Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 333–339

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis, growth, structural, thermal and optical studies of pyrrolidinium-2-carboxylate-4-nitrophenol single crystals

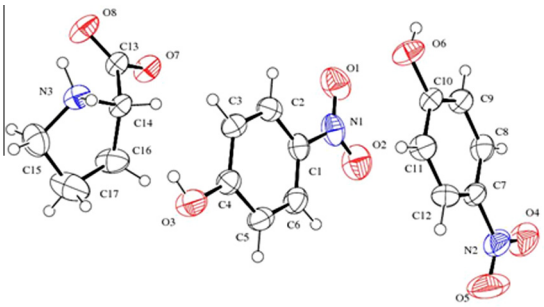
N. Swarna Sowmya [a], S. Sampathkrishnan [a], Y. Vidyalakshmi [b], S. Sudhahar [c], R. Mohan Kumar [c,*]

[a] Department of Applied Physics, Sri Venkateswara College of Engineering, Chennai 602117, India
[b] Department of Physics, Anna University, Chennai 600025, India
[c] Department of Physics, Presidency College, Chennai 600005, India

HIGHLIGHTS

- Organic PCN crystal was grown by slow evaporation method.
- PCN belongs to orthorhombic crystal system with space group $P2_12_12_1$.
- PCN crystal is stable upto 184.68 °C.
- Band gap energy (E_g) of PCN crystal was found to be 3.41 eV.
- SHG efficiency of PCN is 2.33 times that of KDP crystal.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 April 2014
Received in revised form 22 July 2014
Accepted 1 March 2015
Available online 9 March 2015

Keywords:
Crystal structure
Spectral analysis
Thermal analysis
Photoluminescence
NLO material

ABSTRACT

Organic nonlinear optical material, pyrrolidinium-2-carboxylate-4-nitrophenol (PCN) was synthesized and single crystals were grown by slow evaporation solution growth method. Single crystal X-ray diffraction analysis confirmed the structure and lattice parameters of PCN crystals. Infrared, Raman and NMR spectral analyses were used to elucidate the functional groups present in the compound. The thermal behavior of synthesized compound was studied by thermogravimetric and differential scanning calorimetry (TG-DSC) analyses. The photoluminescence property was studied by exciting the crystal at 360 nm. The relative second harmonic generation (SHG) efficiency of grown crystal was estimated by using Nd:YAG laser with fundamental wavelength of 1064 nm.

Introduction

In recent years, organic materials with aromatic rings having high nonlinear optical coefficient, high laser damage threshold, fast response with tailor-made flexibility, low mobility and large band gap find wide applications [1–4]. Organic nonlinear optical (NLO) materials have attracted great attention as they provide the key functions of optical frequency doubling, optical modulation, optical switching and optical memory for emerging technologies in the areas such as optical communication, signal processing and optical information storage devices [5]. In general, the presence of π-electron delocalization in the molecular structure is found to enhance NLO property of the material. Effective materials contain donor and acceptor groups and large π-delocalization have been recognized as a factor leading to larger nonlinearities [6]. Recently, researchers [7–11] have shown much interest in the nitro phenol family crystals due to their intensive applications in the field of optoelectronics. The p-nitrophenol is found to be a best proton acceptor for the metallic hydroxide complexes ($NO_2{\cdot}C_6H_4{\cdot}OX$, X = Na, K, Li, etc.).

* Corresponding author. Tel.: +91 9444600670; fax: +91 44 28510732.
E-mail address: mohan66@hotmail.com (R. Mohan Kumar).

http://dx.doi.org/10.1016/j.saa.2015.03.004
1386-1425/

The p-nitrophenol derivative crystal, sodium 4-nitrophenolate (S4NP) is a class of semi organic NLO material having high value of hyperpolarizability. The nitrophenoxy ion is ionically bonded to sodium ion coupled with intra-molecular hydrogen bonding. Minemoto et al. (1992) and Brahadeeswaran et al. (1998) have studied the crystal growth, topography and chemical etching properties of S4NP [12]. The growth and characterization of Lithium p-nitrophenolate was reported by Milton et al. (2003) [13]. The synthesize, growth and characterization of S4NP NLO single crystal using ethanol solvent have also been reported [14]. Pyrrolidinium-2-carboxylate-4-nitrophenol (PCN), a member of p-nitrophenol family has been reported to have crystallized in orthorhombic system with space group of $P2_12_12_1$ [15]. In this report, we present the synthesis, structural, spectroscopic and optical studies of PCN to understand its efficiency towards optical device fabrications.

Experimental

Synthesis

Pyrrolidinium-2-carboxylate-4-nitrophenol (PCN) was synthesised based on the reaction between the pyrrolidine, carboxylic acid and p-nitrophenol taken in equimolar ratio. The calculated amounts of pyrrolidine and carboxylic acid were dissolved in Millipore water to prepare the pyrrolidinium carboxylate solution. Then p-nitrophenol was added slowly to the pyrrolidinium carboxylate solution with continuous stirring. The solution was stirred for about 12 h to complete the reaction process. The experiment was carried out at room temperature. The purity of synthesized salt was further improved by successive recrystallization processes using water solvent. The synthesis scheme of PCN is depicted in Fig. 1. The recrystallized salt with high purity was collected for crystal growth processes and further characterization.

Solubility

The solubility is one of the important factors which decide the growth rate and growth method for bulk size crystals. The solubility was determined for different temperatures (30–55 °C) with an interval of 5 °C. The solubility for 35 °C was determined by dissolving PCN salt in 100 ml of water taken in an air tight container and kept in a temperature bath at an accuracy of ±0.01 °C with continuous stirring using a magnetic stirrer. The saturation point was confirmed by the formation of undissolved salt at the bottom beaker. Then, 5 ml of the saturated solution was pipetted out and poured in a petridish. It was dried by keeping it in the hot air oven. After the evaporation of the solvent, the petridish was weighted. The difference in the weight was taken into account. The same procedure was repeated to estimate the solubility for different temperatures. The measured solubility data is depicted in Fig. 2. From the graph, it was observed that the solubility of PCN increases with increase in temperature. Since the solubility curve is neither flat nor steep, it is possible to adopt both slow evaporation and slow cooling methods for the growth of PCN.

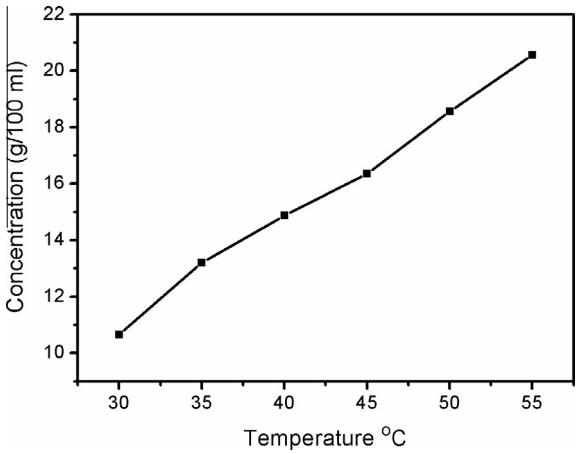


Fig. 2. Solubility curve of PCN in water solvent.

Crystal growth

The purified PCN salt dissolved in the water solvent was kept at 35 °C and the solution was stirred continuously for 8 h using a magnetic stirrer. The homogeneous PCN growth solution was achieved and it was filtered using high quality Whatman filter papers (125 mm) to remove impurities. The growth solution was tightly sealed in a growth container and it was kept in a constant temperature bath which was maintained at 35 °C with an accuracy of ±0.01 °C. The solution was allowed for slow evaporation. The supersaturated solution yielded good quality PCN crystals with size up to about $21 \times 5 \times 3\ mm^3$ in a period of 3–4 weeks. The as-grown PCN single crystals are shown in Fig. 3.

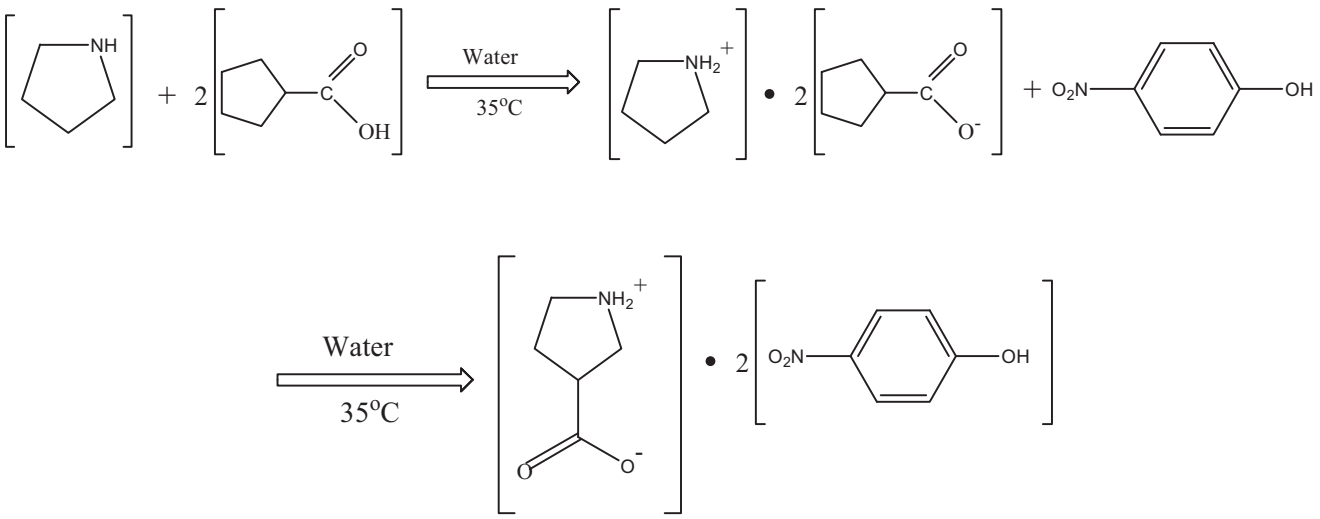


Fig. 1. Synthesis scheme for PCN compound.