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Investigation on Thermal, Optical, Second Order and Third Order NLO Properties of a Nonlinear Optical Single Crystal of L-Leucinium Hydrogen Maleate (LLM)

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ABSTRACT. Organic Nonlinear optical (NLO) single crystals of L-Leucinium Hydrogen Maleate (LLM) have been grown by the slow evaporation solution growth technique at room temperature. The X-Ray diffraction studies proved that the LLM crystals belong to monoclinic system with noncentrosymmetric space group (C_2). The decomposition and thermal strength of the LLM crystals were established by TGA/DTA studies. UV-vis-NIR absorption study shows good transparency of the LLM crystal and the lower cut-off wavelength was found to be 212 nm. The optical band gap, reflectance, refractive index and electrical susceptibility were also calculated. Second order efficiency of the LLM crystal was determined using Kurtz and Perry powder technique. Third order nonlinear studies were performed using Z-Scan technique. Nonlinear parameters such as nonlinear refractive index, absorption coefficient, and nonlinear optical susceptibility were evaluated for the LLM crystal.

Introduction. Amino acid is one of the rich choice for NLO material because of its coherent blue green laser generation and frequency doubling applications. Amino acids are promising candidate for its chirality, weak vanderwaals and hydrogen bonds, the absence of strongly conjugated bonds, wide transparency, bands in the visible and UV spectral regions and zwitter ionic nature of the molecule which is important for crystal hardness [1]. In the crystal engineering and supramolecular point of views L-Leucine is an interesting molecule compared to other amino acid materials and it is an essential branched chain of alpha amino acid [2]. Many optically active aminoacids show highly efficient second harmonic generation. Maleic acid forms crystalline maleate of various organic molecules through hydrogen bonding and π - π interactions. In maleic acid the intramolecular hydrogen bond is very strong and has large π -conjugation has attracted our attention [3]. In this paper, it is reported on growth of L-Leucinium Hydrogen Maleate (LLM) single crystal followed by characterizations like XRD, TG-DTA, UV-Vis-NIR and NLO studies are discussed in detail.

Experimental procedure. A supersaturated solution of L-Leucinium Hydrogen Maleate was prepared using L-Leucine and L-Malic acid in equimolar proportion. The solution was stirred continuously using a magnetic stirrer for 5 hrs. The prepared solution was fitted and kept undisturbed for crystallisation at room temperature. Finally, after 35 days well defined single crystals were obtained by slow evaporation solution growth method. The photograph of the grown crystal of L Leucinium Hydrogen Maleate is shown in fig.1

Results and discussion

X-ray diffraction studies. The powder x-ray diffractometry (XRD) analysis was performed with $CuK\alpha$ radiation. The title compound was crystallizes in monoclinic system with noncentro symmetric

space group of C2 and with lattice parameters $a=21.132 \text{ \AA}$, $b=5.226 \text{ \AA}$, $c=31.452 \text{ \AA}$, $\beta=98.439^\circ$. These values were found to be in good agreement with the reported values [4]. The recorded powder x-ray diffraction pattern of LLM sample is shown in fig.2. The sharp peak and well defined Bragg's peaks at specific 2θ angles shows good crystallinity of the material.

Thermo gravimetric Analysis. Thermal analysis was performed on the powder sample of grown crystal to study the thermal stability and decomposition. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) curves of LLM were obtained in the range between room temperature (28°C) and 700°C at a heating rate of 10°C per min. The experiment was performed in nitrogen atmosphere. From the TGA curves (Fig.3), it is observed that there is no weight loss upto 142°C and there is a single stage of weight loss between 142°C and 574°C . One exothermic peak at 142°C and two endothermic peaks are observed at 478°C and 554°C . The DTA replicate exactly the same change at 142°C by the TG curve. From this the thermogravimetric analysis shows that the material has very good thermal stability up to 142°C [5]. The sharpness of the peak ensures the purity and good crystallinity of the material.



Fig. 1. Photograph of as grown single crystal.

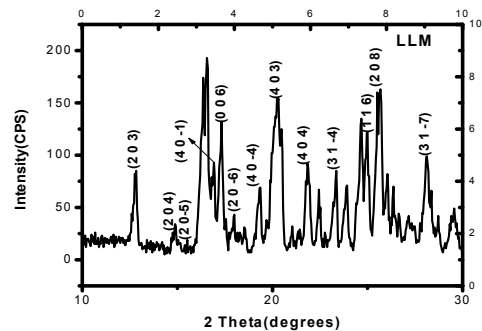


Fig. 2. Powder XRD pattern of the LLM crystals.

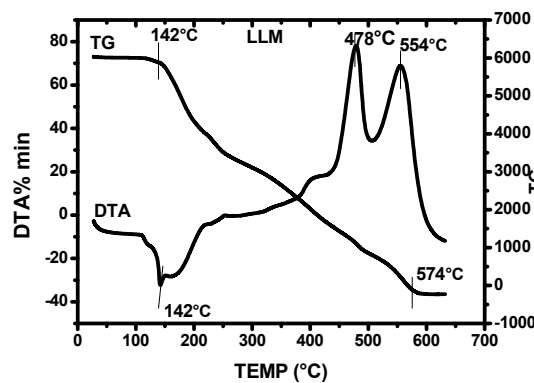


Fig. 3. TG/DTA curve for LLM crystal.

Optical Studies. UV visible spectra are recorded between 200 nm and 1100 nm and is shown in fig.4 (a). The lower cutoff wavelength was found to be around 212nm. The crystals are highly transparent in the entire visible region and it is essential quality for optically active material. Hence the crystals are useful for optoelectronic applications. The recorded optical data was used to calculated band gap of the grown crystal. The absorption coefficient (α) of the LLM crystal was calculated by the relation [6] $\alpha = \text{Absorption}/t$ where 't' is the thickness of the sample. The optical band gap has been evaluated from the relation [6]

$$(\alpha h\nu)^2 = A(E_g - h\nu) \quad (1)$$

Where A is a constant, E_g is the optical band gap, h is the Plank's constant and ν is the frequency of incident photons.

The optical band gap was evaluated by plotting $(\alpha h\nu)^2$ Vs $h\nu$ is as shown in fig.4(b). and the band gap value is found to be 5.42 eV. The extinction coefficient (k) is calculated using the following relation $K = \lambda\alpha/4\pi$. The linear refractive index to energy band gap relation is given by $E_g e^n = 36.3$. The Reflectance value is evaluated from the refractive index (n) [7] is given by

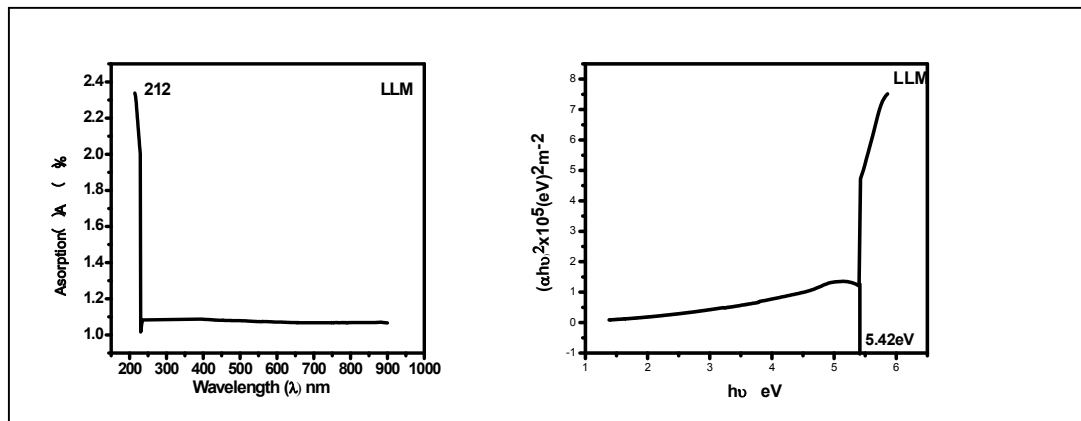


Fig. 4. (a) UV-Vis absorption spectrum of LLM. Fig. 4. (b) Plot of $(\alpha h\nu)^2$ versus $h\nu$ of LLM.

$$R = \left(\frac{n-1}{n+1}\right)^2 \quad (2)$$

The dielectric constant is given by $\epsilon_c = \epsilon_r + \epsilon_i$ where $\epsilon_r = n^2 - K^2 = n^2 - 1$ and $\epsilon_i = 2nk$, here ϵ_r and ϵ_i are real and imaginary part of the dielectric constant. The Electrical susceptibility (χ_e) was evaluated using the following relation [7] $(\chi_e) = \epsilon_r - 1 = n^2 - 1$. The extinction coefficient, linear refractive Index, Reflectance and Electrical Susceptibility of the LLM crystals are 7.8953×10^{-5} , 2.0336, 0.116 and 3.1355 respectively.

Second order NLO Properties. Kurtz and Perry technique was employed to estimate the Second harmonic generation (SHG) efficiency of the grown sample. A high intensity Nd:YAG laser ($\lambda=1064\text{nm}$) with pulse duration of 8 ns a repetition rate of 10Hz was passed through the powdered sample. The incident input energy of 0.7J/s was incident on the crystalline powder and the output signal of 2.98 mW obtained from LLM crystal which was confirmed by green emission (532nm) of the laser beam. It is observed that the SHG efficiency of the grown single crystal is 0.6 times that of the standard KDP crystal (5.03mW).

Third order NLO Properties. The single beam z scan technique is developed by Mansour Sheik Bahae [8] and it is a popular and very accurate method to determine the NLO parameters of the refractive index (n_2), nonlinear absorption coefficient (β) and nonlinear susceptibility ($\chi^{(3)}$) of the grown LLM crystal. Z scan technique play a important role in the development of photonic device for all optical signal processing. In this method, the sample was translated across the $+z$ to $-z$ axial direction along a focussed Gaussian laser beam of wavelength 632.8 nm (He-Ne laser) by using stopper motor to vary the incident intensity falling on the sample. The source light is focused by a lens of focal length 22.5 cm and intensity variation of the transmittance are measured by using digital meter through closed aperture. The recorded results of normalized transmittance measurement for the

LLM crystal of open and closed aperture curves are given in fig. 5(a) and 5(b). In closed aperture curve, the prefocal to post focal peak configuration has the positive third order nonlinear refractive index. This behaviour can be assigned to self focusing effect due to large beam divergence and reduced transmittance through the far field aperture. This is a necessary property for optical switching application.

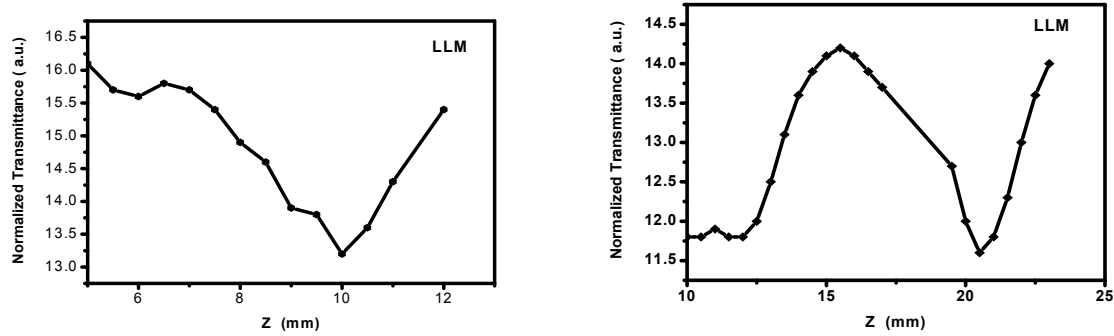


Fig. 5. (a) and (b) open and Closed aperture z-scan spectrum of LLM crystal.

From the z scan data curves the difference between the valley and peak transmittances (ΔT_{v-p}) is written in terms of the on-axis phase shift at the focus ($\Delta\Phi_0$) as [9],

$$\Delta T_{v-p} = 0.406(1-S)^{0.25}|\Delta\Phi_0| \quad (3)$$

where S is the linear aperture transmittance and is given by [9] the equation $S = 1 - \exp[-2r_a^2/\omega_a^2]$ where r_a is the radius of the aperture and ω_a is the beam radius at the aperture. The nonlinear refractive index (n_2) was calculated using closed aperture z scan data and it is given by the simple expression [9]

$$n_2 = \frac{\Delta\Phi_0}{kI_0L_{eff}} \quad (4)$$

where k is the wavenumber ($k=2\pi/\lambda$), I_0 is the intensity of the laser beam at the focus ($z=0$) and the effective thickness of the sample is calculated using formula [9]

$$L_{eff} = [1 - \exp(-\alpha L)] / \alpha \quad (5)$$

where α the linear absorption and L is the thickness of the LLM crystal. From the open aperture curve nonlinear optical absorption coefficient (β) was estimated from the relation [9]

$$B = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \quad (6)$$

where ΔT is the valley point at the open aperture z scan curve. The real and imaginary parts of the third order nonlinear optical susceptibility ($\chi^{(3)}$) were enumerated using the equation [9]

$$\text{Re}\chi^{(3)}(e.s.u.) = \frac{10^{-4}(\epsilon_0 c^2 n_0^2 n^2)}{\pi} \text{ cm}^2/\text{W} \quad (7)$$

$$\text{Im}\chi^{(3)}(e.s.u.) = \frac{10^{-2}(\epsilon_0 c^2 n_0^2 \lambda \beta)}{4\pi} \text{ cm}^2/\text{W}. \quad (8)$$

where ϵ_0 is the vacuum permittivity and c is the velocity of light in vacuum, n_0 is the refractive index of the sample, λ is the wavelength of the He-Ne laser beam.

The third order nonlinear optical susceptibility was calculated using the relation [9],

$$\chi^{(3)} = \sqrt{(\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2} \quad (9)$$

Real susceptibility is directly proportional to the Index of refraction and the imaginary susceptibility is directly proportional to the nonlinear absorption coefficient. The obtained z scan parameters of LIM crystals are shown in table 1.

Table 1. Parameters measured in z scan technique for LLM crystals.

1	Effective thickness (L_{eff})	4.834
2	Nonlinear refractive index (n_2)	$4.26479 \times 10^{-11} \text{ cm}^2/\text{W}$
3	linear absorption coefficient (α)	0.13377
4	Nonlinear absorption coefficient (β)	$2.467 \times 10^{-5} \text{ cm/W}$
5	Third order nonlinear susceptibility ($\chi^{(3)}$)	$19.18 \times 10^{-8} \text{ esu}$
6	Third order nonlinear susceptibility ($\chi^{(3)}$)	$5.58986 \times 10^{-5} \text{ esu}$
7	Third order nonlinear susceptibility ($\chi^{(3)}$)	$0.191 \times 10^{-5} \text{ esu}$

Summary. The L-Leucinium Hydrogen Maleate single crystals were grown by slow evaporation technique. From the X-ray diffraction, it was confirmed that the crystal belongs to monoclinic structure with noncentrosymmetric space group C2. Thermal studies indicate that the LLM is suitable for possible applications upto 142°C . Optical transparency of the crystals was observed by UV-Vis spectral analysis. The band gap, refractive index, reflectance, extinction coefficient and electrical susceptibility were calculated for the UV cut off wave length 212nm. The nonlinear optical property of the grown crystal was found by second order Kurtz Perry powder technique. The third order nonlinear refractive index, absorption coefficient and susceptibility were determined by the Z-scan technique. And it is suitable for NOL applications. From this investigation, it is observed that the grown crystals are useful in nonlinear optoelectronic device applications.

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