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Growth and characterization of Urea succinic acid (USA) single crystal by using slow evaporation process

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ABSTRACT

Good optical quality single crystal of urea succinic acid (USA) was grown by slow solvent evaporation technique. The grown crystal was characterized by X-ray diffraction (XRD), Fourier Transform Infra-red (FTIR), thermal analysis (TG-DTA), UV absorption and dielectric studies. The dielectric constant and dielectric loss of the crystal was studied as function of frequency and the results are discussed. The optical absorption studies indicate that for the sample, optical transparency window is quite wide making it suitable for NLO applications.

Keywords: Organic NLO crystal; USA; slow evaporation process; optical studies; dielectric studies.

INTRODUCTION

The crystallization of several families of organic compounds may be of interest for nonlinear optical applications in the visible and UV regions of the spectrum. Urea (H_2NCONH_2) has shown interesting properties for nonlinear optical applications [1]. Its crystallization is difficult, even if, with some efforts, but satisfactory results have been achieved by solution- and vapour-growth. Its optical and mechanical properties are comparable to those of ADP or KDP crystals [2]. Urea and its derivatives are widely used in crystal engineering and supramolecular chemistry for their versatility in the design and synthesis of solid-state structures and functional materials [3,4]. Unlike mineral acids, organic acids form stable hydrogen-bonded systems with urea [5]. 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 [6]. For that reason they usually show irregular growth habits. So in order to get better growth habit we have tried to grow urea succinic acid (USA) single crystals by slow evaporation process followed by characterizations like single crystal X-ray diffraction

(XRD), Fourier transform infrared (FTIR), Optical absorption spectrum (UV), thermal and dielectric studies.

2. 1. Experimental procedure

Equimolar amount of urea and succinic acid were taken in a beaker containing doubly deionized water. The formation of urea succinic acid (USA) is expressed below

$$CH_4N_2O + C_4H_6O_4 \xrightarrow{H_2O} [(CH_4N_2O).C_4H_6O_4]$$

In our present study, USA crystals were grown at room temperature by slow evaporation technique by dissolving stoichiometric ratio of urea and succinic acid in 100 ml of deionized water under magnetic stirring. The temperature was maintained around 35°C to avoid any decomposition of element from the compound. After two weeks, a colorless, transparent crystal was obtained. The photograph of the as-grown crystal is presented in Fig.1.

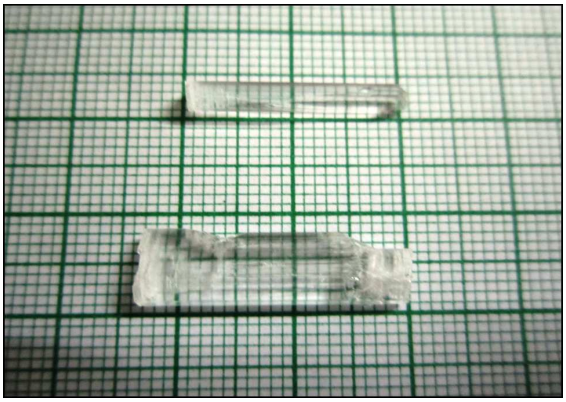

Fig. 1. As grown crystal of Urea succinic acid.

2.2 Characterization

The single crystal X-ray diffraction study of USA single crystals was carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer. Fourier transform infrared (FTIR) spectrum of USA crystal was recorded at a resolution 2 cm^{-1} in the range 400–4000 cm^{-1} employing Bruker IFS-66V spectrophotometer using KBr-pellet technique. The optical absorption spectra of USA crystals were recorded in the range 200 – 2000 nm using Varian Cary 5E spectrophotometer. Thermal stability and physiochemical changes of the sample were analyzed by recording the TGA and DTA spectrum (TGA Q500 V20.10 Build 36 thermal analyzer) in the temperature range 30–385°C in nitrogen atmosphere at a heating rate of 20°C/min. The temperature dependent dielectric constant and dielectric loss of USA crystal was measured using HIOKI 3532 LCR HITESTER in the frequency range 50 Hz –5 MHz. In order to ensure good electrical contact between the crystal and the electrodes, a sample of cross-sectional area 49.377 mm^2 and thickness 3.76 mm was coated with silver paint.

RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis of USA crystal was carried using an X-ray diffractometer, and the calculated lattice parameter values are a=5.61 Å, b=8.22 Å, and c=12.15 Å. The grown USA crystal belongs to monoclinic structure. The Lattice parameter value of USA single crystals are listed in table 1.

Table 1: Lattice parameters of USA crystal

Sample	Lattice Parameters						
	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	V(Å^3)
USA	5.61	8.22	12.15	90.00	96.71.00	90.00	556

3.2 FTIR studies

Fig.2 shows the FTIR spectrum of USA crystal. The broad envelope in the high energy region between 3487cm^{-1} and 2592 cm^{-1} is due to NH_3^+ stretching vibrations. In the frequency range of 2500 to 1600 cm^{-1} an absorption band appears at 1613 cm^{-1} which is attributed to NH_2 deformation. The C = O stretch of carbonyl groups displays its characteristic peak at ~1710 cm^{-1}. The band appearing at 704 cm^{-1} infers the C–O–H stretching of the USA crystals. The peak due to the torsional NH oscillations of NH_3^+ is observed at ~540 cm^{-1}.

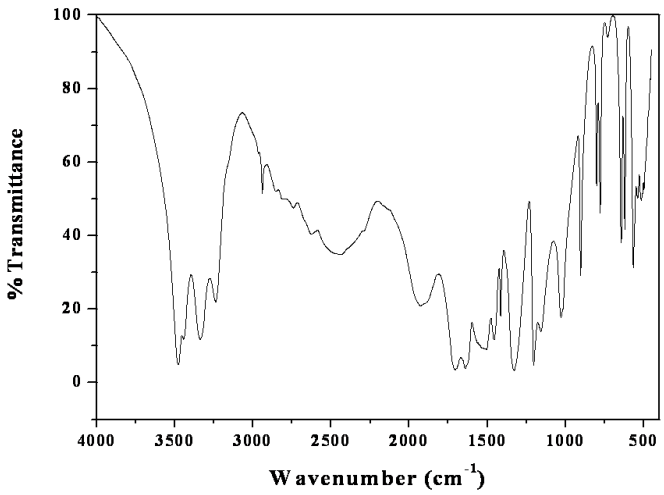

Figure 2 FTIR spectrum of USA

3.3 Thermal studies

Thermo gravimetric and differential thermal analyses give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. The thermo gravimetric analysis of USA crystal was carried out between 30 °C and 300 °C in the nitrogen atmosphere at a heating rate of 20 °C min^{-1} using TGA Q500 V20.10 Build 36 thermal analyzer. The thermogram and the differential thermogravimetric trace of USA are shown in Fig.3. In TGA, there is no weight loss up to 144°C. This indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization. It is seen that the

major weight loss (around 59.82%) starts at 175°C and it continues up to 220°C. The nature of weight loss indicates the decomposition point of the material. Further small weight loss continues up to 250°C (4.783%). However, above this temperature, no weight loss has been observed. In the DTA, the strong exothermic peaks located at ~158°C, 205°C and 242°C depict the crystallization of some of the phases of the decomposed material.

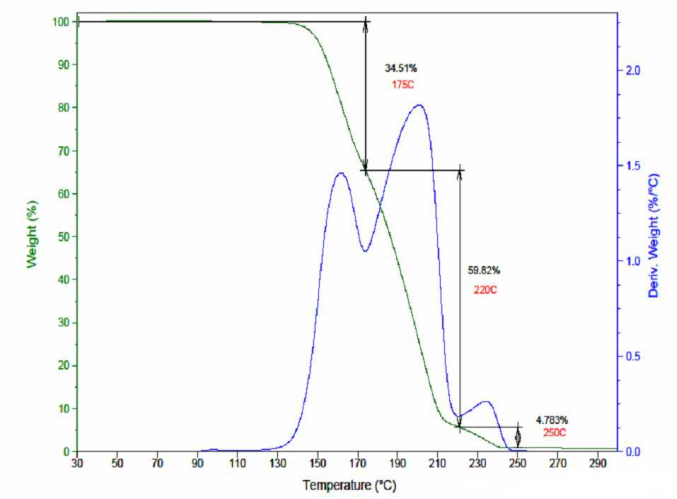

Fig. 3. TGA and DTA thermogram of USA crystal

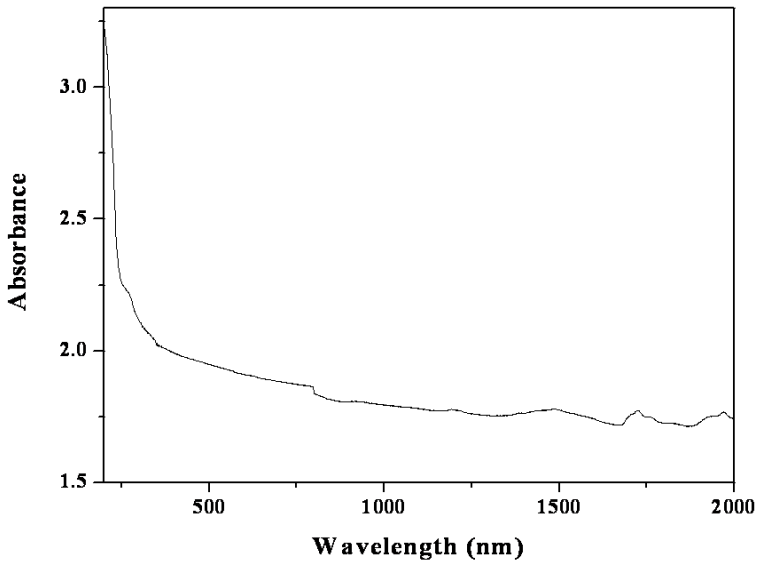

Figure 4 UV absorption spectrum of USA

3.4 UV–Vis–NIR spectrum

Fig. 4 shows the UV-Vis-NIR spectrum recorded with highly transparent single crystal of USA crystal. It is seen from the absorption spectrum that the crystal is transparent in the entire range (240 to 2000 nm) without any absorption peak, which is an essential parameter for NLO crystals. It is further observed that the UV cut-off of USA is at ~241 nm making the applications in the blue region easier with laser. The absence of absorption of light in the visible region is an

intrinsic property of all the amino acids. The low percentage of absorbance in the entire visible region is a desirous property for NLO application. Minimum absorbance is also revealed in the near infrared region.

3.5 Dielectric studies

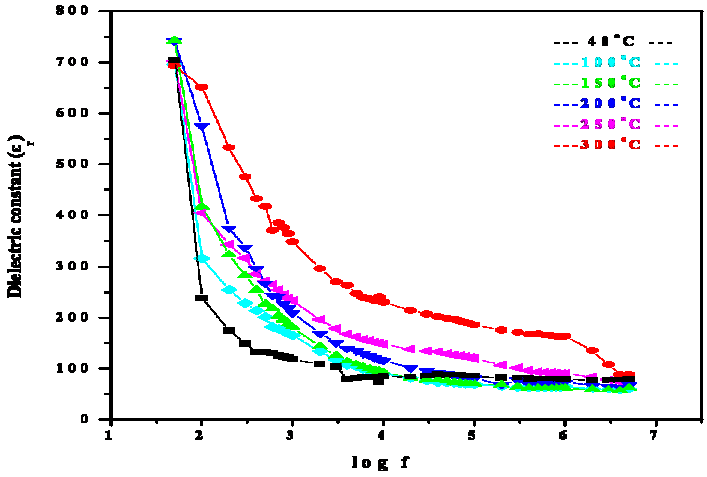

Figure 5 (a) Variation of dielectric constant Vs frequency, for USA single crystals at different temperatures

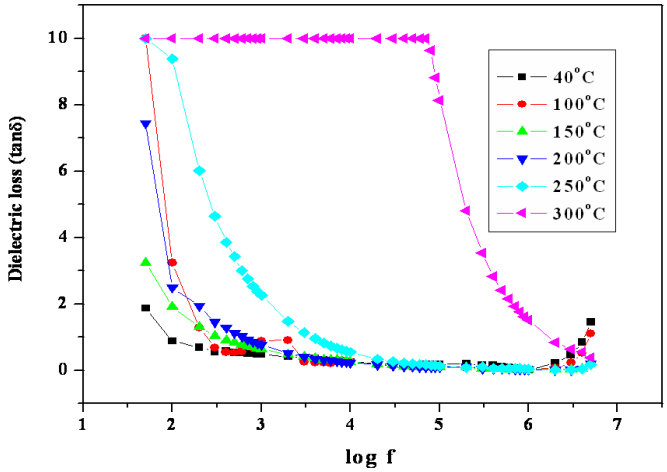

Figure 5 (b) Variation of dielectric loss Vs frequency, for USA single crystals at different temperatures

Figure 5a shows the plot of dielectric constant (εr) versus log frequency. The dielectric constant of the crystal can be calculated using the equation

$$\varepsilon_r = Cd/A\varepsilon_o \qquad (1)$$

where d is the thickness of the sample, A is the area of the sample, C is the capacitance of the sample, ε_o is the permittivity of free space and ε_r is the dielectric constant of the sample. The observed ε_r values are found to be very high at lower frequencies, which may be due to the contribution of all four types of polarizations (space charge, dipolar, ionic and electronic). As the

frequency increases, ε_r decreases sharply up to 1 kHz and then it is constant up to 5MHz. This behaviour of ε_r at higher frequencies may be a result of the negligible space charge and dipolar polarization in this range, where only the ionic and electronic parts survive [7]. The variation of dielectric loss with frequency is shown in Figure 5b. The characteristic of low dielectric loss with high frequency for a given sample suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application [8].

CONCLUSION

Large size and optically transparent single crystals of USA were grown successfully from aqueous solution. The crystal structure was elucidated using the single crystal XRD. The functional groups and the modes of vibrations were identified by FT-IR spectroscopic analysis. It is found that both dielectric constant and loss decrease with increase in frequency. The optical absorption studies indicate that for the sample, optical transparency window is quite wide making it suitable for NLO applications. Based on these observations we can say that USA can be a promising non linear material, which can be possibly used for fabrication of photon devices.

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