



Synthesis, Growth and Characterization of P-Nitroanilinium Sulfanilate

Single Crystals

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ABSTRACT:

P-nitroanilinium sulfanilate (PNASA), a novel nonlinear optical material was synthesized and crystals were grown from the ethanol solvent by slow evaporation solution growth method. The lattice parameters and crystal system of the crystal grown were confirmed by Single Crystal X-ray diffraction analysis. It crystallizes in monoclinic crystal system with space group of P1. The FTIR spectral analysis done to confirm the presence of functional group present in the grown crystals UV–vis-NIR spectral study was performed to analyse optical transparency of PNASA crystal and found that the grown crystal has sufficient transparency in the entire visible region with lower cut-off wavelength of 354 nm. The second harmonic generation test has been confirmed by the Kurtz powder test.

Keywords: SXR, FT-IR, NMR, UV- visible-NIR, band gap, electro-optic material, second harmonic generation.

INTRODUCTION:

Single crystal growth has a major role in the current era of rapid scientific and technical advancement, whereas the application of crystals has infinite limits. In recent years, many substantial achievements have been occurred in the field of nonlinear optics because of the progress of new nonlinear optical crystals of both organic and inorganic (Marder,1991& Zyss,1994). Therefore, amino acid compound single crystals have more practical possibility for NLO applications. The NLO materials are used in the area of opto-electronics, telecommunication and optical storage devices (Peacaut,1993). The main benefit of using organic materials is because of its potential functions in various fields, it also shows a complex phase behaviour, photo and thermal stability, solubility and morphology (Zhao,1999 & Amin,2001). The large optical susceptibilities, inherent ultrafast response time, and high laser damage threshold are the added benefits of organic materials (Chemla ,1987 & Eychmuller,2007).



P-Nitroaniline was chosen due to its applications in pharmaceuticals, pesticides, antioxidants, gum inhibitors, gasoline and poultry medicines (Jerry Donohue, 1956 & Magladena Szostak 2007). 4-nitroaniline is a nitroaniline carrying a nitro group at position 4 (Pubchem ID-7475). It has a role as a bacterial xenobiotic metabolite. In addition to this, sulfanilic acid also has vast applications such as the amide of sulfanilic acid is used in medicine where it is called Streptocid album. Some of the derivatives of sulfanilamide such as albucid, sulfazoles, and sulfidine are used in medicine. It is also used as bleaching agents, plasticizers, pesticides and in paper products (Bharaniraj, 2007). Moreover, organic materials having molecular flexibility and structural diversity are main advantage to improve the nonlinear optical properties in a preferred manner (Datta, 2003). Here, we report the crystal growth and characterization of newly synthesized compound such as P-Nitroanilinium sulfonate which is grown by slow evaporation solution growth technique at room temperature using ethanol as a solvent. The grown crystals were characterized by single X-ray analysis, UV spectral analysis and FTIR analysis. The melting point of the grown crystal was determined and found to be 205°C.

SYNTHESIS AND GROWTH OF PARANITROANILINIUM SULFONATE:

Single crystals of P-nitroanilinium sulfanilate were grown by slow evaporation solution growth method at room temperature. P-nitro aniline and Sulfanilic acid with 1:1 molar ratio was dissolved in deionized water to get a clear solution and the solution was stirred well for homogeneity. The resulting solution was filtered using a Whattman filter paper and the beaker containing the filtrate was kept in a dust free environment for crystallization. Fig.1 gives the reaction scheme for the formation of title compound. After a period of 20 days, colourless crystals of title compound were obtained. The purity of the synthesized crystal was improved considerably by repeating the recrystallization process three times. Fig.2 shows the grown single crystal of the PNASA.

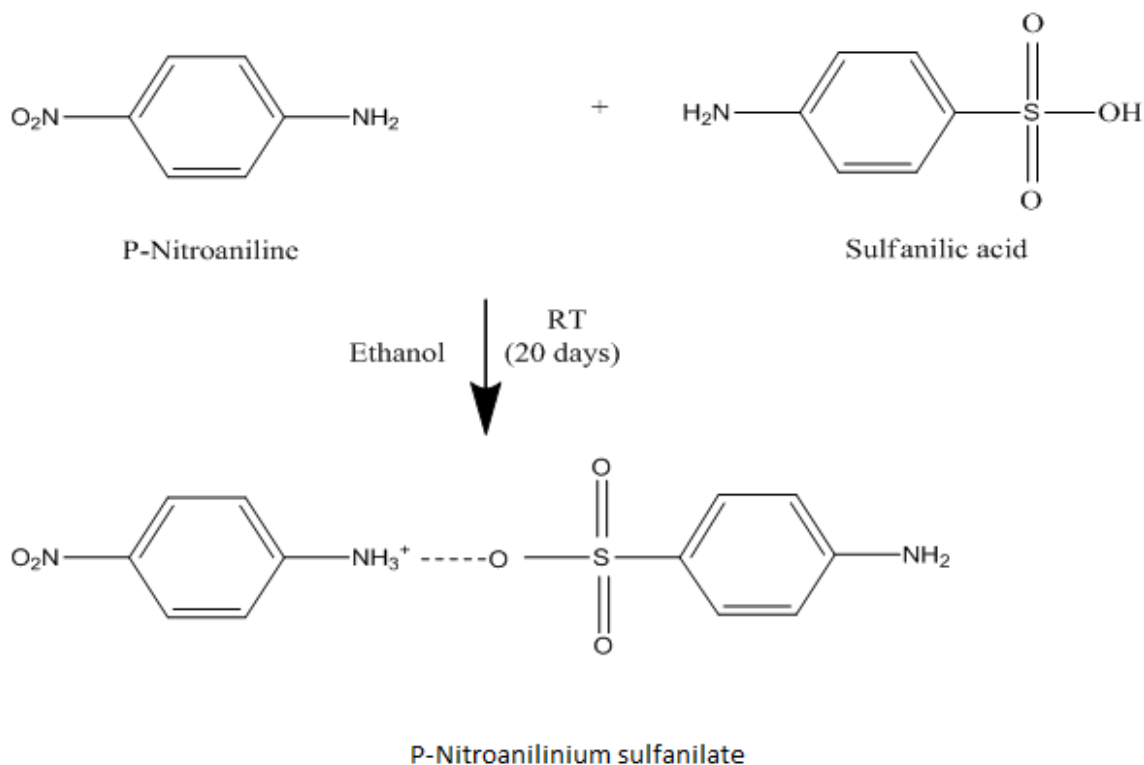


Figure 1: Reaction scheme of p-nitroanilinium sulfanilate

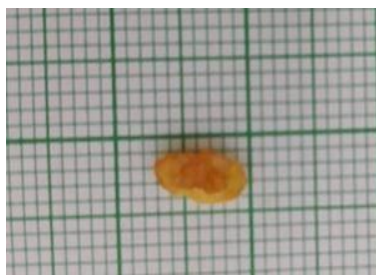


Figure 2: As grown Single crystal of P-nitroanilinium sulfonanilate

RESULTS AND DISCUSSION

Single crystal XRD analysis

The P-nitroanilinium sulfonanilate crystal was subjected to single crystal X-ray diffraction analysis to determine the lattice parameters and space group. In the single crystal XRD data



collection, 9,494 reflections were recorded in the range of 2.68° to 24.99° of which 1887 reflections were unique reflections. The data reveal that the synthesized crystal belongs to the monoclinic crystal system with. The lattice parameters obtained are $a=8.61\text{\AA}$, $b=6.01\text{\AA}$, $c=12.36\text{\AA}$, $\alpha=90^\circ$, $\beta=91.64^\circ$ and $\gamma=90^\circ$. The unit cell volume is 639\AA^3 . The crystallographic data and structure refinement parameters are given in Table 1.

Table 1. Single crystal XRD analysis data of P-nitroanilinium sulfonilate crystal

PNASA	Crystal Data
Molecular Formula	$\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}_3$
Crystal system and space group	Monoclinic, P1
	$a= 8.61\text{\AA}$, $b = 6.01\text{\AA}$
	$c = 12.36\text{\AA}$
Lattice parameters	$\alpha =90.00^\circ$
	$\beta=91.64^\circ$
	$\gamma=90.00^\circ$
Volume	$V=639\text{\AA}^3$

Fourier Transform Infrared Spectral analysis

Fourier transform infrared spectral studies were carried out for the samples to identify the functional groups. The presence of functional groups in the crystal was identified and was shown in Figure 3 & Table 2. The characteristic absorption bands were recorded in the spectral range $4000\text{--}400\text{ cm}^{-1}$ in order to confirm the presence of functional groups in the crystal. CH_2 stretching's observed from the peaks at 2928 cm^{-1} . The N–H stretching was observed from the peaks at 1586.5 cm^{-1} . The C–N stretching was observed at 1279 cm^{-1} and 1108 cm^{-1} . The stretching of the nitro group is affirmed by the peak appeared at 1472 cm^{-1} . The S–O stretching



vibration was observed at 837.3cm^{-1} . The C–S stretching was observed at 698.16 cm^{-1} . The functional groups of the grown material are thus identified.

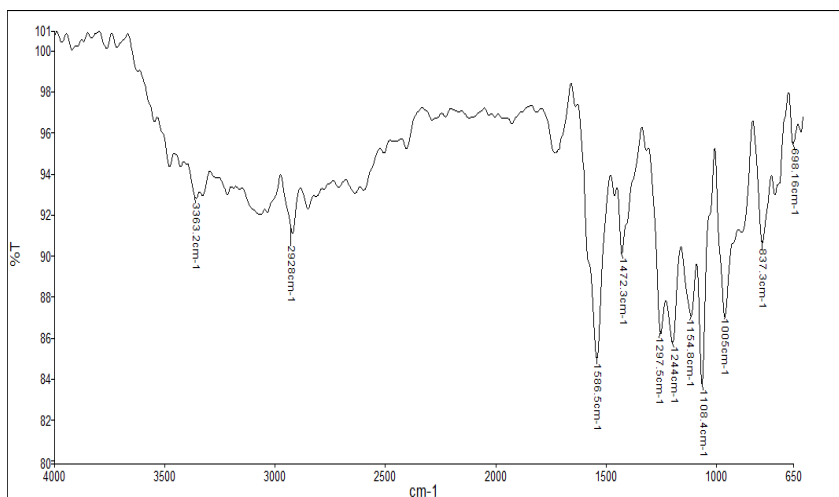


Figure.3. Spectral data and their assignments for P-nitroanilinium sulfanilate

Table.2. Spectral data and their assignments for PNASA

Frequency Cm^{-1}	Assignments
1586.5cm^{-1}	N–H asymmetric stretching and symmetric stretching vibration
2928 cm^{-1}	C–H asymmetric stretching and symmetric stretching vibration
1279 cm^{-1} and 1108 cm^{-1}	C–N stretching vibration
1472 cm^{-1}	asymmetric and symmetric stretching vibration of the nitro
698.16 cm^{-1}	C –S Stretching frequency vibration



837.3 cm ⁻¹	S—O stretching vibration (Kalsi ,1985 &Robert M. Silverstein 2006).
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Determination of Melting point

The melting point of a substance is the temperature at which it changes its state from solid to liquid. It is the way to test whether the compound is pure or not. In order to find the melting point, capillary tube is filled with crystals about 3mm high and placed in any one of the three sample holders of the instrument. Watch the crystals through the magnifying glass and the temperature at which the crystal melts are noted down from the thermometer. The melting point of PNASA single crystals is found to be 205°C.

UV-Visible NIR Spectral analysis

Optical transparency in the entire visible region with a good percentage of transmission is the key properties of an NLO material. The UV-Vis-NIR absorption spectrum of the grown crystal was recorded in the wavelength range of 200–800 nm (Fig.4.1). The higher intensity of the absorption band observed in the UV region may be due to conjugated systems present in the grown material. The absorption is very low near infrared region with cut-off wavelength 354nm. However, 100% transmission is observed onwards. The optical band gap 2.6 (eV) was evaluated using Tauc's relation. The value of band gap energy was estimated from the graph between $(\alpha h\nu)^2$ and $h\nu$ (Fig.4.2) by extrapolating the linear portion of the curve to zero absorption. The optical band gap was measured as 2.6(eV). The higher value of optical band gap suggests that material is dielectric in nature. Only the dielectric material will have wide transparency (Sun, 2008 & Shakir, 2009). The material with wide transparency is required for the fabrication of optical devices.

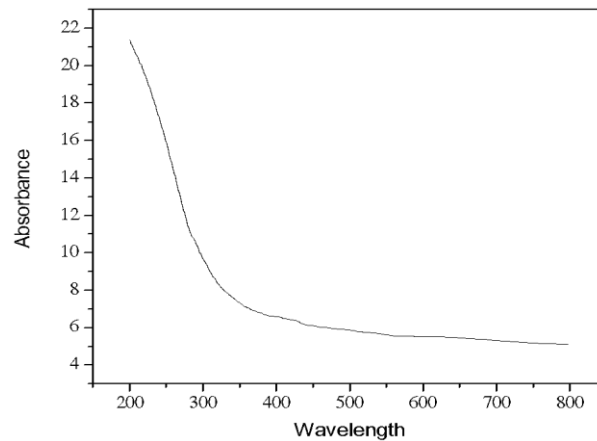


Figure 4.1. UV-Visible NIR Spectrum of grown crystal

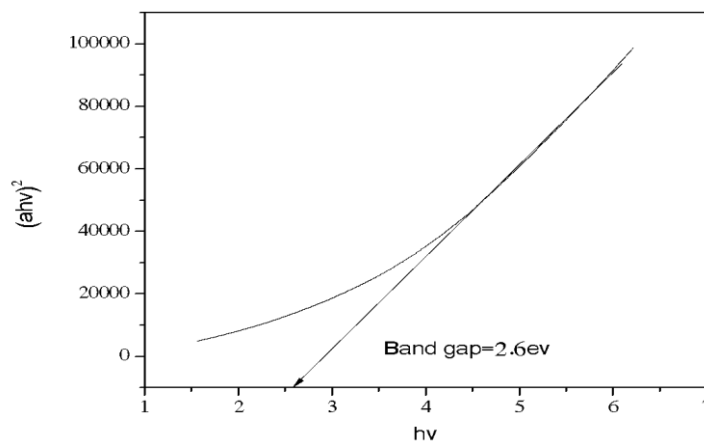


Figure 4.2. Plot of $(\alpha h\nu)^2$ versus Photon energy

SHG efficiency measurements

The SHG efficiency of the grown crystal was measured by a modified Kurtz and Perry technique using Nd: YAG laser with pulse repetition rate of 10 Hz and wavelength 1064 nm. The sample was ground well and tightly packed in a micro capillary tube. The relative SHG efficiency of the grown crystal was measured by comparing the SHG output with the help of a standard KDP (Potassium dihydrogen phosphate) sample of same particle size. The relative efficiency was found to be 0.6 that of standard KDP. SHG was confirmed by the emission of



green radiation (532nm) from the crystal. On a molecular scale the extent of charge transfer (CT) across the NLO Chromophore determines the level of SHG efficiency (Mallik, 2007).

CONCLUSION

The transparent single crystals of PNASA were successfully grown by the slow evaporation solution growth technique at room temperature. The crystallinity of the grown crystal was verified by powder XRD analysis. The cell parameter values are in good agreement with the reported values. The FTIR spectrum revealed the presence of functional groups. The melting point of this PNASA indicates that the sample is stable up to 204°C, so it is used to fabricate high temperature devices. The high optical transmittance in the visible UV region and large beta value makes the crystal a potential material for NLO application. SHG was confirmed by the relative efficiency was found to be 0.6 that of standard KDP. Hence, the grown PNASA single crystal is one of the useful organic crystals for nonlinear optical applications.

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