Growth and Characterization of a Novel Nonlinear Optical Single Crystal of L-Isoleucinium Hydrogen Maleate Hemihydrate

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Abstract: L– Isoleucinium Hydrogen Maleate Hemihydrate (LIM), a nonlinear optical single crystal was grown from aqueous medium by the slow evaporation method at room temperature. The powder XRD analysis reveals that the grown crystal is belongs to monoclinic system with the space group P2₁. The presence of various functional groups in the LIM is confirmed by FT-IR and FT-RAMAN spectroscopy. The second harmonic generation (SHG) efficiency measurements reveal that the LIM is suitable for nonlinear optical (NLO) applications. Thermo-gravimetric and differential thermo gravimetric analysis reveal the thermal stability of the material. The optical transparency has been studied using UV-Vis-NIR spectroscopy and the band gap energy were found out from the absorption studies. The third order nonlinear behavior has been investigated using Z-Scan technique.

Introduction. L- Isoleucine is organic amino acid which is the potential material with excellent optical, thermal and mechanical properties. It is non-polar and aliphatic in nature. L-Isoluecine have been studied and reported in the literature[1]. L-Malic acid is a organic component and it is basically dicarboxilic acid with large π-conjucation has attracted much attention [2]. In the present work L-Isoleucinium hydrogen maleate hemihydrates was grown from aqueous solution by slow evaporation method. The material was characterised by powder XRD analysis, UV-Vis-NIR spectroscopic studies, FT-IR and FT-RAMAN studies, TGA/DTA analysis and Nonlinear optical Studies were discussed.

Crystal growth. LIM crystal was synthesized from L-Isoleucine and L-Maleic acid taken in equimolar ratio. The required quantity of L-Isoleucine and L-Maleic acid was thoroughly dissolved in 2D water and stired well for about six hours using a magnetic stirrer to obtain a homogenoes mixture. Then the saturated solution of LIM was taken in a beaker and kept at room temperature for crystallisation. Finnaly a well defined single crystal was obtained after 40 days by slow evaporation method.

CHARACTERIZATION

Powder x-ray analysis. Powder x-ray diffraction technique is used to show the inner arrangements of atoms molecules in a crystalline material. The XRD study enumerates that the LIM belong to the monoclinic crystal system with space group P2₁ and the lattice parameters are a=11.745 (Å),

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b=6.1011 Å, c=19.2198 Å, α=γ=90°, β=96.7329°. Further the diffraction pattern (Fig.1) of LIM is perfectly matched with the reported literature [1,3].

Optical Analysis. Absorption spectroscopy is one of the best techniques to check the suitability of the grown crystal for optical device fabrication. The absorption spectrum of the grown LIM single crystal is as shown in fig. 2(a). The crystals are transparent in the entire tested region with lower cut off wavelength at 215 nm. The highly transparent is the essential requirement for optically active materials. The recorded optical data was used to calculate the band gap of the grown crystal. The band gap of the LIM crystal is shown in fig. 2(b) and found to be 4.75 eV. The grown LIM crystal can be a suitable candidate for optoelectronic applications because of its large band gap [4].

Fig. 1. Powder XRD pattern of the LIM crystals.

Fig. 2. (a). UV-Vis absorption spectrum of LIM.
Fig. 2. (b). plot of $(\alpha h \nu)^2$ versus $h \nu$ of LIM crystal.

**NLO Studies.** In NLO material Second hormonic generation efficiency is most important [5]. A Q-switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm and a pulse width of 9 ns with a repetition rate of 10 Hz was used. The laser incident input energy of 0.7 mJ/s was illuminate on the crystalline powder, which is filled in an air tight micro capilary tube. The emission of green radiation of wavelength 532nm from the sample confirmed the frequency doubling of LIM. The KDP was used as a reference material and the output energy was found to be 4.48 mW and 5.03mW from grown crystal and reference materials respectively. Hence, from the above discussion second hormonic generation efficincy of LIM crystal was 0.9 times that of standard KDP crystal. Thus LIM is confirmed as a suitable NLO medium for laser generation.

**Third Harmonic Generation.** Third order NLO studies of LIM crystals were performed by a versatile tool of Z scan technique. It is a accurate method to determine the nonlinear index of refraction ($n_2$), nonlinear absorption coefficient ($\beta$) and nonlinear susceptability ($\chi^{(3)}$) of the grown crystal. In this technique a He-Ne laser ($\lambda = 632.8$nm) is used as the light source and is by a lens of focal length 18.5cm. The open aperture mode helps us to calculate the nonlinear absorption coefficient and the closed aperture mode shows the information about the third order nonlinear refractive index and the open and closed aperture modes are shown in fig.4 (a) andfig.4 (b). The nonlinear refractive index ($n_2$), the nonlinear absorption coefficient ($\beta$) and the third order nonlinear optical susceptibility ($\chi^{(3)}$) are calculated and are given in table 1.

Fig. 3. (a)Closed aperture z-scan spectrum of LIM crystal.
Table 1. Parameters in Z scan experiment.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Nonlinear refractive index ($n_2$)</td>
<td>$2.458 \times 10^{-11}$ cm$^2$/W</td>
</tr>
<tr>
<td>Nonlinear absorption coefficient ($\beta$)</td>
<td>$2.438 \times 10^{-5}$ cm/W</td>
</tr>
<tr>
<td>Third order nonlinear susceptibility ($\chi^{(3)}$)</td>
<td>$5.5236 \times 10^{-5}$ esu</td>
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**Thermal Analysis.** The thermal stability of LIM was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) at a temperature range from room temperature to 650°C and the thermogram is shown in fig.4. The TGA and DTA analysis is very important to understand the thermal stability and various transaction of the sample. From TG curve, it has one stage of weight loss. The compound start to decompose at 144°C. The weight loss of approximately 82% occurs between the temperature 144°C - 570°C due to the elimination of a molecule such as CO$_2$, H and O and major weight loss due to decomposition of the crystal. The remaining weight loss occurs above 570°C and the sample is completely decomposed. DTA curve shows two endothermic peaks and three exothermic peaks at 87.6°C, 128°C, 144°C, 489.6°C and 540°C respectively. The sharp peak indicating the purity and crystallinity of the material. The endothermic peak observed at 87°C shows the weight loss is about 7% due to the liberation of water molecules present in the crystal itself. The first exothermic peak observed at 144°C. It is equal to the decomposition point of the TGA curve. The second exothermic peak observed at 489.6°C which is matched with the TGA curve. From the DTA and TGA study, it is observed that the material has water molecules in its crystal lattice and it has thermal stability till its 144°C.

**Vibrational spectral Analysis.** FTIR and FT Raman spectroscopy are very important to analysis the various functional groups in the structure of a compound present in the grown crystal and are shown in fig.5(a) and fig. 5(b). In the high energy region there is a broad band observed from 3600 cm$^{-1}$- 2400 cm$^{-1}$ is assigned for O-H stretching vibration of carboxlic group. It is also over lap with the peaks corresponding to NH assymmetric stretching vibration due to the primary amines of NH$_2$ at 3346 cm$^{-1}$. CH$_3$ assymmetric stretching vibration modes at2964 cm$^{-1}$. The peaks at 2946 cm$^{-1}$ is due to NH$_3$ assymmetric stretching vibration which is also over lap on the OH stretching vibration and the corresponding band in the Raman spectrum is observed at 2942 cm$^{-1}$. Strong band observed at 1739 cm$^{-1}$ contributed of C=O symetric vibration of –COOH group. The peak at 1578 cm$^{-1}$ is due to the NH$_3$ deformation. The bands appeared in the region 1472 cm$^{-1}$ and 1395 cm$^{-1}$ are assigned to COO$^-$ symmetric stretching vibration of –COOH group and the corresponding band is observed at 1453 cm$^{-1}$ in the Raman spectrum. The peaks at 1347 cm$^{-1}$ and 1004 cm$^{-1}$ occurs due to the CN vibration and the corresponding band is observed at 1005 cm$^{-1}$ in the Raman spectrum. The peak observed at 1308 cm$^{-1}$ is due to CH$_2$ wagging vibration and the corresponding peak is also observed at 1302 cm$^{-1}$ in the
Raman spectrum. The NH$_3^+$ rocking vibration observed at 1174 cm$^{-1}$. C-CN symmetric stretching vibration observed at 926 cm$^{-1}$. Very strong band observed at 871 cm$^{-1}$ due to the C-C stretching vibration. The COO$^-$$^1$ wagging and rocking vibrations are observed at 578 cm$^{-1}$ and 483 cm$^{-1}$ respectively and the corresponding band are observed at 540 cm$^{-1}$ and 479 cm$^{-1}$ in the Raman spectrum. The vibrational study confirms the presence of COOH and NH$_2$ group in the LIM crystal.

Fig. 4. TG/DTA curve for LIM crystal.

Fig. 5. (a) FT-IR spectrum of the grown LIM crystal, (b) FT-RAMAN of the grown LIM crystal

Summary. Single crystals of LIM were grown by slow evaporation solution growth method at room temperature. Powder x-ray diffraction analysis was carried out and the lattice parameters were calculated. The Calculated values are good in agreement with the reported values. UV-Vis-NIR study shows that the crystals are transperant in entire visible region and have minimum cut off wavelength of 215nm. Thermal analysis was carried out and it confirms the crystal is stable upto 144°C. Its Second Harmonic Generation efficiency was found to be 0.9 times that of standard KDP. The functional groups present in the LIM crystal is identified by FTIR analysis and it is confirmed by the FT-RAMAN. The nonlinear optical refractive index is ($n_2$) $2.458 \times 10^{-11}$ cm$^2$/W, nonlinear absorption coefficient ($\beta$) is $2.438 \times 10^{-5}$ cm/W and third order nonlinear optical susceptibility ($\chi^{(3)}$) of $5.5236 \times 10^{-5}$ esu are calculated by Z scan technique. Hence LIM single crystals are suitable material for nonlinear optical device fabrication.

References

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