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Structural, optical, thermal, mechanical, dielectric and laser damage threshold studies of a succinate salt of creatinine for nonlinear optical applications

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ABSTRACT

In this work, the structural, optical, mechanical, dielectric, thermal and laser-induced damage threshold (LDT) studies of a promising organic NLO material creatininium succinate (CS) were reported. CS exhibits admirable properties such as good thermal stability (247 °C), low dielectric constant (ε_r=8.5) at higher frequencies and higher LDT up to 5.24 GW/cm^2 (3.5 times greater than urea) which favor this material most suitable for advanced laser applications.

1. Introduction

In current scenario nonlinear optical (NLO) material research concomitantly increases due to its tremendous applications in the area of opto-electronics and development of broadband integrated photonic devices, such as micro resonator filters and modulators [1–3]. Especially, the second-order NLO materials play a major role in the growth of science and technology [4,5]. However, commercial inorganic NLO crystals exhibit remarkable optical nonlinearity, it has some drawbacks such as poor crystal quality and low LDT value which limits the real world applications [6–8]. Consequently, it is desirable to discover a NLO material with high LDT to overcome this difficulty. Organic NLO materials exhibit extremely high nonlinear optical effects, low dielectric constant at higher frequencies, high data storage and high LDT values over inorganic materials [9–11]. The intrinsic defects in organic crystals also enhance the second harmonic generation with the usage of external laser field [12]. Organic single crystals are widely used in solid state laser, electro-optic, light emitting transistor, optical parametric oscillation and tetra-hertz wave generation applications [13–15]. Accordingly, there is a great interest in synthesizing a new organic NLO materials and grow its single crystals with large NLO properties. Creatinine (2-amino- 1, 5-dihydro- 1-methyl-4H-imidazol-4-one, $C_4H_7N_3O$) is synthesized from creatine, a molecule involving in energy production in muscles [16]. It is an excellent proton acceptor, already employed in the synthesis of some proton-transfer complexes [17]. Previously, some of the succinic acid single crystals have been reported with favorable NLO activity [18–21]. Motivated by these facts, creatinine was treated with succinic acid to obtain an organic NLO material, CS. Here, the structural, optical, mechanical, dielectric, thermal and LDT studies of CS were carried out and the results were analysed.

2. Experimental details

Creatinine (56.5 mg, 0.5 M) and succinic acid (59 mg, 0.5 M) were dissolved in 20 ml of deionized water in a 1:1 M ratio (Fig. 1a). The homogeneous solution was prepared and kept for slow evaporation. After 6 days, single crystals were harvested and successive recrystallizations were performed for enhancing the quality.

The ^{1}H and ^{13}C NMR spectra were recorded by Bruker 500 MHz spectrometer using deuterated D_2O as solvent. Powder X-ray diffraction (PXRD) was carried out by PANalytical XPERT-PRO diffractometer with Cu Kα radiation (λ=1.5418 Å). Photoluminescence spectra was recorded using Shimadzu RF5301 spectrofluorometer. The mechanical strength was studied using

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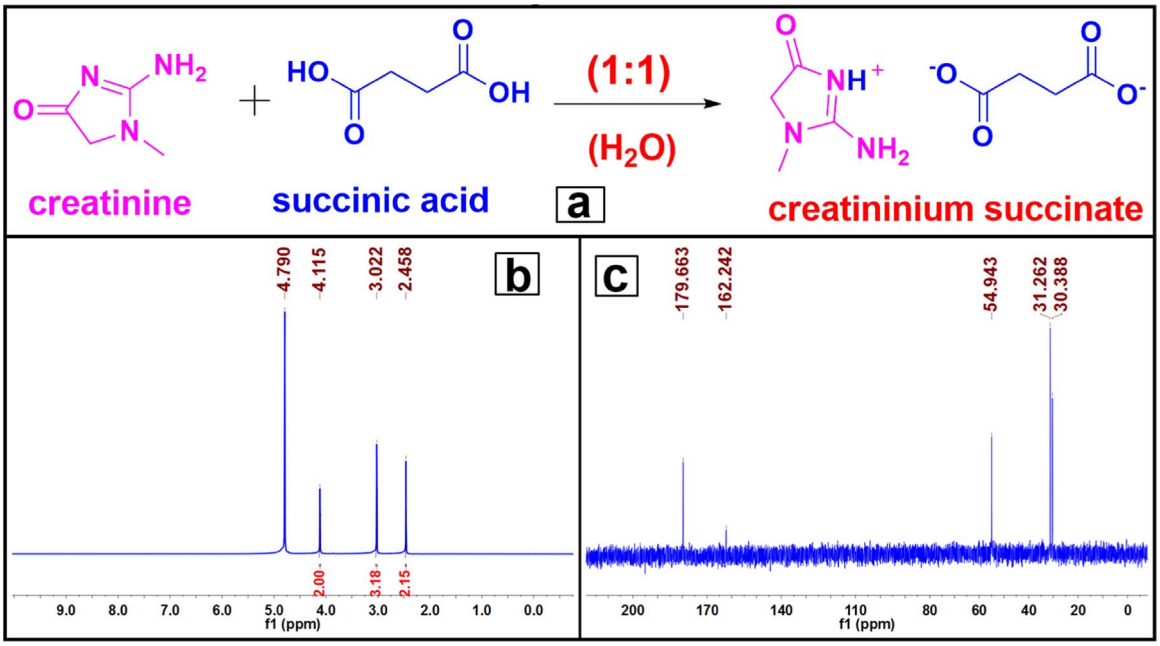

Fig. 1. (a) Reaction scheme of CS, (b) ^{1}H NMR (300 MHz, D_2O) spectrum, (c) ^{13}C NMR (75 MHz, D_2O) spectrum.

the Shimadzu HMV-2000 Vicker's indentation tester. The dielectric property was analysed by the HIOKI 3532-50 LCR HITESTER. Thermal analysis was carried out using NETZSCH STA 409 °C/CD instrument at a heating rate of 10 °C /min.

3. Results and discussion

The ^{1}H NMR (Fig. 1b) obviously specifies the existence of three sets of protons and the chemical shifts (NH_2, OH and NH^+ were exchangeable in D_2O). The singlets observed at 2.45 and 4.11 ppm were attributed to the protons of methylene unit present in the succinate and creatinine moiety, respectively. The protons of the N-methyl unit attached to the creatinine were detected at 3.02 ppm. In ^{13}C NMR (Fig. 1c), the peaks appeared at 30.38 and 54.94 ppm represents the existence of the methylene unit present in the succinate and creatinine respectively. The peaks found at 162.24 and 179.66 ppm (near downfield region) attributes the presence of succinate and creatinine carbonyl unit. Similarly, the peak appeared at 31.26 ppm indicates the presence of the N-methyl unit, which suggest the presence of creatinine ring.

The indexed PXRD pattern of CS (Fig. 2a) was compared with the stimulated pattern (Fig. 2b) obtained from crystallographic file (cif) using the Mercury software. The lattice parameters were calculated using TREOR 90 program and found in good agreement with the single crystal XRD data which are given in Table 1 [22].

The luminescence spectrum (Fig. 2c) shows an intense peak around 361 nm at the ultraviolet (UV) region, which is due to the electronic transition from π^*-π molecular orbital of creatinine. The quaternary nitrogen proton is involved in the rapid proton transfer with carboxylate oxygen, which is predominant in the fluorescence activity. Thus, CS crystal might be useful in UV light emitting

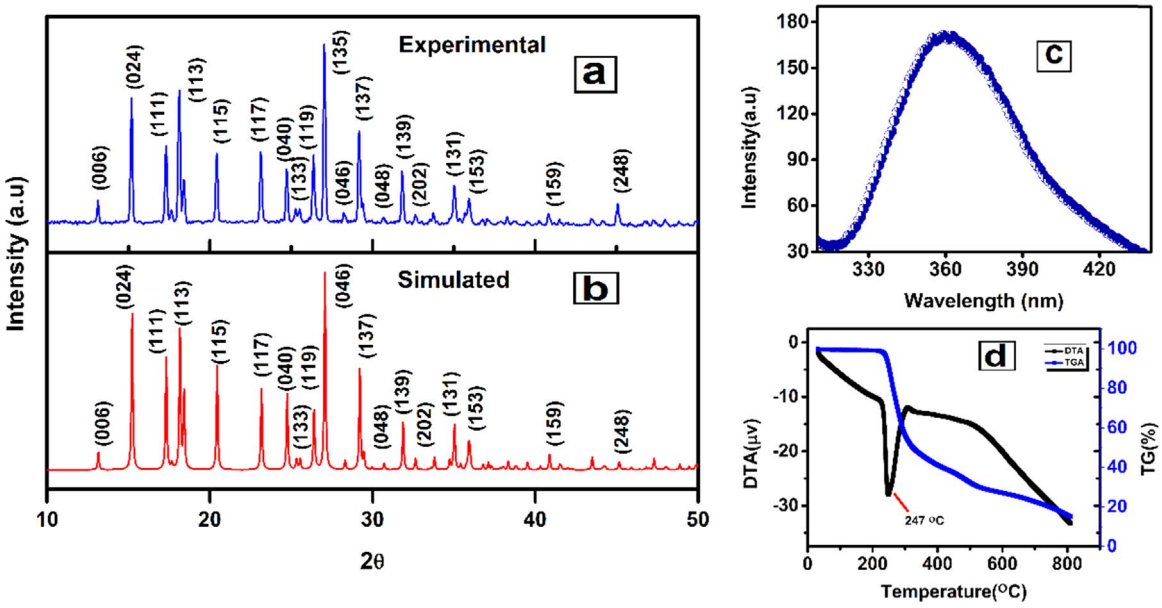

Fig. 2. (a) Experimental/upper line, (b) Simulated/lower line, (c) Luminescence emission spectrum, (d) TGA/DTA curve of CS crystal.