Third order nonlinear studies and other characterization of 4-nitrophenol (4-NP) single crystals

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Abstract. The 4-nitro phenol is an organic NLO material. The commercially available 4-nitrophenol was recrystallized in acetone two times to purify the materials. The single crystal of pure 4-nitro phenol (4-NP) compound was grown by slow evaporation and slow cooling techniques using acetone as a solvent. The grown crystals were subjected to various characterization studies. The powder XRD spectrum of 4-NP shows the good crystalline nature of the grown crystal. The lattice parameter values of the grown 4-NP crystals were calculated from single crystal XRD data as \(a=6.09\,\text{Å}, \ b=8.79\,\text{Å}, \ c=11.61\,\text{Å}, \ \alpha=\gamma=90^\circ, \ \beta=103.15\). 4-NP crystallizes in monoclinic crystal system with the space group of \(P2_1/c\). The crystals obtained by slow evaporation technique were subjected to FTIR spectrum. The resultant FTIR spectrum confirms the various functional groups present in 4-NP. The Vis-IR spectrum of 4-NP shows the cut off wave length of 403nm. The differential thermal analysis of 4-NP shows that the melting point of the compound is 115°C. As it crystallizes in centro symmetric space group, it is suitable for third harmonic generation. The nonlinear absorption coefficient (\(\beta\)) and non linear refractive index (\(n_2\)) were calculated as \(\beta=5.03859\times10^{-6}\,\text{cm/W}\) and \(n_2=1.45967\times10^{-11}\,\text{cm}^2/\text{W}\) respectively by using Z-scan technique.

1. Introduction

Nonlinear optical properties were associated with the ability of a material to undergo nonlinear polarization under the influence of electric fields [1]. Second order NLO effect can be considered as the interaction of the polarizable electrons of the NLO material with two electric fields \(E_1\) and \(E_2\), these fields potentially having different polarizations and potentially oscillating with frequencies \(\omega_1\) and \(\omega_2\) respectively. The second order NLO susceptibility comes only from the polarization of conjugated molecules which were oriented without symmetric center. No such restrictions apply to the third order term nonlinear susceptibility \(\chi^3\). Third order nonlinear optical phenomena, such as nonlinear absorption, nonlinear refraction can be calculated when a thin sample of the material is moved across the focus of a Gaussian laser beam and the transmittance is recorded as a function of the sample position relative to the beam focus. Due to the nonlinear refractive index nature, the material acts as a thin lens changing the beam dimensions as the sample moves across the focus [2]. This Z-scan technique is a well suitable technique to characterize third order NLO response of the materials [3]. The Z-scan technique exploits the distance dependence to probe both real and imaginary parts of \(\chi^3\). The third order nonlinear optical material with weak nonlinear absorption but strong nonlinear refraction have attracted considerable attention because of their potential uses in all optical signal processing devices [4]. However, many materials were limited by large nonlinear absorption values, small non linear refraction and large linear absorption loss. As 4-nitro phenol (4-NP) crystallizes in centro symmetric space group (monoclinic \(P2_1/c\)), the application of 4-NP for SHG is not possible. However by preparing super molecular packing arrangement of 4-NP, (the supermolecular assembly increases the distances of chromophores and inhibits the counteraction between dipoles of centro symmetric molecules) it was made to exhibit SHG even with centro symmetry [5]. In the present
investigation, an effort was taken to study the third order nonlinear refractive index and nonlinear absorption coefficient of 4-NP single crystals.

2. Experimental

2.1 Solubility

The solubility of 4-NP in acetone has been determined by the gravimetric method. A small amount of 4-NP compound was dissolved in 20ml of acetone and it was allowed to stirrer for 2 hrs at 30°C. The stirring was then stopped to allow the undissolved material to settle. From the clear solution, 10ml of sample was carefully taken and placed into a pre weighed container. The solvent was allowed to evaporate at room temperature. The mass of the remaining material was determined. Thus the solubility of 4-NP in acetone at 30°C was obtained. The same process was repeated for various temperatures such as 35, 40, 45 and 50°C and the same was repeated for the solution prepared using another solvent ethyl acetate. Solubility curves of 4-NP in acetone and ethyl acetate solvents were shown in Figure 1.

![Figure 1 Solubility curves of 4-NP](image)

2.2 Growth of 4-NP single crystals

200ml saturated solution of the 4-NP in acetone was prepared at 35°C and the growth was initiated by the controlled evaporation of acetone by using tightly covered sheets. Nucleation started after 20 days. The grown crystals were harvested after the period of 30 days. The temperature of the bath is maintained at constant temperature throughout the growth period. Effort was also taken to grow a crystal by using slow cooling technique but without using any seed crystals. 300ml saturated solution of the 4-NP in acetone was prepared at 35°C and kept inside a constant temperature bath. Growth commences by the controlled cooling rate of 0.01°C/day for two weeks. Then it was kept at the same temperature. After the period of 45 days a well faceted crystal with the dimension of 7x3.4x1.8cm³ was taken out. The crystals have been characterized for their purification and perfection. The crystals obtained with slow evaporation technique and slow cooling technique were shown in Figures 2a and 2b respectively.
3. Characterization

3.1 Powder X-ray diffraction studies of 4-NP

The important application of powder X-ray diffraction pattern is the identification of crystalline compounds by their diffraction pattern. Interaction of X-rays with the sample creates secondary “diffracted” beams of X-rays related to inter planar spacing in the crystalline powder according to a mathematical relation called “Bragg’s Law”: \( n \lambda = 2d \sin \theta \). The powder XRD spectrum of 4-NP crystal was shown in Figure 3. The observed reflection lines were indexed with the help of computer program winplotr.

3.2 Single Crystal X-ray diffraction

The single crystal X-ray diffraction studies were performed on the 4-NP single crystals grown from acetone. From the single crystal X-ray diffraction data it was observed that 4-NP belongs to monoclinic crystal system with P21/c space group. The lattice parameters of 4-NP coincide well with the reported values [6]. The comparison of reported values with the present results were tabulated in Table.1. The morphology of 4-NP indexed from single crystal XRD data was shown in Figure. 4.

Figure 3 Powder XRD spectrum of 4-NP crystals

Figure 4 The morphology of as grown 4-NP crystals
Table 1 Comparison of Lattice parameters of 4-NP with the reported values

| Lattice parameters | Reported values | Present results |
|--------------------|-----------------|-----------------|
| a (Å)              | 6.16            | 6.09            |
| b (Å)              | 8.83            | 8.79            |
| c (Å)              | 11.54           | 11.61           |
| β(°)               | 103.39          | 103.15          |

3.3 FTIR Spectrum of 4-NP

Infra red spectrum of a compound describes the absorption of different IR frequencies by a sample positioned in the path of an IR beam. In the present study, infrared absorption spectrum of the grown 4-NP crystal was recorded in the range 4000–400cm⁻¹ using a KBr disk on a PERKIN–ELMER spectrum RX1 infrared spectrophotometer. The KBr disk was prepared by grounding the 4-NP sample with KBr and made into a disc after drying and then pressing it at high pressures. The FTIR spectrum of as grown 4-NP crystal is shown in Figure 5. The peak assignments from the resultant FTIR spectrum were tabulated in Table 2. There were peaks at 3325cm⁻¹ and 1217cm⁻¹ caused by an O-H stretching vibration and a C-O stretching vibrations respectively. The -OH peak is broadened owing to hydrogen bonding present in phenols. These confirm that the compound consists a phenol group. If a nitro group is attached to an aromatic ring, the N-O stretching bands shift to down to slightly lower wave numbers from 1550-1475 cm⁻¹ and 1360-1290 cm⁻¹. Hence these peaks observed at the region of 1495cm⁻¹ and 1345cm⁻¹ as asymmetric and symmetric stretching vibrations respectively were assigned to N=O group [7]. Compounds that do not have a C=C bond show C–H stretches only below 3000cm⁻¹. But the C–H stretch observed at 3085cm⁻¹ shows the presence of aromatic ring. Also aromatic hydrocarbons show absorptions in the regions 1613 cm⁻¹ and 1590cm⁻¹ due to carbon-carbon stretching vibrations in the aromatic ring. The important infrared modes for nitro compounds(-C-NO₂) were usually observed in the finger print region between 1300-1100cm⁻¹. The peak at 1113cm⁻¹ confirms the presence of C-NO₂ bonding. The bands at 960 cm⁻¹ were assigned to C-H out of plane bending vibrations. All assignments confirm the presence functional groups of 4-NP.

![FTIR spectrum of 4-NP](image-url)
Table 2 Peak assignments of 4-NP

| Wave Number cm\(^{-1}\) | Assignments                      |
|-------------------------|----------------------------------|
| 3325                    | OH stretch                       |
| 3085                    | Aromatic CH                     |
| 1613 \(\text{C=C} \)    | Aromatic ring C=C stretch       |
| 1590                    |                                 |
| 1495 \(\text{N=O} \)    | N=O Asymmetric stretch          |
| 1345 \(\text{N=O} \)    | N=O symmetric stretch           |
| 1217                    | C-OH                            |
| 1113                    | C-NO2                            |
| 960                     | C-H out of plane bending         |

3.4 **Thermo gravimetric analysis of 4-NP**

During thermal analysis mass change of a substance is measured as function of temperature and the mass is lost if the substance contains a volatile fractions. To study the thermal stability of grown 4-NP crystals, the DTA/TGA was carried out between the temperature 0\(^\circ\)C and 500\(^\circ\)C in the nitrogen atmosphere at heating rate 10 oC/min using Netzsch STA 409 c/cd thermal analyzer. The DTA/TGA curves of 4-NP were shown in Figure 5. The DTA curve shows a major endothermic peak, which corresponds to the melting point of the compound at 115 oC. Before the melting point, no weight loss is observed. TGA curve represents decomposition of the sample in a single stage. The second endothermic peak observed at 288 0C indicates decomposition nature of the material at this stage and 8.08% decomposition is recorded. Correspondingly TGA curve shows the full degradation at 300 0C.

![Figure 6 DTA/TGA analysis of 4-NP](image)

![Figure 7 VIS-IR spectrum of 4-NP](image)

3.4 **Linear optical properties of 4-NP**

The visible-IR spectrum of 4-NP single crystal was recorded with Varian Carry 5E UV-visible-IR spectrophotometer. A single crystal of 4-NP with the thickness of 2mm is subjected to the visible-IR spectrum. The visible-IR spectrum of 4-NP single crystal is shown in Figure 7. The hydrogen bonding present in the conjugated 4-NP(aromatic compound which is substituted by a chromophore) stabilizes the excited state, hence electron transfer is facilitated as \(\pi\rightarrow\pi^*\) transition resulting in a shift of the position of absorption by the system to longer wavelengths. From the resultant vis-IR spectrum of 4-NP the observed cutoff wavelength is 403nm and it shows the 80% of transmittance.
3.5 Nonlinear optical properties

Self focusing of an intense Gaussian beam in a non linear medium results in beam distortion, which can be measured. The refractive index $n_2$ value of the medium can be extracted from this distortion. The light transmitted by a small aperture in the far field is then detected [8].

3.5.1 Closed aperture

If a part of the transmitted light is detected due to the presence of an aperture in front of the detector, both nonlinear refractive index and two photon absorption manifest themselves on a so-called closed-aperture Z-scan [9]. The third-order nonlinear refractive index $n_2$ and the nonlinear absorption coefficient $\beta$ of 4-NP single crystals of thickness of 2mm were determined by the Z-scan technique. In close-aperture test, the sample is simply scanned across the focal point of a 632.8 nm laser beam past a short-focal-length lens. As the sample passes through the focal point of the beam, the power density changes. Variation in transmitted intensity is related directly to nonlinear optical (NLO) index coefficient [10]. The sign and magnitude of third-order refractive nonlinearities were calculated from closed aperture data. The closed aperture curve of 4-NP was shown in Figure 8. The peak followed by a valley (normalized transmittance obtained from the closed-aperture Z-scan data) indicates that the sign of nonlinear refraction $n_2$ negative (self-defocusing) at 632 nm. Nonlinear intensity-dependent refractive index ($n_2$) of 4-NP was calculated to be $n_2=1.45967\times10^{-11}$ cm$^2$/W.

3.5.2 Open aperture

In open-aperture Z-scan, the sample is moved through the focus without placing an aperture at the detector and all the light from the sample is transmitted. The Z-scan data with fully open aperture is insensitive to nonlinear refraction. The open aperture curve of 4-NP was shown in Figure 9. From the open-aperture Z-scan data the magnitude of intensity dependent nonlinear absorption is derived and it exhibits an increase of transmittance with respect to the focus($z=0$), result of an induced negative nonlinear absorption effect of 4-NP single crystals. Two-photon absorption coefficient of 4-NP single crystal was found to be $\beta= 5.03859\times10^{-6}$ cm/W.

4 Conclusion

4-NP single crystals were grown by slow evaporation and slow cooling techniques. Grown crystals were subjected to different characterization studies. The solubility of 4-NP in acetone and ethyl acetate was determined by gravimetric method. Crystalline nature of the grown 4-NP crystals was analyzed by powder X-ray diffraction method. The lattice parameters of 4-NP were measured by single crystal X-ray diffraction method. The presence of functional groups of 4-NP was confirmed by FTIR study. According to the vis-IR spectroscopic studies of 4-NP, the lower cutoff wave length and transmittance were found to be 403nm and 80% respectively. The sharp endothermic peak observed at 115°C of DTA curve confirms the melting point of 4-NP as 115°C. The third-order nonlinear refraction and two photon absorption coefficient were measured for the 4-NP using Z-scan technique. The values of nonlinear refractive index, $n_2$ and nonlinear absorption coefficient for 4-NP measured at 632 nm were $n_2=1.45967\times10^{-11}$ cm$^2$/W and $\beta= 5.03859\times10^{-6}$ cm/W respectively. The experiment also confirmed that the nonlinear phenomenon was caused by self defocusing process.
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