Optik 125 (2014) 5695–5700

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Growth, structural, thermal, optical, dielectric, mechanical and laser damage threshold studies of nicotinium tartrate single crystals

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ARTICLE INFO

Article history:
Received 9 October 2013
Accepted 27 May 2014

Keywords:
Powder X-ray diffraction
Organic compounds
FTIR spectroscopy
Nonlinear optical material

ABSTRACT

An organic nonlinear optical nicotinium tartrate (NT) single crystal was grown by slow evaporation solution growth technique. The cell parameters of NT crystal were confirmed by single crystal and powder X-ray diffraction studies. The crystalline perfection of NT crystal was examined from HRXRD studies. The presence of functional groups was identified from FTIR spectral analysis. TGA and DSC studies revealed the thermal stability of NT crystal. UV–vis-NIR spectral studies showed that the NT crystal has wide transmission window in the entire visible region. The dielectric study on NT crystal established the normal dielectric behavior. The mechanical strength of NT crystal was studied by Vickers' microhardness test. The laser damage threshold value of NT crystal was measured using Nd:YAG laser. The relative SHG efficiency of NT was measured to be 1.1 times that of KDP.

1. Introduction

Recently, organic nonlinear optical material (NLO) is attracting a great deal of attention due to their potentially high nonlinearity and rapid response in electro-optic modulation, frequency mixing, second harmonic generation and optical parametric oscillation, etc. over the inorganic NLO material [1–3]. The nonlinear optical crystal is in fact the "polar crystal" in which the macroscopic properties reflect the internal asymmetric relationship. The structural flexibility of organic chromophores easily modifiable through precise chemical synthesis in view to increase the molecular hyperpolarizability and the possible crafting of chirality centers are remarkable assets compared to the difficulties of the engineering route of inorganic materials, in which the requirements of non-centrosymmetry and high susceptibility have to be accounted [4,5]. Most of the organic nonlinear optical crystals have low laser damage threshold values, less thermal stability etc. and hence these materials have been limited for device fabrication process. In order to overcome these properties, a new class of organic nonlinear material, nicotinium tartrate with high laser damage threshold value has been grown. The L-tartaric acid possesses good mechanical strength comparable with inorganic materials [6]. Smith et al. have crystallized the nicotinium tartrate single crystal with noncentrosymmetric space group of $P2_12_12_1$ [7]. In the present investigation, crystal growth aspects, structural, thermal, optical, dielectric, microhardness, laser damage threshold and etching studies were systematically carried out on the NT single crystal for the first time.

2. Experimental

2.1. Synthesis, solubility and crystal growth

Commercially available L-tartaric acid (Merck AR grade 99.5%) and nicotinic acid (SRL AR grade 99.5%) were dissolved in deionized water and solution was mixed thoroughly using magnetic stirrer for about 5 h. The mixture was heated at 45 °C till a white crystalline salt of NT was obtained. The synthesized salt was further purified by repeated recrystallization process. The reaction scheme and their chemical structures are illustrated in Fig. 1.

The solubility of NT in water was assessed as a function of temperature in the range 35–50 °C using constant temperature bath (CTB) with an accuracy of ±0.01 °C. The saturated solution was allowed to reach the equilibrium about two days at a chosen temperature and then the solubility was gravimetrically analyzed. The same process was repeated for different temperatures and the solubility curve was obtained as shown in Fig. 2. It is observed that NT exhibits fair solubility and has positive solubility temperature gradient in water.

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http://dx.doi.org/10.1016/j.ijleo.2014.06.091
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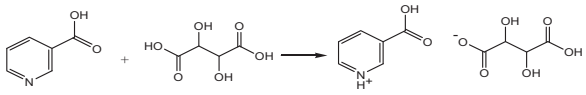

Fig. 1. Reaction scheme for NT.

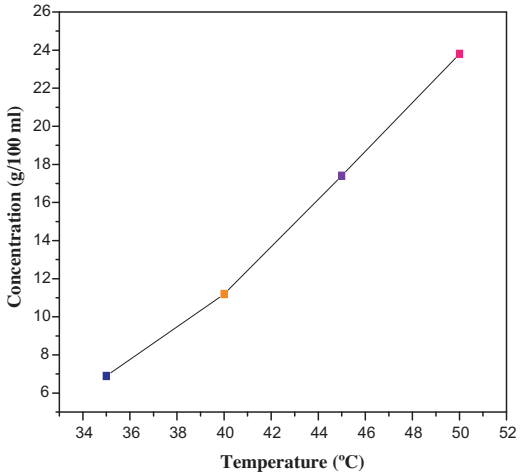

Fig. 2. Solubility of NT compound in aqueous solution.

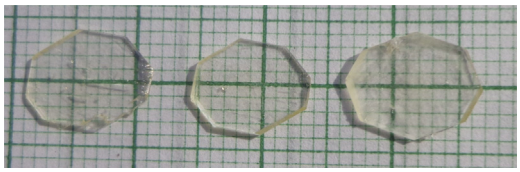

Fig. 3. Photograph of as grown NT crystal.

The saturated growth solution was prepared in accordance with the solubility data. Single crystal of NT was grown from the aqueous solution using slow evaporation method. The prepared solution was kept in a constant temperature water bath with an accuracy of ±0.01 °C. After a span of 19 days, single crystal with the dimension of 14 mm × 5 mm × 4 mm was harvested. The photograph of the grown crystal of NT is shown in Fig. 3.

3. Characterization

The grown NT crystals were subjected to X-ray diffraction studies using Bruker Kappa APEXII single crystal X-ray difffractometer with MoK$_\alpha$ (λ = 0.71073 Å) radiation. Powder X-ray diffraction pattern was recorded for NT crystal using Rich Seifert diffractometer with CuK$_\alpha$ (λ = 1.5405 Å) radiation over the range 10–70° at a scanning rate of 1°/min. The crystalline perfection of the NT crystal was elucidated by HRXRD studies using multicrystal X-ray diffractometry. The various functional groups of NT crystal were identified by the KBr pellet technique using a Perkin Elmer FTIR spectrometer in the range 4000–450 cm^{-1}. The transmission spectrum of the NT crystal was studied in the range 190–900 nm using T90+ spectrophotometer. TGA and DSC experiments were carried out from 30 to 500 °C on NETZSCH STA 409 instrument with a heating rate of 10 °C/min. Samples were weighed in an Al_2O_3 crucible. The dielectric measurement was carried out using HIOKI 3532–50 LCR HITESTER instrument. Microhardness measurement was carried out for NT crystal using Leitz-Wetzlar Vickers' microhardness tester fitted with a diamond pyramidal indenter attached to an optical microscope. The laser damage threshold value of NT was measured using Nd:YAG laser with 8 ns pulse width and 10 Hz repetition rate.

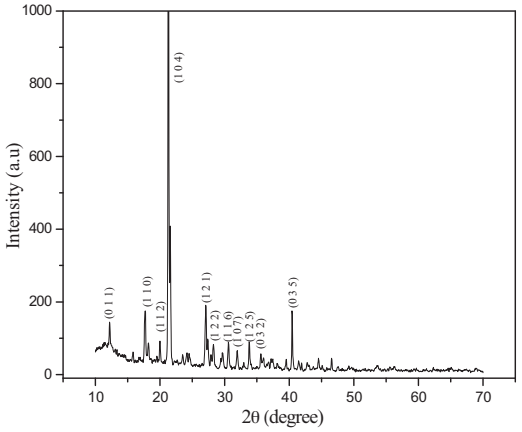

Fig. 4. Powder X-ray diffraction pattern of NT crystal.

Kurtz and Perry powder technique was employed on NT crystal to measure the second harmonic generation efficiency using Nd:YAG laser.

3.1. Single crystal and powder X-ray diffraction studies

The cell parameters of NT crystal were estimated by single crystal X-ray diffraction analysis and the obtained cell parameters are a = 6.547 Å, b = 7.725 Å, c = 21.549 Å, V = 1090 Å^3, with angle $\alpha = \beta = \gamma = 90°$. The grown crystal belongs to orthorhombic crystal system with space group of $P2_12_12_1$. The crystal data of NT are in good agreement with the reported values [7]. From the powder X-ray diffraction pattern, the presence of prominent Bragg peaks at specific 2θ angles confirmed the perfect crystalline nature (Fig. 4).

3.2. High resolution X-ray diffraction study

Fig. 5 shows the high resolution X-ray diffraction curve recorded using MoK$_{\alpha1}$ radiation for a typical NT single crystal specimen. From the figure, it is clear that the curve do not contain a single peak. On deconvolution of the diffraction curve, it is clear that the curve contains an additional peak which is 42 arc s. away from the main peak. The additional peak corresponds to an internal structural very low angle boundary. For a better understanding, the schematic of a structural grain boundary is given in the inset of Fig. 5. As seen in the inset, two regions of the crystal are misoriented by a finite or tilt angle 'α', it may be defined as the misorientation angle between the two crystalline regions on both sides of the structural grain boundary. The two regions may be perfect. If the value of α is ≤1 arc min,

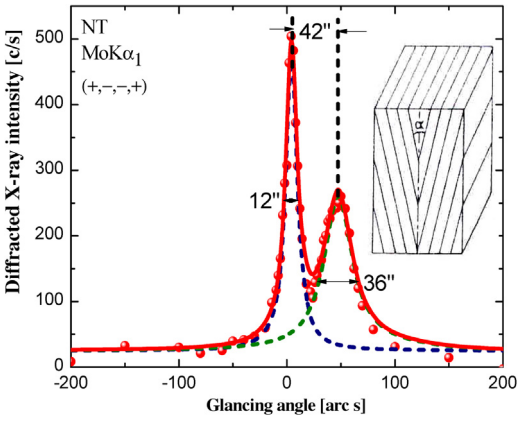

Fig. 5. HRXRD curve of NT crystal.