



Synthesis, growth and characterization of dibromo thiosemicarbazide cadmium (II) chloride monohydrate-A semiorganic nonlinear optical single crystal

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ABSTRACT

One of the metal-organic nonlinear optical materials, dibromo thiosemicarbazide cadmium (II) chloride monohydrate (DBTSCCC) was synthesized. Solubility of DBTSCCC was determined in double distilled water at different temperatures. Three dimensional crystal structure of the grown crystal was determined by single crystal X-ray diffraction study. FT-IR study confirms the formation of the expected compound. Thermogravimetric and differential thermal analyses were carried out to study the thermal stability of the crystal. UV-vis-NIR spectrum recorded from 2 mm thick crystals shows ~65% transmitted in the wavelength region of 390-1100 nm. Linear optical constants such as extinction coefficient and refractive index were calculated. Optical nonlinearities of dibromo thiosemicarbazide cadmium (II) chloride monohydrate were investigated by Z-scan technique with He-Ne laser radiation of wavelength 632.8 nm. Mechanical properties of the grown crystal were studied using Vickers microhardness test. Second harmonic generation efficiency of the powdered dibromo thiosemicarbazide cadmium (II) chloride monohydrate was estimated using Nd: YAG laser and is ~7.0 times that of potassium dihydrogen orthophosphate.

Keywords: Characterization; Growth from solution; Organic compound; Nonlinear optical material

INTRODUCTION

Many new novel organic materials synthesized based on the predictive molecular engineering approach possess potential applications in nonlinear optics, telecommunication, frequency mixing, optical parametric oscillation, optical bi-stability, optical image processing and underwater communication [1, 2]. The advantage of the organic materials is that they offer high degree of synthetic flexibility through structural modification and exhibit high laser damage threshold [3]. In order to achieve good macroscopic nonlinear response in organic crystals, one requires an increase in the number of π -electrons and π -delocalization length, so as to lead to high molecular hyper polarizability and also proper orientation of the molecule in the solid state structure to facilitate high-frequency conversion efficiency. Organic crystals fall short of vital technological properties including mechanical strength, chemical stability and performance at low and high temperature. In order to overcome the shortcoming of the organic materials, some new classes of metal-organic nonlinear optical materials (NLO) have been developed [4,5].

The limitations on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing device grade organic single crystals have egged on scientists to adopt alternate strategies. Obviously began the development of hybrid organic–inorganic materials. The achievement to have high efficient optical quality organic based NLO materials in semiorganic class is to form compound in which a polarizable organic molecule is stoichiometrically bonded to inorganic host [6,7]. Regarding the organic ligands, small π -electron systems such as thiocyanate (SCN^-), urea [$\text{OC}(\text{NH}_2)_2$] and thiourea [$\text{SC}(\text{NH}_2)_2$] have been used with remarkable success. These ligands and their metal (group II B) complexes are always colorless. Potential NLO materials like bithiourea cadmium chloride (BTCC) and triallyl thiourea cadmium chloride (ATCC) are examples of this approach [8,9]. The structural analysis and detailed studies of the physico-chemical behavior of the materials have led to the conclusion that the central metal atoms cannot be ignored in calculating the NLO coefficients [10]. In this work, growth and characterization of one of the semiorganic NLO crystals, dibromo thiosemicarbazide cadmium (II) chloride, is presented.

MATERIALS AND METHODS

Growth of dibromo thiosemicarbazide cadmium(II)chloride monohydrate single crystals

Single crystals of dibromo (thiosemicarbazide) cadmium (II) chloride monohydrate (DBTSCCC) were grown by slow evaporation method from aqueous solution. Bromine solution, cadmium chloride and thiosemicarbazide were mixed in double distilled water in equimolar ratio. The prepared solution was stirred well and refluxed about 5 h, which on cooling yielded colourless salt at the bottom of the beaker. As a first step towards crystallization, the solubility of DBTSCCC in double distilled water was estimated in the temperature range of 30°C - 55°C (Figure 1). Saturated solution of DBTSCCC was taken in a beaker and the mouth was closed with the perforated lid in order to control the rate of evaporation and kept in room temperature for crystallization. One of the better quality crystals obtained from slow evaporation of the solvent at room temperature was used as a seed crystal. One of the transparent DBTSCCC crystals ($3 \times 3 \times 1 \text{ mm}^3$) were obtained from the aqueous solution of DBTSCCC by slow evaporation at room temperature and the same was used as the seed crystal. Slow evaporation at room temperature yielded a good quality single crystal of dimensions $8 \times 7 \times 2 \text{ mm}^3$ from aqueous solution in a growth period of 26 days and is shown in Figure 2.

RESULTS AND DISCUSSION

3.1. Single crystal X-ray diffraction

The X-ray data were collected for a well-shaped optical quality single crystal of DBTSCCC using a computer-controlled Enraf Nonius-CAD 4 single crystal X-ray diffractometer. The cell parameters of the single crystal were determined using 25 reflections. From the data collected for DBTSCCC crystal, it is observed that it belongs to the monoclinic system and the unit cell parameters are $a = 6.982(3) \text{ \AA}$, $b = 14.162(11) \text{ \AA}$, $c = 8.352(16) \text{ \AA}$, $\beta = 101.31(2)^\circ$ and are in good agreement with the reported values of Nicolo *et al.* [11].

3.2 FT-IR spectral analysis

Fourier transform infrared (FTIR) spectrum of DBTSCCC was recorded at room temperature in the spectral range of 4000 cm^{-1} - 400 cm^{-1} by KBr pellet technique using the Perkin Elmer grating Infrared spectrophotometer. The observed spectrum is shown in Figure 3. The absorption peak at 3290 cm^{-1} is due to O—H stretching vibration of water molecule. The peak at 2841 cm^{-1} is due to the C—H stretching vibration. The peak at 781 cm^{-1} is due to the C—Cl stretching vibration. The peak at 526 cm^{-1} is due to the C—Br stretching vibration [12]. The peaks at 1590 cm^{-1} and 1498 cm^{-1} are due to asymmetric and symmetric NH_3^+ bending modes respectively. NH_2 stretching vibration is absent at 2063 cm^{-1} , revealing that amino-nitrogen is one of the coordinate sites [12].

3.3 Linear and nonlinear optical properties.

The optical transmittance spectrum of DBTSCCC crystal of 2 mm thickness was recorded in the range of 200-1100 nm using Varian Cary 5E UV-vis-NIR spectrophotometer and is presented in Figure 4. The recorded UV-vis-NIR transmission spectrum of DBTSCCC shows the lower cutoff wavelength at 390 nm. The direct optical band gap of DBTSCCC is obtained from the relation ,

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where E_g is the optical band gap, α is the absorption coefficient and A is a constant.

The variation of $(\alpha h\nu)^2$ vs $h\nu$ in the fundamental absorption region is plotted in nm and a wide transparency in the entire region which makes the material suitable for second harmonic generation [13]. The transmittance of the crystal is about 65% in the visible and near infrared region. The E_g evaluated by the extrapolation of the linear part to energy axis is 2.4 eV. From the recorded absorption spectra, the linear optical constants like extinction coefficient and refractive index of DBTSCCC were calculated.

The extinction coefficient shows exponential decay as the photon energy increases. Refractive index being the measure of percentage of intensity of light reflected, the reflectance shows an increasing value along the photon energy. From Figures 6 and 7, it is clear that the extinction coefficient and the reflectance depend upon the absorption coefficient.

The Z-scan is a simple and popular experimental technique employed to measure the intensity dependent third order nonlinear susceptibility of the materials. It allows the simultaneous measurement of both the nonlinear refractive index and the nonlinear absorption coefficient. In this method, the sample is translated in the Z-direction along the axis of a focused Gaussian beam from the He-Ne laser wavelength of 632.8 nm and the far field intensity is measured as a function of the sample position. By properly monitoring the transmittance change through a small aperture at the far field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture) one can measure the intensity dependent absorption of the sample. When both the methods (open and closed) are used for the measurements, the ratio of the signals determines the nonlinear refraction of the sample. The third order nonlinear refractive index and the nonlinear absorption coefficient were evaluated by the Z-scan measurements (Figures 8 & 9). A spatial distribution of the temperature in the crystal surface is produced due to the localized absorption of a tightly focused beam propagating through the absorbing sample. Hence a spatial variation of the refractive index is produced which acts as a thermal lens resulting in the phase distortion of the propagating beam.

Table.1 portrays the experimental details and the results of the Z-scan technique for DBTSCCC. The calculated value of the nonlinear refractive index n_2 is $-4.126 \times 10^{-8} \text{ cm}^2/\text{W}$. From the results of the open aperture Z-scan curve, it can be concluded that as the minimum lies near the focus ($Z=0$), the nonlinear absorption is regarded as two photon absorption [14]. The nonlinear absorption coefficient is found to be $3.1 \times 10^{-3} \text{ cm/W}$. The third order susceptibility of DBTSCCC is $2.0 \times 10^{-6} \text{ esu}$.

Kurtz and Perry [15] test was performed to estimate the SHG efficiency of the powdered DBTSCCC crystal. The crystal was illuminated by Spectra Physics Quanta Ray DHS2. Nd:YAG laser output wavelength of 1064 nm with pulse width of 8 ns and repetition rate 10 Hz. The second harmonics signal, generated in the crystal was confirmed from the emission of green radiation by the crystal. The SHG radiations of 532 nm green light was collected by a photomultiplier tube (PMT-Philips Photonics-model 8563) after being monochromated (monochromator-model Triax-550). The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052B). The input laser energy incident on the powdered sample was 3.4 mJ. Powder SHG efficiency obtained for DBTSCCC is about 7.0 times that of potassium dihydrogen orthophosphate. The relatively higher NLO efficiency is due to the crystal structure of DBTSCCC which consists of infinite parallel chains of coordinated cadmium atoms linked to each other by a double bridge of bromine (Br) and sulfur (S). The water molecule is located between the chains and is connected by hydrogen bonds with the nitrogen (N) atoms of the organic ligands. The coordination geometry about Cd is an octahedron formed by three Br, two S and one N atoms [11].

3.4. Thermal analysis

The thermal stability of DBTSCCC was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using SDT Q600 V8.3 Build 101 instrument between the temperatures 50°C and 1100°C at a heating rate of $10^\circ\text{C}/\text{min}$ in Nitrogen atmosphere (Figure 10). The DBTSCCC sample weighing 2.355 mg was taken for the measurement. From the DTA curve it is observed that, the material is stable up to 110°C , the melting point of the substance. Above this point, the material begins to attain an endothermic transition and begins to decompose. The sharp endothermic peak shows a good degree of crystallinity of the sample [16].

3.5. Microhardness analysis

Vickers microhardness test was carried out on DBTSCCC crystal using microhardness tester fitted with a diamond indenter. The indentations were made using a Vickers pyramidal indenter for various loads of 25, 50 and 100 g and the diagonals of the impressions were measured using Shimadzu (Japan); Model HMV-2 hardness instrument. The

microhardness studies were made on the well-developed (101) face. The indentation time was kept as 25 s for all the loads. Vickers microhardness number (H_v) was evaluated from the relation $H_v = 1.8544(P/d^2)$ Kg/mm², where P is the applied load in Kg and d is the diagonal length of the impression in mm. The variation of microhardness values derived as a function of applied load is shown in Figure 11. From the Vicker's microhardness studies, it is observed that the hardness value increases upto a load of 100 g. For load above 100 g cracks started developing around the indentation mark which may be due to the release of internal stresses [17].

Table 1 Measurement details and the results of the Z-scan technique

Measurement details and the results of the Z-scan technique	
Laser beam wavelength	632.8
Focal length of the lens	24 cm
Optical path length	125 cm
Beam radius of the aperture (ωa)	4 mm
Aperture radius (ra)	4 mm
Sample thickness (l)	1.7 mm
Beam radius (ωL)	3 mm
Effective thickness (L_{eff})	1.69 mm
Linear absorption coefficient	0.625
Nonlinear refractive index (n_2)	-4.106×10^{-8} cm ² /W
Nonlinear absorption coefficient (β)	3.153×10^{-3} cm/W
Real part of the third-order susceptibility [$Re(\chi^3)$]	2.30×10^{-6} esu
Imaginary part of the third-order susceptibility [$Im(\chi^3)$]	1.20×10^{-6} esu
Third-order susceptibility (χ^3)	2.015×10^{-6} esu

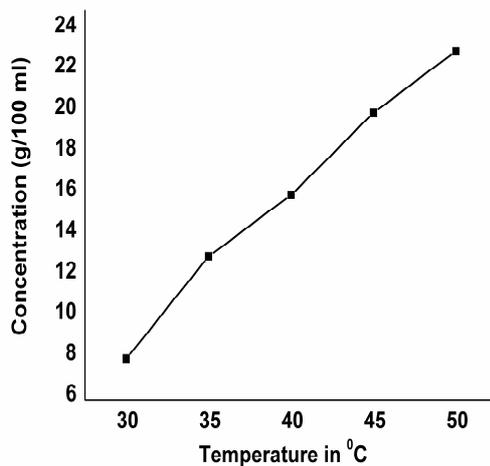


Fig.1 Solubility curve of DBTSCCC

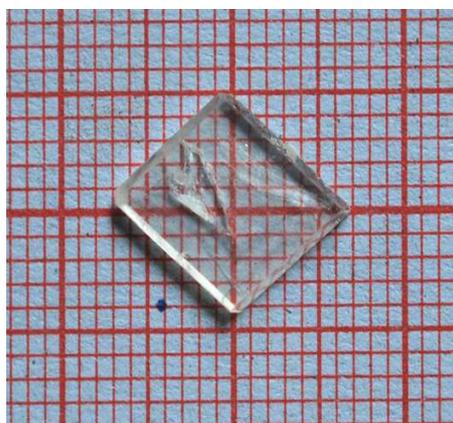


Fig. 2 The as-grown DBTSCCC crystal

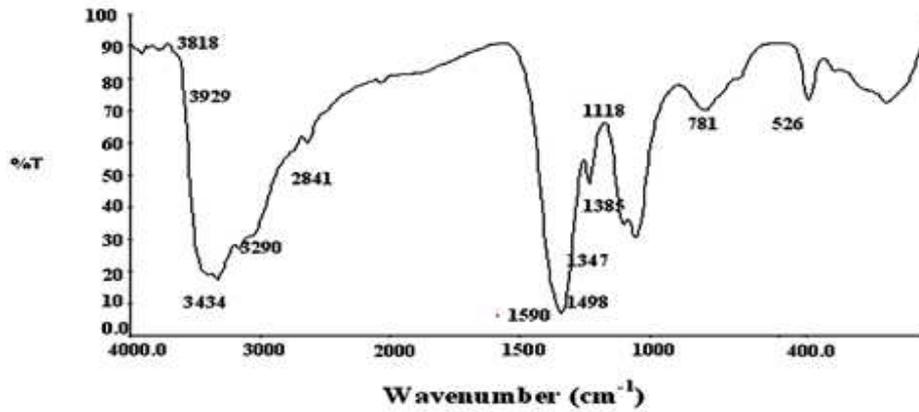


Fig. 3 The FTIR spectrum of DBTSCCC

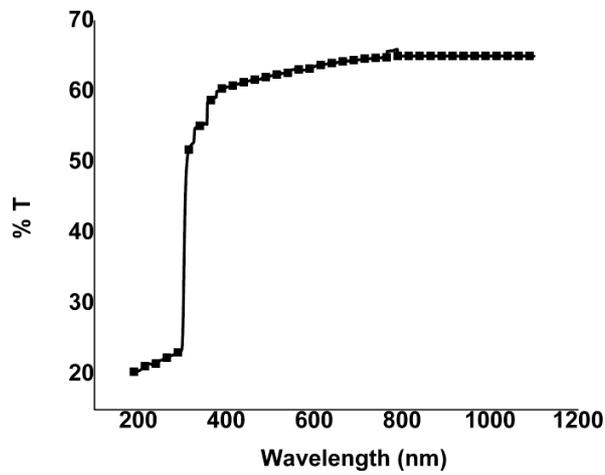


Fig. 4 UV-vis-NIR spectrum

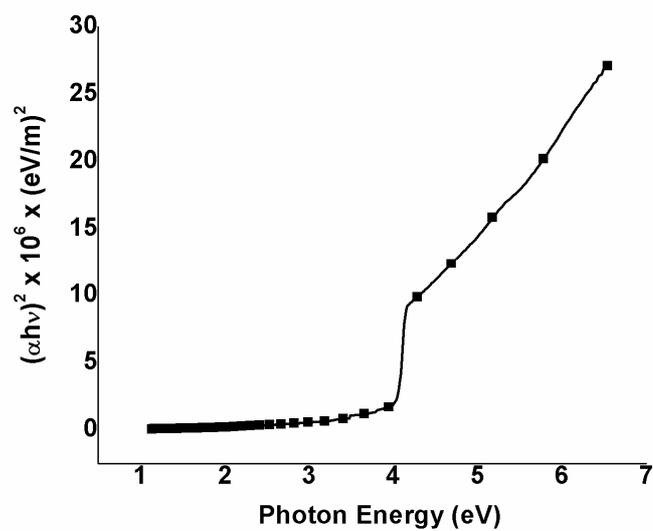


Fig. 5 $(\alpha h\nu)^2$ vs photon energy

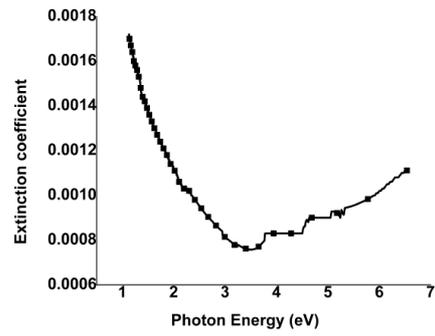


Fig. 6 Extinction Coefficient vs Photon Energy

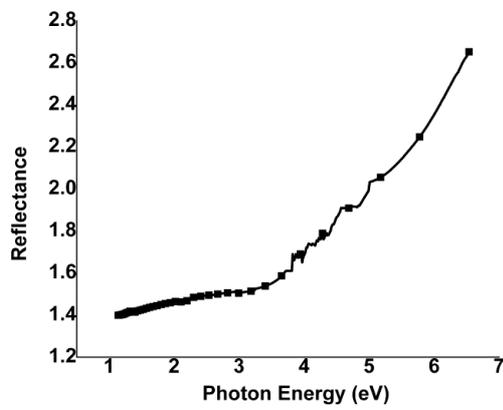


Fig. 7 Reflectance vs Photon Energy

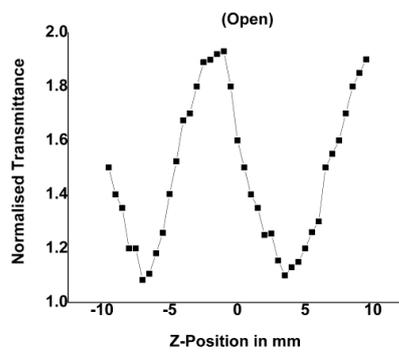


Fig. 8 Open curve of DBTSCCC

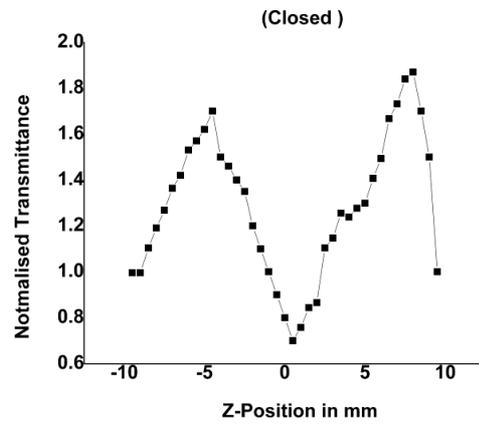


Fig.9 Closed curve of DBTSCCC

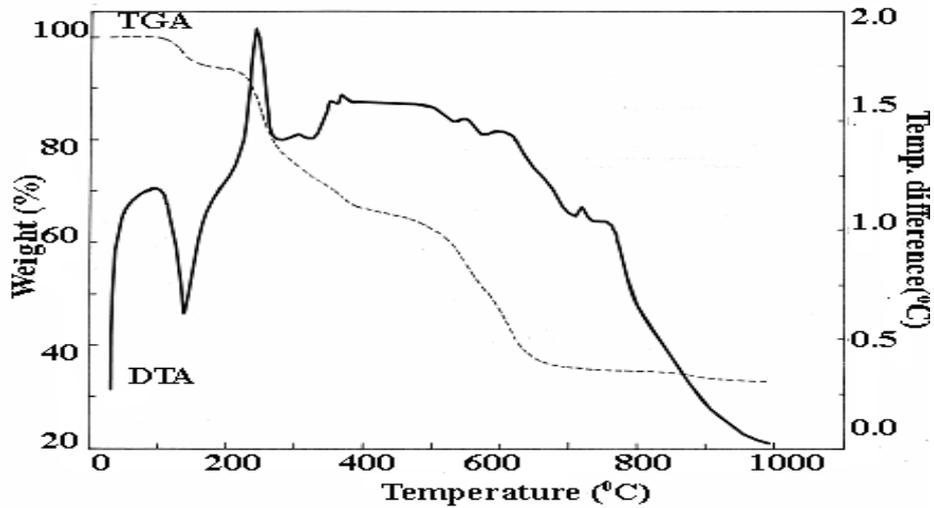


Fig.10 TGA/DTA curve of DBTSCCC

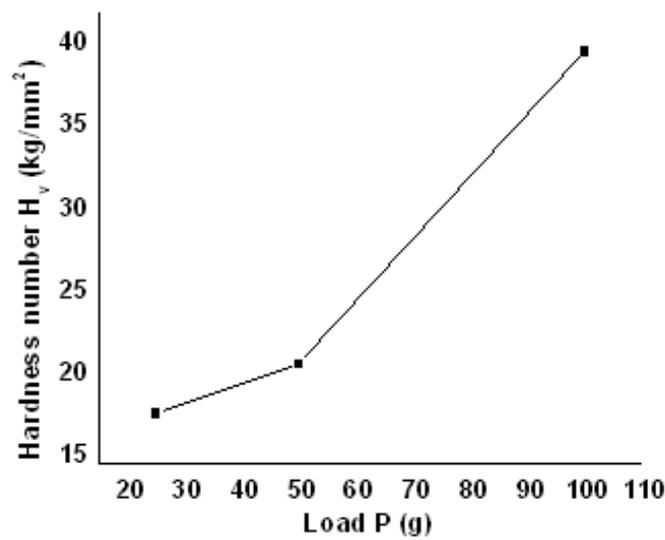


Fig. 11 Microhardness behavior of DBTSCCC

CONCLUSION

Slow evaporation technique at room temperature yielded DBTSCCC single crystal of dimensions $8 \times 7 \times 2 \text{ mm}^3$. Determination of unit cell parameters the single crystal X-ray diffraction technique confirmed the identity of the synthesized material. FTIR spectral studies confirmed the presence of functional groups of DBTSCCC crystal. The range of optical transmittance window and the lower cut off wavelength at 390 nm, identified through UV-vis-NIR spectrum, reveals that DBTSCCC crystal is a potential candidate for second harmonic generation. Vickers microhardness study reveals that the DBTSCCC stands upto 100 g load. TGA and DTA studies show that the compound is stable up to its melting point 150.5°C . Powder SHG efficiency of DBTSCCC estimated is about ~7.0 times that of potassium dihydrogen orthophosphate and is due to the presence of infinite parallel chains of coordinated cadmium atoms linked with bromine and sulfur in a double bridge and hydrogen bonds in the crystal structure.

Acknowledgment

The authors thank to Dr. K. Panchanatheeswaran, Professor in Chemistry (Rtd), School of Chemistry, Bharathidasan University, Tiruchirappalli for fruitful discussion. Authors thank Prof. D. Sasti Kumar, Department of Physics, NIT, Tiruchirappalli, for extending the facilities available in his laboratory for recording the Z-scan measurements.

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