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Growth and characterization of organic nonlinear optical material: 5-Nitroindole (5NI) for optical applications

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ABSTRACT

Single crystals of organic nonlinear optical material 5-Nitroindole (5NI) has been grown by slow cooling solution growth technique using methanol as a solvent. The grown crystal was subjected to single crystal X-ray diffraction technique to determine the lattice parameters. Fourier transform infrared spectrum (FTIR) was recorded to identify the presence of functional groups. The optical properties such as the optical band gap, extinction coefficient (k), refractive index (n) and optical conductivity (σ) were calculated. The optical band gap of 5NI is 2.33 eV. The melting point and thermal stability of the crystal was analyzed from TG/DTA studies. Dielectric studies were carried out at different temperatures and frequencies.

1. Introduction

Organic materials with high second order optical nonlinearities has been given much attention over the past decades because of their potential applications, including optical information processing, optical sensing, electro-optic modulation, frequency conversion, optical parametric oscillations, and telecommunications [1–3]. The main merits of organic materials are flexibility in the methods of synthesis, scope for altering the properties of functional substitution, inherently high non-linearity, high damage resistance etc. [4,5]. In these organic crystals, two requirements are satisfied: (i) they are made of highly polarizable molecules, the so-called conjugated molecules, where highly delocalized π-electrons can easily move between electron donor and electron acceptor groups on opposite sides of the molecule, inducing a molecular charge transfer, (ii) the molecules are adequately packed to build up a non centrosymmetrical crystal structure that provides non vanishing second-order nonlinear coefficients [6]. Nonetheless, the uptake and commercialization of organic nonlinear optical materials (NLO) has been slow, mainly due to competition from existing inorganic materials as well as issues with the long-term stability of organic components when exposed to high intensity light. Consequently, there is still a significant quantity of research needed before the widespread deployment of device-quality low power levels. Hence a great deal of research effort has been focused on organic materials, among which the 5-Nitroindole (5NI) is especially attractive because they posses good optical properties, thermal stability and dielectric properties. 5-Nitroindole is a fused ring heterocyclic compound which is having good second harmonic generation efficiency of 20.5 times larger than that of urea determined by using the powder technique of Kurtz and Perry and is found in reference [7,8]. A material is generally said to be functional/smart if it holds a physical property that is utilizable in applications [9]. To the best of our knowledge, the bulk growth, optical, thermal and dielectric properties of the material were not reported so far which is more important for the material to be utilized in practical applications such as optical window, electro-optic modulator and in optical switches.

This paper reports on growth and characterization of 5NI single crystal. The grown crystals were subjected to various characterizations like single crystal XRD, optical studies, thermal analysis and dielectric properties.

2. Experimental

2.1. Synthesis and growth

The commercially available 5-Nitroindole ($C_8H_6N_2O_2$) was purified by repeated recrystallization process using methanol as a solvent. The solubility of 5-Nitroindole was estimated from 30 to 45 °C in steps of 5 °C. The recrystallized salt of 5-Nitroindole was used as the starting material to prepare the solution. The solution of 5-Nitroindole was prepared at 35 °C, the solution was optimally covered with perforated sheet and placed in a constant temperature bath (accuracy of ±0.01 °C) for two days and the temperature was reduced at a lowering rate of 0.1 °C/day. Good quality single

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Fig. 1. Grown crystals of 5NI.

crystal of size 30 mm × 7 mm × 2 mm were obtained from the mother solution after 15 days. The grown crystal is shown in Fig. 1.

3. Characterization studies

Single crystal X-ray diffraction analysis of 5NI was carried out using Enraf-Nonius CAD-4 diffractometer using MoKα radiation (λ = 0.71073 Å) to determine the unit cell parameters and space group. Optical studies have been carried out using ELICO SL 218 double beam UV–vis spectrophotometer which records optical absorption spectrum in the range of 200–1100 nm. Thermo gravimetric analysis and differential thermal analysis for 5NI have been recorded using a SDT Q600 V8 instrument. The analysis was carried out in an atmosphere of nitrogen at a heating rate of 10 °C/min for the temperature range 30–600 °C. Dielectric measurement was carried out using HIOKI 3532-50 LCR HI TESTER in the frequency range of 50 Hz to 5 MHz at various temperatures ranging from 308 to 403 K. The detailed discussions on the obtained results are presented in the following sections.

4. Results and discussion

4.1. Single crystal X-ray diffraction

From the X-ray diffraction studies, it is found that the grown crystal belongs to orthorhombic system with space group Fdd2 symmetry. The obtained lattice parameters are $a = 24.53$ Å, $b = 27.85$ Å, $c = 4.35$ Å, and $V = 2970$ Å which are in good agreement with the literature report [6].

4.2. Optical properties

To determine the transparency range of the 5NI single crystal, UV–vis absorption spectrum was recorded and is shown in Fig. 2. Optically clear single crystal of thickness 2 mm was used for this study. The cut-off wavelength of the crystal occurs at 478 nm. From the figure, it shows that the crystal was optically transparent in the wavelength range from 479 to 1100 nm, a feature that

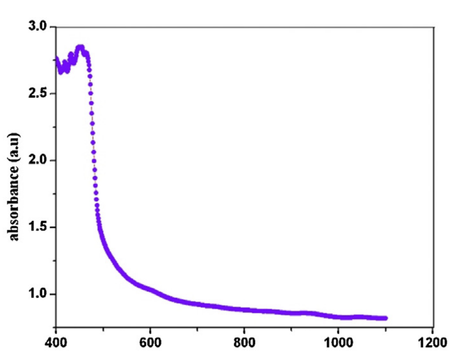

Fig. 2. UV absorbance spectrum.

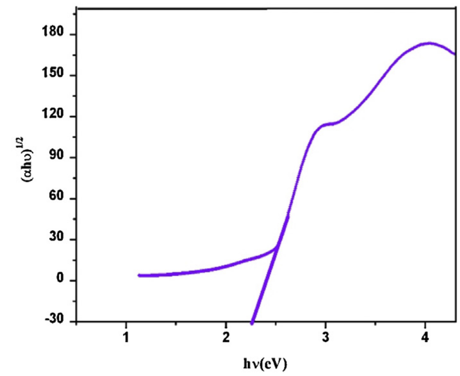

Fig. 3. Plot of $(\alpha h\upsilon)^{1/2}$ vs. photon energy ($h\upsilon$).

promotes possible optical applications in devices operating at the near infrared wavelength range, (i.e.) ultrafast modulators and switches [10]. The crystal has sufficient transmission in the visible and IR region.

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons. The absorption coefficient (α) was calculated using the following relation:

$$\alpha = \frac{2.303 \ \log(1/T)}{t} \tag{1}$$

where T is the transmittance and t is the thickness of the crystal.

The relation between the optical band gap, absorption coefficient and energy ($h\upsilon$) of the incident photon is given by

$$\alpha h\nu = B(h\nu - E_g)^r \tag{2}$$

where E_g the optical energy gap, B is a constant and r is an index which can be assumed to have values of 1/2, 3/2, 2, and 3 depending on the nature of the electronic transition responsible for the absorption. $r = 1/2$ for allowed direct transition, $r = 3/2$ for forbidden direct transition, with $r = 2$ refers to indirect allowed transitions and $r = 3$ refers to indirect forbidden transition. The band gap was calculated from the Tauc's plot between $h\upsilon$ and $(\alpha h\upsilon)^{½}$. It is shown in Fig. 3. The optical band gap value of 5NI is 2.33 eV. The extinction coefficient is a measure of the fraction of light lost due to scattering and absorption per unit distance of the penetration medium. It can be estimated from the values of α and λ using the relation:

$$K = \frac{\lambda\alpha}{4\pi} \tag{3}$$

The extinction coefficient as a function of photon energy is shown in Fig. 4. The extinction coefficient decreases with photon energy shows that light lost during the scattering and absorbance decreases. It is one of the important parameter to determine the light intensity and refractive index. If the light intensity increases,

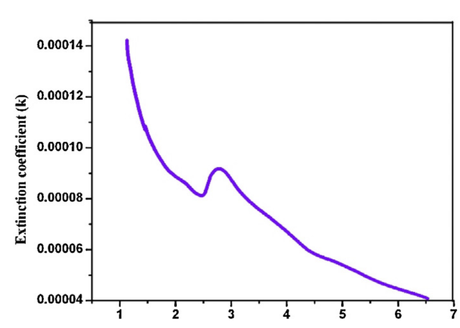

Fig. 4. Plot of photon energy vs. extinction coefficient (k).