



Growth and characterization of an efficient nonlinear optical single crystal: Urea *p*-nitrophenol



A. Rathika¹, R. Ganapathi Raman*

Department of Physics, Noorul Islam Centre for Higher Education, Kumaracoil, Thuckalay, Kanyakumari 629 175, India

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ABSTRACT

An organic nonlinear optical single crystal of urea *p*-nitrophenol has been synthesized and grown by slow evaporation solution growth technique. The grown crystals were characterized by single crystal and powder X-ray diffraction analysis and it was found to be the structure of the crystal belongs to triclinic system. The various functional groups were identified by FT-IR and Raman spectral analysis. Thermal stability of the grown crystal was studied by TGA/DTA. The optical properties of the grown crystals were analyzed by UV–vis. The mechanical properties of the grown crystal were studied by Vickers microhardness measurements. Nonlinear optical property of the crystal was confirmed using the Kurtz and Perry powder technique and a study of its SHG efficiency in comparison with KDP has made.

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1. Introduction

During the decade of crystal research, second order nonlinear optical properties has attracted the attention of many researchers to search for a variety of new types of nonlinear optical (NLO) materials because of the potential application in various engineering technological fields [1–3]. In the search for NLO crystals, conjugated structure compounds with electron donor and acceptor substituents are extensively studied. Due to their delocalised electrons, they generally have a high second harmonic generation (SHG) efficiency. Single crystals are the backbone of the modern technological revolution. The impact of single crystals is clearly visible in industries like semiconductors, optics etc. Most of the high performance optoelectronic devices are made from crystalline materials [4]. Organic compounds are often formed by weak van der Waals and hydrogen bonds and hence possess high degree of delocalization. Urea, a promising organic crystal exhibits large nonlinear optical coefficients, high degree of birefringence and relatively high laser damage threshold [5–8]. Urea has some undesirable mechanical and chemical properties, i.e., mechanically soft and hygroscopic nature. As a result of hygroscopic nature, urea cannot be exposed to

normal atmosphere, and for practical applications it is being used by immersing it in an index-matching fluid with compatible chemical and optical characteristics. Amongst them, the nonlinearity of urea is comparable with that of another important commercial NLO material potassium dihydrogen phosphate (KDP) [9,10]. In the title compound, $C_6H_5NO_3 \cdot CH_4N_2O$, *p*-nitrophenol molecules are linked to urea molecules by $O-H \cdots O$ and $N-H \cdots O$ hydrogen bonds forming network structure [11]. Urea crystals attract the attention of both theoretical and experimental scientists due to their nonlinear optical piezoelectric properties. Urea is highly soluble in water and the corresponding solution has some important features: Urea is representative of one class of materials, which are applicable to photonics and reference material in the diffusive mixing of organic solutions (DMOS) experiment in micro cavity carried out by NASA [12]. They are potentially useful materials for frequency doubling of near IR laser radiation single crystal of the material which have high laser damage threshold [13]. During the past decade researchers have shown much interest in *p*-nitrophenol family of crystals due to their high laser damage threshold, transparency window, extended thermal stability and high NLO coefficient [14–18]. *p*-Nitrophenol totally matches this criterion with its electron donor substituents “–OH” and electron acceptor substituents “–NO₂” and phenyl group form a conjugated molecular configuration. *p*-Nitrophenol derivatives are interesting candidates as they are a typical one-dimensional (1D) donor-acceptor π system, and the presence of phenolic OH favors the formation of salts with various organic and

* Corresponding author. Tel.: +91 9976715576.

E-mail address: ganapathiraman83@gmail.com (R. Ganapathi Raman).

¹ Tel.: +91 9626840787. rathidhanu@gmail.com.

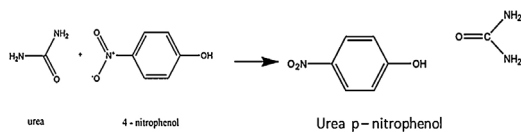


Fig. 1. Reaction scheme of UPN crystal.

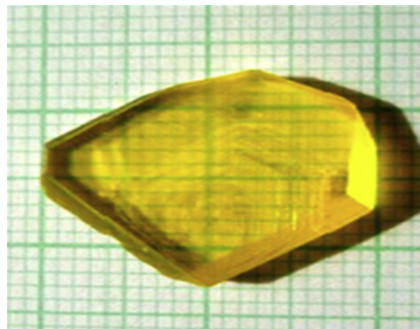


Fig. 2. Grown UPN crystal.

inorganic bases. In this paper, we report the growth and characterization studies of urea *p*-nitrophenol (UPN) single crystal.

2. Experimental

2.1. Synthesis and crystal growth

In the present investigation, Analar reagent (AR) grade of urea ($\text{CH}_4\text{N}_2\text{O}$) and *p*-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$) were taken in the optimized ratio 1:1 as per the reaction. The reaction scheme of the title compound is depicted in Fig. 1. The mixture was stirred well to avoid co-precipitation of multiple phases and which yields the UPN. The solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation solution growth technique at room temperature. Supersaturated solution was prepared in the known amount of methanol and kept at room temperature for controlled evaporation. After the growth period of 25 days, yellow coloured single crystals were harvested with the dimension of $22 \times 25 \times 5 \text{ mm}^3$. The photographs of grown crystals are shown in Fig. 2.

2.2. Characterization studies

The grown UPN single crystals have been subjected to various characterization studies. The Bruker Kappa APEXII single crystal X-ray diffractometer, used to estimate the cell parameters and the powder X-ray diffraction pattern was checked by XPERT-PRO X-ray diffractometer of UPN crystal. The FTIR spectrum of UPN was recorded using a 8400S Shimadzu infrared spectrophotometer using KBr pellet technique in the region $4500\text{--}500 \text{ cm}^{-1}$. The FT-Raman spectrum was recorded using a BRUKER: RFS 27: standalone FT-Raman spectrometer in the region $4000\text{--}0 \text{ cm}^{-1}$. The TGA/DTA studies showed the thermal properties of grown crystal carried using TA instruments, model: Q600 SDT and Q20 DSC thermal analyzer. The UV-vis transmission spectrum of UPN crystal was studied in the range $400\text{--}900 \text{ nm}$ by PerkinElmer Lambda 35 UV-vis spectrometer. >Microhardness measurement was carried out using Leitz–Wetzlar Vickers' microhardness tester fitted with a diamond pyramidal indenter attached to an optical microscope. Nonlinear optical property of the crystal was confirmed using the Kurtz and Perry powder technique and a study of its SHG efficiency in comparison with KDP has made.

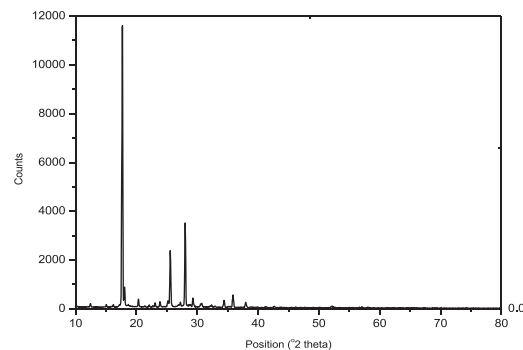


Fig. 3. Powder XRD profile of UPN crystal.

3. Results and discussion

The single crystal X-ray diffraction study was carried out to confirm the cell parameter values of UPN crystal. The estimated cell parameters are $a = 3.7619 \text{ \AA}$, $b = 10.2300 \text{ \AA}$, $c = 11.8100 \text{ \AA}$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$ and volume $V = 442 \text{ \AA}^3$ it belongs to triclinic system with the space group of P1. The unit cell parameters are in good agreement with the reported values [11]. The crystalline nature of the grown crystal was checked by taking the X-ray diffraction pattern of powder samples with $\text{Cu K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The sample was scanned 2θ in the range of $10\text{--}80^\circ$ at the rate of $2^\circ/\text{min}$. The indexed powder XRD pattern is shown in Fig. 3. The appearance of sharp and strong peaks confirmed the good crystallinity nature of the grown sample.

Fig. 4a and b shows the FTIR and Raman spectrum of UPN crystal and the vibrational band assignments are summarized in Table 1. Normally stretching, bending and wagging deformation of NH band appears around $3500\text{--}3000$, $1700\text{--}1600$, $1150\text{--}900 \text{ cm}^{-1}$ respectively in vibrational spectrum [19]. Aromatic compounds commonly exhibit multiple weak bands in the region $3100\text{--}3000 \text{ cm}^{-1}$ due to aromatic C–H stretching vibration. There are six equivalent C=C bonds in benzene and consequently there

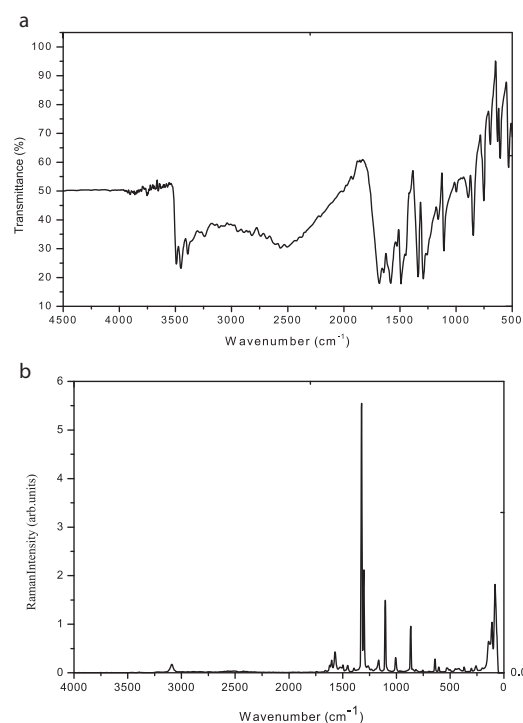


Fig. 4. (a) FTIR spectrum of UPN crystal. (b) FT-Raman spectrum of UPN crystal.

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