



Growth and characterization of organic crystals: Urea L-malate and Zn(II) doped Urea L-malate

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Abstract: Urea L-malate and Zn(II) doped Urea L-malate crystals are grown from aqueous solution at room temperature. The influence of transition metal Zn(II) doping on the structural, optical, mechanical and dielectric properties of Urea L-malate has been investigated. Single crystal X-ray diffraction analysis reveals that both the pure and Zn(II) doped Urea L-malate crystals belong to monoclinic system with the space group $P2_1$. The FT-IR spectral study reveals the presence of functional groups and confirms the small distortion of the structure of the crystals due to doping. The optical absorption studies were carried out to analyze the optical absorption of the grown crystals and confirmed that the absorption is almost negligible in the visible and UV regions for both pure and doped crystals. Kurtz and Perry powder technique has been employed to identify second harmonic generation efficiency of the grown crystals. Hardness Studies were carried out to find the mechanical behavior of the grown crystals. Dielectric studies were employed to find the dielectric constant and dielectric loss of the grown crystals.

Keywords: Crystal growth, XRD, Optical, hardness, Dielectric.

Introduction

The materials which can generate second harmonic blue-green light using laser diodes have been attracting a great deal of interest. Organic nonlinear materials are potential candidates for frequency mixing, electro-optic modulation, optical parametric oscillation etc., due to their large optical non-linearity, low cut off wavelength, short response time and high thresholds for laser power [1-3]. 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 is one of the simplest biological molecule and one of the simplest diamide used in organic chemistry due to its capability in forming transition metal complexes. Urea has shown interesting properties for nonlinear optical applications. Its optical and mechanical properties are comparable to those of semi-organic nonlinear optical crystals. Gomes et al [4] have reported that a urea L-malic acid crystal was found to exhibit second harmonic efficiency three times that of the widely used inorganic crystal, KDP. In search of compounds with similar or better optical and mechanical properties and better growth yield, many scientists have studied the derivatives of urea [5, 6]. The Zn-doped III-V semiconductor layers have been proposed in the recent years as efficient materials suitable for optoelectronic devices [7, 8].

Motivated by the previous works, we have grown single crystals of Urea L-malate (ULM) and Zn(II) doped ULM. In this paper, we report the influence of transition metal Zn(II) doping on the optical, mechanical and dielectric properties of NLO active Urea L-malate crystals grown by slow solvent evaporation method at

32°C. The grown crystals were subjected to single crystal XRD analysis, FT-IR spectral analysis, UV-Visible spectral analysis, Kurtz and Perry SHG test, dielectric and microhardness studies.

Experimental

The organic compound Urea L-malate (ULM) has been synthesized by dissolving 1:1 molar ratio of Urea (AR grade) and malic acid (AR grade) in double distilled water at room temperature (32°C). The prepared solution was homogeneously stirred for about 4 hours using magnetic stirrer. By heating the mixture to dryness below an optimum temperature of 55°C in a temperature controllable water bath, colorless tiny crystalline samples were obtained and were used for the growth of ULM single crystal. To ensure high purity, the material was purified by consecutive crystallization. The synthesized material was thoroughly dissolved in double distilled water to get saturated solution. In order to remove unwanted impurities, the prepared solution was then filtered twice using micro-whatman filter paper and kept in a borosil beaker covered with porous paper to ease the evaporation of the solvent. To ensure constant growth rate, it was placed in a temperature water bath at 32 °C.

In order to grow Zn(II) doped ULM crystal, 5wt% of Zn(II) in the form of ZnSO₄ was added to the saturated solution of urea L-malic acid and the same method was followed as that of pure ULM. In the present work, two drops of H₂O₂ were added to both the solutions of ULM to inhibit the growth of any microorganism. A good quality ULM single crystal of size 20mm×8mm×4mm was obtained in a period of 30 days at room temperature and is shown in Figure 1(a). At the same period of time, good quality single crystal of Zn(II) doped ULM with the size 24mm×14mm×7mm was obtained and is shown in Figure 1(b).

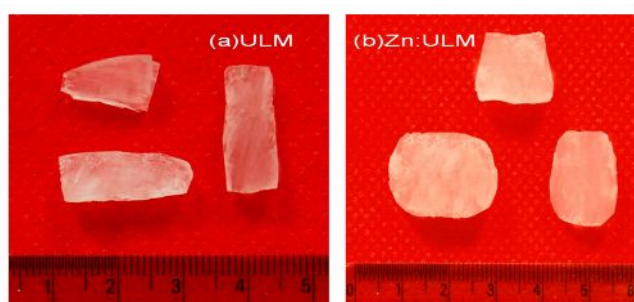


Figure 1. (a) As grown ULM and (b) Zn(II) doped ULM crystal

Results and Discussion

Single crystal XRD study

To confirm the crystal structure and lattice parameters, single crystal XRD study was carried out using BRUKER AXS kappa apex2 CCD diffractometer using MoK α radiation source of wavelength 0.7107 Å. The X-ray crystallography data confirms that the ULM crystal belongs to monoclinic system with P2₁ space group and V= 924(3) Å³. The lattice parameters are a= 9.24(2) Å, b=7.23(5) Å, c=13.86(3) Å, $\alpha = \gamma = 90^\circ$ and $\beta = 93.40^\circ$. A slight increase in dimensions has been observed in case of Zn(II) doped crystal and this may be due to the presence of dopant in the lattice of pure ULM crystal. The observed crystal parameters are specified in Table 1.

Table 1. Crystallographic data of ULM and Zn(II) doped ULM

| Cell parameters | ULM crystal | Zn:ULM crystal |
|----------------------|------------------------------|------------------------------|
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2 ₁ | P2 ₁ |
| Unit cell dimensions | a = 9.24(2) Å | a = 9.28(5) Å |
| | b = 7.23(5) Å | b = 7.20(2) Å |
| | c = 13.86(3) Å | c = 13.95(7) Å |
| | $\alpha = \gamma = 90^\circ$ | $\alpha = \gamma = 90^\circ$ |
| | $\beta = 93.40^\circ$ | $\beta = 93.39^\circ$ |
| Volume | V= 924(3) Å ³ | V= 930(12) Å ³ |

FT-IR Spectral Analysis

Fourier Transform Infrared (FTIR) spectrum was recorded using Perkin Elmer spectrometer using KBr pellet technique in the range 4000 to 400 cm^{-1} . FTIR spectra of pure and Zn(II) doped ULM crystals are depicted in Figures 2 and 3. Both the pure and doped crystals show almost similar outcome. Spectral bands are interpreted and compared with the known spectra of the functional groups [9, 10]. The FT-IR spectra of ULM crystal shows a strong and intense peak at 3483 cm^{-1} , which is ascribed to O–H stretching of carboxylic acid and the presence of water molecule in the crystal. The peaks at 3357 and 3230 cm^{-1} are due to NH and C–H stretching vibrations in ULM. The strongest peak observed at 1719 cm^{-1} indicates the presence of C=O stretching of carbonyl group. The peaks at 1646 and 1543 cm^{-1} are assigned to asymmetric and symmetric stretching vibration of COO^- . The strong peaks at 1268 and 1225 cm^{-1} are due to presence of asymmetric and symmetric stretching vibration of C–O functionality. Another strong peak observed at 1114 cm^{-1} is due to the existence C–N stretching vibration. The peak at 800 cm^{-1} is due to C–C stretching vibration. In case of Zn(II) doped ULM crystal, slight shifts in some of the characteristic vibrational frequencies are observed which may be due to the effect of doping. The important bands that support our interpretations are listed in Table 2.

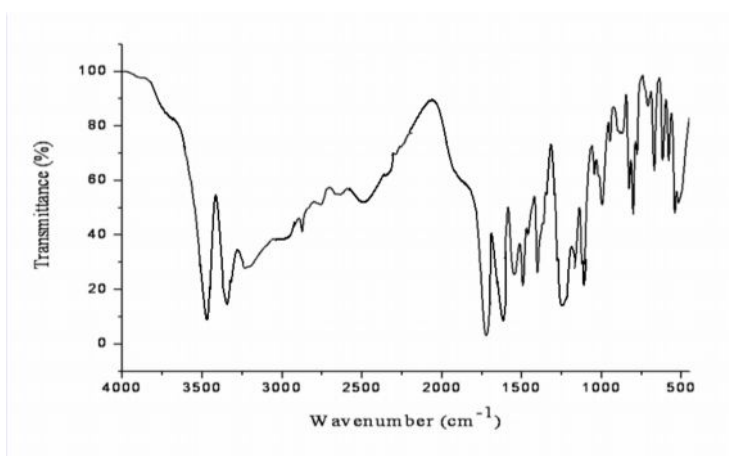


Figure 2. FT-IR spectra of ULM crystal

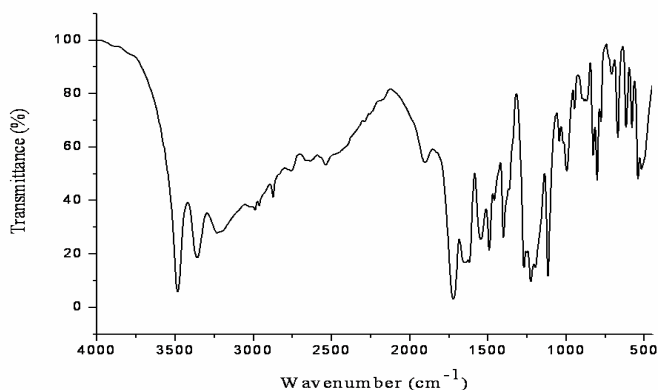


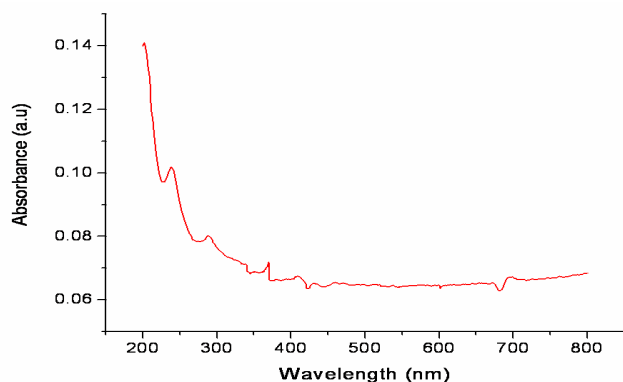
Figure 3. FT-IR spectra of Zn(II) doped ULM crystal

Table 2. FT-IR spectral assignment of ULM and Zn(II) doped ULM crystal

| Wavenumber (cm ⁻¹) | | Assignments |
|--------------------------------|--------|---|
| ULM | Zn:ULM | |
| 3483 | 3479 | O–H stretching |
| 3357 | 3354 | N–H stretching |
| 3230 | 3228 | C–H stretching |
| 1719 | 1717 | C=O stretching |
| 1646 | 1645 | Asymmetric stretching of COO ⁻ |
| 1543 | 1540 | Symmetric stretching of COO ⁻ |
| 1268 | 1266 | Asymmetric stretching of C–O |
| 1225 | 1225 | Symmetric stretching of C–O |
| 1114 | 1112 | C–N Stretching |
| 800 | 797 | C–C Stretching |

UV-Visible spectral studies

The optical absorption spectra were recorded using Varian Carry–5E UV-vis spectrophotometer in the wavelength range 200–800 nm for both the crystals. The recorded absorption spectra are shown in Figures 4 and 5. From the observed spectra, it has been found that the grown crystals are absolutely transparent in the entire UV and visible regions with minimum optical absorption, which will enable the crystals to be excellent materials for second harmonic generations and optoelectronic applications. A sharp fall in absorption is observed in the spectra of pure ULM crystals at 231 nm and this corresponds to the lower cut-off wavelength or fundamental absorption of the crystal. In case of Zn(II) doped crystal, the lower cut-off wavelength is slightly shifted to 228 nm. It is also observed that the optical absorption still becomes minimum in Zn(II) doped crystal which shows that optical transparency is enhanced by doping.

**Figure 4. Optical absorption spectrum of ULM crystal**

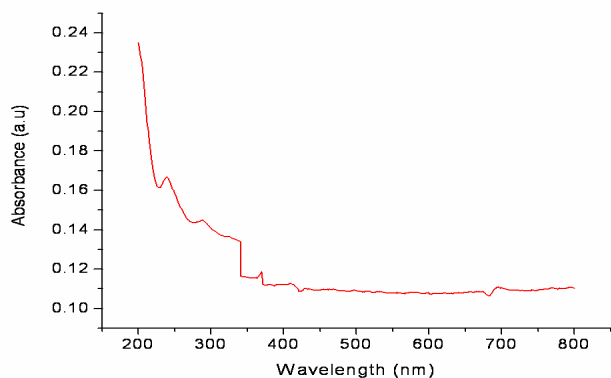


Figure 5. Optical absorption spectrum of Zn(II) doped ULM crystal

SHG study

The Second Harmonic Generation (SHG) efficiencies of ULM and Zn(II) doped ULM crystals were measured by the Kurtz and Perry powder technique [11]. In this technique, the grown crystals were grounded into fine microcrystalline powders and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser operating at the fundamental wavelength 1064nm with 8 ns pulse width and 10 Hz pulse rate has been used for this purpose. The highly intensive laser beam was made to fall normally on the sample cell. The output beam from the samples was displayed on the oscilloscope. The second harmonic signal generation was confirmed by the emission of green radiation from the samples. Powdered KDP sample has been used as reference material during output measurement. It has been observed that the SHG efficiency of ULM crystal is 2.0 times more than that of KDP. The SHG efficiency of Zn(II):ULM is 2.20 times more than that of KDP sample.

Microhardness studies

Microhardness testing is very useful technique to understand the mechanical behavior of materials [12]. Mechanical property of the material was analyzed by measuring the microhardness number with different loads. In the present work, Leitz Wetzlar Vickers microhardness tester, fitted with diamond Vickers pyramidal indenter has been used. The static indentations were made on the grown crystals for different loads at room temperature with a constant indentation time of 15 s. Due to the development of cracks at higher loads; the maximum applied load has been limited to 100 g. The Vickers microhardness number H_V of LHM crystal was determined using the formula $H_V = 1.8544 P/d^2$ kg/mm² where P is the applied load in kg and d is an average diagonal length of the indentation in mm.

A plot is drawn between hardness number (H_V) and applied load (P) for ULM and Zn(II) doped ULM crystals and are shown in Figure 6. It has been observed from the plot that the hardness increases with increasing load for both crystals. This type of behavior wherein the hardness number increases with applied load is called reverse indentation size effect (RISE). Similar hardness behavior was observed in some of organic materials such as 4APM [13] and CCBA [14]. From the graph, it is observed that hardness has been significantly increased in the Zn doped ULM crystal.

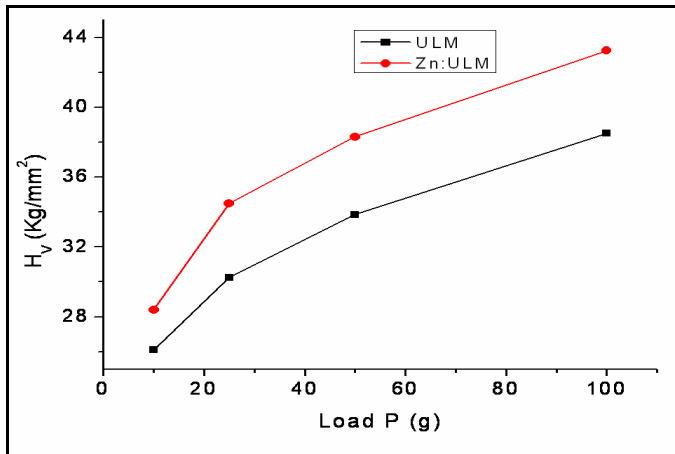


Figure 6. Plot of Hardness number (H_v) Vs load (P) for ULM and Zn(II) doped ULM

Dielectric studies

The grown ULM and Zn(II) doped ULM single crystals were subjected to dielectric studies using HIOCKI 3532-50 LCR HITESTER instrument. The cut and polished single crystals of ULM and Zn(II) doped ULM were used for dielectric measurements. The experiments were carried out in the frequency range from 50 Hz to 5 MHz at different temperatures.

Variations of dielectric loss with log frequency at different temperatures for both the crystals are shown in Figures 7 and 8. As the frequency increases, the dielectric loss decreases and at higher frequencies it almost becomes zero. The dielectric constant and dielectric loss show similar responses with frequencies at all temperatures. The low value of dielectric loss at high frequencies implies that both crystals possess better optical quality with lesser defects and this parameter is crucial for NLO materials in their application [15].

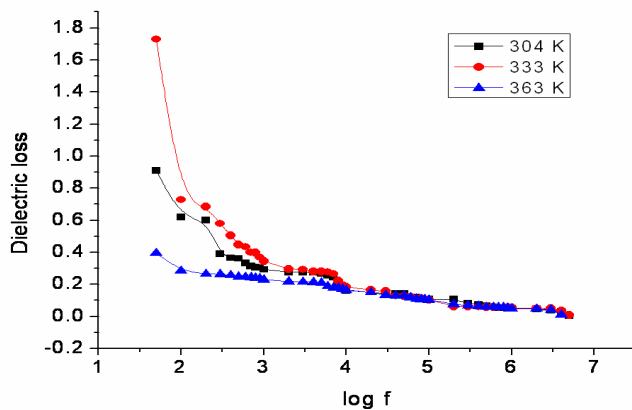


Figure 7. Variation of dielectric loss with log frequency for ULM

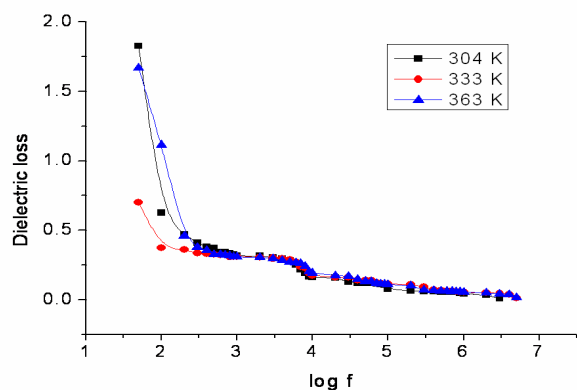


Figure 8. Variation of dielectric loss with log frequency for Zn(II) doped ULM

Conclusion

In this work, pure and transition metal Zn(II) doped ULM crystals were grown by slow solvent evaporation method at room temperature in a period of 30 days. The single crystal XRD study confirms that the grown crystals belong to monoclinic system with the space group $P2_1$. A close observation of the crystallographic data shows a marginal increase in the lattice parameters and volume for the doped crystal. The presence of various functional groups and the modes of vibrations were identified by FTIR spectroscopy. The UV-visible spectral study shows that the optical absorption is very low for both the crystals in the entire UV and visible regions. The transparency of ULM crystal is increased by the incorporation of dopant. The SHG efficiency of ULM and Zn:ULM crystals are 2.0 and 2.20 times more than that of KDP sample. Microhardness study shows that the hardness of ULM crystal has been significantly increased with Zn(II) doping. Low value of dielectric loss at high frequencies implies that both crystals possess better optical quality with lesser defects and this parameter is crucial for nonlinear optical materials in their applications.

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