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Investigations on Structural and optical properties of 4-chloro2-nitroaniline crystals for Nonlinear Optical Applications

K. Sangeetha[1], R. Mathammal[2]*, L.Guru Prasad[3]

[1] Periyar University, Department of Physics, Government Arts College, Salem-7, India
[2] Periyar University, Department of Physics, Sri Sarada College for Women, Salem-16, India
[3] Periyar University, Department of Science & Humanities, M. Kumarasamy College of Engineering, Karur, India

Abstract: Single crystals of 4-chloro 2-nitroaniline have been grown by slow evaporation solution growth technique method using ethanol as solvent. The crystallinity and parameters of the grown crystal are determined with the powder x-ray diffraction result. The optical transparency and lower cut off value of UV transmission were ascertained by recorded UV-Visible spectrum of 4Cl2NA crystals. The existence of second harmonic generation (SHG) of the grown crystal was confirmed by Kurtz-powder technique and the efficiency of frequency doubling was found to be 3 times than that of KDP. The TGA/DTA studies shows the thermal properties of the crystals.
Keywords: Crystal growth, powder XRD, UV-VIS, TGA-DTA, SHG.

Introduction

4-chloro2-nitroaniline (4Cl2NA), a trisubstituted benzene derivative, has been extensively studied because of its exceptional nonlinear optical (NLO) properties. Organic crystals have been shown to have potential applications in nonlinear optics. Nonlinear optical (NLO) materials capable of generating the second harmonic frequency play an important role in the domain of optoelectronics and photonics [1,2]. Nowadays, NLO organic crystals are competing with widely used inorganic materials because their preparation is less expensive, non-linear susceptibilities are high, their large birefringence to use as frequency converters and laser damage thresholds are fairly high. Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications. Within the last decade much progress has been made in the development of these NLO organic materials having large nonlinear optical coefficients [3,4]. Due to the technological importance of these nonlinear crystals the needs for high quality organic crystals have grown dramatically in the last decade. With rapid progress in the crystal growth technology, crystals having attractive nonlinear properties are being discovered.

Aniline and substituted anilines are widely used as a starting material in a vast amount of pharmaceutical and many other industrial processes. The understanding of their molecular properties as well as natures of reaction mechanisms they undergo is of great importance. Hence, the investigation on the structures, and the vibrations of aniline and substituted anilines are still being carried out, increasingly. The inclusion of a

substituent group in aniline leads to the variation of charge distribution in the molecule, and consequently, this greatly affects the structural, electronic and vibrational parameters [5].

2. Experimental details

Crystal growth

The compound under investigation namely 4Cl2NA is purchased from Alfa Aesar Company, U.S.A. which is of spectroscopic gauge with a stated purity of 98% and was used to grow the crystals. Number of crystal growing methods are available to grow single crystals, but the choice of the method greatly depends upon the physical and chemical properties of the material. Out of all methods, solution growth technique is inexpensive and easier. In this method, the crystal growth is performed using a supersaturated solution of the material with a suitable solvent.

Fig.(1) The grown single crystal of 4Cl2NA.

From the solubility test it was observed that ethanol is a suitable solvent for crystal growth of 4Cl2NA crystals. Here a supersaturated solution of 4Cl2NA has been obtained by dissolving the sample in ethanol with continuous stirring at room temperature. The prepared solution was filtered using filter paper, slightly warmed and allowed to evaporate very slowly. Consecutively, to ensure the slow evaporation the beaker was covered with perforated polythene paper. After about 5-10 days, good quality transparent reddish needle shaped 4Cl2NA crystals were obtained and is shown in Fig.1.

The room temperature FTIR spectrum of the title compound is measured in the region 4000-400 cm^{-1} with the scanning speed of 10 cm^{-1} min^{-1} and the spectral resolution of 4.0 cm^{-1} by employing perkin-Elmer spectrometer. The FT-Raman spectrum of the compound is recorded using Bruker FRA 106/S instrument equipped with Nd: YAG laser source operating at 1064 nm line widths with 100mW power. The spectrum has been recorded in the range of 4000–10 cm^{-1}. ^{1}H and ^{13}C NMR (400 MHz; $CDCl_3$) spectra are recorded using BRUKER TPX-400 FT-NMR spectrometer. The optical absorption spectrum is recorded using Perkin-Elmer Lamda 935 UV-VIS-NIR spectrometer.

3. Results and discussion

3.1 Powder X-ray diffraction

Powder X-ray diffraction study is used for the identification of crystallinity of the grown crystal. The purified samples of the grown crystals have been crushed to a uniform fine powder and subjected to SEIFERT 3003 TT powder X-ray diffractometer with Cu Kα (λ=1.540598 Å) radiation for structural analysis of the crystal. The sample was scanned in the range between 10 and 80ºC. The indexed diffraction pattern of pure 4Cl2NA is shown in Fig.2. The sharp intensity peaks found in spectra shows good crystalline nature and purity of the grown crystal. The observed peaks were found to be in good agreement with the data available in JCPDS file no:52-2054.

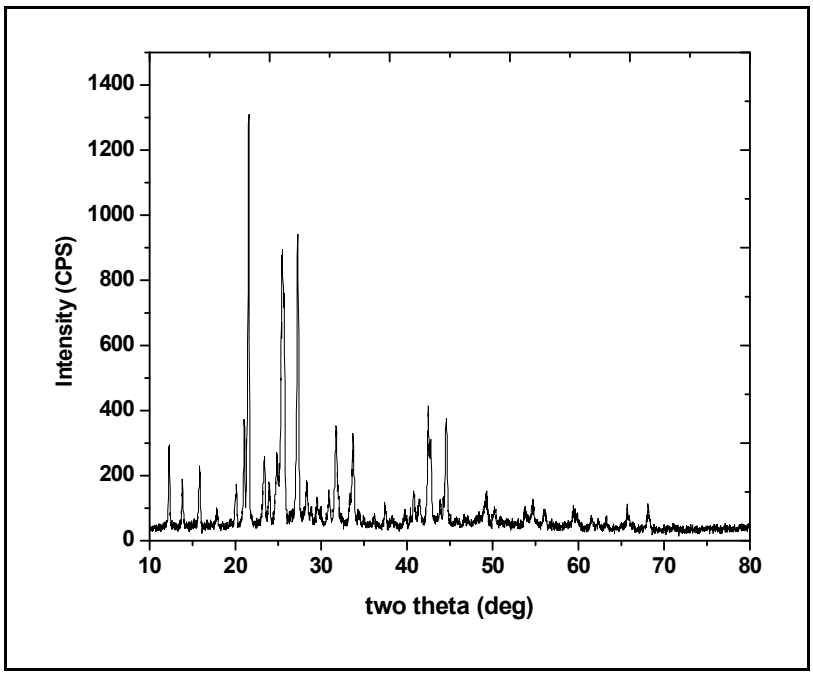

Fig.2. Powder XRD pattern of 4Cl2NA

Lattice Parameters

From the powder XRD measurement, it is found that the grown crystal belongs to the monoclinic system and has a centrosymmetric nature with the space group of P21/n. The determined cell dimensions are a=8.518Å, b=3.807Å, c=22.602Å, and α=90.00º, β=97.22º and γ=90.00º. The cell volume is V=727.228 $Å^3$.

3.2. UV-Vis-NIR spectral analysis

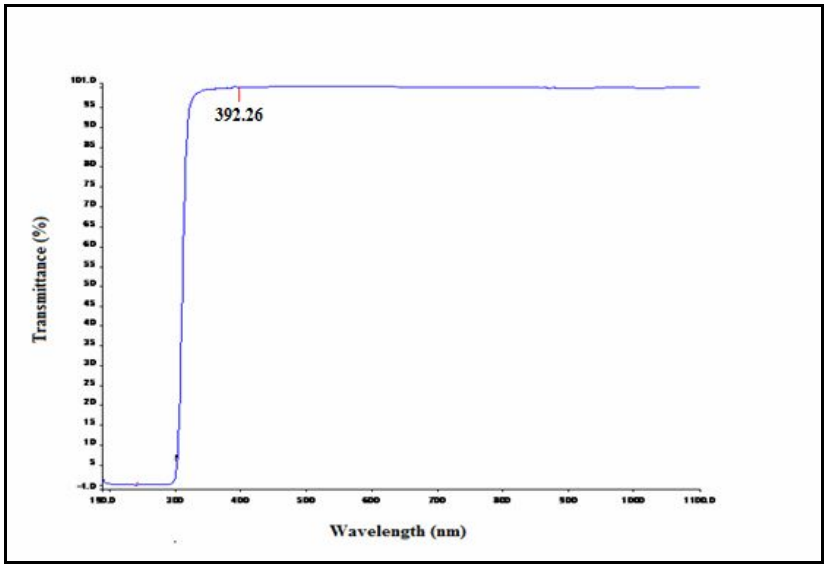

Figure 3a: Optical transmittance of 4Cl2NA single crystal.

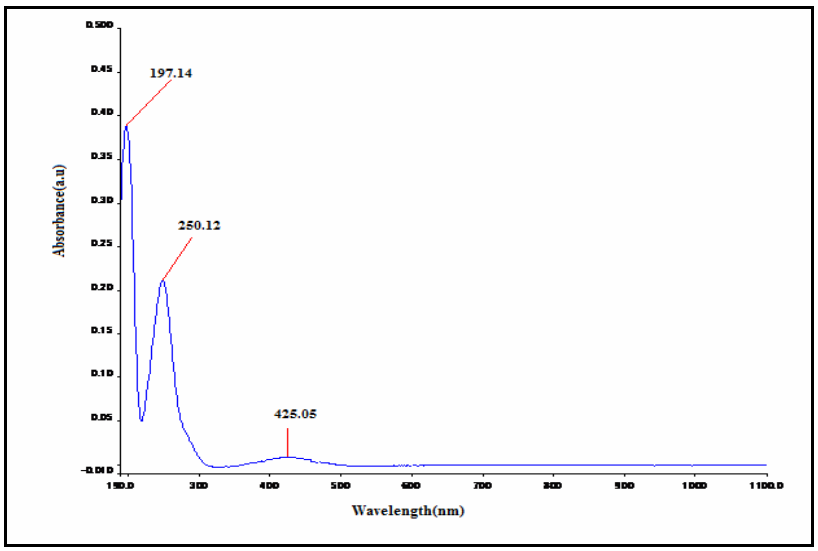

Figure 3b: Optical absorbance of 4Cl2NA single crystal.

From Fig.3.a. it is observed that the grown crystal has wider transparency in the entire visible and NIR region and the lower cutoff wavelength is found at 392nm. Higher transparency and lower cutoff wavelength ensures the usefulness of the grown material for nonlinear optical applications. The absorbance was reduced drastically between the wavelength of 490 nm and 1100 nm due to its good optical behaviour. The absorbance spectrum is shown in the Fig. 3.b. An absorption peak observed at 392 nm arises due to electron transition between n → π* states. Energy gap of 4Cl2NA is calculated by using the formula [6]

$$E = \frac{1.243 \times 10^3}{\lambda_{max}} eV$$

Where, λ is the lower cutoff wavelength and the energy gap value is found as 3.17 eV.

3.3. Powder SHG Measurement

The nonlinear optical conversion efficiency has been carried out using modified setup of Kurtz and Perry **[7]** at the Indian Institute of science, Bangalore. A Q-switched Nd:YAG laser beam of wavelength 1064nm was used with an input power of 5.5 mJ and pulses of width 8ns with a repetition rate of 10 Hz. The grown single crystals of 4Cl2NA were ground to a uniform particle size of 125-150µm and then packed in a microcapillary of uniform bore and expressed and exposed to laser radiations. Second harmonic radiation generated by the randomly oriented microcrystals was focused by a lens and detected by a photomultiplier tube. The generation of the second harmonic was confirmed by the emission of green light.. It was observed that, the output voltage was 205mV for the 4Cl2NA crystal and the value of KDP was 67mV. The SHG conversion efficiency of 4Cl2NA is found to be 3 times that of KDP.

4. Thermal analysis

Thermogravimetric analysis measures the change in mass of a sample on heating and useful to study the crystallization. Thermo-gravimetry (TG) and differential thermal analysis (DTA) are quite useful, since they provide reliable information on the physico-chemical parameters, characterizing the processes of transformation of solids or participation of solids in processes of isothermal or non-isothermal heating [8,9]. The TG/DTA spectrum recorded for the present study is shown in the Fig.4. The measurement indicates that the material exhibits single-stage weight loss starting at 165° C, which may be due to the decomposition of 4ClNA, and below this temperature, no significant weight loss is observed. The DTA analysis of 4Cl2NA was also performed between 40 to 400° C in the nitrogen atmosphere. The resulting spectrum is shown in the same Fig.11. The heating rate was maintained at 10° C min^{-1}. In DTA there is a sharp endotherm at 117° C, which is assigned to the melting point of the specimen. Below this endotherm, no exothermic or endothermic peak is observed. The sharpness of the endothermic peak observed in DTA shows good degree of crystallinity [10] of the specimen

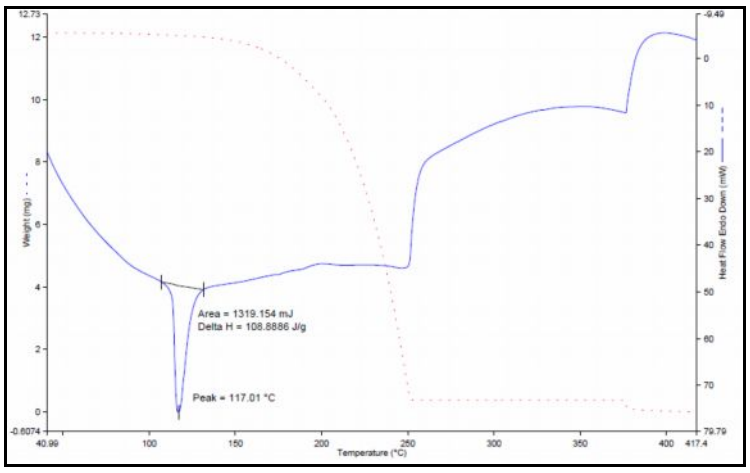

Fig.4. TGA curves of 4Cl2NA

5. Conclusion

Optically transparent 4Cl2NA single crystals have been grown by slow solvent evaporation method. The lattice parameters of 4NA are calculated by using single crystal XRD data and they agree well with reported values. The UV-Vis-NIR absorption spectrum shows that the cut-off wavelength lies at 398 nm with energy gap of 3.16 eV and the grown crystal has wide transparency in the range of 390 and 1200 nm, which confirms the suitability of the crystal for NLO applications. The title compound exhibited good NLO property and are much 3 times greater than that of KDP. A comparison of the result of experimental and theoretical study gave us a full description of the geometry and vibrational properties of the compound. The calculated HOMO and LUMO energies shows that charge transfer occurs within the molecule. ^{1}H and ^{13}C NMR chemical shifts are compared with experimental values.The stability and intramolecular interactions have been interpreted by NBO/NLO analysis and the transactions give stabilization to the structure which have been identified by second order perturbation energy calculations. Mulliken atomic charges and the natural atomic charges obtained are tabulated which gives us a proper understanding of the atomic theory. The electric dipole moment, polarizability and the first order hyperpolarizability of the title compound were calculated. The ^{13}C chemical shifts of all the carbon atoms and ^{1}H NMR chemical shifts of all the aromatic protons are in good agreement with the experimental values.

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