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Investigations On the Growth, Spectral, Photoluminescence, Laser Damage Threshold and NLO Studies Of Sodium 3,5-Dinitrobenzoate Single Crystals

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ABSTRACT

Nonlinear optical single crystal of Sodium 3,5-dinitrobenzoate has been grown using the slow evaporation solution growth technique at ambient temperature. A single crystal x-ray diffraction study revealed that the crystal belongs to the Trigonal system with space group P3121. The functional groups in the material were identified using Fourier transform infrared (FT-IR) spectroscopy and KBr pellet techniques. The optical assessment of the title compound was analysed using UV-Vis-NIR spectral analysis. Based on the absorbance data, the lower cutoff wavelength was determined to be 332 nm, and the optical bandgap was found to be 3.7 eV. The grown crystal exhibits good optical transparency throughout the entire region. Analysis of the photoluminescence spectrum indicates broad emission peaks, suggesting violet emission. The laser damage threshold (LDT) was tested using a Nd: YAG laser, and the second harmonic generation efficiency was evaluated using the Kurtz-Perry powder technique.

Keywords: Crystal Growth, X-ray diffraction, FT-IR, Optical studies, Laser damage threshold

1. INTRODUCTION

In recent times, there has been a growing interest among scientists and technicians in nonlinear optical (NLO) crystals due to their potential applications in photonics, optoelectronics, optical information processing, frequency conversion, and communications. The search for such optical materials is ongoing, leading to the discovery of numerous organic compounds with enhanced nonlinear optical (NLO) efficiency. The presence of active π bonds in organic systems is the main reason behind the high efficiency of nonlinear optical effects. However, organic materials have limitations such as suboptimal mechanical strength, susceptibility to laser damage, and limited thermal stability. Various engineering methods have led to the development of numerous organic

molecules to address these constraints, and ongoing efforts are focused on optimizing their properties [1-5].

The nitro groups are typically bonded to metal ions through a conjugated π-electron bonding system of donor and acceptor ions, leading to high optical nonlinearity effects, such as when the Na^+ ion is bonded with the NO_2 group in the crystal. 3,5-dinitrobenzoic acid's nitro-substituted aromatic acid has been utilized to produce chiral crystalline adduct materials with physical properties that are potentially valuable for applications like nonlinear optics. It has a relatively strong proton donor-acceptor due to the presence of the COOH carboxylic group. The structure is trigonal, and the benzoate ion possesses twofold crystallographic symmetry, passing through the carboxylate group, as depicted in Figure 1. The compound in question exhibits significant biological activity, with a minimum inhibitory concentration against fungi. It is used to prepare metal complexes to enhance their biological effects. There is little existing literature on the bonding of 3,5-dinitrobenzoic acid to metals such as magnesium [6], manganese [7], lithium [8,9], and potassium [10,11].

The current study involved growing a single crystal of sodium 3,5-dinitrobenzoate (NaDNB) using the low-temperature solution method (SEST). The grown crystals were then characterized using single-crystal X-ray diffraction, Fourier transform infrared (FT-IR) spectroscopic analysis, UV-Visible-NIR analysis, Photoluminescence (PL), Laser Damage Threshold studies (LDT), and Second Harmonic Generation (SHG) studies.

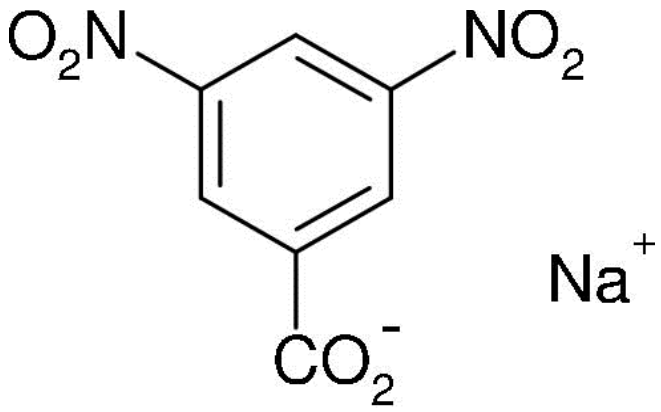

Figure 1. Molecular structure of Sodium 3,5-dinitrobenzoate

2. MATERIALS AND METHODS

The commercially available 3,5-dinitrobenzoic acid (Aldrich, 99%) was dissolved in a 1:1 ratio with sodium hydroxide (NaOH) solution to synthesize sodium 3,5-dinitrobenzoate (NaDNB) compound. Initially, the measured quantities of NaOH and 3,5-DNBA were dissolved in double-distilled water. The solution was thoroughly mixed using a motorized magnetic stirrer for 12 hours. Afterward, repeated recrystallization was performed to improve the optical quality of the crystals and eliminate suspended impurities. The homogenous solution was carefully filtered and placed in a constant temperature bath (±0.01°C). After 45 days, good-quality single crystals were harvested from the mother solution, as shown in Figure 2.

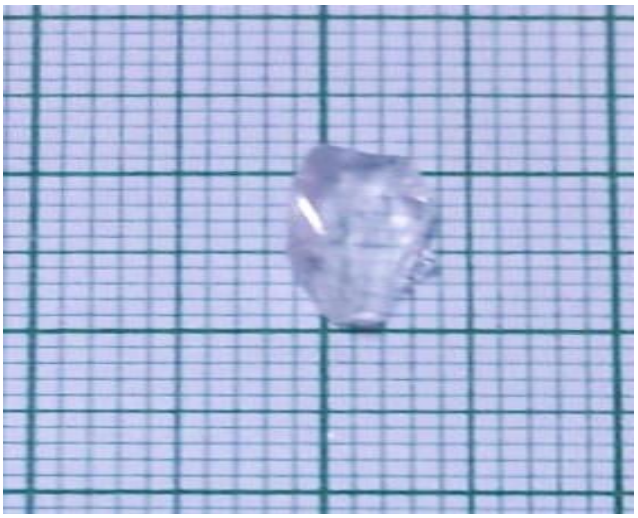

Figure 2. As grown single crystal of sodium 3,5-dinitrobenzoate

3. RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction analysis

The as grown single crystal of NaDNB was subjected to X-ray diffraction using Bruker Kappa APEX II diffractometer with MoKα (λ = 0.71073 Å). From the studies, it crystallizes in the trigonal system with space group P_{3121}. The calculated cell parameters a = b = 10.688Å, c = 6.3526 Å, α = β = 90°, γ=120° and volume V = 646 Å^3 are matched with the reported literature values [12]. which is tabulated in Table 1.

Table 1 Crystallographic information of NaDNB

Lattice parameters	Present work	Helen P Jones et.al (2005)
a = b	10.68 Å	10.77 Å
c	6.490 Å	6.350 Å
Crystal system with space group	Trigonal, P_{3121}	Trigonal, P_{3121}
α = β	90°	90°
γ	120°	120°
Volume	646 Å^3	638 Å^3

3.2 FT-IR spectroscopic analysis

The FT-IR spectrum of the title compound was recorded in the range of 400 to 4000 cm^{-1} using a Bruker AXS FT-IR spectrophotometer, as shown in Figure 3. The band at 2942 cm^{-1} and 2880 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the C-H group. The robust asymmetric stretching mode at 1630 cm^{-1} indicates the presence of carboxylic salt of COO- and its symmetric stretching is at 1417 cm^{-1}. The peak at 1111 cm^{-1} is due to C-C bending vibration, and the bending vibration of C-N appears at 905 cm^{-1}. The strong C=H out-of-plane bending vibration is observed at 679 cm^{-1}, and the C-O wagging vibration is observed at 497 cm^{-1}. These are all the vibrational assignments of the title compound.

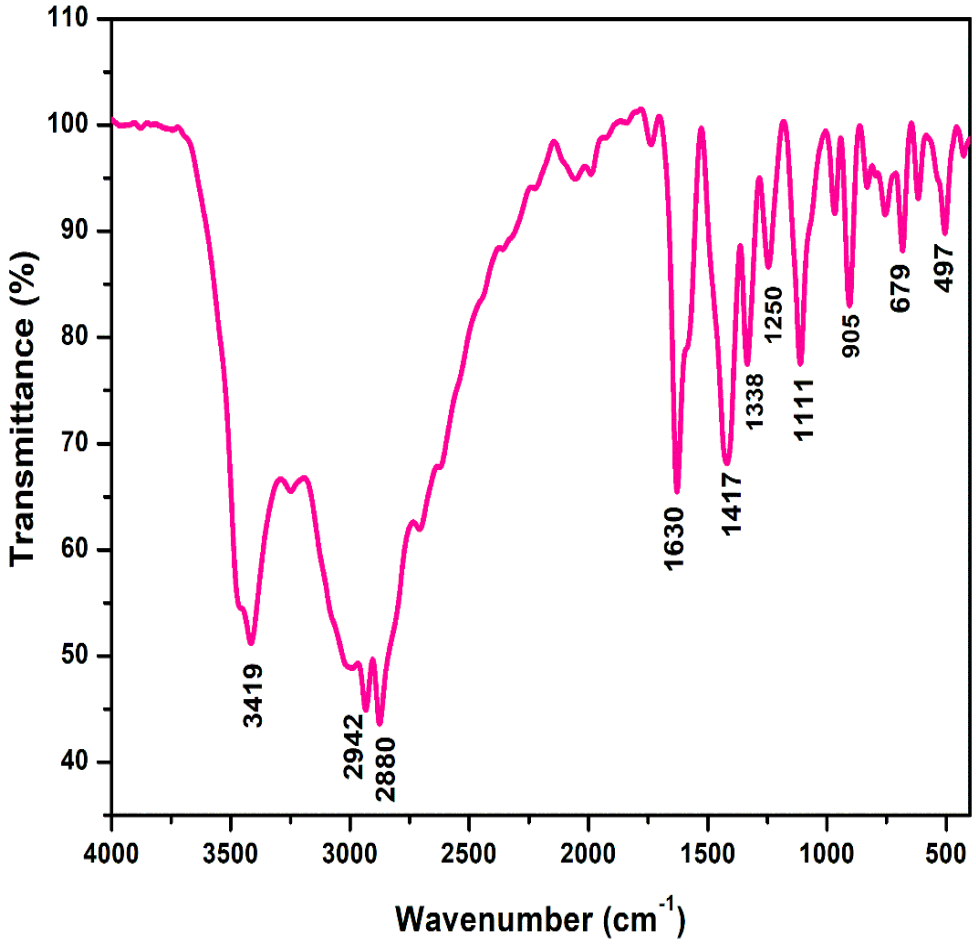

Figure 3. FT-IR spectrum of sodium 3,5-dinitrobenzoate

3.3 UV-Visible-NIR analysis

The optical properties of the materials were closely related to their atomic structure, electronic bandgap, and electrical properties. UV-visible spectrum was utilized to analyse the characteristic peak of the compound, indicating electronic transitions between molecules [13]. The optical studies were conducted using a Perkin-Elmer Lambda-35 UV-Visible NIR spectrophotometer in the wavelength range of 250 – 1200 nm. The UV-visible spectrum provides information about the molecule's structure because the absorption of UV and visible light involves the promotion of the electron from the ground state to higher states. The optical absorption and transmittance spectrum of the title compound are depicted in Figures 4 and 5, respectively. From the spectrum, the lower cut-off wavelength was observed at 332 nm. The grown crystal exhibited good transmittance throughout the entire visible and near-infrared region.

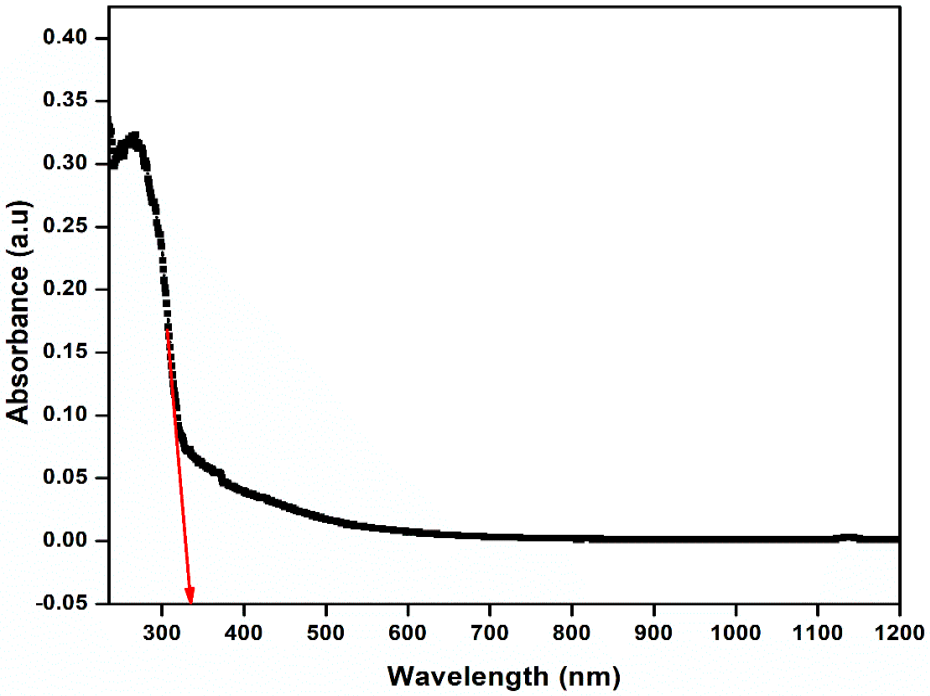

Figure 4. UV-Visible-NIR absorbance spectrum of sodium 3,5-dinitrobenzoate

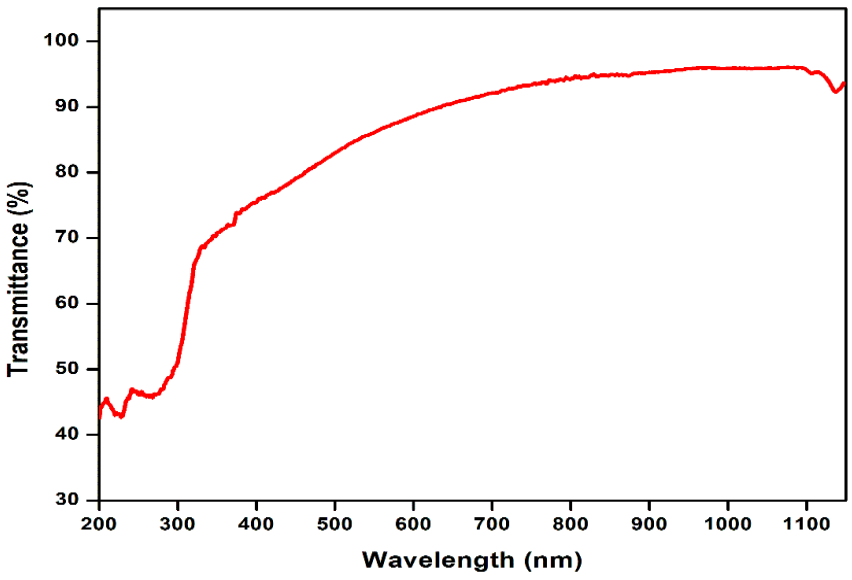

Figure 5. UV-Visible-NIR transmittance spectrum of sodium 3,5-dinitrobenzoate

The UV-Visible absorbance data was used to calculate the optical band gap, which is shown in Figure 6. The plot of energy (hυ) versus $(\alpha h\upsilon)^{1/2}$, where "α" represents the absorption coefficient, helped determine the optical band gap energy, which was found to be 3.7 eV by extrapolating the slope region where it intersects the x-axis. For a direct transition, "n" equals 1/2 or 3/2, depending on whether the transition is allowed or forbidden in a quantum mechanical sense. The

graph plotted between the absorption coefficient and the incident photon energy at room temperature demonstrates a linear behaviour, indicating evidence of the direct transition. In Figure 7, the relationship between refractive index (n) and wavelength (λ) is depicted. The spectrum shows the refractive index (n) as a function of wavelength (λ).

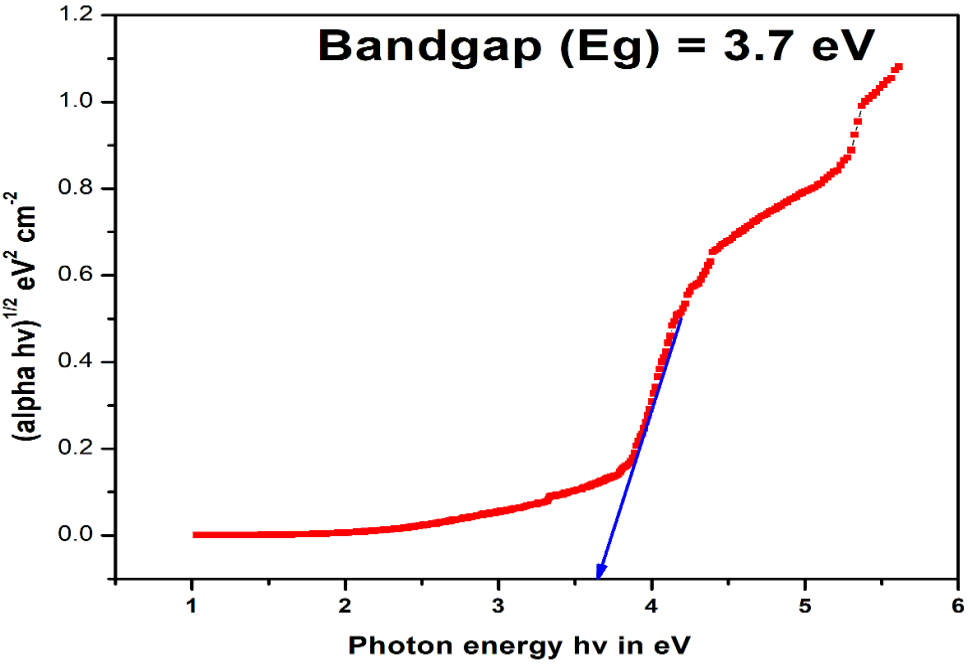

Figure 6. Variation of Photon energy (hν) with $(\alpha h\nu)^{1/2}$

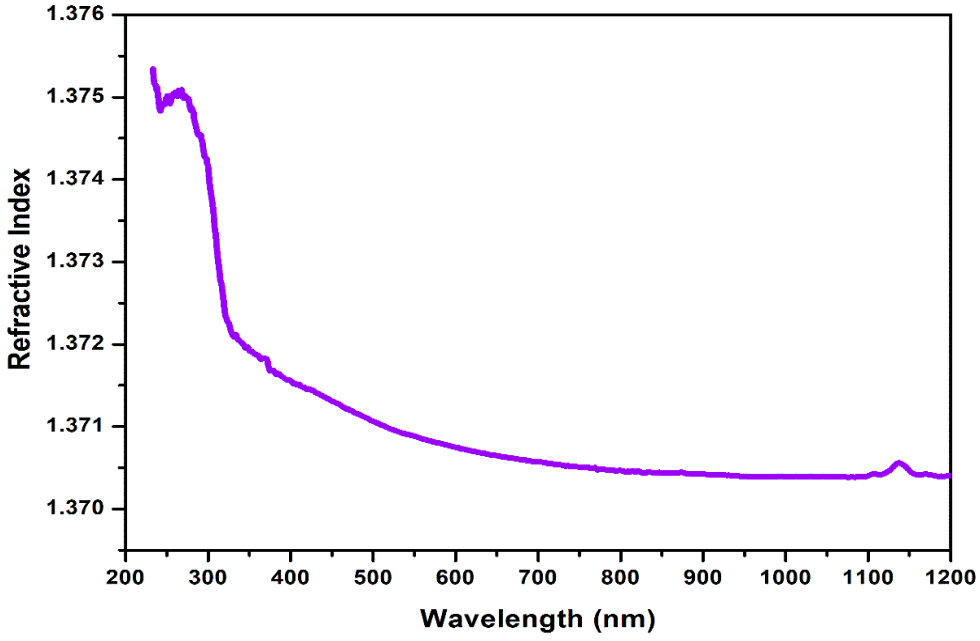

Figure 7. Wavelength dependence of sodium 3,5-dinitrobenzoate

3.4 Photoluminescence studies

The NaDNB sample was examined using the Jobin Yvon-Spex Spectrofluorometer to measure its photoluminescence spectrum. Photoluminescence refers to the emission of light radiation resulting from the absorption of photons [14]. In this analysis, the NaDNB sample was excited at 325 nm, and the resulting emission spectrum was recorded between 350 and 650 nm, as shown in Figure 8. This luminescence emission falls within the violet region, indicating the emission of violet light, with the intensity of the emission peak decreasing after 450 nm. The strong peak in the spectrum suggests that the synthesized material is pure and suitable for laser-assisted applications.

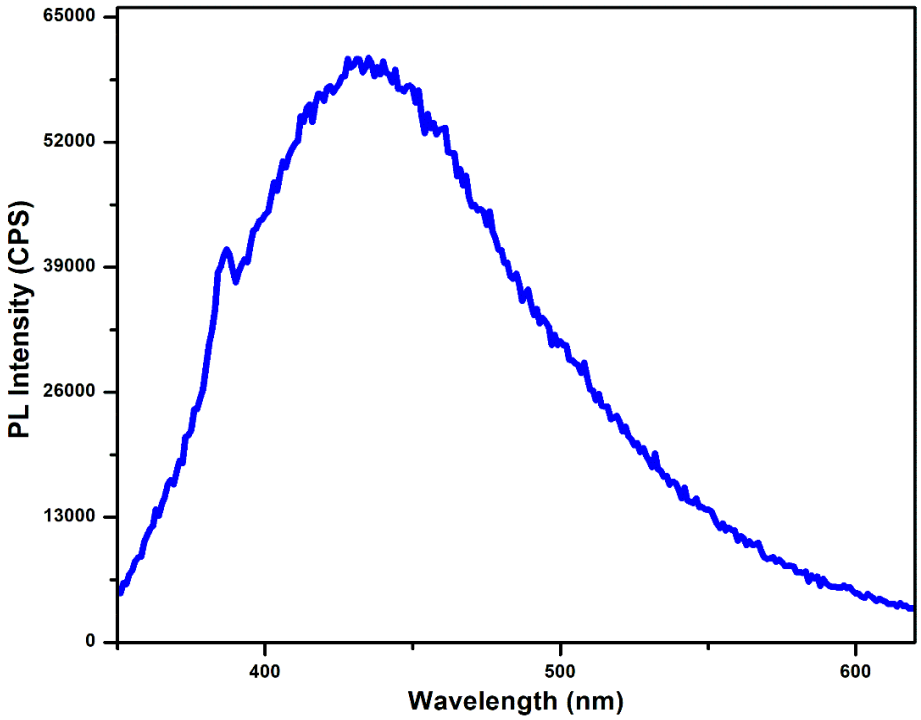

Figure 8. PL spectrum of sodium 3,5-dinitrobenzoate

3.5 Laser Damage Threshold Studies

The laser damage threshold (LDT) value indicates the minimum amount of energy a material can withstand before it is damaged. This value is crucial for assessing the performance of optical systems in laser applications. In a recent study, a Q-switched Nd:YAG laser operating at 1064 nm wavelength, with a transverse mode frequency of 10 Hz and a pulse duration of 6 ns, was utilized to measure the LDT of a grown crystal. The crystal's well-polished surface was irradiated using a 1 mm diameter laser beam, which was controlled by a variable attenuator. The crystal was positioned at the focal point of a converging lens with a focal length of 10 cm. Damage to the crystal surface was observed visually as the input laser energy density reached 12.2 mJ on the power meter.

3.6 Nonlinear Optical studies

Kurtz-Perry powder technique [15] was used to determine the second harmonic generation (SHG) efficiency of the compound. This allowed us to compare the SHG efficiency of the title compound to the standard potassium dihydrogen phosphate (KDP). In this study, a 1064 nm Q-switched Nd: YAG laser beam with an input energy of 0.70 J, a pulse width of 6 ns, and an input repetition rate of 10 Hz was utilized. The grown specimen was powdered with an average particle size range, placed in a micro-capillary tube with a uniform bore, and exposed to laser radiation to confirm the non-linear optical (NLO) property. The output from the sample was monochromate to measure the 532 nm component intensity. The second harmonic signal generated in the crystalline sample was verified by the emission of green radiation with a wavelength of 532 nm from the crystalline powder sample. Comparison with KDP showed that the SHG efficiency of the sample was 0.5 times that of standard KDP. It was noted that the second-order nonlinear efficiency varies with the particle size of the powder sample [16].

4. CONCLUSION

A bulk semi-organic nonlinear optical single crystal of sodium 3,5-dinitrobenzoate was cultivated using the slow evaporation solution growth technique at room temperature. The crystal's unit cell parameters were verified through single crystal X-ray diffraction analysis, and various functional groups were identified via FT-IR spectral analysis. The optical properties were examined, revealing a lower cut-off wavelength of 332 nm and an optical band gap of 3.7 eV. The material's suitability for violet emission applications was confirmed through photoluminescence studies. Furthermore, the laser damage threshold value was assessed, resulting in observed surface damage. Finally, the SHG efficiency was evaluated using the Kurtz-Perry technique and compared with that of the KDP crystal.

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