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Growth and characterization of pure and doped urea L-malic acid

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ABSTRACT

Pure and Lanthanam(La^{3+}) doped Non Linear Optical single crystals of Urea L-Malic acid(ULMA) were grown successfully by slow evaporation technique. Crystalline natures of the grown crystals were confirmed by Powder XRD analysis. Doping has not altered the monoclinic structure of crystals. UV-Vis-NIR spectroscopic studies showed that, doped crystals exhibit low absorption in the visible region of the spectrum than the pure crystals. FT-IR analyses exhibit the presence of various functional groups in the grown crystal. Dielectric studies showed the low value of dielectric constant / dielectric loss at high frequency region. Second Harmonic Generating (SHG) efficiency of pure and doped crystals is found as 3.0 times and 3.96 times than KDP.

INTRODUCTION

Nonlinear optical (NLO) organic materials play an important role for optical second harmonic generation (SHG) due to their applications in the domain of optoelectronics and photonics [1]. Organic NLO materials are potential candidates for frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability etc., due to their large optical non-linearity, low cut off wavelength, short response time and high thresholds for laser power [2]. Organic single crystals are the model systems to study effects caused by ion impact, because they occupy an intermediate position between inorganic crystals and polymers. Urea L-malic acid (ULMA) is a NLO organic material which is reported to exhibit second harmonic efficiency three times that of the widely used inorganic crystal, KDP. Hence, this material is selected for detailed investigation and the results obtained are discussed. This chapter contains details of single crystal growth and characterization of pure and Lanthanum (La^{3+}) doped ULMA. In the present investigation, the grown crystals are subjected to powder XRD to estimate the crystal structure and space group. The content of the dopant was determined by ICP analysis. FT-IR, UV-Vis-NIR and dielectric studies were carried out for the grown pure and doped crystals. The SHG efficiency of the pure and doped ULMA crystals were also studied using Nd:YAG Q-switched laser. The results of these investigations are discussed in this chapter.

MATERIALS AND METHODS

Synthesis and solubility

From aqueous solution with equimolar proportion of urea and L-malic the product compound ULMA ($CO(NH_2)2C_4H_6O_5$) is formed. The growth of metal substituted crystal is achieved by using the same procedure by adding dopant of 2 mol % concentration of La^{3+} to the ULMA solution. The synthesized salt of pure and doped ULMA was utilized for the measurement of its solubility in water. The solubility of pure and doped ULMA in double distilled water was measured at six different temperatures (30, 35, 40, 45 and 50°C) using a constant temperature bath of accuracy ±0.01 °C. The amount of ULMA salt dissolved in 100 ml of water at the above

mentioned temperatures has been plotted as a function of temperature (Figure 1). From the solubility curve, it is observed that the solubility of both pure and doped samples of ULMA increases with increase in temperature. The incorporation of dopant into the parent solution has promoted the growth rate of the crystals. Bulk crystals were grown by successive recrystallisation and the crystals are found to be transparent and free from defects. Figure .2 shows the photograph of as grown pure and doped crystals in a period of 50 days.

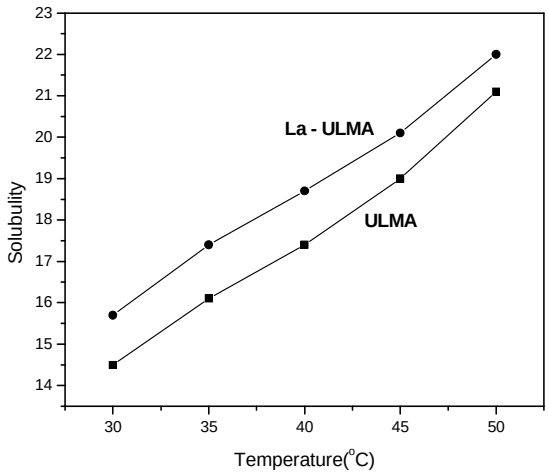


Figure 1 Solubility curves of pure and La^{3+} doped ULMA crystal

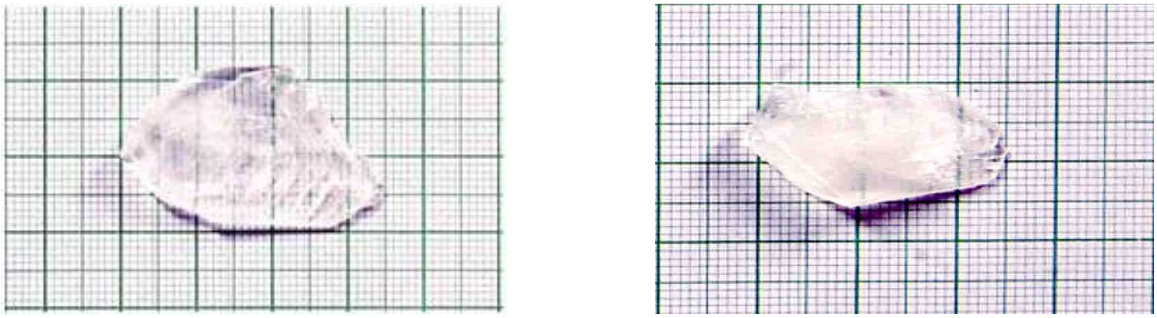


Figure 2 Photograph of as grown pure and La^{3+} doped ULMA crystal

RESULTS AND DISCUSSION

Powder XRD studies

The structural properties of single crystal of pure and doped ULMA have been studied by X-ray powder diffraction technique. Powder X-ray diffraction studies of the grown crystals were carried out, using Rich Siefert & Co X-ray diffractometer with Cu K_α (λ = 1.5406 Å) radiation. The samples were scanned for 2θ values from 10˚ to 40˚ at a rate of 2˚ /min. Figure 3 shows the Powder XRD pattern of pure and doped ULMA crystal. The diffraction patterns of the crystals were indexed by least square fit method. The lattice parameter values of pure and doped ULMA crystal were calculated and are well matched with the reported literature [3]. The lattice parameters are shown in Table 1. There are slight variations in the lattice parameters and cell volume of the pure and doped crystals. These variations are due to the incorporation of the dopant in the ULMA crystal lattice.

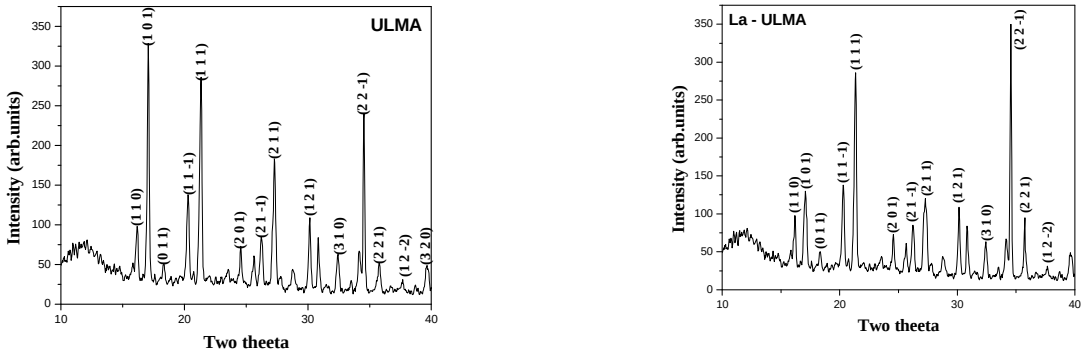


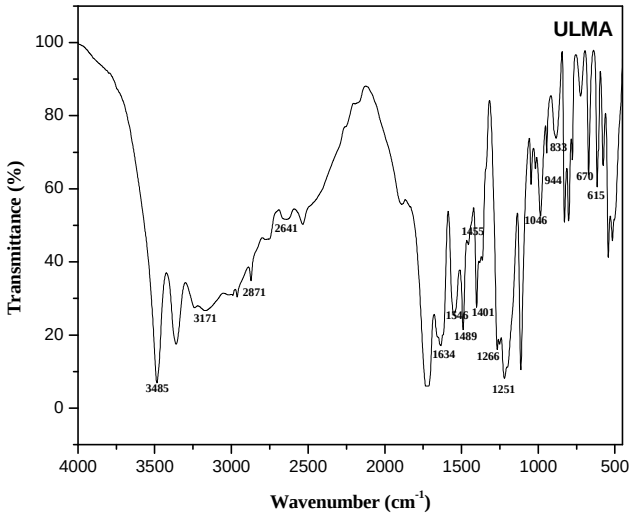
Figure.3 Powder XRD pattern of pure and La^{3+} doped ULMA crystal

Table .1 Lattice parameters for pure and La^{3+} doped ULMA crystal

Lattice parameters	Pure ULMA	La^{3+} -ULMA	ULMA de Matos Gomes et al, 2000
a (Å)	9.055	9.011	9.034
b (Å)	6.941	6.912	6.936
c (Å)	6.888	6.891	6.801
α(º)	90	90	90
β(º)	94.66	94.69	94.67
γ(º)	90	90	90
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$

Inductively coupled plasma analysis

In order to determine the weight percentage of doped ULMA crystal, 10 mg of fine powder of the crystal was dissolved in 100 ml of triple distilled water. This prepared solution was taken for the ICP analysis. The results obtained from ICP show that 1.33% of La^{3+} (133 µg/100ml) was present in the solution. It is observed that the amount of dopant incorporated into the crystal lattice is below its original concentration (2%) in the solution.



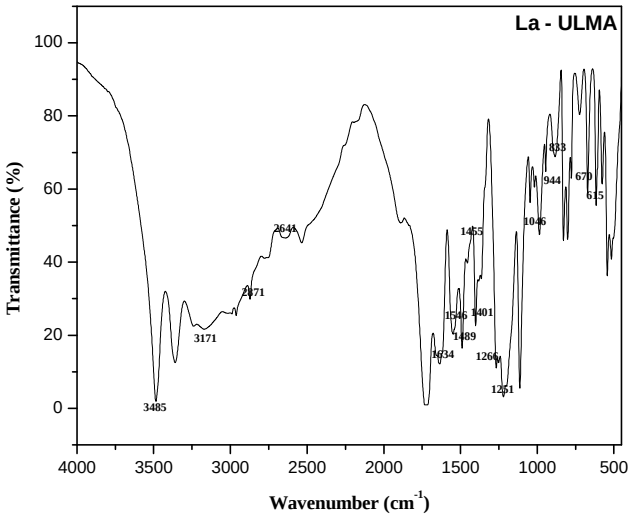


Figure 4 FT-IR spectrum of pure and La^{3+} doped ULMA crystal

FT-IR analysis

The middle infrared spectra of pure and doped ULMA are shown in Figure 3.4. Both the pure and doped compounds show similar trend. The spectra show NH-CH stretching vibration characteristics from 3500-2300 cm^{-1}. The intense peak at 1634 is due to the presence of NH_2 group. The peaks at 1455 and 1401cm^{-1} is due to COO^{-1} symmetric stretching. The peaks due to COO^{-1} vibrations are formed at 1266, 1251 and 1219cm^{-1}. The peak at 883 is due to C-C stretching. FT-IR spectral assignment of pure and doped ULMA is shown in table 2.

Table.2 FT-IR spectral assignments of ULMA

Wavenumbers (cm^{-1})		Assignments
Pure ULMA	**La^{3+}-ULMA**	
3500-2300	3500-2300	NH & ch stretching vibraton
1634	1635	Presence of NH_2 group
1546	1547	COO^- symmetric stretching
1489	1490	Symmetric NH_3 deformation
1455	1456	COO^- symmetric deformation
1401	1402	COO^- symmetric deformation
1266	1267	COO^- vibration
1251	1252	COO^- vibration
1219	1220	COO^- vibration
1046	1047	C-N stretching
944	945	CH_2 Rocking
883	884	C-C stretching
670	671	NH_2 out of plane
615	616	NH_2 wag(out of plane)

UV-Vis-NIR spectrum

Optical absorption data were taken on the polished crystal samples of about 4mm to 6mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200nm – 2000nm. The spectra (Figure.5) indicate that the pure and doped ULMA crystals have minimum absorption in the entire visible region. The cut-off wavelengths for pure and doped crystals are 265nm and 260nm respectively. Interestingly the doped crystal has reduced absorption and reduced cut-off wavelength. Moreover the La^{3+} doped crystal shows an improved transparency window. The required properties for NLO activity are minimum absorption and low cut-off wavelength. These properties are improved in the doped crystal. Both the pure and doped crystals possess good transparency for the wavelengths of sources which are used for photonic devices. The band gap of pure and doped crystals were found to be 4.916 and 4.83 eV respectively (Figure 6)

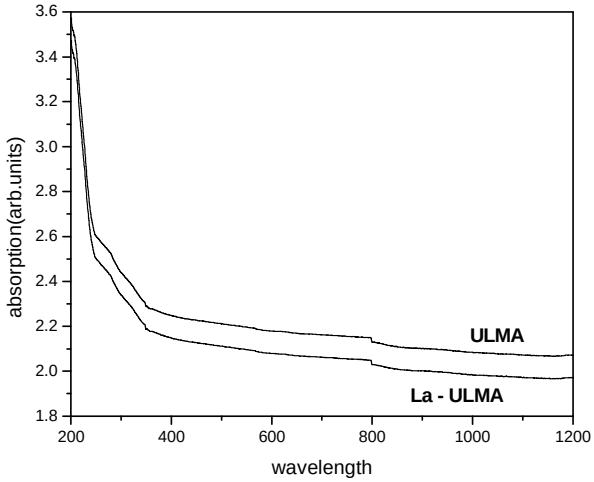


Figure 5 Absorption spectrum of pure and La^{3+} doped ULMA crystal

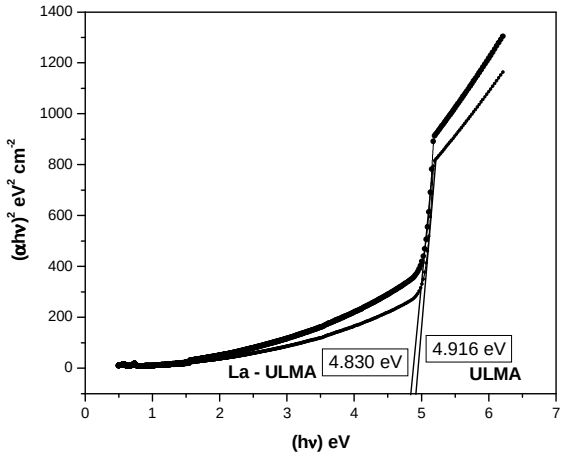


Figure 6 Band gap of pure and La^{3+} doped ULMA crystals

NLO studies

Kurtz and Perry powder [4] SHG test was carried out on pure and doped ULMA single crystals to study its NLO properties. The sample was illuminated using Q–switched, mode locked Nd:YAG laser with input pulse of 6.2 mJ. The emission of green radiation from the crystal confirmed the second harmonic signal generation in the crystal. The second harmonic signal of 283.71 mW and 345.2 mW respectively were obtained for pure and doped ULMA with reference to KDP (91.66 mW). Thus, the SHG efficiency of pure and doped ULMA crystals is 3.0 and 3.76 times respectively more than KDP. Thus, the La^{3+} has increased the efficiency of pure ULMA.

Dielectric studies

The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 5 MHz at room temperature. Figure 7 shows the plot of dielectric constant versus applied frequency of pure and doped ULMA. The applied frequency has been represented by logarithmic values in the plot. The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency and increases with different temperatures. This is due to the presence of space charge polarization which depends on purity and perfection of the sample. Displacement of an ion from an equilibrium position is equivalent to the placing of the fictitious dipole at the state with the ion in equilibrium. Although positive and negative ions displace in opposite directions in an

electric field, the induced moments all have the same sign. Since ionic polarization is related to the oscillation of ions, the proper frequencies are much lower than those of electrons due to large differences between masses. The dielectric loss is also studied as a function of frequency. The curves are shown in Figure 8 suggesting that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of the dielectric constant. This behaviour is common in the case of ionic systems. The low value of dielectric loss indicates that the grown pure and doped ULMA crystals have lesser defects [5].

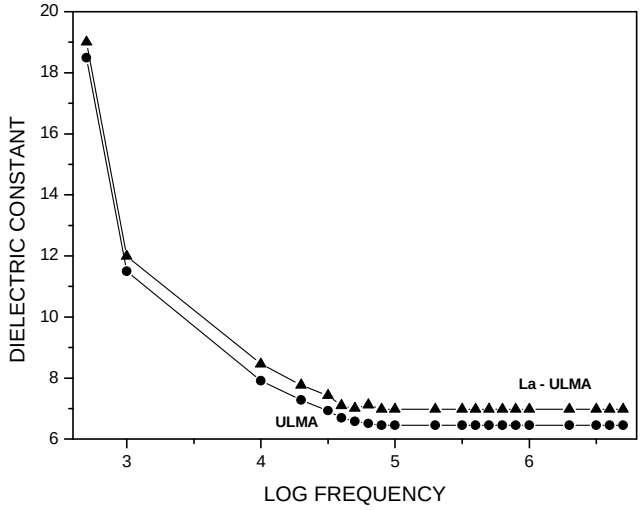


Figure 7 Variation of Dielectric constant for pure and La^{3+} doped ULMA crystal

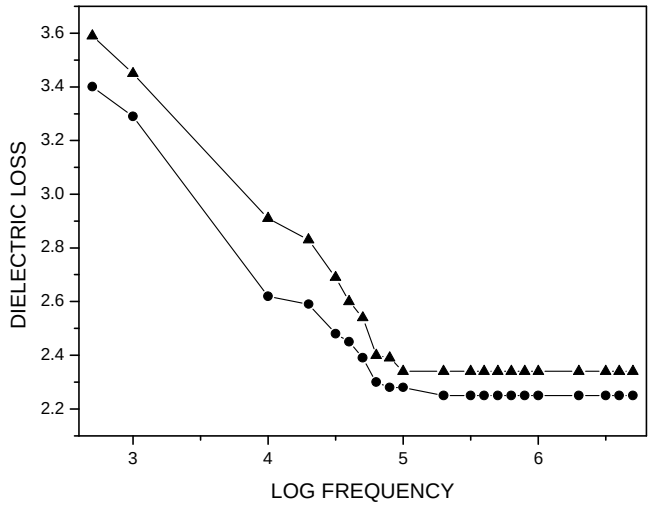


Figure 8 Variation of Dielectric loss for pure and La^{3+} doped ULMA crystal

CONCLUSION

In the present work, the growth of promising NLO crystal of both pure and La^{3+} doped ULMA single crystals were achieved by slow evaporation technique. Powder X-ray diffraction studies were carried out, and the lattice parameters were determined. The presence of functional groups in pure and La^{3+} doped ULMA were analyzed by FT-Infrared studies. The UV-Vis-NIR spectra of the pure and doped ULMA shows good optical transmittance in the entire visible region and the dopants have increased the percentage of transmission in ULMA. The SHG efficiency

of both pure and doped ULMA was found to be thrice than that of KDP. dielectric studies reveal the low value of dielectric constant / dielectric loss of the crystal at high frequency region. SHG efficiency of pure and doped ULMA crystals is 3.0 and 3.76 times greater than that KDP.

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