Optics & Laser Technology 71 (2015) 108–113

Contents lists available at ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Growth and characterization of a new organic nonlinear optical crystal: 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one

P.S. Patil [a,*], P. Ajay Kumar [b], S. Venugopal Rao [b], G. Bhagavannarayana [c]

[a] Department of Physics, K. L. E. Institute of Technology, Opposite Airport, Gokul, Hubli 580030, India
[b] Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Hyderabad 500046, India
[c] Crystal Growth & X-ray Analysis, CSIR-National Physical Laboratory, New Delhi 110012, India

ARTICLE INFO

Article history:
Received 24 January 2015
Accepted 5 March 2015

Keywords:
Organic compounds
Nonlinear optical material
Two-photon absorption

ABSTRACT

Organic nonlinear optical single crystal of 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one (Ci3NC) with dimensions $25 \times 15 \times 10$ mm^3 was successfully grown for the first time by the slow evaporation solution growth technique (SEST). The structural perfection of the grown crystals has been analyzed by high-resolution X-ray diffraction (HRXRD) rocking curve measurements, and it was found that the crystalline perfection is reasonably good having very low angle (tilt angle $\leq 1'$) internal structural grain boundary. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were used to study its thermal properties. Powder test with Nd:YAG laser radiation shows second harmonic generation which is about 7 times that of urea. The optical transmittance window and the lower cutoff wavelength of the Ci3NC have been identified by UV–vis–NIR studies. Third-order nonlinear optical (NLO) response of Ci3NC has been examined using Z-scan technique with femtosecond (fs), MHz pulses at wavelengths of 870 nm and 900 nm. Various NLO coefficients such as two-photon absorption (2PA) coefficient (β), three photon absorption (3PA) coefficient (γ), and nonlinear refractive index (η_2) were evaluated.

1. Introduction

The current optoelectronics industry is highly motivated to discover new nonlinear optical (NLO) materials since they are vital for advanced display technologies, telecommunications and the laser industry [1]. Specifically, NLO materials are key sources of red, green and blue light for RGB displays and laser application, on account of their ability to act as wavelength converter. Different types of molecular and bulk materials have been examined for nonlinear optical properties [2]. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power as compared with inorganic materials [2,3]. Organic molecules with significant nonlinear optical activity generally consist of a π-electron conjugated structure. The conjugated π-electron moiety provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Fictionalization of both ends of the π-bond systems with appropriate electron donor and acceptor group can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical nonlinearity [4–7].

In view of the importance of organic nonlinear materials and also as a part of our ongoing work [8–10], the investigation of growth and characterization of 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one (Ci3NC) is undertaken. We have already reported synthesis and single crystal structure of Ci3NC [11]. Ci3NC ($C_{17}H_{13}NO_3$, Mr=279.28) crystallizes in the orthorhombic space group $P2_12_12_1$ with lattice parameters $a=7.0167$ (1) Å, $b=12.1953$ (2) Å, $c=16.1081$ (3) Å and there are four molecules per unit cell [11]. As a part of extensive characterization, we present in this article, the investigation of the crystal growth, transmission cutoff, the SHG efficiency, nonlinear absorption and refraction, thermal expansion and HRXRD of this material.

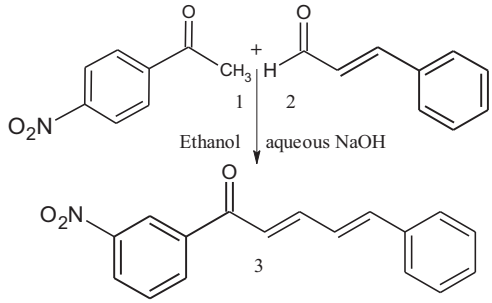
2. Experimental procedure

2.1. Material synthesis

The general synthetic strategy employed to prepare 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one was based on Claisen–Schmidt condensation, which has been previously reported [11]. The chemical structure of Ci3NC and the schematic representation of the reaction is given in Scheme 1.

* Corresponding author. Fax: +91 836 2330688.
E-mail address: pspatilcrystal@gmail.com (P.S. Patil).

http://dx.doi.org/10.1016/j.optlastec.2015.03.002
0030-3992/



Scheme 1. Chemical structure (3) and synthesis scheme of 1-(3-Nitrophenyl)-5-phenylpenta-2,4-dien-1-one.

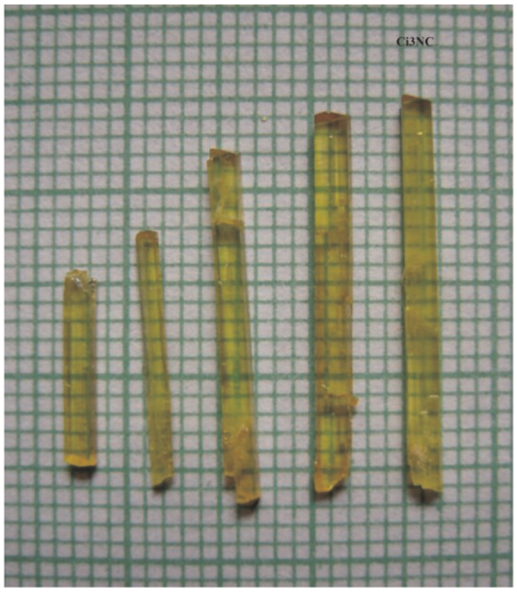


Fig. 1. Photograph of as grown Ci3NC crystals.

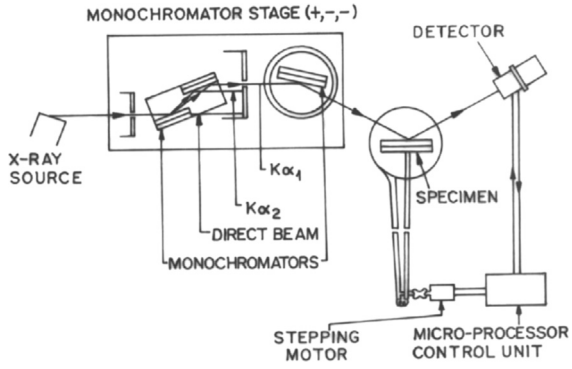


Fig. 2. Schematic line diagram of the multi-crystal X-ray diffractometer.

2.2. Crystal growth

Large sized good quality single crystals are essential to evaluate their physical properties reliably. Selection of suitable solvent and optimization of growth conditions are crucial for this purpose. It was found that Ci3NC was insoluble in water, moderately soluble in acetone and highly soluble in dimethylformamide (DMF). The solution of the growth material was prepared in DMF. After filtration by using Whatman filter paper, the solution was transferred into a crystal growth vessel. Next, it was kept for crystallization by slow evaporation at room temperature (30 °C). At the period of super saturation, tiny crystals were nucleated. They were allowed to grow to maximum possible dimensions and then harvested. Transparent thick needles like crystals appeared in the growth vessels within 15 days of solution evaporation. Fig. 1 shows the photograph of as grown crystals. The crystals obtained are nonhygroscopic, stable at room temperature and exhibit a needle like shape. The needle-like structure of the crystal is considered to play an active role in the second harmonic process [12].

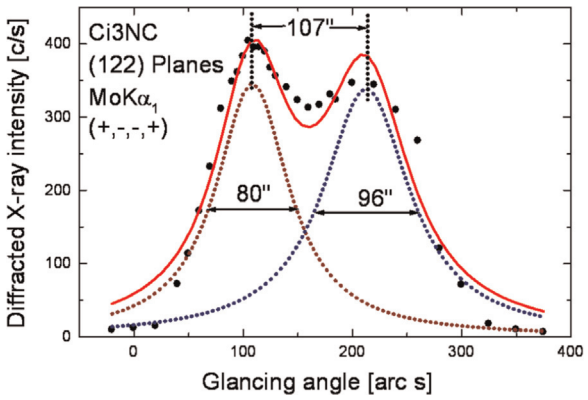


Fig. 3. Diffraction curve recorded for Ci3NC single crystal for (122) diffracting planes by employing the multi-crystal X-ray diffractometer with MoKα_1 radiation.

2.3. Characterization

To reveal the crystalline perfection of the grown crystals, a multi-crystal X-ray diffractometer (MCD) developed at NPL [13] has been used to record high-resolution diffraction curves (DCs). Fig. 2 shows the schematic diagram of the multi-crystal X-ray diffractometer. In this system a fine focus (0.4×8 mm^2; 2 kW Mo) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was employed. The well-collimated and monochromatic MoKα_1 beam obtained from the three monochromator (111) Si crystals set in dispersive $(+,-,-)$ configuration has been used as the exploring X-ray beam. This arrangement improves the spectral purity ($\Delta\lambda/\lambda \ll 10^{-5}$) of the MoK$\alpha_1$ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be $\ll 3''$. The specimen crystal is aligned in the $(+,-,-,+)$ configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve of the specimen crystal is insignificant. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of $0.5''$. The diffracted intensity is measured by using an in-house developed scintillation counter. To provide two-theta ($2\theta_B$) angular rotation to the detector (scintillation counter) corresponding to the Bragg diffraction angle (θ_B), it is coupled to the radial arm of the goniometer of the specimen stage. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B starting from a suitable arbitrary glancing angle. The detector was kept at the same angular position $2\theta_B$ with wide opening for its slit, the so-called ω scan.

For the optical transmission study, the UV–vis NIR spectra were recorded in the range of 300–1100 nm using Shimadzu UV-1061 UV–vis spectrophotometer. The spectra were recorded for DMF solution of Ci3NC in a quartz cell of 10 mm length. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the Ci3NC crystals were carried out using the Shimadzu DT-40 simultaneous DTA/TGA analyzer with a heating rate of 10 °C/min.