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Synthesis, Experimental and Theoretical Investigations on Nonlinear Optical Urea L-malic acid Single Crystals

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ABSTRACT

Efficient organic non linear optical material Urea L-malic acid (ULMA) single crystals had been grown by slow evaporation from aqueous solution. In the present investigation, the grown crystal was subjected to powder XRD to estimate the crystal structure and space group. FT-IR, UV-Vis-NIR, thermal and microhardness studies were carried out for the grown pure and doped crystals. The SHG efficiency of ULMA crystals were also studied using Nd:YAG Q-switched laser. We report for the first time the first order hyperpolarizability of ULMA determined with the aid of density functional theory calculations at B3LYP/6-31G(d,p) level.

Key words: Crystal growth; XRD, FT-IR, DFT

INTRODUCTION

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 [1-2]. 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 [3]. Hence, this material is selected for detailed investigation and the results obtained are discussed.

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 synthesized salt of ULMA was utilized for the measurement of its solubility in water. The solubility 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 ºC [4]. 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). Figure 2 shows the photograph of as grown crystal in a period of 50 days.

RESULTS AND DISCUSSION

3. Characterization

3.1 Powder XRD studies

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 ULMA crystal. The diffraction patterns of the crystals were indexed by least square fit method. The lattice parameter values of ULMA crystal were calculated and are well matched with the reported literature [3].

3.2 FT-IR analysis

The middle infrared spectrum of ULMA is shown in Figure 4. The spectrum shows 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 & 1401cm^{-1} is due to COO^{-1} symmetric stretching. The peaks due to COO^{-1} vibrations are formed at 1266, 1251 & 1219cm^{-1}. The peak at 883 is due to C-C stretching.FT-IR spectral assignment of ULMA is shown in table 1.

3.3 UV-Vis-NIR spectrum

Optical absorption data were taken on the polished crystal sample of about 4mm to 6mm thickness using a Varian carry 5E model dual beam spectrophotometer between 200nm – 2000nm. The spectrum (Figure 5) indicate that the crystal have minimum absorption in the entire visible region. The cut-off wavelength is 265nm. The required properties for NLO activity are minimum absorption and low cut-off wavelength.

3.4 NLO studies

Kurtz and Perry powder SHG test [5] was carried out on ULMA single crystal 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 345.2 mW was obtained for ULMA with reference to KDP (91.66 mW). Thus, the SHG efficiency of ULMA crystal is 3.76 times more than KDP.

3.5 First order Hyperpolarizability:

The first hyperpolarizability (β_0) of this of novel molecular system of ULMA is calculated using standard basis set. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensorthat can be described by a 3 x 3 x 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [6]. The components of β are defined as the coefficients in the Taylor series expansionof the energy in the external electric field. The first order Hyperpolarizabilitiy of ULMA is 7.3578 x 10^{-30} esu.

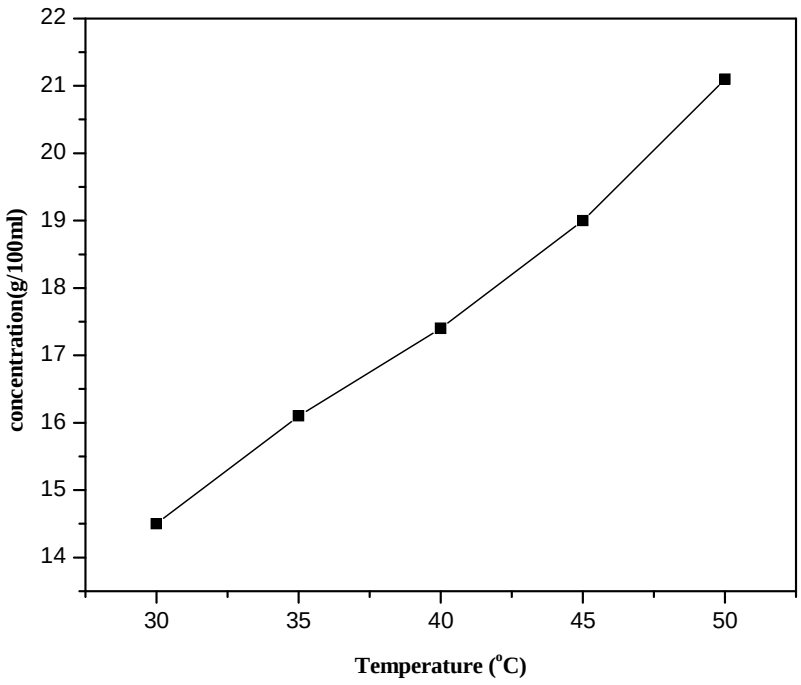

Fig. 1 Solubility curve of ULMA crystal

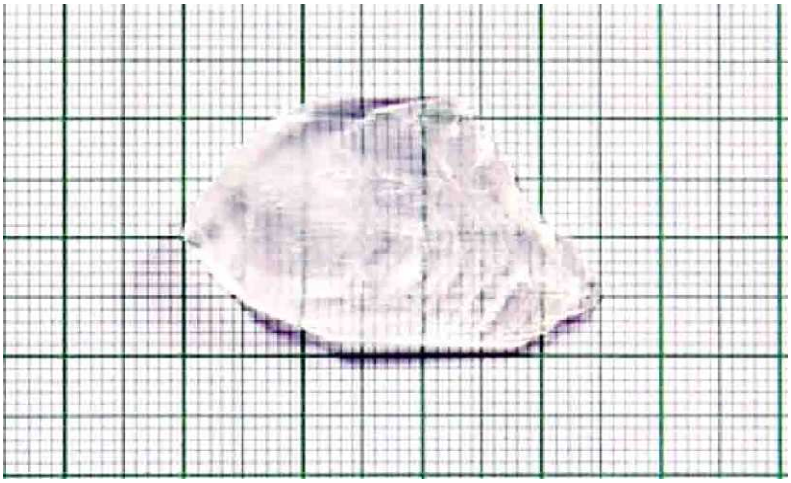

Fig. 2 Photograph of as grown ULMA crystal

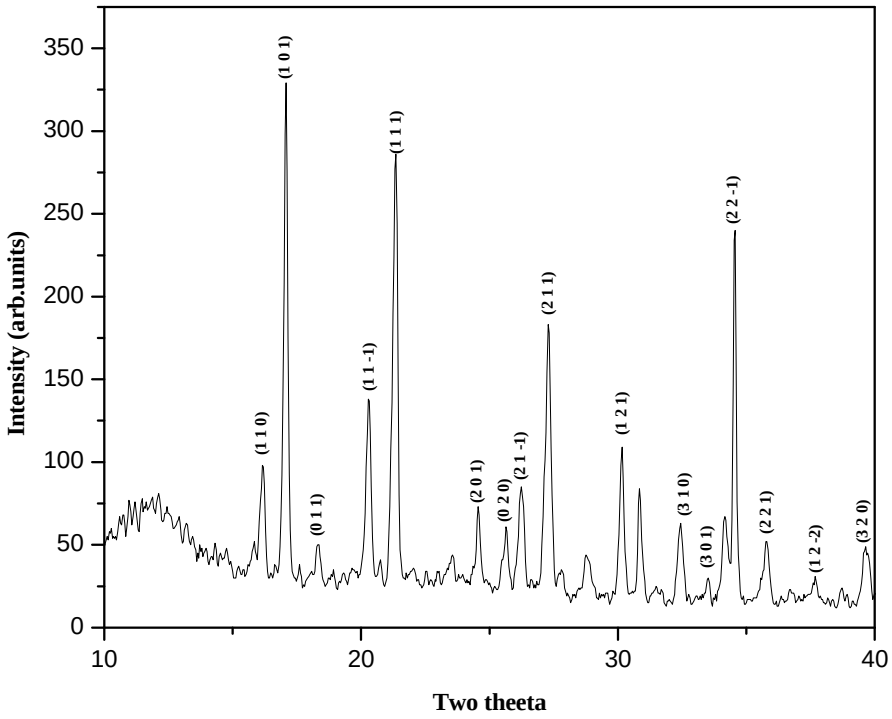

Fig. 3 Powder XRD pattern of ULMA crystal

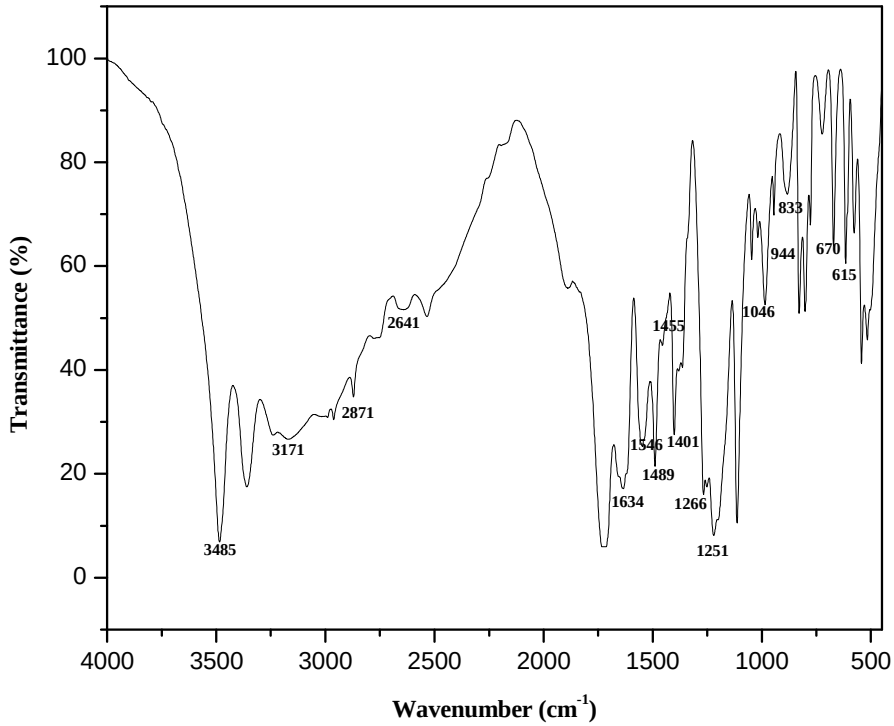

Fig. 4 FT-IR spectrum of ULMA crystal

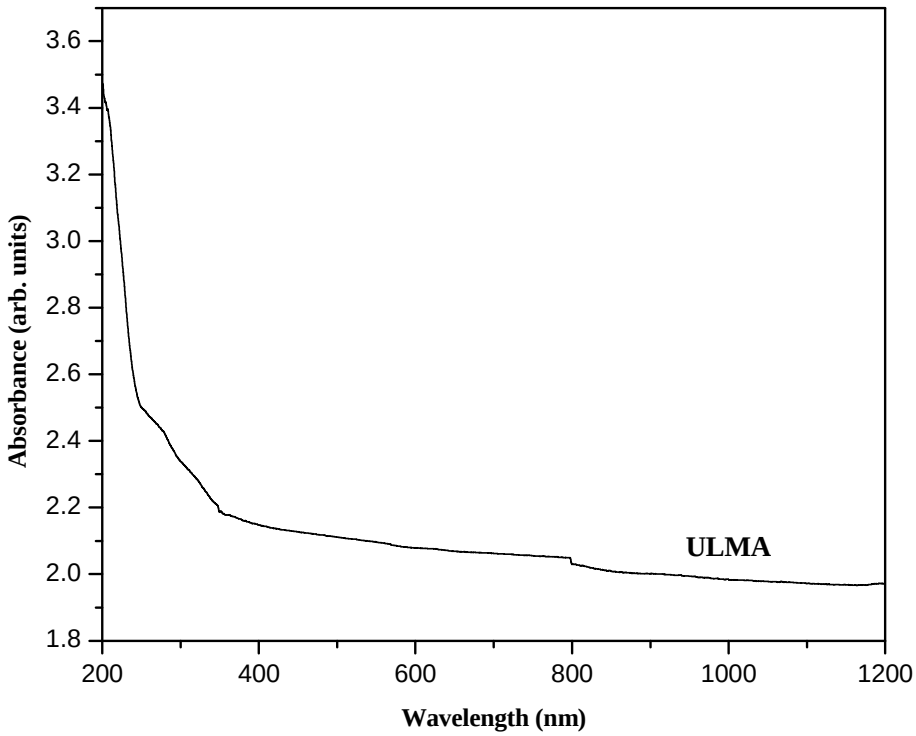

Fig. 5 UV–Vis–NIR Absorption Spectra

Table 1. FT-IR spectral assignments of ULMA

Wavenumbers (cm^{-1})	Assignments
3500-2300	NH & ch stretching vibraton
1634	Presence of NH_2 group
1546	COO^- symmetric stretching
1489	Symmetric NH_3 deformation
1455	COO^- symmetric deformation
1401	COO^- symmetric deformation
1266	COO^- vibration
1251	COO^- vibration
1219	COO^- vibration
1046	C-N stretching
944	CH_2 Rocking
883	C-C stretching
670	NH_2 out of plane
615	NH_2 wag(out of plane)

CONCLUSION

In the present work, the growth of promising ULMA single crystal was achieved by slow evaporation technique. Powder X-ray diffraction studies were carried out, and the lattice parameters were determined. The presences of functional groups in ULMA were analyzed by FT-Infrared studies. The UV-Vis-NIR spectrum of ULMA shows good optical transmittance in the entire visible region. The SHG efficiency of ULMA was found to be thrice than that of KDP.

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