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Growth, spectral, thermal, electrical, mechanical and nonlinear optical properties of organic single crystal 4–Amino–(1–methylphenyl) pyridinium bromide

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ABSTRACT

A recently identified organic nonlinear optical material, 4–Amino–(1–methylphenyl) pyridinium bromide (4A1MPB) was synthesized and attempts were made to grow good quality single crystal by slow evaporation solution growth technique which crystallizes in orthorhombic system with a non–centrosymmetric space group $P2_12_12_1$. Studies such as microanalysis and powder XRD were performed for this material to ascertain its composition and phase respectively. The FT–IR spectral study, which was performed to analyze and assign the vibrational frequencies, enumerated various characteristic functional groups present in the crystal. The NLO efficiency was measured by Kurtz and Perry powder technique using Nd:YAG laser of wavelength 1064 nm and it was found to be about 0.73 times that of standard KDP material. TG/DTA and DSC analyses showed that the grown crystal was thermally stable up to about 197 °C. The UV–vis–NIR spectral data and fluorescence spectrum of the crystal were recorded to explore its optical transmission and emission properties respectively. The dielectric constant, dielectric loss, and ac conductivity of the grown crystal were evaluated as a function of frequency for various temperatures. The photoconducting nature of the grown crystal was analyzed and confirmed to be positive. The hardness studies were performed on (001) plane of the crystal at room temperature using Vickers micro-hardness tester, from which mechanical stability was analyzed through the classical Meyer's relation that revealed the moderate hardness of the title compound.

1. Introduction

In recent decades, many investigations are being carried out to synthesize new compounds with noncentrosymmetric space group and grow the single crystals for technological applications [1,2]. Research on organic NLO materials has become vital field of interest owing to their relatively higher NLO and electro–optic coefficients as compared to their inorganic counterparts, small dielectric constant (and hence faster response), ease of synthesizing new molecules due to inherent flexibility, higher laser damage threshold (> 10 GW/cm^2), possible integration into devices to realize their applications in the fields such as optical communication, Terahertz wave technology, etc [3–5]. Further, the physico–chemical properties such as spectral,

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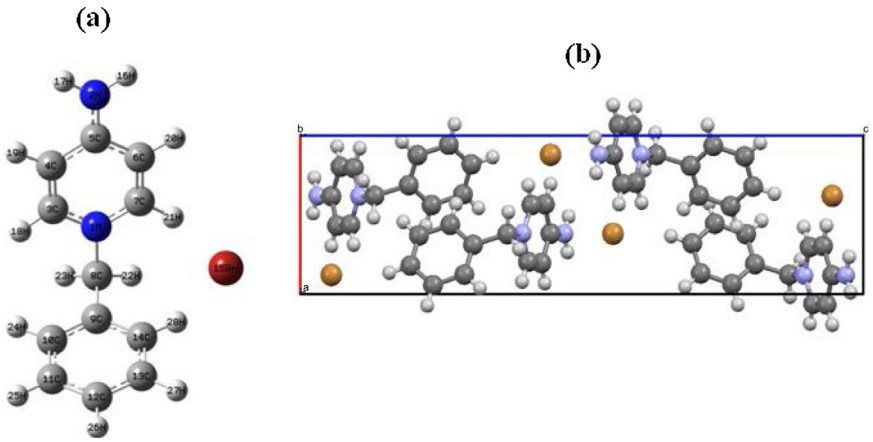

Fig. 1. (a) Molecular structure of 4A1MPB with atom numbering scheme (b) Unit cell packing of 4A1MPB viewed along b–axis.

thermal, electrical, mechanical and nonlinear optical properties are essential to study the ability of the organic compound being explored for its stability at ambient conditions [6–8]. However, organic crystals possess relatively weak intermolecular bonding and hence it is difficult to grow high quality and large size crystals. In general, acentric organic molecules consist of highly delocalized π–electron conjugated moiety suitably substituted by a donor group at one end of the conjugated structure and an acceptor group at the other end, forming a "push-pull" conjugated structure and exhibit evidence for high value of second order optical nonlinearity [9,10]. In this direction, several 4–Aminopyridinium based organic crystals have been investigated for their NLO properties and among them 4–Aminopyridinium maleate ($P2_1$) [11], 4–Aminopyridinium hydrogen maleate ($P2_1$) [12], 4–Aminopyridinium monophthalate ($P2_12_12_1$) [13], 4–Aminopyridinium tetrafluoroborate (C2) [14], 4–Aminopyridinium P–Aminobenzoate dihydrate (Cc) [15], 4–Aminopyridinium P–Aminobenzenesulfonate P–Ammoniobenzenesulfonate monohydrate (C2) [16] and 4–Aminopyridinium 4–nitrophenolate 4–nitrophenol ($P2_1$) [17] are noteworthy as they have been found to crystallize in non–centrosymmetric space group and, consequently, exhibiting second order nonlinearity. Further, in the year 2006, Seethalakshmi.et.al, identified another pyridine based compound namely, 4–Amino–(1–methylphenyl) pyridinium bromide (4A1MPB), and solved its structure which was reported to have crystallized in orthorhombic crystal system with a non–centrosymmetric space group of $P2_12_12_1$ [18]. The molecular structures of 4A1MPB with atom numbering scheme and its corresponding packing arrangement inside a single unit cell viewed along b–axis are shown in Fig. 1(a) and Fig. 1(b) respectively. The 4A1MPB belongs to π–Donor–Acceptor type molecular compound wherein benzyl bromide acts as donor and 4–Aminopyridine acts as acceptor. This asymmetric system consists of 4–Aminopyridine molecules in protonated form and benzyl bromide in mono–ionized state. The intermolecular N—H ···Br hydrogen bonds link individual pair of cation and anion and the structure is further stabilized by an extensive network of weak intermolecular C—H ···Br hydrogen bonds. However, apart from the studies on crystal structure, there are no reports available on the crystal growth, microanalysis, second harmonic generation, optical, dielectric, photoconductivity and mechanical properties of the title compound. Since these informations are expected to provide in–depth knowledge on the physico–chemical properties of 4A1MPB, detailed studies were performed on this compound and the results are provided, to the best of our knowledge, for the first time.

2. Experimental procedures

2.1. Synthesis and crystal growth

All chemicals and reagents used for the synthesis were of analytical grade (purity ≥ 98%), procured from Merck, India and used as received without any further purification. The title compound (4A1MPB) derived from 4–Aminopyridine and Benzyl bromide was synthesized according to the similar procedure as described in Ref. [18]. The calculated amount of the starting materials taken in 1:1 molar ratio dissolved separately in acetone were thoroughly mixed and stirred well continuously for 2 h using a motorized magnetic stirrer to prepare a homogeneous mixture of the solution. The white crystalline precipitate that settled at the bottom of beaker was separated, washed with dry acetone and then dried in a hot air oven to obtain the stable white microcrystalline powder. The material thus synthesized was re–crystallized two or three times in ethanol to enhance the purity and kept in an airtight pack which was then utilized for further growth. The reaction scheme involved in the chemical synthesis of the title compound is shown in Scheme 1. The solubility of 4A1MPB was analyzed in methanol, ethanol, acetone, acetonitrile and toluene however ethanol was found to possess moderate solubility and hence the solubility in ethanol was estimated gravimetrically at different temperatures (25 °C to 40 °C) with an interval of 5 °C using a water bath equipped with a programmable Eurotherm temperature controller having an accuracy of ± 0.01 °C (Fig. 2). A saturated solution of the title compound was prepared at room temperature (30 °C) by dissolving the