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Studies on the crystal growth and characterization of urea L-malic acid single crystals grown from different solvents

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Abstract

Crystals of urea L-malic acid (ULMA) were grown by solvent evaporation technique at ambient temperature using different solvents like water, methanol and ethanol. For identification of elements present in ULMA crystal, CHN test was carried out followed by characterization like XRD, optical transmission, SHG efficiency measurement and dielectric studies. A remarkable morphological change was observed for crystals grown from different solvents. But XRD studies did not reveal any change in lattice parameters for these ULMA crystals. Optical transmittance was found to be increased for crystals grown from water. Both the dielectric constant and dielectric loss vary slowly with frequency.

Keywords: Optical materials and properties; Crystal growth; X-ray techniques; Dielectrics

1. Introduction

Urea is one of the simplest biological molecule and one of the simplest diamide used in organic chemistry because of its capability in forming transition metal complexes [1]. Urea has shown interesting properties for nonlinear optical applications [2]. Its optical and mechanical properties are comparable to those of semiorganic NLO crystals. In search of compounds with similar or better optical and mechanical properties and better growth yield many scientists [3–6] have studied the derivatives of urea. The growth of urea and its derivatives like most organic materials is problematic owing to its polar electrical characteristics, which enhance the interaction between growth surfaces and molecules of solvent and solute. For that reason they usually show irregular growth habits. So in order to get better growth habit we have tried to grow the crystals of urea L-malic acid (ULMA) in different solvents followed by characterization like XRD, optical spectrometry, SHG efficiency and dielectric measurement. Single crystal growth of ULMA has already been reported by Dixit et al. [7], but there is no such report on the growth of ULMA crystals in different solvents.

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2. Experimental procedures

2.1. Synthesis and identification

To get the binary organic compound of urea L-malic acid (ULMA), we first prepared two homogeneous aqueous solutions of urea and malic acid by dissolving equivalent amount of urea (Merck, purity 99.5%) and L-malic acid (Merck, purity 99%) in warm water. The two solutions so formed were then mixed with constant stirring for 6–7 h and heated at a temperature of 40 °C. The hot solution was then filtered out and kept undisturbed. After few weeks, crystalline powder sample of ULMA was separated out from the solution, which was dried in vacuum oven. To ascertain that the material obtained is surely that of ULMA, CHN analysis was carried out in a CHN analyzer (2400 Series II CHN analyzer PERKINELMER-precisely, USA).

2.2. Crystal growth

In this present investigation, the single crystal of ULMA was grown by solvent evaporation method at constant temperature. Before growing the crystals, appropriate selection of solvents for the growth of material is of prime importance. The solubility test of ULMA in different organic solvents revealed that ULMA is

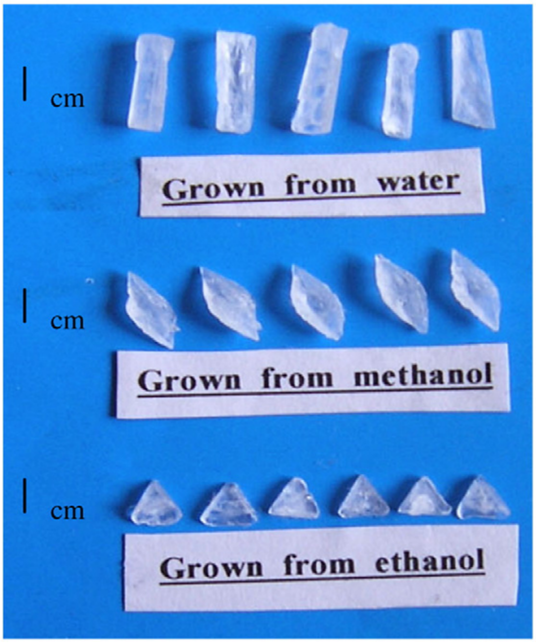

Fig. 1. As-grown crystals of ULMA grown from different solvents by solvent evaporation method.

soluble both in water and alcohol. So we prepared three different solutions of ULMA taking water, methanol and ethanol as solvents. After 40–45 days, clear crystals of ULMA were obtained.

2.3. X-ray diffraction analysis

To confirm the crystallinity of grown crystals and also the unit cell parameters of ULMA, X-ray diffraction analysis was carried out with crystalline powder sample of ULMA. Powder X-ray diffraction pattern was recorded using a microprocessor controlled X-ray diffractometer (SEIFERT XRD 3000P) using nickle filtered CuK_{α} radiation (36 kV, 20 mA). Data were recorded over a 2θ range 8°–50° using step scan of 0.02° for a time interval of 2 s. From X-ray diffraction pattern, all the observed reflection lines were indexed and the required cell parameters were calculated using 2θ values of these reflections with the help of computer program Winplotr [8].

2.4. Optical transmission studies

The UV–Visible spectrum of ULMA was recorded on a SHIMADZU UV-2401PC spectrophotometer in the range 200–800 nm. Single crystals of ULMA of thickness 2.0 mm grown from water, methanol and ethanol were used for these studies.

2.5. SHG efficiency

The SHG efficiency of ULMA crystals was determined by powder technique of Kurtz and Perry [9]. The second harmonic output was generated by irradiating the powder samples of grain size 110 μm–150 μm by pulsed laser beam of Nd–YAG laser of pulse width 8 ns and pulse energy 4 mJ. The emission of green radiation from the sample confirmed the second harmonic generation in the crystal. The output beam from the sample was filtered by an IR filter to remove the fundamental beam (1064 nm) and the second harmonic beam (532 nm) was focussed by a lens and measured by a CRO.

2.6. Dielectric studies

Dielectric properties of organic NLO materials are important for their fast switching times in electro-optic applications. So the dielectric studies of ULMA crystal grown from aqueous solution were undertaken in this work. The dielectric constant of ULMA was found by measuring the capacitance of the samples with Solatron S11260 impedance analyzer and calculating the dielectric constants assuming that each samples behave like a parallel plate capacitor. Measurements were made at room temperature from 100 kHz to 10 MHz.

3. Results and discussions

The experimental results of CHN test shows that the percentage composition of C, H, N present in the synthesized material is in good agreement with that of calculated values of ULMA, thus confirming the molecular formula of the compound as $CO(NH_2)_2C_4H_6O_5$.

Fig. 1 shows grown crystals of ULMA from different solvents. Initial investigation shows that ULMA crystals exhibit a range of habits and of varying quality. The morphological changes may be caused due to the intermolecular interactions between solute and solvent molecules at the various crystal/solution interfaces. Since the extent of such interactions depends upon the nature of the solvent and the detailed chemistry of the various faces, substantial variations in crystal habit from one solvent to another may be expected. In our present study, ULMA crystals grown from three different solvents have different morphologies. ULMA crystals grown from water are rectangular in shape that from methanol rhombohedral and ULMA grown from ethanol has triangular shape. From the solubility graph (Fig. 2), it was observed that ULMA has highest solubility in water and lowest in ethanol. This is because we know that solubility of a compound in solvent increases with the dielectric constant of the solvent. Here we observed that the thickness of crystals was affected by the dielectric constant of the solvents. Lower the dielectric constants of the solvents lower is the thickness of the grown crystals.

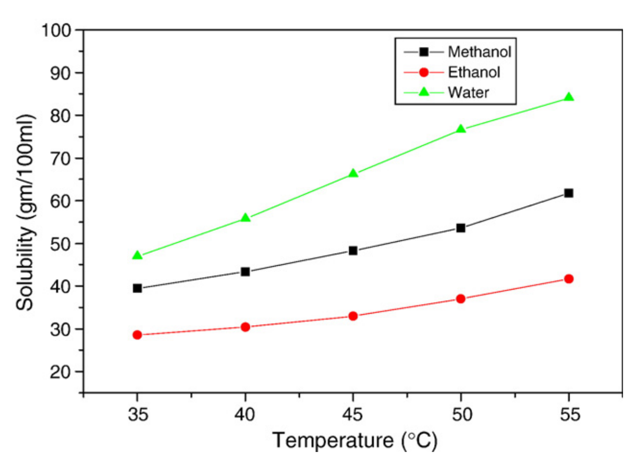

Fig. 2. Solubility curve of ULMA in different solvents.

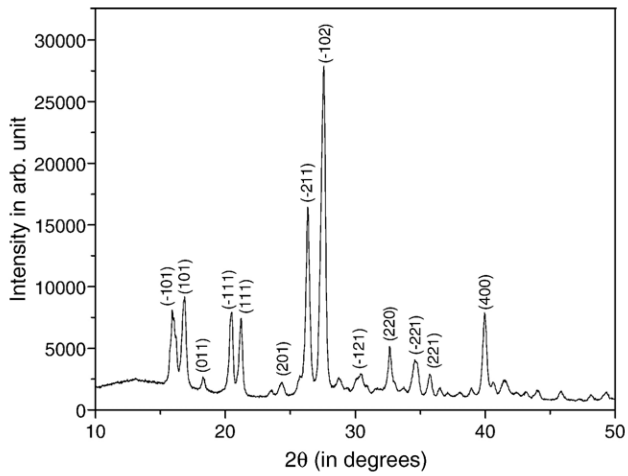

Fig. 3. Powder diffraction pattern of ULMA.

Fig. 3 shows powder XRD pattern of ULMA grown from water. The values of cell parameters a=9.037 Å, b=6.931 Å, c=6.800 Å, β=94.61° calculated from 2θ values of this X-ray diffraction pattern agree very well with the reported values [6]. No significant variation was observed for lattice parameters of the ULMA crystals grown from methanol and ethanol.

Fig. 4 shows the optical transmission spectra of ULMA crystals grown from different solutions. The figure shows that all the crystals are optically transparent in the UV–Vis region with 90% transmission for ULMA crystal grown from water. Lower percentage of transmission for crystals grown from methanol and ethanol may be due to the inhomogeneties arise due to solvent inclusion and also observed by Dhanasekaran et al. [10] in case of POM crystal. On the other hand the electronic absorption in UV (cut off 210 nm) region, ruled by amino-carboxylic group transition is largely the same for all the crystals grown from different solvents and attributed with certainty to intrinsic absorption of the material.

The SHG intensity is comparable to that of urea and almost same for all ULMA crystals grown from different solvents.

Fig. 5(a) shows the variation of dielectric constant (ε_1) as a function of frequency. From the curve, it is observed that the dielectric constant (ε_1) decreases slowly with increasing frequency. The same trend is observed in the case of variation of dielectric loss with frequency (Fig. 5(b)). The low value of dielectric loss indirectly indicates that ULMA crystal grown from aqueous solution is qualitatively better than that grown from other solvents and in agreement with the results of optical transmission studies.

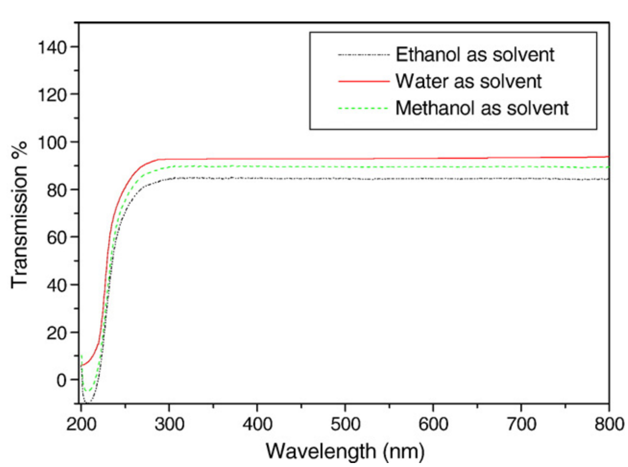

Fig. 4. UV–Vis transmission spectra of ULMA.

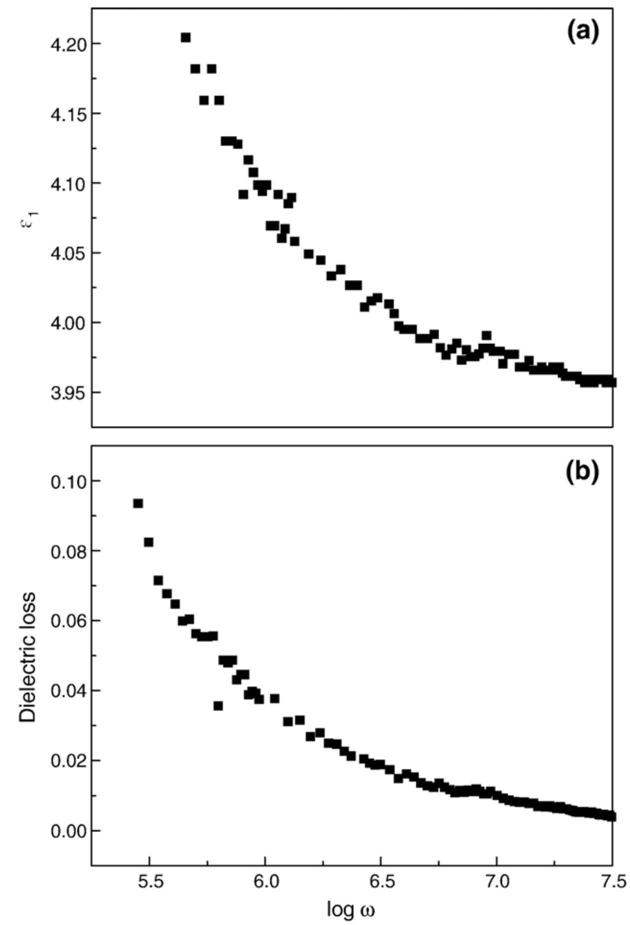

Fig. 5. (a) Variation of dielectric constant (ε_1) of ULMA with frequency (ω). (b) Variation of dielectric loss of ULMA with frequency (ω).

4. Conclusion

Single crystal of binary organic compound urea L-malic acid was grown by solvent evaporation technique at ambient temperature using different solvents like water, methanol and ethanol. The grown crystals exhibit different morphologies and qualities with change of solvents, which are attributed due to the intermolecular interactions between solute and solvent molecules at the interface. Optical transmittance was slightly enhanced for ULMA crystal grown from water showing the good optical quality of this crystal compared to those grown from methanol and ethanol and also supported by the result of dielectric studies. The values of SHG efficiency for all ULMA crystals grown from different solvents do not show any remarkable change and comparable to that of urea. The growth experiment in large scale with water as solvent is expected to yield bulk crystals suitable for laser fusion experiments and SHG device application.

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