4-Aminopyridinium Salicylate- An organic single crystal for third harmonic generation applications

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Abstract:

In the present work, Non-linear optical organic single crystal, 4 aminopyridinium salicylate (APSA) is grown by slow evaporation method using methanol as solvent. The as grown single crystal was subjected to various characterizations such as XRD, FTIR, UV, dielectric studies and the results are studied. The photoconductivity measurements reveal that the conductivity of APSA is positive. The thermal stability of the as grown crystal was studied with TG/DTA analysis. Z-scan studies were carried out to determine parameters of THG such as non-linear refractive index and non-linear absorption coefficient. The antioxidant property of APSA against DPPH and H₂O₂ was identified. The non-linear property of the crystal was confirmed through the above studies.

Key Words: XRD, FTIR, UV, THG(Third harmonic generation), non-linear refractive index, non-linear absorption coefficient.

1. Introduction

After the invention of the laser in 1940, there has been a steady development in the frequency doubling process, nearly for the last five decades. Materials with high NLO characteristics are of great interest in view of their vital applications such as second and third harmonic generation, electro-optical amplitude modulation, high density optical data storage, ultra compact lasers, optical switching, optical limiting, optical logic, THz wave generation, frequency shifting, optical parametric generation, medical diagnosis and biophotonics [1-3]. In this regard already a great number of inorganic, organic and semi-organic crystals have been grown and their NLO properties are reported. But still, the quest for more efficient nonlinear optical materials is on the increase for the future development of the optoelectronics and photonics technology. Organic materials are considered to be promising NLO candidates since they have several advantages such as high crystalline nature, flexibility of molecular design, high laser damage threshold and large second order hyperpolarizability (β) when compared to inorganic counterparts. Particularly charge transfer complexes (CT) of organic materials are considered for the reason that the special type of interaction is accompanied by a transfer of an electron from the donor to the acceptor.
Also, this CT complex is based on the π-π interaction which leads to high electron density which has a fast response in electro-optic effect that makes more flexible than inorganic materials [4-7].

Based on these facts in the present work pyridine-acid based (donor-acceptor) crystal 4-aminopyridinium salicylate was grown and the third order nonlinear optical parameters like nonlinear refractive index and nonlinear absorption coefficient have been calculated and the obtained results are discussed in detail.

2. Experimental details

2.1 Material synthesis

The Pure specimens of 4-aminopyridine and salicylic acid were used without further purification for material synthesis. The two reactants were dissolved separately with 1:1 molar ratio in methanol and mixed together. The resulting solution was stirred well for about 1 hour. The obtained microcrystalline product was filtered off and then purified by repeated recrystallization process in methanol. The recrystallized compound was used for single crystal growth by the solvent evaporation technique.

2.2 Crystal growth

It is easy to grow single crystals of optical quality of APSA using a standard slow evaporation technique. A saturated solution of APSA in methanol was prepared and stirred well about one and half hour to dissolve the material completely. The solution was then filtered through a quantitative Whatman 41 grade filter paper to remove the suspended impurities. The beaker containing the filtrate was covered using thin polyethylene sheet to prevent the evaporation quickly. The perforations were made to regulate the evaporation. The beaker was kept aside unperturbed in an atmosphere most suitable for the growth of single crystals. Proper care was taken to minimize mechanical disturbance and temperature fluctuations. In a normal growth period of 12 days, single crystals of the title material were harvested and subjected to the characterization. The photograph of the grown crystal is shown in Fig 1.

![As grown crystals of APSA.](image)
3. Results and Discussion

3.1 XRD Studies

The as-grown single crystals of APSA were subjected to single crystal XRD using an Oxford-Diffraction Xcalibur with a sapphire CCD detector and enhance diffractometer (MoKα radiation, graphite monochromator; λ=0.71073Å). Results indicate that the title compound belongs to the orthorhombic system with a space group of Pbca. The lattice parameter values are found to be $a = 12.5804$ Å, $b = 11.4154$ Å, $c = 15.7562$ Å and $Z = 8$. The volume of the APSA crystal was found to be 2262.75 (Å$^3$) [8].

Powder X-ray diffraction pattern of the grown crystals was carried out by using Rich Seifert diffractometer. Diffraction pattern data were collected on the diffractometer equipped with monochromated CuKα radiation (1.540598Å) and detected by a scintillation counter. The grown crystals were finely crushed into powder and subjected to analysis. The sample was scanned over the 2 theta range of 10-50° at a scan rate of 3/min. Fig. 2 depicts the powder X-ray pattern for the APSA crystal. The sharp and well defined Bragg’s peaks at specific 2theta angle testinomies the crystalline nature of the sample. The various planes of reflections (hkl) were indexed using TREOR 90 program.

![Fig.2. Powder XRD spectrum of APSA.](image)

3.2 FTIR analysis

The Middle infrared (FTIR) spectrum of the APSA was recorded at room temperature in the range of 400 to 4000 cm$^{-1}$ using a Bruker FTIR 4100 spectrometer by a standard KBr pellet method. The functional groups present in the grown crystal were identified by infrared (FTIR) spectral studies. The recorded spectrum is depicted in Fig.3. A strong peak observed at 3426 is assigned for NH stretch of the primary amine group of 4-aminopyridine. The peaks at 3775 and 3105 are due to OH stretching vibration. The C-C stretching vibration was observed at 1462, 2049 and 1954 respectively. The COO- asymmetric
and symmetric stretching vibrations were observed at 1524 and 1581. The band at 1650 indicates that NH bending vibration. The peak at 1024 is assigned for C-H in-plane bending vibration. The bending vibration of C-H is assigned at 1382 and 1335. The bands at 1189 and 1134 are assigned to C-O stretching vibration. The NH wagging vibration is assigned 1252. The C-N stretching vibration pyridine is assigned at 1252. The vibrations at 2667 and 1024 are attributed to CH stretching and OH bending vibration. The COO- of carboxylate was observed at 764. Peaks at 660 and 552 are due to NH out of plane bending and OH out of plane bending vibrations.

![Fig.3. FTIR spectrum of APSA.](image_url)

3.3 UV-Vis studies

Optical transmittance studies for the grown crystals were recorded using a Perkin-Elmer lambda 35 spectrometer in the range 200-1100 nm. Recorded optical transmittance spectrum is shown in Fig.4. the lower cut-off wavelength of the crystal was observed at 380 nm. The absence of absorption and transparency in the visible region illustrate the suitability of APSA crystal for optoelectronic applications [9].
3.4 Dielectric Studies

Dielectric studies for the grown crystals were carried out in the frequency range from 50Hz to 5MHz using Hioki LCR meter (3532-50). Cut and polished crystals were used for the measurement. The dielectric constant of the crystal was calculated by the given formula

\[ \varepsilon_r = \frac{Cd}{\varepsilon_oA} \]  

Where \( C \) is the capacitance of the crystal, \( d \) is the thickness of the crystal, \( \varepsilon_o \) is the free space permittivity and \( A \) is the cross sectional area of the sample. Fig.5a shows the dielectric constant Vs frequency for the grown crystal. the dielectric constant is very low at high frequency and decreases slowly at higher frequencies and finally attains a constant value at very high frequencies (Above 1 MHz). It may be due to all four polarizations namely electronic, ionic, space charge and orientation. Out of these polarizations, space charge polarization mainly depends upon the purity of the sample. Hence high value of dielectric constant at a low frequency is attributed to space charge polarization [10, 11]. Fig.5b shows dielectric loss with respect to frequency. The dielectric loss is very low at high frequency. This low value suggests that sample possesses enhanced optical quality for nonlinear device applications.
3.5 Photoconductivity

Photoconductivity measurement for the grown crystals was taken at room temperature using Keithley 6517B electrometer. Crystals were cut and polished in a regular shape and used for the measurement. The thin copper wire was connected to the opposite faces of the crystals using electronic grade silver paste. This copper wire was connected to electrometer DC supply. The input voltage was increased from 10V to 100V. For dark current measurement sample was protected from all the radiation and corresponding dark current was recorded. Then the sample was exposed to illumination from 100W halogen lamp containing iodine vapour and tungsten filament. The photocurrent was recorded for the same input applied voltage. Fig.6 depicts the dark and photocurrent measurement for APSA crystal with respect to applied input voltage. It is concluded from the figure that photocurrent is higher than dark current. This type of behaviour is called positive photoconductivity, it may be due to the increase of charge carriers in the presence of illumination. Further, it can be explained by Stockman model. Positive photoconductivity materials can be used for solitons wave communications [12].
3.6 TG/DTA analysis

Thermograms of APSA crystals shows that there is no loss in weight up to 245 °C, hence the material is thermally stable, which indicates no possibility of co-ordinated water molecules (Fig. 7). APSA crystals start melting at around 245 °C and slow and gradual weight loss is observed. Then after, slow decomposition is observed from 245°C to 300 °C, and then a sudden loss in weight is observed from 500 °C. It was confirmed from DTA curve that CRSU underwent endothermic transition at 247.8°C corresponding to their melting point. From the TGA/DTA analysis, it is corroborated that the decomposition of material is 245°C. Hence, for any application, the crystal can be used up to 245°C.

Fig. 7. TG/DTA spectrum of APSA.
3.7 Z-Scan studies

The z-scan technique is a standard technique for the simultaneous measurement of both the nonlinear refractive index ($n_2$) and the nonlinear absorption coefficient ($\beta$) [11]. The cut and polished crystals of APSA were taken for the measurement. The sample was moved across a focal region (-Z to +Z) along the axial direction, which was the direction of propagation of the laser beam. The intensity dependent absorption of the material was measured by moving the sample through the focus and without placing an aperture at the detector (open aperture). The amplitude of the phase shift was determined carefully by monitoring the change in the transmittance through a small aperture at the far field position (closed aperture). The measurements of an open and closed aperture of the normalized transmittance (T) are presented in Figs. 8 (a-b). The absolute value of $\chi^{(3)}$ was calculated from the following relation.

$$|\chi^{(3)}| = \left[ (Re\chi^{(3)})^2 + (Im\chi^{(3)})^2 \right]^{1/2} \quad (6.2)$$

The estimated nonlinear refractive index ($n_2$), nonlinear absorption coefficient and third order susceptibility values of APSA single crystal was $1.6103 \times 10^{-7}$ cm/W and $0.000615$ cm$^2$/W and $3.38 \times 10^{-7}$ esu indicates that the material reveals a positive refractive index, it results in the self-focusing nature and exhibits the two-photon absorption process of the crystal. This is one of the essential parameters for optical limiting applications.

![Figs. 8 (a) Normalized transmittance with open aperture as a function of Z position](image)
![Figs. 8 (b) Normalized transmittance with closed aperture as a function of Z position.](image)

3.8 Antioxidant Studies

The DPPH method is a simple, rapid and convenient method for scavenging of free radical. This method is widely used to examine the antioxidant properties of the compound. In the presence of a compound, the stable DPPH radicals are capable of donating hydrogen atoms. Hence, the radical property is destroyed. The free radical scavenging ability of the synthesized compound with DPPH radical is studied in this analysis. The ascorbic acid is used as standard
complex for comparison of results. The results of antioxidant activity by DPPH free radical scavenging activity is depicted in Figure 9. The result confirms that the synthesized compound can reduce the concentration of the initial free DPPH radicals. This study confirms that the synthesized compound is capable of scavenging free radicals.

4. Summary

4-aminopyridinium salicylate single crystal was grown from methanol solvent by slow evaporation technique. The single crystal X-ray diffraction study reveals that grown crystal belongs to the orthorhombic system. The crystalline nature of grown crystal was confirmed by powder XRD studies. The functional groups present in the compound are confirmed by FTIR spectral studies. The crystal exhibits absence of absorption in the visible region. Dielectric constant increases with respect to temperature. The photoconductivity study reveals positive photoconductivity nature of the crystal. Z-scan measurements reveal the self-focusing nature. Also, the crystal exhibits good antioxidant property against DPPH and H₂O₂ radicals. All above results suggesting that the grown APSA can act as a potential candidate for optoelectronics and biological applications.

References


