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Synthesis, growth, structural, optical and thermal properties of a new organic nonlinear optical crystal: 2-amino 5-chloropyridinium-L-tartarate

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ABSTRACT

A new organic nonlinear optical crystal 2-amino-5-chloropyridinium-L-tartarate [2A5CPLTA] has been synthesized and the crystals were grown by slow evaporation solution technique at room temperature using methanol as solvent. The crystal structure of the title compound has been determined by the single crystal X-ray diffraction study and it belongs to the monoclinic system with noncentrosymmetric space group $P2_1$. The presence of functional groups was ascertained by Fourier transform infrared analysis. The transmittance and lower cut off of the grown crystal was ascertained by the UV–vis–NIR spectroscopy. Thermal studies reveled that 2A5CPLTA crystal is thermally stable up to 144 °C. The dielectric measurements of the grown crystal were carried out with different frequencies and temperatures. Vickers micro hardness measurement was carried out to study the mechanical behavior of the grown crystal. The second harmonic generation of the title crystal was confirmed by the Kurtz–Perry powder test employing the Nd: YAG laser as the source.

1. Introduction

In the last decades, organic molecular crystals have been considered potential substitutes for inorganic crystals in nonlinear optical applications, because they have high values for the nonlinear coefficients, large birefringence values, high damage thresholds in laser beams, and a large transparency domain [1]. Recently, organic nonlinear optical crystals have been recognized for hybrid photonic integrated circuitry and it is generally versatile since they are often formed with intramolecular hydrogen bonds and hence possess high degree of delocalization [2,3]. Non-linear optical crystals are of particular interest for the design and formation of different laser operated optoelectronic materials such as modulators, deflectors, optical triggers, optically operated fibers, etc. This is due to their large second-order optical susceptibilities, ultra-fast response time (sub-picosecond) and high optical damage thresholds. The development of nonlinear optics have enhanced in parallel with the introduction of lasers, because laser beam possess the energy density necessary to produce nonlinear effects [4].

Aromatic derivatives are a group of organic compounds that could be interesting for the optical nonlinear applications because of the delocalized cloud of π electrons. Pyridine heterocyclic and their derivatives are present in many large molecules having photo chemical, electro chemical and catalytic applications. They are possessing nonlinear optical properties [5] and 4-N, N-dimethylamino-4′-N′-methylstilbazoliumtosylate (DAST) is used in generating and detecting terahertz (THz) frequencies [6]. 2-amino-5-chloropyridine is a non-hygroscopic simple organic material and the crystal has been grown by slow evaporation method and these crystals are promising low dielectric constant material Suthan et. al. [7]. Additionally because of their chelating abilities, 2- amino pyridine is commonly used as ligands in inorganic and organo metallic chemistry [8]. This class of compounds and their derivatives are valuable synthetic target compounds and their synthesis have been extensively reviewed [9,10].

In this article, we present the synthesis, bulk crystal growth, structure, optical, thermal and dielectric properties of organic nonlinear optical crystal 2-amino-5-chloropyridinium- L-tartrate single crystal from aqueous solution by slow evaporation method for the first time.

2. Experimental procedure

2.1. Synthesis, solubility and crystal growth

The title compound was synthesized by taking 2-amino-5-chloropyridine (Sigma-Aldrich 99%) and L-Tartaric acid (Merck 99%) in an

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equimolar ratio. The calculated amount of 2-amino-5-chloropyridine was first dissolved in methanol. L-Tartaric acid was dissolved in double distilled water and then added to the solution slowly by stirring. To obtain the homogenous solution it was continuously stirred for 6 h and filtered using Whatman filter paper. This filtered solution was allowed to dry at room temperature and the salts were obtained. The dried salt was collected and used for the further growth of 2A5CPLTA crystal. The reaction scheme of this compound is shown in Fig. 1. The purity of the synthesized salt was further improved by successive recrystallization process. 2-amino-5-chloropyridine is a base which gains a proton in acidic solution and forms salt of the respective acid. During the proton transfer reaction, a proton is transferred from the electron donor group of L-tartaric acid to the electron acceptor group of 2-amino-5-chloropyridine.

Selection of suitable solvent and solubility equilibrium are crucial for the growth of bulk and optically good quality single crystals. The solubility of 2-amino-5-chloropyridinium-L-tartarate was assessed using methanol solvent at different temperatures ranging from 25–50 °C. The amount of 2A5CPLTA required to make the saturated solution at different temperatures was estimated gravimetrically and the obtained solubility curve of 2A5CPLTA is shown in Fig. 2. From the solubility study, it is found that the title compound exhibits positive solubility in methanol solvent.

The saturated solution of 2A5CPLTA was prepared at room temperature in accordance with the solubility data. The pH value of the solution was measured and it was found to be 5.2. The saturated solution was filtered by using Whatmann filter paper. The filtered solution was then transferred in to the 300 ml beaker and tightly covered with perforated sheets. The prepared solution was kept in a constant temperature bath (CTB) at 35 °C to stabilize the temperature and to avoid the effect of fluctuation in room temperature. The solvent was allowed to evaporate, to get the good quality crystal. After a span of 25 days, bulk crystal of 2A5CPLTA of size $17 \times 8 \times 5$ mm^3 was harvested and it is shown in Fig. 3.

3. Results and discussion

3.1. Single crystal X-ray diffraction studies

The single crystal X-ray diffraction studies of 2A5CPLTA was performed using Bruker AXS Kappa APEX II CCD diffractometer equipped with graphite monochromated Mo Kα radiation (λ= 0.71073 Å) at room temperature. The single crystal of size $0.35 \times 0.30 \times 0.25$ mm^3 was used for the study. Accurate unit cell parameters were determined from the reflections of 36 frames measured in three different crystallographic zones by the method of difference vectors. Data collection, data reduction and absorption correction were performed by APEX2, SAINT-plus and SADABS programs [11]. A total of 4357 reflections were recorded with 2θ range from 2.51 to 28.25° of which 2688 reflections are considered as unique reflections with $I > 2\sigma(I)$. The structure was solved by direct method procedure using SHELXS-97 program and refined by Full-matrix least squares procedure on F^2 using SHELXL-97 program [12]. The final refinement converges to R-values of R_1= 0.0339 and WR_2=0.0922. The crystallographic data and the refinement details for 2A5CPLTA are summarized in Table1. Fig. 4 shows the ORTEP plot of the molecule drawn at 50% probability thermal displacement ellipsoids with the atom numbering scheme. All the hydrogen atoms were positioned geometrically [C–H=0.93 Å – 0.96 Å, N–H=0.86 Å–0.88 Å] and were refined. The asymmetric unit of the title compound consists of a neutral

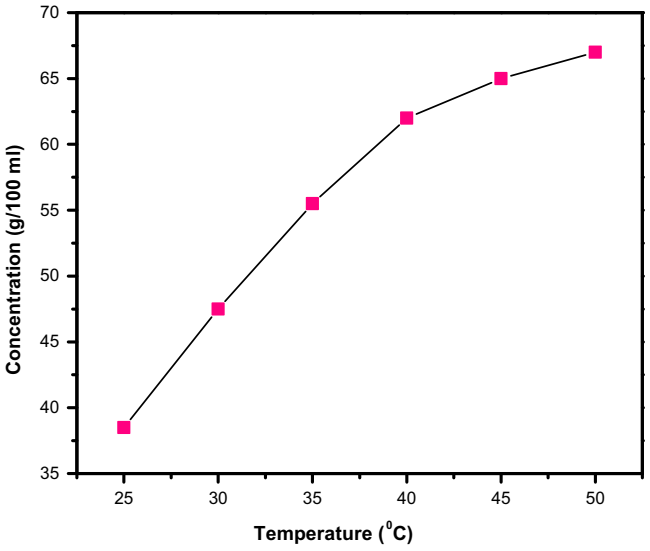

Fig. 2. Solubility curve of 2A5CPLTA in methanol solvent.

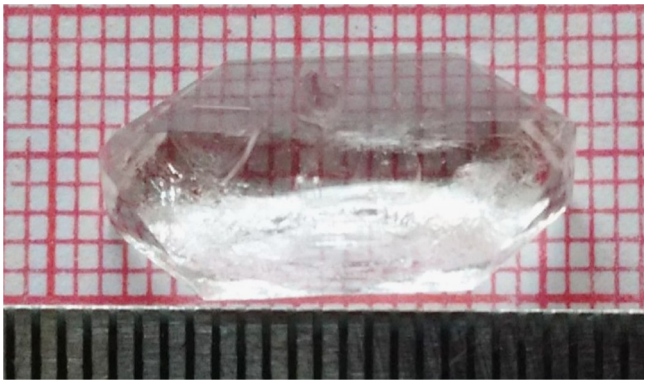

Fig. 3. Photograph of as-grown 2A5CPLTA crystal.

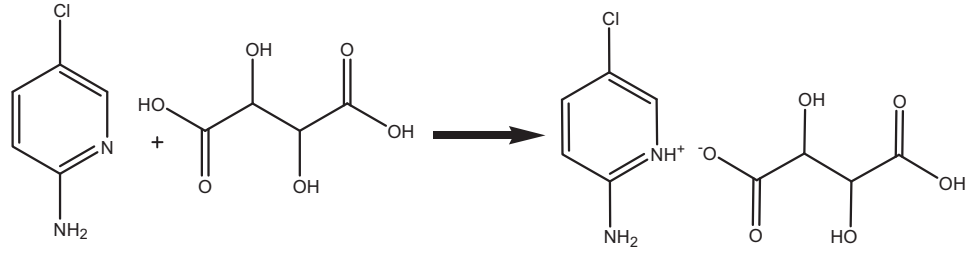

Fig. 1. Reaction scheme of 2A5CPLTA compound.