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Studies on synthesis, growth and characterization of a novel third order nonlinear optical 4-Dimethylaminopyridinium p-Toluenesulfonate single crystal

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ABSTRACT

Good quality single crystals of 4-Dimethylaminopyridinium p-Toluenesulfonate (4DMAPPTS) possessing third order nonlinearity were grown by slow evaporation solution technique (SEST). Single crystal X-ray diffraction analysis reveals that 4DMAPPTS belongs to monoclinic crystal system with centrosymmetric space group $P2_1/n$. FT-IR spectral studies were carried out to identify the functional groups present in 4DMAPPTS. NMR spectral study confirms the molecular structure of the grown crystal. Dielectric measurements were made over a wide range of frequencies for different temperatures. The grown crystal was subjected to Vickers microhardness test to study the mechanical property. The etching studies reveal the growth pattern and dislocations present in the grown title crystal. The important optical parameters such as absorption coefficient, extinction coefficient, refractive index and optical band gap were estimated from UV–Visible spectral analysis. The negative third order nonlinear optical parameters like refractive index (n_2), absorption coefficient (β) and susceptibility ($\chi^{(3)}$) were estimated by *Z*-scan studies.

1. Introduction

The search for organic material with high order nonlinear optical property has attracted significant attention because of their possible applications in optoelectronic and optical devices such as optical limiters optical switches and optical modulators [1,2]. In recent years a large variety of materials have been investigated for third-order nonlinear optics, among them organic materials are advantageous because of their optical and electronic properties which can be tuned and tailored by structural modification [3]. Pyridine and its derivatives play a central role in technological, industrial areas as well as in bio chemistry. As such, pyridine compounds are considered to be an optical material. 4-dimethylaminopyridine (4DMAP) is found to be an excellent charge transfer organic molecule and crystal structures of about 40 salts have been reported earlier [4].

The crystal structure of the title compound 4-Dimethylaminopyridinium p-Toluenesulfonate (4DMAPPTS) was reported by John McAdam and Simpson [5]. It crystallizes in the monoclinic crystal system with centrosymmetric space group $P2_1/n$ and has the molecular formula $C_7H_{11}N_2^+ \cdot C_7H_7SO_3^-$. In the donor–acceptor series, 4-Dimethylaminopyridinie p-Toluenesulfonate (4DMAPPTS) is one such compound in which 4-Dimethylaminopyridine acts as the acceptor and p-Toluenesulfonic acid as the donor. In 4DMAPPTS crystal structure N—H···O hydrogen bonds link individual pairs of cations and anions and the structure is further stabilized by an extensive network of C—H···O hydrogen bonds. However, to the best of our knowledge no systematic studies of 4DMAPPTS have been made. In the present investigation we report bulk growth, FTIR, crystalline perfection, thermal, dielectrical, mechanical, linear and nonlinear optical properties of 4DMAPPTS.

2. Experimental procedure

2.1. Synthesis and crystal growth

The 4DMAPPTS salt was synthesized by dissolving 4-Dimethylaminopyridine and p-Toluenesulfonic acid in the ratio 1:1 in methanol at room temperature. The synthesized 4DMAPPTS salt has been obtained by the following chemical reaction:

$$C_7H_{10}N_2 + C_7H_8SO_3 \rightarrow C_7H_{11}N_2^+ \cdot C_7H_7SO_3^-$$

(4-Dimethylaminopyridine) + (p-Toluenesulfonic acid)
→ (4-Dimethylaminopyridinium p-Toluenesulfonate)

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The reaction scheme of 4-Dimethylaminopyridinium p-Toluenesulfonate (4DMAPPTS) is depicted in Fig. 1.

The prepared saturated solution of 4DMAPPTS was filtered by using Whatman filter paper (grade NO. 1). The beaker containing solution was then optimally closed and kept at room temperature for slow evaporation. After a period of 40 days, block-like single crystals of size 32 mm × 13 mm × 4 mm were obtained and it is shown in Fig. 2a. Molecular structure of 4DMAPPTS with atomic number scheme is shown in Fig. 2b.

3. Characterization

As grown 4DMAPPTS crystals have been subjected to various characterization studies to analyze the structural, optical and mechanical properties. The unit cell parameters and crystal structure of 4DMAPPTS were determined from single crystal X-ray diffraction analysis. The functional groups were identified using FT-IR spectral studies. FT-NMR (^{1}H NMR and ^{13}C NMR) analysis helps to confirm the molecular structure of 4DMAPPTS compound. The grown crystal was subjected to Vickers hardness test and the stiffness constant, yield strength were estimated. The etching studies were carried out to reveal the growth pattern and dislocations present in the grown 4DMAPPTS crystal. The optical behavior of the grown crystal was analyzed by UV–Visible study. The Photoconductivity of the material was measured. Third order nonlinear parameters such as nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and susceptibility (χ^3) were estimated by *Z*-scan studies.

4. Results and discussion

4.1. X-ray diffraction studies

The grown crystal of 4DMAPPTS was subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 X-ray diffractometer. The single crystal XRD study enumerates that the grown 4DMAPPTS belongs to the monoclinic crystal system with space group $P2_1/n$ and the lattice parameters are $a = 8.938$ (4) Å, $b = 17.567$ (8) Å, $c = 9.795$ (6) Å. The obtained single crystal XRD data are well matched with the reported literature values [5].

4.2. FT-IR spectral analysis

The Fourier transform infrared (FT-IR) spectrum of 4DMAPPTS was recorded at room temperature in the region 400–4000 cm^{-1} using FT-IR Spectrometer with single reflection ATR accessory (Perkin Elmer Spectrum two, USA) in order to analyze the synthesized compound qualitatively and the presence of functional groups in the molecule. The corresponding spectrum of 4DMAPPTS is shown in Fig. 3. The frequency assignment of FTIR spectrum is presented in Table 1. In the FT-IR spectrum, the band at 3208 cm^{-1} is attributed to N—H stretching vibrations. The peaks at 3065 cm^{-1}, 2914 cm^{-1}, 2668 cm^{-1} are due to the C—H stretching vibrations and the peak at 1492 cm^{-1} is due to the C=N stretching vibration. The peaks at 1000 cm^{-1}, 515 cm^{-1} correspond to the SO_3^- symmetric stretching whereas 1211 cm^{-1} indicates SO_3^- asymmetric stretching. The peaks appearing at 1396 cm^{-1} and 678 cm^{-1} are owing to C—S stretching vibration. The C—C out of plane bending occurs at 808 cm^{-1} whereas the peak observed at 1444 cm^{-1} is due to C—H in plane bending. The peak at 555 cm^{-1} is due to the N—H torsional oscillation.

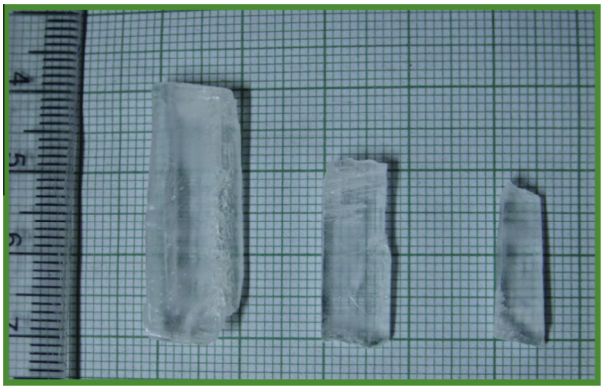

Fig. 2a. As grown single crystal of 4-Dimethylaminopyridinium p-Toluenesulfonate.

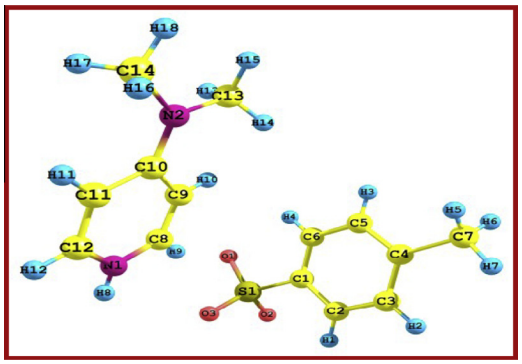

Fig. 2b. Molecular structure of 4DMAPPTS with atomic number scheme.

4.3. NMR spectral analysis

To confirm the molecular structure of 4DMAPPTS, ^{1}H and ^{13}C NMR spectral studies were performed using MeOD as solvent using

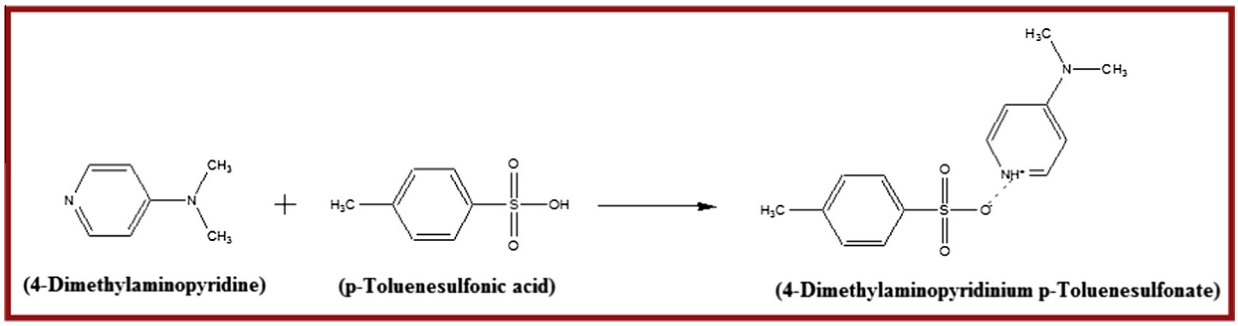

Fig. 1. Reaction scheme of 4-Dimethylaminopyridinium p-Toluenesulfonate.