

Fig. 2. (b). plot of $(\alpha hv)^2$ versus hv of LIM crystal.

NLO Studies. In NLO material Second harmonic 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 capillary 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 harmonic generation efficiency 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 (β) and nonlinear susceptibility ($\chi^{(3)}$) of the grown crystal. In this technique a He-Ne laser ($\lambda=632.8\text{nm}$) 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) and fig.4 (b). The nonlinear refractive index (n_2), the nonlinear absorption coefficient (β) and the third order nonlinear optical susceptibility ($\chi^{(3)}$) are calculated and are given in table 1.

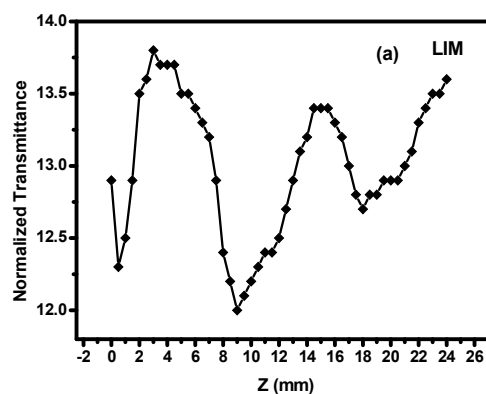


Fig. 3. (a) Closed aperture z-scan spectrum of LIM crystal.

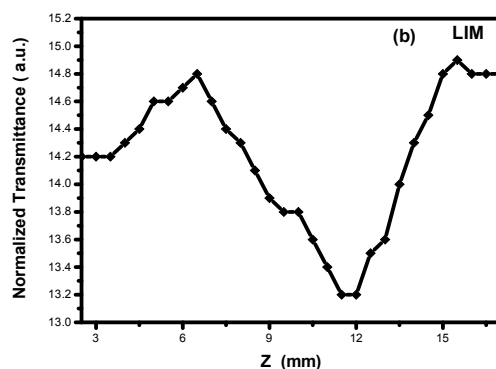


Fig. 3. (b) open aperture z-scan spectrum of LIM crystal.

Table 1. Parameters in Z scan experiment.

Nonlinear refractive index (n_2)	$2.458 \times 10^{-11} \text{ cm}^2/\text{W}$
Nonlinear absorption coefficient (β)	$2.438 \times 10^{-5} \text{ cm/W}$
Third order nonlinear susceptibility ($\chi^{(3)}$)	$5.5236 \times 10^{-5} \text{ esu}$

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 CO₂, 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 carboxylic group. It is also over lap with the peaks corresponding to NH asymmetric stretching vibration due to the primary amines of NH₂ at 3346 cm⁻¹. CH₃ asymmetric stretching vibration modes at 2964 cm⁻¹. The peaks at 2946 cm⁻¹ is due to NH₃ asymmetric 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 symmetric vibration of -COOH group. The peak at 1578 cm⁻¹ is due to the NH₃ deformation. The bands appeared in the region 1472 cm⁻¹ and 1395 cm⁻¹ are assigned to COO⁻¹ 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 CH₂ 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.

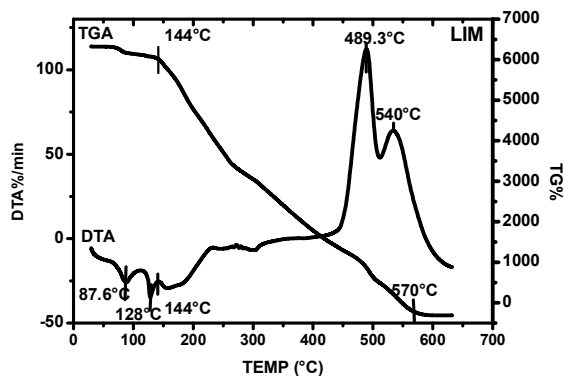


Fig. 4. TG/DTA curve for LIM crystal.

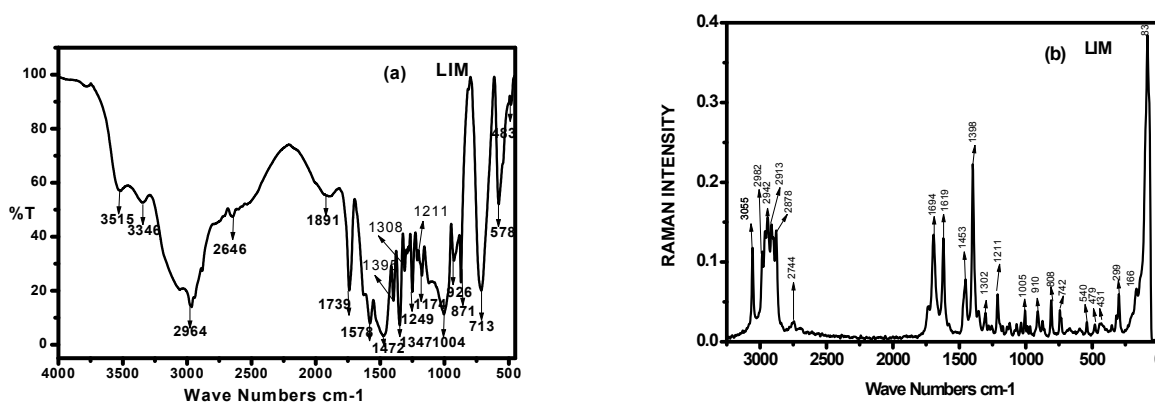


Fig. 5. (a) FT-IR spectrum of the grown LIM crystal, (b) FT-RAMAN of the grown LIM crystal

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 transparent 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) $2.458 \times 10^{-11}\text{ cm}^2/\text{W}$, nonlinear absorption coefficient (β) is $2.438 \times 10^{-5}\text{ cm}/\text{W}$ and third order nonlinear optical susceptibility $(\chi^{(3)})$ of $5.5236 \times 10^{-5}\text{ esu}$ are calculated by Z scan technique. Hence LIM single crystals are suitable material for nonlinear optical device fabrication.

References

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