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Synthesis, Crystal growth and characterizations of third order NLO active single crystal - Aminomethylpyridinium Trichloroacetate

A. Kiruthiga[1], A. Priyadharshini[1]

[1]*Department of physics, Auxilium College, Vellore -632006, India*
[*]*Corresponding author: priyadharshini@auxiliumcollege.edu.in*

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ABSTRACT:
Background: Organic non-linear optical (NLO) materials have attracted considerable attention due to their potential applications in photonics, optoelectronic devices, and optical communication systems. The development of high-quality organic NLO single crystals with good optical transparency and stable structural properties is essential for efficient device performance.
Purpose: The present work aims to grow and characterize an organic NLO single crystal of 2-Amino-6-methylpyridinium 2,2,2-trichloroacetate (AMPTCA) and to investigate its structural, optical, dielectric, and third-order non-linear optical properties.
Method: Single crystals of AMPTCA were grown from methanol solution by the slow evaporation solution growth technique at room temperature. The structural purity and lattice parameters were determined using single crystal and powder X-ray diffraction (XRD) studies. The crystal belongs to the monoclinic system with space group $P2_1/n$ and lattice parameters a = 11.636(8) Å, b = 14.663(12) Å, c = 13.710(4) Å, and β = 96.326(4)°, with a unit cell volume of V = 2365.4(9) Å^3. Optical properties were analyzed using UV–Vis–NIR spectroscopy in the wavelength range of 200–1000 nm, revealing a UV cut-off wavelength at 250 nm with a transparency of about 92%. The crystalline perfection was examined through chemical etching analysis, while dielectric measurements were carried out to study the electrical properties. The third-order NLO properties of the grown crystal were evaluated using the single-beam Z-scan technique.
Conclusion: The grown AMPTCA single crystal exhibits good crystalline quality, high optical transparency, and promising dielectric and third-order NLO properties. These characteristics indicate that the material is a potential candidate for applications in non-linear optical and photonic devices.

Keywords: Third order Non-Linear optical (NLO) Materials, Dielectric studies, Etching analysis, Z-scan measurement

1. Introduction

Nonlinear optical (NLO) crystals have emerged as a highly intriguing area of recent research due to their vital applications in various fields, including signal processing, telecommunications, optical modulation, and optical switching, especially when it comes to organic materials [1,2]. Especially, Pyridine heterocycles and their derivatives are present in many large molecules has a noticeable enhancement in the field of nonlinear optical (NLO) [3,4]. In order to validate this statement, we have successfully synthesised centrosymmetric 2-Amino-6-methylpyridinium 2,2,2-trichloroacetate (AMPTCA) organic single crystal by the adoption of slow evaporation technique. The title crystal consists of two crystallographically independent protonated 2-amino-6- methylpyridinium cation and trichloroacetate anion which is more beneficial for enhancing the nonlinear optical (NLO) coefficient. Currently, the design and synthesis of charge transfer organic molecules are receiving concentrated attention, primarily due to their exceptional optical nonlinearities, which arise from the extensive interaction between the cation and anion [5]. The structure of AMPTCA was previously reported by Syed Suresh Babu [6]. The

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crystal has been characterized by various techniques, such as single crystal and powder X-ray analysis, FTIR analysis, UV-Visible spectroscopy, chemical etching, dielectric and the Z-scan.

2. Methods and Material

2.1. Reagents:

2-Amino-6-methylpyridine, Trichloroacetic acid and Methanol were purchased from commercial sources and used without further purification.

2.2. Material Synthesis and Crystal Growth:

2-Amino-6-methylpyridinium 2,2,2-trichloroacetate single crystal was synthesized by slow Evaporation method by using the 2-amino-6-methylpydrine and trichloroacetic acid stoichiometric ratio [1:1] and dissolved in methanol. The above prepared solution was stirred about 3 hours using magnetic stirrer to ensure homogeneous mixture, and then the solution is filtered by using whatman filter paper to remove the impurities from the solution. The solution was then transferred into beaker and covered with aluminum sheet with tiny holes to ensure the slow evaporation. The solution was dried at room temperature to obtain the colorless single crystal. The purity of the synthesized material is improved by repeated recrystallisation process and filtration. After the growth period, the colorless transparent single crystals were harvested from the mother solution. **Scheme 1.** illustrates the synthetic route of AMPTCA compound. The photographic image of AMPTCA crystal and its corresponding morphology are shown in Fig. 1(a & b), respectively.

3. Results and Discussion

3.1. Instrumentation

In the present investigation, the lattice parameters of AMPTCA single crystal were found by single XRD analysis the Powder XRD analysis was made on the finely crushed powder of AMPTCA by using a BRUKER X-ray diffractometer with Cu K_α (λ=1.5406 Å) radiation, with a step size of 0.02^0 S-1 over a 2θ range 10^0 to 40^0, and the identical diffraction peaks are indexed with the help of Powder- X software package. The FT-IR spectrum of the AMPTCA sample was scanned at the middle infrared region of 400 - 4000 cm^{-1} using a SHIMADZU IRAFFINITY spectrometer. For the optical studies, the absorption spectrum of AMPTCA sample was recorded on a Varian Carry ELICO SL 218 double beam UV–Vis–NIR spectrometer in the spectral region 200–1000 nm. The dielectric properties were studied by dielectric measurement. The crystalline perfection was identified by etching analysis. The third order NLO properties of AMPTCA crystal have been investigated by Z-scan measurement employing the continuous He-Ne laser operated at 632.8 nm wavelength.

3.2. Single Crystal X-Ray Diffraction Analysis

From the single crystal XRD measurement, we found that the grown crystal belongs to a monoclinic system and has a centrosymmetric nature with the space group of $P2_1/n$. The calculated lattice parameters are a = 11.636 (8) Å, b = 14.663 (12) Å, c = 13.710 (4) Å and β = 96.326 (4) Å. The volume of the crystal is V = 2365.4 (9) Å. The observed values are consistent with the previously reported values (CCDC-988938) [6].

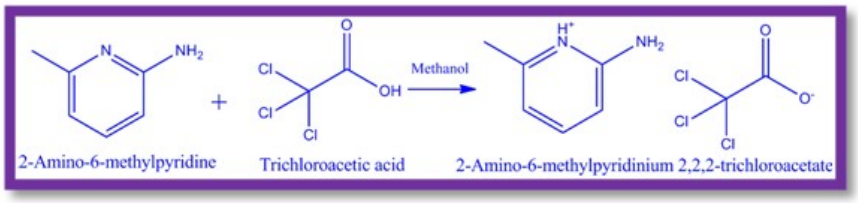
3.3. Powder X-Ray Diffraction Analysis

From the powder X-ray diffraction, the phase purity of AMPTCA crystal compounds has been confirmed; the powder X-ray diffraction (PXRD) patterns of AMPTCA compound were checked at room temperature. The simulated and experimental PXRD patterns of AMPTCA are shown in Fig 2. The peaks of the measured diffraction position are in good agreement with those of the simulated diffraction position generated from single crystal XRD data. The high intensity well defined sharp peaks at specific 2θ angle reveal the high crystalline perfection and phase purity of the AMPTCA crystal.

3.4. FTIR-Spectral Analysis

Fourier transform infrared spectroscopy (FT-IR) plays a crucial role in understanding the diverse functional groups, chemical bonding, and molecular structure of the grown crystal. The FT-IR spectrum of the powdered AMPTCA sample is presented in the Fig 3, the spectral analysis of AMPTCA crystals reveals various vibrational modes associated with specific wave

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Scheme 1. Synthesis of AMPTCA

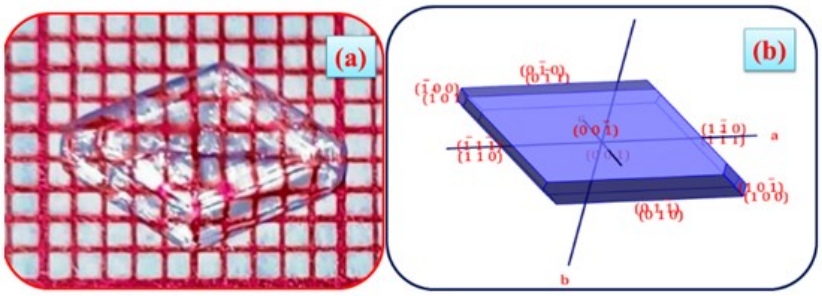


Figure 1: (a) Photographic image of AMPTCA crystal and (b) Morphology of the grown Crystal Obtained using the WinXMorph Software.

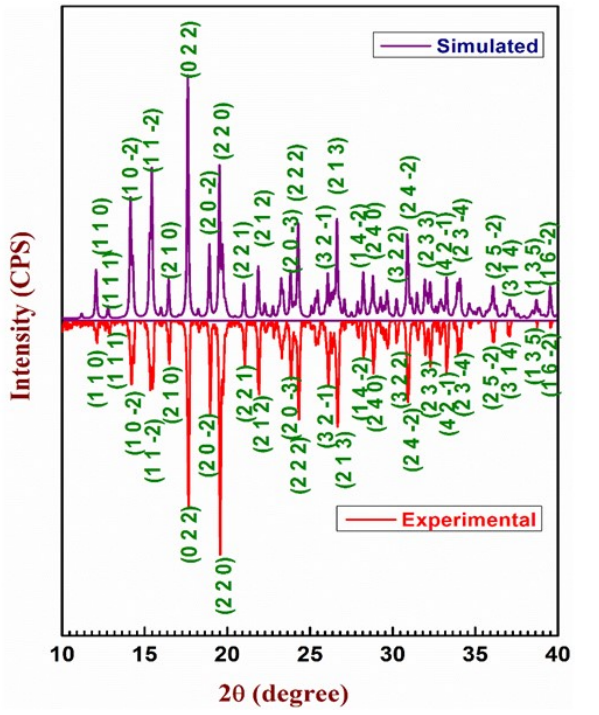


Figure 2: Simulated and Experimental Powder X-Ray Diffraction Patterns of AMPTCA Crystal

numbers. The N-H stretching vibration is observed at 3185 cm^{-1}, while the C-H stretching appears at 2974 cm-1. A strong band at 1631 cm^{-1} corresponds to the C=C stretching mode. The symmetric stretching of the COO^- group is identified at 1352 cm^{-1}, and C-H in-plane bending is noted at 1254 cm^{-1}. The C-N stretching vibrations are assigned to the bands at 1268 cm^{-1} and 1035 cm^{-1}. Furthermore, the C-H out-of-plane bending vibrations are observed at 861 cm^{-1}, 785 cm^{-1}, and 689 cm-1. Finally, the vibrations of the COO^- group are seen at 602 cm^{-1}, 530 cm^{-1}, and 430 cm^{-1}.

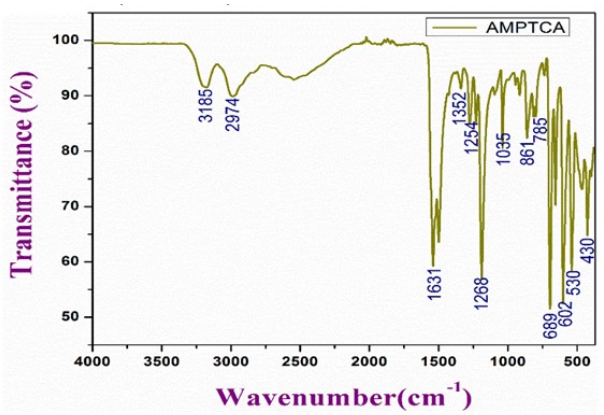


Figure 3: FTIR Spectrum of AMPTCA crystal.

3.5. UV- Visible NIR Spectral Analysis

Absorption and transmittance studies are crucial for identifying potential nonlinear optical (NLO) materials. Ideally, a crystal with minimal absorption and high optical transparency across the electromagnetic spectrum is highly desirable for various optical applications [7,8]. The UV-visible absorption spectrum of the AMPTCA crystal reveals a lower cutoff wavelength of approximately 250 nm, which is good agreement with the reported value [4]. Furthermore, the transmittance spectrum (Fig.4) shows a broad transmission

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window between 200-1000 nm, with a maximum transmittance of up to 92%. Notably, no characteristic absorptions are observed in this region, indicating that the AMPTCA crystal is well-suited for photonic and optical applications.

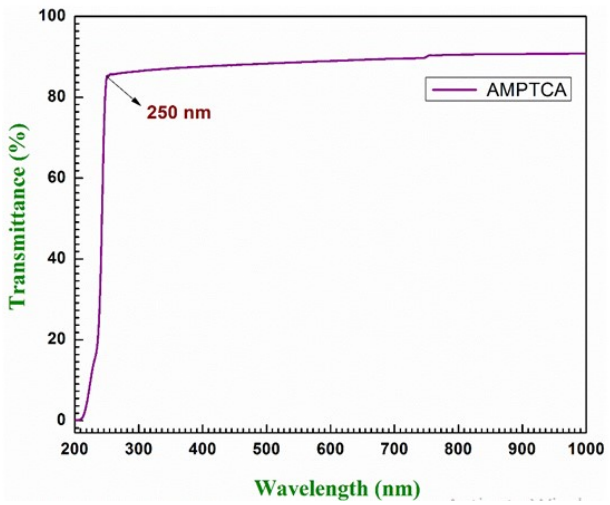


Figure 4: Optical Transmission Spectrum of AMPTCA Single Crystal.

3.6. Chemical Etching Analysis

This worthy study plays a role of a thesaurus for the identification of the crystalline perfection. The defected crystal destroyed its original mechanical and electrical properties. The etching is an indispensable popular appliance for the investigation of the surface dislocation, spiral, growth hillocks, slip patterns and grain boundaries of the grown crystal. The Imperfection crystals are not suitable for the nonlinear optical properties of SHG and THG efficiencies, laser threshold damage, etc [8,9]. In the present snoop of etching, carried out on the flat surface of AMPTCA crystal.

When the crystal dissolved in a particular solvent, the reversal of the growth taking place by giving the perfect etches pits. The etching time (10 s & 20 s) is responsible for the solubility of the AMPTCA crystalline material immerse in the methanol solvent. The surface etchant of the title crystal was removed gently by using the tissue paper, and then the feature of the crystal surface taken for the examination under the Carl Zeiss optical microscope in a reflection mode with 50x magnification. During the etching process, the weak surface of the layer removed due to the vacancy of the atom present on the surface of the specimen. Fig.5 depicts the etching mechanisms of AMPTCA crystal enable to develop the elongated growth striations with visual of a steep slope. Thus, the minimum deformation of title crystals is suitable for the device fabrication [10].

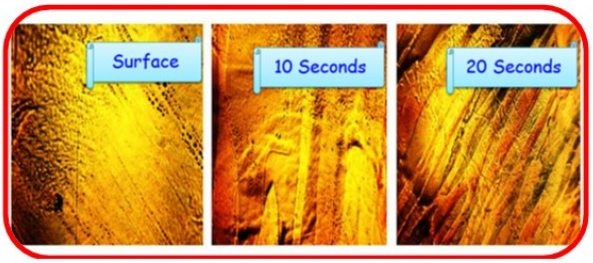


Figure 5: Recorded micrographic image of the AMPTCA crystal:(a) surface of the grown crystal before etching; (b) surface etching after 10s; (c) surface etching after 20s

3.7. Dielectric Measurement

The measurement of dielectric is a well-established tool for the identification of the materials polarization based on the external electrical field [10-12]. A well-shaped cut and polished defect free good quality of AMPTCA crystal was taken for dielectric measurement. In which the high-grade silver paste applied on the parallel surfaces of the crystals that enhance the uniform electrical contact between the two electrodes. Fig (6) and Fig (7) shows the frequency dependents dielectric measurement carried out for the different temperature.

The dielectric constant and dielectric loss can be calculated using the relation

$$\varepsilon' = \frac{Cd}{A\varepsilon_0}$$

Where C is the capacitance measured in microfarad, d is a thickness of the crystal in mm. ε_0 is constant of permittivity in free space. Fig.6 shows the high dielectric constant at low frequency and then it decreases gradually with increase the frequency and finally it may attain saturation dielectric constant for further increasing the frequency. Fig.7 shows the low dielectric loss (Tan δ) at the high-frequency hints reveals that the grown crystal has good optical quality with a lesser defect. Thus, these crystals are crucial

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for the optoelectronic applications and NLO devices [12-14].

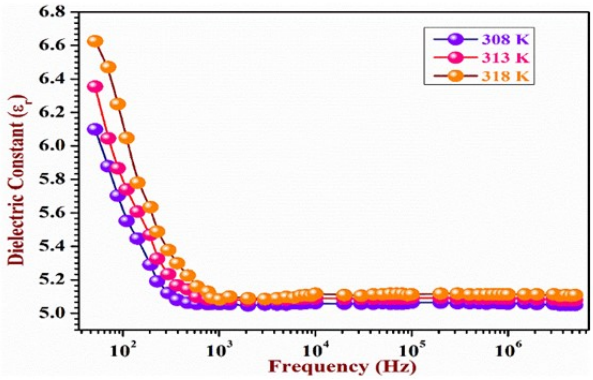


Figure 6: Frequency dependence dielectric constant of AMPTCA crystal at different temperatures.

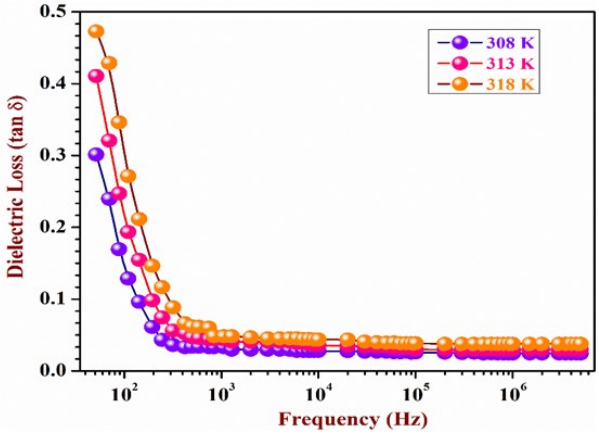


Figure 7: Frequency response of dielectric loss (tan δ) of AMPTCA crystal at different temperature

3.8. Third Order NLO Properties By Z-Scan Measurement

Single-beam Z-scan technique was employed to measure the third-order optical nonlinearities of the AMPTCA crystal. This method was first developed by Sheik-Bahae et al [14]. The experiments were performed using a continuous He-Ne laser of the wavelength of 632.8 nm, which was focused by a 30 mm focal length lens. The laser beam waist at the focus is measured to be 12.05 μm and the Rayleigh length is 0.72 mm. The sample was mounted on a translation stage (-Z to +Z) that was controlled by the computer to move along the Z-axis with respect to the focal point. An aperture 1.75 mm radius was placed in front of the transmission detector, and the transmittance was recorded as a function of the sample position on the Z-axis i.e., closed aperture (CA) Z-scan. For measuring the NLO absorption, the Z-dependent sample transmittance was taken without the aperture i.e., open aperture (OA) Z-scan. Actually, the nonlinear absorption coefficient (β) and nonlinear refractive index (n_2) could be assessed by OA and CA Z-scan. The obtained results of the Z-scan curves in open and closed aperture modes are shown in Fig.8 and Fig.9

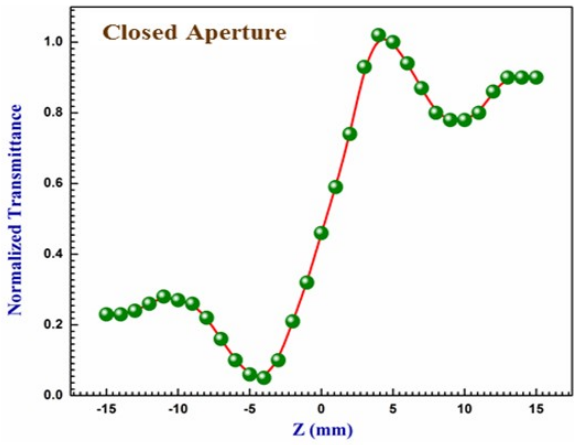


Figure 8: Self-Focusing Closed Aperture (CA) Z-Scan Spectrum of AMPTCA crystal.

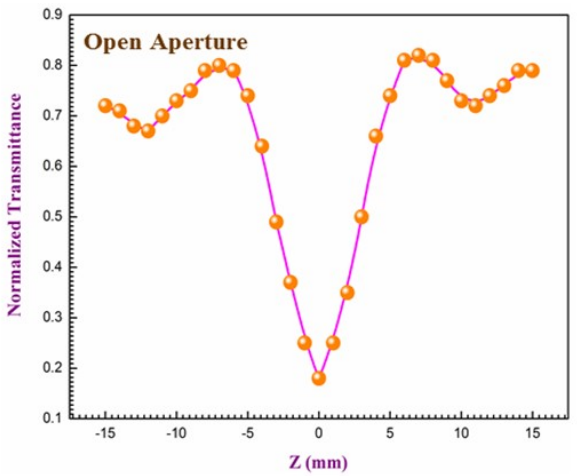


Figure 9: Open Aperture (Reverse Saturable Absorption) Z-scan Spectrum of AMPTCA crystal.

The nonlinear refractive index (n_2) can be obtained by the relation given by,

$$n_2 = \frac{\Delta\Phi_o}{KI_oL_{eff}} \quad (1)$$

focal point (I_o = 26.40 MW /m^2), and L_{eff} is effective thickness of the grown crystal can be estimated as

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$L_{eff} = [1- \exp(-\alpha L)]/\alpha$, where L is the thickness of the crystal and α is the linear absorption coefficient. From the OA curve line, the nonlinear absorption coefficient (α) was estimated by,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_o L_{eff}} \quad (2)$$

where Δ T is the valley value at the OA data. The absolute value of the third-order nonlinear optical susceptibility ($\xi^{(3)}$) was calculated by using the equation,

$$\left|\chi^{(3)}\right| = \left[\left(Re(\chi^{(3)})\right)^2 + \left(Im(\chi^{(3)})\right)^2\right]^{1/2} \quad (3)$$

where Re and Im represent the real and imaginary parts of the optical susceptibility. From the Z-scan data, the calculated values of $\chi^{(3)}$ are 4.21×10^{-5} esu, n_2 is 2.676×10^{-11} m^2/W, and β is 2.437×10^{-5} m/W.

Thus, the overall experimental results indicate that the AMPTCA crystal possesses significant NLO properties. The grown AMPTCA crystal exhibits excellent third-order nonlinear optical properties, making it highly suitable for optical limiting and photonic device fabrication applications [10–15].

4. Conclusion

An organic charge transfer single crystal of AMPTCA was grown by the slow evaporation method. The single crystal and powder X-ray diffraction studies confirmed centrosymmetric space group ($P2_1/n$) and crystallinity of the title crystal. The UV-Vis-transmittance study reveals that the crystal has good transparency (92 %) with the cut-off wavelength at 250 nm. FT-IR spectral studies confirm the presence of various functional groups in AMPTCA. The crystalline perfection was identified by etching analysis. Dielectric studies confirm the good optical quality of the crystal with lesser defect. The Z-scan measurement provided the detailed information about the third order NLO activity of the grown crystals.

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