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Growth and characterization of Cadmium Thiosemicarbazide Bromide crystals for antibacterial and nonlinear optical applications

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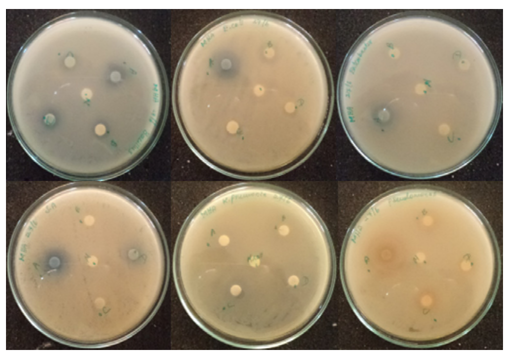
HIGHLIGHTS

- Growth of CTSB crystals has been achieved.
- Load dependent hardness parameters are calculated.
- Optical band gap has been estimated.
- Antibacterial efficiency of CTSB was analyzed by "Well Diffusion method".

GRAPHICAL ABSTRACT



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ABSTRACT

Semiorganic nonlinear optical crystals of Cadmium Thiosemicarbazide Bromide was grown by slow evaporation solution growth technique. The unit cell parameters were estimated by subjecting the crystals to single crystal X-ray diffraction. The grown crystals were subjected to Powder X-ray diffraction for analyzing the crystalline nature of the sample. FTIR studies reveal the functional groups and the optical characters were analyzed by UV–Vis spectral studies. Mechanical stability of the sample was assessed by Vicker's micro hardness test. The presence of surface dislocations was identified by chemical etching technique. Antibacterial study was carried out against ACDP declared harmful pathogens. SHG efficiency of CTSB crystal was tested using Nd: YAG laser and it was found to be ~1.8 times that of potassium dihydrogen phosphate.

Introduction

Materials with high optical nonlinearity are the target to researchers in the recent years. The intense search on NLO materials revolutionized the fields of telecommunications, medical diagnostics, high density optical recording and display systems manufacturing [1–3]. The field of Molecular engineering has succeeded in controlling the NLO properties of materials which promoted the growth and characterization of novel NLO materials [4]. NLO response is larger in organic materials when compared to inorganic materials due to the presence of active π bonds.

Organic molecules containing π electron conjugation systems asymmetrized by the electron donor and acceptor groups are highly polarizable entities for NLO applications [5]. Yet these materials have poor mechanical strength, thermal stability and laser damage threshold. Also organic NLO crystals are constituted by weak Van der Waals and hydrogen bonds with conjugated π electrons. In order to overcome these limitations, a new class of hybrid materials called the semiorganic crystals were explored and proposed as new candidates with interesting nonlinear optical

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response. Semiorganic crystals possess high thermal and mechanical stability than the organics. The various sub-networks in the semiorganic materials induce noncentrosymmetry and enhance the thermal and mechanical stabilities through hydrogen bonding interactions [6–8]. Semiorganic materials have received extensive attention owing to their fundamental and practical interest such as second order nonlinear optical (SONLO) responses, magnetism, luminescence, photography and drug delivery [9].

Single crystals of organic complex of thiosemicarbazide have suggested much interest in the last few years due to their nonlinear optical properties [10–13]. Thiosemicarbazide molecule is centrosymmetric in nature but when combined with inorganic salts it yields complexes that are non centrosymmetric [14]. Metal organic complexes offer high environmental stability combined with greater diversity of tunable electronic properties by virtue of the coordinated metal center [15,16].

Reported by a number of researchers, thiosemicarbazide complex is an interesting semiorganic nonlinear optical material which is gaining more attention day by day. Thiosemicarbazide along with its metal complex Cadmium Chloride was reported for the first time in literature by Sankar et al. [17], Maadeswaran et al. [18] studied the structural, optical, fluorescence properties of Cadmium Thiosemicarbazide Bromide single crystals. The birefringence properties of Thiosemicarbazide Cadmium Chloride monohydrate (TCCM) crystals was researched and reported by Maadeswaran et al. [19]., Not only the inorganic complexes but also the organic complexes of thiosemicarbazide were explored by numerous researchers [20–22]. Metal complexes of thiosemicarbazide were widely analyzed and their hybrid properties were published in many works. Thiosemicarbazide coordinates well with the alkali metal halides viz., Lithium Chloride and Potassium Chloride [23,24]. In a work reported by Maadeswaran et al., the dielectric constant of Thiosemicarbazide Potassium Chloride increases with the increase in temperature and the maximum dielectric constant was observed at 150 °C [23]. Organometallic complex crystal of thiosemicarbazide (thiosemicarbazide cadmium acetate) was grown by Selvaraju et al. [25] and the work reports the structural, optical, thermal and the SHG analysis of TSCA. The present work deals with the synthesis, growth, structural and optical characterization of the semiorganic nonlinear optical Cadmium Thiosemicarbazide Bromide single crystals. The article also highlights the mechanical stability, chemical etching analysis and the resistance offered by the title material against some harmful bacteria.

Experimental

Crystal growth

All the precursors and the solvent used in the experiment were highly pure. Cadmium Thiosemicarbazide Bromide was synthesized by taking Cadmium Bromide (Merck AR grade 99.8% pure) and Thiosemicarbazide (SRL AR grade 99.7% pure) in equimolar ratio. The title compound was synthesized according to the reaction

$$CdBr_2 + CN_3H_5S \longrightarrow Cd\ (CN_3H_5S)\ Br_2$$

The calculated amount of cadmium bromide was dissolved in deionized water and continuous stirring was carried out for 3 h. After 3 h thiosemicarbazide solution was added slowly and the mixture was maintained at 80 °C in order to avoid decomposition of the solute molecules. The solution gets homogenized after 8 h of agitation at 80 °C. The prepared solution was filtered after the complete dissolution of the precursors and left standby for 14 days on a constant temperature bath for the growth of CTSB crystals. A uniform temperature of 35 °C was maintained throughout the growth period. The as grown CTSB crystal is shown in Fig. 1.

Characterization

The lattice parameters of CTSB single crystal were estimated by subjecting the samples to single crystal X-ray diffraction analysis. The grown CTSB crystals were subjected to Powder X-ray diffraction analysis in order to find the particle size, and the crystalline nature of the sample. The presence of functional groups was identified by FTIR spectral studies. The optical characters of the sample were assessed by UV Visible spectral analysis. The mechanical characters of the sample were evaluated by Vicker's micro hardness test. The presence of dislocations on the surface of the sample was detected by chemical etching technique. The resistivity of the samples against ACDP (Advisory Committee on dangerous pathogens) declared harmful bacteria was tested by Antibacterial Study by "Well Diffusion method". The second harmonic generation efficiency of the sample was studied by Kurtz and Perry experimental set up for NLO testing.

Single crystal X-ray diffraction

The unit cell parameters of the grown crystals were estimated using ENTAF NONIUS CAD4 X-ray diffractometer equipped with Mo Kα radiation. The analysis was carried out at room temperature. The structure was solved by direct method and refined by full matrix least squares technique using SHELXL program. CTSB crystallizes in triclinic system with the space group P1. The estimated lattice parameter values are $a = 5.05$ Å, $b = 6.20$ Å, $c = 7.44$ Å, $\alpha = 76.15°$, $\beta = 76.20°$, $\gamma = 83.56°$ and $V = 232.94$ Å^3. The obtained lattice parameters agree very well with the reported values [18].

Powder X-ray diffraction

The powder XRD data were collected for the grown crystals using JEOL (JDX-8030) X-ray diffractometer equipped with Cu Kα radiation. The wavelength of the radiation used was 1.5406 Å. The sample was scanned at 25 °C in step scans with the scan rate and step size of 2 °C/min and 0.1 respectively within the range of 10–75°. The high crystalline nature of the sample was well revealed by the prominent peak at specific 2θ angle. The crystallite size was calculated using the Scherrer formula.

$$D = k\lambda/\beta\cos\theta$$

where k is a constant (0.9), λ is the X-ray wavelength, β is the broadening of diffraction line measured at half of its maximum intensity and θ is the Bragg's angle. The calculated average crystallite size of

Fig. 1. As grown CTSB single crystal.