Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 135 (2015) 39–45

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Studies on the growth, structural, spectral and third-order nonlinear optical properties of Ammonium 3-carboxy-4-hydroxy benzenesulfonate monohydrate single crystal

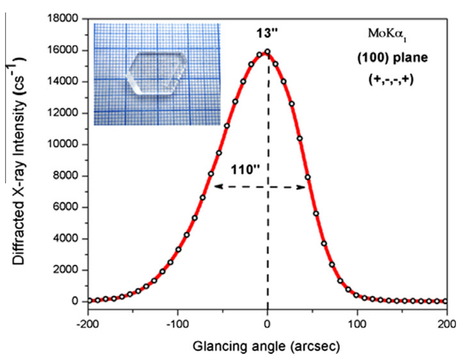
A. Silambarasan [a], M. Krishna Kumar [a], A. Thirunavukkarasu [a], R. Mohan Kumar [a,*], P.R. Umarani [b]

[a] Department of Physics, Presidency College, Chennai 600005, India
[b] Kunthavai Naacchiyaar Govt. Arts College (Women), Thanjavur 613 007, India

HIGHLIGHTS

- Single crystal of ACHBS size up to $20 \times 14 \times 5$ mm^3 was grown by solution growth method.
- FWHM of ACHBS crystal was found to be 110 arc sec on (100) plane.
- Cut-off wavelength of ACHBS was found to be 342 nm.
- NLO parameters $n_2 = 1.204 \times 10^{-11}$ m^2/W, and $\beta = 0.528 \times 10^{-3}$ cm/W were measured.
- ACHBS Vicker's hardness test showed the mechanical tolerance load up to 125 g.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 May 2014
Received in revised form 25 June 2014
Accepted 2 July 2014
Available online 10 July 2014

Keywords:
Crystal growth
Infrared spectroscopy
High-resolution X-ray diffraction
Z-scan technique
Thermal properties

ABSTRACT

An organic nonlinear optical bulk single crystal, Ammonium 3-carboxy-4-hydroxy benzenesulfonate monohydrate (ACHBS) was successfully grown by solution growth technique. Single crystal X-ray diffraction study confirms that, the grown crystal belongs to P2$_1$/c space group. Powder X-ray diffraction and high resolution X-ray diffraction analyses revealed the crystallinity of the grown crystal. Infrared spectral analysis showed the vibrational behavior of chemical bonds and its functional groups. The thermal stability and decomposition stages of the grown crystal were studied by TG-DTA analysis. UV–Visible transmittance studies showed the transparency region and cut-off wavelength of the grown crystal. The third-order nonlinear optical susceptibility of the grown crystal was estimated by Z-scan technique using He—Ne laser source. The mechanical property of the grown crystal was studied by using Vicker's microhardness test.

Introduction

Organic materials are attractive due to their electronic and optical properties and the molecular structure can be easily modified for suitable applications [1]. In recent years, organic nonlinear optical (NLO) crystals have great attention as they provide the key functions of optical frequency doubling, optical modulation, optical switching and optical memory for emerging technologies in the areas such as optical communication, signal processing and optical information storage devices [2,3]. The organic compounds are optically more nonlinear than inorganic materials, because of their hydrogen bonds and weak van der Waal's force, also it possess a high degree of delocalization [4]. The microscopic

* Corresponding author. Tel.: +91 9444600670; fax: +91 44 28510732.
E-mail address: mohan66@hotmail.com (R. Mohan Kumar).

http://dx.doi.org/10.1016/j.saa.2014.07.002
1386-1425/

origin of nonlinearity in these materials is due to the presence of delocalized π-electron systems, which are responsible for enhancing their asymmetric polarizability [5]. Investigations on third-order nonlinear optical materials are relatively less compared to second-order nonlinear optical materials. Efforts have been made to synthesis novel third order NLO materials for their efficient optical switching behavior [6]. The aim for designing the molecules with large third-order nonlinearity is to incorporate them into devices for optical signals processing applications [7,8]. The presence of benzenesulfonate and hydroxyl functional groups plays a vital role in nonlinearity of the grown crystal [9,10]. The Z-scan technique is useful to measure the contribution of nonlinear refraction, nonlinear absorption and third-order nonlinear susceptibility ($\chi^{(3)}$) of the molecular crystals [11,12]. Due to continuous miniaturization of the modern devices based on single crystals, the assessment of crystalline perfection becomes more important. In this report, the π-conjugated Ammonium 3-carboxy-4-hydroxy benzenesulfonate monohydrate (ACHBS) single crystal was grown by slow evaporation technique with optimized growth condition. The growth aspects, structural, spectral, optical and mechanical properties of grown crystal have been reported for the first time.

Materials and methods

Single crystal of ACHBS was grown from aqueous solution using high pure precursors such as ammonia and 5-sulfosalicylic acid. The crystal system and lattice parameters were determined using BRUKER KAPPA APEX II single crystal X-ray diffractometer at 293 K. BRUKER AXS CAD 4 with Cu K_α radiation was used to record the powder X-ray diffraction pattern of the grown crystal. High resolution X-ray diffraction curve was recorded by using PANalytical X'Pert PRO MRD system with Cu $K_{\alpha 1}$ radiation to assess the crystalline perfection. Infrared spectrum of the grown crystal was recorded by KBr pellet technique using BRUKER IFS FT-IR spectrometer in the region 4000–500 cm^{-1}. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using SDT Q600 V8 instrument from 30 °C to 1000 °C. UV–visible spectrum was recorded for the grown crystal using VARIAN CARRY 5E model spectrophotometer. The Z-scan technique was employed to determine third-order nonlinearity of grown crystal by using He—Ne laser source of 632.8 nm. Vicker's microhardness measurement test was carried out on the grown crystal by using Shimadzu HMV-2000 fitted with Vicker's pyramidal indenter.

Experimental

Synthesis and crystal growth

Ammonium 3-carboxy-4-hydroxy benzenesulfonate monohydrate (ACHBS) compound was synthesized from high pure (AR grade) ammonia (NH_3) and 5-sulfosalicylic acid ($C_7H_6O_6S$). The calculated amounts of reactants in equimolar ratio were thoroughly dissolved in deionized water (Fig. 1). After continuous stirring for homogenous mixture, the prepared solution was allowed for slow evaporation. The spontaneous nucleations were occurred in the period of 3–4 weeks and the resulting ACHBS salt was collected. The recrystallization process was used to purify the synthesized salt. The saturated growth solution was prepared by dissolving purified salt in water solvent and it was magnetically stirred for about 6 h to achieve the homogeneity. Then, the ACHBS solution was filtered for further purification using high quality filter paper in order to remove any impurities present in the solution. The crystallizer containing growth solution was kept at constant temperature of 40 °C using a constant temperature bath with an accuracy of ±0.01 °C. The evaporation of the solution was controlled by covering the crystallizer with pinhold polythene sheet. After the evaporation of 3–4 weeks period, the supersaturated solution yielded optical quality single crystal with good morphology. The as-grown single crystal with dimension up to 20 × 14 × 5 mm^3 is shown in Fig. 2.

Results and discussion

X- ray diffraction studies

The single crystal X-ray diffraction analysis was carried out on the grown crystal at 293 K. It reveals that ACHBS belongs to

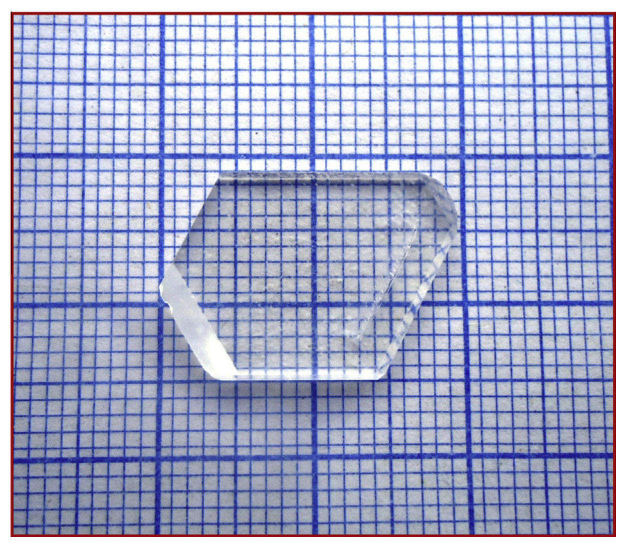


Fig. 2. Photograph of ACHBS single crystal grown by slow evaporation method.

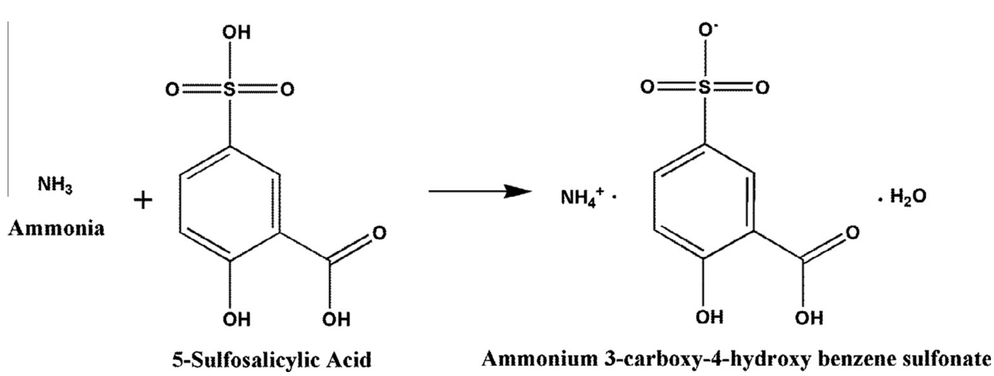


Fig. 1. Material synthesis scheme for ACHBS.