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Optical, Spectral and Thermal Investigations on N-3-Nitrophenyl Acetamide (3-NAA) Single Crystals.

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ABSTRACT

Good quality single crystals of N-3-nitrophenyl acetamide (3-NAA) is grown successfully using slow evaporation solution growth technique. Powder XRD studies were carried out for the grown crystals and it was observed that 3-NAA belongs to monoclinic system with $P2_1$ space group. Optical absorption spectrum of the crystals shows minimum absorption in 330 nm - 800 nm. First order hyperpolarizability of 3NAA is calculated as 4.024860812 $\times 10^{-30}$esu and found useful in molecular designing. NLO studies shows that grown crystal is 4 times greater efficient than KDP. A frontier molecular orbital analysis gives the HOMO-LUMO energy gap value as -0.10134 a.u. TGA and DTA studies were carried out for the grown crystals and it's found that it exhibit single stages of weight loss.

Keywords: optical, spectral, 3-NAA.

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INTRODUCTION

In recent years extensive research is being carried out on organic nonlinear optical NLO materials due to their high nonlinearity, fast response times, facile modification of molecular properties through precise synthetic methods, high optical damage thresholds and better laser damage resistance as compared to their inorganic counterparts. The microscopic origin of nonlinearity in these molecular NLO materials is due to the presence of delocalized p-electron systems connecting donor and acceptor groups which enhance the necessary asymmetric polarizability[1]. Materials with high nonlinear optical (NLO) activity are very useful as electro-optic switching elements and for optical information processing. The field of NLO organic molecules is dominated by donor acceptor substituted asymmetric linear molecules [2]. Organic NLO materials are formed by weak Van der Waals and hydrogen bonds with conjugated π electrons and are more advantageous than their inorganic counterparts due to high conversion efficiency for second harmonic generation and transparency in the visible region, high resistance to optical damage and so on. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. Traditionally, crystals of organic materials have been grown from the melt or from vapor or solution. Even though many organic compounds are reported for their second harmonic generation (SHG), the title compound N-3-nitrophenyl acetamide (3NAA) is found to be an interesting organic non-linear optical (NLO) material. Hence we made an attempt to report the growth and characterization of 3NAA.

Synthesis and Solubility of 3NAA

The 3NAA compound was synthesized by the direct combination of N-(3-nitrophenyl) acetamide and acetic anhydride in methanol at room temperature on the basis of the following stoichiometric equation.

$$C_6H_6N_2O_2 + C_4H_6O_3 \longrightarrow C_8H_8N_2O_3 + CH_3COOH$$

The synthesized compound was further purified by repeated recrystallisation using acetone as a solvent because the solubility of 3NAA is very high in acetone. Purified salt of 3NAA were collected and further used for bulk single crystal growth. The solubility of 3NAA was initially carried out using acetone and methanol as solvents. It was found that the solubility of 3NAA in acetone was high than methanol at ambient temperature (30º C). The solubility of 3NAA was measured for various temperatures in the range of 30°C to 50°C. According to the solubility curve, the saturated solution of 3NAA was prepared by dissolving the source material in the mixed solvent. On reaching saturation, the beaker containing the growth solution was optimally closed for controlled evaporation. Transparent single crystals were obtained from the growth solution after 10 days. The as grown crystal is shown in the Fig.1 of size measuring 18 x 3 x 3 mm^3.

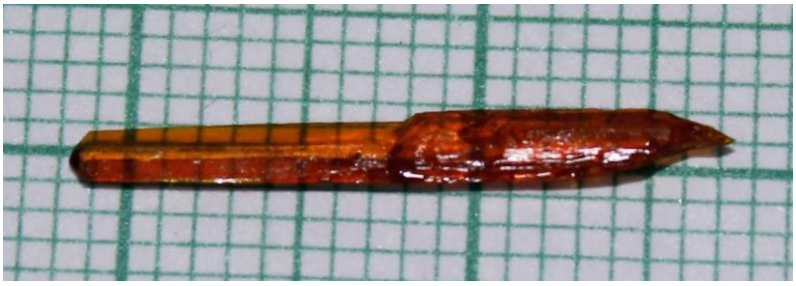

Figure 1: Photograph of as grown 3NAA single crystal

Powder X-ray diffraction studies

Finely crushed powder of 3NAA crystal was subjected to powder X-ray diffraction analysis using CuK_α (λ = 1.5418 Å) radiation. The sample was scanned over the range 10° to 45° at a scan rate of 2° /minute. The recorded X-ray diffraction pattern of 3NAA is shown in Fig .2.Using the simulated hkl values and the experimental 2θ - intensity values, the lattice parameters were estimated and the results indicated that 3NAA crystal retained its monoclinic structure with lattice parameters value a = 9.762 Å, b =13.287 Å, c =13.226 Å, and β = 102.99°.

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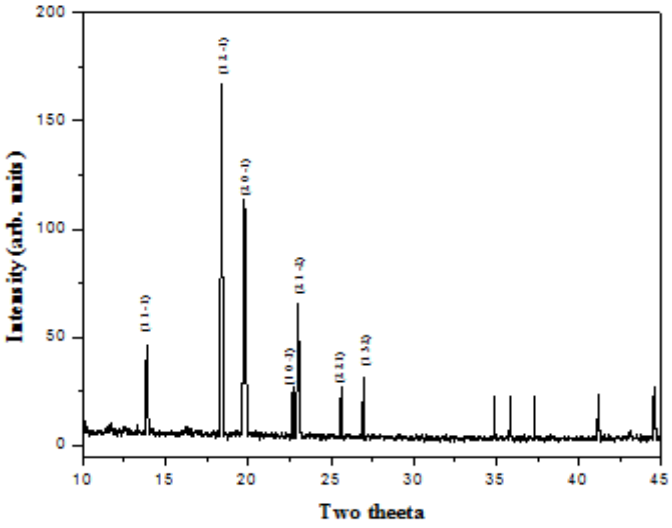

Figure 2: Powder XRD pattern of 3NAA crystal

Optical absorption spectrum

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 3NAA are pale yellowish orange color and transparent indicating the absence of absorption in the visible region. The UV-Vis spectral absorption was studied using a Varian Cary 5E UV-Vis-NIR spectrophotometer with a single crystal of 3mm thickness in the range of 200–1200nm. The recorded spectrum is shown in Fig. 3. The crystal has sufficient transmission in the entire visible and IR region. The lower cut off wavelength is around 240 nm.

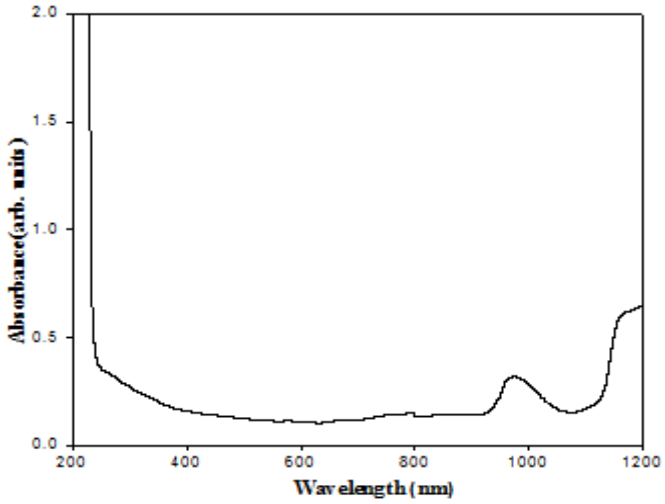

Figure 3: Optical absorption spectrum of 3NAA crystal

Thermal studies

Thermo Gravimetric (TG) and Differential Thermal Analysis (DTA) curves for 3NAA crystal were recorded in the temperature range of 30° to 800°C as shown in Fig.4. The studies were performed in nitrogen atmosphere at a heating rate of 20°C min^{-1}. The DTA curve shows a narrow endothermic peak at 113.7°C, which corresponds to the TG curve. The TG curve indicates the decomposition temperature at 113° - 203°C and after that the material becomes volatile. TG curve reveals that the material is stable up to 113°C and the decomposition takes place in one single stage. The decomposition is completed by 203°C with a total weight loss of 99.1 %.

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NLO studies

Kurtz and Perry powder technique remains an extremely valuable tool for initial screening of materials for second harmonic generation. The fundamental beam 1064nm from Q-switched Nd:YAG laser is used to test the second harmonic generation (SHG) property of the 3NAA crystal by using Kurtz powder technique. Pulse energy of 6.2 mJ/pulse and pulse width of 10 ns and repetition rate of 10 Hz is used. The fundamental beam was filtered by using IR filter. A photo multiplier tube (Philips Photonics) was used as detector. It is observed that the measured SHG efficiency of 3NAA crystal was 4 times that of KDP.

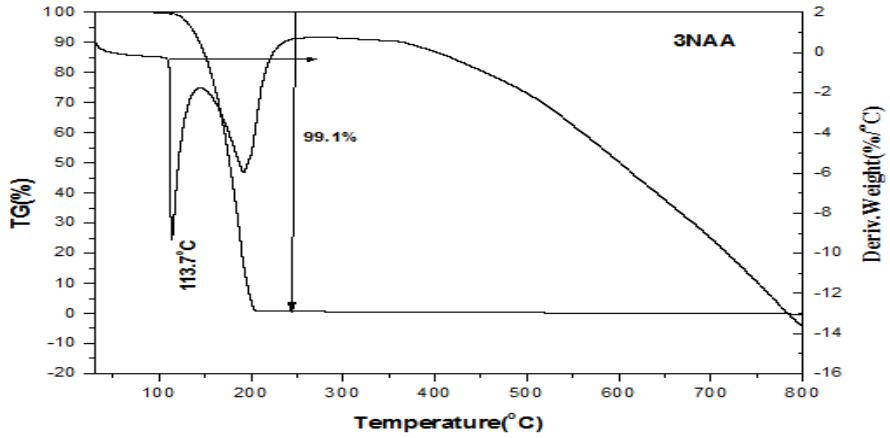

Figure 4: TGA and DTA curves of 3NAA crystal

HOMO-LOMO Analysis

The frontier molecular orbital play an important role in the electric and optical properties, as well as in UV–Vis spectra and chemical reactions [3]. Molecular orbital (HOMO and LUMO) and their properties such as energy are very useful for physicists and chemists and are very important parameters for quantum chemistry. Both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plays a significant role in chemical stability [4]. The HOMO–LUMO energy gap of 3NAA (Fig .5) was calculated at B3LYP/6-31G (d, p) level, which reveals that the energy gap reflects the NLO activity of the molecule. Charge transfer interaction through π conjugated bridge results in substantial ground state donor–acceptor (DA) mixing and the appearance of a charge transfer band in the electron absorption spectrum. The following molecular energy value for 3NAA is obtained as.

HOMO energy = -0.16717 a.u.
LUMO energy = -0.06583 a.u.
HOMO–LUMO energy gap = -0.10134 a.u.

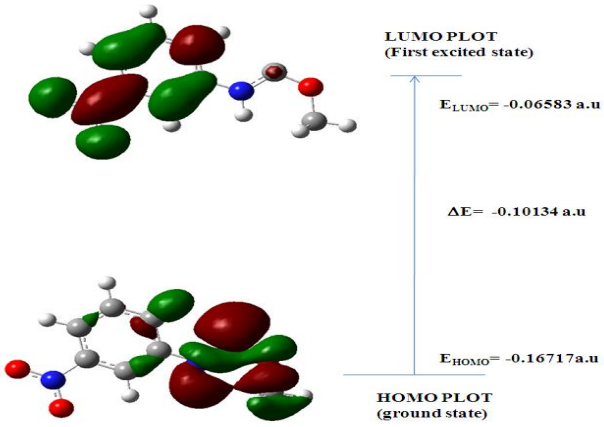

Figure 5: HOMO – LUMO plot of 3NAA molecule

Hyperpolarizability studies

The second-order polarizability or first hyperpolarizability and dipole moment was calculated by B3LYP using 6-31G (d, p) basis set on the basis of the finite-field approach. Theoretical calculations on molecular hyperpolarizability become one of the key factors in the second-order NLO materials design [5,6]. Theoretical determination of hyperpolarizability provides a guideline to experimentalists for the design and synthesis of organic NLO materials. Nonlinearity in organic chromophores can be synthetically modulated by varying the composition or length of conjugated p-systems, and by evaluating the effects of various electron-donor and electron-acceptor groups. They determine not only the strength of molecular interactions (long-range interaction, dispersion force, etc.) and the cross sections of different scattering and collision process but also the NLO properties of the system [7,8] . 3NAA is an excellent NLO material which is understood from the values of hyperpolarizability listed in Table 1

Table 1: Hyperpolarizability of 3NAA in esu

β_{xxx}	-275.705
β_{xxy}	-109.758
β_{xyy}	-187.947
β_{yyy}	-9.47754
β_{xxz}	-0.0259567
β_{xyz}	-0.00107375
β_{yyz}	-0.0120082
β_{xzz}	6.55646
β_{yzz}	-30.2164
β_{zzz}	0.0216665
β_{tot}	$4.024860812 \times 10^{-30}$ esu

CONCLUSION

Single crystal of N-(3-Nitrophenyl) Acetamide (3NAA) was grown successfully by slow evaporation technique using the mixed solvent of acetone and methanol (1:1). Powder X-ray diffraction studies confirmed that 3NAA crystals are monoclinic in structure with $P2_1$ space group. Existence of strong hydrogen bond in the donor accepter coupling was understood from bond lengths. A frontier molecular orbital analysis gives the HOMO-LUMO energy gap value as -0.10134 a.u. The UV-Vis spectrum reveals minimum absorption in the entire visible region. Thermal studies indicated that 3NAA is thermally stable up to 280°C. The SHG efficiency of the 3NAA is four times than that of KDP. With high thermal stability low dielectric loss and high SHG efficiency, 3NAA could be a potential material for photonics device fabrication when compared with other nonlinear optical organic materials.

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