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Characterization of Urea L-Malic Acid (ULMA) Crystals Grown in Water, Acetone and Ethanol

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Abstract

Urea L-malic acid (ULMA) salt was synthesized by dissolving urea and L-malic acid in the molar ratio 1:1 in de-ionized water heated at 45°C. The solubility of the synthesized salt was found in different solvents such as de-ionized water, ethanol and acetone in the temperature range 30-50°C. In accordance with the solubility data, saturated solutions for ULMA salt in different solvents were prepared and single crystals of ULMA were grown by solution method with slow evaporation technique at room temperature (30°C). It is noticed that the morphology of ULMA crystals is altered when they are grown in different solvents. The grown crystals were characterized by several studies such as X-ray diffraction (XRD) studies, solubility studies, UV-visible-NIR transmittance studies, microhardness studies. Second Harmonic Generation (SHG) studies reveal the Nonlinear(NLO) activity of the grown crystals.

Keywords: Urea L-malic acid; Crystal Growth; Solution method; Single crystal; Characterization; NLO; XRD; SHG; Microhardness

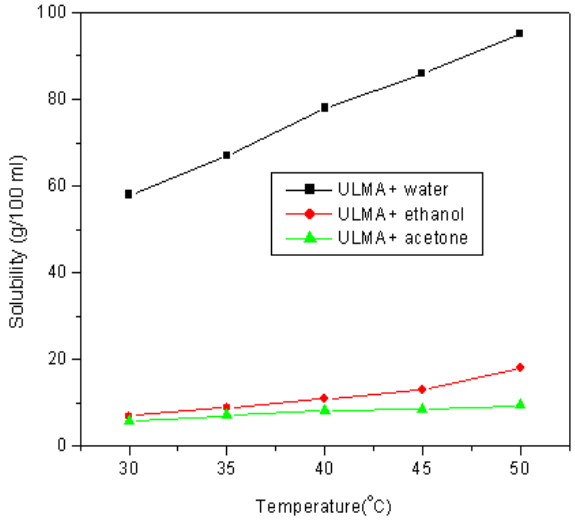
Introduction

The present day technological society requires cost effective and efficient nonlinear optical (NLO) materials for device fabrication. NLO materials can be classified as organic, inorganic and semi-organic materials. Among these, organic NLO materials are gaining attention in the recent years because they have de-localized conjugated electrons which induce efficient NLO behavior. At the molecular level, the presence of a finite value of molecular hyperpolarizability is the fundamental requirement for third-rank NLO processes and this is achieved by having a large difference in the electron distribution between the ground and first-excited states [1]. Moreover organic materials offer flexibility and show moderate resistance to optical radiation. Urea L-malic acid is an organic NLO material and it is a derivative of urea. It shows efficient nonlinear optical properties and broad transparency as that of urea. Its SHG efficiency is roughly three times that of KDP [2]. Various properties of ULMA and NLO crystals have been reported by many authors [3-6]. Dixit et al has reported that prismatic habit dominates in the growth of ULMA crystals if the saturation level was slightly increased [7]. This paper deals with the synthesis and growth of Urea L-malic acid crystals in different solvents and various studies on X-ray diffraction (XRD), UV-visible-IR studies, Microhardness studies and SHG studies of the grown crystals are reported.

Synthesis, Solubility and Growth

Analar Reagent (AR) grade chemicals such as urea and L-malic acid were taken in 1: 1 molar ratio and dissolved in de-ionized water and stirred using magnetic stirrer for about 2 hours. The solution was heated till the synthesized salt of ULMA was obtained. During the synthesis, temperature of the solution was maintained at 45 °C in order to avoid the oxidation of sample. The purity of the synthesized salt was improved by repeated re-crystallization. Solubility study was carried out using a hot-plate magnetic stirrer and a digital thermometer. A voltage regulator was attached with hot-plate magnetic stirrer in order to maintain the temperature constant (Here accuracy is $\pm$ 0.1°C). Initially, the temperature was maintained at 30°C. The twice re-crystallized salt of ULMA was added step by step to 50 ml of de-ionized water in an air-tight container kept on the hot-plate magnetic stirrer and stirring was continued till a small precipitate was formed. This gave confirmation of supersaturated condition of the solution. Then, 25 ml of the solution was pipetted out and taken in a petri dish and it was warmed up at 50°C till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility (in g/100 ml) of ULMA sample in de-ionized water was determined and this method of measuring solubility is known as gravimetrical method [8,9]. The same procedure was followed to find solubility of ULMA salt at various temperatures and in other solvents like acetone and ethanol. The variations of solubility with temperature for ULMA salt in different solvents like de-ionized water, ethanol and acetone are presented in the figure 1. From the figure, it is observed that the solubility of ULMA sample in water is the highest compared to acetone and ethanol and for all the solvents considered in this work, the solubility increases with temperature. Thus, ULMA salt has positive temperature coefficient of solubility in water, acetone and ethanol.

Fig.1: Solubility curves for ULMA crystals dissolved in de-ionized water, ethanol and acetone.



Single crystals of the re-crystallized salt of ULMA were grown by solution method with slow solvent evaporation technique at room temperature (30°C) in different solvents like water, acetone and ethanol. In accordance with the solubility data, saturated solutions of ULMA sample were prepared separately in de-ionized water, acetone and ethyl alcohol. The solutions were constantly stirred well using a magnetic stirrer and were filtered using micro Whatmann filter papers. Then the filtered solutions were kept in three separate borosil beakers covered with porous papers for slow evaporation. The grown crystals were harvested after 35 days.

Characterization Techniques

Powder X-ray diffraction patterns of the samples were obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K_a radiations (λ= 1.54056 Å) at 35 KV, 10 mA). The samples were scanned over the required range for two-theta values(10 – 50°). Second Harmonic Generation (SHG) test for the grown ULMA crystals was performed by the powder technique of Kurtz and Perry [10] using a pulsed Nd:YAG laser (Model: YG501C, λ=1064 nm). Pulse energy of 4 mJ/pulse, pulse width of 10 ns and

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repetition rate of 10 Hz were used. The grown crystals were ground to powder of grain size 1500-1800 µm and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a capillary tube. Mirocrystalline material of Potassium Dihydrogen Phosphate (KDP) was used as reference in this experiment. Second Harmonic Generation (SHG) from the samples was detected using an optical cable attached to a fluorescence spectroscope (Model: DID A-512 G/R). A Varian Cary 5E UV-Visible-NIR spectrophotometer was used for spectral transmission studies. A crystal thickness of about 2 mm was used for transmission studies.

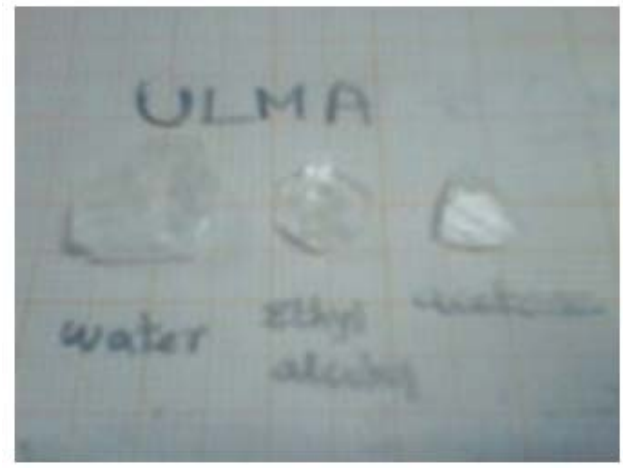
Vickers hardness measurements were carried out on ULMA crystals using ultra microhardness tester fitted with a diamond indentor. The indentations were made using a Vickers pyramidal indentor for various loads from 25 to 200 gm. Several trials of measurements were made on the prominent face and the average diagonal length was calculated for indentation of 5 seconds. The Vickers micro hardness number was calculated using the relation H v = 1.8544 P / d kg/mm^2 where P is the applied load and d is the diagonal length of the indentation impression[11,12].

Results and Discussion

Morphological appearance

The crystals grown in de-ionized water, ethanol and acetone are displayed in the figure 2. It noticed that there are morphological changes when ULMA crystals are grown in different solvents. Frequent reference in the literature of crystallization indicates that a change of solvent often results in a change of crystal habit. It is noticed that the thickness is large and transparency is high for the crystal grown in de-ionized water compared to the crystals grown in acetone and ethyl alcohol. It is reported that the thickness of the growth layers on certain ionic crystals was affected by the dielectric constant of the aqueous solution. The ULMA crystals from ethyl alcohol and acetone are found to have reduced height and this is because the dielectric constant of acetone and ethyl alcohol is less than that of water. Hence, the crystals grown in de-ionized water are observed to larger compared to those are grown in acetone and ethyl alcohol in same period of the growth.

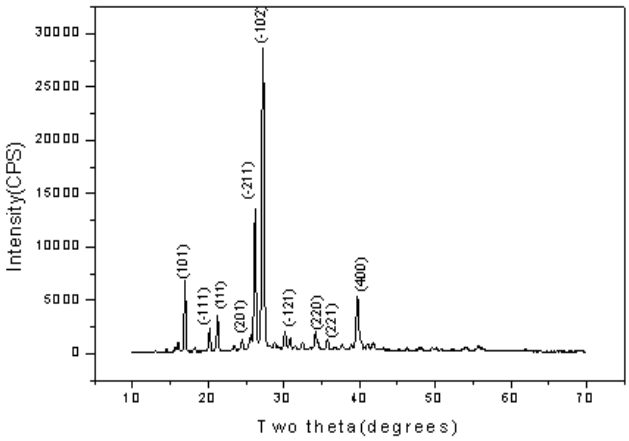
Fig 2: A photograph of the crystals of ULMA grown in water, ethanol and acetone



XRD studies

Fig 3. shows the powder XRD pattern of ULMA crystal grown from water. The well-defined peaks at specific 2θ values show high crystallinity of the grown crystals. All the reflections of powder XRD patterns of this work were indexed using the TREOR software package following the procedure of Lipson and Steeple [13]. The lattice parameters were obtained from the data of powder XRD pattern using UNITCELL software package. In this work, the values of lattice parameters are found to be a=9.0374 A°, b=6.9346 A°, c=6.8037 A°, β=95.68° and these values are observed to be in close agreement with data reported in the literature [2]. The powder XRD patterns were also taken for the crystals grown in acetone and ethyl alcohol and these patterns are observed to be the same as that of ULMA crystal grown in de-ionized water and hence they are not presented in the figure.

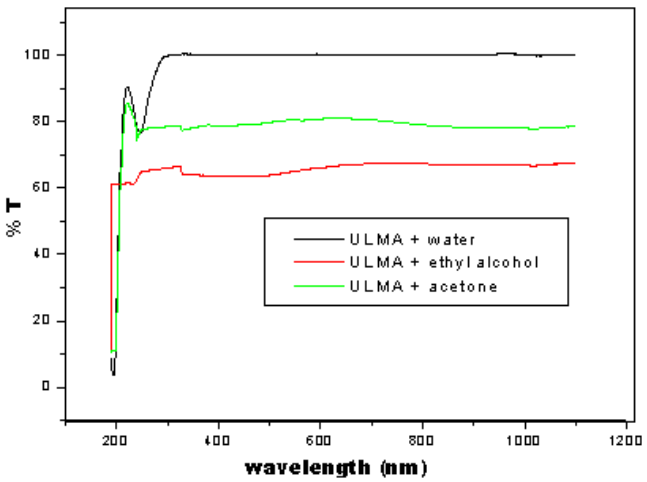
Fig.3: Powder XRD pattern for ULMA crystal grown in de-ionized water



UV-visible-NIR transmittance studies

Fig. 4 shows the UV-visible-NIR transmission spectra of ULMA crystals grown from different solvents. For all optical applications in general and especially for SHG the material considered must be transparent in the wavelength region of interest. Measurements of the optical absorption in ULMA crystals from different solvents shows range of transparency in visible region. All crystals of ULMA from water, ethyl alcohol and acetone can be utilized for second harmonic generation in all visible wavelengths since the transparency is good in that range. The lower cut-off which corresponds to the fundamental absorption occurs at 190 nm for ULMA crystals from different solvents of our study. The short cut-off wavelength facilitates the grown crystals of this work to be potential nonlinear optical materials for second harmonic generation by Nd:YAG laser. The transmittance is very good with 100% for ULMA crystals from water and comparatively very low around 62% for ULMA from ethyl alcohol and around 80% for ULMA from acetone. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples. Using the formula E_g = 1240 / λ (nm), the band gap is calculated to be 5.636 eV for all the grown three samples.

Fig. 4: UV-visible-NIR transmittance spectra for the crystals grown in water, ethanol and acetone



Microhardness studies

Vickers hardness number (H_v) was evaluvated from the relation H_v =1.8544 P/d^2 Kg/mm^2 where H_v is Vickers hardness number, P is the indenter load in kilogram and d is the diagonal length of the impression in millimetre. Fig. 5 shows the variation of Vickers microhardness number (H_v) with applied load (d) for ULMA crystals

grown in water, ethyl alcohol and acetone. It is noticed from the figure that the hardness value increases with increasing load for the crystals of this work. For loads above 200 g cracks developed on the surface of the crystal due to release of internal stress generated locally by indentation. Mayer's law [14] relates load and size of indentation as $P=a\ d^n$,where a and n are the constants. The plot of log d versus log P is drawn (Fig. 6) and from plots, the hardening coefficient (n) was determined. The value of n is found to be 2.733 for ULMA crystals grown in ethyl alcohol solvent and 6.936 for ULMA crystals grown in acetone solvent and 3 for ULMA crystals grown in de-ionized water. According to Onitsch, n should be between 1 and 1.6 for hard materials and above 1.6 for softer ones [15]. Hence ULMA crystals grown in different solvents belong to soft category of materials.

Fig.5: Variation of microhardness number with load for ULMA crystals grown in water, ethanol and acetone.

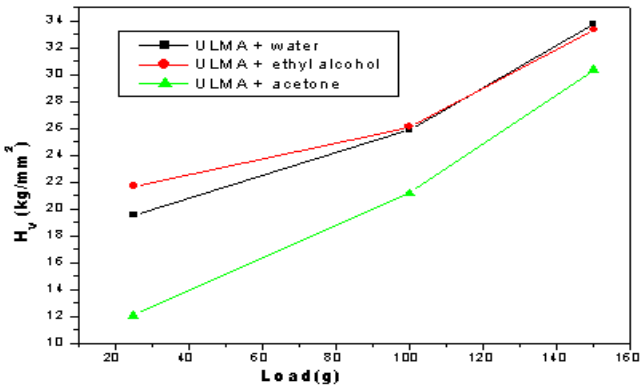
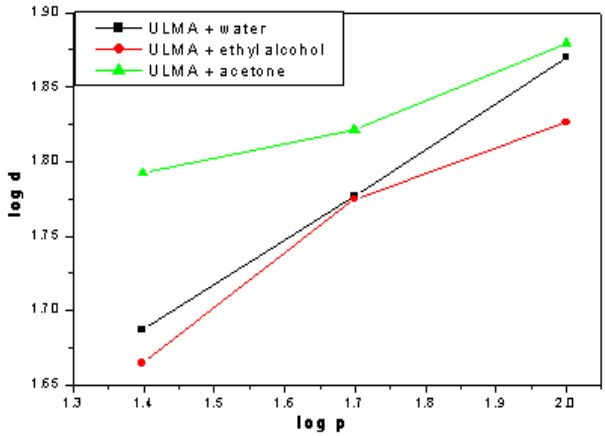


Fig.6: Plots of log d versus log P for ULMA crystals grown in water, ethanol and acetone.



Second Harmonic Generation (SHG) studies

SHG test on the crystals was performed by Kurtz powder method [10]. The LAHC crystal was powdered with uniform particle size using a ball mill and it was packed densely between two transparent glass slides. An Nd:YAG laser with a modulated radiation of 1064nm was used as a light source. This laser device can be operated in two different-modes. In the single-shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulse at a repetition rate of 10 Hz. To make relevant comparison with known SHG material, KDP was also ground and sieved into the same particle size ranges. The doubling of frequency was confirmed by the green radiation of 532 nm. It is observed that the SHG intensity is almost same for all ULMA crystals grown from different solvents.

Conclusions

Urea L-Malic acid(ULMA) salt was synthesized and single crystals of ULMA were grown in different solvents by solution method. The external appearance (morphology) appears to be different and internal crystal structure is not changed when ULMA crystals are grown in different solvents. The grown crystals are observed to be transparent and colourless and they crystallize in monoclinic crystal system. Microhardness study indicates that ULMA crystals grown from water has more mechanical strength compared to ULMA crystals grown from ethyl alcohol and acetone. From the data of microhardness studies, work hardening coefficient of the crystals was determined. The UV-visible-NIR transmittance spectra show that the grown crystals have good optical transmittance in the entire visible region, which indicates ULMA crystals are the promising material for nonlinear application. From SHG studes, it is concluded that the ULMA crystals grown in different solvents such as water, ethyl alcohol and acetone show the same SHG efficiency.

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