Synthesis, Growth, Thermal and Optical Properties of Urea L-Malic Acid (ULMA) NLO Crystal

[1]S.R.Niranjana, [1]M. Victor Antony raj, [1]*J.Madhavan
[1]Department of Physics, Loyola College, Chennai-34.
[2]Department of Physics, National College, Trichy-1.

Abstract **- Urea L-malic acid, a new second order nonlinear optical crystal, has been synthesized and grown by slow evaporation solution growth technique. X-ray diffraction showed that the candidate material crystallized in monoclinic crystal system a noncentrosymmetric with $P2_1$ space group. Optical absorption spectra of the grown crystal revealed the lower cut-off wavelength and wide transparency of the grown crystal. Thermo gravimetric Analysis of the grown crystal shows three stages of weight loss and the decomposition temperature is found as 185°C. Second harmonic generation (SHG) efficiency of the grown crystal at a fundamental wavelength of 1064 nm is calculated as three times greater than that of KDP.**

I. INTRODUCTION

Organic Non Linear Optical materials are good candidate for signal processing, optical switching and modulating devices and these materials offer flexibility of molecular design, virtually an unlimited number of crystalline structures and a high damage resistance to optical radiation[1]. Over the past two decades nonlinear optical (NLO) materials have been intensely investigated for their application in optical communications and optoelectronics. NLO materials endow the expansion of the circumscribed spectral regime of lasers. Some organic crystals are highly polar, which form non-centrosymmetric crystal structure. Hence, these materials might make it desirable to replace electronic switching circuits in computing and telecommunication systems with purely optical devices [2]. Organic NLO materials are formed by weak Van der Waals and hydrogen bonds with conjugated π electrons and are more advantageous than their inorganic counterparts due to high conversion efficiency for second harmonic generation and transparency in the visible region, high resistance to optical damage and so on [3]. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. In the present work, an attempt is made to synthesize grow and characterize an efficient NLO material ULMA single crystal.

II. EXPERIMENTAL PROCEDURE

To grow bulk crystals from solution by slow evaporation technique, it is desirable to select a solvent in which it is moderately soluble. The size of a crystal depends on the amount of material available in the solution, which in turn is decided by the solubility of the material in that solvent. Using a constant temperature bath of accuracy ±0.01 °C the solubility of ULMA in double distilled water was measured at five different temperatures (30, 35, 40, 45 and 50°C). The solubility of ULMA as a function of temperature is shown in Figure 1. From aqueous solution with equimolar proportion of Urea and L-malic the product compound $CO(NH_2)_2C_4H_6O_5$ (ULMA) is formed. Bulk crystals were grown by successive recrystallization and the crystals are found to be transparent and free from defects Figure 2 shows the photograph of as grown crystal in a period of 35 days.

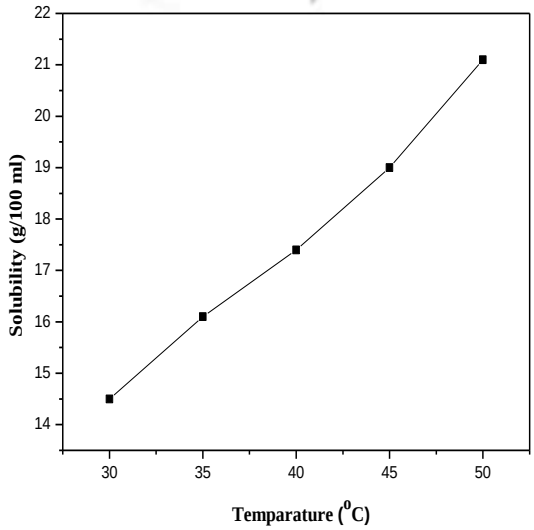

Figure 1 Solubility Curve of ULMA

Figure 2 Photograph of as grown ULMA crystal

III. RESULTS AND DISCUSSION

XRD analysis

Powder X-ray diffraction (PXRD) analysis was performed on ULMA crystals. The data were collected by using a SIEFERT X-ray Diffractometer using CuKα (Kα = 1.540598) radiation. The sample was scanned for a 2θ range of 10–40° and at a scan rate of 1 ° min^{-1}. All the observed reflections in PXRD are indexed and the unit cell parameters were calculated. Figure 3 shows the powder XRD pattern of as grown crystal. The XRD data of ULMA crystal indicates that it crystallizes in monoclinic system with $P2_1$ space group. Unit cell parameters of the grown crystal are found as a=9.055 Å, b=6.941 Å, c=6.88 Å and α=γ=90 ° β=94.66°.

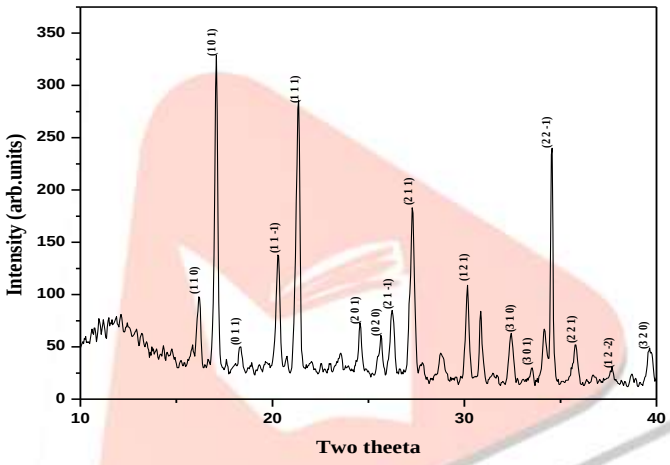

Figure 3 Powder XRD pattern of ULMA crystal

Optical absorption spectrum

The UV-Vis analysis was made between 200 and 2000 nm, which covers near-ultraviolet (200-400 nm), visible (400-800 nm) and then far-infrared (800-1200 nm) regions. The plot of absorption vs. wavelength (nm) is shown in Fig. 4. The crystal has sufficient transmission in the entire UV, visible and IR region. The lower cut off wavelength for ULMA is around 350 nm. The spectrum further indicates that the crystal has wide optical transmission window from 350 nm to 1400 nm Absence of absorption in the region between 400 and 1400 nm is an advantage as it is the key requirement for materials having NLO properties [4]. From the absorbance spectra band gap was evaluated. The *E*g could be estimated from the plots of $h\nu$ versus $(\alpha h\nu)^2$. A plot of $h\nu$ versus $(\alpha h\nu)^2$ is shown in Figure 5 and the optical band gap (*E*g) value was obtained from the interception of the linear portion of the curve with *X*-axis. This gives the *E*g values of 3.767eV for Urea L-Malic Acid single crystal.

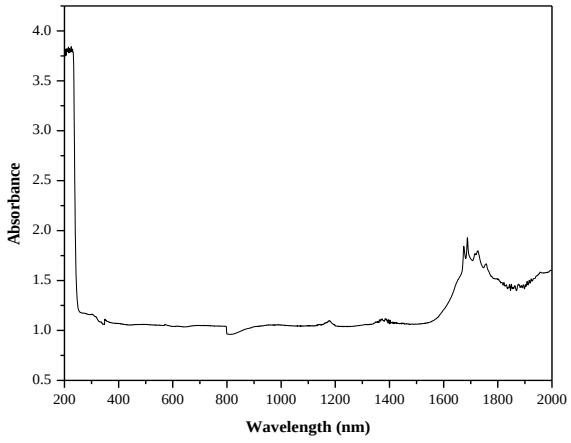

Figure 4 Optical absorption spectrum of ULMA crystal

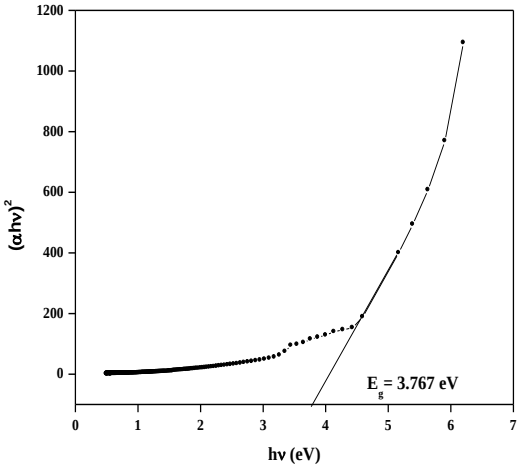

Figure 5 Energy band gap of ULMA

Thermal studies

Thermo gravimetric and derivative thermo gravimetric analyses on ULMA were carried out from room temperature to 850° C using the instrument NETSZCH STA 409C at a heating rate of 20°C /min in nitrogen atmosphere. Figure 6 shows the Thermo-gravimetric Analysis (TGA) curves and Derivative Thermogram (DTG) for the ULMA sample. The TGA shows three stages of weight loss. The materials starts decomposing at 185°C, the DTG peaks coincide well with the TGA plot. The sharpness of the peaks shows good degree of crytstallinity of the grown crystal.

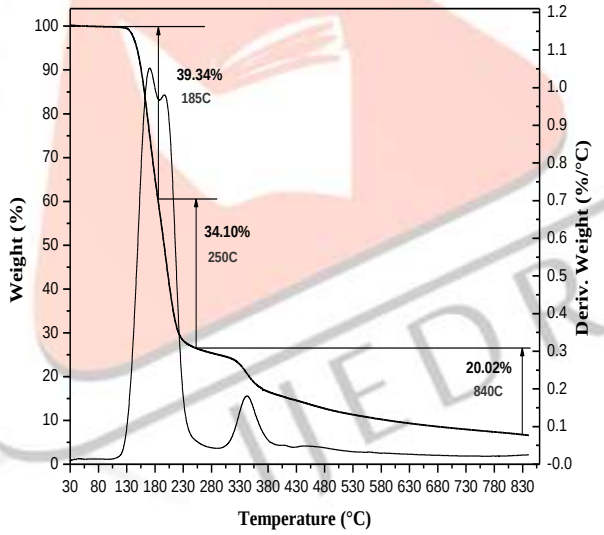

Figure 6 TGA and DTA curves of ULMA crystal

NLO studies

The quadratic non-linear optical property of ULMA was confirmed, and the SHG efficiency in the powdered form was measured using the Kurtz and Perry powder method [5]. The crystal was crushed into powder and it was packed densely between two transparent glass slides. An Nd: YAG laser was used as a light source. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse width with 10 Hz pulse rate was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter. The transmitted fundamental wave was passed over a monochromator which separates 532 nm (second harmonic signal) from 1064 nm. The green light was detected by a photomultiplier tube and displayed on a storage oscilloscope. KDP crystal was powdered to the identical size and was used as reference materials in the SHG measurement. The SHG relative efficiency of ULMA crystal was found to be 3 times higher than that of KDP.

IV. CONCLUSION

Good optical quality ULMA single crystals of dimension up to 16×12×11 mm^3 have been grown successfully by the isothermal solvent evaporation technique. The solubility curves of ULMA in different temperatures have been measured gravimetrically. The structure of the crystal is confirmed by powder X-ray analysis and it is found that the crystal belongs to the monoclinic system with $P2_1$space group. Optical absorption spectrum was recorded for the given crystal and it is found that it has minimum absorption between 240-1400 nm. The optical band gap of the material is found as 3.767 eV. TG and DTG studies confirmed the

three stage weight loss. The output of green light confirmed its non-centrosymmetric structure and its SHG efficiency is 3 times higher than potassium di hydrogen phosphate (KDP).

V. REFERENCES

[1] S. Senthil, S. Pari, R. John Xavier and J. Madhavan, "Linear and nonlinear optical properties of N-(3-nitrophenyl) acetamide single crystals", Optik, Vol 123, pp 104–108, 2012.
[2] Chemla D. S, Zyss, J. Nonlinear Optical Properties of Organic Molecules and Crystals. Academic Press. Orlando, 1987.
[3] J.Madhavan, S.Aruna, A.Anuradha, D.Prem Anand, I.Vetha Potheher, K. Thamizharasan, P. Sagayaraj "Growth and characterization of a new nonlinear optical L-histidine acetate single crystals", Optical Materials, Vol. 29, pp 1211-1216, 2007.
[4] N.Vijayan, R.Ramesh Babu, R.Gopalakrishnan, S.Dhanuskodi, Ramasamy P. "Growth of semicarbazone of benzophenone single crystals," J. Crystal Growth, Vol. 236, p.407, 2002
[5] S.K Kurtz and T.T. Perry, "A Powder Technique for the Evaluation of Nonlinear Optical Materials", J. Appl. Phys., Vol. 39, p.3798, 1968.