



Synthesis, growth, characterisation and laser damage threshold studies of *N,N*-dimethylanilinium-3-carboxy-4-hydroxybenzenesulphonate crystal: An efficient SHG material for electro-optic applications



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ABSTRACT

An NLO active organic proton transfer complex salt, *N,N*-Dimethylanilinium-3-carboxy-4-hydroxybenzenesulphonate has been synthesized and single crystals grown by slow solvent evaporation solution growth technique at ambient temperature. The synthesized salt was characterized by UV–visible absorption, UV–vis–NIR transmission spectral studies and elemental analysis. The formation of the salt and the crystal structure have been confirmed by single crystal X-ray diffraction (XRD) analysis and the title crystal belongs to monoclinic crystal system with the non-centrosymmetric space group, *Pc*. The FT-IR spectrum was recorded to confirm the presence of various functional groups in the grown crystal. The molecular structure of the crystal was further confirmed by ^1H and ^{13}C NMR spectra. The TG/DTA analyses were carried out to establish the thermal stability of the title crystal. The dielectric constant and dielectric loss have been studied as a function of frequency at different temperatures. The presence of SHG and its conversion efficiency was measured by employing the modified Kurtz and Perry powder technique. The laser damage threshold value of the title crystal was determined using a Nd:YAG laser with the wavelength of 1064 nm.

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1. Introduction

The discovery of new NLO materials embedded with desirable physical properties such as optical transparency, thermal, optical and mechanical stabilities, etc., is an important objective in nonlinear optics. Organic crystalline materials are the target to develop NLO materials owing to their large optical nonlinearity, high laser damage threshold and potential applications in optical signal processing, frequency conversion, organic superconductors, color displays, laser remote sensing, ultra compact lasers, molecular electronics, electro-optical amplitude modulation, high density optical data storage, optical switching, optical signal processing, optical communication, photonics and bio photonics [1–3]. These organic crystals, especially crystals containing aromatic components are versatile due to availability of π - electrons and extension

of delocalization of π - electrons through conjugation which directs to enhance the second order polarizability (β). Furthermore, they often form a variety of hydrogen bonding interactions and offer a high degree of delocalization of the π -conjugated electrons by tailoring proper an electron donor and an acceptor groups at the two opposite ends of the conjugated aromatic system to acquire acentric crystal structure [4,5]. Hydrogen bonding is also an important driving force which plays a crucial role in the creation of non-centrosymmetric structures of crystals that is mainly responsible for the nonlinear optical property of the materials [6,7]. The hydrogen-bonded systems lead to form novel structures that have unique physical and chemical properties [8] and have a wide range of applications in molecular recognition, crystal engineering, supra molecular assembly, materials science and biological systems [9–12]. The protonation of donor by the acceptor is a most important route for the formation of acid-base ion pair products to form non-centrosymmetric structures for NLO applications [13–15]. The acid part of the ion pair or molecular crystals is responsible for thermal and mechanical properties due to strong

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hydrogen bond interactions [16]. The acid strength of aromatic sulphonic acids ensures formation of proton transfer compounds resulting from their reaction with most Lewis bases which may be useful to build potential optical materials [17]. Moreover, the sulfonate group provides three available O atoms as proton-accepting centres for hydrogen bonding associations thereby enhancing its utility for supramolecular assembly. Due to strong acidic nature, 5-sulfosalicylic acid with three functional groups (the sulfonic, carboxylic and phenolic groups) may also be useful to build potentially optical materials. Based on these aspects, we present the synthesis, growth and spectroscopic characterisation of SHG active organic hydrogen bonding organic salt crystal *N,N*-Dimethyl anilinium-3-carboxy-4-hydroxybenzenesulphonate (DMABS). Single crystals of the title material were grown and characterized through electronic, vibrational, nuclear magnetic resonance spectral studies, TG/DTA, Nonlinear optical and laser damage threshold studies.

2. Experimental details

AR grade *N,N*-dimethyl aniline and 3-carboxy-4-hydroxybenzenesulphonic acid were used as starting materials for the synthesis of title compound. Equimolar solutions of *N,N*-dimethyl aniline and 3-carboxy-4-hydroxybenzenesulphonic acid were prepared separately in pure methanol and Millipore water of resistivity 18.2 m Ω respectively and henceforth mixed together. The resulting solution was stirred well to attain the uniform concentration and heated slightly to dissolve all the undissolved substance. Then the solution was filtered through a quantitative Whatmann 41 grade filter paper to remove the suspended impurities. The clear filtrate so obtained was collected in a 100 mL beaker and kept aside unperturbed in an atmosphere opt for the growth of single crystals of the title compound. Well grown good optical quality single crystals (8 × 2 × 3 mm³) were harvested at the end of tenth day. The reaction scheme and the photograph of as-grown title crystals are presented in Figs. 1 and 2 respectively.

The synthesized material was subjected to various characterisation techniques such as Elemental analysis (Perkin Elmer 240C elemental analyzer), UV–Visible absorption spectrum (DMSO solvent, SHIMADZU 1601 UV–Vis spectrophotometer, 200–600 nm, Resolution: 1 nm), UV–Vis–NIR transmittance spectrum (Powdered material, JASCO UV–Vis–NIR Spectrophotometer, 200–1500 nm, Resolution: 1 nm), Photoluminescence spectrum (Horiba Jobin Yvon model FL3-22 Fluorolog spectrofluorimeter, 325 nm), FT-IR (Perkin Elmer FT-IR 8000, 4000–400 cm⁻¹, KBr pellet, spectral resolution: 2 cm⁻¹), ¹H and ¹³C NMR (Bruker AV III, 500 MHz, DMSO solvent, TMS standard), TG/DTA (35–500 °C, NETZSCH STA 409 C/CD, TG resolution: 0.1 μ g, DTA resolution: 0.1 mV), Hardness (Vickers microhardness tester, HMV SHIMADZU,

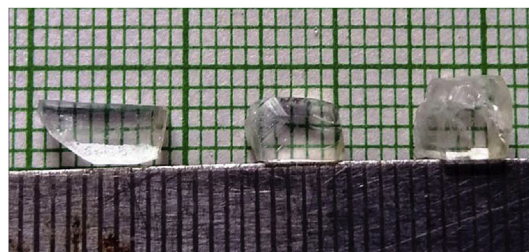


Fig. 2. As-grown single crystals of DMABS crystal.

make: HMV-2T), Dielectric studies (50 Hz to 5 MHz, Hioki LCR 3532-50 LCR meter, silt width: 2 nm), SHG test (modified Kurtz and Perry powder technique) and Laser damage threshold studies (J-50-MB-YAG, QUANTA RAY Model LAB-170 - 10). Single crystal X-ray diffraction data of DMABS compound was collected at room temperature on a Bruker Diffractometer equipped with a fine focused sealed tube. The unit cell parameters were determined and the data collections of DMABS were performed using a graphite monochromated Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) by ϕ and ω scans. The structure of the crystal was solved by direct method [18] using SHELXS-97, which revealed the position of all non-hydrogen atoms and was refined by full matrix least squares on F^2 (SHELXL-97) [19]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed in calculated positions and refined as riding atoms.

3. Results and discussion

The purity and stoichiometric proportion of the elements (CHN) present in the synthesized compound were determined by elemental analysis. The result of the analysis indicates that the DMABS salt crystal contains C, 53.15% (53.09%); H, 5.09% (5.05%); N, 4.21% (4.13%). The data show a good agreement between the experimentally determined and theoretically calculated values (given within brackets) within the limits of permissible error. The result further indicates that DMABS crystal is free from impurities and devoid of water molecules in any form. UV–Visible absorption spectrum of DMABS crystal was recorded in the wavelength range from 200 to 800 nm using DMSO as solvent and shown in the Fig. 3. The spectrum exhibits strong absorption bands attributed to π - π^* and the weak bands of n - π^* transitions occurring in the salt crystal. The strong and intense absorption bands at 210 and 230 nm are assigned to the π - π^* transitions. The weak absorption band at 310 nm is attributed to the symmetry forbidden n - π^* transition. To determine the transmission range and to know the suitability of the crystals for optical applications, the UV–vis–NIR transmission

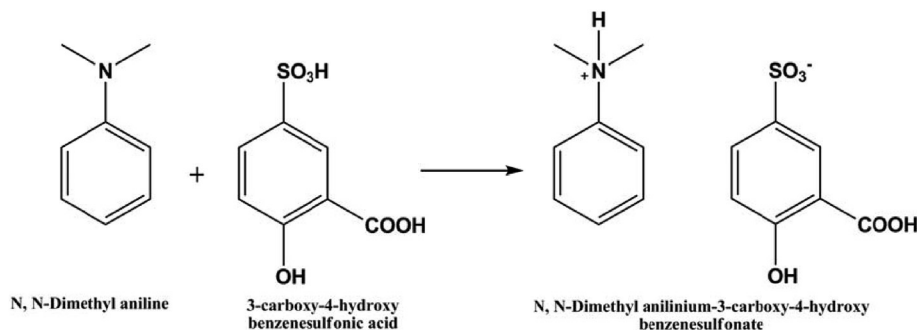


Fig. 1. Reaction scheme of DMABS crystal.

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