

Figure 4: EDAX Spectra of pure and  $\text{Ag}^+$ -doped LAM crystals

### 3.5 UV – Vis – Nir Spectral Studies

UV – Vis – NIR transmittance Spectrum of pure and  $\text{Ag}$  – doped LAM single crystal of thickness 2 mm was used to record the spectrum in the wavelength range 200 - 1100 nm using Lambda 35 UV – Vis – NIR spectrophotometer. A nonlinear optical material can be used for practical application only if it has a wide transparency window. Fig.5(a) shows the transmittance spectrum of pure and  $\text{Ag}^+$ -doped LAM single crystals. The lower cut-off wavelength occurs at 196 nm and 194 nm for pure and  $\text{Ag}^+$ -doped LAM respectively. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample.

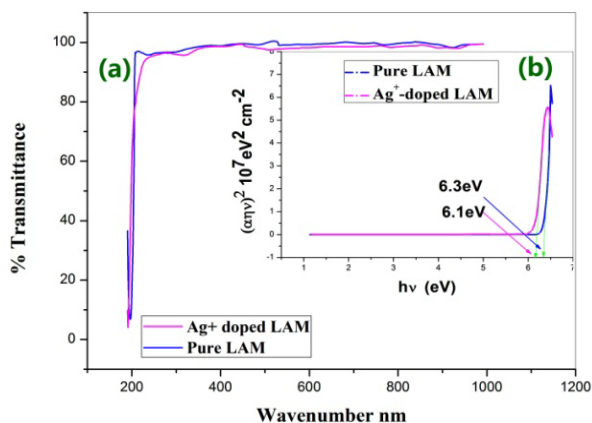


Figure 5: (a) UV – Vis - NIR transmittance spectrum and (b) Plot of  $(\alpha hv)^2$  versus  $h\nu$  of pure and  $\text{Ag}^+$  - doped LAM crystals.

The optical absorption coefficient ( $\alpha$ ) was calculated from the transmittance spectrum using the following relation,  $\alpha = 1/t \log(1/T)$  where,  $T$  is the transmittance and  $t$  is the thickness of the crystal. The direct optical band determined using the relation  $\alpha = A(h\nu - E_g)^{1/2}/(h\nu)$  where,  $E_g$  is optical band gap energy of the crystal and  $A$  is a constant. The plot of  $(\alpha hv)^2$  versus  $h\nu$  is shown in Figure 5(b).  $E_g$  is evaluated by the extrapolation of the linear part of the graph. The calculated band gap energy is found to be 6.3 eV for pure LAM and  $\text{Ag}^+$ -doped LAM is 6.1 eV.

### 3.6 Dielectric Studies

The dielectric study of pure and  $\text{Ag}^+$ -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. The dielectric constant was calculated using the formula  $\epsilon_r = (Ct)/(\epsilon_0 A)$ , where  $C$  is capacitance (Farads),  $t$  the thickness (m),  $A$  the area ( $\text{m}^2$ ),  $\epsilon_0$  is the absolute permittivity in the free space. Fig.7 Shows the variation of the dielectric constant ( $\epsilon_r$ ) with applied frequency. The value of dielectric constant is high in the lower frequency region and then it decreases with increase of frequency.

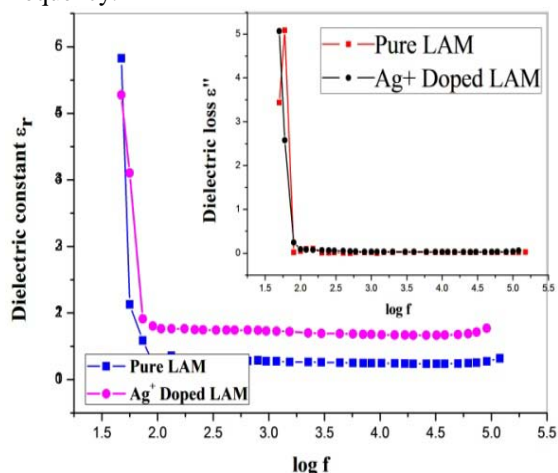
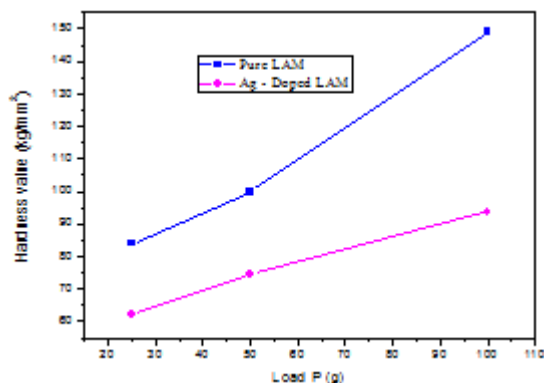


Figure 7: Dielectric constant & Dielectric loss of a pure and  $\text{Ag}^+$ -doped LAM crystals.

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 [9]. Similarly, the dielectric loss was calculated using the relation  $\epsilon'' = \epsilon_r \tan \delta$ . The variation of dielectric loss with frequency is shown in Fig. 7. In the case of  $\text{Ag}^+$ -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  $\text{Ag}^+$  metal ion dopant.

### 3.7 Vicker's Microhardness Studies

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  $\text{Ag}^+$ -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. The Vicker's hardness ( $H_v$ ) numbers at different loads were calculated using the following relation,  $H_v = 1.8544/d^2(\text{kg}/\text{mm}^2)$  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.

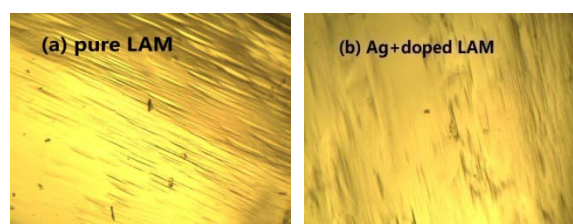


**Figure 9:** Microhardness behaviour of pure and Ag<sup>+</sup>-doped LAM crystals.

The value of hardness increases with increase in applied load and above 100 g cracks were developed around the indentation mark for pure and doped LAM due to the release of internal stress generated locally by indentation. From the results, it is observed that the value of hardness of the pure LAM crystal is higher than the hardness value of Ag<sup>+</sup>-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 is shown in Fig. 9.

### 3.8 Etching Analysis

The Chemical Etching studies were carried out on the grown crystals of pure LAM and Ag<sup>+</sup>-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 10s in water etchant for etching. The etch patterns recorded using motic camera are presented in the Figure 11(a) and (b). The shape of the etch pits may be changed by varying the amount of the solvent. The etch patterns obtained also depend upon the nature of the etchant.



**Figure 11:** Etch patterns of (a) pure LAM and (b) Ag<sup>+</sup>-doped LAM crystals for.

## 4. CONCLUSION

The single crystals of pure and Ag<sup>+</sup> doped L - Asparagine monohydrate single crystals were grown from aqueous solution by slow evaporation technique at room temperature. Single crystal X - ray diffraction studies confirm that both pure and Ag<sup>+</sup>-doped LAM crystals crystallize in orthorhombic crystal system. The UV cut - off wavelength of pure LAM and Ag<sup>+</sup>-doped LAM is observed at 196 nm and 194 nm respectively. The FTIR spectrum confirms the presence of functional groups of the grown single crystals.

The incorporation of Ag<sup>+</sup> 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 value of microhardness increases with the increase of applied load for both pure and Ag<sup>+</sup> doped LAM single crystals. It is interesting to note that the incorporation of dopant have slightly decreased the hardness of the parent. Etch patterns of grown Ag<sup>+</sup>-doped LAM crystal shows the crystalline perfection.

## Reference

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