Journal of Crystal Growth 441 (2016) 18–25

Contents lists available at ScienceDirect

Journal of Crystal Growth

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

Synthesis, growth and characterization of a new organic three dimensional framework: Piperazin-1-ium 4-aminobenzenesulfonate

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ARTICLE INFO

Article history:
Received 14 November 2015
Received in revised form
30 January 2016
Accepted 2 February 2016
Communicated by M. Roth
Available online 10 February 2016

Keywords:
A1. Crystal structure
A1. Crystal morphology
A2. Growth from solution
B1. Organic compounds
B2. Nonlinear optical materials

ABSTRACT

Piperazinium p-aminobenzenesulfonate (PPABS), a new nonlinear optical material was synthesized and crystals were grown from the methanol solvent by slow evaporation solution growth method. Single crystal X-ray diffraction study elucidated the crystal structure of PPABS. It crystallizes in orthorhombic crystal system with space group of Pbca. UV–vis-NIR spectral study was performed to analyze optical transparency of PPABS crystal and found that the grown crystal has sufficient transparency in the entire visible region with lower cutoff wavelength of 321 nm. The thermal stability and decomposition stages of the sample were studied by TG/DTA analyses. The different environmental carbon and hydrogen atoms of the proposed structure were identified by NMR spectral studies. The electric field response of crystal was determined from the dielectric studies. From the Z-scan measurements, the third order nonlinear optical properties of grown crystal were studied.

1. Introduction

Aromatic organic crystalline compounds are most promising candidate for nonlinear optical applications because of their conjugated system. The flowing of delocalized π electrons between donor and acceptor groups on opposite sides of the molecules may induce a large molecular charge transfer. The intermolecular charge transfer and the depolarization of π electrons in organic molecules can cause huge and fast optical nonlinear responses [1]. In recent years, the research interest in finding more in the second order NLO materials was compared more to the third order nonlinear phenomena in molecular materials. Nowadays the research interest in exploring the third order nonlinear optical material has been stimulated among the researchers due to their potential applications such as optical signal processing, optical switching, three-dimensional (3D) fluorescence imaging, 3D optical data storage, 3D lithographic micro fabrication and optical power limiting [2–7]. Piperazine is an achiral organic weak base with the space group $P2_1/n$ [8]. It is a cycloaliphatic secondary amine with two protonated NH groups in a six membered saturated ring [9]. It is an excellent hydrogen-bond acceptor and due to this nature, it is capable of yielding both second and third order NLO properties, mainly in the combination with carboxylic group [10]. Recently, piperazinium crystals such as piperazinium L-tartrate, piperazine (bis) p-toluenesulfonate, piperazinium perchlorate and 4-hydroxytetramethylpiperazinium picrate have been reported [11–14]. 4-Aminobenzosulfonic acid exists as zwitterions and it has a deprotonated SO_3^- group and a protonated NH_3^+ group. This dipolar nature makes them suitable candidate for NLO applications. The sulphanilate crystals such as 4-aminopyridinium p-aminobenzenesulfonate, sodium sulphanilate dihydrate, lithium sulphanilate hydrate with good nonlinear optical properties have been reported [15–17]. In the present investigation, synthesis, growth, thermal, linear and nonlinear optical properties of piperazin-1-ium 4-aminobenzenesulfonate have been reported for the first time.

2. Experiment

2.1. Materials synthesis and crystal growth

The title compound was synthesized using analytical grade precursors piperazine (Spectrochem, 99%) and p-aminobenznesulfonic acid (Merck India, 99.5%) in an equimolar ratio. The stoichiometrically weighed starting materials were dissolved in methanol solvent at room temperature and stirred well for 4 h. The beaker containing solution was kept in a constant temperature water bath at 40 °C and allowed for evaporation. The reaction of title compound is shown in Fig. 1. After a period of 10 days, brown colored crystalline salt was obtained and recrystallized it many times to get purified salt. Solvent selection is the important criteria to grow bulk and transparent single crystals. The solubility of piperazin-1-ium 4-aminobenzenesulfonate

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http://dx.doi.org/10.1016/j.jcrysgro.2016.02.005
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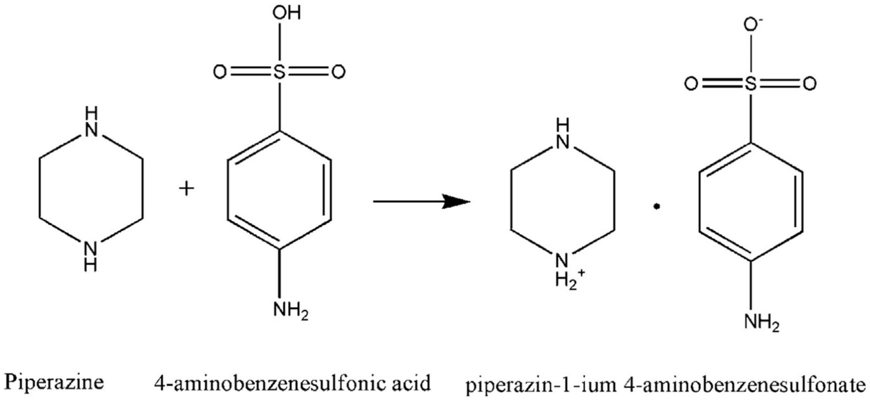

Fig. 1. Reaction scheme of PPABS.

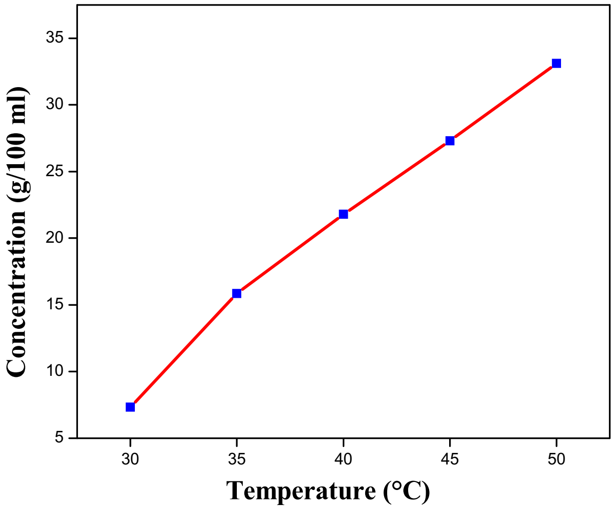

Fig. 2. Solubility of PPABS in methanol solvent.

was determined using methanol solvent at different temperatures ranging from 30 to 50 °C. The required amount of PPABS taken to make the saturated solution at different temperatures was estimated gravimetrically and the obtained solubility of PPABS is depicted in Fig. 2. From the solubility data, it is found that the title compound shows positive solubility gradient in methanol solvent.

In order to perform the crystal growth experiment, growth solution was prepared and saturated at room temperature. After a growth period of 20 days, good quality PPABS crystals are obtained as shown in Fig. 3.

3. Characterization

As-grown PPABS crystals have been subjected to various characterization studies to analyze the structural, thermal, optical, dielectric and mechanical properties. The crystal structure of PPABS was determined from the single-crystal X-ray diffraction data using a Bruker kappa APEXII single crystal X-ray diffractometer with a graphite monochromated MoKα radiation ($\lambda=$ 0.71073 Å) at 293 K [18]. Optical transmittance of grown PPABS crystal was measured by a T 90+ Lab India UV–vis double beam spectrometer for the wavelength range of 190–900 nm. ^{1}H NMR and ^{13}CNMR spectra of PPABS were recorded using a Bruker Avance III 500 MHz FT-NMR spectrometer. The dielectric study of PPABS was carried out using a HIOKI 3532-50 LCR Hitester in the frequency range from 50 Hz to 5 MHz for the temperature range from 313 to 373 K. Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out in nitrogen atmosphere using a NETZSCH STA 409PC/PG instrument with a heating rate of 10 °C/min starting from 30 to 600 °C. Differential scanning calorimetry technique carried out using a NETZSCH DSC 204 calorimetry in the temperature range from 30 to 300 °C. Z-scan measurement was carried out on PPABS crystal using a He–Ne laser source with the wavelength of 632.8 nm under closed and open aperture modes.

4. Results and discussion

4.1. X-ray diffraction studies

The crystal structure PPABS was solved by the direct method and refined by the full matrix least-squares technique on employing the SHELXL 97 program package [19]. The crystallographic data for structure analysis of the title compound are listed in Table 1. N–H…O hydrogen bonds link the ionic units into a chain, and forming sheets (Fig. 5). The asymmetric unit of the piperazin-1-ium 4-aminobenzenesulfonate compound comprises of a piperazine cation and a 4-aminobenzenesulfonate anion (Fig. 4). It was observed that the chemical composition of the crystal is $(C_6H_6NSO_3{}^-)\cdot0.5(C_4H_{12}N_2{}^+)$, and the PPABS crystallizes in orthorhombic crystal system with space group Pbca. The cell parameters were found to be $a=10.192(2)$ Å, $b=8.470(2)$ Å, $c=21.584(5)$ Å, $\alpha=\beta=\gamma=90°$and volume, $V=1863.3(7)$ Å^3. The crystal structure of PPABS is deposited at the Cambridge Crystallographic Data Centre (CCDC 1422300).

The title compound was found to have similar crystal structure of organic piperazine (bis) p-toluenesulfonate single crystal. The complete molecular structure was situated across a crystallographic inversion center (Fig. 4). The non-aromatic heterocyclic adopts a chair conformation ($^1C_4$, $^{N1}C_{N2}$) according to a conformation analysis [20]. The piperazine ring adopts a chair conformation with the puckering parameters Q, θ and φ having values of 0.581(2) Å, 0.12(1)° and 0°, respectively [21]. For an ideal chair conformation, θ has a value of 0° or 180°. All bond lengths and angles are normal [22]. The average N–C bond length in the piperazine ring is 1.490(3) Å indicating the single bond nature. The dihedral angle between piperazine ring and benzene (C1–C6) ring is 66.92(9)°. In the sulfamate anion, the S–O distances vary from 1.4327(2) to 1.4599(2) Å , and O–S–O angles vary from 108.8 (2)° to 114.6(2)°. All the four H atoms of amino group in the cation of PPABS are hydrogen bonded to the oxygen atoms of the carboxylate groups of the anions. One H atom forms a trifurcated hydrogen bond to all the oxygen atoms of carboxylate group of anion, whereas the other three H atoms form single hydrogen bond to oxygen atom of the carboxylate group of anions (Fig. 5). These N–H…O hydrogen bonds link the ionic units into a chain, and forming sheets lying parallel to