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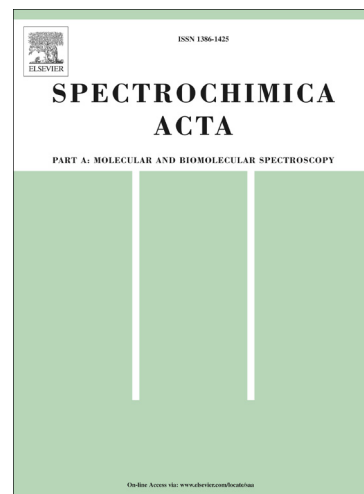
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Synthesis, growth and characterization of a new promising organic nonlinear optical crystal: 4–nitrophenyl hydrazone

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Abstract

4-nitrophenyl hydrazone single crystals were grown by slow evaporation of solvent method using acetone as a solvent. The grown crystals were subjected to various characterizations such as X-ray diffraction studies, UV-visible studies, thermogravimetric analysis and differential thermal analysis (TGA/DTA) and second harmonic generation (SHG). The cell parameters were calculated by using single crystal XRD measurement and the crystal system was found as orthorhombic with non-centro-symmetric space group $Pca2_1$. The crystallinity of the grown crystal was confirmed by powder X-ray diffraction analysis. The Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) studies confirmed the presence of functional groups in the sample. The optical transmittance spectrum shows that the crystal is transparent in the visible wavelength range. The scanning electron microscopy (SEM) was used to study the surface morphology of the grown crystal. The chemical composition of the grown crystal was confirmed by energy dispersive X-ray (EDX) analysis. The TGA/DTA results showed that the material is stable up to 146 °C. The NLO property of the crystal was confirmed by Kurtz and Perry method and SHG conversion efficiency is 15.39 times when compared to KDP crystal.

Highlights

- New NLO crystal is grown by slow evaporation of solvent at room temperature.
- The sample crystallizes in orthorhombic space group $Pca2_1$.
- NMR and FTIR studies confirm the purity and functional groups of the grown crystal.
- Second harmonic generation efficiency is 15.39 times higher than KDP.

Keywords

Nonlinear optical materials, X-ray diffraction, Crystal structure, Optical properties, SHG

1. Introduction

In the recent past, growing the non-linear optical (NLO) single crystals has emerged as one of the most attractive fields of research in view of its potential applications in the area of laser technology, optical communication, optical data storage, optical signal processing, optical switching, optical computing, optical bi-stability etc [1-4]. The organic nonlinear optical materials are very interesting and promising for high-speed electro-optic applications in future telecommunication networks. Recently, a large number of organic compounds with nonlocalized π electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibilities larger than the inorganic optical materials. The basic structure of organic NLO materials is based on π bond systems and due to the overlapping of π orbital, delocalization of electronic charge distribution leads to a high mobility of the electron density. Functionalization of both ends of the π bond system with appropriate electron donor

and acceptor groups can enhance the asymmetric electronic distribution in either or both the ground and excited states, these leading to an increased optical nonlinearity [5-7]. Hydrazone derivatives are an important class of organic compounds and tend to form crystals in non-centro-symmetric space groups and motivated to investigate non-linear properties [8]. Some of hydrazone derivatives were used in nonlinear optics for the preparation of crystals and Langmuir–Blodgett films. Some of nitrophenyl hydrazone crystals exhibit a large macroscopic optical nonlinearity with optimal molecular packing for electro-optics and terahertz-wave generation [10-13]. The synthesis and structure of various phenyl hydrazone compounds are investigated and their photochemical and photophysical properties are studied systematically [14-19]. In the present work we emphasize the involvement and interplay of the hydrazone moiety (–CH=N–NH–) with additional functional groups, in forming intermolecular interactions through spectroscopic technique. Based on extensive use of phenyl hydrazone compounds for various photophysical properties, in this paper for the first time, we report the synthesis, characterization and NLO property of 4-nitrophenyl hydrazone.

2. Experimental

2.1. Synthesis of 4-nitrophenyl hydrazone

The mixture of 99 % purity of 4-nitroacetophenone (5 gm, 30 mmol) and 98 % purity of phenyl hydrazine (3.26 ml, 30 mmol) was dissolved in 50 ml of methanol and 2-3 drops of glacial acetic acid was added. The reaction mixture was then heated for 30 min in water bath. After the completion of the reaction and up on cooling the reaction mixture, the product was separated out as red crystalline solid. The product thus obtained was then filtered, washed with ethanol and dried to get pure 4-nitrophenyl hydrazone in good yield. The chemical reaction is shown in the following scheme:
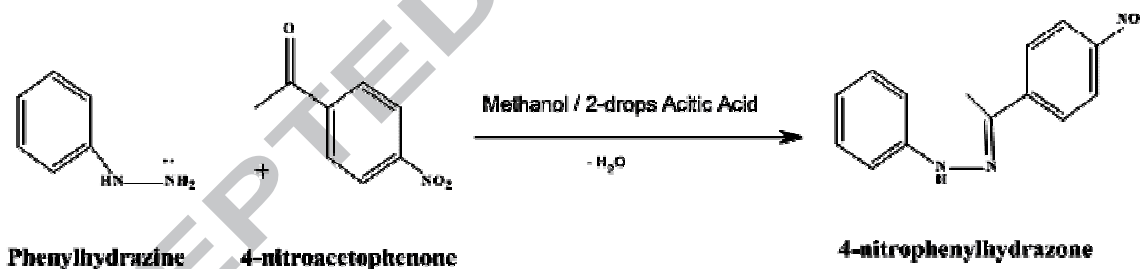
2.2. Single crystal growth and characterization

The dried product of 4-nitrophenyl hydrazone was dissolved in acetone and the total content was covered by a perforated sheet to facilitate the evaporation of the solvent at room temperature. In about 24 hours, we obtained needle shaped crystals as shown in Fig. 1. The grown crystal was confirmed by single crystal and powder XRD analysis. The single crystal XRD data was recorded by using Nonius CAD-4/MACH3 diffractometer, with Mo-Kα radiation (λ=0.71073 Å). The powder XRD study was carried out to demonstrate the crystallinity of the sample by using a Rigaku-Miniflex X-ray diffractometer with Cu-Kα radiations (λ=1.5406 Å). The FTIR spectrum of the grown crystal was recorded in the frequency range from 400–4000 cm^{-1} using FTIR-8400S spectrophotometer, Shimadzu model under a resolution of 4 cm^{-1} and with the scanning speed of 2 mm/sec following KBr pellet technique. The ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrums of the grown crystals were recorded using a Bruker-AMX 400 MHz in (CH$_3$)$_2$CO as solvent. The optical transmittance spectrum of 4-nitrophenyl hydrazone crystal was recorded using Perkin-Elmer

UV-visible spectrophotometer in the range of 350 – 800 nm. The SEM images and EDX pattern of the grown crystals were recorded using Quanta 200 with Genesis eds software. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using TA instruments Q600 SDT in the nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The study of nonlinear optical conversion efficiency has been carried out using the modified setup of Kurtz and Perry at Indian institute of Science (IISc), Bangalore [20].
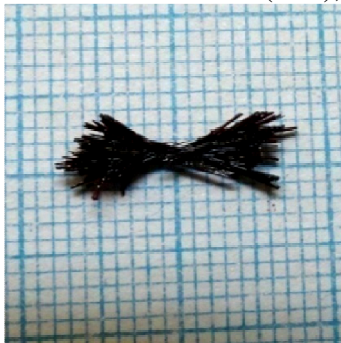

Fig. 1. The photograph of the as-grown 4-nitrophenyl hydrazone crystals.

3. Results and discussion

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis of 4-nitrophenyl hydrazone crystal have been carried out to identify the structure and to estimate the lattice parameters. The title compound crystallizes in orthorhombic crystal system with space group Pca2$_1$ which is recognized as non-centro-symmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals. The structural details of the crystal are given in table 1.

Table 1. Crystal structure details of 4-nitrophenyl hydrazone.

Crystallographic data of 4-nitrophenyl hydrazone	
Formula	$C_{13}H_{11}N_3O_2$
Crystal structure	Orthorhombic
Space group	Pca2$_1$
a (Å)	10.31(3)
b (Å)	9.54(2)
c (Å)	8.20(4)
α $^{(\circ)} = \beta$ $^{(\circ)} = \gamma$ $^{(\circ)}$	90.00(0)
Cell volume (Å^3)	789.7753
Density (gm.cm^{-3})	1.428
Molecular weight	241

3.2. Powder X-ray diffraction

The powder X-ray diffraction analysis was carried out to confirm the crystallinity of the sample. The grown crystal was crushed to a uniform fine powder and subjected to powder X-ray diffraction. The XRD pattern of the grown crystal was recorded and is shown in Fig. 2. The intensity versus 2θ was recorded by varying from 10° to 90° at a rate of 5°/min by

employing continuous scan mode. The sharp and well defined peaks at specific 2θ values indicate the good crystalline nature of the sample.
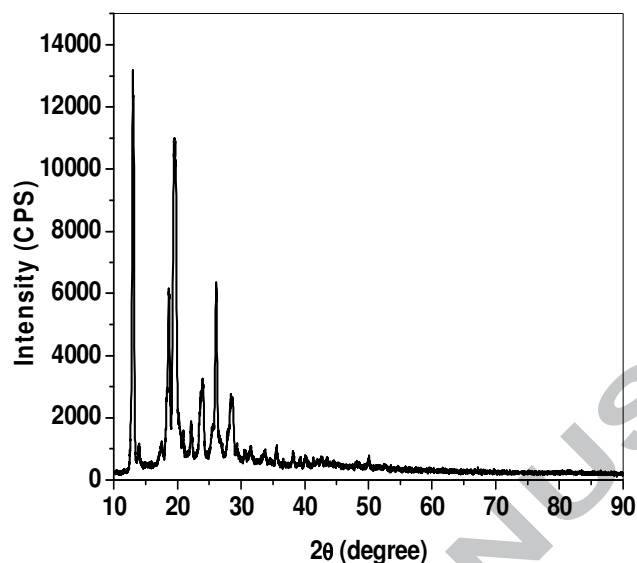

Fig. 2. Powder XRD pattern of 4-nitrophenyl hydrazone crystal.

3.3. FTIR Spectral Measurement

The Fourier transform infrared spectroscopy was used to identify the functional groups present in 4-nitrophenyl hydrazone crystal. The FTIR spectrum of the grown crystal was recorded in the frequency range of 400–4000 cm^{-1} and is shown in Fig. 3, it can be seen that, an absorption peaks at 3333.10 cm^{-1} is due to the stretching frequency of N-H group. The peak at 3022.55 cm^{-1} corresponding to stretching absorption of =CH group in aromatic rings. The spectrum shows the absorption band at 1491.92 cm^{-1} due to bending vibration of CH_3 group. Further the peaks correspond to C=O group in the region 1640-1700 cm^{-1} disappeared and new peak appears at 1595.18 cm^{-1} indicates the formation of C=N group. N-H and C=N stretching at 3333.10 cm^{-1} and 1595.18 cm^{-1} confirm the sample has hydrazone derivatives [21]. Absorptions at 1548.89 cm^{-1} and 1323.21 cm^{-1} correspond to symmetrical and asymmetrical vibrations for -NO_2 group. The resultant spectrum confirms the presence of all functional groups in the material.
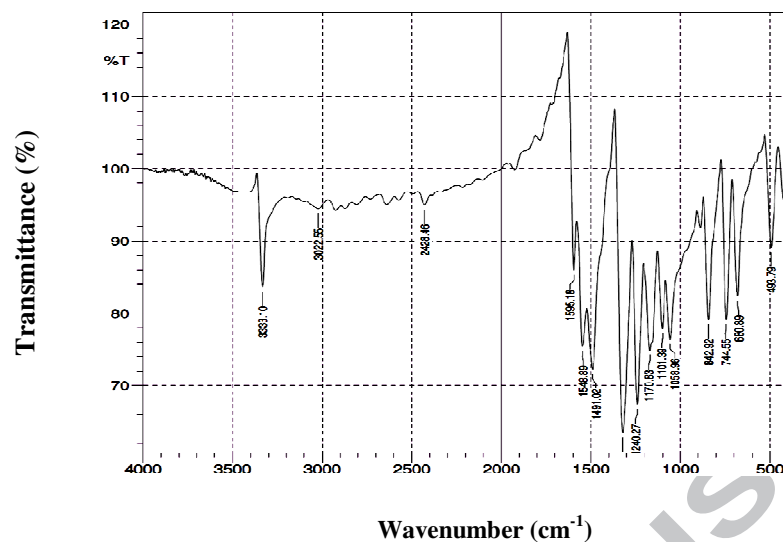
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Fig. 3. FTIR spectrum of 4-nitrophenyl hydrazone crystal.

3.4. NMR Spectral Measurement (^1H and ^{13}C)

The NMR spectroscopy is a powerful tool in terms of structural information derived from the spectrum. It involves the change of the spin state of a nuclear magnetic moment when the nuclear magnetic field is changed. Thus, NMR techniques are used to detect the presence of particular nuclei in a compound for a given nuclear species [22]. The ^1H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectrums of the grown crystal are shown in fig. 4 and fig.5 respectively. The ^1H-NMR spectrum (Fig. 4) indicates four kinds of proton signals related to the main functional groups. The singlet at $\delta = 2.349$ ppm is corresponds to the methyl protons ($-CH_3$). Also the ^1H-NMR spectrum shows that the singlet as a broad signal at $\delta = 9.077$ ppm strongly assignable to amino proton ($-NH$). The protons of unsubstituted phenyl appear as two multiplets signals in the region of $\delta = 6.845$ to 7.338 ppm. However, the protons of 4-nitrophenyl appear as two doublets. The doublet of the protons adjusted to the nitro group appear in down field at 8.219 ppm with coupling constant J=7.6 Hz and the other doublet appear at 8.075 ppm with coupling constant J=7.6 Hz as shown in Fig. 4.
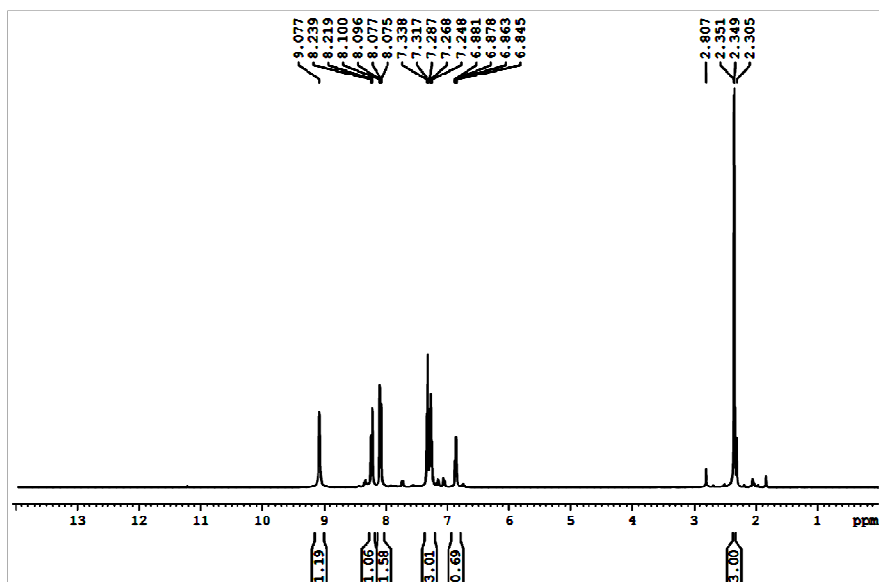
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Fig. 4. The ^{1}H-NMR spectrum of 4-nitrophenyl hydrazone crystal.

The ^{13}C-NMR spectrum of the grown crystal (Fig. 5) is in accordance with the proposed structure. The spectrum shows that the singlet at δ = 12.12 ppm corresponds to the carbon atom of methyl group. The aromatic carbon atoms appear in the region at δ = 113.51 to 146.64 ppm. The singlet at δ = 147.58 ppm was assignable to carbon atom of (C=N). The signals which appear at 30.38 ppm and 206.07 ppm are known to the carbon atoms of acetone solvent.
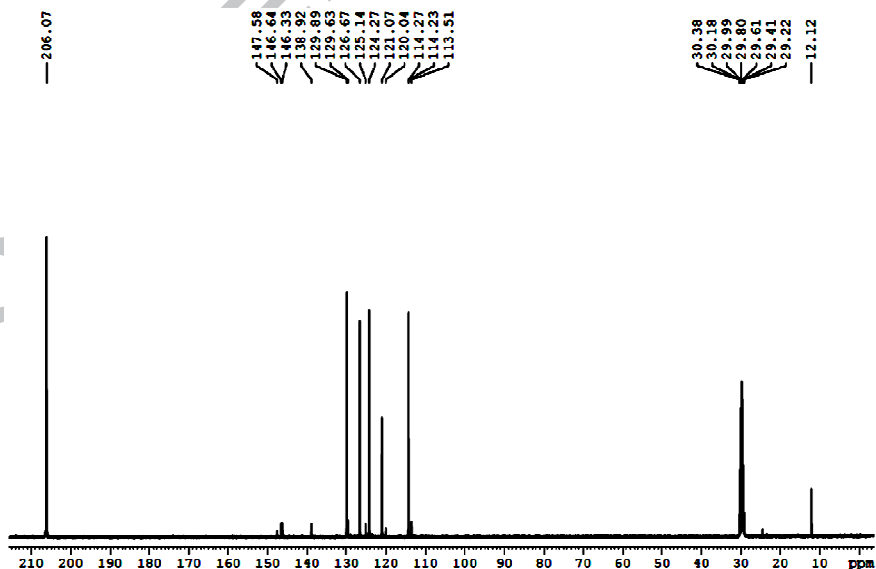

Fig. 5. The ^{13}C-NMR spectrum of 4-nitro phenyl hydrazone crystal.

6

3.5. UV-visible spectral measurement

The UV-visible spectral study is a useful tool to determine the transparency, which is an important requirement for a material to be optically active. The UV–visible spectrum of the grown crystal was recorded in the range between 350–800 nm. The optical transmittance spectrum of 4-nitrophenyl hydrazone crystal is shown in Fig. 6. The short wavelength cut-off occurs at 488 nm and there is no appreciable absorption of light in the entire visible region. The colored compounds absorb UV visible light generally with a strong absorbence in the visible range. The absorption band obtained in the visible region is assigned to $n \rightarrow \pi^*$ electronic transition of hydrazone (–CH=N–NH–) group present in the 4-nitrophenyl hydrazone molecules [23,24] The good transmittance property of the crystal in the entire visible region ensures its suitability for second harmonic generation application [25].
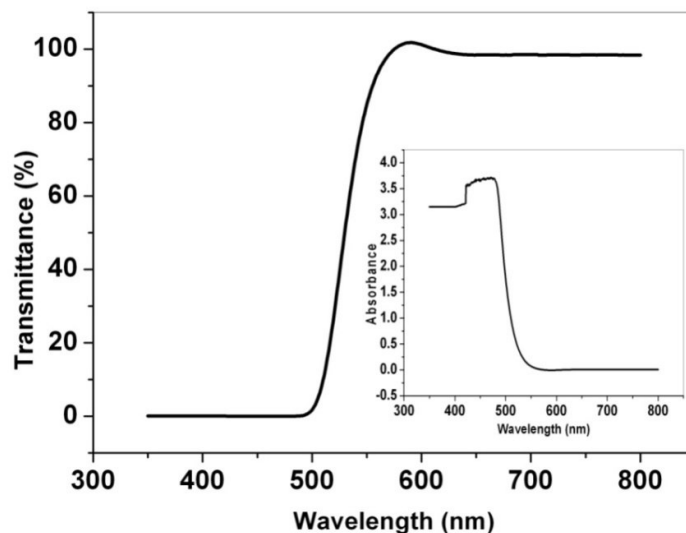

Fig. 6. UV-visible spectrum of 4-nitrophenyl hydrazone crystal.

The optical energy gap of the grown crystal is determined from the transmittance spectrum using the equation;

$$\alpha h v = A(h v - E_g)^n \tag{1}$$

where A is a constant which varies with transitions, E_g is the band gap of the material and n is an index which can have the values 1/2, 3/2, 2, or 3 depending on the nature of the electronic transitions. Here, the value of n is assigned as 1/2 for an allowed direct transition and α is the absorption coefficient, which is calculated from the equation;

$$\alpha = \frac{Abs}{t} \tag{2}$$

where Abs is the absorbance of the material and t is the thickness of the sample. From the transmittance spectrum, a graph is drawn between $h v$ and $(\alpha h v)^2$ and is shown in Fig. 7. The band gap energy of the grown crystal is evaluated by extrapolation a straight line in the linear region of the graph at $(\alpha h v)^2 = 0$. The band gap energy calculated was found to be 2.45 eV for the grown crystal.
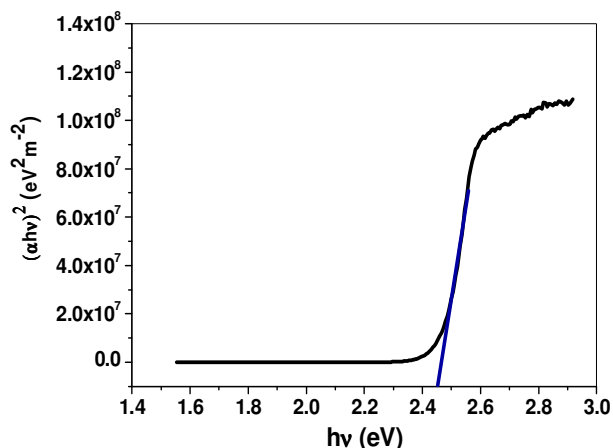
Fig. 7. The plot of $(\alpha h \nu)^2$ vs photon energy hν.

3.6. Scanning electron microscopy (SEM) measurement

The SEM micrographs of the grown crystals were taken at different magnification values are shown in Fig. 8. It gives information about surface morphology and the presence of imperfections in the crystals. Fig. 8 clearly shows the grain distribution over the surface and a few microcrystals present on the surface of the grown crystal.
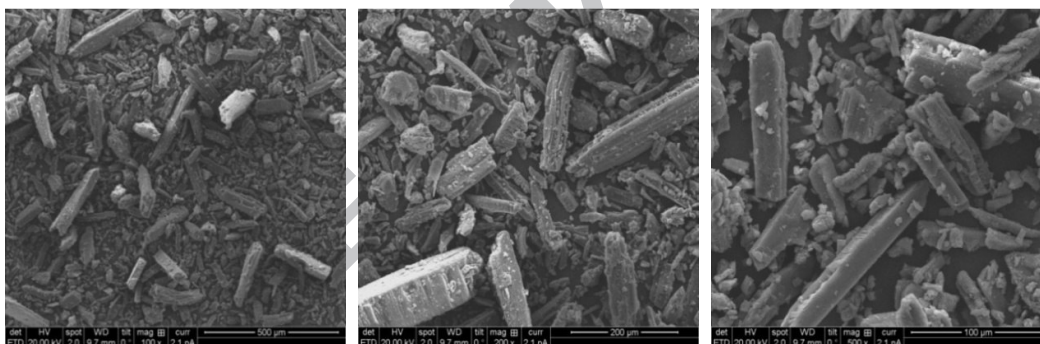

Fig. 8. SEM micrograph of 4-nitrophenyl hydrazone crystal.

3.7. Energy dispersive X-ray (EDX) measurement

An elemental analysis was carried out for 4-nitrophenyl hydrazone by employing the energy dispersive X-ray (EDX) in order to confirm the composition of carbon (C), nitrogen (N) and oxygen (O) in the crystal. Fig. 9 illustrates the EDX spectrum of the grown crystal. The weight percentages (wt %) of C, N and O as obtained from EDX analysis is listed in table 2.
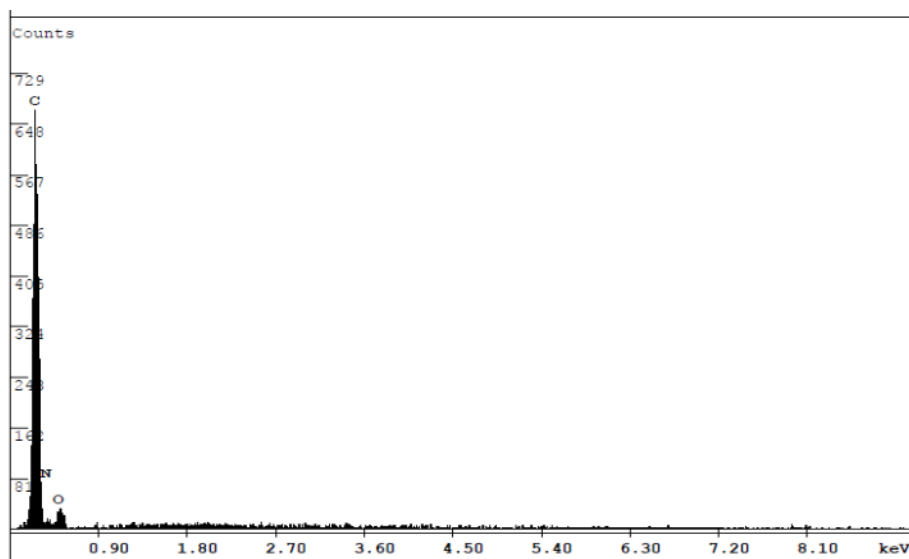
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Fig. 9. EDX spectrum of 4-nitrophenyl hydrazone crystal.

Table 2. EDX quantification of 4-nitrophenyl hydrazone crystal.

Element	Wt (%)	At%
Carbon	76.31	79.97
Nitrogen	12.51	11.24
Oxygen	11.18	8.79
Total	100.00	100.00

3.8. Thermal measurements

The thermo gravimetric (TG) and differential thermal analysis (DTA) are important as far as the fabrication technology is concerned, as they provide thermal stability since considerable amount of heat is generated during the cutting process. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of the grown crystals were carried out between 30 $^{\circ}$C to 987 $^{\circ}$C. Fig. 10 shows the thermograms illustrating simultaneously recorded TGA and DTA. The DTA curve shows a major endothermic peak, which corresponds to the melting point of the material at 146 $^{\circ}$C. The sharpness of the peak at 146 $^{\circ}$C indicates the high purity of the grown crystal. Another important observation is, there is no phase transition until the material melts and this enhances the temperature range for the utility of crystal for NLO applications. The absence of water in the molecular structure is indicated by the absence of weight loss around 100 $^{\circ}$C. There are two peaks detected at 327.2 $^{\circ}$C and 486.7 $^{\circ}$C, may be due to the decomposition stage of the compound. From the TGA curve, it can be seen that there are three stages of weight loss. The first weight loss (stage I) is a sharp one starting at about 135.8 $^{\circ}$C, which indicates the beginning of the melting. This is followed by a weight loss (stage II) occurring between 296.7 $^{\circ}$C and 557.4 $^{\circ}$C. The weight loss (stage III) above 557.4 $^{\circ}$C is assigned to the decomposition of the compound.
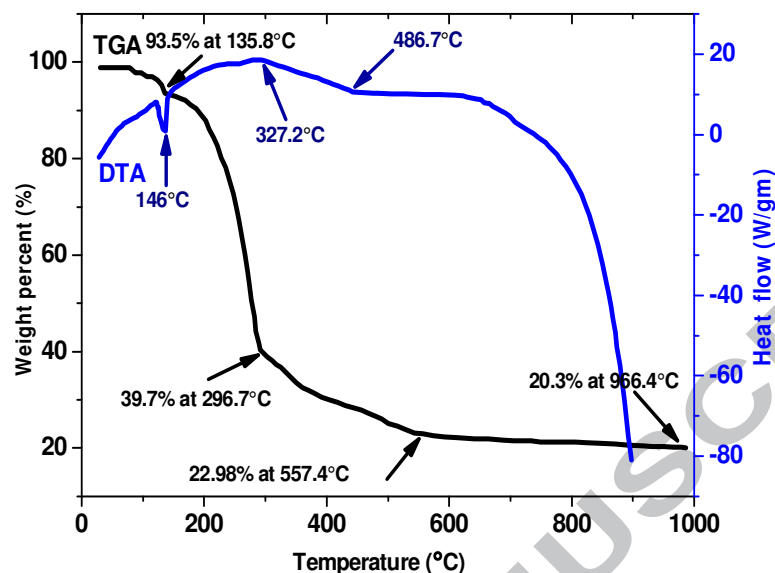
Fig. 10. TGA/DTA curves of 4-nitrophenyl hydrazone crystal

3.9. Powder SHG measurement

The study of nonlinear optical conversion efficiency has been carried out using the modified setup of Kurtz and Perry method. A Q-switched Nd:YAG laser beam of wavelength 1064 nm with an input power of 3.25 mJ/pulse and pulse width of 10 ns with a repetition rate of 10 Hz were used. The grown crystals of 4-nitrophenyl hydrazone were powdered and then packed in a micro capillary of uniform bore and exposed to laser radiations. The second harmonic radiation generated by the randomly oriented microcrystals were focused by a lens and detected by a photo multiplier tube. The emission of green radiation of wavelength 532 nm from the crystal confirmed the second harmonic signal generation. A sample of potassium dihydrogen phosphate (KDP) was used as a reference material for the present measurement. The signal amplitude in mV on the oscilloscope indicates the SHG efficiency of the grown crystal. A second harmonic signal of 1000 mV was obtained from 4-nitrophenyl hydrazone, with reference material KDP (65 mV). The SHG conversion efficiency of 4-nitrophenyl hydrazone was found to be 15.39 times when compared to that of KDP.

4. Conclusions

The needle shaped crystals of 4-nitrophenyl hydrazone were grown by slow evaporation technique using acetone as a solvent. The single crystal X-ray crystallographic data indicates that the crystal belongs to orthorhombic crystal system with non-centro-symmetric space group Pca2$_1$. The powder X-ray diffraction pattern confirmed the crystallinity of the sample. The FTIR, ^{1}H NMR and ^{13}C NMR spectrums show the presence of different functional groups in the grown crystal. The UV-visible spectrum revealed that the grown crystal was moderately transparent in the entire visible region. Therefore grown crystals were suitable for second harmonic generation applications. The chemical composition of the grown crystal was ascertained by EDX measurement. The SEM shows that a few microcrystals were randomly distributed on the surface of the crystal. Thermal analysis revealed that the title compound is stable up to 146 °C and hence the grown crystal can be used for SHG applications up to 146 °C. The SHG property of the grown crystal was tested and found to be 15.39 times when

10

compared to KDP crystal. Therefore, the aforesaid results make 4-nitrophenyl hydrazone crystal is a good candidate for NLO applications.
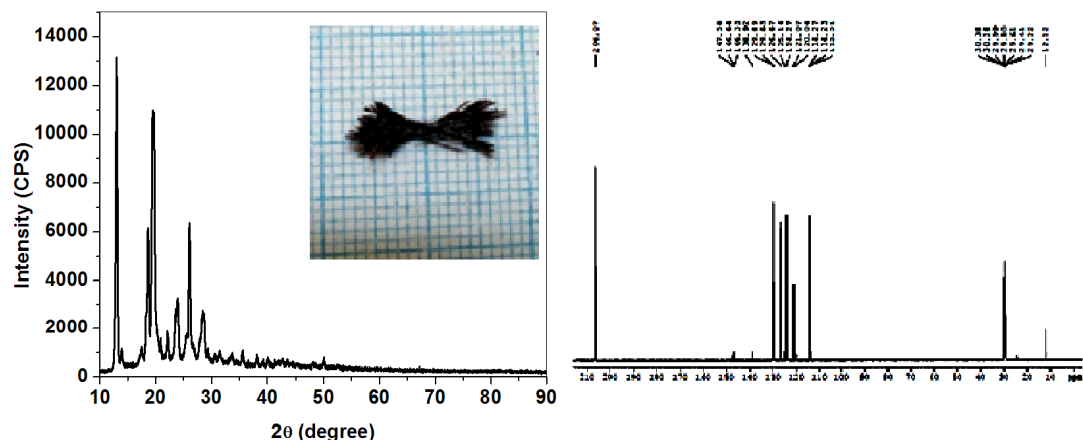
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