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Ethylenediaminium di(2-nitrophenolate) single crystals as materials for optical second harmonic generation

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ABSTRACT

An organic second harmonic generation (SHG) active material, ethylenediaminium di(2-nitrophenolate) (EDA2NP) was synthesized through proton transfer reaction. Good quality single crystals of dimension $6 \times 4 \times 2$ mm^3 were grown by solvent evaporation method using ethanol as a solvent for the first time in literature. The lattice parameters of the grown crystals were determined by X-ray diffraction studies. Fourier Transform Infra Red (FT-IR) spectrum was recorded to identify the presence of various functional groups and the molecular structure was confirmed by nuclear magnetic resonance (NMR) spectrum. Thermal analyses of the grown crystal were carried out using thermo gravimetric–differential thermal analysis (TG–DTA) and differential scanning calorimetry (DSC) curves. Optical (UV–vis–NIR) analysis shows that the grown crystals were found to be transparent (450–2500 nm) in the entire visible region. The existence of second harmonic generation signals was observed by using Nd:YAG laser with fundamental wavelength of 1064 nm.

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1. Introduction

Identification of efficient molecular assemblies with suitable optical nonlinearities represents an active field of research at the interface of modern physics, chemistry and materials science [1]. Engineering of new nonlinear optical (NLO) materials capable of second-harmonic generation with enhanced figures of merit has developed as a major force to realize the theoretical phenomena into realistic devices. The challenges confronted by materials scientists is in designing these types of functional materials by intellectual construction of molecular assemblies (acentric and chiral solids) exhibiting second order nonlinear optical effects. In this aspect, organic NLO materials are drawing more attention due to their high nonlinear coefficient and rapid response to electro-optic effect [2,3].

The design of organic polar crystals for quadratic nonlinear optical applications is of greater importance as these molecules containing π electron systems asymmetrized by electron donor and acceptor groups are highly polarizable entities [4]. Especially, the extension of benzene derivatives has permitted an increase in the number of π electrons as well as their delocalization length, so as to lead to prodigious enhancement in first order hyperpolarizability [5]. In particular, nitrophenol derivatives are interesting candidates, as they are a typical one-dimensional (1D) donor–acceptor π system, and the presence of phenolic OH favours in formation of salts with various organic and inorganic bases. The conjugated base, thus formed has increased molecular hyperpolarizability because of the better electron donating property of phenolate O^- (Hammett coefficient $\sigma = -0.81$) [6] than that of phenolic OH (Hammett coefficient $\sigma = -0.38$) [7]. Recently, a series of phenol–ammonium salts including ethylenediaminium nitrophenolate were successfully synthesized by Liu et al., [8]. Although plenty of research works on 4-nitrophenolates and their derivatives [9,10] has been extensively carried out, 2-nitrophenol based compounds are lesser in focus. Among the phenolates, ethylenediaminium di(2-nitrophenolate) is an newly identified noncentrosymmetric system, whose crystal structure was successfully solved by Liu et al., [8]. On this basis, in the present investigation, the systematic studies of synthesis, bulk growth, spectral, thermal, optical and second harmonic generation properties of SHG active ethylenediaminium di(2-nitrophenolate) [EDA2NP] is reported in detail.

2. Experiment

2.1. Synthesis and crystal growth

Synthesis of EDA2NP is a typical proton transfer reaction where a proton is transferred from the electron donor group of 2-nitro

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phenol to the electron acceptor group of Ethylenediamine as depicted in the reaction scheme (Fig. 1) hinted by Liu et al., [8]. All the materials were of analytical grade and were used as purchased. Ethylenediamine (2.90 mmol) was dissolved in methanol (5 mL) and added to a solution of 2-nitrophenol (7.19 mmol) dissolved in methanol (50 mL). The stoichiometric amount of the reactants was stirred well for three hours and a yellow solid was precipitated with a yield of 94%. The product was filtered, washed and dried at 40 °C for 12 h.

The solubility of EDA2NP in ethanol was assessed as a function of temperature in the temperature range 25–50 °C. Fig. 2 shows the solubility curve of EDA2NP. The title compound exhibits good solubility and a positive solubility temperature gradient (direct solubility) in ethanol solvent. Hence, single crystals of EDA2NP were grown by solvent evaporation by using ethanol as solvent. The purity was improved by repeated recrystallization process since high-quality crystals are very much essential for evaluating the nonlinear optical properties of molecular materials. Good quality crystals (Fig. 2) with dimension $6\times4\times2\ mm^3$ were obtained after a period of 15 days.

2.2. Characterization

The structure of the grown crystal was confirmed by single crystal X-ray diffraction using a ENRAF NONIUS CAD4 diffractometer, with Mo$K\alpha$ radiation ($\lambda=0.7107$ Å). The powder sample was subjected to powder XRD analysis using a Rigaku diffractometer with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). The computer program AUTOX was used to index all the observed reflection in the XRD pattern and to calculate the corresponding lattice parameters. The elemental analysis of the grown sample was carried out using CHN elemental analyses to confirm the chemical composition of synthesized compound. Molecular structure of the sample was studied by ^1H and ^{13}C NMR spectra recorded using a Joel GSX 400 MHz FT-NMR spectrometer. Various functional groups in the compound were identified using a JASCO FTIR spectrometer in the range 400–4000 cm^{-1}. Thermal analysis on the sample was performed by Thermo gravimetric (TG), differential thermal (DTA) and differential scanning calorimetry (DSC) using a Seiko thermal analyzer in nitrogen atmosphere at a heating rate of 20 °C min^{-1} in the temperature range 30–1000 °C. The UV–vis–NIR transmittance on a 2 mm thick crystal was measured using a Lambda 35 spectrometer in the wavelength range of 200–2500 nm with the resolution of 1 nm at 30 °C. A preliminary study on the powder SHG measurements were performed by using a modified Kurtz technique using a Q-switched Nd:YAG laser (1064 nm, 5 ns, 10 Hz).

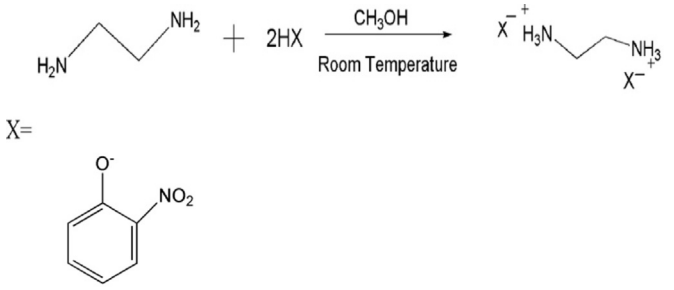

Fig. 1. Reaction Scheme of EDA2NP.

3. Results and discussion

3.1. Crystal structural analysis

The single crystal X-ray diffraction analysis reveals that the grown crystal crystallizes in orthorhombic system with space group Pccn having four molecules in the unit cell. The determined lattice parameters are $a=26.038$ Å [26.047 Å], $b=6.8164$ Å [6.8351 Å], $c=8.4841$ Å [8.4637 Å], $\beta=90.01$ [90]° with volume 1505.2 $Å^3$ [1506.8 $Å^3$]. The values given in the square brackets are the corresponding values already reported by Liu et al., [8]. The recorded PXRD pattern of the compound is depicted in Fig. 3. All the observed Bragg's diffraction peaks were indexed for the

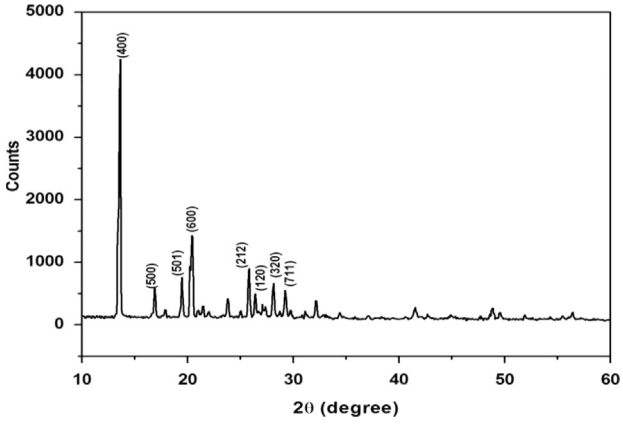

Fig. 3. Powder XRD Pattern of EDA2NP.

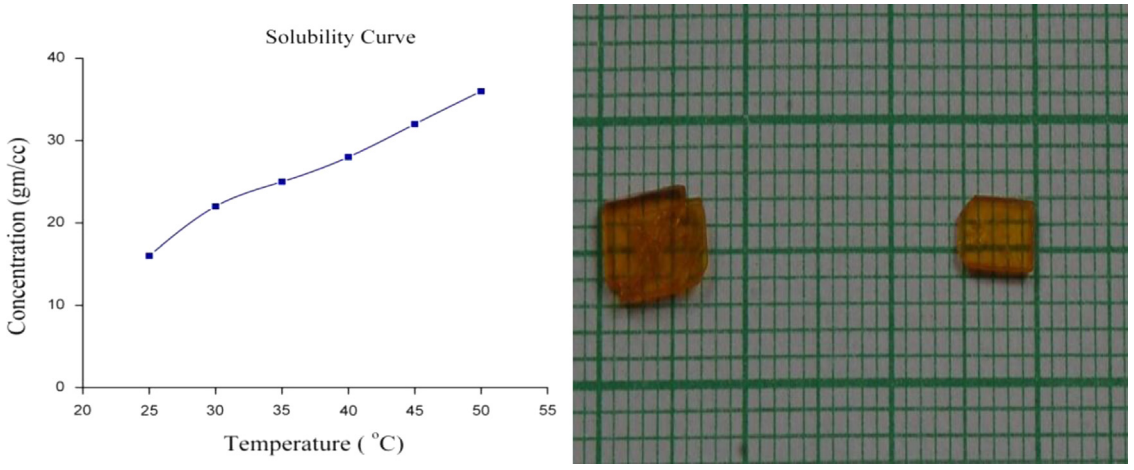

Fig. 2. Solubility curve and the grown single crystals of EDA2NP.

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