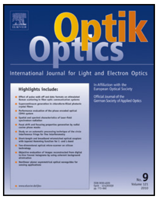
Optik 126 (2015) 2348–2353

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo



Studies on the growth and characterizations of 2-amino 4-methylpyridinium tartrate monohydrate single crystals

J.V. Jovita[a,*], A. Ramanand[b,1], P. Sagayaraj[b,2], K. Boopathi[c,3], P. Ramasamy[c,4]

[a] Department of Physics, Queen Mary's College for Women(A), Chennai, India
[b] Department of Physics, Loyola College, Chennai, India
[c] Centre for Crystal Growth, SSN College of Engineering, Chennai, India

ARTICLE INFO

Article history:
Received 20 April 2014
Accepted 29 May 2015

Keywords:
Organic compounds
Crystal growth
FTIR analysis
Optical properties
Thermal analysis

ABSTRACT

A noncentrosymmetric, organic single crystal, 2-amino 4-methylpyridinium tartrate monohydrate was synthesized and grown by slow evaporation solution technique at room temperature using methanol as a solvent. The cell parameters of the grown crystal were determined by single crystal X-ray diffraction method. The various functional groups present in the crystal and the different types of protons and carbons were identified by the FTIR and NMR spectral analyses. Optical properties were determined by UV–vis–NIR spectroscopic and photoluminescence studies. The second harmonic generation of the grown crystal was observed by Kurtz Perry powder technique. Photoconductivity studies were carried out for various voltages applied on the grown crystal. The thermal and mechanical stabilities of the 2-amino 4-methylpyridinium tartrate monohydrate single crystal were investigated by TGA–DTA and Vickers microhardness measurements, respectively.

1. Introduction

Organic materials received appreciation and attention due to their power over fast response time, high optical damage threshold and versatility in molecular design, have much opportunity for improving the SHG response. In the organic molecules, donor and acceptor groups and conjugated molecules, with the aid of hydrogen–bond interactions have proved to be the most important, useful and reliable, because of their strength and directional properties. The ability to control the orientation of the hydrogen–bond by choosing appropriate donor and acceptor species enables the design of new and interesting crystal structure [1,2]. Pyridine and its derivatives exhibit hydrogen–bond interactions and this property plays an important role in heterocyclic chemistry. The synthesis, growth, structure and properties of single crystals of 2-amino 4-picolinium toluene sulfonate, 2-amino-4-picolinium 4-aminobenzoate, 4-amino pyridinium maleate, Picolinium maleate, Picolinium tartrate monohydrate have been reported with their enhanced nonlinear optical property [3–7]. The growth and structures of 2-amino 4-methylpyridinium with salicylic acid, trifluroacetic acid, pyridine-2, 6-dicarboxylic acid, methanol solution of mercury chloride and also with a mixture of ammonium vanadate, cobalt nitrate hexahydrate and boric acid have also been reported, highlighting proton exchange interactions which finds applications in biomedicine [8–12]. These interesting applications and ongoing research in the applications of the structurally similar compounds intrigued the authors to select such materials for their research. The synthesis, growth, structure and properties of organic single crystal, 2-amino 4-methylpyridininum tartrate monohydrate (AMPTM) are reported here in. The prominent properties such as photoconductivity, nonlinear optical and thermal properties of the grown crystals find its potential applications in optical device processing.

2. Experimental

2.1. Material synthesis and crystal growth

AMPTM was synthesized by the reaction of equimolar ratio of 2-amino 4-methylpyridine (Aldrich) with tartaric acid (Spectrochem). A saturated solution of 2-amino 4-methylpyridine in

---

[*] Corresponding author. Tel.: +91 44 22601427/+91 9444107954; fax::: +91 4428443052.

E-mail addresses: jovitaqmc@gmail.com (J.V. Jovita), ramanand_aroor@yahoo.com (A. Ramanand), psagayaraj@hotmail.com (P. Sagayaraj), boopathi.chemist@gmail.com (K. Boopathi), ramasamyp@ssn.edu.in (P. Ramasamy).

[1] Tel.: +91 044 24800761.
[2] Tel.: +91 9962868517.
[3] Tel.: +91 9940714175.
[4] Tel.: +91 9283105760.

http://dx.doi.org/10.1016/j.ijleo.2015.05.143
0030-4026/© 2015 Elsevier GmbH. All rights reserved.

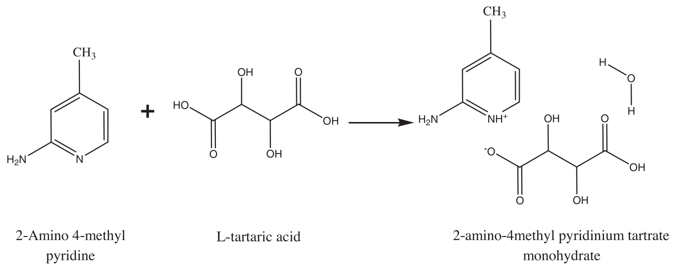


Fig. 1. Reaction scheme of AMPTM.

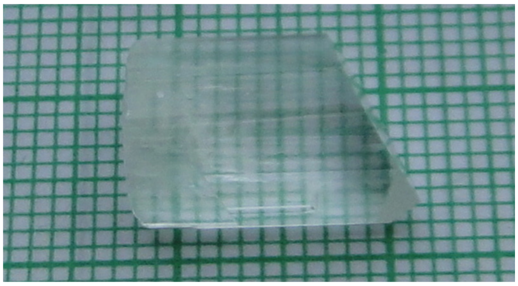


Fig. 2. As-grown crystal of AMPTM.

acetone was prepared and tartaric acid was added to the same solution, hydrogen bonded salt was synthesized in the form of pale pink precipitate. The precipitate was dried and powdered. It was observed that the methanol was a suitable solvent to grow AMPTM single crystal. The saturated solution of AMPTM in methanol was prepared at room temperature. The solution was stirred for 6 h to get homogeneous solution, filtered and kept for slow evaporation at room temperature. Nucleation started after a period of 10 days. The slow evaporation process was allowed for a period of four weeks. The grown crystals of size 10 × 10 × 5 mm^3 were harvested and recrystallized to obtain pure crystals for further studies. The reaction scheme and the photograph of as-grown AMPTM crystals are given in Figs. 1 and 2, respectively.

3. Characterization studies

The single crystal XRD data of the grown AMPTM crystal was obtained using a Bruker AXS (Kappa Apex II) diffractometer with Mo*K*α (0.71073 Å) radiation at room temperature. The FTIR spectrum of AMPTM is recorded using a JASCO FT-IR 410 spectrometer by the KBr pellet method. The ^{1}H and ^{13}C NMR spectrum of 2A5NPTFA was recorded using DMSO as solvent on a Bruker 300 MHz (Ultra shield) TM instrument at 23 °C (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) to confirm the molecular structure. The UV–vis–NIR spectrum was studied by Perkin-Elmer Lambda35 spectrometer with AMPTM single crystal of 1 mm thickness in the range of 200–1100 nm. The photoluminescence spectrum was measured with the JOBIN YVON FLUROLOG-3-11 spectrofluorometer with 180–1550 nm PMT detector using Xenon Lamp of 450 W as an excitation source. The SHG behavior of the grown crystals was observed using a Q-switched Nd:YAG laser of wavelength 1064 nm, Quanta ray series supplied by Spectra Physics and Coherent Molectron power meter USA. The photoconductivity studies were carried out on the AMPTM single crystal using Keithley 485 picoammeter. The TGA–DTA of AMPTM was recorded by using PerkinElmer Diamond TG–DTA instrument. A platinum crucible was used for heating the sample and analysis was carried out in a nitrogen atmosphere at a heating rate of 10 °C min^{-1} in the temperature range of 30–275 °C. Vickers micro-hardness measurements were performed on 2A5NPTFA crystal using MATSUZAWA model MMT-X series micro hardness tester fitted with diamond indenter.

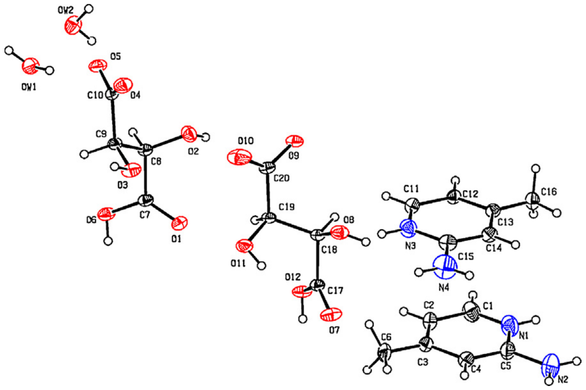


Fig. 3. ORTEP diagram of the AMPTM.

4. Results and discussion

4.1. Single crystal X-ray diffraction study

The AMPTM material crystallized in triclinic system with noncentrosymmetric space group P1. The unit cell dimensions are $a = 7.176(3)$ Å, $b = 9.9359(18)$ Å, $c = 10.716(2)$ Å, $\alpha = 117.528°$, $\beta = 104.792°$, $\gamma = 91.701°$ and volume (V) = 645.3(3) Å^3. The ORTEP diagram with 30% probability level along with its atom labeling scheme of AMPTM is given in Fig. 3. Crystallographic data of AMPTM has been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 938314].

4.2. FTIR spectral analysis

The FTIR spectrum of AMPTM is shown in Fig. 4. The characteristic absorption bands were recorded in spectral range 4000–400 cm^{-1} in order to confirm the presence of functional groups in the molecular structure. In AMPTM, there was a formation of strong H bond between 2-amino 4-methyl pyridine and tartaric acid. The tartrate anion donates H^+ to pyridine moiety to form N^+—H bond. The peak at 3310 cm^{-1} assigned to O—H stretching vibrations. The peaks at 3122 cm^{-1} and 1622 cm^{-1} are assigned to N^+—H stretching vibration. Aromatic C—H stretching occurs at 2991 cm^{-1}. The C—H vibration of tartrate group occurs at 2784 cm^{-1}. The C=C carbonyl stretching occurs at 1875 cm^{-1}. The peak at 1753 cm^{-1} assigned to C—C carbonyl stretching. The C=N stretching occurs at 1676 cm^{-1}. The aromatic C=C stretching occurs at 1481 cm^{-1}. The peaks at 1388 cm^{-1} and 1308 cm^{-1} are due to asymmetric and symmetric stretching vibrations of C—C, respectively. The asymmetric and symmetric vibrations of COO^- occur at

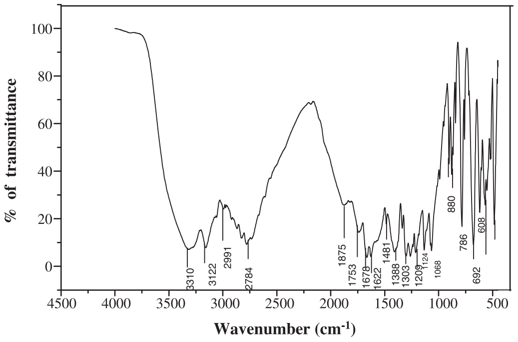


Fig. 4. FTIR spectrum of AMPTM.