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Studies on the nonlinear optical single crystal: Ammonium D,L-tartrate ($C_4H_9NO_6$)

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ABSTRACT

The organic nonlinear optical material ammonium D,L-tartrate single crystal has been successfully grown by slow evaporation solution technique (SEST). The grown crystals were characterized by single crystal XRD and the lattice parameters have been confirmed. The structural perfection of the grown crystal was analyzed by high-resolution X-ray diffraction measurement. The optical transmittance spectrum shows that the material has a good optical transparency in the entire visible region with the UV cut-off wavelength at 234 nm. Thermogravimetric and differential scanning calorimetric measurements were performed to study the thermal properties of the grown crystal. Chemical etching studies were attempted to determine the dislocation density of the grown crystal. Mechanical behavior was assessed using Vickers hardness testing carried out on (0 0 1) crystallographic plane. The Kurtz–Perry powder SHG technique confirms the NLO property of the grown crystal and the efficiency of AMT crystal was found to be 1.3 times that of standard KDP crystal.

1. Introduction

Great efforts have been devoted to the research and design of highly efficient nonlinear optical (NLO) materials due to their widespread applications such as high-speed information processing, optical communications and optical data storage [1]. The potential applications of this field have not been realized due to lack of development of NLO materials. In the past two decades many organic and inorganic materials have been developed in this field. Organic materials have attracted much attention in the field of nonlinear optics in recent years. Ammonium derivatives are promising NLO materials and have been used as optical modulators and frequency converters [2]. In recent times, the growth and NLO properties of ammonium derivatives have been reported [3–5]. Likewise a number of tartaric acid complexes was studied as promising materials for second harmonic generation (SHG) such as L-histidinium-L-tartrate hemihydrates [6], 2-amino-5-nitropyridinium monohydrogen L-tartrate [7], L-lysine-L-tartaric acid [8], guanidinium L-hydrogen tartrate [9] and urea-tartaric acid [10]. Recently, the vibrational spectra and structural studies of ammonium D,L-tartrate (AMT) crystal were reported by Vidya et al. [11]. However, to our knowledge, no systematic studies appear to have been carried out on the crystals of AMT. The present work deals with the crystal growth of AMT with various characteristic studies such as single crystal X-ray diffraction, powder X-ray diffraction, high resolution X-ray diffraction (HRXRD), optical transmittance, thermal analyses (TG/DSC), chemical etching and microhardness.

2. Experimental

2.1. Material synthesis and crystal growth

AMT is one of the hydrolysis products of glutamine in acidic aqueous solution containing tartaric acid. It is expected that tartaric acid would share its hydrogen with the amide group of glutamine to form AMT. AMT ($C_4H_9NO_6$) was synthesized from L-glutamine and L-tartaric acid taken in equimolar ratio. The calculated amounts of salts were thoroughly dissolved in Millipore water (18.2 MΩ cm) and stirred well using a magnetic stirrer at room temperature. Optically good crystal having dimensions 13 mm × 4 mm × 2 mm with perfect external morphology was harvested within a period of 1 week and the grown crystal is shown in Fig. 1.

2.2. Solubility

AMT was dissolved in Millipore water and kept in a constant temperature bath controlled at an accuracy of ±0.01 °C with a cryostat facility for cooling below room temperature. It is continuously stirred using immersed magnetic stirrer to achieve homogeneity concentration throughout the volume of the solution. Solubility was measured at different temperatures of 25, 30, 35, 40, 45 and 50 °C. The solubility curve is shown in Fig. 2. From the solubility curve

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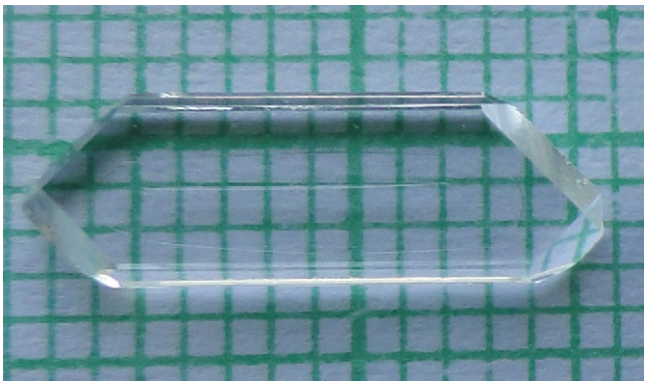

Fig. 1. Photograph of ammonium D,L-tartrate crystal grown from aqueous solution by slow evaporation method.

it is found that the AMT crystal possesses positive solubility coefficient since its solubility increases with the temperature.

3. Results and discussion

3.1. Single crystal X-ray diffraction

X-ray diffraction studies for the AMT crystal were carried out using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation. The goniometer equipped with the diffractometer is four circle goniometer with φ, χ, ω and 2θ axes by which the crystal is rotated. The crystal of size 0.30 mm × 0.25 mm × 0.25 mm was cut and mounted on a glass fiber using cyanoacrylate. The unit cell parameters were determined by collecting the diffracted intensities from 36 frames measured in three different crystallographic zones and using the method of difference vectors. From the single crystal X-ray diffraction measurements it is found that AMT crystal belongs to the orthorhombic system with non-centrosymmetric space group $P2_12_12_1$. The unit cell parameters are a = 7.60 Å, b = 7.79 Å, c = 11.00 Å, $\alpha = \beta = \gamma = 90^\circ$ and volume V = 651 Å^3 which is found to be in very good agreement with the previously reported values [11].

3.2. Powder X-ray diffraction

The grown crystals have been characterized by X-ray powder diffraction technique using a Rich seifert X-ray powder diffractometer with Cu Kα radiations of λ = 1.5408 Å. The 2θ range was analyzed from 10° to 70°, employing the reflection mode for scanning. The prominent peaks have been indexed. Fig. 3 represents the X-ray powder diffraction pattern for the grown AMT crystal.

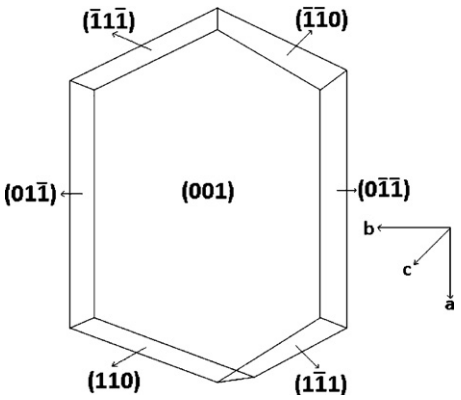

Fig. 2. Morphology of AMT crystal.

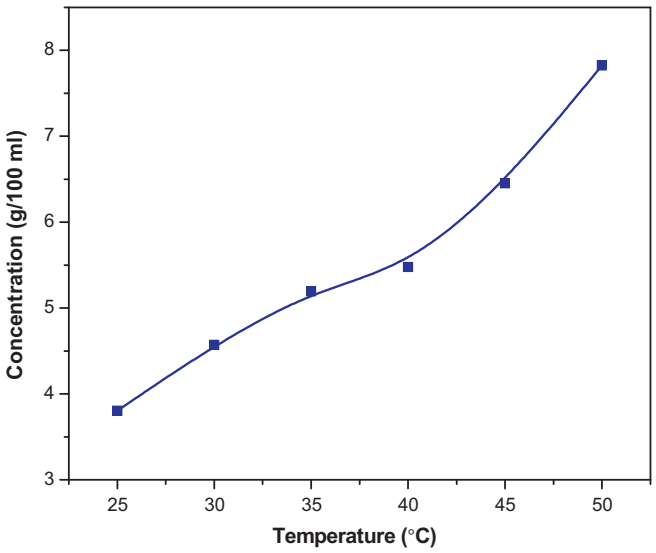

Fig. 3. Solubility curve.

3.3. Crystal morphology

The unit cell dimensions are determined from accurately measured 2θ values (the angular deviation from the direct undeviated beam) of about 25 reflections using an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation employed with $\omega/2\theta$ scan mode. Accurate unit cell parameters and orientation matrix for the crystal was obtained by a least-squares fit of several reflections in the range $15 < \theta < 25^\circ$. According to the chemical bonding theory of single crystal growth, the crystallographic structure controls single crystal growth behaviors [12,13,2,14–16], which warrants us a useful tool to study the growth history of single crystals. From the collected reflections the external morphology of the AMT crystal was drawn and the crystal faces were identified using the recorded set of h, k, l reflections. The external appearance or morphology of the grown crystals seems to be polyhedron in shape with eight symmetrically independent facets. Among these facets, the crystal has three prominent flat facets. The major flat facet is indexed as (0 0 1) plane and the other two developed planes have been indexed as (0 1 −1) and (0 −1 −1). It was observed that the growth rate of AMT along the a-axis is much higher than that along the b- and c-axis, which resulted in elongation along the ⟨0 1 0⟩ direction. The indexed morphology of AMT is shown in Fig. 4.

3.4. HRXRD analysis

To evaluate the crystalline perfection of the AMT crystal, high resolution X-ray diffraction (HRXRD) analysis was carried out. In this system, a fine focus (0.4 mm × 8 mm; 2 kW Mo) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was employed. The well-collimated and monochromated Mo $K\alpha_1$ beam obtained from the three monochromator Si crystals set in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. This arrangement improves the spectral purity ($\Delta\lambda/\lambda \ll 10^{-5}$) of the Mo $K\alpha_1$ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be ≪3″. The specimen crystal is aligned in the (+,−,−,+) configuration. Due to dispersive configuration of the third monochromator crystal with respect to the second monochromator, the spectral