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Structural, optical, thermal, photoconductivity, laser damage threshold and fluorescence analysis of an organic material: β-P-amino benzoic acid single crystal

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ABSTRACT

β-P-amino benzoic acid, an organic single crystal was grown by slow evaporation technique. Single crystal X-ray diffraction studies show that the grown crystal has β-polymorph of P-amino benzoic acid [β-PABA] form and the lattice parameters are $a = 6.30$ Å, $b = 8.61$ Å, $c = 12.43$ Å $\alpha = \gamma = 90°$ and $\beta = 100.20°$. FTIR analysis confirms that bands at 1588 cm^{-1}, 1415 cm^{-1} are assigned to ring skeletal vibrations of title compound. The molecular structure of the grown crystal has been identified by Nuclear Magnetic Resonance spectral study. The optical absorbance spectrum from 200 to 1100 nm shows that there is an edge absorbance in UV region. Optical band gap of the crystal has been assessed from the absorbance spectrum. The thermal properties of crystals were evaluated from TG-DTA analysis, it exhibits that there is no weight loss up to 187 °C. Laser damage threshold indicates that the grown crystal has no surface damage up to 35 mJ. Photoconductivity and fluorescence spectral experiments are also carried out and the results are discussed.

1. Introduction

Crystals occupy a major part in the areas of advanced applied science, detectors, optical, lasers, sensors, electrical devices and components [1–4]. Recently, researchers have been showing their keen interest in synthesis and growth of novel substances because of their optoelectronic and photonic applications [2–4]. P-amino benzoic acid (PABA) is a biological molecule and it has UV absorption and photosensitive nature [5–7]. PABA is a member of vitamin Bx and it acts as a bacterial cofactor involved in the synthesis of folic acid [6,7]. It is used in pharmaceuticals. Apart from this, PABA uses include perfumes, dyes, sunscreen agents and feedstock additives. In medicine, it is used as a protective drug against UV-irradiation. This property of P-aminobenzoic acid has the capacity of inducing endogenous interferon, which open new possibilities for its application in medicine [7,8]. P-amino benzoic acid ($C_7H_7NO_2$) is the simplest aromatic carboxylic acid. The derivatives of PABA are one of the interesting materials due to its polymorphic structure. Polymorphs are solid phases which have the same chemical composition but differ in crystal structure. Many materials have different structures without any change in chemical composition but they have different properties such as different crystal shapes, melting points, densities, stabilities, solubility and bioavailability [6]. PABA exhibits two kinds of polymorphs: (i) α-PABA, which looks like a needle (ii) β-PABA, which looks like a prism. Formations of these polymorphic shapes depend on the solvent used [6,9]. Gracin and Rasmuson reported that with many organic solvents α-PABA forms only needles but with water forms needles and prisms [9]. Initially, the crystal structure of the β-polymorph of PABA was determined by Alleaume et al. (1966). However, the precision structure of the β-polymorph of PABA was redetermined by Gracin and Fischer (2005). The β-PABA has hydrogen bonded three dimensional network [7]. The Hydrogen bonding plays an important role in molecular recognition and crystal engineering research [3,4]. Investigations on organic single crystals have been considerably increased due to their technological importance in the field of optical memories, scintillators, semiconductors, thermoelectrics, colour displays, optical memories, molecular electronics and so on [10–12]. The derivative of aminobenzoic acid has several applications such as the design of innovative pharmaceuticals, semiconductors, the study of bioactive nanoparticles and the development of novel electronic devices [13]. The molecular structure of PABA consists of an aromatic ring and it contains amino (NH_2) donor group and the carboxyl acid (COO^-) acceptor group. Electron donor–acceptor or charge transfer complexes are significant in physical properties like non linear optical effects and electrical conductivity. These physical properties are potently depending on degree and nature

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of the charge transfer interaction [14,15]. Aromatic acids (aminobenzoic acid, aromatic amino acids, phenolic acids, etc.) possess strong absorption bands in the UV range and can be subjected to photochemical transformation [16]. Fluorescence analysis is an important technique to investigate the molecular interaction, dynamics of biomolecules, electronic structure of materials and energy gap states [17–23]. Fluorescence has many applications in the area of molecular state, photochemistry of solid materials, biochemical, and medical and chemical research fields for analyzing organic compounds [23]. The photoconductivity is an optical process in which a material becomes more conductive owing to the absorption of visible light and UV light [10]. In this paper photoconductivity measurement is carried out between UV and NIR region. Photodetection in photosensitive materials are very crucial in military applications. In addition these fields require proper understanding of the basic principles of photoconductivity processes [24]. Photosensitivity of PABA is highly concentration dependent. The photosensitizing properties of PABA are technologically very important and it needs further analysis [5]. The surface laser damage threshold value of organic polymeric material is greater than 10 GW/cm^2 with picoseconds pulses [25]. For the optical application defect free single crystals are important because a small defect can affect the performance of the optical devices. Defect of the crystals can be identified by defect studies. There are various techniques invented to identify the defects in crystals. Among them chemical etching is one of the methods to find out the etch patterns. The derivatives of aminobenzoic acid possess good fluorescence, high quantum yield, photosensitivity and UV light absorption properties [5,16–18,26]. Due to these important optical properties of derivatives of aminobenzoic acid, the present paper discusses FTIR, UV–Vis–NIR, photoconductivity, laser damage threshold, fluorescence and optical microscope analysis of β-P-amino benzoic acid single crystal and also study of title compound is of interest as its structure contains electron donating groups and electron accepting groups which exhibit several physical properties.

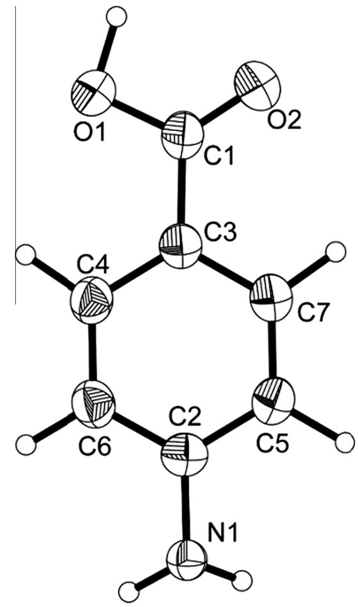

Fig. 1. Chemical structure of PABA.

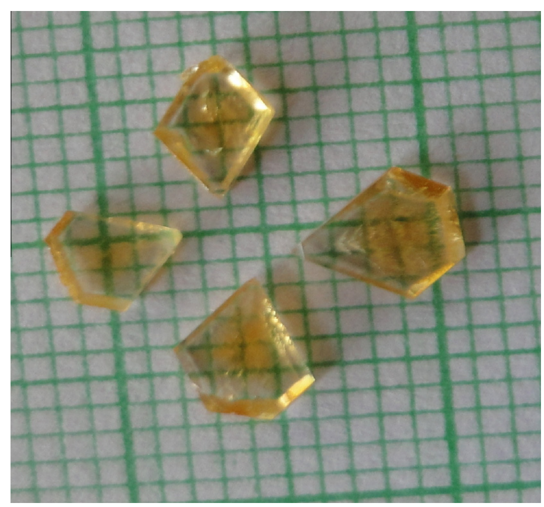

Fig. 2. β-PABA single crystals.

2. Materials and methods

2.1. Crystal growth

β-P-aminobenzoic acid crystals were grown by slow evaporation technique. The commercially available P-aminobenzoic acid was purified by repeated recrystallization using deionised water as solvent which has resistivity of 18.2 MΩ cm. The solution was stirred well for 12 h until homogeneous mixture of clear solution was obtained. Then the solution was filtered using filter paper and transferred to a glass vessel and evaporation was allowed to take place at room temperature. After two weeks 1 mm^3 seed crystals were obtained from super saturated solution. Defect free single crystals are selected as seed for growing large size single crystals. Seed crystals were located at the bottom of the beaker containing the supersaturated solution. The beaker was kept in a constant temperature bath to maintain the growth solution at constant temperature 28 °C with accuracy ±0.01 °C. Prism single crystals have been harvested in a growth period of 45 days. When amino group materials are kept for a long growth period its solution is predominantly affected by fungus. In order to avoid fungus some drops of hydrofluoric acid were added to mother solution. The chemical structure [7] and grown crystals of PABA are shown in Figs. 1 and 2 respectively.

2.2. Characterization

The single crystal X-ray diffraction studies of β-PABA single crystals were carried out using Bruker AXS Kappa APEX II CCD Diffractometer, equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. The obtained single PABA crystals were finely ground and subjected to powder X-ray diffraction studies using XPERT-PRO X-ray diffractometer with Cu Kα (λ = 1.54060 Å) radiation at 25 °C. The sample was scanned for 2θ values from 10° to 60° at a rate of 2°/m. The FTIR spectrum of the β-PABA crystal was recorded using Bruker ALPHA FTIR spectrometer in the wavelength range 500–4000 cm^{-1} by single reflection ATR accessory mode. To find the position of proton and carbon in β-PABA, Proton Nuclear Magnetic Resonance (^{1}H NMR) and carbon Nuclear Magnetic Resonance (^{13}C NMR spectra) were recorded using a Bruker FT-NMR 400 MHz spectrometer and DMSO d_6 used as a solvent. The absorption spectrum of the β-PABA was made in the region 200–1100 nm using Perkin Elmer Lambda 35 spectrometer at room temperature. The surface laser damage threshold measurements have been made on β-PABA single crystals using the high-power Q-switched Nd:YAG laser with 10 Hz pulse repetition rate and the pulse width of the laser is 7 ns for 532 nm. The thermal stability of β-PABA was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using Perkin