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Synthesis, growth, spectral, photoluminescence and VSM properties of a semiorganic nonlinear optical crystal-cadmium thiourea bromide [CTB]

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Single crystals of cadmium thiourea bromide (CTB), a novel semiorganic nonlinear optical material were grown from aqueous solution by slow evaporation method. Powder X-ray diffraction pattern and FT IR spectrum analysis confirmed the formation of crystal. CTB has good optical transmission in the entire visible region, which is an essential requirement for a nonlinear crystal. Fluorescence spectra analysis was carried out on the crystal. The optical second harmonic generation conversion efficiency of CTB was determined using Kurtz powder technique. The magnetic property of the crystal was investigated.

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1. Introduction

Nonlinear optics (NLO) is a new frontier area of science and technology which will play a major role in the emerging technology of photonics, the technology of this century. Nonlinear optical processes provide the key functions of frequency conversion and optical switching [1]. Most of the NLO organic crystals usually have poor mechanical and thermal properties and are susceptible for damage during processing even though they have large NLO efficiency and it is difficult to grow larger size optical-quality crystals of these materials for device applications. Purely inorganic NLO materials have excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity because of the lack of extended p-electron delocalization [2-3]. Interests have been centered on semiorganic crystals which combine the positive aspects of organic and inorganic materials resulting in useful nonlinear optical properties. The obvious development of semi-organic materials, where the organic ligand is ionically bonded with inorganic host refined the search of new materials with high optical nonlinearities which is an important area due to their optical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reaction, laser remote sensing, color display, medical diagnostics, etc., [4]. Recent studies have shown that thiourea derivatives have potential coordination behavior with transition metals [5]. In the recent past, the nonlinear optical properties of some products of thiourea [6, 7] include the advantages of both organic and inorganic part of the complex which have attracted great interest. The thiourea molecule is an interesting organic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds. The centrosymmetric thiourea molecule yields non-centrosymmetric complexes, which has nonlinear optical properties.

In the present study, thiourea is combined with cadmium bromide to form a semiorganic nonlinear optical material. Here we report the growth of single crystals of cadmium bromide thiourea by slow evaporation technique and its characterization.

2. Synthesis and crystal growth

In the present investigation, cadmium thiourea bromide crystals were grown by slow evaporation solution growth of thiourea in saturated aqueous solution of cadmium bromide in the equimolar ratio 1:1 as per the reaction

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

The synthesis of the material was covered at room temperature. Initially thiourea was dissolved in deionized water followed by cadmium bromide, since thiourea has the coordinating capacity to form different phases of metal-thiourea complexes, the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. For slow evaporation, few holes were made on the paper and kept undisturbed. The CTB crystal was obtained by self nucleation using saturated solution which is optically transparent and free from macroscopic devices. Transparent needle shaped crystals were harvested after a typical growth period of 15-20 days. The purity of the

solution was improved by successive recrystallization process.

3. Results and discussion

3.1 X-ray powder diffraction studies

X-ray powder patterns of the crystal were recorded on a JEOL JDX services diffractrometer using CuK_α (λ=1.5406 Å) radiation. The sample was scanned for a 2θ range 10-70º and at a scan rate of 2º /min. The powder X-ray diffraction pattern of CTB is shown in Fig.1.The disclosure of well-defined Bragg's peaks at specific 2θ angle shows high crystallinity of CTB crystals. The d-spacing and their relative intensities of the diffraction peaks are tabulated (Table 1) in the pattern list.

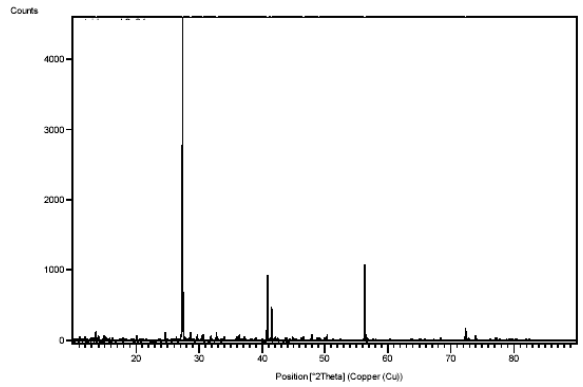

Fig. 1. powder XRD patterns of CTB crystals.

Table 1. X- Ray powder diffraction data of CTB crystals.

2θ	FWHM	d-spacing
13.7209	0.9792	6.44865
27.3959	0.1428	3.25291
28.6722	0.2040	3.11094
30.5507	0.3264	2.92380
32.7888	0.3264	2.72916
40.8628	0.0816	2.20662
41.4965	0.0816	2.17437
46.6101	0.4896	1.94703
49.0739	0.6528	1.85489
56.3708	0.0816	1.63086
72.3639	0.1632	1.30481

3.2 FT IR spectra

Fourier transform spectroscopy is effectively used to determine the molecular structure and identify the functional groups in the synthesized compound. In order to analyze quantitatively the presence of functional groups in the crystal, FT IR spectra was recorded using Thermo Nicolet V-200 FT IR spectrometer by KBr pellet method in the region 4000-400 cm^{-1} as shown in Fig. 2. When compared with the spectra of thiourea, a few peaks were found to be slightly shifted. Thiourea is potentially capable of forming co-ordinate bonds through sulfur and nitrogen. Most of the metals form a complex through sulfur [8]. The broad envelope positioned between 3433 and 3201 cm^{-1} corresponds to the symmetric and symmetric stretching modes of NH2 grouping of thiourea. The well resolved peak at 1613 cm^{-1} is due to the NH_2 bending vibration. The narrow and strong bands at 1490 and 1436 cm^{-1} are attributed to the stretching vibration of C-N and C-S. The band at 1093 cm^{-1}can be ascribed to C-N stretching vibration. There is an intense sharp peak at 712 cm^{-1}due to N-H wagging vibration. There is an intense sharp peak at 473 cm^{-1} assigned to N-C-S stretching vibration. The increase in C-N stretching and N-C-N bending vibrational modes confirms the C=N double bond character and the metal ion Cd^{2+} is coordinated with thiourea through the sulfur atoms. Assignments of corresponding wavenumber are shown in Table 2.

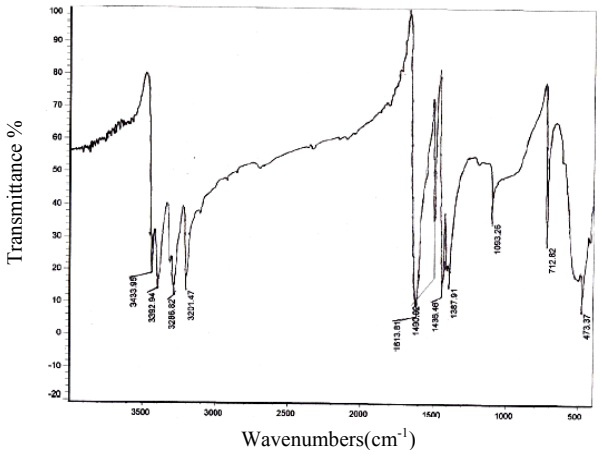

Fig. 2. FT IR Spectrum of CTB crystals.

Table 2. FT IR spectral data of CTB crystals.

Wavenumber (cm^{-1})		Assignments
Thiourea	CTB	
3376	3392, 3433	N-H stretching
3280	3286	NH2 asymmetric stretching
3167	3201	NH2 symmetric stretching
1627	1613	NH2 bending
1472	1490	C-N asymmetric stretching
1417	1436, 1387	C-S asymmetric stretching
1089	1093	C-N symmetric stretching
740	712	C-S symmetric stretching
469	473	N-C-S bending

3.3 UV-visible absorption

Absorption spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. The UV-Visible spectra for the grown CTB crystal were recorded using JASCO V-530 dual beam spectrophotometer in the wavelength region 200-800nm with a scanning speed of 400nm/min. The percentage of absorption versus wavelength is shown in Fig. 3. The CTB crystal show good transmission in the entire visible region and the lower cutoff wavelength is 237 nm. The absence of absorption in the entire visible region between 400-800 nm is a favorable circumstance and desirous properties for NLO activity.

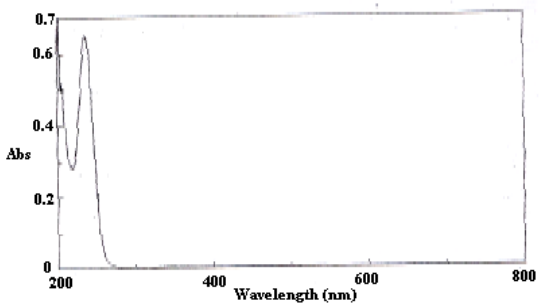

Fig. 3. UV-Vis spectrum of CTB crystals.

3.4 Photoluminescence

Photoluminescence (PL) technique, the spectrum emitted by the radioactive recombination of photogenerated minority carriers, is a direct way to measure the band gap energy. However, large amount of impurities induces a large free carrier density in the bands. Consequently, a different carrier interaction causes remarkable modification of the line shape and spectral energy of the PL feature [9]. The excitation and emission spectra of CTB were recorded in (FP-6500) spectrofluorometer. The excitation spectrum was measured in the range of (260-300) nm, the sample was excited at 280nm, a peak at 361 and 381nm was observed in the emission spectrum (Fig. 4). The calculated band gap energy was about 3.2 eV.

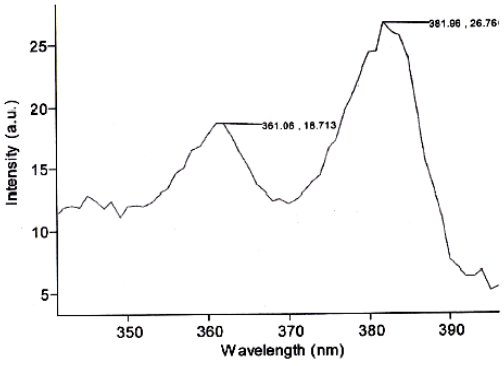

Fig. 4. Emission spectrum of CTB crystals.

3.5 Nonlinear optical test

In order to confirm the NLO property of CTB, second harmonic efficiency test was performed by the Kurtz and Perry [10]. Powder technique using Q- switched mode locked Nd: YAG laser operating at the fundamental wavelength 1064 nm. The crystal was ground into powder and densely packed between two transparent glass slides. The specimen was illuminated using the Nd: YAG laser which serves as source. Microcrystalline materials of KDP were used as reference. The output from the Q-switched laser was focused onto the sample. The output could be seen as a bright green flash emission from the second harmonic generation in the crystal.

3.6 Vibrating sample magnetometer

The vibrating sample magnetometer is a widely used instrument for determining magnetic properties for a large variety of materials: diamagnetics, paramagnanetics, ferromagnetics and antiferromagnetics [11]. The magnetic property of CTB crystal was investigated using VSM (Lakeshore 7404 series). Field Vs momentum curve reveals that the CTB crystal exhibits less diamagnetic property.

4. Conclusions

Optically good quality crystals of cadmium thiourea bromide were grown using the slow solvent evaporation technique. Chemical composition of the synthesized material was confirmed by CHNS analysis. FT IR studies show that in the spectra of CTB there is a shift in the frequency band in the low frequency region which reveals that thiourea form sulfur to cadmium bonds in the crystal. Optical absorption spectra revealed the optical properties of the grown crystals. Fluorescence spectra were investigated using the emission property of the crystal. The NLO property of the crystal was examined by performing Kurtz powder test using Nd: YAG laser. The CTB crystal exhibits diamagnetic property. The studies expose that CTB is a suitable material for opto-elctronic applications.

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