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Photoconductivity and IR Studies of 3-Nitroacetanilide Single Crystal : A Potential Organic Non-linear Optical Material

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3-Nitroacetanilide was grown by slow evaporation technique using acetone as a solvent. In order to calculate the lattice parameter values, powder X-ray diffraction studies were carried out on the grown sample. Various functional groups of the 3-nitroacetanilide was identified by FTIR studies. Photoconductivity of the grown sample was studied.

Key Words: 3-Nitroacetanilide, Photoconductivity, Solution growth.

INTRODUCTION

Organic non-linear optical (NLO) materials were thoroughly studied in the last few decades due to their potentially high nonlinearities and rapid response in electro optic effect compared to inorganic NLO materials[1-4]. Recently a variety of organic NLO materials with non-localized *p*-electron systems with a large dipole moment have been synthesized with non-linear susceptibilities higher than the inorganic optical materials[3-5]. It is essential to identify and grow large size crystals of new organic NLO materials in order to realize its non-linear optical applications. In this paper, the studies on crystal growth and characterization of 3-nitroacetanilide (3NAA), a promising material for NLO applications is reported. 3-Nitroacetanilide ($C_8H_8N_2O_3$) crystallizes in monoclinic system with space group $P2_1$ and the lattice parameter values[6] are a = 9.767 Å, b =13.298 Å, c =13.272 Å, β = 102.991°.

EXPERIMENTAL

Crystal growth: The commercially purchased source material (E-Merck, India Ltd.) was purified twice by recrystallization process in acetone. Crystal growth experiments were conducted in two solvents such as acetone and methanol. On the basis of quality of the grown crystal, acetone was selected as a suitable solvent for the bulk growth of 3NAA

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single crystals. Hence a systematic investigation has been made to grow bulk single crystals of 3NAA using acetone as a solvent. Saturated solution of 3NAA was prepared in acetone and allowed for solvent evaporation. The saturated solution was filtered using A-grade Zero haze filter paper. The filtered, saturated solution was taken in an airtight container and preheated to 5 °C above the saturation and left for 1 h under stirring condition to ensure the homogeneity. The tightly covered saturated solution was kept in a constant temperature bath with an accuracy of ± 0.1 ºC. Nucleation was observed within the next 20 h. Then the crystal was allowed to grow further and harvested from the crystallizer after getting a reasonable size. Crystal has good optical transparency with pale yellow colour in nature.

RESULTS AND DISCUSSION

Powder X-ray diffraction study: Grown 3NAA crystal was finely crushed with the aid of mortar and the crushed powder was subjected to X-ray diffraction analysis. The sample was scanned by X-ray diffractometer with CuKα radiation (λ = 1.54178 Å) radiation over the range 10 to 60 º at a scan rate of 2 º/min. The recorded X-ray diffraction spectrum of 3NAA is shown in Fig. 1. Using the simulated hkl values and the experimental d values, the lattice parameters were calculated and compared with the literature[6]. Experimental d values and the corresponding (hkl) values are tabulated in Table-1. The calculated values are in well agreement with the literature and the calculated values are a = 9.7664 Å, b =13.2976 Å, c =13.272 Å, β = 102.9912°. This indicates that 3NAA crystal retains its own crystal system.

TABLE-1
XRD DATA FOR 3-NITROACETANILIDE (3NAA) SAMPLE

Peak No.	2θ	d-values (Å)	hkl values
1	12.126	7.292	(1 1-1)
2	16.727	5.295	(1 2-1)
3	18.365	4.827	(2 0-1)
4	20.949	4.237	(1 0-3)
5	21.410	4.146	(2 1-2)
6	25.112	3.542	(2 2 1)
7	27.232	3.272	(1 3 2)
8	35.632	2.517	(2 0-5)

FTIR spectral analysis: The FTIR spectrum was recorded for the grown sample using Jasco-460 plus FTIR spectrometer at room temperature in the range of 4000 to 400 cm^{-1}. The spectrum shows the symmetric and asymmetric stretching modes of free NH_2 group, which are observed

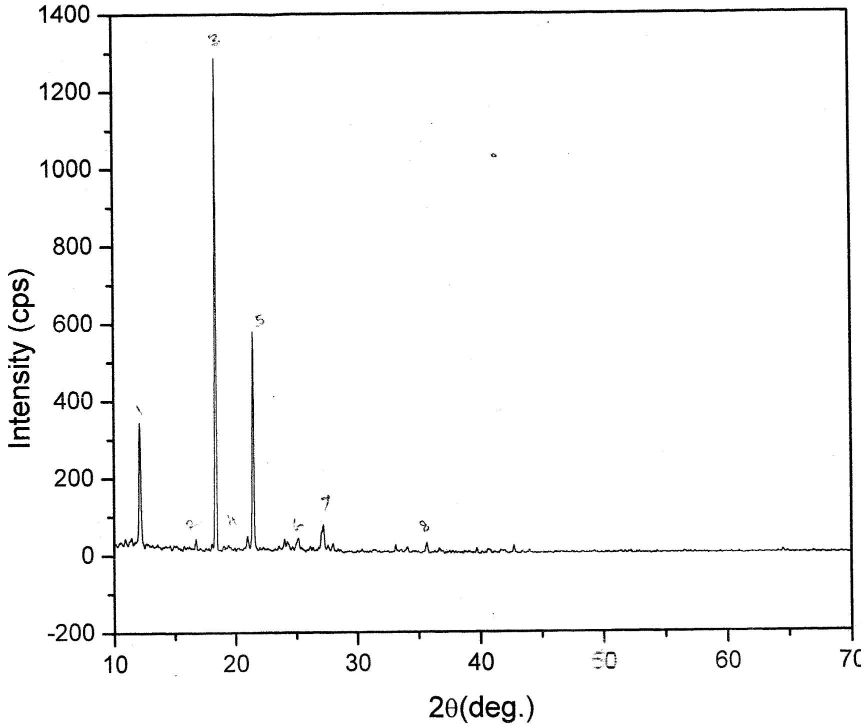

Fig. 1. X-ray powder diffraction spectrum of 3-nitroacetanilide crystal

at 3303 and 3263 cm^{-1}. Aromatic C-H stretching was observed at 3130 and 3097 cm^{-1}. In the anilide structure there is competition between the ring and the (C=O) for the non-bonded electron pair of the nitrogen. The (C=O) absorption of oxides occurs at longer wavelengths than normal carbonyl absorption due to the resonance effect. From the spectrum the absorption at 1673 cm^{-1} is due to (C=O) stretching vibration. The (N-H) out of plane bending vibration was observed at 1600 cm^{-1} and the in plane bending of (N-H) was observed at 1548 cm^{-1}. Aromatic skeletal vibration is observed at 1600 cm^{-1}. Two doublets were observed around 1545 and 1345 cm^{-1} due to asymmetric and symmetric stretching of (N=O). Peak at 1260 cm^{-1} is due to combination of δ(N-H) and ν(C-N) vibration. The peak between 805 and 741 cm^{-1} shows the *meta* position of the substituted molecule (NO_2) in the benzene ring of 3-nitroacetanilide. A well-resolved peak at 604 cm^{-1} represents the C-N-O stretching vibration. The characteristic FTIR absorption bands observed are consistent with the functional groups present in the compound.

Determination of melting point and density: Melting point of the grown crystal was measured using a melting point apparatus and found to be 151.8 °C. The density ρ was calculated as 1.425 g/cc from the crystallographic data using the formula ρ = MZ/NV, where M = molecular weight, Z = the number of molecules per unit cell, N = Avogadro's number and V = the volume of the unit cell. Experimentally sink or Swim method[7] was employed and the density value of 1.4245 g/cc was determined. The values determined by theoretical and experimental methods are in line.

Photoconductivity studies: Photoconductivity of the crystal was studied using Keithley 485 picoammeter. The experiment was performed at room temperature. Electrical contacts were made at a spacing of about 0.106 cm on the samples using silver paint. The DC input was increased from 20 to 400 volts in steps and the corresponding dark currents 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 (I_p) and dark current (I_d) with applied field are shown in Fig. 2. Both the photo and dark currents of 3-nitroacetanilide crystal increase linearly with applied field. It is observed from the plot that the dark current is less than photocurrent, thus suggesting that 3-nitroacetanilide exhibits positive photoconductivity. In general positive photoconductivity is attributed to generation of mobile charge carriers caused by the absorption of photons[8].

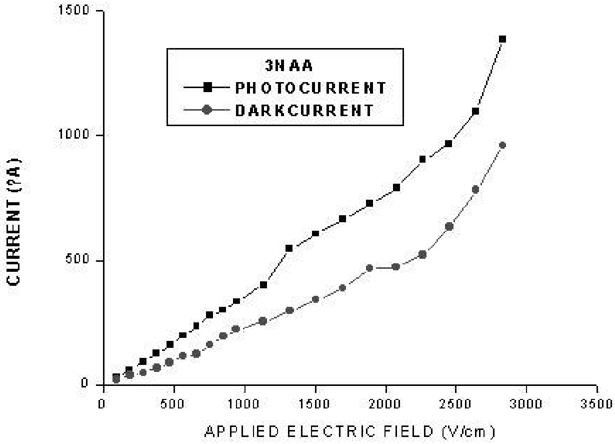

Fig. 2. Variation of dark and photo current with applied field for 3NAA

Conclusion

Optical quality 3-nitro acetanilide (3NAA) was grown by slow evaporation method using acetone as a solvent. The cell parameters of the grown crystal were calculated by powder X-ray diffraction analysis. Presence of various functional groups in the grown crystal was identified by FTIR. From the photoconductivity studies, it was observed from the plot that the dark current is less than photocurrent thus the material exhibits positive photoconductivity.

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