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Synthesis, Growth and Characterization of Benzophenone Added Sodium Acid Phthalate Crystal—A Potential Material for Nonlinear Optical Applications

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Abstract

Sodium acid phthalate $C_8H_5NaO_4$ is one of the suitable semiorganic single crystals hired in second harmonic generation conversion applications. In the present work, optically transparent Benzophenone doped with sodium acid phthalate (SAPB) single crystals were grown successfully by slow evaporation solution technique. Single crystal XRD analyses exposed that the crystal lattice of SAPB crystal is a monoclinic crystal system with unit cell parameters a = 6.77 Å, b = 9.31 Å, c = 13.58 Å, and space group B2cb. The crystalline nature of SAPB material was confirmed by powder XRD pattern. The functional groups present in the grown crystals were identified by the FTIR analysis ranging between 4000 and 500 cm^{-1}. The optical transparency and band gap of grown crystals were measured from UV-Visible spectroscopy. The fluorescence emission spectrum of the SAPB crystal having a strong Yellow emission peak at 574 nm and the red emission at 631 nm are identified. The Vickers microhardness number (H_v) increases with increasing load. Meyer's index number (n) calculated from H_v shows that the material belongs to the soft material category. Preliminary measurement using Kurtz powder technique with Nd-YAG laser light of wavelength 1064 nm indicates that their second harmonic generation (SHG) efficiencies of the grown crystals were presented 2 times in comparison with Potassium Dihydrogen Phosphate (KDP) was confirmed.

Keywords

Growth from Solution, UV-Vis, FTIR, Powder XRD, Fluorescence, SHG

1. Introduction

Recent interest in research focuses much on the search for highly efficient second order nonlinear optical (NLO) materials due to their potential applications in data storage devices, optical communication, optical switches, optical frequency conversion, laser-based images, optoelectronics, telecommunication [1] [2]. The desired nonlinear optical material must exhibit large second-order optical nonlinearities, Semiorgani NLO crystals have a wide range of applications like high transparency range and the material is sodium acid phthalate ($C_8H_5NaO_4$) doping of external impurity plays a crucial role in tuning the properties of the host crystal, the most effective strategy to gain improvement in intrinsic properties of SAPB crystal is to incorporate benzophenone ($C_{13}H_{10}O$) impurities in a selected quantity [3] [4] [5] [6] [7]. To enhance the physical properties of single crystals impurities is playing a vital role. The fact motivates the abundant benzophenone chosen as dopant [8]. The excellent applications and use of titled material in various optical devices encourage us to grow good quality single crystals using dopant with improved optical properties for future technological application.

In this present work, we report the repercussion of benzophenone in sodium acid phthalate single crystals for SHG applications [9]. The method used for the growth of benzophenone doped sodium acid phthalate was the conventional method which can also be called as slow evaporation solution growth method. The grown crystal was subjected to various characterization studies such as the structural studies were made on the grown crystal by single crystal X-ray diffraction studies [10] [11] [12] [13] [14]. The crystalline nature and functional group were identified by powder X-ray diffraction, Fourier transform infrared analysis, UV-absorption studies, and the fluorescence study exhibits that material having a yellow color emission, Vickers microhardness, Finally, the NLO property of the SAPB crystal was studied using Kurtz powder technique.

2. Experimental Procedure

Synthesis and Crystal Growth

All the reagents were purchased from Sigma Aldrich and used without further purification. The title compound was synthesized by sodium hydroxide and phthalic acid at 1:1 equimolar ratio. The calculated amount of sodium hydroxide and phthalic acid was added to double distilled water according to the solubility. The benzophenone was dissolved in deionized water according to the solubility and stirred for 2 hour, and finally, both solutions was mixed with continuous stirring for about 3 hour using magnetic stirrer and to obtain a homogenous mixture. The completely dissolved solution was filtered using whattman filter paper to remove the suspended impurities and allowed to crystallize by solution growth method at room temperature for about 16 days. Finally a well-defined single crystal with the dimensions of $5 \times 6 \times 2$ mm^3 was obtained. The photograph of grown SAPB crystal is shown in **Figure 1**.

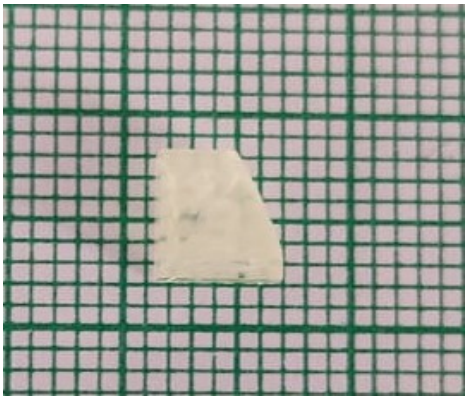

Figure 1. Photograph of as grown SAPB crystal.

3. Result and Discussion

3.1. Powder X-Ray Diffraction

The powder X-ray diffraction analysis of SAPB was recorded by using a powder X-ray diffractometer with CuKα_1 radiation (λ = 1.5460 m). Figure 2 shows the powder X-ray diffraction pattern that confirms the crystalline nature of the grown crystal [15] [16] [17] [18]. From the spectrum, it is observed that the peaks are turned up in between 10' - 60' degrees. From the above investigation, we can propose that the grown crystal is a combination of reflections from (110), (011), (020), (111), (210) and (131) diffraction planes, which appeared at the 2θ of 16.54, 19.06, 22.28, 23.38, 28.52 and 39.79 respectively, the sharp and prominent peak at 19.06 is assigned to the (001) crystal plane of SAPB. The high intensity and low full width half maxima of the peaks confirm the good crystalline nature of the crystal.

3.2. Single Crystal X-Ray Diffraction

The single crystal XRD studies are carried out with more dependable information on lattice parameters as compared to the powder XRD studies. The apt size of a single crystal was selected for the XRD analysis and to evaluate the cell parameters [19]. The SCXRD result declares that benzophenone doped with sodium acid phthalate crystal belongs to the monoclinic crystal system [20]. The unit cell dimensions and X-ray intensity data of SAPB were founded using Bruker D8 Venture Scxrd equipped with MoKα radiation (λ = 0.71073 Å). The single crystal XRD result revealed that lithium benzophenone doped Sodium acid phthalate crystal belongs to the monoclinic system with a space group of B2cb having non-centro symmetry. The obtained lattice parameters are shown in Table 1.

3.3. FTIR Analysis

FTIR spectroscopy is an effective tool to identify and confirm a compound by analyzing the functional groups present within the spectrum. The molecular interactions between the reagents can be well explained by examining different

modes of vibrations [21]-[28]. The spectrum of synthesized material, SAPB is recorded in the region of 4000 and 500 cm^{-1} and is depicted in **Figure 3**. The frequency of 350.10 cm^{-1} is due to OH overtones of the water molecule. The characteristic stretching vibrations of CH_2 are observed at 2854.21 cm^{-1} and 2454.23 cm^{-1}. The peaks obtained at 1598.42 cm^{-1} and 1626.01 cm^{-1} are due to C=O stretching of the COO group. The aromatic ring structure of the SAPB occurs at 1571.15 cm^{-1} and aromatic amine stretching at 1297.06 cm^{-1}. The NH bonding vibration occurs at 1626.01 cm^{-1}. The skeletal vibrations of the aromatic ring of benzophenone were observed at 1598.42 cm^{-1} and 1571.15 cm^{-1}. The vibrations proved the presence of expected functional groups in the synthesized compound.

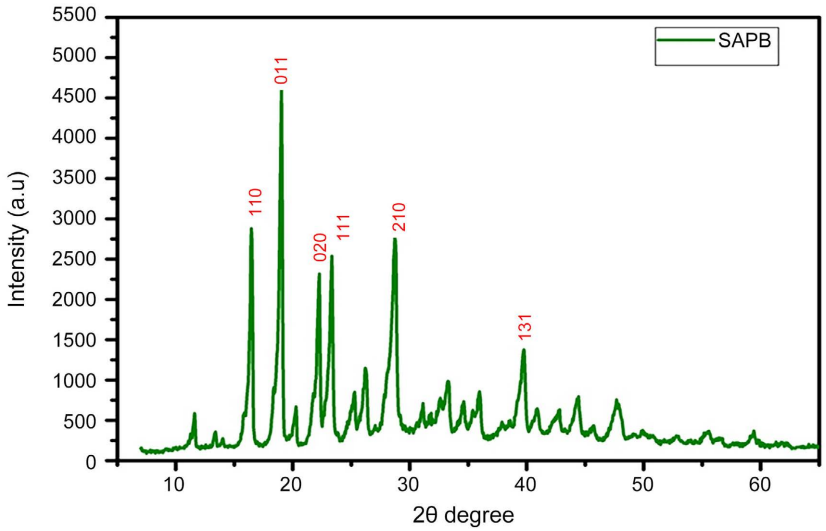

Figure 2. Powder X-ray diffraction pattern of SAPB crystal.

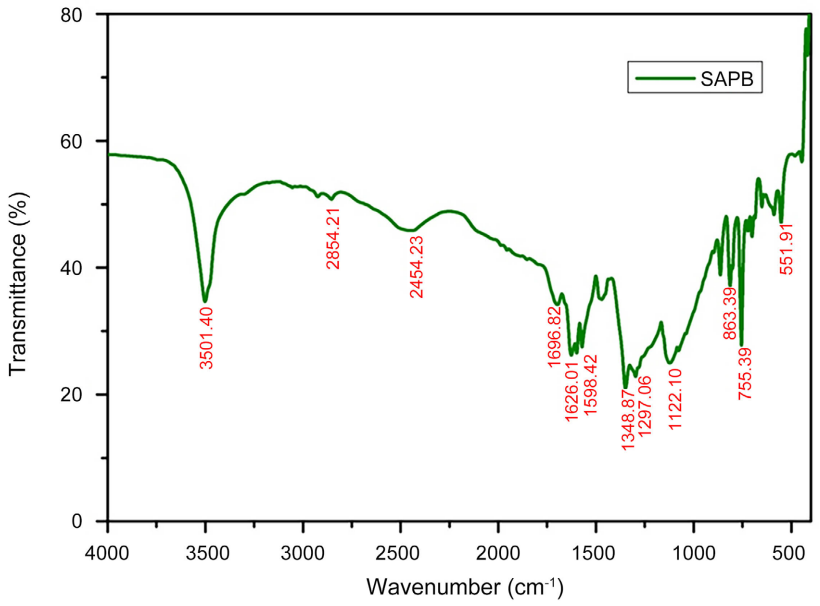

Figure 3. FT-IR spectrum of SAPB crystal.

Table 1. Single crystal data of SAPB grown crystal.

Lattice Parameters	SAPB
a	6.77 Å
b	9.31 Å
c	13.58 Å
α	90.05˚
β	104.34˚
γ	90.04˚
Volume	829 Å^3
Crystal system	Monoclinic
Space group	B2cb

3.4. UV-VIS NIR Spectral Analysis

The grown crystal of benzophenone doped sodium acid phthalate dissolved in distilled water was subjected to spectral studies within 200 - 1200 nm wavelength range using Varian Cary 5E-UV spectrometer. The optical transmittance range and lower cut-off wavelength of a single crystal are vital factors for optical applications. The obtained optical transmittance and absorption spectrum are shown in **Figure 4(a)** and **Figure 4(b)**. The absorption and transmission spectra help us to identify the nature of the molecule by analyzing the transition of electrons in σ and π orbital's between the ground state and higher excited states with the energy absorbed [29] [30]. The SAPB single crystal showed 93% in the entire visible region with the cut-off wavelength of 277 nm. The spectrum indicates that the crystal to be used as a promising aspirant for a higher order of non-linear optical generations and terahertz applications.

The property of electronic optical band gap energy can be well exploited in the fields of terahertz generation and electro optical device applications [31] [32] [33]. The absorption coefficient α can be determined from the transmission spectrum based on the relation,

$$\alpha = \frac{2.303\log\left(\frac{1}{T}\right)}{t} \tag{1}$$

where, α is the absorption coefficient, T is the transmittance and t is the thickness of the crystal. The band gap was estimated from the transmission spectrum and the optical absorption coefficient α near the absorption edge was calculated using the relation,

$$h\gamma\alpha = A\left(h\gamma - E_g\right)^{1/2} \tag{2}$$

In this equation A is a constant, E_g is electronic band gap energy, h is plank's constant, γ is frequency of the incident photon. Hence the optical band gap energy can be calculated from the Tau's plot between $(h\gamma\alpha)^2$ and the photon

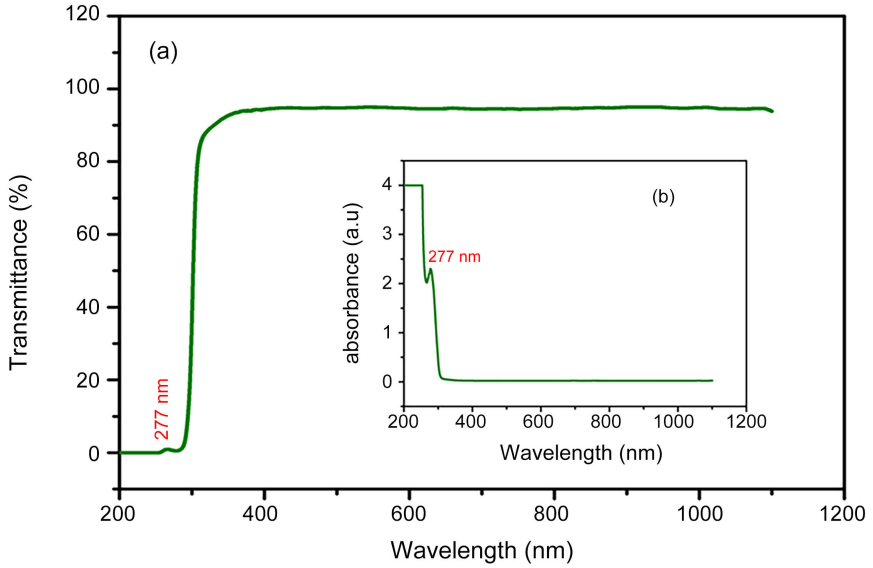

Figure 4. (a). UV-Vis transmission and (b) absorption spectrum of SAPB single crystal.

energy $h\gamma$ (eV) as exhibited in **Figure 5**. Then, by extrapolating the linear portion of Tauc's plot to the axis $\alpha h\gamma = 0$, the value for optical band gap can be obtained [34] [35] [36] [37]. The band gap of SAPB crystal estimated by extrapolation of the linear part of the graph is 4 eV. The band gap and transmittance in the entire visible region enables the crystal suitable for optoelectronic and photonic applications.

3.5. Fluorescence Study

Fluorescence study is a prominent instrument to decide the actual properties of a material at the molecular level, including crystallinity and purity. The fluorescence spectrum was interpreted for SAPB crystal using Varian Cary Eclipse Fluorescence Spectrometer at room temperature. The fluorescence discharge range was recorded in the scope of 500 to 850 nm, shown in **Figure 6**. The SAPB crystal showed a strong yellow emission peak at 574 nm and the red emission at 631 nm are identified [38] [39] [40]. A higher power ratio in the luminescence spectrum is an evidence of better purity, crystallinity, and structural perfection of the SAPB crystal; hence this semiorganic molecule with promising fluorescence emission can be exploited for NLO applications.

3.6. Vickers Microhardness Analysis

The mechanical properties of the crystal are very important for the practical device fabrication. The transparent SAPB single crystals free from cracks, with flat and smooth faces are chosen for static indentation Vickers microhardness test. In the present study, the applied loads (P) are 25 g, 50 g and 100 g respectively and indentation time is fixed 10 s for all indentations. For each load, the average of two diagonal lengths (d) of the indentation mark was measured with the help of calibrated micrometer attached to a metallographic microscope. The Vickers

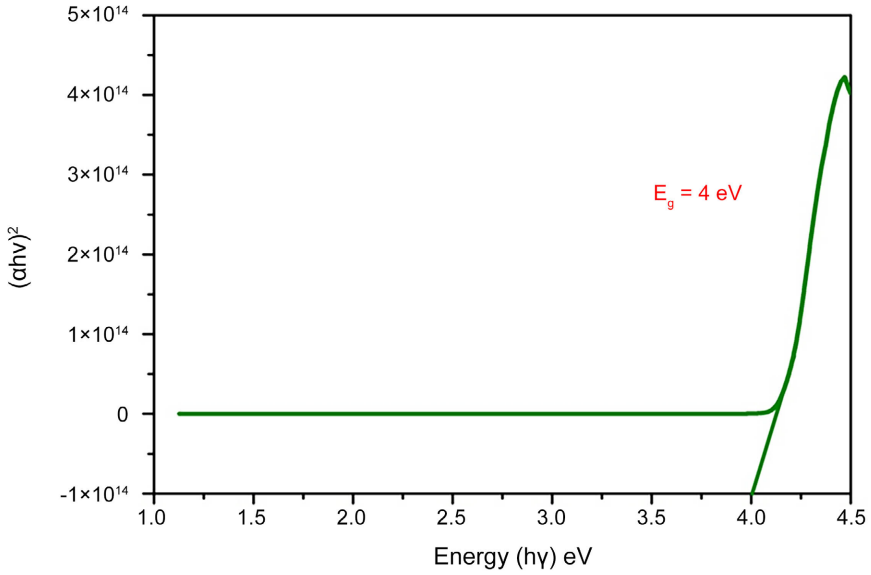

Figure 5. Tauc's plot of SAPB.

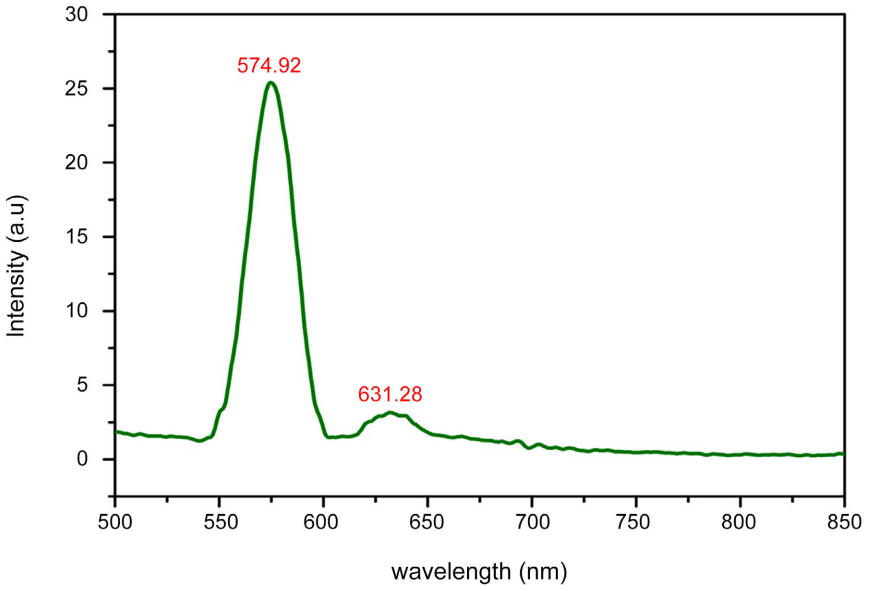

Figure 6. Fluorescence study of SAPB crystal.

hardness number (H_v) value was calculated from the formula, $H_v = 1.8544(P/d^2)$ Kg/mm^2 where d is the diagonal length of the impression in mm and P is the applied loads in Kg. As a function of applied load (P), the change in microhardness value H_v and the plot of log$d$ vs. log$P$ are shown in **Figure 7** and **Figure 8** respectively. Further, the microhardness value increase of load and it is in agreement with the reverse indentation size effect [41] [42]. For above 100 g of applied load, micro cracks were observed due to the release of internal stress generated because of indentation process. The "n" vale was calculated by using Mayer's law given by following relation $P = Ad^n$ where A is constant value and n is the work hardening co-efficient. The Mayer's graph is shown in **Figure 8**. The

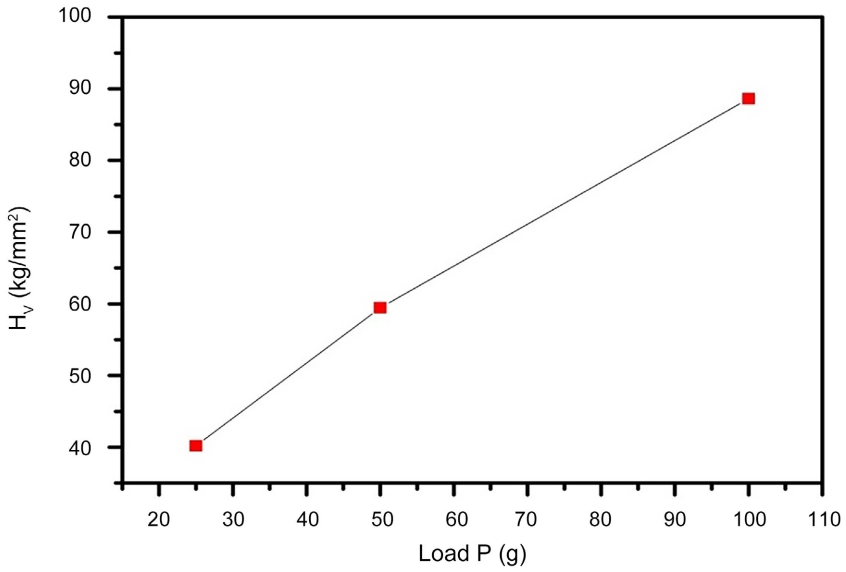

Figure 7. Variation of H_v versus load P.

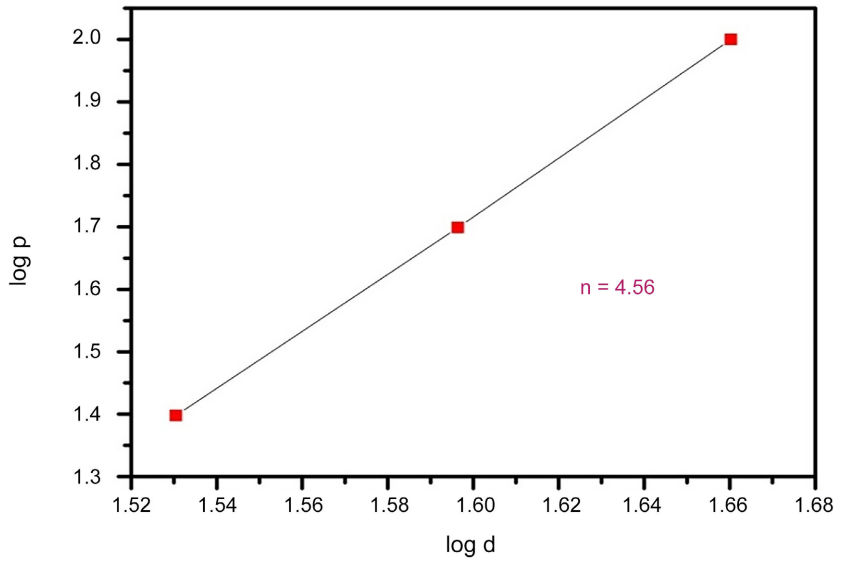

Figure 8. Graph between log$P$ versus log$d$.

work hardening co-efficient (n) of the SAPB crystal has been determined from the slope of the straight line and it is found to be 4.56. According to Onitsch and Hanneman the value of n comes out to be 1 - 1.6 for hard materials and more than 1.6 for soft nature category. Hence, that grown SAPB single crystal belongs to the soft material category.

3.7. Second Harmonic Generation Efficiency Test

The non-linear optical activity of the grown crystal is investigated through the Kurtz-Perry powder method by performing out the SHG test. The frequency conversion effectiveness of material emphatically blends with the impurities, cationic deformities, and the intermolecular charge transfer interaction within the

crystal lattice [43] [44]. The crystals are ground to powder and packed in a capillary tube and were exposed to the continuous wave mode bolted Q-switched Nd-YAG laser of fundamental wavelength 1064 nm delivering 10 ns laser pulses following a repetition rate of 10 Hz. The SHG behavior in these crystals was confirmed from the outflow of exceptional green radiation (λ = 532 nm) by the sample. The determined SHG efficiency of SAPB of crystal as 2 times superior to KDP crystal.

4. Conclusion

Optically good quality single crystal of benzophenone doped sodium acid phthalate crystals has been grown by slow solution evaporation technique. The sharp distinct Bragg's peaks confirm the crystalline nature of the synthesized material. The crystallographic contemplates were completed out utilizing the Single XRD structural pattern and found that SAPB crystal belongs to monoclinic system with B2cb as the non-centrosymmetric space group. The functional groups of the SAPB crystal have been detected by FTIR spectroscopy. UV-Vis spectrum confirms the wide optical transparency of the compound of wavelength with optical band gap 4 eV, which guarantees the ability of the material to create higher harmonic frequencies in non-linear optical applications. The luminescence property of the material was examined from Fluorescence studies with an emission peak at 574.72 nm exhibits its utility in yellow light emitting diodes. The value of Mayer's index was calculated as 4.56, which suggests that SAPB belongs to soft material category. The nonlinear optical test revealed that SAPB determined SHG efficiency of 2 times that of KDP. The above investigations conclude that the benzophenone doped sodium acid phthalate crystal could be advantageous for applications of various frontier technological photonic devices utilized in optical limiting systems, night vision sensors, optical logic switching, signaling, and modulating system.

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Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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