Development and Evaluation of an Efficient Second Order Non-Linear Optical Single Crystal – 2-(3-Aminopyridinium-1-yl)-3-carboxyproponate monohydrate

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Abstract—A slow evaporation solution approach was used to create high-quality single crystals of 2-(3-aminopyridinium-1-yl)-3-carboxyproponate monohydrate (3ACPM). The single crystal X-ray diffraction was used to determine the crystal system and lattice characteristics. Software called Krystal Shaper was used to mimic the morphology of the 3ACPM. To evaluate the optical transmittance, UV-vis spectral analysis was used. The Nd:YAG laser was used to assess the laser-induced surface damage threshold (LISDT) of 3ACPM single crystal. The presence of second harmonic generation (SHG) was evaluated using the Kurtz-Perry powder method.

Research and development of highly efficient organic nonlinear optical (NLO) materials have received much attention because of their numerous applications, including optical communications, optical data storage, and high-speed information processing [1]. Due to its highly aligned and stable dipolar NLO chromophore, several investigations have lately been carried out worldwide to design new compounds and create single crystals with non-centrosymmetric space groups. For the construction of our devices, we need crystals with bulk size, excellent optical quality, mechanical stability, no flaws, and high NLO nonlinearity. Generally speaking, various crystal shapes have been produced under ambient conditions using the slow evaporation solution technique (SEST). Organic compounds exhibiting π-electron delocalization are crucial to the study of nonlinear optics. Sergiu Draguta [3] and colleagues demonstrated the 3-aminopyridine 4-nitrophnenol adduct crystal structure. The adduct mentioned above was investigated in terms of growth, characterization, and quantum chemical studies, particularly emphasizing second harmonic generation (SHG).

In this perspective, 2-(3-aminopyridinium-1-yl)-3-carboxyproponate monohydrate (3APCM) single crystal structure was first reported by G.M. Corrales and his co-workers [4]. As far as we know, neither quantum chemical calculations nor the experimental investigation of the material referenced in the title have been published. There is no information on the growth, linear optical property, laser damage threshold, and SHG nonlinearity of the titular material except from studies on crystal structure. In this viewpoint, 3ACPM was developed in bulk form to begin with. To determine the lattice parameters and crystal system, the generated single crystal of 3ACPM underwent single-crystal X-ray diffraction analysis. The crystal morphology was simulated using the Krystal Shaper platform. The titular material's linear and non-linear optical characteristics were assessed for their suitability for device fabrication. The laser-induced surface damage threshold was performed to determine the resistance of 3ACPM to laser interaction.

By using a slow evaporation process and low-temperature solution growth, the high-quality single crystal of 3ACPM was produced. By mixing 3-aminopyridine (Hi-Media) and fumaric acid (Hi-Media) in methanol in an exact proportion (1:1), a single crystal of 3ACPM was created, and the reaction scheme is presented in Fig. 1(a).

(a)

$$C_5H_6N_2 + C_4H_4O_4 \xrightarrow{MeOH} C_9H_{10}N_2O_4.H_2O$$

(b)

Fig. 1. (a) Scheme of synthesis of 3-ACPM; (b) Snapshot of as grown 3-ACPM single crystal.

Initially, methanol was used to dissolve the predicted amount of fumaric acid. Fumaric acid dissolved in methanol was added to this, along with the predicted amount of 3-aminopyridine, and the resulting orange-colored solution was left to stir for roughly three hours to establish homogeneity. This solution was transferred to a

clean beaker using a Whatmann filter to remove any contaminants. A perforated aluminum foil was placed over the beaker to stop the solution from quickly evaporating. The complete setup was placed in a spotless environment and was not disturbed. Twenty-two days later, 3ACPM single crystals of excellent grade were collected. Fig. 1(b) shows a snapshot of an as-grown 3-ACPM single crystal.

X-ray diffraction analysis of a single crystal of 3ACPM revealed that the material crystallizes in an orthorhombic crystal system with the non-centrosymmetric space group $Pna2_1$. In this way, the titular material satisfied the main SHG requirement. Further observation shows that the volume V = 1017.67 (7) Å^3 and the lattice parameters were discovered to be a = 7.47 (4) Å, b = 19.49 (2) Å, and c = 6.99 Å with Z=4. The reported data and the observed outcomes were determined to be consistent [4]. It is envisioned that chains along the axis are connected by COO—H...OOC motifs rather than centrosymmetric dimeric hydrogen-bonded units based on the geometry accepted by the eponymous substance, $C_9H_{10}N_2O_4.H_2O$. These chains are held together by the water of crystallization and the N—H...O and O—H...O hydrogen bonds between the carboxylic acid and carboxylate units [4]. The development of SHG is facilitated by the presence of the aforementioned hydrogen bonds and the crystallization of the title substance in a non-centrosymmetric space group. Figure 2 displays the 3ACPM's molecular structure.

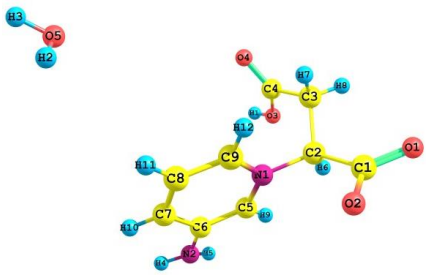

Fig. 2. Molecular structure of 3ACPM.

Crystal morphology offers fundamental details on the bulk crystal's growth rate and creation of notable growth facets. Additionally, because crystals are naturally anisotropic, they can be cut into noticeable facets with better properties for usage in applications focused on devices. The Krystal Shaper program was used to provide some information on crystal morphology. The CIF [4] was developed as a starting point to forecast the 3ACPM morphology. The projected 3ACPM morphology is made up of the six aspects with Freidel pairs (1 0 0), (-1 0 0), (0 0 1), (0 0 -1), (0 1 0), and (0 -1 0). The inferred crystal shape of 3ACPM is shown in Fig. 3.

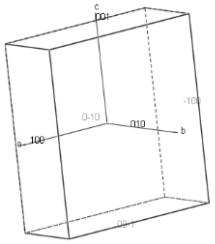

Fig. 3. Deduced morphology of 3ACPM.

To deploy NLO crystals in the field of SHG-oriented applications, they must have a cut-off wavelength below the operating wavelength of 532 nm and a wide transmission window. Furthermore, at the operating wavelength, there should be no significant absorption. UV-vis spectral analysis was performed on the titular material to illuminate its optical transmission spectrum. Fig. 4 depicts the UV-vis transmission spectrum of a 3ACPM single crystal.

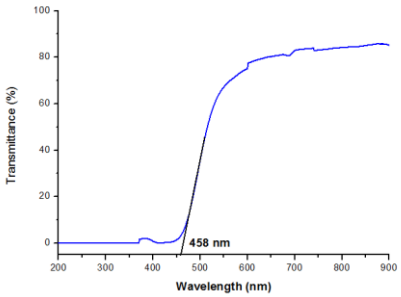

Fig. 4. UV-vis transmission spectrum of 3ACPM.

According to Fig. 4 of the UV-vis transmission spectrum of 3ACPM, the cut-off wavelength was discovered to be 458 nm, with an optical transparency of around 80%. Fig. 4 also shows that there are no significant absorptions near the fundamental or second harmonic wavelengths, which contributes to the conversion efficiency in those wavelengths.

The laser-induced surface damage threshold (LISDT) was measured on a single crystal of 3ACPM as grown. The LISDT analysis was performed using a 1064 nm Nd:YAG laser with a pulse width of 10 ns and a repetition rate of 10 Hz. A 2 mm diameter laser beam was focused on the crystal. A single 3ACPM crystal was placed at the focus of a planoconvex lens with a focal length of 30 cm. With a polarizer and a half-wave plate, an attenuator was used to vary the energy of the laser pulses. The pulse energy of each shot was measured using a phototube and an oscilloscope in combination. The laser-induced surface damage threshold of the as-grown 3ACPM single crystal was calculated by the relation:

$$P_d = E / (\tau\pi r^2), \quad (1)$$

where E is the input energy (mJ), τ is the pulse width (ns), and r is the laser spot radius (mm). 3ACPM's laser-induced surface damage threshold was determined to be 0.582 GW/cm^2.

The existence of second harmonic generation (SHG) in the 3ACPM powdered crystalline sample was validated by the Kurtz-Perry powder technique [5]. This technique ensures the SHG execution of novel materials comparable to standard SHG material potassium dihydrogen phosphate (KDP). To investigate the SHG analysis of the titular material, a Q-switched Nd:YAG laser with a wavelength of 1064 nm, a pulse width of 10 ns, and a repetition rate of 10 Hz was used. The crystalline samples of 3ACPM and reference material KDP were individually stuffed in separate micro-capillary tubes of 125-150 micrometers. The yield may be viewed as a shining green streak emanating with the escalated 532 nm wavelength. After being converted into an equivalent electrical signal, the SHG yield was displayed on a digital storage oscilloscope. The photomultiplier tube's optical wave occurrence was converted into voltage yield. The 3ACPM crystalline sample recorded a SHG wave intensity of 13.6 mV, whereas the KDP powdered crystalline sample measured 5.9 mV for an input energy of 2.7 mJ/pulse. The SHG nonlinearity of the powdered crystalline sample of 3ACPM is approximately 2.30 times more than that of the KDP standard reference material. The relative SHG nonlinearities of titular material with 3-Aminopyridine 4-Nitrophenol (3AP4NP) in line with KDP equaling 1.0 is presented in Table 1.

Table 1. Relative SHG nonlinearities of titular material with reported data

NLO Crystals	Space Group	SHG nonlinearities	References
3ACPM	$Pna2_1$	2.30	Current Work
3AP4NP	$P2_1$	2.72	[6]

In conclusion, we described 3ACPM, an NLO single crystal that was synthesized, grown, and characterized. By employing methanol as a solvent and a slow evaporation process, the superior quality single crystals of 3ACPM were created. It was discovered that the formed 3ACPM single crystal crystallizes in an orthorhombic crystal system with a non-centrosymmetric space group using single-crystal X-ray diffraction research. With the help of six facets, the 3ACPM crystal's shape was anticipated. According to the UV-vis transmittance spectral analysis, the titular material has about 80% optical transparency in the working wavelength. It was established that the 3ACPM single crystal's laser-induced surface damage threshold was 2.58 GW/cm^2. It was revealed that the 3ACPM powdered sample's SHG nonlinearity was 2.30 times more than that of KDP, the standard reference material. The deployment of the titular material in SHG applications is made possible by this outcome. The titular compound is suggested as a prospective option in the field of nonlinear optics because of its promising crystal formation and linear and nonlinear optical properties.

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