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Crystallization and Characterization of Nonlinear Optical Crystals of Urea

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ABSTRACT

Single crystals of Urea family such as Urea L-malate and Zn(II) incorporated Urea L-malate were synthesized and grown by slow solvent evaporation method in aqueous solution at an ambient temperature. Effect of metal dopant Zn(II) on physicochemical properties of Urea L-malate crystal has been studied. Crystal structure was analyzed by powder and single crystal X-ray diffraction techniques which indicate that both the pure and Zn(II) doped Urea L-malate crystals are of monoclinic crystal system with P2 space group. Optical transmittance analysis was carried out to identify the optical behaviour of the grown crystals. It has been observed that the transmittance is adequate for both the crystals in the UV and visible regions. Kurtz powder method has been employed to find out the second harmonic generation efficiency of the grown crystals. The thermal decomposition and purity of the samples were studied by thermogravimetry and differential scanning calorimetry techniques. Dielectric nature of the as grown crystals Urea L-malate and Zn(II) doped Urea L-malate were studied in the frequency range of 100 Hz to 5 MHz at different temperatures.

Keywords: Crystallization, Powder crystal XRD, TG-DSC, Dielectric.

INTRODUCTION

Single crystals have strong influence in the recent technology which is clear from the modern developments in the fields of nonlinear optics, solid state lasers, semiconductors, photosensitive materials and crystalline thin films for computer and microelectronics engineering. Since the discovery of nonlinear optical phenomenon for the first time in 1961, nonlinear optical frequency conversion materials have played major role in many fields, such as optical communication, laser technology, optical data storage, optical information processing, image manipulation etc [1–3]. In recent years, generation of second harmonic wavelengths using laser diodes has been attracting a great deal of interest due to its potential applications. Organic materials are potential candidates for the above applications due to their large optical non-linearity, low cut off wavelength, short response time and high thresholds for laser power [4–6]. Organic single crystals occupy an intermediate position between inorganic crystals and polymers and hence they are the model systems to study effects caused by ion impact.

Urea exhibits promising characteristics for nonlinear optical applications due to its ability in forming transition metal complexes. It has been observed that the second harmonic efficiency of urea L-malic acid crystal was three times higher than that of the widely used KDP crystals [7]. Derivatives of urea with similar or better physicochemical properties with better growth yield have been reported [8, 9]. In continuance of the previous

works, we have grown single crystals of Urea L-malate and Zn(II) doped Urea L-malate. In the present analysis, the crystal growth, XRD, optical, thermal and dielectric nature of Urea L-malate and Zn(II) doped Urea L-malate crystals were reported.

MATERIALS AND METHODS

Analytical reagent (AR) grade chemicals of Urea and L-malic acid were obtained from Merck India Ltd. Double distilled water was used as the solvent for the growth of the title compounds. Urea L-malate was synthesized by dissolving equimolar ratio of urea and L-malic acid at room temperature (32°C). The prepared solution was continuously stirred using magnetic stirrer around 5 hours. The prepared solution was heated to dryness below an optimum temperature of 50°C. After heating to required level, colorless tiny crystalline samples were obtained in a temperature controllable water bath. To attain high purity of the compound, the samples were purified by successive crystallization process. For the purpose of growing single crystals, tiny crystalline samples with good optical transparency were used.

In order to synthesize Zn(II) doped Urea L-malate, 5wt% of Zn(II) in the form of ZnSO₄ was mixed to the saturated solution of urea L-malic acid and the same procedure was followed as that of pure crystal. During the growth process, few drops of hydrogen peroxide were added to the solutions to hinder the growth of any microorganism. Good quality Urea L-malate single crystal of dimension 20mm×8mm×4mm and Zn(II) doped Urea L-malate of dimension 24mm×14mm×7mm were obtained in a period of 30 days and are shown in Figure 1.

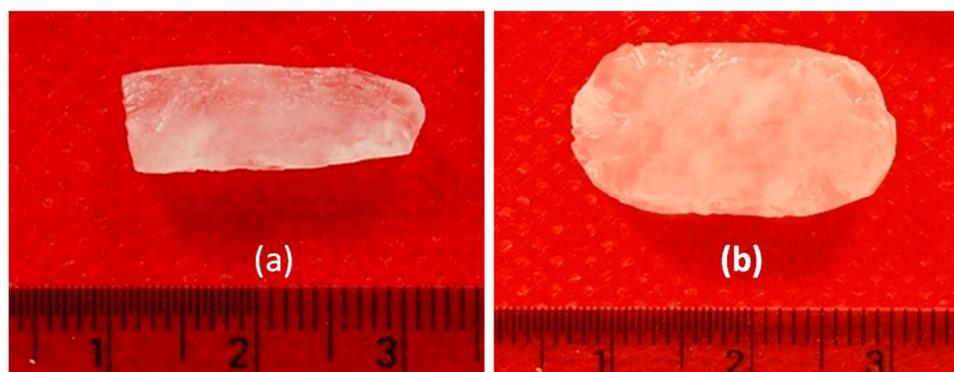


Figure 1 (a) As grown Urea L-malate and (b) Zn(II) doped Urea L-malate crystals

RESULTS AND DISCUSSION

Powder and single crystal XRD analysis

The internal arrangement of atoms or molecules in a crystalline compound can be studied by X-ray diffraction technique. The given samples were analyzed by powder XRD and single crystal XRD techniques. The powdered samples of pure and doped Urea L-malate were scanned between the 2θ ranges from 10° to 80° at a scan speed of 3 deg/min using a continuous mode X-ray diffractometer with Cu_K-beta (30 kV, 100 mA) radiation. The obtained XRD patterns are displayed in Fig. 2 and 3. In case of Zn(II) doped crystal, some additional peaks are observed in the diffraction pattern. Miller indices of the planes have been calculated and Bragg's peaks have been indexed. The peaks intensities with full width half maximum (FWHM) values, 2θ values, d-spacing and miller indices are listed in Tables 1 and 2 for pure and Zn(II) doped Urea L-malate crystals. The results were analyzed using PROSZKI software package from which it has been found that the pure and Zn(II) doped crystals belong to monoclinic system with the space group P2. The sharp nature of the diffraction peaks illustrates good crystallinity of the compounds [10].

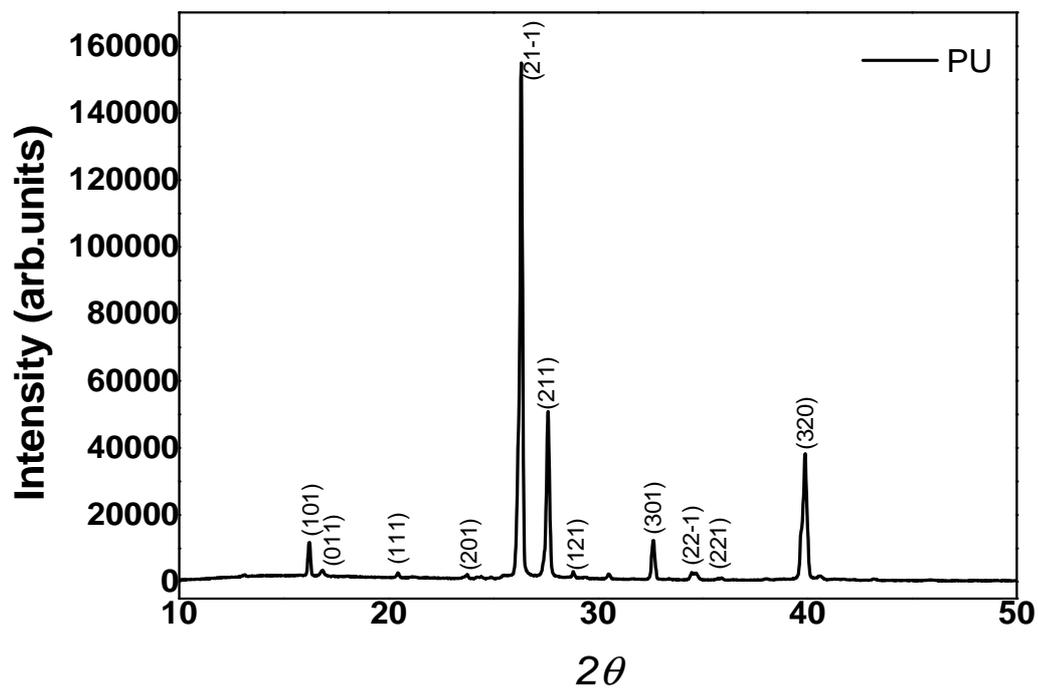


Figure 2 Powder XRD pattern for Urea L-malate

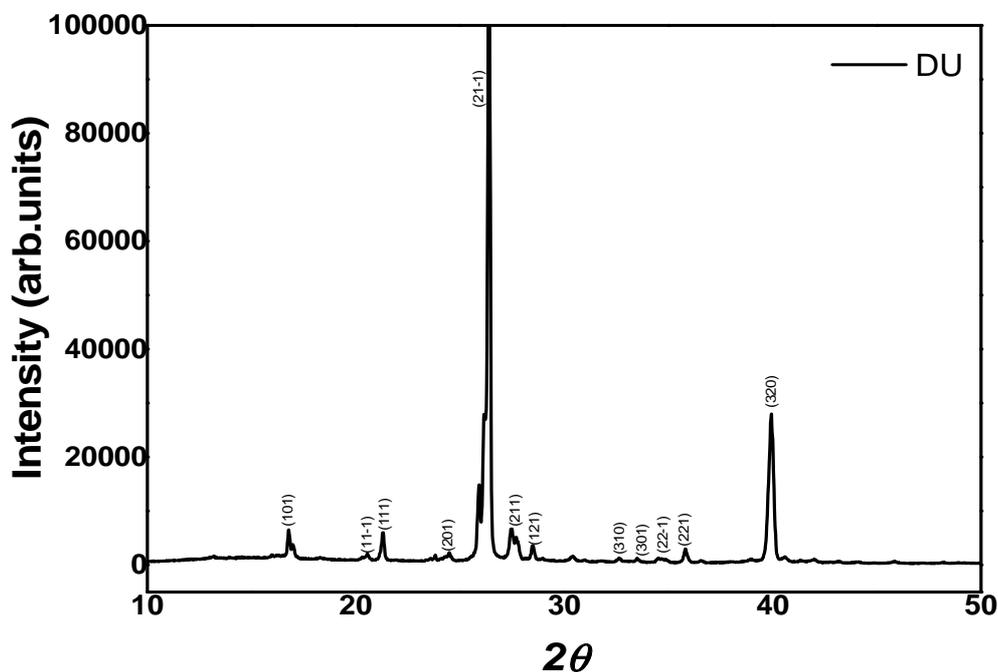


Fig.3 Powder XRD pattern for Zn(II) doped Urea L-malate

Table 1 Powder XRD data for Urea L-malate

2-theta (deg)	Height (cps)	FWHM (deg)	d-spacing (Å)	hkl
16.201(3)	7305(135)	0.1238(18)	5.4666(8)	101
16.802(12)	1124(53)	0.185(11)	5.272(4)	011
20.429(4)	1250(56)	0.083(7)	4.3437(8)	111
23.756(8)	965(49)	0.092(15)	3.7425(12)	201
26.3309(8)	127602(565)	0.0857(15)	3.38200(10)	21-1
27.601(3)	38062(308)	0.139(3)	3.2291(4)	211
28.815(6)	1661(64)	0.086(9)	3.0959(6)	121
32.622(4)	9609(155)	0.138(3)	2.7427(3)	301
34.681(13)	1430(60)	0.25(3)	2.5845(9)	22-1
35.82(3)	364(30)	0.29(3)	2.505(2)	221
39.8975(14)	26153(256)	0.125(5)	2.25774(7)	320

Table 2 Powder XRD data for Zn(II) doped Urea L-malate

2-theta (deg)	Height (cps)	FWHM (deg)	d-spacing (Å)	hkl
16.748(3)	3651(96)	0.079(6)	5.2893(8)	101
20.558(5)	801(45)	0.169(13)	4.3168(10)	11-1
21.312(5)	3765(97)	0.143(5)	4.1657(10)	111
24.460(11)	930(48)	0.217(15)	3.6362(17)	201
26.3848(11)	106229(515)	0.0953(14)	3.37521(13)	21-1
27.455(8)	3983(100)	0.196(11)	3.2461(9)	211
28.472(9)	2218(74)	0.128(10)	3.1324(10)	121
32.622(15)	457(34)	0.187(18)	2.7427(12)	310
33.503(11)	561(37)	0.12(2)	2.6726(9)	301
34.49(2)	475(34)	0.451(19)	2.5986(17)	22-1
35.822(8)	1916(69)	0.155(8)	2.5047(5)	221
39.924(2)	19555(221)	0.2466(17)	2.25630(13)	320

The crystalline nature of pure and Zn(II) doped Urea L-malate were also confirmed by single crystal XRD analysis. The single crystal X-ray crystallography data confirms that the Urea L-malate crystal belongs to monoclinic system with P2 space group and $V = 924(3) \text{ \AA}^3$. The lattice parameters are $a = 9.24(2) \text{ \AA}$, $b = 7.23(5) \text{ \AA}$, $c = 13.86(3) \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 93.40^\circ$. The doped crystal also belongs to the same distal system with the volume $V = 930(9) \text{ \AA}^3$. The lattice parameters of Zn(II) doped crystal are $a = 9.28(5) \text{ \AA}$, $b = 7.20(2) \text{ \AA}$, $c = 13.95(7) \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 93.37^\circ$. A slight increase in dimensions has been observed in case of Zn(II) doped crystal and this may be attributed to the presence of dopant in the lattice of pure crystal.

Optical transmittance studies

Suitability of the crystals in the transmittance range for optical applications has been identified using UV-Visible spectral analysis [11, 12]. The transmittance spectra were recorded in the wavelength range 200–800 nm. The recorded optical spectra are shown in Figures 4 and 5. From the optical spectra, it has been observed that both crystals are totally transparent in the near UV and visible spectral regions. In the spectra of pure Urea L-malate crystal, a sharp fall in transmittance is observed at 232 nm and this specifies it's the lower cut-off wavelength. In case of Zn(II) doped crystal, the lower cut-off wavelength is shifted to 228 nm. In case of Zn(II) doped crystal, the optical transmittance still becomes better which enable the crystal to be suitable materials for second harmonic generations and optoelectronic applications.

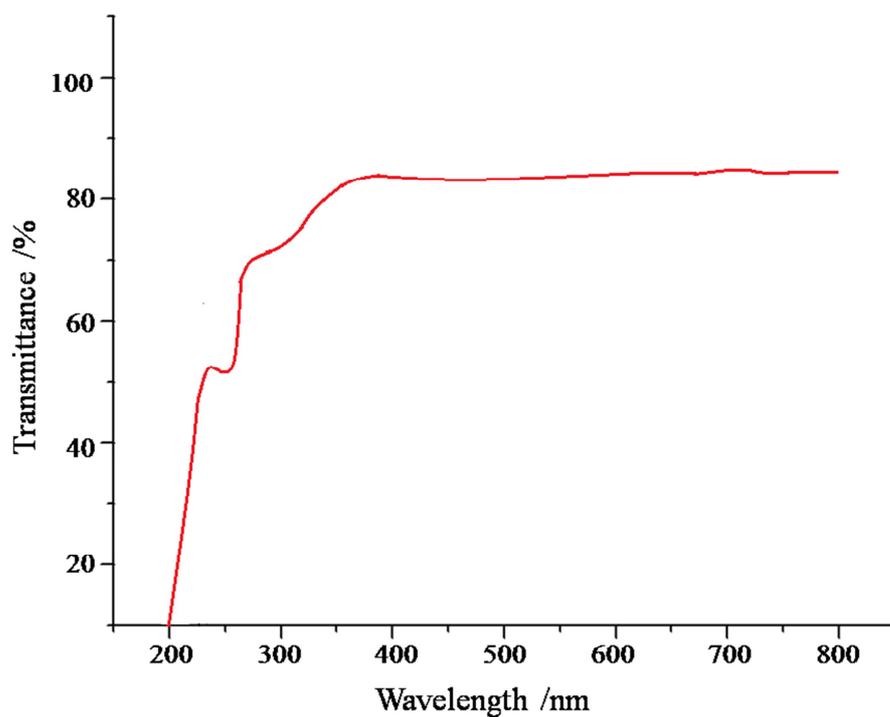


Figure 4 Optical transmittance spectrum of Urea L-malate

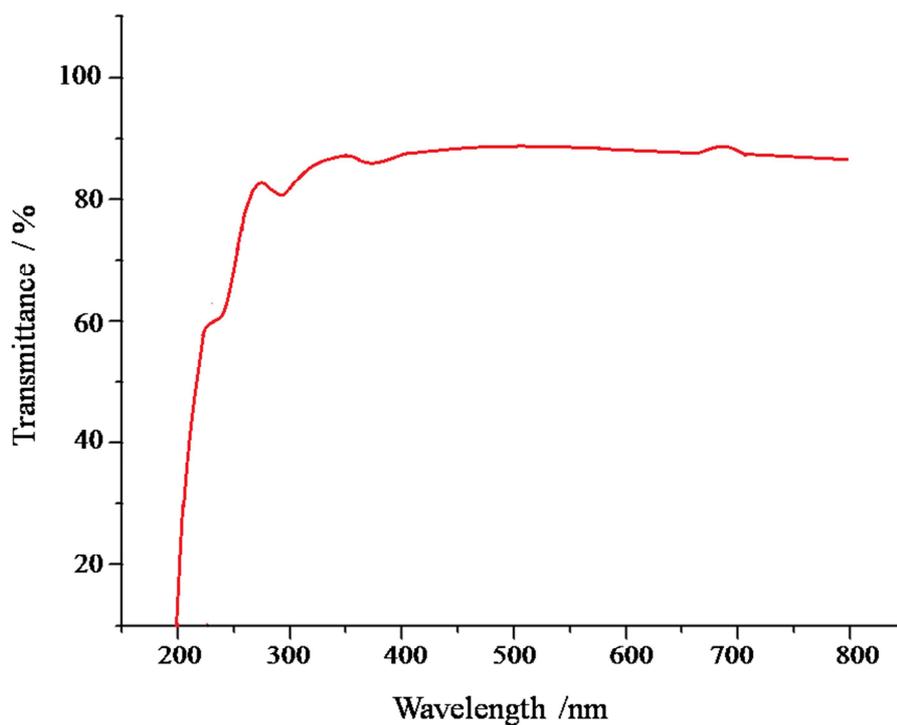


Figure 5 Optical transmittance spectrum of Zn(II) doped Urea L-malate

Second Harmonic Generation Study

The conventional Kurtz and Perry powder technique has been used for the measurement of Second harmonic generation efficiencies of pure and Zn(II) doped Urea L-malate crystals [13]. The grown crystalline samples were grounded into fine microcrystalline powders and densely packed between two transparent glass slides. The samples were exposed to Q-switched Nd:YAG laser operating at the fundamental wavelength 1064nm with 8 ns pulse width and 10 Hz pulse rate. The highly intensive laser beam was allowed to fall normally on the sample cell. The emission of green radiation from the sample confirms the second harmonic generation by the crystals. Powdered KDP samples were used as reference material for the output measurement. Measurements show that the SHG efficiency of Urea L-malate crystal is 2.0 times more than that of KDP. In case of Zn(II) doped crystal, it is 2.20 times higher than that of standard KDP

Thermal analysis (TG and DSC)

Thermogravimetric and Differential Scanning Calorimetry (TG-DSC) analyses are of much significant methods as far as fabrication technology is concerned, as they provide thermal stability of the compounds for fabrication purpose, where a substantial amount of heat is generated during the cutting process [14]. Thermal analysis was performed on the grown pure and doped Urea L-malate crystals to study the thermal degradation and melting point. The TG and DSC analyses were simultaneously carried out for both the crystals using NETZSCH STA 449F3 thermal analyzer with Al₂O₃ crucible in the temperature range 25–1400°C at a heating rate of 10°C/min. The readings were taken under nitrogen atmosphere and the simultaneously recorded TG-DSC traces are depicted in figures 6 and 7.

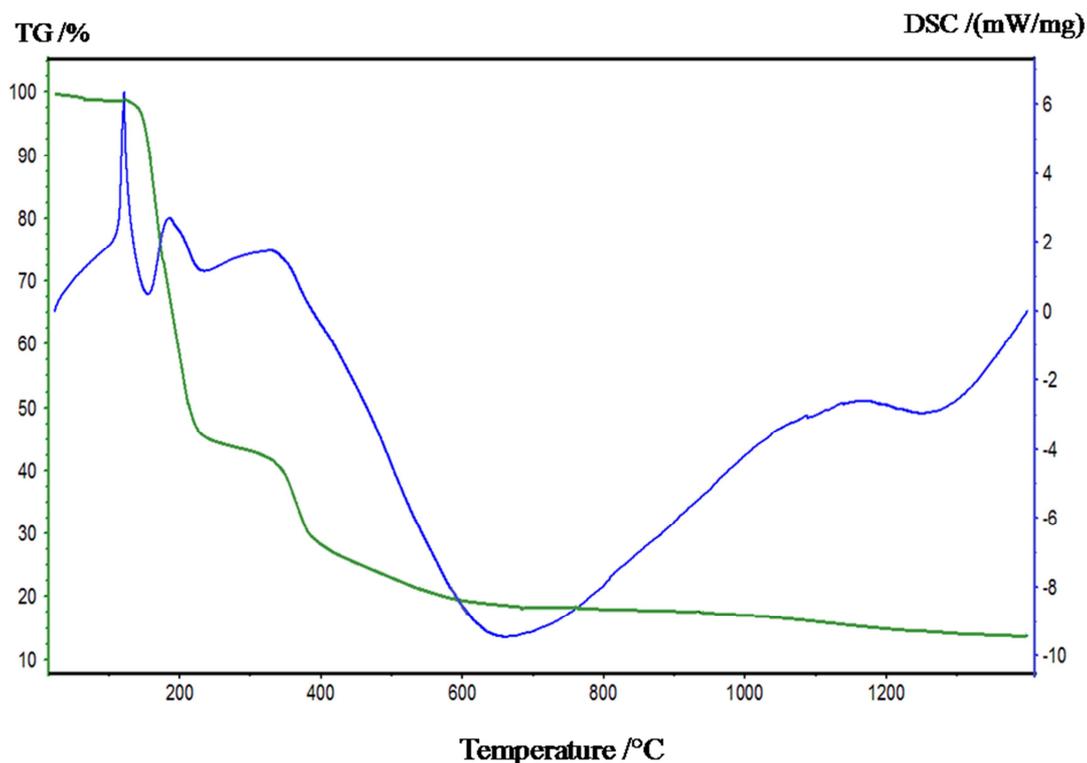


Figure 6 TG-DSC traces for Urea L-malate

The TG trace of pure Urea L-malate appear almost straight upto 122°C and then it shows a major mass loss (55.61%) in the temperature range 122°C –295°C, which is attributed to melting and partial degradation of the compound. In the TG trace, another mass loss of compound (21.25%) occurring in between 295 and 510°C corresponds to complete degradation and partial volatilization of the substance. In the subsequence steps, there is a mass loss (13.68%) between 510 and 1400°C, due to the decomposition of remaining substance and release of

gaseous products. The initial mass of the compound subjected for the analysis was 3.684 mg and the remaining final mass after the study was only 9.46% of the initial mass and it shows bulk decomposition of the substance. But, in the case of Zn(II)-doped Urea L-malate crystal, the first stage of major mass loss take place in the temperature range 130–300°C and the second stage of mass loss takes place at around 300–520°C.

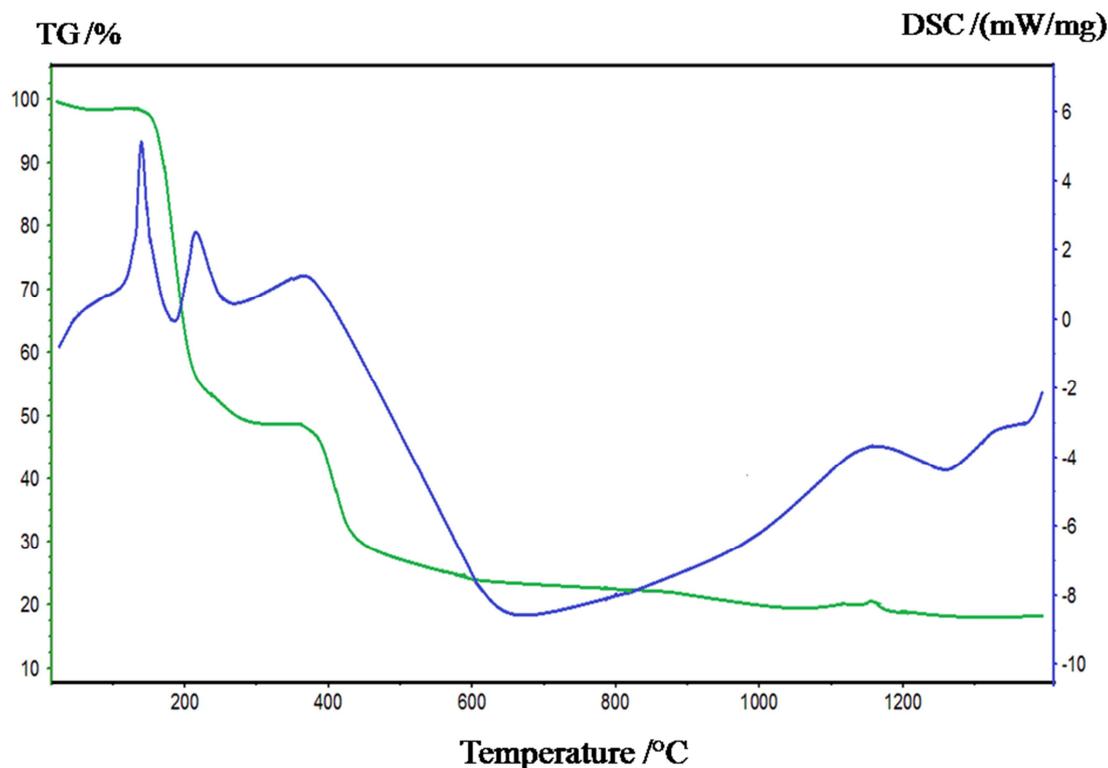


Figure 7 TG-DSC traces for Zn(II) doped Urea L-malate

In the temperature range 122°C –295°C, the DSC trace for pure Urea L-malate shows two sharp endothermic peaks, one at 122°C and another peak at 185°C which are attributed to the removal weakly entrapped water and partial degradation of compound. This is followed by another peak at around 328°C which shows the decomposition of the remaining compound. The DSC trace of the doped crystal also shows the same endothermic peaks which are slightly shifted and appear at 128 and 195°C. This indicates that the melting point of Urea L-malate crystal has been slightly increased with the inclusion of Zn(II) dopant in the pure crystalline material.

Dielectric studies

In order to study the lattice dynamics in the crystal, the dielectric measurements were carried out for the grown compounds. Polished single crystals of Urea L-malate and Zn(II) doped crystals were used for dielectric measurements. The experiments were carried out in the frequency range from 50 Hz to 5 MHz at 304 K, 333 K and 363 K temperatures. The variations of dielectric constant with log frequency at different temperatures are shown in Figures 8 and 9. It has been observed that the dielectric constant of Urea L-malate crystal is higher at lower frequencies and decreases exponentially with increasing frequency and reaches a minimum value at higher frequencies. This can be understood on the basis of polarization mechanism. Usually, at low frequencies the contributions of electronic, ionic, dipolar and space charge polarizations are significant. As the frequency increases, space charge cannot follow the external field and hence polarization decreases, giving rise to smaller values of dielectric constant. Dielectric constant is almost same at higher frequencies for all temperatures. The dielectric constant of Zn(II) doped Urea L-malate crystal shows the same trend as that of pure crystal but its value is less than pure crystal.

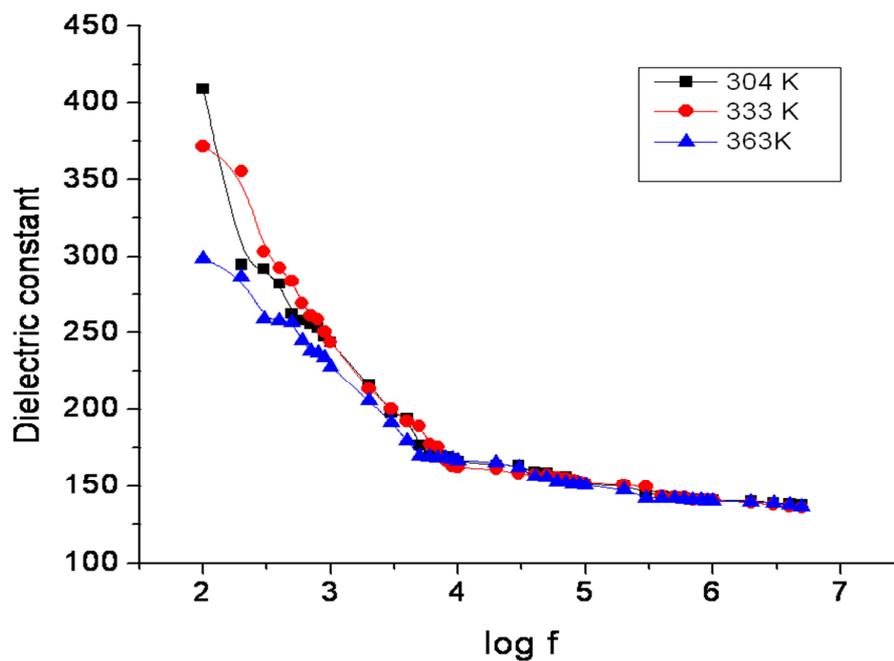


Figure 8 Variation of dielectric constant with log frequency for Urea L-malate

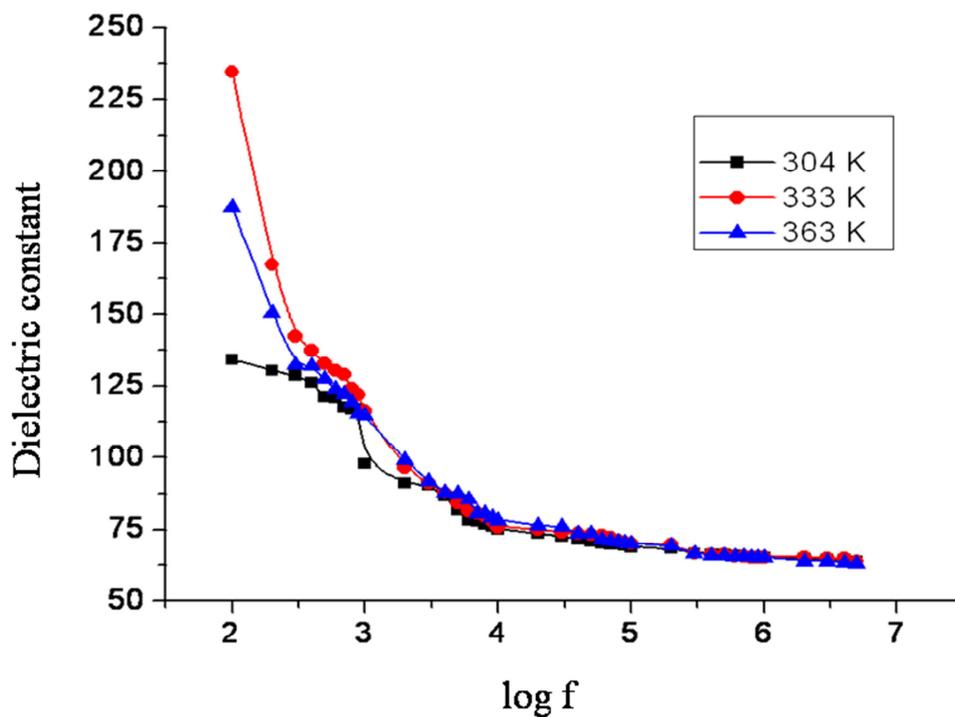


Figure 9 Variation of dielectric constant with log frequency for Zn(II) doped Urea L-malate

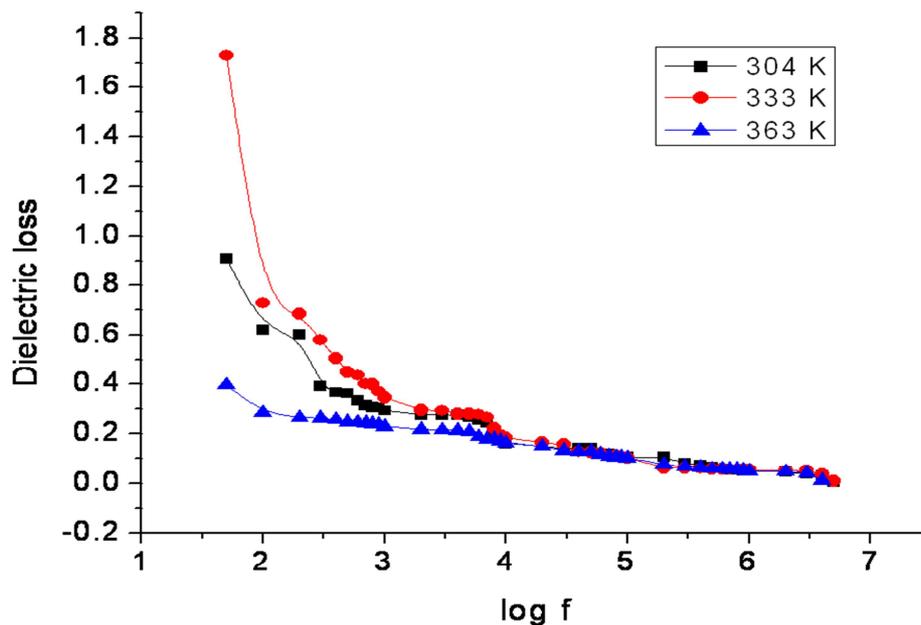


Figure 10 Variation of dielectric loss with log frequency for Urea L-malate

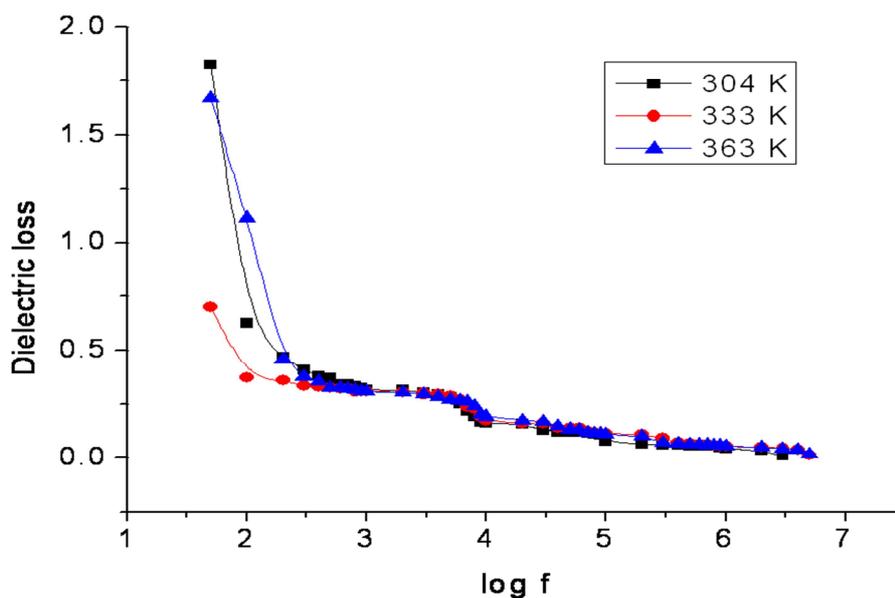


Figure 11 Variation of dielectric loss with log frequency for Zn(II) doped Urea L-malate

Variations of dielectric loss with log frequency at at 304 K, 333 K and 363 K temperatures are shown in Figures 10 and 11. Dielectric loss decreases as the frequency increases and it almost becomes zero at higher frequencies. The dielectric constant and dielectric loss show same trends with varying frequencies. The small values of dielectric loss at high frequencies mean that both pure and doped Urea L-malate crystals possess enhanced optical quality with lesser defects [15].

CONCLUSION

Single crystals of Urea L-malate and Zn(II) incorporated Urea L-malate were grown from aqueous solution by slow evaporation technique at room temperature in a period of 30 days. The powder and single crystal XRD studies substantiate that the grown crystals are of monoclinic system with the space group P2. The UV-visible spectral analysis reveals that the optical transmittance is fairly good for the pure and doped Urea L-malate crystals in the entire UV and visible regions. It also shows that the optical transparency of Urea L-malate crystal is slightly increased by the incorporation of Zn(II) dopant. The nonlinear optical property is confirmed by SHG measurements. Thermal studies indicates that Zn(II) doped Urea L-malate crystal is more stable than pure crystal. Dielectric studies shows that the dielectric constant for pure and Zn(II) doped Urea L-malate crystals found to be decreasing at high frequencies. Due to the existence of wide optical transparency and enhanced SHG efficiency, these crystals may be useful for nonlinear applications.

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