its lattice parameters are $a=5.597 \text{ \AA}$, $b=9.819 \text{ \AA}$, $c=11.792 \text{ \AA}$ and $V=648.05 \text{ \AA}^3$. The molecule is in the zwitter ionic form and is linked together by seven distinct hydrogen bonds forming a three dimensional network. Several metal, organic and inorganic acid were complexed with LAM

crystals have been synthesized and reported, which gives as hope to synthesize new complexes. Asparagine complexes such as L – asparagine – L - tartaric acid (LALT) [7], L - asparaginium picrate (LASP) [8], L - asparaginium nitrate (LAsN) [9] and L - asparagine cadmium chloride monohydrate [10] are proved to be good NLO materials. Recently, investigation of Mn^{2+} doped L - asparagine monohydrate single crystal has been found to improve the crystallinity, optical transparency and mechanical strength that are useful for optoelectronic application as reported by Shakir et al. [11]. In view of this we have undertaken the growth and characterization of pure and Cs doped LAM crystals. In this work, we have presented the growth, structural, optical, thermal, mechanical, dielectric and etching of Pure Cs - doped LAM single crystals grown by slow evaporation method.

Experimental

Crystal growth

Analar grade L – Asparagine monohydrate and Cesium nitrate salts were used to grow the single crystals. Saturated solution of L – Asparagine monohydrate was prepared at room temperature.

The solution was continuously stirred for about six hours using the magnetic stirrer and this solution was filtered using whatman filter paper. The filtered solution was kept in a dust free atmosphere to allow evaporation. Good quality single crystals of pure LAM is harvested after the growth period of 11 days. The size of the grown LAM crystal $5 \times 3 \times 3 \text{ mm}^3$ is shown in **Figure 1 (a)**. The growth of Cs - doped LAM crystals were successfully grown by slow evaporation technique. Saturated solution of AR grade LAM and one mole percentage of CsNO_3 was prepared. The prepared solution was filtered and placed in an undisturbed area. The Cs - doped LAM single crystals of size $10 \times 4 \times 4 \text{ mm}^3$ were harvested after the growth period of seven days is shown **Figure 1 (b)**.

Results and Discussion

Single crystal X-ray diffraction

In order to identify the lattice parameters of the grown crystals, single crystal X-ray diffraction study was performed by using ENRAF - NONIUS CAD 4 diffractometer with $\text{CuK}\alpha$ radiation source ($\lambda=1.5404 \text{ \AA}$). The single crystal XRD data shows that both pure and Cs - doped LAM crystals belongs to orthorhombic crystallographic system. The lattice parameters of LAM crystals are in good agreement with the reported values [5]. The observed lattice parameter values of the pure and Cs - doped LAM crystals were compared and is presented in **Table 1**. A marginal decrease in the lattice parameters and volume has been observed for the Cs - doped LAM crystal in comparison with the pure LAM crystal.

FT-IR analysis

The FT - IR spectrum of pure and Cs - doped LAM crystals were recorded on Perkin - Elmer FTIR spectrometer using KBr pellet technique in the range of $4000 - 400 \text{ cm}^{-1}$. The FTIR spectra of both pure and Cs - doped LAM crystals are shown in **Figure 2**. A peak appeared at 3781 cm^{-1} indicating the presence of O - H stretching vibration. The intense and fairly sharp band at 3383 cm^{-1} is assigned to the NH_2 asymmetric stretching vibration. The appearance of the broad band at 3110 cm^{-1} is due to the NH_2 symmetric stretching vibration. The N - H symmetric stretching vibration is observed in 2000 cm^{-1} . The asymmetric and symmetric stretching type vibration of ionised carboxylate group COO^- are observed at 1642 cm^{-1} and 1430 cm^{-1} respectively.



Figure 1a As grown LAM crystal.

Table 1 Single crystal X-ray diffraction data of pure and Cs-doped LAM crystals.

Cell Parameters	Pure LAM	Cs - doped LAM
a	5.593 (Å)	5.597 (Å)
b	9.827 (Å)	9.819 (Å)
c	11.808 (Å)	11.792 (Å)
α	90°C	90°C
β	90°C	90°C
γ	90°C	90°C
V	648.996 Å ³	648.05 Å ³
Crystal system	Orthorhombic	Orthorhombic

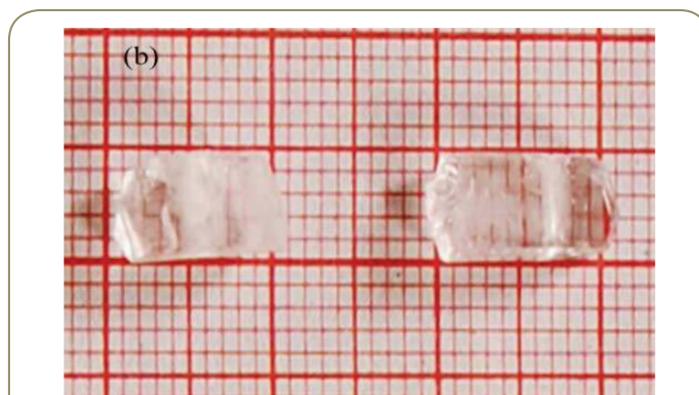


Figure 1b As grown Cs - doped LAM crystal.

The band observed at 1358 cm^{-1} is assigned to CH_2 twisting type of vibration. The band at 1148 cm^{-1} is attributed to the rocking type of vibration of NH_3^+ . The band corresponding to C-N and C-C stretching vibrations appeared at 1083 and 836 cm^{-1} respectively. The of vibrational peak observed at 597 and 511 cm^{-1} are due to torsional oscillation of NH_3^+ . Although the spectrum of Cs - doped LAM provides similar features as that of pure LAM, there is slight shifting observed suggesting that it may be due to the incorporation of Cs ions in the lattice of LAM.

EDAX analysis

Energy Dispersive X - rays Analysis (EDAX) is a technique used for identifying the elemental composition of the specimen. In this study, the grown crystals were analyzed by FEI QUANTA 200F energy dispersive X - ray microanalyzer. The incorporation of Cs in the doped specimen was confirmed by EDS qualitative analysis as clearly seen in **Figure 3**. Analysis of the surface at different sites reveals that the incorporation of Cs is non-uniform over the host crystal surface.

UV-Vis - NIR Spectral studies

UV - Vis - NIR transmittance Spectrum of pure and Cs - doped LAM single crystal of thickness 2 mm was recorded in the wavelength range $200 - 1100 \text{ nm}$ using Lambda 35 UV - Vis - NIR spectrophotometer. It gives limited information about the structure of the molecule because the transmittance of UV and Visible light involves promotion of the electrons from the ground state to a higher energy state. A nonlinear optical material can be used for practical application only if it has a wide transparency window. **Figure 4** shows the transmittance spectrum of pure and

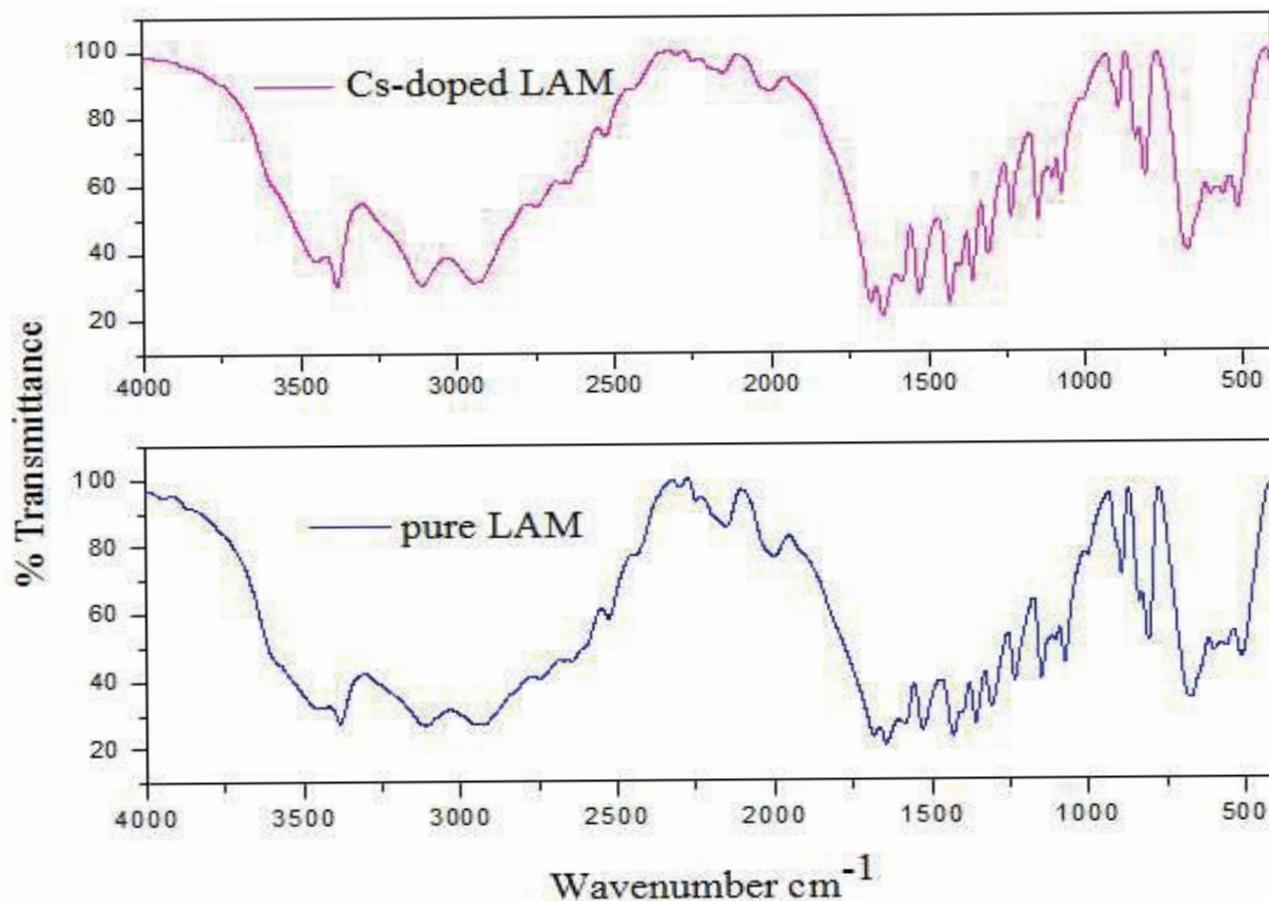


Figure 2 FTIR spectrum of pure LAM and Cs - doped LAM crystals.

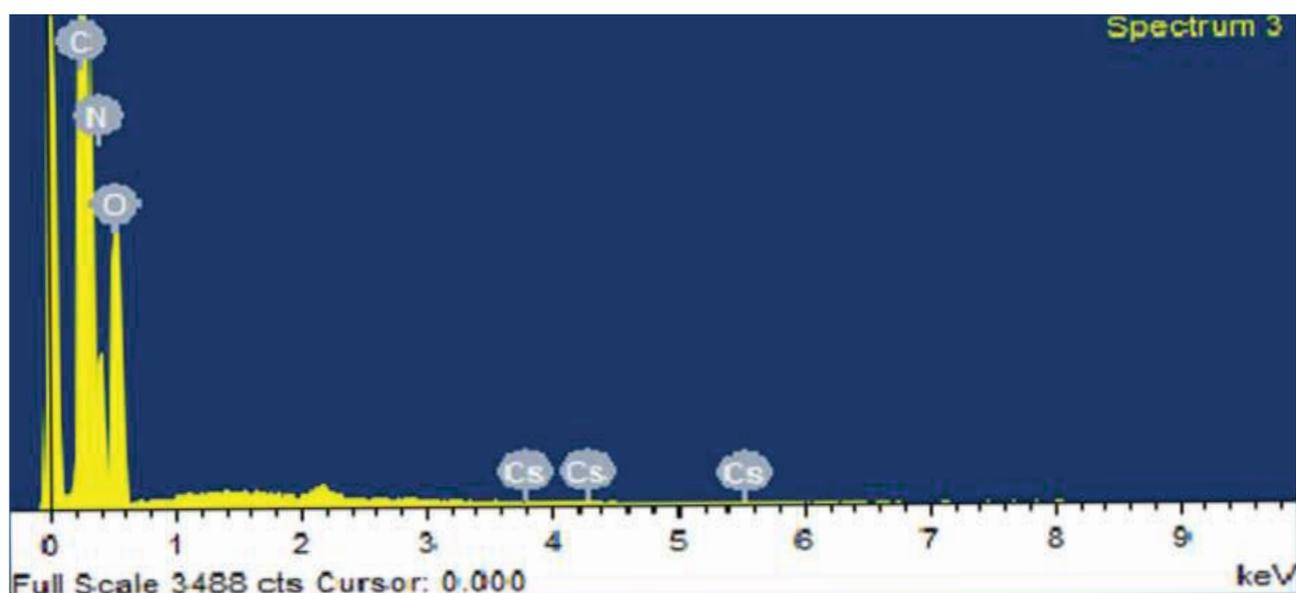


Figure 3 EDAX Spectra of pure and Cs - doped LAM crystal.

Cs - doped LAM single crystals. The lower cut-off wavelength is found to be at 196 nm and 221 nm for pure and Cs - doped LAM respectively. LAM crystal has good optical transparency in the

complete UV - visible region. Whereas the percentage of optical transmittance decreases slightly for Cs - doped LAM. Absorption in the near ultraviolet region arises from electronic transitions

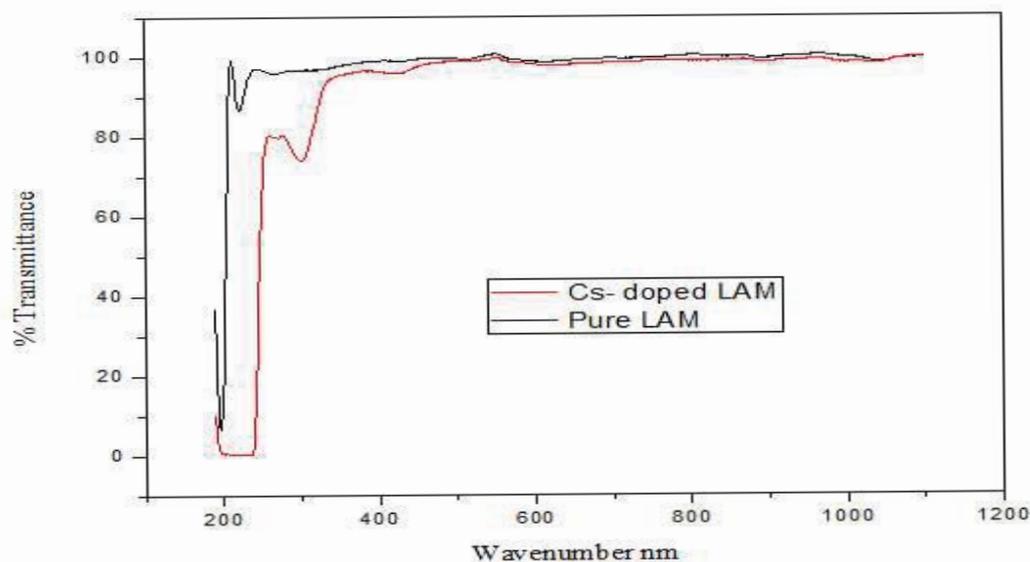


Figure 4 UV-Vis - NIR transmittance spectrum of a pure and Cs - doped LAM crystals.

associated within the sample. The optical absorption coefficient (α) was calculated from the transmittance spectrum using the following relation,

$$\alpha = \frac{1}{t} \log \left(\frac{1}{T} \right)$$

Where, T is the transmittance and t is the thickness of the crystal. Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$),

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}$$

Where, E_g is optical band gap energy of the crystal and A is a constant. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in **Figure 5**. E_g is evaluated by the extrapolation of the linear part of the graph with x-axis. The calculated band gap energy is found to be 6.3 eV for pure LAM and Cs - doped LAM is 6.1 eV.

Dielectric studies

The dielectric study of pure and Cs - doped LAM single crystals were carried out using the instrument HIOKI 3532 - 50 LCR HITESTER. A sample of dimension $4 \times 2 \times 2 \text{ mm}^3$ having graphite coating on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency from 50 Hz to 200 KHz at room temperature. **Figure 6** Shows the variation of the dielectric constant (ϵ_r) with applied frequency. The dielectric constant is calculated using the formula

$$\epsilon_r = \frac{Ct}{\epsilon_0 A}$$

Where C is capacitance (F), t the thickness (m), A the area (m^2), ϵ_0 is the absolute permittivity in the free space having a value of $8.854 \times 10^{-12} \text{ Fm}^{-1}$. The dielectric constant has high value in the lower frequency region and then it decreases with increase of frequency. The high value of dielectric constant at low frequencies may be due to the presence of all the four polarizations and its low

value at high frequencies may be due to the loss of significance of these polarizations gradually [12]. Similarly, the variation of dielectric loss with frequency is shown in **Figure 7**. In the case of Cs - doped LAM the same trend is observed with reference to pure LAM. However it is marginally altered in the dielectric behaviour of pure LAM, which may be due to the incorporation Cs metal ion dopant. It is confirmed that the grown crystals possesses optical quality with fewer defects, and this parameter is vital importance role for various second harmonic generation application.

Vicker's microhardness studies

Mechanical strength is one of the important properties of any material used for device fabrication. Hardness is the resistance offered by a material against the plastic deformation caused by scratching or indentation. The Vickers microhardness measurements were carried out on pure and Cs - doped LAM crystal using SHIMADZU HMV - 2000 microhardness tester. The static indentation were made at room temperature with a constant indentation time 3 s. The diagonal impressions of the indentation marks made on the surface by varying load from 25 g to 100 g were measured. To get accurate measurements for microhardness values at each load the experiment was repeated and the average value of diagonal length of indentation for pure and Cs - doped LAM crystals were calculated. The hardness was calculated using the following expression:

$$H_v = \frac{1.8544 P}{d^2} \text{ (kg/mm}^2\text{)}$$

where P is applied load in kg, 1.8544 is a count of a geometrical factor for the diamond pyramidal indenter and d is the average diagonal length of the indenter impression in mm. The hardness number was found to increase with increase in applied load and above 100 g cracks were developed on the smooth surface of the crystal due to the release of internal stress generated locally by indentation. The microhardness (H_v) values increases with load

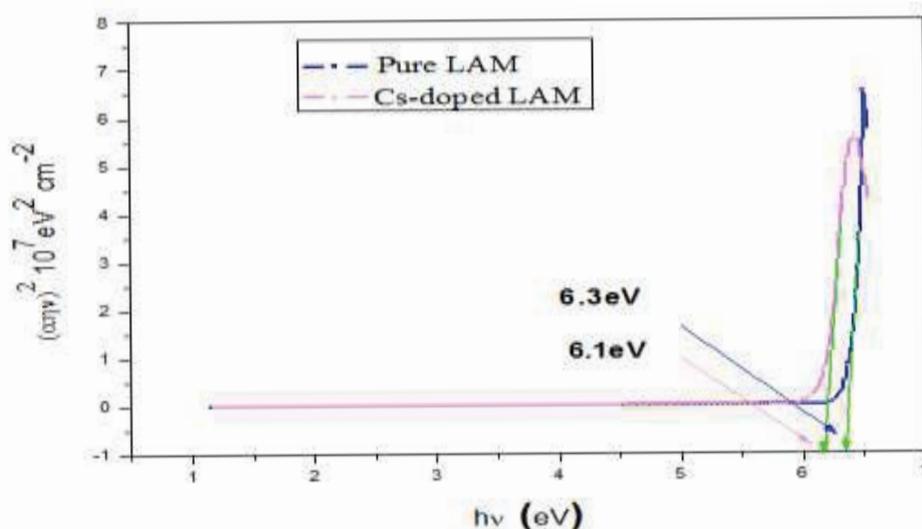


Figure 5 Plot of $(\alpha hu)^2$ versus hu of pure and Cs - doped LAM crystals.

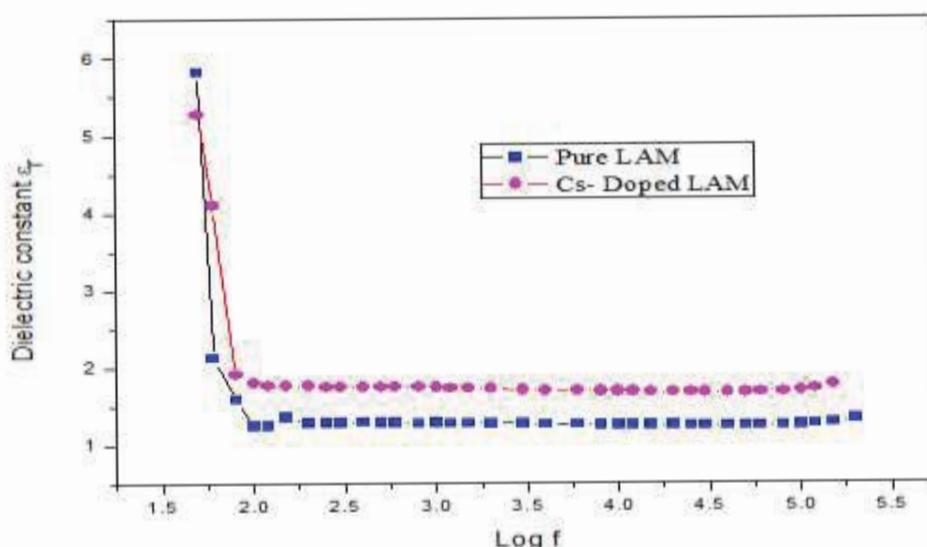


Figure 6 Dielectric constant of a pure and Cs - doped LAM crystals.

for both pure and cesium doped L-Asparagine monohydrate. From the results, it is observed that the value of hardness of the pure LAM crystal is higher than the hardness value of Cs - doped LAM single crystals for all loads. This decrease in the hardness value of doped sample can be attributed to the incorporation of the impurity in the lattice of the LAM crystal. The plot drawn between the corresponding loads and hardness values of pure and Cs - doped LAM is depicted in **Figure 8**. The hardness value of the material increases with the increase of applied load. Such a phenomenon was referred to as reverse indentation size effect (RISE). In order to analyze the ISE one needs to fit the experimental data according to the Meyer's law

$$P = Ad^n$$

which correlate the applied load P and indentation length d . Where A is a constant parameter for a given material n is called the Meyer's index or work hardening coefficient. In the present work the plot obtained between $\log P$ and $\log d$. The work hardening coefficient (n) was calculated from **Figure 9** by the least square curve fitting method. The work hardening coefficient (n) was calculated to be 1.2 for pure LAM and 1.1 for Cs - doped LAM respectively. According to Onitsch [13], the value of n lies between 1 and 1.6 for hard materials and for soft material if is above 1.6. So the crystal pure and Cs - doped LAM can be accepted as hard material.

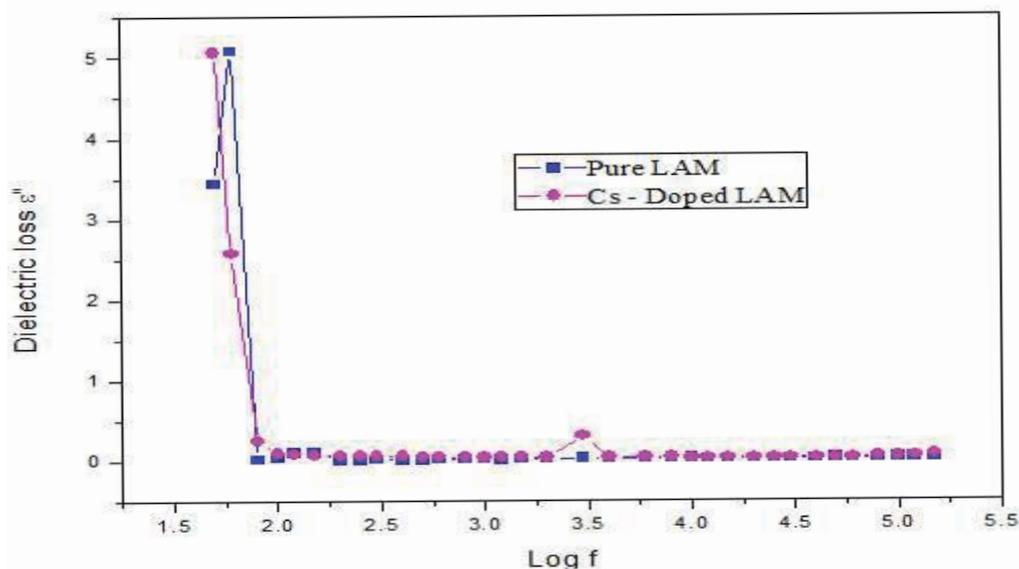


Figure 7 Dielectric constant of a pure and Cs - doped LAM crystals.

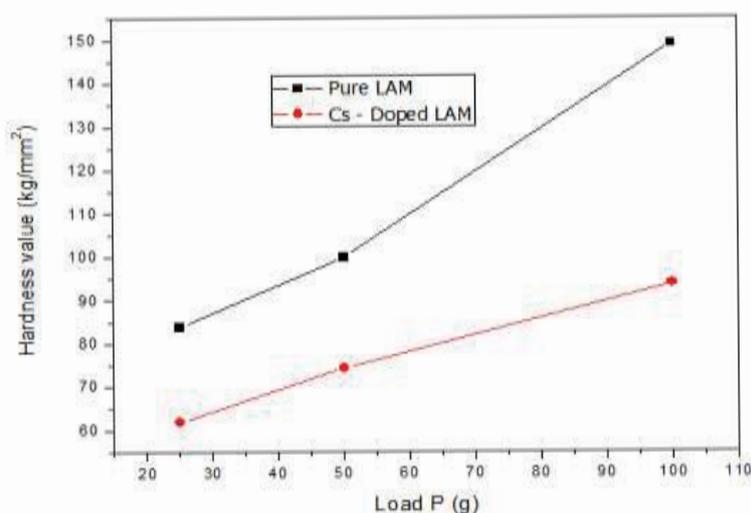


Figure 8 Microhardness behaviour of pure and Cs - doped LAM crystals.

Thermal analysis

The Thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning Calorimetry (DSC) techniques were employed to identify the phase transition, different stages of decomposition and melting point of the grown crystals. The TGA and DTA of pure and doped LAM crystals were carried out in nitrogen atmosphere in the temperature range 25°C - 1000°C, at a heating rate of 10°C, using the instrument SDT Q600 V20.9 Build 20 analyzer. **Figures 10 and 11** show the simultaneously recorded TGA, DTA and DSC curves of pure and Cs - doped L-Asparagine monohydrate crystals. TGA curve shows three stages of weight loss for pure Cs-doped LAM. The compound is stable upto 106°C. The first stage of decomposition between 106°C and 233°C is

about 11% due to the evaporation of lattice water. The second stage is between 283°C and 342°C with a weight loss of 25% due to the decomposition L-Asparagine. The third weight loss upto 900°C is about 27% is due to the decomposition of remaining residue which is up to 900°C.

From DTA curve of pure L - Asparagine shows a strong endothermic peak at 120.68°C and 257.16°C. The endothermic peaks of Cs doped LAM crystals are slightly shifted and observed at 125.96°C and 256.97°C. The two endothermic peaks in pure and Cs-doped LAM coincides exactly with the decomposition patterns observed in TGA. From the analysis it is concluded that the crystal decomposes before melting. DSC curve of both pure and Cs Doped LAM crystal shows three phase transition. The

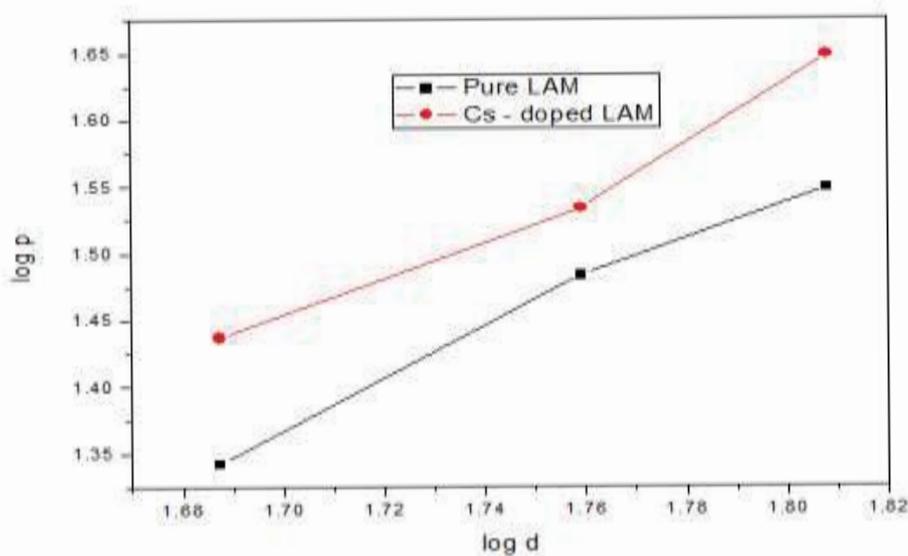


Figure 9 log P versus log d for pure and Cs - doped LAM crystals

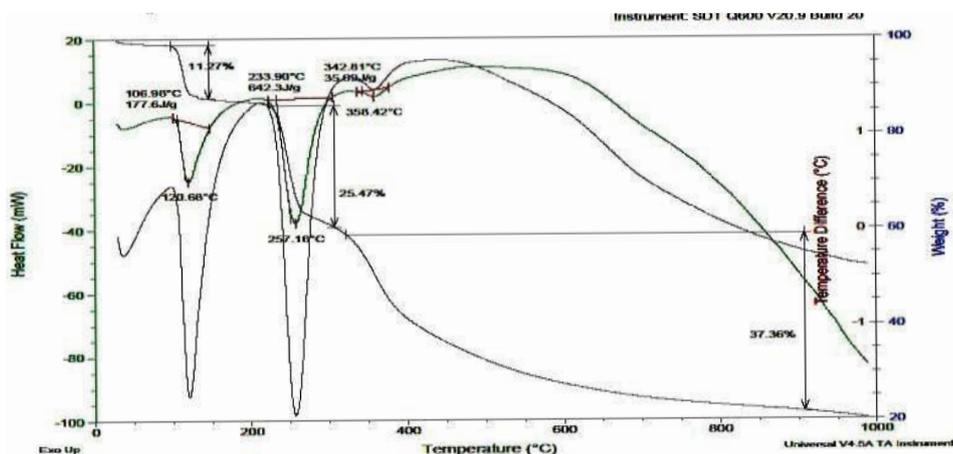


Figure 10 TGA/DTA and DSC curve of pure LAM crystal.

peaks of doped LAM crystal are slightly lower in value and shifted accordingly. This supports the fact of incorporation of Cs ion in the host crystal [14]. There is a reduction in the decomposition temperature of the doped crystal which is attributed to the decreased lattice energy caused by the addition of metal ion [15].

Etching analysis

Etching is a technique used to reveal the defects in crystals like dislocations, twin boundaries and point defects etc. Normally when the crystal is dissolved in the solvent, well defined etch pits are formed. The formation of the etch pit is assumed to be the reverse of growth process. The etching studies were carried out on the grown crystals of pure and doped LAM crystals using polarized High resolution optical microscope. The surface of the crystal was polished finely before the etching process. The photographs were taken with an etching time of 10 seconds for pure and 20 seconds for Cs doped LAM crystals the etch

patterns are shown in **Figure 12 (a) and (b)**. The etching shows predominant straight striations on the grown crystal. The size of the pit increases with the increase of etching time. The pit pattern remains the same. The observed etch pits are due to the layered growth of the crystal. This shows how the crystal would have been formed from the solution [16].

Conclusions

The single crystals of pure and Cs - doped L - Asparagine monohydrate single crystals were grown from aqueous solution by slow evaporation technique at room temperature. The grown crystals are transparent and have well defined external appearance. Single crystal X - ray diffraction studies confirm that both pure and Cs - doped LAM crystals crystallize in orthorhombic crystal system. The UV cut - off wavelength of pure LAM and Cs - doped LAM is observed at 196 nm and 221 nm respectively. The FTIR spectrum confirms that the presence of functional groups

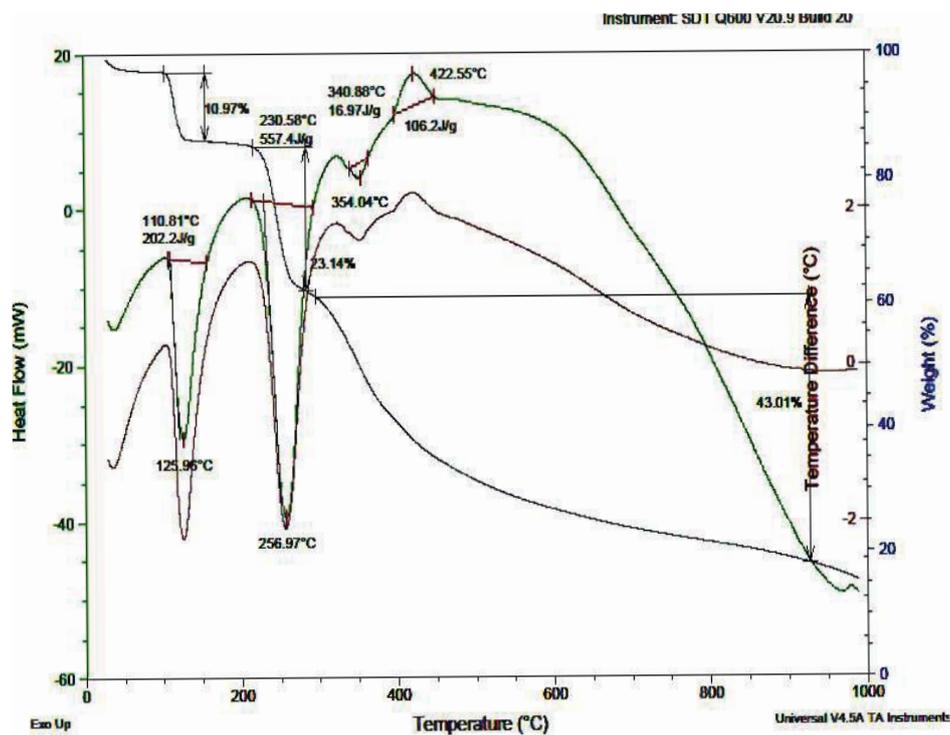


Figure 11 TGA/DTA and DSC curve of Cs - doped LAM crystal

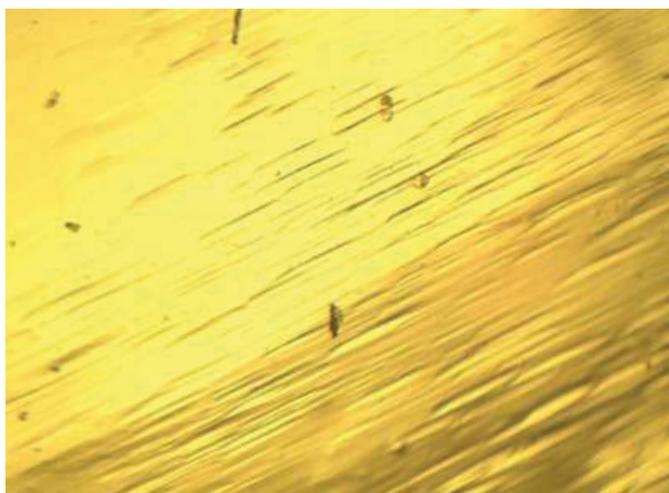


Figure 12a Etch pattern 10 Seconds for pure LAM crystals.



Figure 12b Etch pattern 20 Seconds for Cs - doped LAM crystals.

of the grown single crystals. The incorporation of Cs metal ion in the LAM crystal is confirmed by EDAX spectral analysis. The dielectric studies reveals that the value of dielectric constant and dielectric loss of the crystal is low at high frequency region. The

microhardness study indicate that the hard nature of the crystals. It is interesting to note that the incorporation of dopant have slightly improved the hardness of the parent. Etch patterns of grown Cs - doped LAM crystal shows the crystalline perfection.

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