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Effect of Cu2+ ions on the Linear optical properties of Undoped Lithium sulphate Monohydrate

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Abstract: *Undoped and copper doped Lithium sulphate monohydrate(LSMH) single crystals have been grown by slow evaporation of an aqueous solution of deionized water at room temperature. The monoclinic structure of the grown crystals is confirmed by powder X – ray diffraction analysis. The presence of functional group vibrations in the grown crystals are identified through FTIR analysis. Tauc plot of the grown crystals were obtained from UV – Vis spectral analysis to test the insulating behavior of the crystals. Linear optical parameters such as absorption coefficient, extinction coefficient, reflectance, refractive index, susceptibility, real and imaginary part of dielectric constant, electronic polarizablity, optical and electrical conductivity of the grown crystals were calculated.*
Keyword: *Inorganic crystals, NLO crystals, Optical constants, Slow evaporation, UV studies.*

I. Introduction

Piezoelectric, Pyroelectric and NLO materials find wide applications in the field of Optoelectronic technology. Inorganic crystals have sufficient strength, high physico-chemical stability and better mechanical and thermal properties. Recently it is confirmed that the effect of dopants have made remarkable changes in the properties of Inorganic crystals[1-3].. The properties of the materials such as transparency, reflectance, refractive index, optical conductivity , electrical conductivity, electrical susceptibility, dielectric constant, Meyer's number, stiffness constant, yield strength, fracture toughness and Brittle index is varied by adding dopants to the undoped inorganic crystals. Effect of Cu2+ ions on the structural and optical properties of Undoped Lithium sulphate Monohydrate is discussed in this paper.

II. Experimental Procedure

Single crystals of undoped and copper doped LSMH are obtained by slow evaporation technique. Aqueous solution of LSMH and LSMH containing 0.5% of copper sulphate pentahydrate were prepared for growing undoped and copper doped LSMH crystals. The solutions were stirred with a magnetic stirrer well to attain homogeneity. The saturated solutions were filtered using filter paper. After filtration the beakers containing the saturated solutions were covered with a perforated sheet for controlled evaporation. They were allowed to undergo slow evaporation which gradually led to supersaturated condition for nucleation resulting in the formation of transparent tiny crystals. After a period of 30 days good quality crystals of undoped LSMH and copper doped LSMH were harvested. The photograph of the grown crystals was shown in fig 1.

III. Result and Discussion

3.1 Powder XRD Analysis

X-ray diffraction studies were carried out for the powdered sample of Undoped and copper (Cu) doped LSMH with Cu Kα radiation of wavelength 1.5406Å.Fig 2 shows the XRD spectrum of Undoped LSMH and Cu doped LSMH. The XRD pattern of Cu doped LSMH is similar to the XRD pattern of undoped LSMH. The obtained pattern reveals that the effect of doping slightly changes the structure of the compound by having shift in their peaks and different peak intensities. By using the JCPDS software the hkl values are indexed. The crystal structure of the grown crystals is monoclinic with the space group $P2_{1.}$ The lattice parameters of the grown crystals were presented in Table 1.

3.2 FT-IR spectral Analysis

FT-IR spectra for the powdered samples of the grown crystals were recorded in order to study its nature of bonding. The recorded IR spectrum gives the details of the molecular structure of the grown crystals. IR bands are observed at the wave numbers 648.72,1072,1620 and 3450 cm^{-1}. The broad band at 3450 cm^{-1} corresponds to symmetric stretching mode of water molecules. The band at 1620 cm^{-1} is due to bending vibration of water molecules. The peak at 1072 cm^{-1} is assigned to stretching vibration of SO_4. The peak at

648.72 cm^{-1} corresponds to triply degenerate vibrations of SO_4. The above peak assignment to the particular wave number agrees very well with that already reported [4-5].

3.3 UV-Vis spectral Analysis

The recorded UV-Vis spectra of the powdered samples of the grown crystals in the wavelength range from 200-1100 nm are shown in the Fig 4 (a). A nonlinear material must have high transparency in the entire visible region. Undoped LSMH and Cu doped LSMH have high transparency in the visible region. Therefore the grown crystals satisfy the basic requirement of NLO property. The absorption coefficient is calculated using the relation (1) Where 't' is the thickness of the sample and T is the measured transmittance The absorption graph which is shown in fig 4(b) gives cutoff wavelength of the grown crystals and it is 232 nm for Undoped LSMH and 242 nm for Cu doped LSMH. This low cutoff wavelength of the grown crystals shows their suitability for optical applications [6].

Their band gap energies were calculated using the formula (2). Their band gap energies of undoped and Cu doped LSMH were 5.34 eV and 5.12 eV respectively. These values were in close agreement with the values obtained from Tauc plot. With the evidence of direct band gap, the Tauc plot is drawn between photon energy ($h\nu$) and $(\alpha h\nu)^2$ as shown in fig (4c) and the obtained band gap energies are 5.54 eV and 5.48 eV for pure and Cu doped LSMH. The band gap energies were calculated by extrapolating the linear portion of the Tauc plot to the energy axis. This larger band gap energy of the crystals [7] proves that the crystals are insulator and have wide transmission in the visible region. These properties of the crystals are used in the fabrication of many optoelectronic devices. The values of $(\alpha h\nu)^2$ is found by equation (3) Where Eg is a band gap energy and A is a constant. When an electromagnetic wave propagates through a material, there will be a loss in absorption [8]. The absorption loss is given by extinction coefficient. The relation between absorption coefficient (α) and extinction coefficient (K) is given by equation (4) Where λ is the wavelength of light. A graph is plotted between $h\nu$ and extinction coefficient (K) for pure and Cu doped LSMH in fig (4d)

The Reflectance (R) [8] is calculated using the following relation and a graph is drawn between energy $h\nu$ and Reflectance(R) of pure and Mg doped LSMH as shown in fig (4e)

The refractive index [8] in terms of reflectance (R) can be written as in equation (6) Fig (4g) shows the variation of refractive index (n) as a function of photon energy $h\nu$ for undoped and Cu doped LSMH. Fig (4d) and (4e) show that the extinction coefficient decays exponentially upto 5.1eV and 4.4 eV for undoped and Cu doped LSMH crystals respectively. The reflectance and refractive index remains constant upto 5.1eV and 4.4 eV for undoped and Cu doped LSMH crystals respectively. The extinction coefficient and reflectance increases suddenly with the photon energy beyond 4.5 eV. The grown crystals have low reflectance and low extinction coefficient values. This property of the grown crystals makes it suitable for device fabrication.

The electric susceptibility [8] of the grown crystals can be obtained using the equation (7) and it is calculated for various wavelengths and the variation with respect to photon energy is shown in fig 4(h). The optical property [8] of the material is characterized by its complex dielectric constant. The real part ($\varepsilon 1$) provides information about dispersion, while the imaginary part ($\varepsilon 2$) gives a measure of the dissipation rate of the wave in the medium and it is given by equation (8) and (9). The real and imaginary parts of the dielectric constants are calculated at various wavelengths using the following relation (10). The variation of real and imaginary part of the dielectric constant as the function of photon energy is shown in fig (4i) and (4j) respectively.

The optical and electrical conductivity [8] of the grown crystals were calculated using the equation (11) and (12). A graph is plotted for optical and electrical conductivity of the grown crystals as a function of energy and is shown in figure (4k) and (4l) respectively. Where n is the refractive index of the grown crystals and c is the velocity of the light. The electronic polarizability is calculated using the obtained real dielectric constant in the optical region by Clausius-Mosotti relation [9]. The variation of electronic polarizability with photon energy is shown in fig 4(f)

The optical constants of undoped and Cu doped LSMH crystals were calculated and the values are tabulated in Table 2 for a particular wavelength (λ=1000 nm)

IV. Equations

$\alpha = 2.303 \log(1/T)/t$ --------------------------------- -(1)

$Eg = 1240/\lambda$ eV ------------------------------------ -(2)

$(\alpha h\nu)^2 = A (h\nu - Eg)$ ----------------------------------- (3)

$K = \alpha\lambda/4\pi$ --- (4)

$R = 1 \pm (1-\exp(-\alpha t) + \exp(\alpha t))^{1/2})/(1+\exp(-\alpha t))$ (5)

$n = -(((R+1) \pm (3R^2+10R-3)^{1/2})/(2(R-1)))$ ------------ (6)

$\chi_c = (n2 - K^2 - \varepsilon_0)/4\pi$-----------------------------------(7)

$\varepsilon_{r=} (n+iK)^2$-- (8)

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$\varepsilon_r = n^2 - K^2 + i2nK$-- (9)
$\varepsilon_1 = n^2 - K^2$ and $\varepsilon_2 = 2nK$ ----------------------------- (10)
$\sigma_{opt} = \alpha nC/4\pi$ -- (11)
$\sigma_{elec} = 2\lambda\sigma_{opt}/\alpha$ --- - (12)

V. Figures and Tables

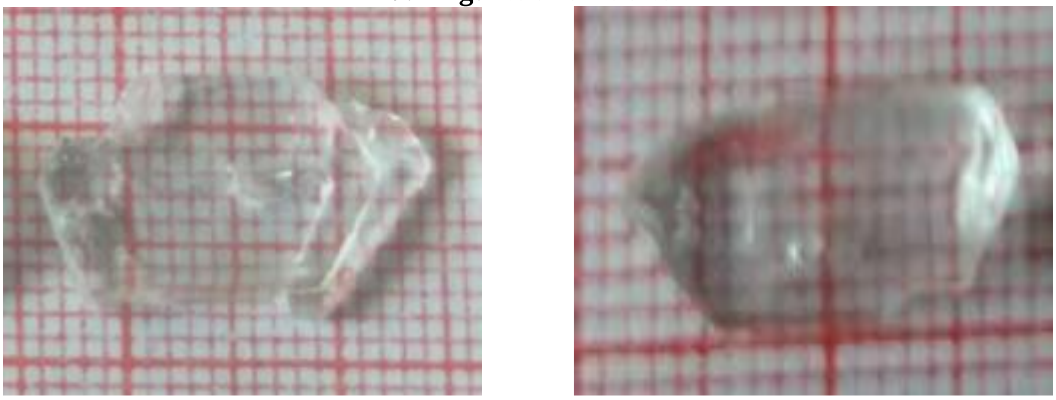

Fig1. (a) Undoped LSMH single crystal and (b) Cu doped LSMH single crystal

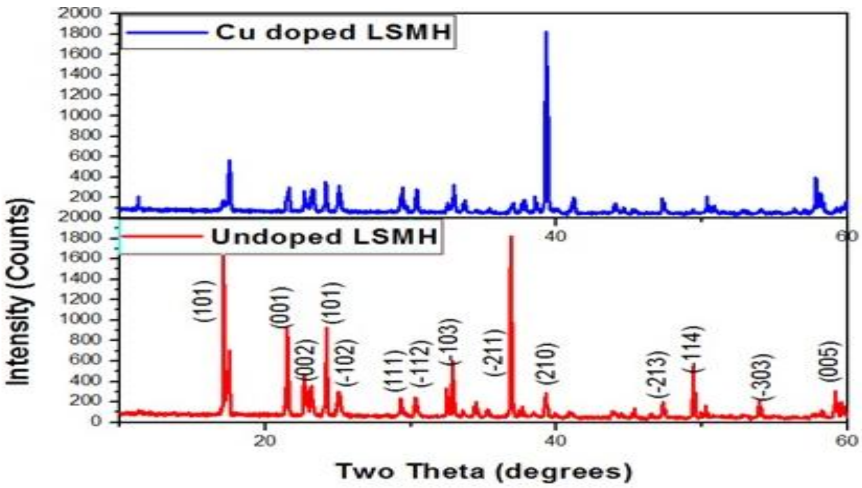

Fig 2. XRD pattern of (a) Undoped LSMH and (b) Mg doped LSMH

Table1: Comparison of Cell parameters of grown crystals with JCPDS File.

Crystal	a Å	b Å	c Å	β	V
Undoped LSMH	5.445	4.863	8.157	107.23	206.28
Cu doped LSMH	5.443	4.846	8.161	107.25	205.59
JCPDS	5.430	4.830	8.140	107.58	203.51

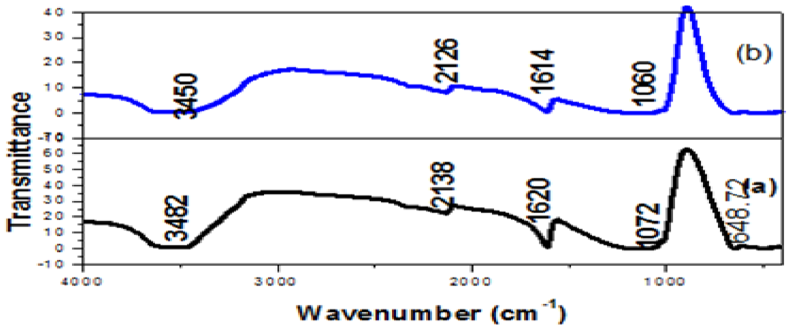

Fig 3 (a) FT-IR spectra of Undoped LSMH (b) FT-IR spectra of Cu doped LSMH

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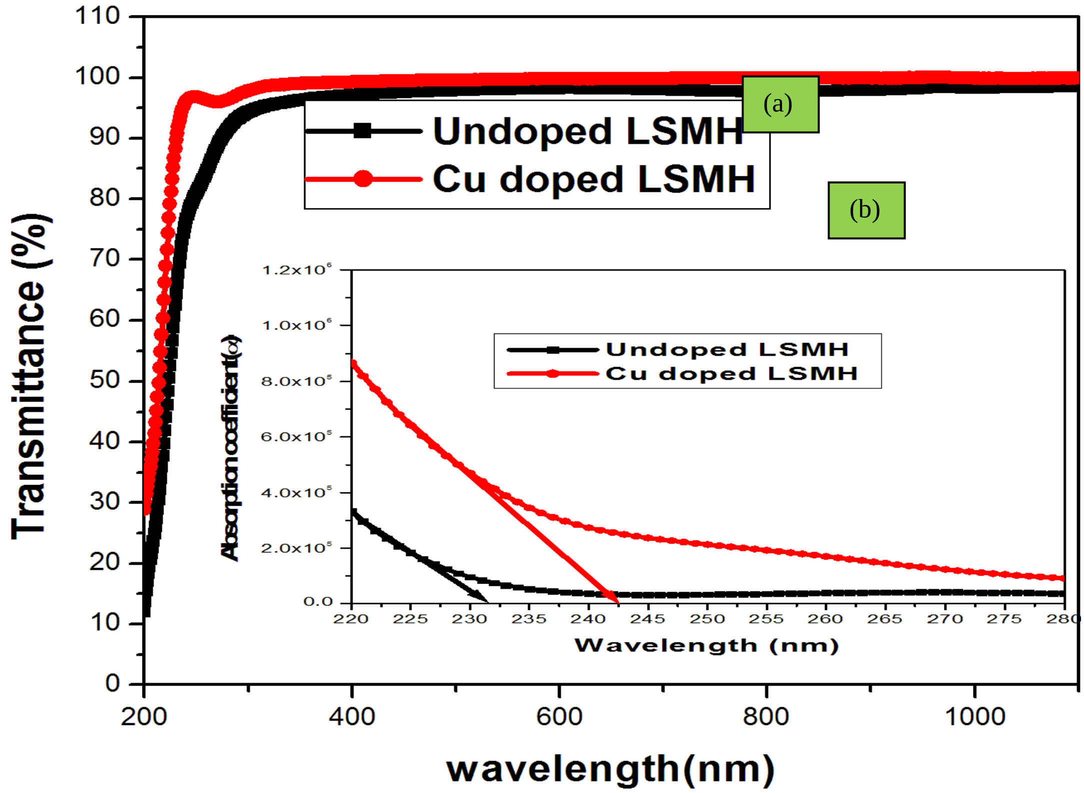

Fig 4 (a) UV-Vis spectra of undoped and Cu doped LSMH 4(b) Absorption Graph of undoped and Cu doped LSMH

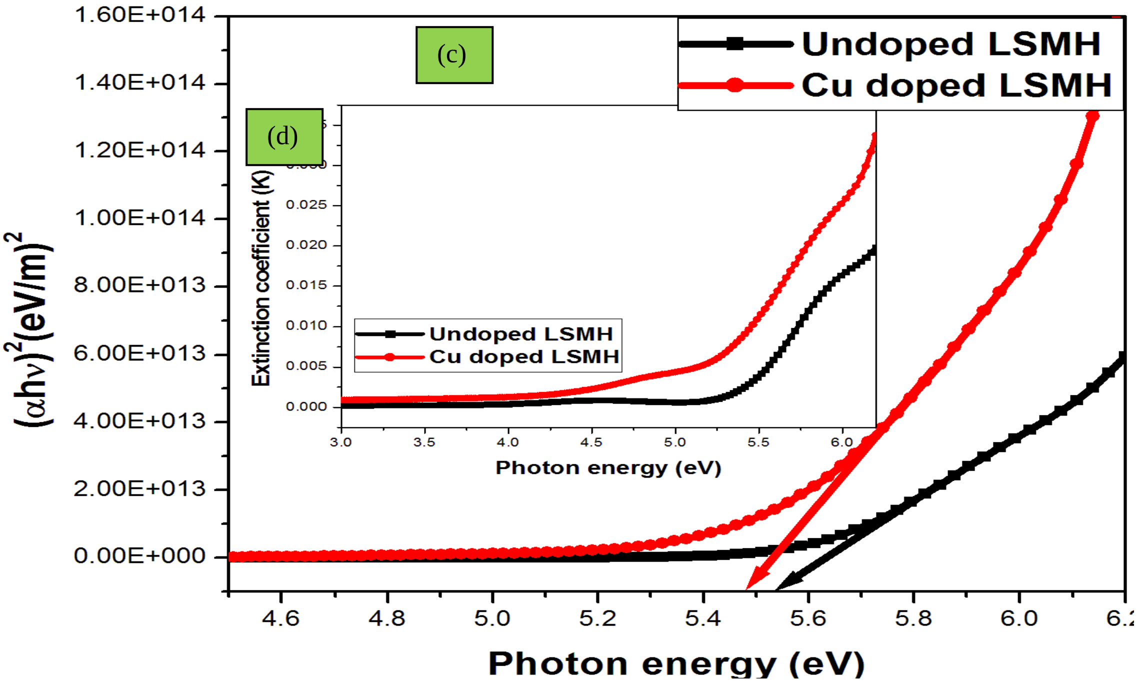

Fig 4 (c) Tauc plot of undoped and Cu doped LSMH 4(b) Extinction coefficient Graph of undoped and Cu doped LSMH

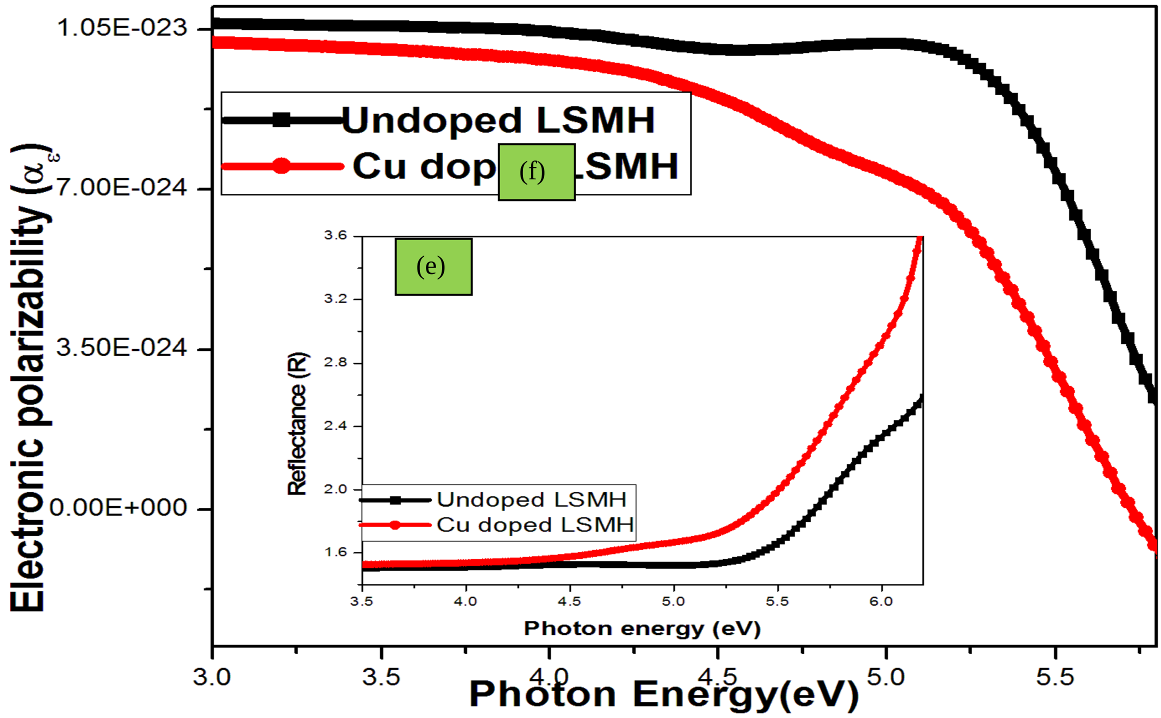

Fig 4 (e) Reflectance of undoped and Cu doped LSMH 4(f) Electronic polarizability Graph of undoped and Cu doped LSMH

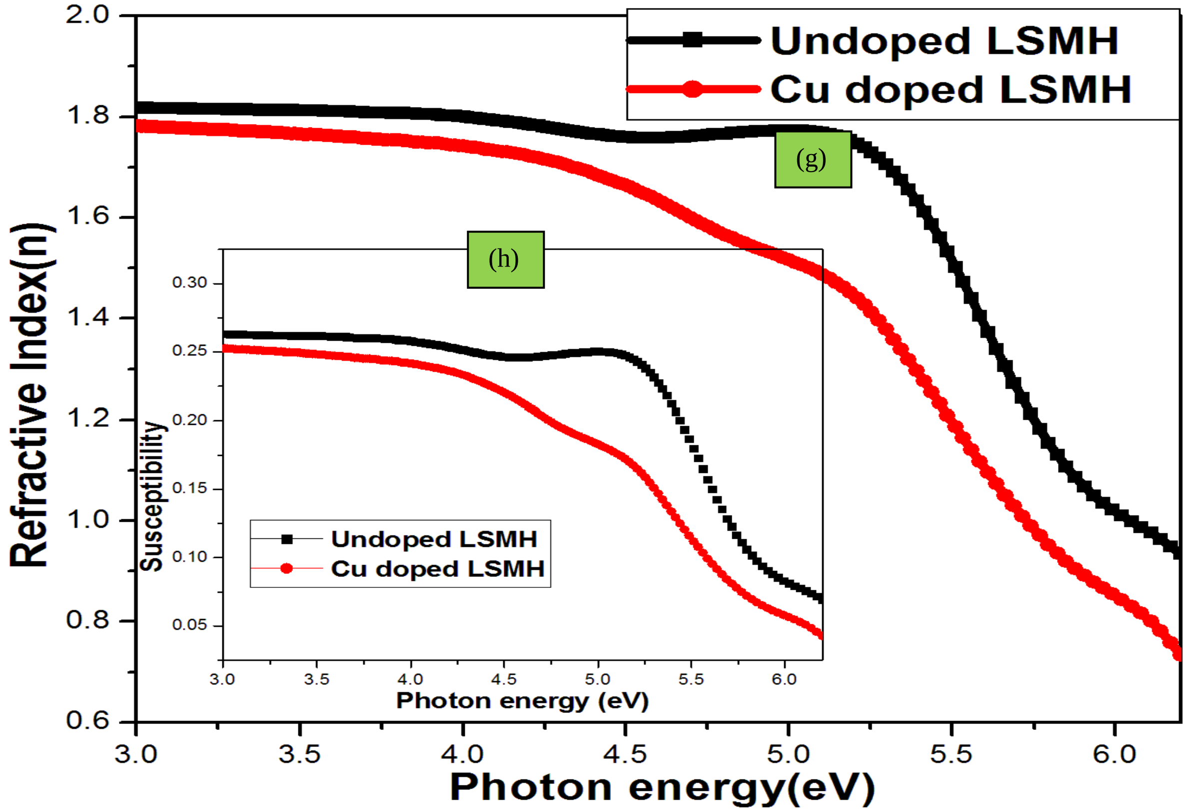

Fig 4 (g) Refractive index graphs of undoped and Cu doped LSMH 4(h) Susceptibility Graph of undoped and Cu doped LSMH

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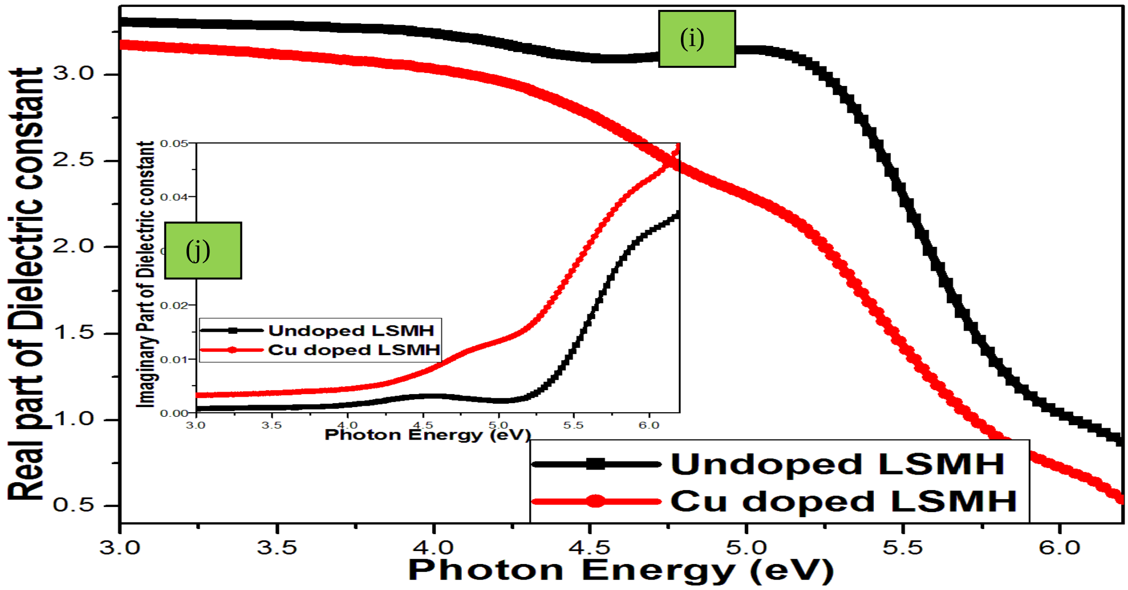

Fig 4 (i) Real Dielectric constant graph of undoped and Cu doped LSMH 4(j) Imaginary Dielectric constant Graph of undoped and Cu doped LSMH

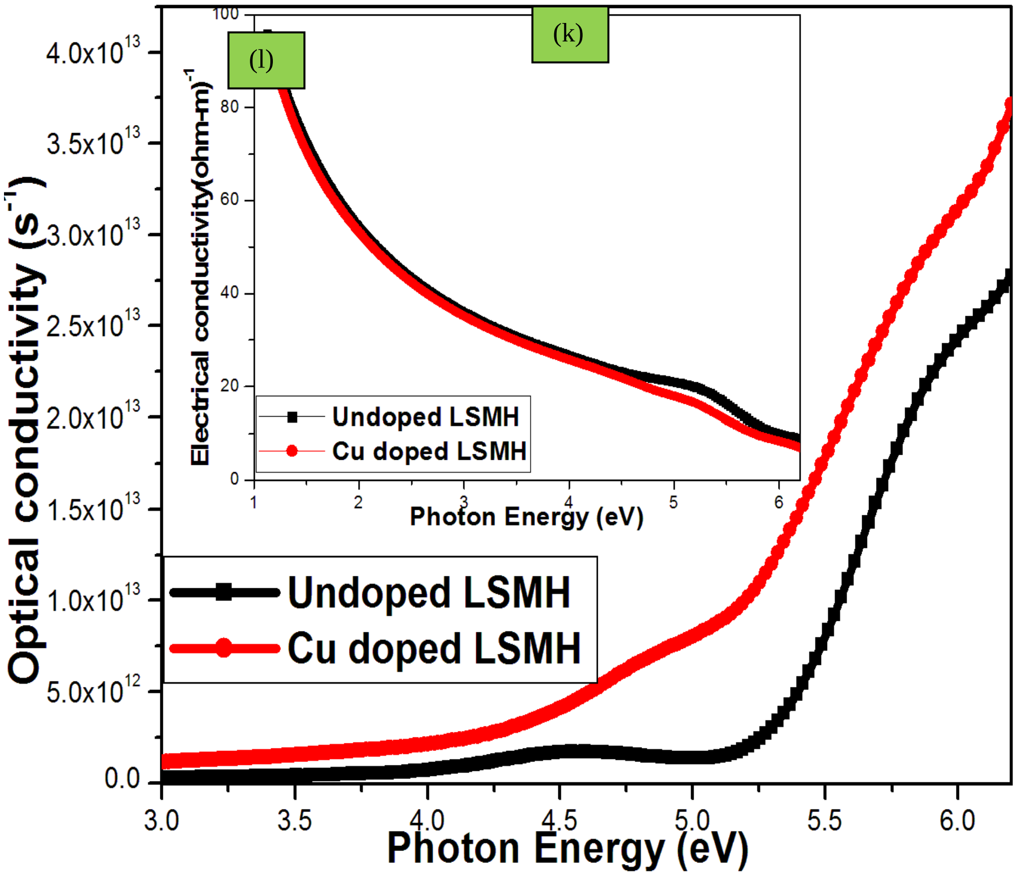

Fig 4 (k) Optical conductivity graph of undoped and Cu doped LSMH 4(l) Electrical conductivity Graph of undoped and Cu doped LSMH

Optical parameters	Pure LSMH	Mg doped LSMH
Cut off wavelength (nm)	232	242
Band Gap Energy (eV)	5.54	5.48
Extinction coefficient (K)	9.56E-05	0.001349
Reflectance (R)	1.5009007	1.51271
Refractive index (n)	1.827909	1.7995
Electrical Susceptibility (χ_e)	0.266023	0.2578
Real part of Dielectric constant	3.341253	3.2382
Imaginary part of Dielectric constant($\varepsilon2$)	0.000349	0.00485
Optical conductivity (σ_{opt})	5.24E10	7.28E11
Electrical conductivity (σ_{elec})	87.32	85.964

Table 2: Optical parameters of Undoped and Cu doped LSMH

VI. Conclusion

Pure LSMH and Mg doped LSMH crystals were grown from aqueous solution by isothermal slow evaporation technique. The powder X-ray diffraction studies confirm that the grown crystals belong to non centrosymmetric monoclinic structure with the space group $P2_1$. FTIR studies of the grown crystals confirm the presence of functional groups. Optical studies show that the grown crystals have wide transmission range. The absorption coefficient, optical band gap, extinction coefficient, reflectance, refractive index, electric susceptibility, Real and imaginary part of dielectric constant, optical and electrical conductivity have been calculated as a function of energy.

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