Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 33–39

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Structural, optical, thermal and mechanical properties of Urea tartaric acid single crystals

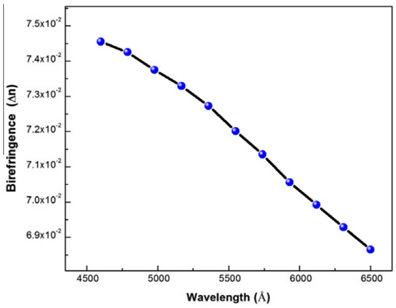
P. Vinothkumar, K. Rajeswari, R. Mohan Kumar, A. Bhaskaran *

Department of Physics, Presidency College, Chennai 600 005, India

HIGHLIGHTS

- Urea tartaric acid crystal has been grown by slow evaporation technique.
- Optical band gap of UT was estimated using UV–Vis–NIR spectral data.
- SHG efficiency of UT was found to be 3.2 times that of KDP and close to Urea.
- Birefringence values of UT were measured as a function of wavelength.
- Laser damage threshold value of UT was determined using Nd:YAG laser.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form 16 February 2015
Accepted 17 February 2015
Available online 27 February 2015

Keywords:
Solubility
X-ray diffraction
Recrystallization
Single crystal growth
Nonlinear optical material

ABSTRACT

Urea tartaric acid (UT) an organic nonlinear optical (NLO) material was synthesized from aqueous solution and the crystals were grown by the slow evaporation technique. The single crystal X-ray diffraction (XRD) analysis revealed that the UT crystal belongs to the orthorhombic system. The functional groups of UT have been identified by the Fourier transform infrared spectral studies. The optical transparent window in the visible and near the IR regions was investigated. The transmittance of UT has been used to calculate the refractive index (n) as a function of the wavelength. The nonlinear optical property of the grown crystal has been confirmed by the Kurtz powder second harmonic generation test. The birefringence of the crystal was determined using a tungsten halogen lamp source. The laser induced surface damage threshold for the grown crystal was measured using the Nd:YAG laser. The anisotropic in mechanical property of the grown crystals was studied using Vicker's microhardness tester at different planes. The etch pit density of UT crystals was investigated. The thermal behavior of UT was investigated using the TG–DTA and DSC studies.

Introduction

Organic materials like DAST, Urea and p-hydroxybenzoic acid exhibit large nonlinear susceptibilities, due to π-conjugation and molecular electronic properties [1]. Urea crystal belongs to the tetragonal crystal system with a needle like shape. The polar properties of Urea molecules contribute to their nonlinear optical characteristics, but at the same time, contribute strongly to an anisotropic growth. The Urea crystal possesses large nonlinearities, very good transparency up to 200 nm and large birefringence. Hence, it is a useful material for the processes of generation and mixing of frequencies, in a large range of the spectrum including UV [2–4]. However, the hygroscopic nature of Urea constrains its usage in growth processes and devices. Urea derivatives can be considered as important materials because of their nonlinearities, optical transparency, adequate birefringence and environmental stability.

---

* Corresponding author. Tel.: +91 9840800250; fax: +91 44 2235 2870.
E-mail address: abhaskaran_68@yahoo.co.in (A. Bhaskaran).

http://dx.doi.org/10.1016/j.saa.2015.02.063
1386-1425/

The Urea molecule is planar in crystal structure and the oxygen atom of Urea has more electronegativity compared to the nitrogen atom due to the lone pair of N atoms with π-electron on carbonyl results, causing a decrease in the electron density around the N atoms. Due to the charge transfer among the C, H and N molecules, the H^+ ions become weaker and O^- become stronger. Complex formation with Urea is possible in two ways. One through the N molecule, and the other through the O atom, which leads to ionic and addict complexes respectively. The chiral molecule or carboxylic acid binds with the O of Urea through O–H and forms many addiction complexes.

Urea tartaric acid is an additive compound formed by small organic molecules of Urea and the chiral molecule of L-tartaric acid. The crystal structure of UT is stabilized by a strong hydrogen bond (O–H···O) in three dimensional networks, between Urea and tartaric acid. The short O–H···O interactions of Urea and tartaric acid molecules can lead to an inclusion complex with non-centrosymmetrical structure.

The UT crystal is more rigid and is expected to enhance the optical nonlinearity due to cross linking of multidirectional hydrogen bonds or multi bond character in C–N and C–O bonds [5,6]. In this paper, the synthesis, growth and characterizations, such as X-ray diffraction (XRD), Fourier transform infrared spectrum (FTIR), UV–Vis–NIR spectroscopy studies, second harmonic generation (SHG), birefringence, thermal and laser damage threshold studies of the UT crystal have been investigated and reported.

Experimental details

Synthesis

The Urea and L-tartaric acid were taken in 1:1 molar ratio and dissolved in methanol separately at 40 °C and 35 °C, respectively. The solutions were stirred well for 4 h, and a clear solution was obtained. The prepared two solutions were mixed at 45 °C and the hot solution was allowed to cool at 30 °C using constant temperature bath. After 10 days, the white precipitation of Urea tartaric acid compound was formed as per the following reaction.

$$CO(NH_2)_2 + C_4H_6O_6 \rightarrow C_4H_6O_6 \cdot CH_4N_2O$$

The chemical composition of the UT compound determined using Perkin Elmer result analyser reveals that it contains 28.63% carbon (28.71%), 4.74% hydrogen (4.79%), 13.32% nitrogen (13.33%) where the figures in bracket represent the theoretical composition. These values are well agreed with calculated values Urea tartaric acid compound.

Crystal growth

The solution was left for slow evaporation, resulting in the formation of a compound of white microcrystalline organic salt. The synthesized salt was then purified by repeated recrystallization process using deionised water. The solubility of UT in deionised water was determined in the temperature range of 30–55 °C as illustrated in Fig. 1. The solubility curve reveals that the synthesized compound displays a positive temperature gradient of solubility. A saturated solution of the UT compound was prepared at 40 °C in an aqueous solution at pH 3 and kept in constant temperature bath for slow evaporation. Transparent UT crystals of average dimension 12 × 4 × 5 mm^3 were obtained, after a typical growth period of 45 days, as shown in Fig. 2. The grown crystal was stable in the environment without sacrificing its transparency.

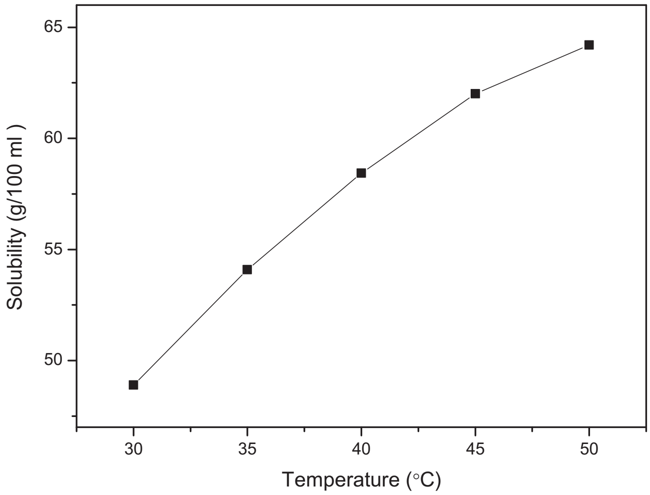


Fig. 1. Solubility curve of UT crystal.

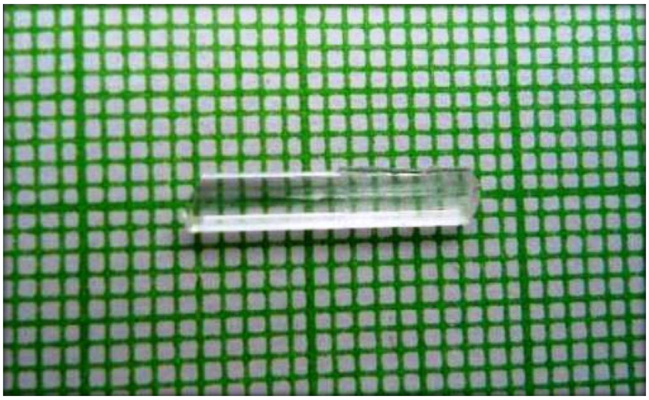


Fig. 2. As grown UT crystal.

Results and discussion

X-ray diffraction and morphology studies

The X-ray diffraction data was collected for a well-shaped single crystal of UT using a CAD-4, Enraf Nonius-FR590 automatic X-ray diffractometer, with MoK_α (λ = 0.7170 Å) radiation. The reflections from a finite number of planes were collected. It was observed that the crystal belongs to the orthorhombic system, with the following cell dimensions: a = 5.072 (3) Å, b = 9.792 (2) Å and c = 17.231 Å with unit cell volume V = 855.77 $Å^3$ and space group $P2_12_12_1$. The observed lattice parameter values are closely in agreement with the reported values [7], confirming the identity of the grown crystal. The typical morphology of the UT crystal is depicted in Fig. 3.

It was observed that the crystal has four prominent morphological faces, namely (230), (100), (010), and (001) with a-axis along the length of the crystal. Among them, (010), (001) are the thinnest crystallographic planes. The unit cell has the shortest dimension along the a-axis. It was inferred that the fastest growth of the crystal occurs along the shortest crystallographic axis [8].

FT-IR studies

The FT-IR spectral analysis was carried out to identify the chemical bonding and molecular structure of the material. The FT-IR spectrum of UT was recorded using a BrukerIFS-66V spectrophotometer in the region 400–4000 cm^{-1}, by KBr pellet technique.