Growth and characterization of a semiorganic nonlinear optical crystal- Cadmium thiosemicarbazide bromide

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Nonlinear optical single crystal of cadmium thiosemicarbazide bromide (CTSB) has been grown from solution growth method by slow evaporation technique at room temperature. Chemical composition of synthesized material was confirmed by CHNS analysis. The CTSB crystals were characterized by single crystal X-ray diffraction study and powder X-ray diffraction analysis. The presence of functional groups was identified by FT IR spectral study. The optical properties of the crystals were reveled by UV-Visible absorption spectra. The fluorescence spectrums of CTSB were recorded and the band gap was calculated. The second harmonic generation efficiency measurement is found to be higher than that of KDP crystal.

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1. Introduction

In the recent years, an intense worldwide effort has been focused on the research of design and development of materials with large optical nonlinearity. The fast development in the field of opto-electronics includes optical frequency conversion, optical data storage and optical switches in the initially confined laser fusion systems has stimulated the search for highly nonlinear optical crystals for efficient signal processing. The nonlinear optical (NLO) materials possess wide range of applications in the field of telecommunications, high density optical recording, color display, medical diagnostics, etc., [1-3]. The overwhelming success of molecular engineering in controlling NLO properties has promoted the growth and characterization of a variety of new types of NLO materials [4]. The search for new frequency conversion materials over the past decades has concentrated primarily on organic and inorganic compounds. The inherent limitations on the maximum attainable nonlinearity in inorganic materials comparing to organic crystals in technological properties such as mechanical strength enhanced chemical stability and performance at low and high temperature. These limitations made scientist adopt alternate strategies which led to the discovery of new class of semiorganic nonlinear optical materials for device fabrication technology, owing to large nonlinearity, high resistance, too large induced damage, less deliquescence, low angular sensitivity and good mechanical hardness [5-7].

Organic-inorganic hybrid materials have received extensive attention in recent years owing to their great fundamental and practical interest such as second order nonlinear optical (NLO) responses, magnetism, luminescence, photography and drug delivery [8]. Single crystals of organic complex of thiosemicarbazide have suggested much interest in the last few years due to their nonlinear optical properties [9-12]. The centrosymmetric thiosemicarbazide molecule when combined with inorganic salts yields noncentrosymmetric complexes, which has nonlinear optical properties [13]. Metal complexes of thiourea, commonly called semiorganic combines the high

optical nonlinearity and chemical flexibility of organics with physical ruggedness of inorganic. Metal organic complexes offer high environmental stability combined with greater diversity of tunable electronic properties by virtue of the coordinated metal center [14-15].

In the present investigation, the growth of cadmium thiosemicarbazide bromide crystal has been achieved by solvent evaporation technique at room temperature. Characterization studies such as CHNS analysis, single crystal XRD, powder XRD, FT IR, UV-Vis, and fluorescence was carried out. The NLO property of the single crystal has been confirmed by SHG test.

2. Synthesis and growth technique

All the starting materials were highly pure and the synthesis and growth process were carried out in aqueous solution. The cadmium thiosemicarbazide bromide has been synthesized by taking cadmium bromide and thiosemicarbazide in a 1:1 stoichiometric ratio. Cadmium thiosemicarbazide bromide crystal was synthesized according to the reaction.

$$CdBr_2 + NH_2\text{-}NH\text{-}CS\text{-}NH_2 \text{ ---------> } Cd\,(NH_2\text{-}NH\text{-}CS\text{-}NH_2)\,Br_2$$

The calculated amount of cadmium bromide was first dissolved in deionized water. Then thiosemicarbazide was added to the solution slowly. The solution was agitated with a magnetic stirring device and filtered after complete dissolution of the starting materials. The prepared solution was left standby for several days at room temperature, thereby colourless crystals were obtained in 25 to 30 days (Fig. 1). The priority of the synthesized crystal was improved by successive recrystallization processes.

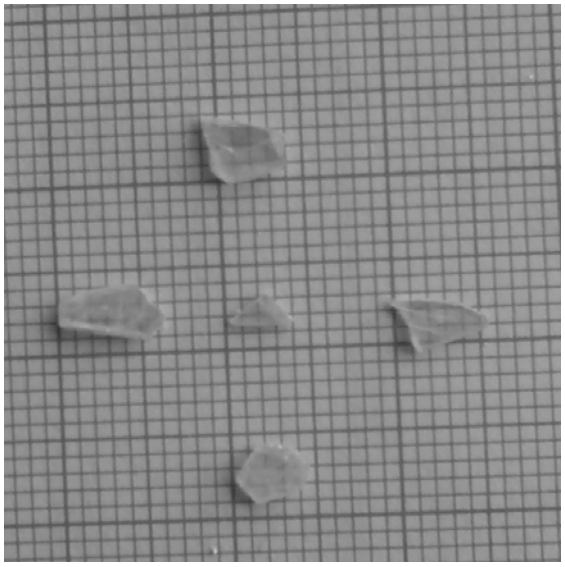

Fig. 1. As-grown CTSB crystals.

3. Results and discussion

3.1 CHNS analysis

To confirm whether the material synthesized was surely the above-named compound, analysis of carbon, hydrogen, nitrogen and sulfur was carried out on the sample employing Vario EL III Elementar. The experimental and calculated values of C, H, N and S agree well with each other thus confirming the formation of CTSB and are represented in Table1.

Table 1. Elemental analysis of CTSB crystals.

Element	Experimental values (%)	Theoretical values (%)
C	3.42	3.30
H	1.51	1.38
N	12.86	11.56
S	15.02	13.41

3.2 Single crystal XRD analysis

The unit cell parameters of grown crystal were carried out using Enraf Nonius-CAD4 diffractometer with Mo Kα radiation at room temperature. The structure was solved by direct method and refined by full matrix least squares technique using SHELXL-97 program [16]. The title material CTSB crystallizes in triclinic system with space group P1, the lattice parameter values are a=5.09 Å, b=6.14 Å, c=7.53 Å, α=77.80°, β=77.20 °, γ=84.00 °, V=225 $Å^3$.

3.2 X-ray powder diffraction analysis

The powder X-ray diffraction data were collected for the grown single crystals. The pattern was recorded using a JEOL JDX services instrument with CuK_α. (K_α =1.5406Å) radiation. The sample was scanned in the range 10-90 °C at a scan rate of 2° /min. The finely powdered materials of the grown CTSB crystal were used for the analysis. The powder X-ray diffraction pattern with diffraction indices is shown in Fig. 2. The prominent well resolved Bragg's peak at specific 2θ angle reveals the high crystalline nature of the crystal. The crystallite size (D) was calculated using Scherer's formula from the full width at half maximum (FWHM)

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

Where, β→the broadening of diffraction line measured at half of its maximum intensity, λ→X-ray wavelength (1.5406Å), θ→Bragg's angle, k→constant (0.9). The calculated average crystallite size is about 89 nm.

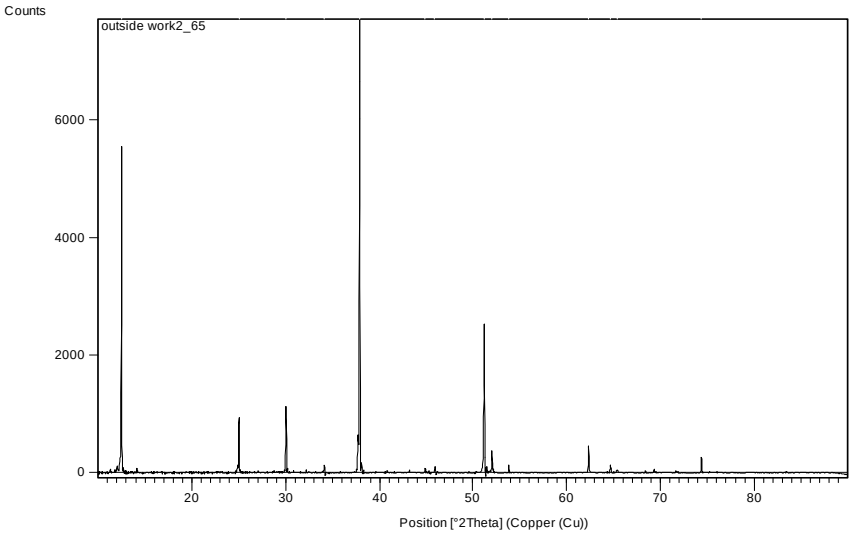

Fig. 2 powder XRD patterns of CTSB crystals.

Table 2. X- Ray powder diffraction data of CTSB crystals.

2θ	d-spacing [Å]	FWHM
12.4914	7.08045	0.0612
25.0210	3.55601	0.0816
30.0390	2.97243	0.1020
34.1168	2.62590	0.0816
37.8737	2.37361	0.0816
44.8569	2.01898	0.1224
45.9358	1.97404	0.2448
51.2374	1.78153	0.1020
52.0635	1.75519	0.1020
53.8550	1.70096	0.0816
62.3608	1.48783	0.0816
64.6885	1.43980	0.1224
65.3979	1.42589	0.4896
74.3755	1.27443	0.0816
12.4914	7.08045	0.0612
25.0210	3.55601	0.0816

3.3 FTIR studies

The Fourier transform infrared analysis was carried out between 4000 and 400 cm^{-1} by recording the spectrum using Thermo Nicolet V-200 FTIR spectrometer by KBr pellet technique in order to reveal the metal complex coordination. The broad envelope positioned between 3289 and 3168 cm^{-1} corresponds to the asymmetric and symmetric stretching vibrations of NH_2 group Fig. 3. The NH_2 bending 1641 cm^{-1}, vibrational mode was almost observed in the same frequencies as in thiourea, suggesting that the nitrogen to metal bond is not present in the coordination complex. The absorption at 1562 cm^{-1} is due to N-C-N asymmetric stretching. The symmetric and asymmetric stretching of C=S are observed at 1457 and 748 cm^{-1} respectively, and the absorption peak at 683 cm^{-1} is due to the C-Br stretching. The assignments confirm the presence of various functional groups present in the material, tabulated in Table 3.

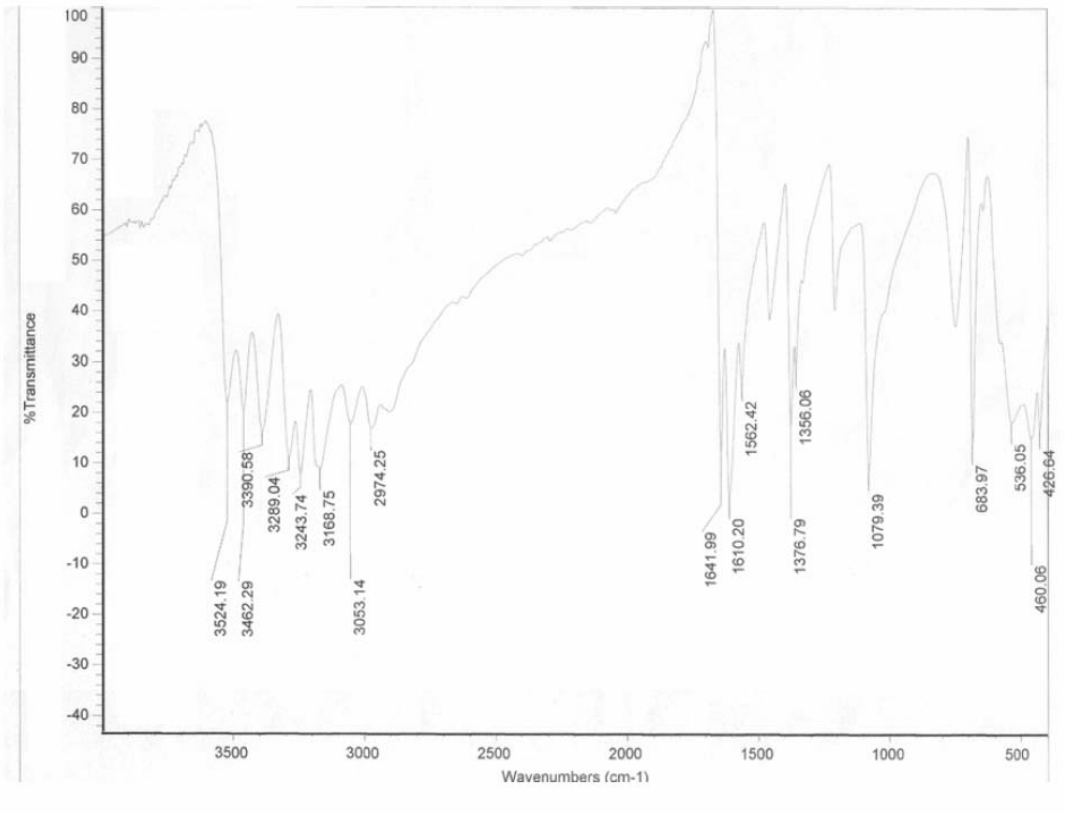

Fig. 3 FT IR Spectrum of CTSB crystals.

Table 3. FT IR spectral data of CTSB crystals.

Wavenumber (cm^{-1})		Assignments
Thiourea	CTSB	
3280	3289	Asymmetric NH_2 stretching
3167	3168	Symmetric NH_2 stretching
1627	1641	NH_2 bending
1593	1562	Asymmetric N-C-N stretching
1472	1457	Asymmetric C=S stretching
1089	1079	Asymmetric N-C-N stretching
740	748	Symmetric C=S stretching
648	683	C-Br stretching

3.4 UV-Vis spectral analysis

To understand the optical transparency of the CTSB crystal in the UV-Visible region of the electromagnetic spectrum, an optical absorption spectrum of CTSB crystal was recorded. The

spectrum was recorded by employing JASCO V-530 dual beam spectrophotometer at room temperature in the range 200 -800 nm with a scanning speed of 400 nm/min. The lower cut-off wavelength was found to be 236nm. In the entire visible region the optical absorption spectrum is flat and constant. This transparent nature in the visible region is a desirable and useful property for NLO applications (Fig. 4.).

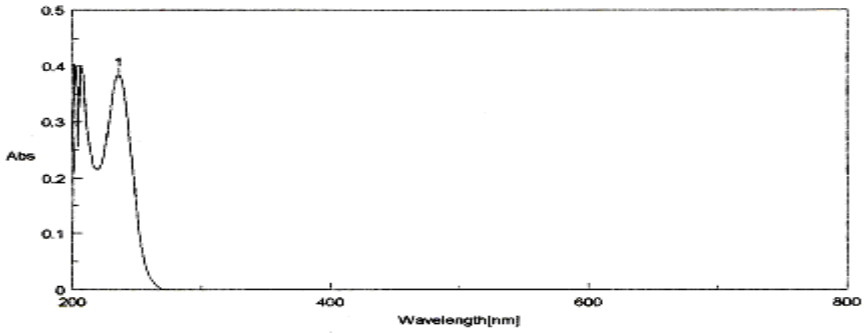

Fig. 4 UV-Vis spectrum of CTSB crystals

3.5 Photoluminescence

The excitation and emission spectra of CTSB were recorded. The excitation spectrum was recorded in the range of (260-300) nm as shown in Fig. 5. The sample was excited at 280 nm, a peak at 380 nm was observed in the emission spectrum Fig. 6. The result indicates that CTSB crystals have violet fluorescence emission.

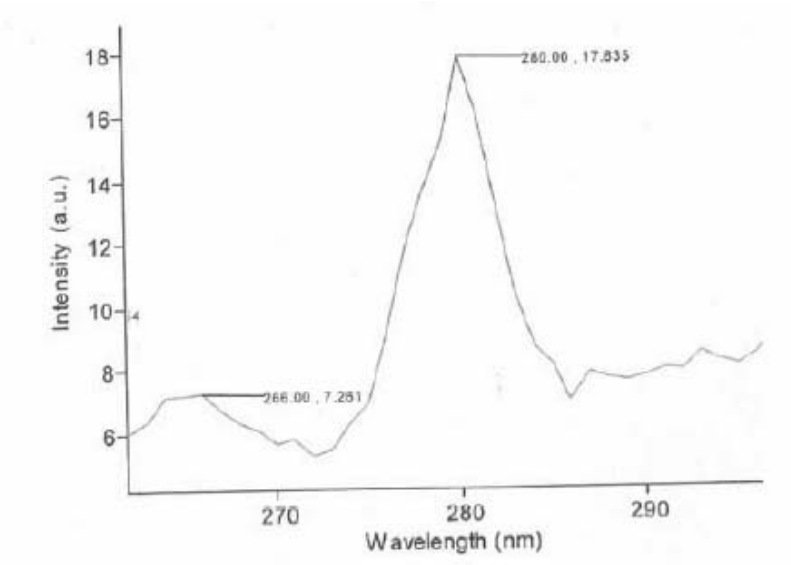

Fig. 5. Excitation spectrum of CTSB crystals

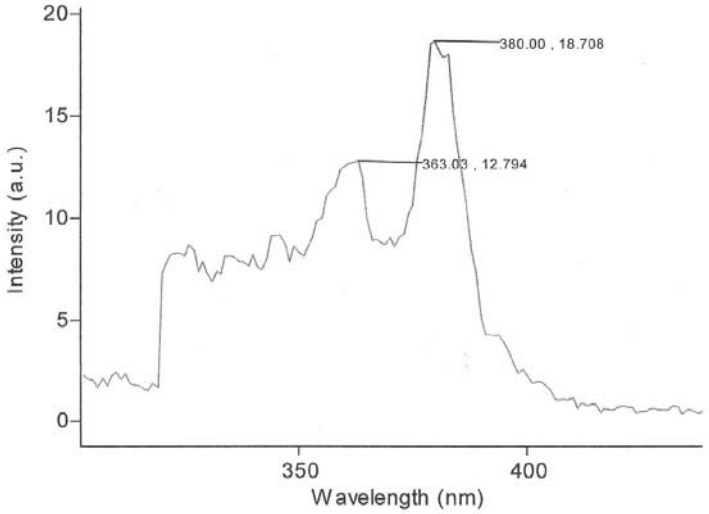

Fig. 6 Emission spectrum of CTSB crystals.

3.6 Nonlinear optical studies

Nonlinear optical property of the crystal was determined by the modified version of powder technique developed by Kurtz and Perry [17]. The crystal was ground into fine powder and packed in the micro capillary tube. A Q-switched Nd:YAG laser (1064 nm) has been used. The input pulse energy of 3.2 mJ/pulse and pulse width 8ns was incident on the crystalline powder. The SHG signal at 532 nm is detected using a photomultiplier tube (PMT). The generation of the second harmonics was confirmed by the emission of green radiation. The present result shows that SHG conversion efficiency of KDP is 105 mV and for CTSB is 198 mV.

4. Conclusion

Cadmium thiosemicarbazide bromide, a new semiorganic material has been synthesized by solvent evaporation technique at room temperature. Chemical composition of the synthesized compound was established by CHNS analysis. Lattice parameter values were determined by using single crystal XRD. The sharp well defined Bragg's peak confirms the crystalline nature of the materials and calculated average crystallite size is about 89 nm. The FT IR analysis verified all the functional groups and molecular strength of the crystal. The optical transparency and the lower cutoff wavelength were identified from the recorded UV-Vis spectrum. The violet fluorescence emission of the crystal confirms its fluorescence behavior. The Kurtz powder second harmonic generation test shows that the crystal is a promising candidate for optical second harmonic generation applications.

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