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Growth, spectral, optical, thermal, surface analysis and third order nonlinear optical properties of an organic single crystal: 1-(2-Methyl-6-nitro-4-phenyl-3-quinolyl) ethanone

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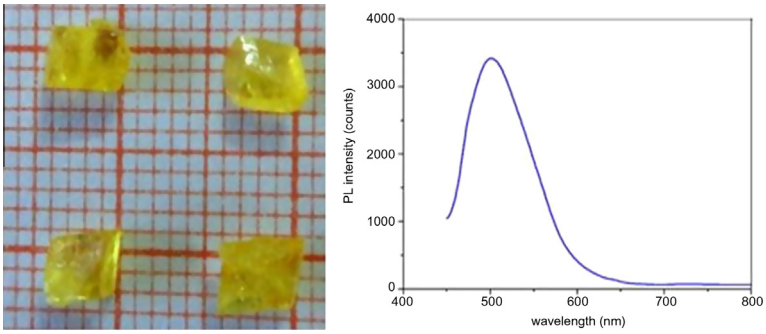
HIGHLIGHTS

- 2M6NQE have grown by slow evaporation solution growth technique.
- The absorption edge of the crystal has found to be 371 nm.
- The melting point of the material is 170 °C, and it has stable up to 263 °C.
- PL spectral shows green emission in the crystal.
- Etching and Z-scan study was discussed in this manuscript.

GRAPHICAL ABSTRACT



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ABSTRACT

Single crystal of 1-(2-Methyl-6-nitro-4-phenyl-3-quinolyl) ethanone was grown using slow evaporation solution growth technique. Single crystal X-ray diffraction study reveals the lattice parameters of the grown crystal. The modes of vibration of different molecular groups present in 2M6NQE were identified by FTIR spectral analysis. Its optical behavior was examined through UV–vis–NIR absorption and PL emission spectrum. They signify that the crystal has transparency in the region between 383 and 1100 nm. The PL spectrum of the title compound shows green emission in the crystal. From the thermal analysis, 2M6NQE has found to be thermally stable up to 263 °C, and the melting point of the material is 170 °C. The estimations of third order non-linear optical properties like non-linear absorption coefficient (β), non-linear refractive index (n_2) and susceptibility [$\chi^{(3)}$] were calculated using Z-scan technique. It has observed that, crystal exhibits reverse saturation absorption and self-defocusing performance. Etching study was carried out for the grown crystal using different solvents.

Introduction

In recent years, the interest in organic complexes was widely applied due to a great extent to the possibility of tailoring their nonlinear response by manipulation of their chemical structure, and state of aggregation [1]. The search for new materials with high optical nonlinearities were the important task, because of their practical applications in optical switching, optical bistability and optical limiting, phase modulation and other signal processing [2–5]. Nonlinear absorption materials were attracted extensive attentions in the different applications of science and technology [6–9]. Nevertheless, the ideal material for a third order nonlinear

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applications must meet several specifications as a high optical nonlinearity, a broadband response, a high threshold for laser induced damage and a low intensity threshold to activate the nonlinear process. Quinoline is a powerful pharmacodynamic material, and it has reported possessing a wide variety of important biological properties such as antimicrobial, antimalarial, anti HIV and anticancer activities [10–13]. The title compound, 1-(2-Methyl-6-nitro-4-phenyl-3-quinolyl) ethanone (2M6NQE) is one of the most significant derivative, exhibits third order nonlinear optical (NLO) property which can be used in optical switching and optical limiting devices [14,15]. Single crystals of 2M6NQE were grown using the solution growth technique. The grown crystal was then subjected to single crystal XRD, UV–vis–NIR, FTIR spectral analysis, thermal analysis and etching studies respectively. The third-order optical nonlinearity of the quinoline derivative was determined using a standard Z-scan technique. This technique, known for its simplicity and sensitivity, relies on the distortions induced in the spatial and temporal profile of the input beam on passing through the sample. It has widely used in material characterization because it provides not only the magnitudes but also the sign of real and imaginary parts of third-order nonlinear susceptibility [$\chi^{(3)}$].

Experimental procedure

Synthesis and growth of 2M6NQE

The material was synthesized by following the method of Loh et al. [16]. A mixture of 5-nitro-2-amino-benzophenone (0.01 M) acetyl acetone (0.01 M) and 0.15 ml of concentrated HCl has irradiated under microwave for about 8 min at 240 W. The resultant solid was filtered, dried and purified by column chromatography using 1:1 mixture of ethyl acetate and petroleum ether.

The purified material was then dissolved in the solvent chloroform and stirred continuously for 3 h using a magnetic stirrer. The beaker containing the saturated solution was optimally covered with perforated sheet for controlled evaporation of the solvent. Slow evaporation of the chloroform induces the spontaneous nucleation in the solution, and tiny single crystals were obtained. The transparent yellow single crystals of size 4 mm × 3 mm × 3 mm were harvested. The as grown 2M6NQE crystals were shown in Fig. 1.

Results and discussion

Single crystal XRD

Single crystal X-ray diffraction analysis of 2M6NQE material was carried out using Enraf Nonius CAD-4 X-ray diffractometer. The lattice parameters are a = 13.189 Å, b = 7.735 Å, c = 16.953 Å and β = 129.076. It has observed that 2M6NQE single crystal belongs to the monoclinic system and space group $P2_1/c$. The space group suggests that the crystal belongs to centrosymmetric group and the absence of second order nonlinearity in the material. The result of single crystal XRD study was found to be in good agreement with the reported values [16].

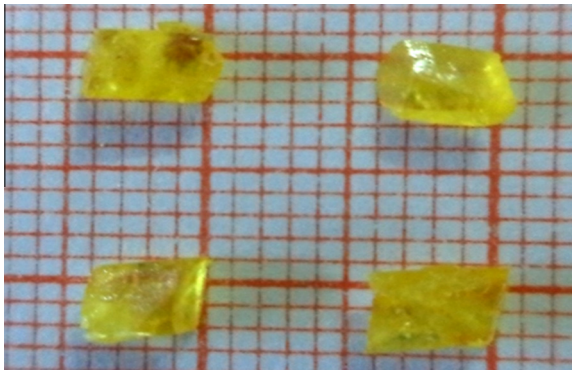

Fig. 1. As grown crystal of 2M6NQE.

FTIR spectral analysis

The FTIR analysis of the grown crystal was recorded in the range 400–4000 cm^{-1}. It was carried out using FT-IR 4100 type-A spectrophotometer employing KBr pellet technique at room temperature. The recorded FTIR spectrum is shown in Fig. 2. The presence of C—H stretching vibration is assigned to the peaks at 852.54 cm^{-1} and 867.97 cm^{-1}. The vibration of the C—N group was confirmed by the peak observed at 1201.65 cm^{-1}. The sharp peaks observed at 1029.99 cm^{-1}, and 1049.28 cm^{-1} is due to C—C bond present in the compound. The presence of a methyl group (CH_3) was confirmed by the peak observed at 1373.32 cm^{-1} and 2995.45 cm^{-1}. The C═O stretching band observed at 1707 cm^{-1} indicates the presence of carboxylic acid group. The peak observed at 1529.55 cm^{-1} is assigned to the presence of NO_2 group present in the compound. The presence of pyridine was confirmed by the peak observed at 3034.03 cm^{-1}.

Optical absorption studies

The optical absorption spectrum of the grown crystal was recorded using ELICO SL 218 double beam UV–vis spectrophotometer in the wavelength range of 190–1100 nm. A sample of 2.5 mm thickness was used for measurement without polishing the crystal surface. The recorded UV–visible spectrum at room temperature is shown in Fig. 3. The absorption edge of the grown crystal was found to be 382 nm. The crystal shows its complete transparency in the visible region. Optical band gap value was calculated from the Tauc's plot between the absorption coefficient $(\alpha h\nu)^{1/2}$ and photon energy ($h\nu$). The band gap graph of 2M6NQE is shown in Fig. 4. The optical band gap value of 2M6NQE is 2.99 eV.

TG/DTA studies

The thermal stability of the grown crystal was measured using thermo gravimetric (TG) analysis and Differential thermal analysis (DTA) simultaneously from room temperature to 1000 °C. It was carried out in a nitrogen atmosphere using SDT Q600 V8 apparatus at a heating rate of 10 °C/min. The recorded TG spectrum was shown in Fig. 5. TG curve precisely shows there is no weight loss up to 263.50 °C. The thermo gram spectrum reveals that the significant weight loss starts at 263.50 °C, and it continues up to 303.99 °C. The second stage of weight loss starts at 355.93 °C, and it continues up to 379.90 °C. The weight losses are due to the acetyl function present in the molecule. In DTA spectrum, (Fig. 6) the endothermic peak observed around 170.56 °C corresponds to the melting temperature of the material. From the results of thermal analysis, it has established that no transformation and weight loss observed before 263.50 °C. Hence the material can be exploited for any suitable applications up to 263.50 °C.

Photoluminescence

The photoluminescence spectrum was recorded using a Jobin Yvon-Spex spectrofluorometer (Fluorolog version 3: Model FL3-11). The sample compartment module equipped with a Xenon lamp operates at 450 W. The sample was excited at 370 nm. The emission spectrum was recorded between 400 and 800 nm. The Photomultiplier (PM) tube was used for detecting the output sig-