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Synthesis, Growth and Characterization of N-(3-Nitrophenyl) Acetamide Crystal-Find it Optical Uses

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Abstract

Single crystals of N-(3-nitrophenyl)acetamide (3-NPA) were successfully grown by slow evaporation method at a constant temperature 32°C from acetone and methanol mixed solvent. The suitability of the selected mixed solvent was justified by the growth of large size, transparent single crystal of 3-NPA. The solubility studies for 3-NPA were estimated. The cell dimensions were obtained by powder crystal X-ray diffraction (XRD) study. The functional groups have been confirmed using Fourier transform infrared (FTIR) analysis. UV-visible and fluorescence spectral analyses were carried out for the grown crystals. Thermo gravimetric analysis and differential thermal investigation were carried out to find out the thermal properties of the as grown crystal. The Second Harmonic Generation (SHG) efficiency of 3-NPA was also determined using Kurtz-Perry method.

Keywords: Solution Growth, Powder X-Ray Diffraction, Single Crystal Growth, Organic materials, Nonlinear Optics

Introduction

Nonlinear optical materials (NLO) have established to be an attractive candidate for a number of applications such as second harmonic generation, frequency mixing, electro-optic modulation, etc. Rapid development in the field of opto-electronics have necessitated the search for new and efficient non-linear optical (NLO) materials, which can be used for various applications like optical computing, optical data storage, optical communications and electro-optic shutters. Recently a variety of organic NLO materials with non-localized π-electron systems with a large dipole moment have been synthesized with non-linear susceptibilities higher than the inorganic NLO materials [1–5]. The advantages of organic materials over inorganic materials are the scope for altering the properties by functional substitutions, high degree of nonlinearity and high laser damage threshold. Organic crystals with the required conjugated π-electrons are attractive candidates, because of the large nonlinear optical coefficients [6-10]. 3-nitro acetanilide (3-NPA) is a potential material among the many organic compounds reported for second harmonic generation (SHG) applications. These crystals can be grown into bulk form with good applied optical transparency in blue-green region, which are mechanically hard and chemically stable for second harmonic generation (SHG). To possess NLO property organic materials should contain highly conjugated pi electron system affected by electron donor and acceptor groups. Hence, in this class one such acetanilide derivatives, 3-NPA was taken under study that showed efficient NLO property. Some of the acetanilide derivatives such as Acetoacetanilide [7,8] and p-aminoacetanilide [9] were found to exhibit NLO properties. 3-NPA is a meta substituted aromatic compound with molecular formula $C_8H_8N_2O_3$. The molecular structure of 3-NPA, given in Figure 1, this compound crystallizes in the monoclinic system in the chiral space group P21 with four independent molecules in the asymmetric unit. In this paper, we report the material solubility, crystal growth, powder crystal X-ray diffraction (powder-XRD), Fourier Transform Infrared Spectroscopy (FTIR), optical, Fluorescence, hardness and NLO studies of 3-NPA.

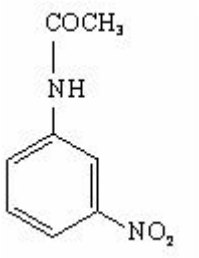

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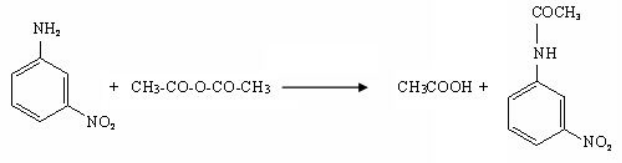
Figure 1. Molecular structure of 3-NPA.

Experimental

Synthesis of 3-NPA

The label compound was synthesized from analytical re-agent (AR) 3-nitroaniline and acetic anhydride. Required quantity of 3-nitroaniline was dissolved in acetic anhydride at room temperature. The direct reaction between them as shown in the format immediately yielded yellow colour compound. The precipitated product was clean and dehydrated using vacuum filtration. Recrystallization processes repurified the material.



Format 1. Synthesis of 3-NPA

Solubility Curve

The solubility of 3-NPA was determined by means of acetone and methanol as mixed solvent, since this is found to be a suitable solvent to grow considerable size crystals. Recrystallized salt was dissolved in mixed solvents and the solution was maintained at 32°C in a constant temperature bath and stirred continuously to ensure homogenization of the solution. On reaching the saturation, the amount of the salt in the solution was analyzed gravimetrically. The same procedure was repetitive for the temperatures 35°C, 40°C, 45°C and 50°C and upto 60°C results are shown in **Figure 2**. The 3-NPA exhibits good solubility and encouraging solubility-temperature gradient in acetone and methanol mixed solvent.

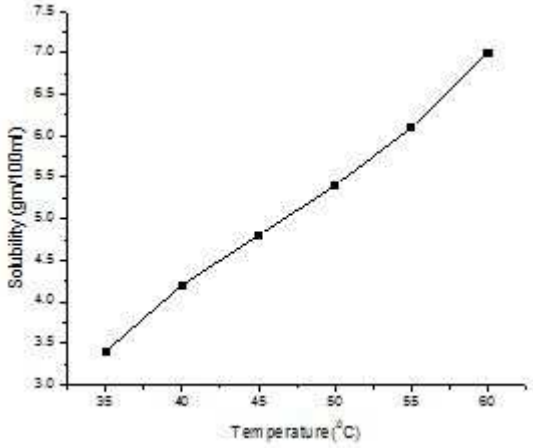


Figure 2. Solubility diagram of 3-NPA

Crystal Growth

The saturated solution of 3-NPA was prepared by dissolving the source material in the mixed solvent at 32°C. The homogeneity of the solution was realized with continuous stirring of the solution using a magnetic stirrer at temperature (32°C) by using constant temperature bath. On reaching saturation, the beaker containing the growth solution was optimally closed for controlled evaporation. Transparent single crystal was obtained from the growth solution after 10 days. The grown crystal is shown in the **Figure 3**. Based on the experimental observation during this investigation, which revealed the difficulty involved in the crystallization, high optical quality 3-NPA single crystal of size measuring 7 x 5 x 3 mm^3 has been successfully grown by slow evaporation technique from acetone and methanol mixed solvent. The suitability of the selected mixed solvent was justified by the growth of large size, transparent single crystal of 3-NPA.

Figure 3. Photograph of as grown crystals of 3-NPA

Results and Discussions

Powder X-ray Diffraction Studies

Grown 3-NPA crystal was finely crushed with the aid of mortar and the crushed powder was subjected to powder X-ray diffraction analysis. The sample was scanned by X-ray diffractometer with CuKα radiation (l = 1.54178 Å) radiation over the range 10 to 60 º at a scan rate of 2 %min. The recorded X-ray diffraction spectrum of 3-NPA is shown in **Figure 4.** Powder crystal XRD reveals that 3-NPA belongs to monoclinic system. The unit cell parameters obtained are a = 9.762 Å**,** b =13.287 Å, c =13.226 Å, and β = 102.99°.

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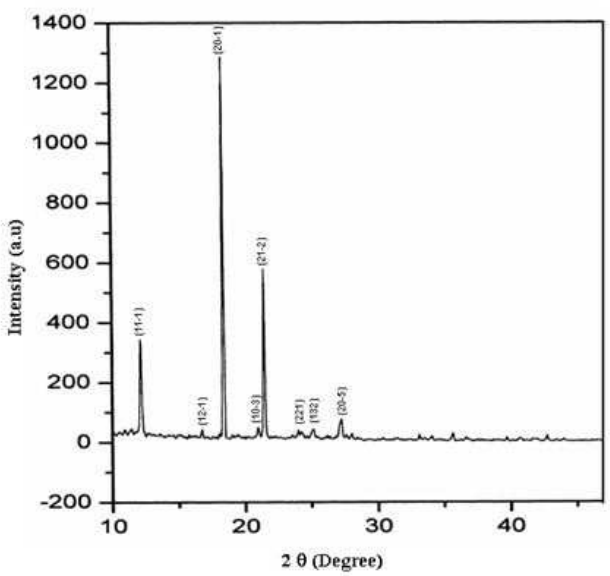

Figure 4. Powder XRD Spectrum of 3-NPA crystals

FTIR Spectral Analysis

The FTIR spectrum was recorded on the grown 3-NPA crystal at room temperature in the range of 400cm^{-1} – 4000 cm^{-1} as shown in the **Figure 5**. The spectrum shows the symmetric and asymmetric stretching modes of free NH_2 group, which are observed at 3303cm^{-1} and 3263 cm^{-1}. The absorptions at 1673 cm^{-1} are due to ketone stretching vibration. The aromatic skeletal ring is observed at 1600 cm^{-1}. A well-resolved peak at 604 cm^{-1} represents the C-N-O stretching vibration. Peak at 1260 cm^{-1} is due to N-H bending and C-N stretching vibrations [11]. The vibration observed between 886 and 670 cm^{-1} are usually associated with the presence of benzene rings in the NA molecule. The peak between 741 and 805 cm^{-1} shows the meta position of the substituted. The peaks at 1531 and 1350cm^{-1} are due to the vibration of NO_2 stretching modes. As either the N-H stretching modes or NO_2 stretching modes are not much broad, their interaction with the neighboring molecule is recognized to be weak bonds.

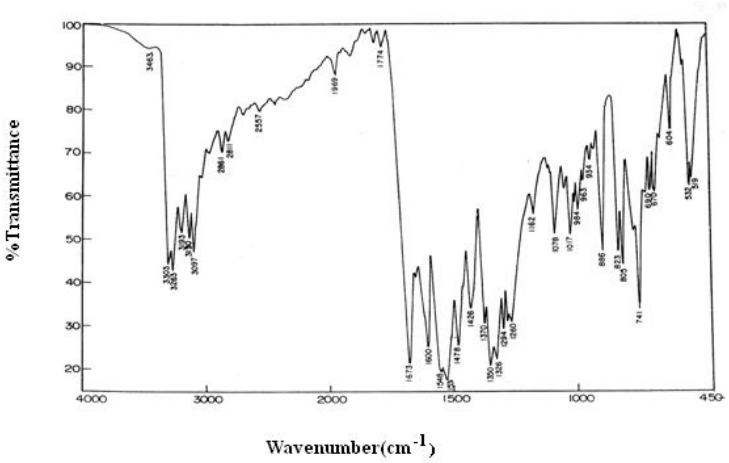

Figure 5. FTIR Spectrum of 3-NPA crystal

UV-Vis Studies

In order to determine the optical transmission characteristics of the grown crystal UV-Vis spectrum was recorded on the cut and polished grown sample. The grown crystals of 3-NPA are pale yellowish orange colour and transparent indicating the absence of absorption in the visible region. UV-Vis transmission spectrum presented in **Figure 6** shows that the crystal has good transparency in the range 380 nm - 1100 nm, which indicates that this crystal can be employed in the NLO applications in the entire visible and IR region. The absence of the absorption in the visible region is the necessity for this compound as it is to be exploited for NLO applications in the room temperature.

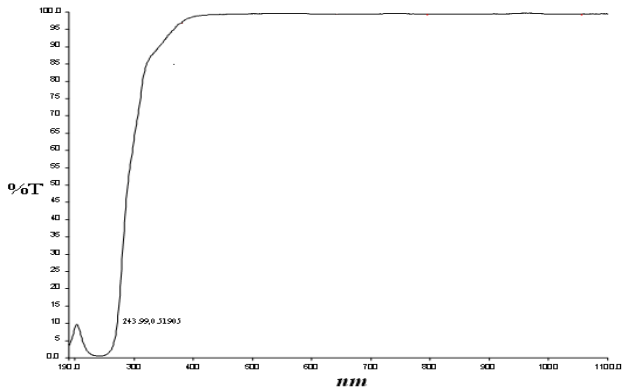

Figure 6. UV-Vis Spectrum of 3-NPA crystal

Photoconductivity Studies

Photoconductivity of the 3-NPA crystal was studied using Keithley 485 picoammeter. The experiment was performed at room temperature. Electrical contacts were made at a spacing of about 0.126 cm on the samples using silver paint. The DC input was increased from 20 to 400 volts in steps and the corresponding dark currents

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were noted from the electrometer. The sample was illuminated with a halogen lamp (100 W) and the corresponding photocurrent was recorded for the applied voltage as in the previous case. The variations of photocurrent (Ip) and dark current (Id) with applied field are shown in Fig. 7. Both the photo and dark currents of 3-NPA crystal increase linearly with applied field. It is observed from the plot that the dark current is less than photocurrent, thus suggesting that 3-NPA exhibits positive photoconductivity. In general, positive photoconductivity is recognized to generation of mobile charge carriers caused by the absorption of photons.

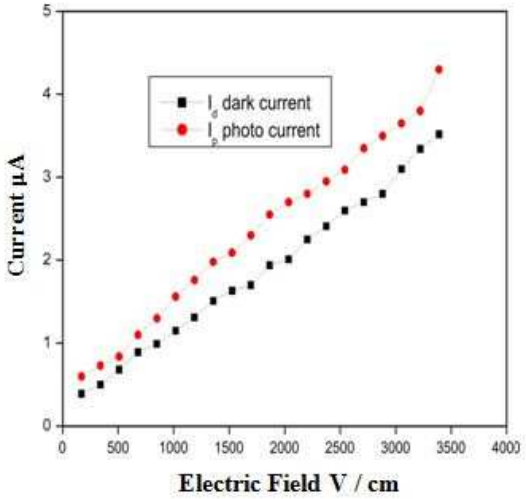

Figure 7. Photocurrent versus applied electric field

Microhardness study of 3-NPA Crystals

Microhardness studies have been carried out on the 3-NPA single crystal using a Leitz microhardness tester fitted with a Vickers diamond pyramidal indentor. Vicker's microhardness values have been calculated using $Hv = (1.8544^* p) / d^2$ kg.mm^{-2}, where p is the applied load and d is the mean diagonal length of the indentor impression. Hardness values have been taken for various applied loads.

A graph has been plotted between hardness number (Hv) and applied load as shown in the figure . It is observed from the graph that the hardness value increases and then attains almost saturation with the increase of the applied load [14].

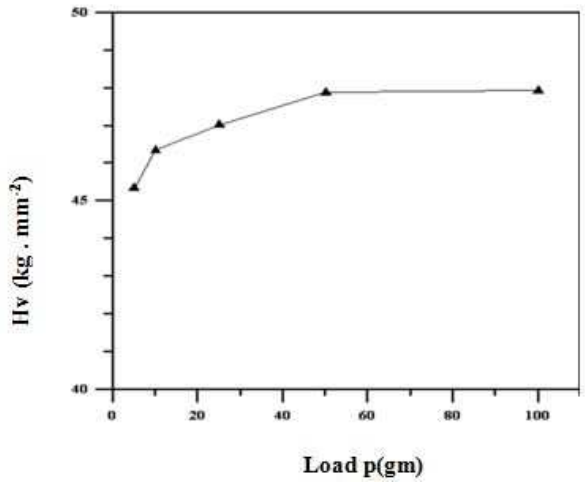

Figure 8. Hardness Vs. Load p (gm)

Non linear optical studies

This is sufficient for SHG laser radiation of 1064 nm or other applications in the blue region. Kurtz powder SHG test confirmed the nonlinear property of crystal. In this technique, the sample was packed as a polycrystalline powder into cell sandwiched between two glass slides and exposed to a Q-switched Nd:YAG laser emitting 1064 nm, 10ns laser. The SHG output power was absorbed with respect to a standard KDP crystal, which gave greenish colour[12].

Conclusions

Single crystal of 3-NPA was grown by slow evaporation method. Bulk crystals were grown by slow evaporation technique. Lattice parameter values have been evaluated by powder X-ray diffraction studies. Various functional groups present in the grown sample were identified by FTIR analysis. Hardness studies confirmed that 3-NPA is a relatively soft material. Photoconductivity studies showed that 3-NPA exhibits positive photoconductivity. SHG test confirmed that 3-NPA is an NLO material. Optical absorption studies reveal the suitability of the material for nonlinear optical applications.

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