Research Article

Crystal Growth, Optical and Thermal Studies of 4-Nitroaniline 4-Aminobenzoic Acid: A Fluorescent Material

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Abstract

The organic single crystals of 4-nitroaniline 4-aminobenzoic acid (4NAABA) were grown from ethanol solvent. The grown crystals have been confirmed from single crystal XRD analysis. The UV absorption was carried out which shows the cutoff wavelength around 459 nm. The optical band gap of the crystal has been evaluated from the absorption spectra and absorption coefficient by extrapolation technique. The fluorescence spectral analysis is carried out for 4NAABA crystals. The thermal stability of the crystal was evaluated from thermogravimetric and differential thermal analysis.

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Introduction

The research on efficient organic single crystal for the wide range of optical applications has been increased considerably because of their efficient physicochemical properties such as molecular nonlinearity over a broad frequency range, low cost, with better processability, ease of fabrication and possible integration into devices [1]. However, organic crystals have relatively weak intermolecular bindings and it is too difficult to grow high quality large size crystals compared with inorganic crystals. 4-aminobenzoic acid (4-aba) is one of the well known carboxylic acids promoting molecular self assembly by means of strong hydrogen bonding through its carboxylic acid group and the ring substituted amino group of 4-nitroanilne (4-na) [6-10]. Strong hydrogen bonds occur due to the polarizable hydrogen atom covalently bonded to an electron-withdrawing donor nitrogen atom and interact with a partially negatively charged and comparatively less polarisable acceptor oxygen atom, which will also increase the molecular hyperpolarizability [2]. Graham smith et al [3] reported the structure of 4naaba. However, this paper reports for the first time the growth of large size organic single crystal of 4-nitroaniline 4-aminobenzoic acid with molecular formula $c_{13}h_{15}n_3o_4$. The grown crystal was characterized by single crystal xrd, uv-vis-nir absorption spectroscopy and fluorescence analysis. Thermogravimetric and differential thermal analysis were carried out to determine the thermal property of the grown crystal.

Experimental Procedure

Synthesis and Crystal Growth

The title compound was synthesized by dissolving equimolar ratio of commercially available AR grade 4-aminobenzoic acid and 4- nitroaniline in ethanol at 318 K. The synthesized material was further purified by repeated recrystallization process in ethanol. The solubility studies in different solvents showed that the compound is insoluble in water, and highly soluble in ethanol. The Solubility of 4NAABA was found to be 11.10 g/100 ml at 40 ^{0}C. To grow single crystals of 4NAABA slow evaporation solution growth technique (SEST) was employed. Saturated solution of the compound with ethanol as a solvent was prepared and the temperature of the solution has been increased while stirring the solution in order to have high homogeneity. The solution was filtered to remove any impurities present

and was kept undisturbed. Consecutively, to ensure the slow evaporation the beaker was covered with perforated polythene paper. The transparent yellowish single crystal has been grown in a span of 15 days. The grown crystal is shown in **figure 1**. The grown crystal has been confirmed using single XRD studies. The present result is in close agreement with the reported results [3] which are shown in **table 1**.

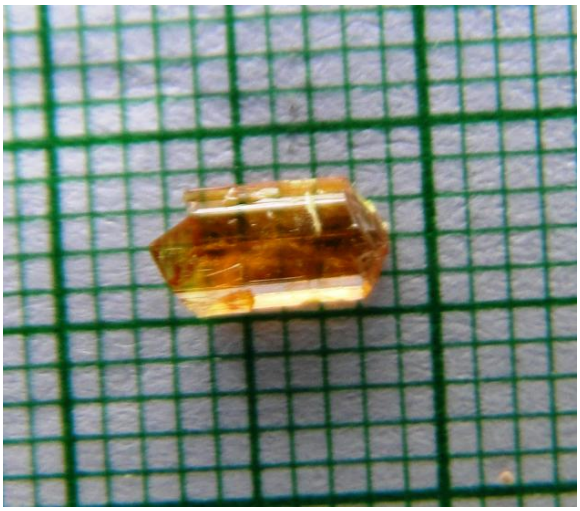

Figure 1 Grown 4NAABA crystal

Table 1 Single crystal XRD result of reported and present study

Parameter	Reported[3]	Present
a (Å)	4.869	4.84
b (Å)	31.25	31.10
c (Å)	8.637	8.59
α	90.00^{υ}	90.00^{υ}
β	93.69^{υ}	93.56^{υ}
γ	90.00^{υ}	90.00^{υ}
Volume ($Å^3$)	1311	1290
System	Monoclinic	Monoclinic
Space group	$P2/_1C$	$P2/_1C$

Results and Discussions

Optical studies

The optical absorbance and transmission were recorded from UV to IR in the wavelength range of 200-1100 nm^{-1} using Perkin Elmer UV- Vis- NIR spectrophotometer at room temperature. UV-Vis-NIR spectrum occurs due to the electronic transitions of the molecule. Figure 2 shows the recorded optical absorption and transmission spectrum of grown crystal in which characteristic absorption band of 4NAABA crystal occurs below 450 nm. The thickness of the sample used for measurement was 2 mm. The absorbance was reduced drastically between the wavelength of 490 nm

and 1100 nm due to its good optical behavior. The measured absorbance (A) was used to calculate the absorption coefficient (α) using the formula,

$$\alpha = \frac{2.303 \log A}{t} \quad (1)$$

Where, A is the absorption and t is the thickness of the sample. The absorption coefficient was calculated at different location of the grown crystal. Similar absorption coefficient was observed in different sites of the grown crystal.

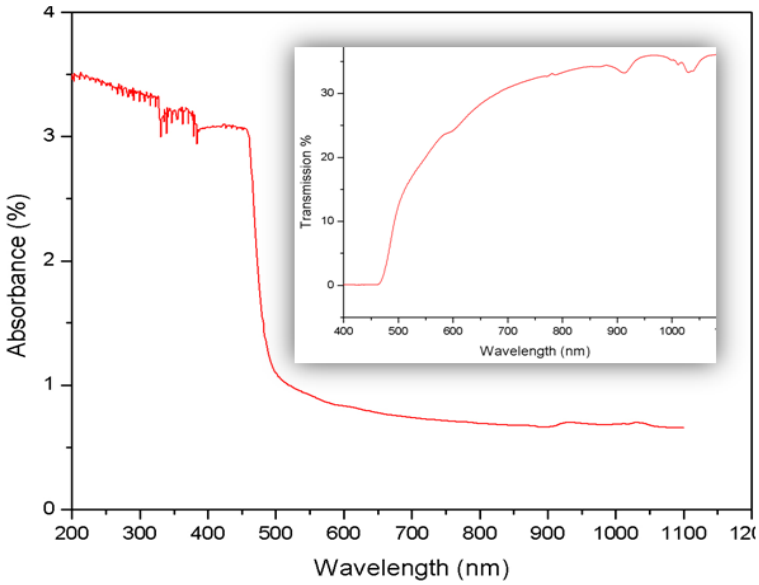

Figure 2 Uv-vis spectrum of grown crystals

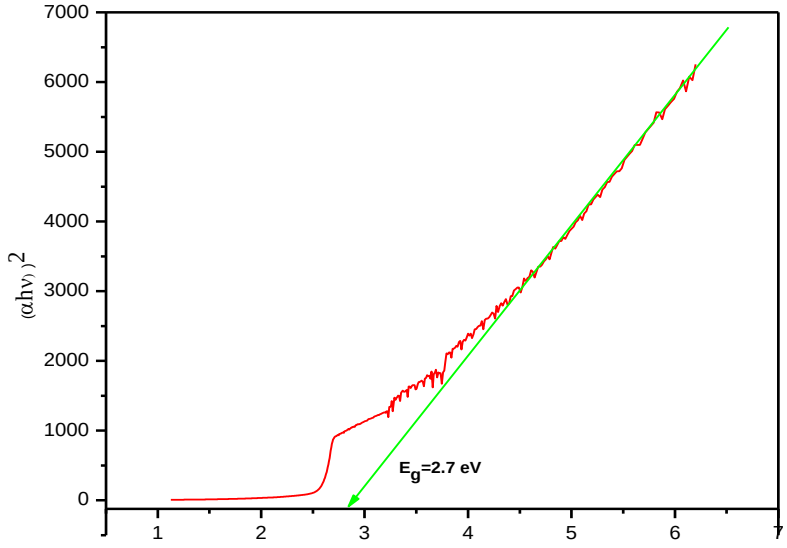

Figure 3 Variation of photon energy (hν) with $(\alpha h\nu)^2$

The optical band gap (E_g) has been estimated from the optical absorption coefficient (α) near the absorption edge for the direct transition given by

$$(\alpha h\nu)^2 = A(E_g - h\nu) \quad (2)$$

where A is a constant, E_g is the optical band gap, h is the Planck's constant and ν is the frequency of incident photons. The optical band gap was evaluated by plotting $(\alpha h\nu)^2$ vs. hν as shown in figure 3 and extrapolating the linear portion of absorption edge $(\alpha h\nu)^2$ in the photon energy axis gives the optical band gap of the crystal [1]. From the figure 3, it is obtained that the optical band gap value of the 4NAABA single crystal is 2.7 eV.

Fluorescence analysis

The compounds containing aromatic functional groups of low energy $\pi \rightarrow \pi^*$ transition levels have high intense fluorescence behaviour [4]. Jasco FP-6300 spectrofluorometer was used to record the fluorescence spectrum of the 4NAABA crystal at room temperature with 450 W high pressure xenon lamp as an excitation source. The grown 4NAABA crystal was excited at 395 nm. The emission spectrum is measured in the range of 450–750 nm which is shown in **Figure. 4**. The broad band centered at 470 nm and sharp band at 590 nm are observed in the emission spectrum. The band gap energy was calculated using the formula, $E_g = hc/\lambda e$. Here h, c, and e are constant; λ is the wavelength of absorbed fluorescence. The band gap energy calculated is about 2.65 eV for the crystal. The result indicates that the 4NAABA crystal is a yellow light emitting material.

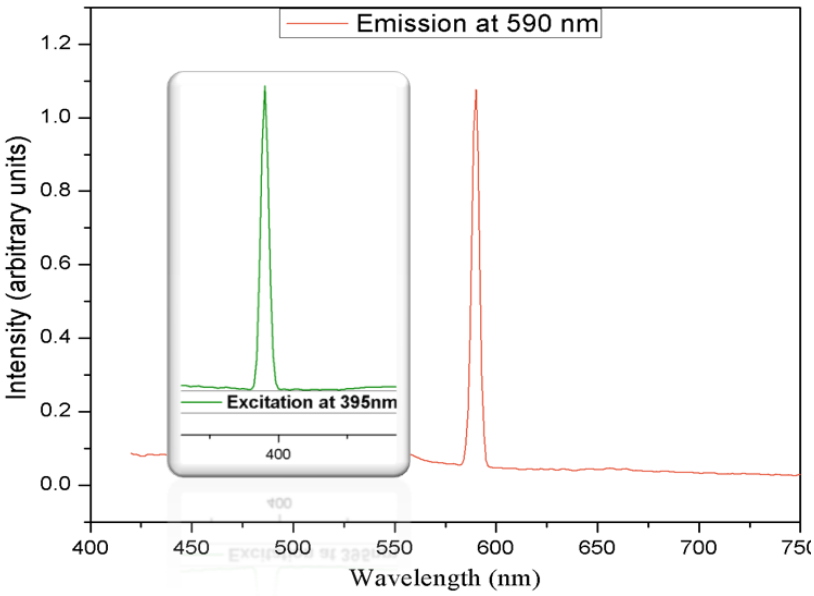

Figure 4 Fluorescence spectrum of 4NAABA.

Thermal analysis

The thermal analysis of grown crystal was carried out between 35 and 365 °C at a heating rate 10 °C min^{-1} in nitrogen ambient using PerkinElmer Diamond TG/DTA instrument. The thermal analyses are used to find out the weight loss (TGA) and melting point (DTA) of the grown 4NAABA single crystal. The TG/DTA curves are shown in the **figure 5**. In differential thermal analysis, the material undergoes an irreversible sharp endothermic transition at 151 ^{0}C,

which corresponds to its melting point. Below the melting point there is no endothermic or exothermic peak, which illustrates the absence of isothermic transition in grown single crystal. The material dissociates after melting. The TGA curve indicates that the sample is stable and there is no phase transition upto 160 ^{0}C. This is a strong indication of the purity of the crystal as well as its perfection.

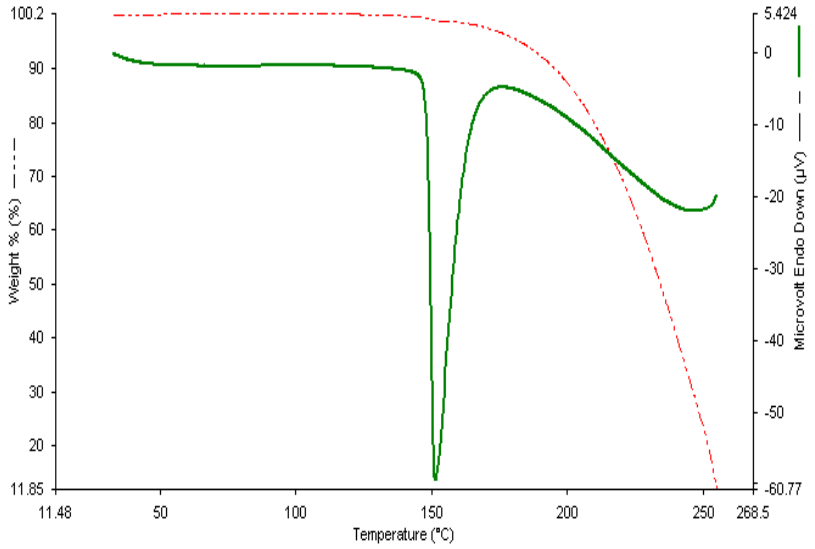

Figure 5 TG\DTA curve of grown crystals.

Conclusions

4NAABA single crystals were grown from ethanol solvent by SEST technique. The lower cutoff wavelength and transmission from entire NIR to visible region was determined from the UV – Vis – NIR absorbance spectrum. The yellow fluorescence emission of the crystal confirmed its fluorescence behavior. The results of DTA analysis pointed out the thermal stability of the grown crystal upto 160 ^{0}C. The sharp endothermic peak indicates the high quality of the crystal as well as its perfection. This study will be helpful to grow the 4NAABA crystals for optical applications.

References

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