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Effect of potassium iodide on the growth and characterization of L-asparagine monohydrate single crystals

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ABSTRACT

Single crystals of pure and KI doped L – Asparagine monohydrate (LAM) were grown by slow evaporation method at room temperature. Transparent, bulk single crystals of size 10 × 3 × 3 mm^3 were harvested in ten days. The lattice parameters were calculated by single crystal X – ray diffraction analysis. The effect of KI doping on the growth, optical and mechanical properties have been investigated. The presence of various functional groups has been identified by FTIR spectral analysis. UV – Vis – NIR spectrum was recorded to study the optical transmittance and absorbance of grown crystal. The mechanical strength of the grown crystal was estimated from Vickers microhardness test. The dielectric constant and dielectric loss measurements were carried out on the grown crystal for various temperatures. Chemical etching study was carried out using optical microscopy to study the dislocation, surface defects and morphology.

Keywords: Crystal growth, XRD, UV – Vis - NIR Spectrum, Dielectric study.

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 sufficient large NLO coefficient, transparent in UV region and high laser damage threshold power easily grow with large dimensions (1, 2). Amino acid families of crystals are under extensive investigations in recent times owing to their favorable nonlinear optical properties (3) L-asparagine monohydrate (LAM) single crystal have orthorhombic structure (4) and belong to space group $P2_12_12_1$ with four molecules per unit cell and lattice parameters: *a* = 5.593 Å, *b* = 9.827Å, *c* = 11.808 Å. The molecule is in the zwitterions form and is linked together by seven distinct hydrogen bonds forming a three dimensional network. It is an interesting material to investigate as it crystallizes in structures exhibiting a complex network of hydrogen bonds among asparagines and water molecules (1). Based on this, asparagine complexes such as L-asparagine-L-tartaric acid (LALT) (5) and L-asparagine cadmium chloride monohydrate (6) 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. (7-8). In this perspective the present work involves the growth of single crystals of pure and KI doped LAM by solution growth technique. Single crystal X-ray diffraction study was carried out to confirm the cell parameters. The functional groups present in the crystals were confirmed by FTIR studies. The optical, dielectric, microhardness and etching studies of both pure and doped LAM crystals were carried out.

MATERIALS AND METHODS

Crystal Growth

Analar grade L – Asparagine monohydrate and Potassium Iodide salts were used to grow the pure and doped LAM single crystals. Saturated solution of L – Asparagine monohydrate was prepared at room temperature. The solution was continuously stirred for about three hours using the magnetic stirrer and this solution was filtered using whatman filter paper. The filtered solution was kept in dust free atmosphere to allow evaporation. The good quality single crystals of size 17 × 12 × 3 mm^3 of pure LAM were harvested after the growth period of 11 days is shown in Fig.1. Saturated solution of 1 mole % of KI doped LAM was papered. Slow evaporation of the solution yielded single crystals of size 10 × 4 × 4 mm^3. The crystals harvested after the growth period of seven days is shown Fig.2.

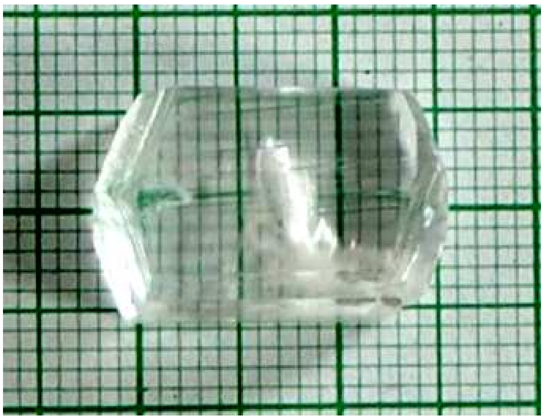

Figure 1. As grown Pure LAM

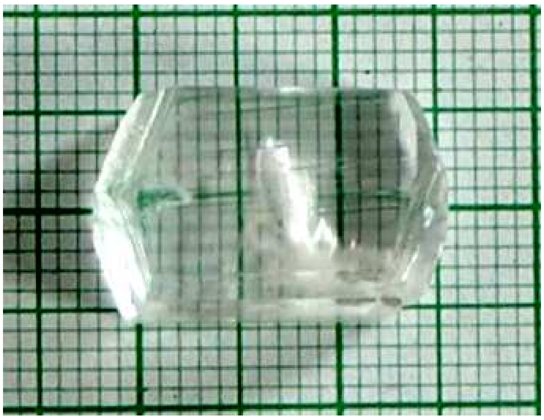

Figure 2. KI - doped LAM crystals

RESULT 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 CuKα radiation source (λ = 1.5404Å). The single crystal XRD data shows that both pure and KI - doped LAM crystals belongs to orthorhombic crystallographic system with non- centrosymmetric space group $P2_12_12_1$. The lattice parameters of LAM crystals are in good agreement with the reported values (4). The observed lattice parameter values of the pure and KI – 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 KI – doped LAM crystal in comparison with the pure LAM crystal.

Table 1: Single crystal X – ray diffraction data of pure and KI – doped LAM crystals

Cell Parameters	Pure LAM	KI doped LAM
a	5.593 (Å)	5. 604 (Å)
b	9.827 (Å)	9.841(Å)
c	11.808 Å)	11. 8792 (Å)
α	90˚	90˚
β	90˚	90˚
γ	90˚	90˚
V	648.996 $Å^3$	654.05 $Å^3$
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$

FT - IR analysis

The FT - IR spectrum of pure and KI - doped LAM crystals were recorded on Perkin - Elmer FTIR spectrometer using KBr pellet technique in the range of 4000 - 400 cm^{-1}. The FT-IR spectra of pure and KI - doped LAM crystals are shown in Figure 3 respectively. A close observation of FT-IR spectra of pure and doped specimens reveal that doping generally results in small shifts in some of the characteristic vibrational frequencies. It could be due to lattice strain developed as a result of doping. 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 stretching vibration. The appearance of the broad band at 2946 and 3110 cm^{-1} is due to the NH_3 asymmetric and symmetric stretching vibration respectively. The N – H symmetric stretching vibration is observed at 2745 cm^{-1}. The band at 2000 cm^{-1} is attributed to N - H stretching vibration (9). The peaks occur at 1769 cm^{-1} is due to symmetric stretching vibrations of C = O. Other characteristic vibrations establishing the identity of the functional groups present in the compounds are represented in Table.2. Although the spectrum of KI - 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 KI ions in the lattice of LAM.

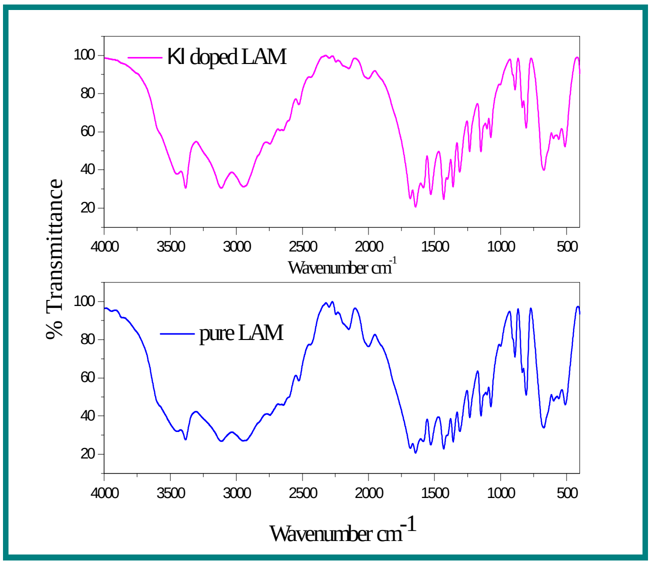

Figure 3. FTIR spectrum of pure LAM and KI doped LAM crystals

Table 2: FTIR Spectral assignments of pure and KI - doped LAM crystals

Pure LAM (cm^{-1})	**KI-doped LAM (cm^{-1})**	**Band assignments**
3781	3781	O–H stretching vibration
3382	3383	NH_2 stretching
3110	3113	NH_3^+ stretching
2948	2946	NH_3^+ stretching
2745	2755	NH symmetric stretching
2148	2149	N - H stretching
2000	2001	N - H stretching
1769	1758	C = O stretching
1358	1359	CH bending
1232	1234	NH_2 rocking
1148	1130	NH_3^+ rocking
836	835	C - C stretching

UV – Vis – NIR Spectral studies

Pure and KI – doped LAM single crystal of thickness 2 mm was used to record the UV – Vis – NIR transmittance Spectrum in the wavelength range 200 - 1100 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 and orbital from the ground state to a higher energy state. Figure 4 shows the transmittance spectrum of pure and KI - doped LAM single crystals. The lower cut-off wavelength is found to be at 196 nm and 200 nm for pure and KI - doped LAM respectively. It is clear that LAM crystal has good optical transparency 95% in the complete UV - visible region. Where as the percentage of optical transmittance decreases to 45% for KI - doped LAM.

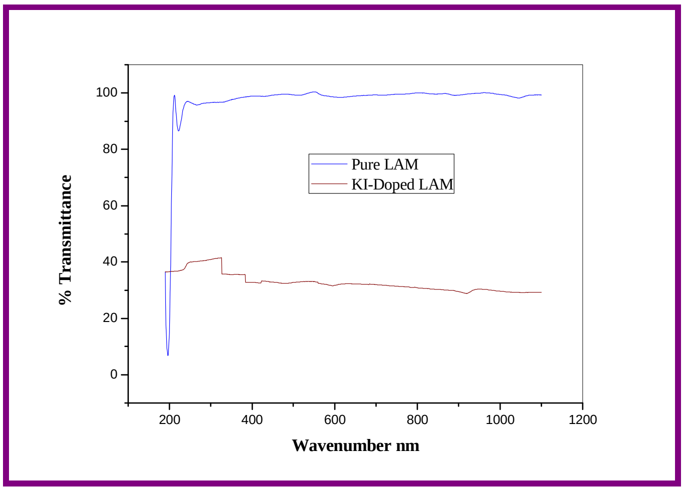

Figure 4. UV – Vis - NIR transmittance spectrum of a pure and KI - doped LAM crystals

Dielectric studies

The dielectric study of pure and KI – doped LAM single crystals were carried out using the instrument HIOKI 3532 - 50 LCR HITESTER. A sample of dimension 4 × 2 × 2 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. Fig.5 Shows the variation of the dielectric constant (ε_r) with applied frequency. The dielectric constant is calculated using the formula $\varepsilon_r = Ct/\varepsilon_o A$ where C is capacitance (Farads), t the thickness (m), A the area (m^2), ε_o is the absolute permittivity in the free space. 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 (10). Similarly, the variation of dielectric loss with frequency is shown in Fig.5. In the case of KI 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 KI of metal ion dopant.

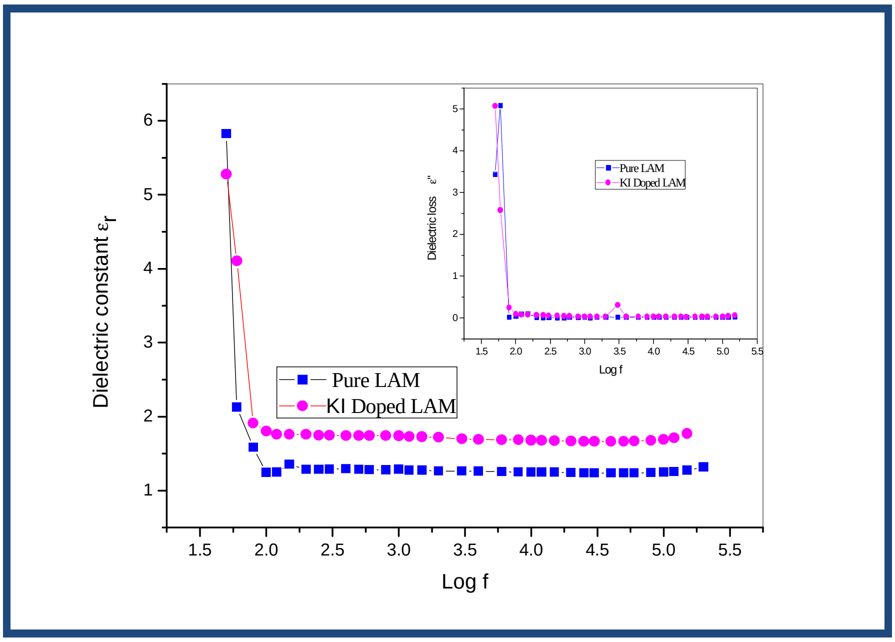

Figure 5. Dielectric constant & Dielectric loss of a pure and KI – doped LAM crystals

Vicker's Microhardness Studies

Mechanical strength is the 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 KI – doped LAM crystal using SHIMADZU HMV - 2000 microhardness tester. The static indentation were made at room temperature with a constant indentation time 3s. The diagonal impressions of the indentation marks made on the surface by varying load from 25g to 100g 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 KI - doped LAM crystals were calculated. The hardness value was calculated using the following expression:

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

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 (Hv) values increases with load for both pure and KI doped L-Asparagine monohydrate increases and reaches a saturation values at higher loads. From the results, it is observed that the value of hardness of the pure LAM crystal is lower than the hardness value of KI - 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 KI – doped LAM is shown in Fig. 6.

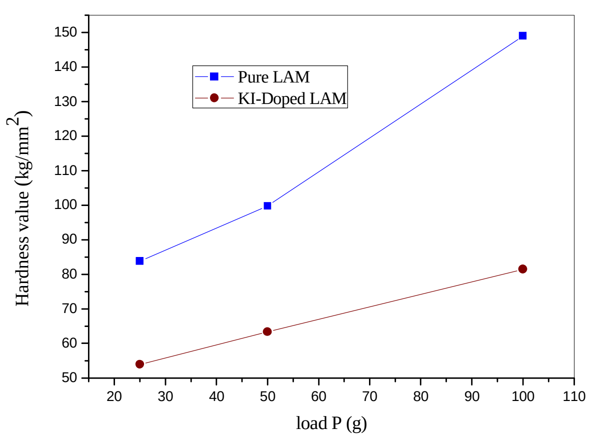

FIG. 6. Microhardness values vs. load for KI crystal

ETCHING ANALYSIS

The chemical etching studies were carried out on the grown crystals of pure LAM and KI – doped LAM using polarized High resolution optical microscope to study the symmetry of the crystal face from the shape of etch pits and distribution of structural defect in the grown crystals. The surface of the crystal was polished finely before the etching process. The crystal was dipped for 10s in double distilled water as etchant for etching. The crystal was immediately dried using tissue paper. The etch patterns' recorded for pure and KI doped LAM single crystal using polarized optical microscope in the transmittance mode are presented in figure 7(a) and 7(b) respectively. Cluster of narrowly spaced individual lines called ship bands are observed in both pure and KI doped LAM crystals. The ends of the ship bands shows the phenomenon of fragmentation.

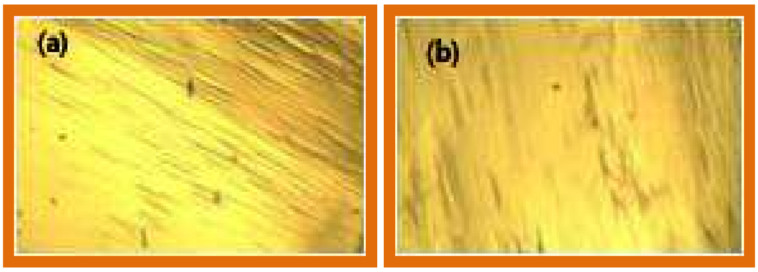

Figure 7. (a) Etch pattern of pure LAM crystal 10 seconds (b) KI doped LAM crystal 10 seconds

CONCLUSION

The single crystals of pure and KI 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 KI doped LAM crystals crystallize in orthorhombic crystal system. The UV cut - off wavelength of pure LAM and KI doped LAM is observed at 196 nm and 200 nm respectively. FTIR spectrum confirms that the presence of functional groups of the grown single crystals. The incorporation of KI 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 decreased the hardness of the parent. Etch patterns of grown KI doped LAM crystal shows the crystalline perfection.

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