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Structural, Optical, and Dielectric Properties of 2,5-DCAP Single Crystals

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ABSTRACT

The organic nonlinear optical (NLO) material 2,5-Dichloroanilinium Picrate (2,5-DCAP) was synthesized and grown as a single crystal using the slow solvent evaporation method. The structure was confirmed via single-crystal X-ray diffraction, revealing a monoclinic system with non-centrosymmetric space group Cc, suitable for second harmonic generation (SHG). Optical studies using UV-Vis-NIR spectroscopy demonstrated excellent transparency and a UV cut-off wavelength at 215 nm, with an optical band gap of 5.77 eV. SHG analysis confirmed efficient frequency doubling, with an SHG output 1.2 times that of potassium dihydrogen phosphate (KDP), indicating phase-matchable behavior. Vickers micro-hardness testing revealed load-dependent mechanical properties, with the material classified as soft based on the work hardening coefficient. Dielectric measurements indicated low dielectric constant and loss at high frequencies, reflecting high optical quality and low defect density. The combined structural, optical, mechanical, and dielectric properties suggest that 2,5-DCAP is a promising candidate for photonic and electro-optic device applications.

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1. INTRODUCTION

Blue light sources that are versatile are essential for uses such as laser displays, medical operations, and optical data storage. Optical second-harmonic generation (SHG) is still a crucial technique for producing strong, coherent blue and green light with excellent beam quality, despite the quick advancement of blue laser diodes [1]. Large delocalized electron systems with strong donor and acceptor groups have been shown to improve second-order molecular nonlinearity [2,3]. Organic molecules have a high degree of electron delocalization and weak hydrogen and Van der Waals interactions. As a result, they exhibit more optical nonlinearity than inorganic materials. Organic materials have several advantages, including flexibility in synthesis methods, the ability to change characteristics by functional substitution, innately high nonlinearity, and high damage tolerance [4].

Second-harmonic generation (SHG) efficiency of organic materials is much higher than that of inorganic ones. Because of its three nitro groups, picric acid (2,4,6-trinitrophenol), which is used in explosives, dyes, and ammo, is an appropriate π-acceptor for neutral donor molecules [5-7]. Known by its TNP moniker, this organic nonlinear optical crystal is efficient and has a high damage threshold, a strong nonlinear coefficient, good optical quality, UV transparency, and a low cut-off wavelength [8]. Picric acid's structure includes both activating AOH groups and deactivating nitro groups. Picric acid serves as both an acceptor for π stacking complexes with other aromatic compounds and an acidic ligand for salt formation via electrostatic or hydrogen bond interactions [9].

The exceptional second-order nonlinear optical (NLO) activity and strong hyperpolarizability of most picric acid compounds can be attributed to their acentric packing. Yoshio et al.'s study used ultraviolet-visible spectroscopy to examine and validate the transfer of charge between picric acid and 2,5-dichloroaniline [10]. Meng et al provided structural information about 2,5-DCAP [11]. The crystal of 2,5-dichloroanilinium picrate (2,5-DCAP), the chemical $C_6H_6Cl_2N^+.C_6H_2N_3O_7^-$. Both structures connect the component ions into continuous two-dimensional zigzag layers by the phenoxide oxygen atoms accepting two N-H hydrogen bonds in a bifurcated pattern and revealed the structure of 2,5-Dichloroanilinium Picrate [11]. 2,5-DCAP crystallizes structurally in space group Cc, a monoclinic system, with unit cell parameters a = 4.3288(18) Å, b = 23.372(10) Å, c = 15.292(6) Å, and β = 94.606(7)°. Slow solvent evaporation is the method used in this work to grow a single crystal of 2,5-DCAP. XRD, UV-Vis-NIR, SHG, microhardness and dielectric experiments were performed on the resultant crystal, and the results are explained.

2. SYNTHESIS OF 2,5-DCAP

Stoichiometric quantities of 2,5-dichloroaniline and picric acid were dissolved in double distilled water at a 1:1 ratio to create an aqueous solution of 2,5-DCAP. These chemicals react to generate 2,5-DCAP in deionized water. C6H5Cl2N+C6H3N3O7 ⟶ C6H6Cl2N+.C6H2N3O7-

The 2,5-DCAP salt was synthesized by evaporating the solvent from the solution, causing the salt to precipitate. The precipitate was then collected from the bottom of the container after the solvent had fully evaporated.

3. GROWTH OF 2, 5-DCAP

Single crystals of 2,5-DCAP were produced from their aqueous solution utilizing the slow solvent evaporation method. Through the perforated cover of the container, the solvent from the supersaturated solution was allowed to evaporate. In 5-7 days, optically clear small crystals developed as a result of spontaneous nucleation. Defect-free and well-formed crystals were carefully selected to serve as seed crystals for further growth experiments. Over a period of 35-40 days, using the slow evaporation method, a high-quality, colorless crystal with optical-grade clarity and dimensions of up to 7 x 4 x 2 mm was successfully grown. Figure 1 shows an image of as-grown 2,5-DCAP single crystals.

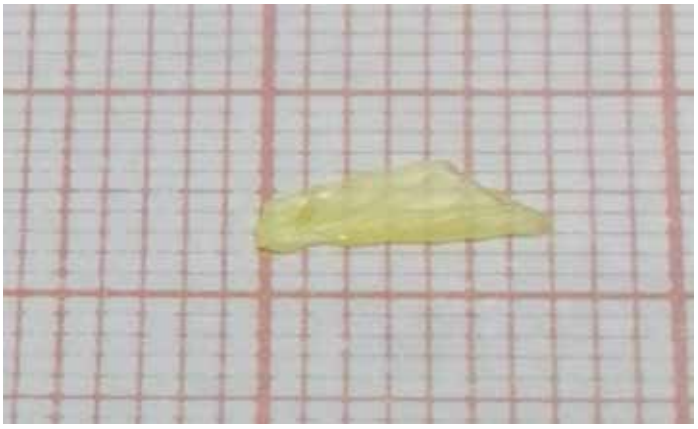


Figure 1. Photograph of as grown 2,5-DCAP

4. RESULT AND DISCUSSION

4.1 Single crystal X-ray diffraction

The 2,5-DCAP crystal was subjected to a single crystal X-ray examination using an automatic X-ray diffractometer. Using graphite-monochromated MoKα radiation (λ = 0.71073 Å), 25 reflections were collected using a random search method to estimate the unit cell characteristics of 2,5-DCAP. Short vectors were used for indexing, and least squares were used for refining after that. 2,5-DCAP is a member of the monoclinic crystal system with non-centrosymmetric space group Cc, according to the study. The cell dimensions are as follows: a = 4.33 Å, b = 23.37 Å, c = 15.28 Å, β = 94.61°, and the cell volume is V = 1546.22 Å^3. The XRD data from this investigation are consistent with values that Gao-Xiang Meng et al. previously published [11].

4.2 Linear optical study

The optical absorption spectra of 2,5-DCAP (Figure 2) highlight its suitability for second harmonic generation due to strong absorption in the visible range. The UV cut-off wavelength is around 215 nm, with a reduced cutoff at 200 nm due to π–π* transitions. The decreased absorption near the Nd:YAG laser's fundamental wavelength enhances the material's resistance to laser damage. The drop in transmittance at 255 nm is likely due to electronic excitation in the COO^- group. Despite no significant absorption in the visible range, 2,5-DCAP is suitable for use as a window in spectroscopic instruments. The crystal demonstrates high optical quality, with near-zero transmittance below the 215 nm cutoff and 90% transparency between 410-1100 nm (Figure 3). A hump between 255 and 410 nm is due to π–π* and n–π* transitions. The UV cutoff at 215 nm makes it suitable for second harmonic generation from a Nd:YAG laser (λ = 1064 nm). The direct band gap, estimated using Tauc's relation (Figure 4), is 5.77 eV.

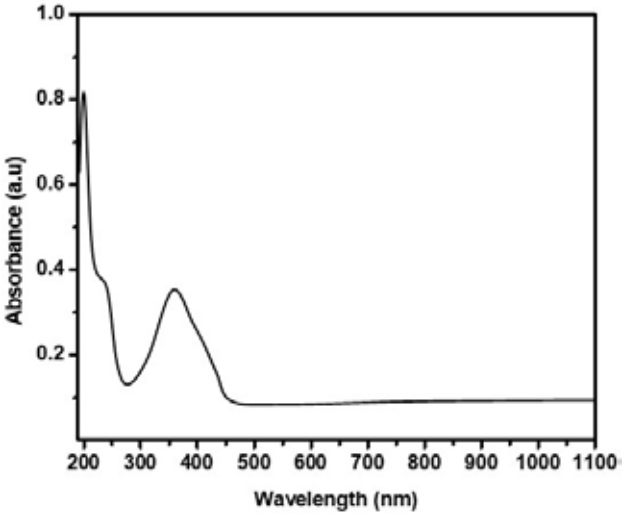


Figure 2. Optical absorption spectrum of 2,5-DCAP

4.3 Nonlinear optical study

A second harmonic generation (SHG) test on 2,5-DCAP was conducted using the Kurtz and Perry technique. A microcrystalline powder sample (average particle size 50-150 μm) was placed in a 0.154 mm capillary tube and irradiated with a Q-switched Nd:YAG laser (1064 nm, 8 ns pulse width, 10 Hz). Microcrystalline KDP of similar size served as a reference. With a laser input of 3.2 mJ, 2,5-DCAP exhibited a non-zero SHG signal, indicating its noncentrosymmetric structure. The SHG efficiency of 2,5-DCAP (192 mV) was found to be 1.2 times higher than that of KDP (160 mV). SHG intensity increased with particle size, peaking around 150 μm, after which it stabilized. This size dependency is characteristic of phase-matchable materials, confirming that 2,5-DCAP can be phase-matched, making it suitable as an effective frequency doubler and optical parametric oscillator.

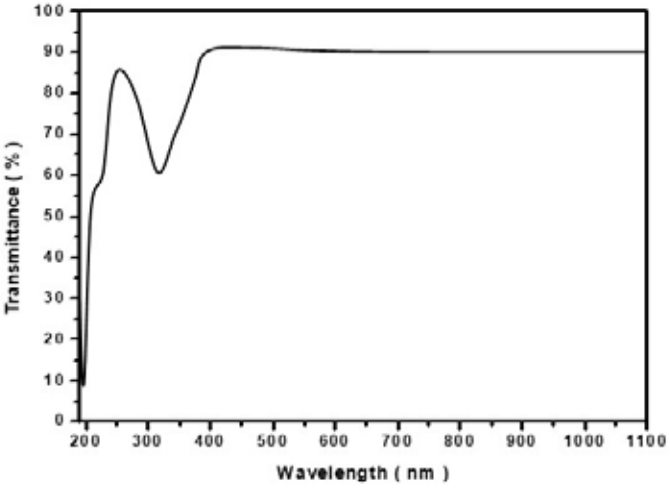


Figure 3. Optical transmission spectrum of 2,5-DCAP

4.4 Microhardness studies

Microhardness measurements are performed on 2,5-DCAP single crystals to investigate their mechanical properties. Mechanical testing is used to examine the mechanical properties of crystals, revealing specific mechanical characteristics. Hardness measurement is the simplest and most efficient method of mechanical testing. The Vickers hardness test is one of the most widely used testing methods. A Vickers microhardness tester with a diamond pyramidal indentor was used to conduct the study. A Leitz micro hardness tester with a diamond pyramidal indentor was used to conduct micro hardness measurements. Single crystals of 2,5-DCAP were tested for microhardness on orientation. The applied force ranged from 10 to 50 g with a constant indentation time of 10 s. The Vicker's hardness number (Hv) is computed as

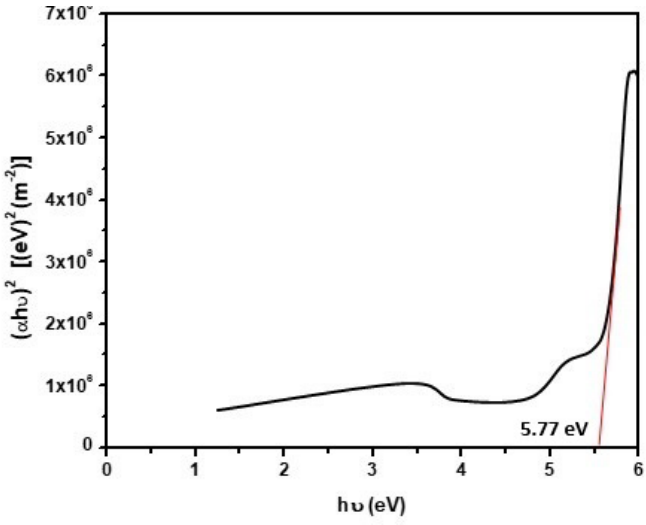


Figure 4. Tauc's plot of 2,5-DCAP

Hv = 1.8544 P/d2 kg/mm2,

where P represents the indentor load in kg and d represents the impression diagonal length in mm. Figure 5 shows that the microhardness of 2,5-DCAP increases with applied load. The observed decrease in microhardness values with increasing stress aligns with the indentation size effect (ISE). Plotting log p vs. log d (Figure 6) reveals a work hardening coefficient n = 2.71, indicating that the crystal is classified as a soft material [12].

4.5 Dielectric studies

Dielectric properties are closely related to the electro-optical characteristics of crystals (Boomadevi et al., 2004). A polished sample of 2,5-DCAP was tested using an HIOKI 3532-50 LCR HiTESTER, with air-drying silver paste applied to both sides to form a parallel plate capacitor. Experiments were conducted at ambient temperature up to 333 K and frequencies from 100 Hz to 5 MHz, measuring capacitance (c) and dissipation factor (d). Figures 7–8 show the frequency dependence of the dielectric constant and loss at various temperatures. The dielectric constant is high at low frequencies and decreases with increasing frequency, attributed to enhanced ionic conductivity. The dielectric constant comprises four components: electronic, ionic, orientational, and space charge polarization [13].

All contributions may be active at low frequencies, with the dielectric constant's fluctuation reflecting the sample's characteristics. In 2,5-DCAP, the dielectric constant is approximately 27.04 at 100 Hz, decreasing with frequency and stabilizing above 5 kHz at all temperatures. At 1 MHz, it drops to around 1.86. This decline in the dielectric constant with increasing frequency is attributed to electronic, ionic, orientational, and space charge polarizations. Figure 4.10 shows the exponential decrease in dielectric loss (tanδ) of 2,5-DCAP with increasing frequency. As temperature rises, the dielectric constant also significantly increases (Figure 9), a trend that continues for dielectric loss as well (Figure 10). The low dielectric loss indicates high-quality crystals [14]. Higher loss values at lower frequencies may result from space charge polarization due to lattice defects [15]. A low dielectric constant and loss at high frequencies suggest improved optical quality with fewer defects, which is crucial for many nonlinear optical materials and applications.

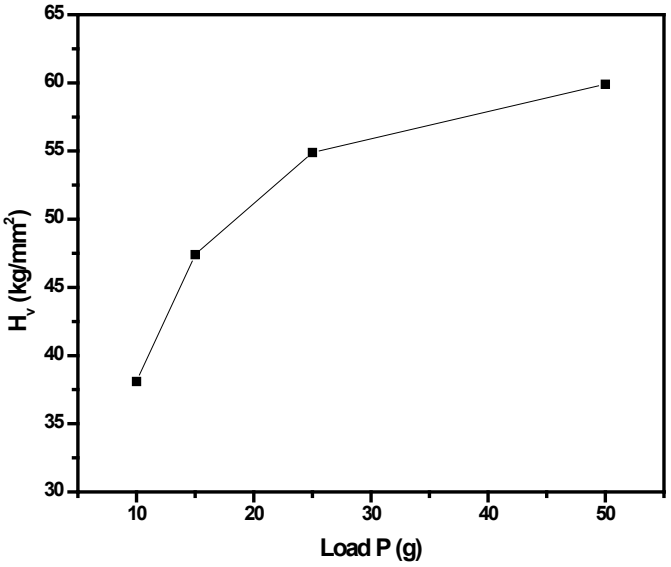


Figure5.Vickershardnessprofileof2,5-DCAPasafunctionof applied load

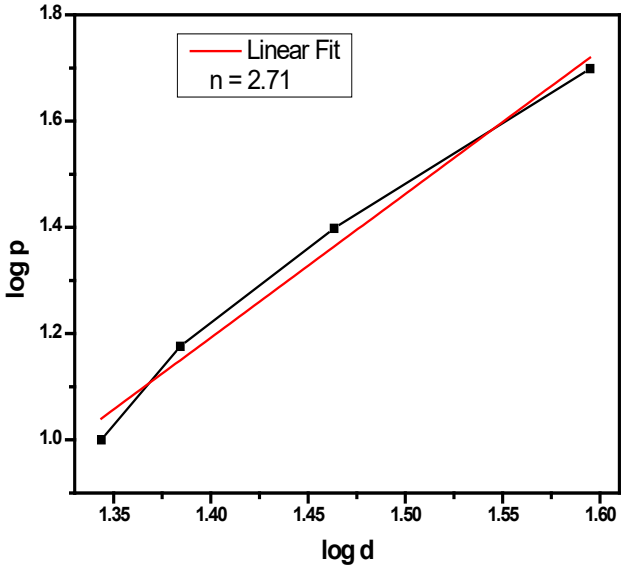


Figure 6. Plot of log d Vs log p for 2,5-DCAP single crystal

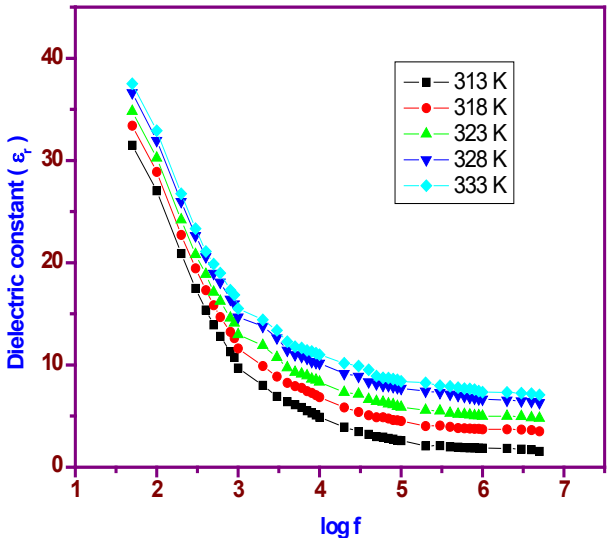


Figure 7. Variation of dielectric constant with log frequency at different temperatures for 2,5-DCAP single crystal

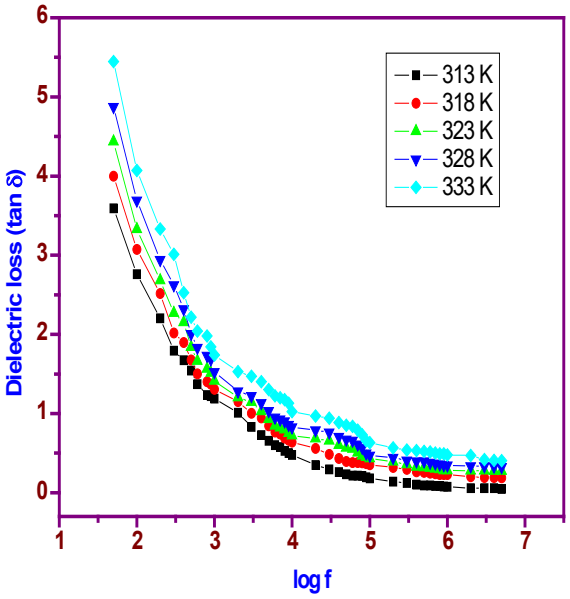


Figure 8. Variation of dielectric loss with log frequency at different temperatures for 2,5-DCAP single crystal

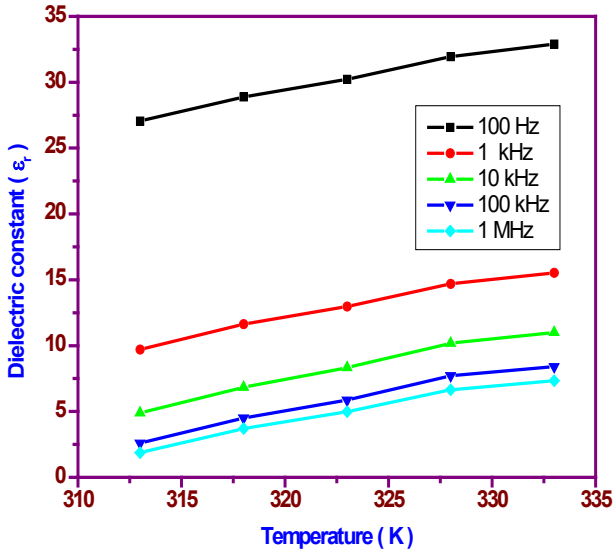


Figure 9. Temperature dependence of dielectric constant for 2,5-DCAP single crystal

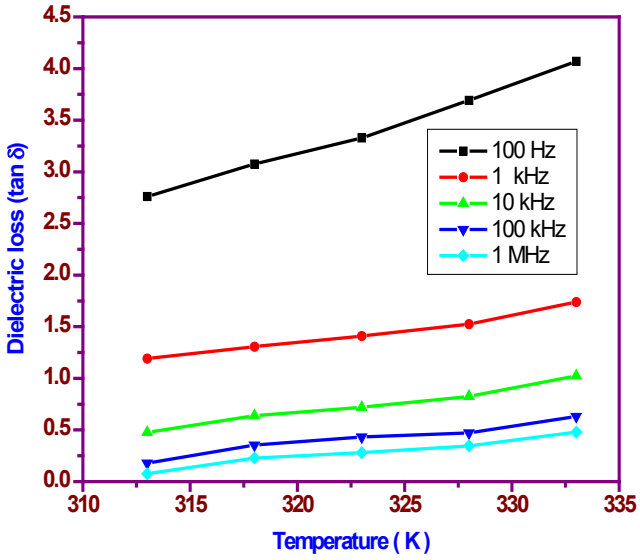


Figure 10. Temperature dependence of dielectric loss for 2,5-DCAP single crystal

5. CONCLUSION

Single crystals of 2,5-DCAP were successfully grown using the slow evaporation method. X-ray diffraction confirmed its monoclinic structure with a noncentrosymmetric space group. UV-Vis-NIR spectroscopy showed excellent optical transparency. Hardness studies indicated decreasing hardness with increasing load. The powder SHG study revealed that

2,5-DCAP is 1.6 times more efficient than KDP. Dielectric characterization indicated a low dielectric constant at higher frequencies. These favorable properties suggest that 2,5-DCAP is a promising material for photonic, electro-optic, and SHG device applications.

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