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Synthesis, crystal growth, structure and characterization of a novel third order nonlinear optical organic single crystal: 2-Amino 4,6-Dimethyl Pyrimidine 4-nitrophenol

P. Karuppasamy[a,*], T. Kamalesh[a], K. Anitha[b], S. Abdul Kalam[c], Muthu Senthil Pandian[a], P. Ramasamy[a], Sunil Verma[d,e], S. Venugopal Rao[c]

[a] SSN Research Centre, SSN College of Engineering, Chennai, 603110, Tamil Nadu, India
[b] Department of Physics, Madurai Kamaraj University, Madurai, 625021, Tamil Nadu, India
[c] Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Gachibowli, Hyderabad, 500046, Telangana, India
[d] Laser Materials Section, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, 452013, Madhya Pradesh, India
[e] Homi Bhabha National Institute, Anushakti Nagar, Mumbai, 400094, Maharashtra, India

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ABSTRACT

Good quality single crystals of 2-amino-4,6-dimethylpyrimidine 4-nitrophenol (AMP4N) were successfully grown by slow evaporation solution technique (SEST) at room temperature using methanol as solvent. The grown crystal was subjected to single crystal XRD (SXRD) and its structure was solved by the direct method using SHELXS program and refined using SHELXL program. The Hirshfeld surfaces analysis was carried out to define theoretically electron density boundary surfaces between the molecules in a grown crystal, which are useful to analyze and view the intermolecular interactions. The powder XRD (PXRD) was carried out to identify the crystalline planes and its strain was also calculated by the Williamson–Hall equation. ^{13}C and ^{1}H NMR were recorded to interpret the environment of the molecular structure of the AMP4N crystal. Functional groups of AMP4N crystal were confirmed by Fourier transform infrared (FTIR) spectral analysis. The optical quality of the grown crystal was analyzed by UV–Vis NIR spectral analysis. The grown crystal has good optical transparency in the range 410–1100 nm. The thermal behaviour of the crystal has been investigated by thermogravimetric and differential thermal analysis (TG-DTA). Chemical etching study was carried out and the etch pit density (EPD) was calculated. The laser damage threshold (LDT) was measured under single-shot mode using an Nd: YAG laser at 532 nm. The third-order nonlinear optical properties such as refractive index (n_2), absorption coefficient (β) and susceptibility ($\chi^{(3)}$) were studied using the Z-scan technique at 532 nm with a continuous wave (CW) solid-state laser.

1. Introduction

In the last couple of decades there has been considerable research attention towards the synthesis of novel nonlinear optical (NLO) materials with superior properties because of their wide applications in the area of photonics, optoelectronics, optical information processing, THz wave generation, laser remote sensing, optical switching, pharmaceutical, color displays and frequency conversion, etc. [1,2]. The continuous research on organic NLO materials prompted researchers to explore many new NLO complexes engineered by the coupling of different organic molecules. When one uses chromophores with highly delocalized π electron systems, they lead to good macroscopic NLO response and high molecular hyperpolarizability. The pyrimidine and aminopyrimidine derivatives are biologically important compounds and they manifest themselves in nature as components of nucleic acids. The functions of nucleic acids are explicitly determined by hydrogen bonding patterns including base pairing which is responsible for genetic information transfer [3]. 4-nitrophenol is a phenolic organic compound of one-dimensional donor-π-acceptor (D-π-A) system which contains both electron accepting (NO_2) and electron-donating (OH) groups linked via aromatic benzene ring. The presence of OH groups favours the formation of new salts with various organic and inorganic bases [4]. 4-nitrophenol derivatives are promising NLO materials as they possess the linear D-π-A conjugated chains which give strong π-electron delocalization effect and these are prone to the formation of strong hydrogen bond interactions [5]. These interactions are known to play an

* Corresponding author. Tel.: +91 9791552297.
E-mail address: karuppasamyp75@gmail.com (P. Karuppasamy).

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important role in composing structures of co-crystals, structure of molecular crystals, biological systems, molecular recognition and crystal engineering research [6]. Hydrogen bonding is recognized as the most powerful force to organize molecules in the solid state and its employment is now emerging as an important design strategy [7]. In this case, the 2-amino-4,6-dimethylpyrimidine molecule is hydrogen bonded to the 4-nitrophenol molecule to form the novel co-crystalline material due to the strong interaction between pyrimidine and phenol. The main advantage of co-crystals is their ability to generate a variety of solid forms of a drug that have distinct physicochemical properties from the solid co-crystal components. These properties include but are not limited to, solubility, dissolution, bioavailability, hygroscopic nature, hydrate/solvate formation, crystal morphology, fusion properties, chemical and thermal stabilities, and mechanical properties [8]. Recently, π-conjugated organic systems have been extensively attracting candidates for synthesizing new efficient second and third order materials due to their quick NLO response. It must possess the enhanced figure of merit, large laser damage threshold (LDT) and low dielectric constant at higher frequencies [9].

In the present work, we have attempted to the synthesise new compound and grow optically transparent crystals of 2-amino-4,6-dimethylpyrimidine 4-nitrophenol (AMP4N) by slow evaporation solution technique (SEST). The grown crystals were characterized by single crystal X-ray diffraction (XRD), powder XRD, Nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), UV-Visible-NIR, thermogravimetric (TG) and differential thermal analysis (DTA), Vickers microhardness, chemical etching, Laser damage threshold (LDT) and third order nonlinear optical (NLO) studies (Z-scan).

2. Experiment

2.1. Material synthesis, crystal growth and morphology

Analytical reagent (AR) grade 2-amino-4,6-dimethylpyrimidine (AMP) and 4-nitrophenol (4NP) were taken in the stoichiometric ratio 1:1 for the synthesis of 2-amino-4,6-dimethylpyrimidine 4-nitrophenol co-crystalline compound. Initially, the calculated amount of AMP and 4NP were dissolved in methanol solvent. The solutions were mixed together using mechanical stirring for about 5 h. After that, it appeared as a light yellow colour solution. The prepared saturated solution was filtered twice into the crystallization dish by using Whatman filter paper and it was allowed to controlled evaporation at room temperature. After few weeks, the transparent yellow colour crystals were harvested. Then the purity of the synthesized material was further improved by successive recrystallization process to eliminate impurities. The optically transparent AMP4N single crystals have been grown over a period of 20 days. The reaction mechanism of the synthesized AMP4N crystal is depicted in Fig. 1. The photograph of as-grown AMP4N crystals is shown in Fig. 2. The morphology of the grown AMP4N crystal was indexed by a WinXMorph software program. The indexed morphology of AMP4N is shown in Fig. 3.

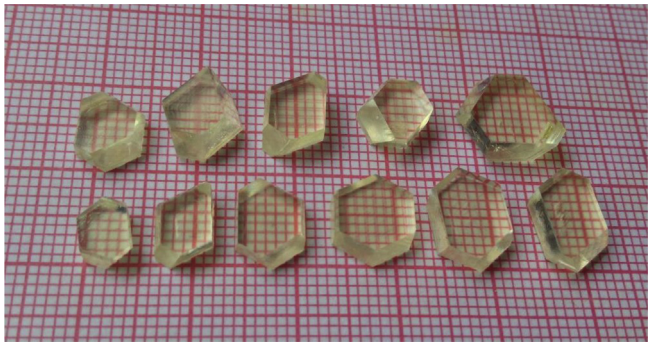

Fig. 2. As grown AMP4N single crystal.

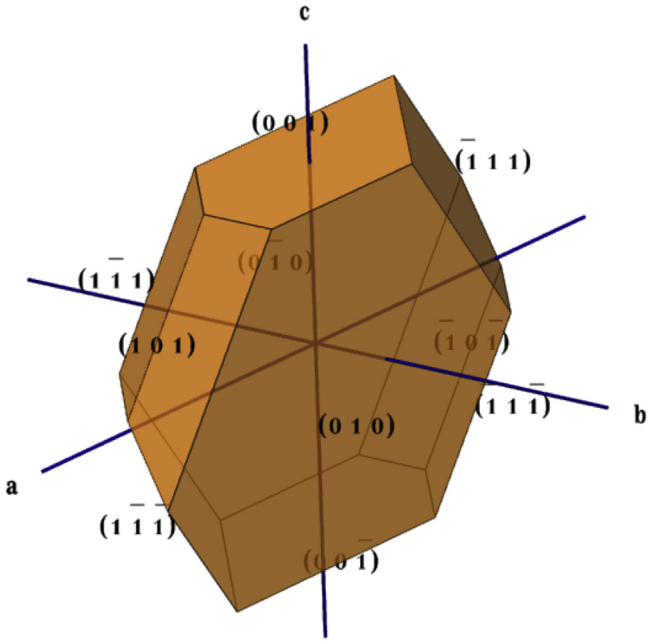

Fig. 3. Morphology of AMP4N single crystal.

2.2. Solubility

The solubility measurement is essential for the growth of bulk size single crystal. The solubility of the AMP4N crystal was determined for different temperatures ranging from 35 °C to 60 °C. This process has been carried out in a constant temperature bath (CTB) with the accuracy of ± 0.01 °C. Initially, the CTB was maintained at 35 °C. The solubility was determined by dissolving the recrystallized salts in 100 ml of methanol solvent in an airtight conical flask. The solution was continuously stirred by the help of immersible motorized magnetic stirrer.

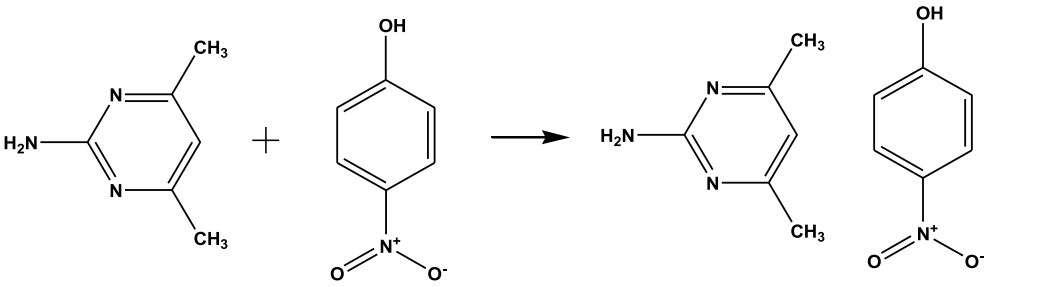

Fig. 1. Reaction scheme of AMP4N.