



Growth, structural, optical, thermal and mechanical properties of cytosinium hydrogen selenite: A novel nonlinear optical single crystal



P. Jaikumar^a, S. Sathiskumar^b, T. Balakrishnan^{b,*}, K. Ramamurthi^c

^a PG & Research Department of Physics, National College (Autonomous), Tiruchirappalli, 620 001 Tamil Nadu, India

^b Crystal Growth Laboratory, Department of Physics, Periyar EVR College (Autonomous), Tiruchirappalli, 620 023 Tamil Nadu, India

^c Crystal Growth & Thin Film laboratory, Department of Physics & Nanotechnology, SRM University, Kattankulathur, 603 203 Kancheepuram, Tamil Nadu, India

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ABSTRACT

A novel nonlinear optical single crystal of cytosinium hydrogen selenite was grown from aqueous solution of cytosinium hydrogen selenite by slow solvent evaporation method at room temperature. The structural properties of grown crystal have been studied by single crystal and powder X-ray diffraction analysis. Presence of various functional groups was identified from Fourier transform infrared spectroscopy. The optical transmittance and absorbance spectra were recorded by UV–vis-NIR spectrometer and the grown crystal possesses good transparency in the entire visible region. The dielectric constant and dielectric loss of the crystal were calculated as a function of frequency at different temperatures. The mechanical strength of the cytosinium hydrogen selenite crystal was estimated using Vicker's microhardness tester. Etch patterns of the cytosinium hydrogen selenite crystal were obtained using distilled water as etchant for different etching time. Second harmonic generation efficiency tested using Nd:YAG laser is about 1.5 times that of KDP.

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1. Introduction

Two main types of bases found in DNA are purines and pyrimidines. Each of the two categories, cytosine and thymine, are pyrimidine derivatives, while guanine and adenine are purine derivatives [1]. But pyrimidine based organic materials are yet to be investigated for optical applications. Cytosine is one of the pyrimidine derivatives which consists of heterocyclic compound along with aromatic amine and keto groups [2,3]. Cytosine plays an important role in DNA/RNA base pairing, through several hydrogen-bonding patterns and controls the essential features of life as it is involved in genetic codon of 17 amino acids [4]. Cytosine is important not only in biological process but also in the areas of biosensors, nanomaterials and device fabrication [5]. The three dimensional single crystal structure of anhydrous cytosine [6] and cytosine monohydrate [7] was reported. Lee and Wang [8] reported the screening, manufacturing, photoluminescence, and molecular recognition of co-crystals of cytosine with dicarboxylic acid. Babulal Das and Baruah [9] reported the self assemblies of

hydrogen bonded single crystals of cytosine by changing the functional groups in polycarboxylic acid. Reji Thomas and Kulkarni [10] studied the hydrogen bonding in proton transfer complexes of cytosine with trimesic acid and pyromellitic acid. Single crystal structure of metal complexes of cytosine with cobalt chloride [11], copper chloride [12] and calcium chloride [13] have been reported. The single crystal structure of cytosinium hydrogen selenite (CHS) was reported by Takouachet et al. [14]. A survey of literature shows no systematic works available on the growth and characterization of cytosinium hydrogen selenite single crystal. Hence in this work we report on the synthesis and growth of CHS single crystal and characterization of the grown crystal for its structural, optical, mechanical, nonlinear optical, dielectric, thermal and etching properties for the first time.

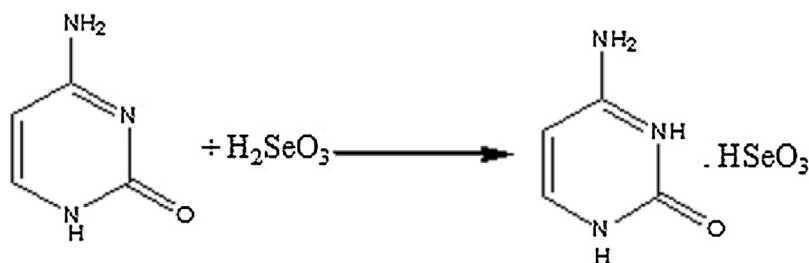
2. Experimental details

2.1. Synthesis

Aqua solution of CHS was prepared from equimolar amounts of AR grade cytosine and selenic acid (E-Merck). The reactants were thoroughly dissolved in doubly distilled water and stirred well for about three hours using temperature controlled magnetic stirrer to

* Corresponding author.

E-mail address: balacrystalgrowth@gmail.com (T. Balakrishnan).



Scheme 1. The reaction mechanism involved in the synthesis of CHS.

obtain a homogeneous mixture of solution. Evaporation of the prepared solution at room temperature yielded the product of CHS. Successive re-crystallization process was adopted to improve the purity of the synthesized CHS. The reaction mechanism of the synthesis of CHS material is shown in [Scheme 1](#).

2.2. Crystal growth

Saturated solution of CHS was prepared at room temperature using recrystallized salt in double distilled water and filtered using Whatman filter paper. The filtered solution was taken in a fresh beaker, closed with perforated polythene sheet and kept in a dust free atmosphere for crystallization. Slow evaporation method yielded single crystals of $4 \times 2 \times 2 \text{ mm}^3$ size in a growth period of 15 days. The grown CHS crystals are shown in [Fig. 1](#).

3. Results and discussion

3.1. X-ray diffraction studies

The grown single crystal was subjected to single crystal X-ray diffraction analysis at room temperature using Enraf Nonius CAD4 X-ray diffractometer with Mo K α ($\lambda = 0.7107 \text{ \AA}$) radiation to estimate the unit cell parameters. Single crystal structure studies show that CHS crystal belongs to orthorhombic system with a non-centrosymmetric space group PCa $_2$. The unit cell parameters obtained are $a = 7.024 \text{ \AA}$ (7.005 \AA), $b = 8.661 \text{ \AA}$ (8.634 \AA), $c = 12.741 \text{ \AA}$ (12.713 \AA) and $V = 771 \text{ \AA}^3$ (768 \AA^3) and these values agree well with the corresponding values reported by Takouachet et al. [14] given in parenthesis. Powder X-ray diffraction pattern of the CHS crystal was recorded on Reich Seifert diffractometer using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. The powdered sample was scanned over a 2θ range $10\text{--}80^\circ$ at a scan rate of $1^\circ/\text{min}$. The recorded powder X-ray diffraction peaks were indexed using AUTOX 93 software. The indexed powder X-ray diffraction pattern of CHS is given in [Fig. 2](#).



Fig. 1. As grown CHS crystals.

3.2. Fourier transform infrared spectral analysis

The Fourier Transform Infrared spectral analysis of CHS crystal was carried out in the range of $400\text{--}4000 \text{ cm}^{-1}$ using PerkinElmer FT-IR spectrometer by the KBr pellet method to study the presence of various functional groups. The recorded FT-IR spectrum is shown in [Fig. 3](#). The peak appears at 3316 cm^{-1} is assigned to NH $_2$ asymmetric stretching vibration. The peak at 3218 cm^{-1} is assigned to the frequency of NH $_2$ symmetric stretching vibration. The intense peak at 1727 cm^{-1} establishes the presence of C=O stretching vibration. The NH $_2$ in-plane deformation vibration mode appears at 1644 cm^{-1} . The C–NH and C=C stretching vibrations are observed at 1497 cm^{-1} and 1368 cm^{-1} respectively. The peak at 1237 cm^{-1} occurs due to C–N stretching vibration. The strong band observed at 821 cm^{-1} , 631 cm^{-1} and 428 cm^{-1} are due to the Se–O stretching vibration [15]. The observed wave numbers and the frequency assignments are presented in [Table 1](#).

3.3. UV–vis–NIR Spectral analysis

The UV–vis–NIR spectrum gives information about the changes in electronic structure of the molecule because the absorption of UV and visible light involves promotion of the electrons from the ground state to higher energy states. The UV–vis–NIR transmittance and absorbance spectrum was recorded in the wavelength range of $190\text{--}1100 \text{ nm}$ using Varian Cary 5E spectrophotometer. The UV transmittance spectrum recorded for CHS crystal of thickness 2 mm is shown in [Fig. 4](#). The lower cutoff observed in the CHS crystal is at 210 nm and the crystal shows about 90% transmittance in the wavelength range of $\sim 350\text{--}1100 \text{ nm}$. The absorption coefficient (α) was evaluated from the equation $\alpha = (1/t) 2.303 \log (1/T)$, where t is the thickness and T is the transmittance of the crystal. The direct band gap (E_g) was determined from the relation $\alpha = B (h\nu - E_g)^{1/2}/h\nu$, where $h\nu$ is the photon energy and B is the constant related to material. A plot of variation of $h\nu$ versus $(\alpha h\nu)^2$ was drawn and presented as an inset of [Fig. 4](#). The optical band gap (E_g) is obtained by extrapolating the linear part of the graph to the X-axis. This gives a band gap value of 5.2 eV for CHS crystal.

3.4. Dielectric studies

The dielectric constant of a material gives useful information about the nature of atoms, ions and their bonding in the material. The dielectric constant and dielectric loss of the CHS crystals were studied at three different temperatures using a HIOKI 3532 LCR HITESTER instrument in the frequency range $50\text{--}2 \text{ MHz}$. Cut and polished crystal of dimension $0.5 \times 0.4 \times 0.2 \text{ cm}$ was used for dielectric study. A two terminal copper electrode was used as a sample holder and the sample was held between the electrodes. The temperature of the sample was controlled and measured using a thermocouple. The thermocouple was fixed in the vicinity of

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