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Synthesis, crystal growth and characterization of an organic material: 2-Aminopyridinium succinate succinic acid single crystal

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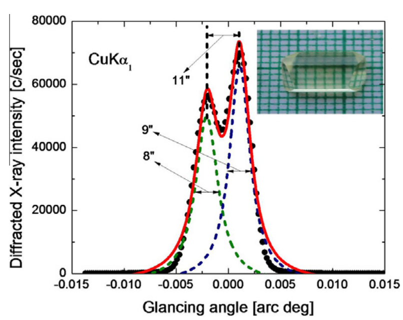
HIGHLIGHTS

- Transparent 2APS single crystal has been grown by solution growth method.
- Crystal perfection has been taken by high resolution X-ray diffraction spectrum.
- The optical band gap value is calculated to be 3.4 eV.
- The grown crystal is thermally stable up to 165 °C.
- Laser damage threshold value is calculated to be 0.8 GW/cm^2.

GRAPHICAL ABSTRACT

Figure shows HXRD spectrum of grown 2APS single crystal.



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ABSTRACT

The 2-aminopyridinium succinate succinic acid (2APS) single crystal was synthesized and grown by slow evaporation method. The crystal structure has been confirmed by powder X-ray diffraction as well as single crystal X-ray diffraction analysis. The crystal perfection has been evaluated by high resolution X-ray diffraction (HRXRD). The grown crystal is transparent in the visible and near infrared region. The optical absorption edge was found to be 348 nm. The fluorescence study was carried out by spectrofluorophotometer. The thermal stability of grown crystal was analyzed by thermal gravimetric and differential thermal gravimetric (TG–DTA) analysis. Vicker's hardness study carried out at room temperature shows increased hardness while increasing the load. Laser damage threshold value was determined by Nd:YAG laser operating at 1064 nm. The grown 2APS crystal was characterized by etching studies using water as etchant.

Introduction

Materials exhibiting large optical nonlinearity are of great interest for applications such as frequency conversion, telecommunication, optical computing, optical information processing and high optical disk data storage [1–3]. The common wisdom has been that an optical material should have a large charge transfer and the optical transparency with less dislocation density. In recent years, search for organic single crystal in the application of telecommunication, frequency doubling and optoelectronics has been increased considerably [4–8]. This is because of their efficient physicochemical properties such as molecular nonlinearity over a broad frequency range, low cost, low dielectric constant, inherent synthetic flexibility, high optical damage threshold (>10 GW/cm^2), ultrafast response with better processability, ease

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of fabrication and possible integration into devices. However, organic crystals have relatively weak intermolecular bindings and it is too difficult to grow high quality large size crystals compared with inorganic crystals. Hydrogen bonding plays a key role in molecular recognition [9] and crystal engineering research [10]. Succinic acid is a common metabolite formed by plants, animals and microorganisms and belongs to C4 dicarboxylic acid produced as an intermediate of the tricarboxylic acid cycle (TCA) and also as one of the fermentation products of energy metabolism [11]. In general, succinic acid can exist in neutral state as succinic acid or in ionized state as succinate. In the ionized state it forms a very strong intramolecular hydrogen bond with other molecule. Similarly 2-aminopyridine molecules can exist in neutral and protonated or cationic state. The structure of 2-aminopyridine and succinic acid in stoichiometric 1:1 ratio has already been studied [12]. The photopyroelectric properties of 2-aminopyridine succinate succinic acid (2APS) crystal were also studied using improved photopyro electric (PPE) technique PPE [4]. In addition to above studies, presently single crystals of 2-aminopyridine succinate succinic acid have been grown by slow evaporation technique and investigations such as solubility, PXRD, SXRD, HRXRD, UV–Visible–NIR, TG–DTA, Hardness studies, laser damage threshold (LDT) and Etching studies were carried out.

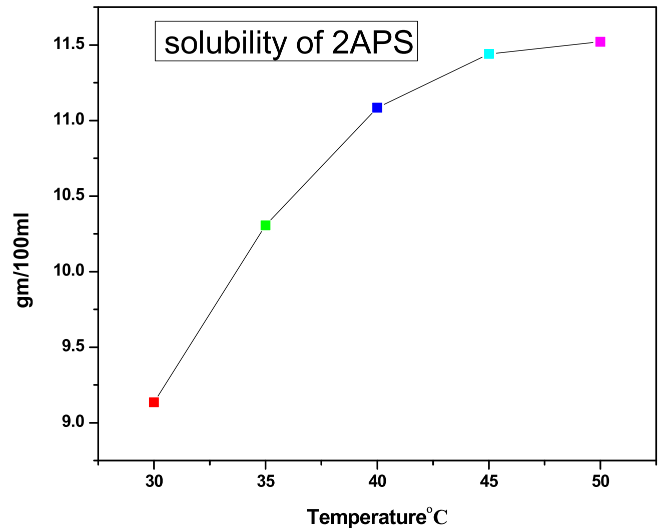

Fig. 1. The solubility of 2APS single crystal.

Material synthesis and crystal growth

The 2APS material was prepared by mixing 2-aminopyridinium and succinic acid in a 1:1 M ratio in water at room temperature. After synthesis, solubility of 2APS was gravimetrically determined as a function of temperature. The solubility was carried out in a constant-temperature water bath with a cryostat facility with an accuracy of ±0.01 °C. The solubility was determined in water for different temperatures (30–50 °C) with the interval of 5 °C and the variation in solubility along with temperatures is depicted in Fig. 1. In accordance with the solubility studies, the saturated solution was prepared and stirred continuously for several hours at room temperature. The solution was filtered in a beaker using Whatman filter paper. The beaker was tightly closed with perforated polyethylene sheet. The solution was allowed for slow evaporation under room temperature condition. The rectangle shaped crystal was grown over a couple of weeks. The material was further purified by repeated recrystallization process in triple distilled water. Finally light yellowish transparent crystals were obtained as shown in Fig. 2.

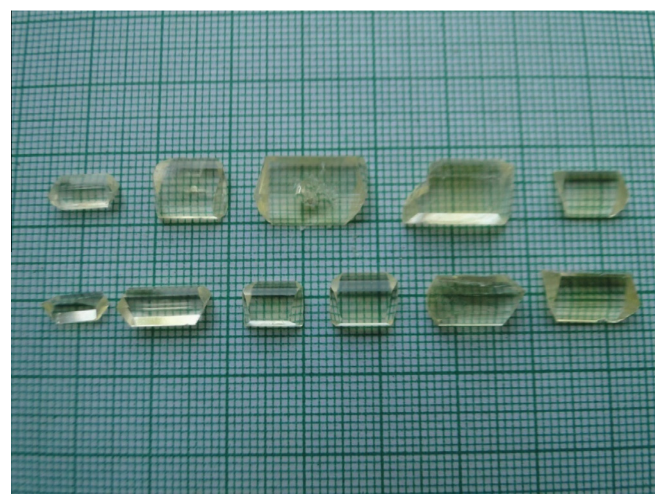

Fig. 2. As grown 2APS single crystal.

Result and discussion

Powder XRD and single crystal XRD

Powder XRD is useful to identify the crystalline nature and phase purity. The powder XRD pattern is determined by REICH SEIFERT X-ray diffractometer employing CuKα (1.54058 Å) with a scan speed of 1°/min and planes are indexed by using 'TWO THETA' refinement software. The indexed powder X-ray diffraction is shown in Fig. 3. The grown crystal was subjected to single crystal X-ray diffraction study using NONIUS CAD-4/MACH 3 diffractometer with MoK_α radiation in the wavelength 0.71073 Å to estimate the lattice parameter values. The cell parameters were obtained from least-squares refinement of the setting angles of 25 reflections. The determined unit cell parameters are in close agreement with reported value [12]. The crystal belongs to monoclinic system with space group $P2_1/c$.

$$a = 10.1923\ \text{Å}, \quad b = 5.1604\ \text{Å}, \quad c = 18.947\ \text{Å}.$$

$$\alpha = \gamma = 90^\circ, \quad \beta = 103.32^\circ,$$

$$V = 969.73\ \text{Å}^3$$

UV–Vis-NIR

The optical transmission and absorption spectrum of 2APS crystal was recorded in the range 200–1100 nm using Lambda 35 spectrophotometer. A 1 mm thick sample was used for UV–Vis–NIR spectrum measurement. It has transparency in entire visible and near infrared region. The fundamental absorption edge was observed at 348 nm. A similar value is seen in the UV–Vis spectrum reported in [4]. There is no absorption in the entire visible region of the spectrum as shown in Fig. 4. Hence, the title crystal can be used for various optical applications owing to its wide transparency window in the entire visible and near infrared regions. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula:

$$\alpha = \frac{2.3026 \log(1/T)}{t}$$