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Growth and Optical properties of BisThiourea Sodium Cadmium chloride-A non-linear optical Crystal

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Abstract;*A new semi organic nonlinear optical material BisThioureasodium cadmium Chloride (BTSCC) has been synthesized. The solubility studies have been carried out in the temperature range 30- 55 C. Single crystals of BTSCC have been grown by slow evaporation of saturated aqueous solution at room temperature. The structural parameters of the grown crystals have been determined by powder crystal X– ray diffraction technique. The UV-Vis-NIR transmittance spectrum has been recorded in the range 200 – 1400 nm. The second harmonic generation has been confirmed by the Kurtz powder test.The FT-IR spectrum has been recorded in the range 400 – 4000 cm-1 and the spectral bandshave been compared with similar thiourea complexes.*
Keywords*: BisThioureasodium cadmium chloride, FT-IR, nonlinear optical material, SHG.*

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I. Introduction

The search for new and efficient NLO materials has resulted in the development of a new class of materials called semi organics. A materials which have large optical non linearity, high second harmonic generation (SHG) coefficients and stable physicochemical properties are known as semi organicmaterials. Among the semi organic NLO materials, the thiourea metal complexes deserve a special attention because of their interesting crystalline perfection, electronic properties and optical quality [**1**]. They have the double advantage of both the organic and inorganic components [**2**].In addition to that these complexes exhibit ligand to metal charge transfer (LMCT) by an electron movement from ligand to metal and metal to ligand (MLCT) owing to the pi electron delocalization which is an essential property for a crystal to exhibit NLO activity [**3**] has been reported. Often these have high melting points and high degree of chemical inertness are driven by their interesting properties and potential utility in various applications, such as molecular magnets, optical limiting traits, luminescence materials sensors [**4**], and catalysis. Some of the potential thiourea-metal complexes reported are bis(thiourea)cadmium chloride (BTCC) [**5, 6**]. In ionic doping, Na^+ is an important metal ion with defined thermal stability and ionic conductivity properties and is a versatile dopant. Further, Na^+ ion doping utilized for enhancing optical efficiency and thermal stability of bimetallic coordination complex in the optoelectronic applications [**7**]. However, there are very few reports on the semi organic bimetallic thiorea doped metal halide crystals for higher order optical applications.Hence in the present study, an attempt has been extended to grow bisthiorea sodium (I) cadmium (II) chloride single crystals by slow evaporation method at 4 pH to increase its quality and size than those reported previously. In order to prove the as grown bimetallic material (BTSCC) is optically active, the title compound has been subjected to various characterizations such as powder crystal XRD, FT-IR, UV-Vis-NIR, DSC, THG and dielectric studies.

II. Experimental

2.1 Materials and methods

The high-purity elements such as cadmium chloride (LOBA Chemie, 99.95 % Assay), sodium chloride (LOBA Chemie, 99.95 % Assay) andThiourea (LOBA Chemie, 99.99 % Assay) with AR grade were used as the starting materials in the slow evaporation chemical reaction method at a temperature of 28˚C. Double distilled deionised water was used as the solvent material to carry out the solubility state of the required reactants, maintaining the pH.at 4.0 of the temperature range of of 28˚C-55˚C.

The X-ray diffraction (XRD) patterns of the prepared samples were recorded using an X'PERT-PRO diffractometer with Cu Ka (1.54060 A °) at room temperature. The analysis was carried out at room temperature. The FTIR analysis was carried out using a PERKIN ELMER FTIR spectrometer by KBr pellet technique for deducing the presence of functional groups and the coordination of disodium copper oxalate dihydrate. The spectrum was recorded within the range of 400 cm^{-1} to 4000 cm^{-1}.

The optical characterization ofbisthioureasodium cadmium chloride crystal was carried with the help of a LAMBDA 35 UV Visible spectrophotometer. The absorption spectrum was traced to the range of 190 to 1100 nm. EDS is a chemical microanalysis technique utilizes X-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analysed volume. This method can detect elements from Na upward in the periodic table. The NLO property and phase matching property of the grown crystals have been confirmed by Kurtz and Perry second harmonic generation (SHG) test using Quanta ray spectra physics Nd: YAG laser.

2.2 Growth of $NaCd_{(0.5)}$ $[CS (NH_2)_2]_2Cl_2$

Bisthioureasodium cadmium chloride (BTSCC) single crystals wasproduced by dissolving thiourea, sodium chloride and cadmium chloride in 2:1:0.5 ratio in an aqueous medium.Calculated quantities of the reactants were dissolved thoroughly in the double distilled deionised water. Using magneticstirrer, the prepared solution was stirred thoroughly toavoid co-precipitation of multiple phases, as thioureais a strong coordinating material to form different phases ofmetal-thiourea complexes. The solution was thoroughlyfiltered by maintaining the pH at 4.0 to increasethe growth rate of the crystaland kept in a dust free environment atroom temperature.When sodium chloride and cadmium chloride are reacted with thiourea, bisthiourea sodium cadmiumchloride is produced **[8]** according to the following reaction (1).

$$NaCl+\frac{1}{2}CdCl_2 +2[CS\ (NH_2)_2]\longrightarrow NaCd_{(0.5)}\ [CS\ (NH_2)_2]_2Cl_2 \quad (1)$$

BTSCC crystals of dimension 8mmx5mmx3mmwere harvested in a period of24-30 days. Grown crystals are shown in **Fig. 1**.The yield of the crystal is 99%.

Figure1: crystal growth size of the BTSCCcrystal

III. Results And Discussion

3.1 Powder X-ray diffraction Analysis

The powder x-ray diffraction spectrum of Bisthiourea sodium cadmium chloride crystal is shown in **Fig.2**. The Powder XRD patterns identified that the formed crystals are in the single phase with good crystalline nature. As seen from the XRD pattern, each peak has got a finite width. The calculated hkl values of the bisthioureacadmium chloride crystal with respect to the two theta values of the as-grownbisthiourea sodium cadmium chloride crystals are shown in the **Table 2**. The diffraction peaks observed for BTSCC crystals are well agreed with the reported values [**9**] confirmed that the grown BTSCC crystal belongs to the orthorhombic system with space group $Pna2_1$. The calculated lattice parameters of the as-grown crystal$NaCd_{(0.5)}[CS(NH_2)_2]_2Cl_2$were a=5.94A°, b=6.50 A°, c=13.23 A°, and$\beta = 90°$revealed that the structure and space group of the purebisthiourea cadmium chloride and sodium doped bisthiourea cadmium chloride are identical with each other.

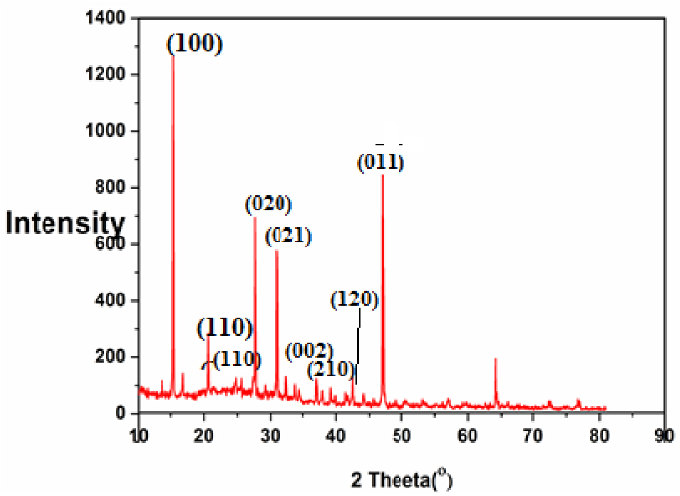

Figure 2: Powder XRD spectrum of BTSCC crystal

3.2 FTIR Spectral analysis

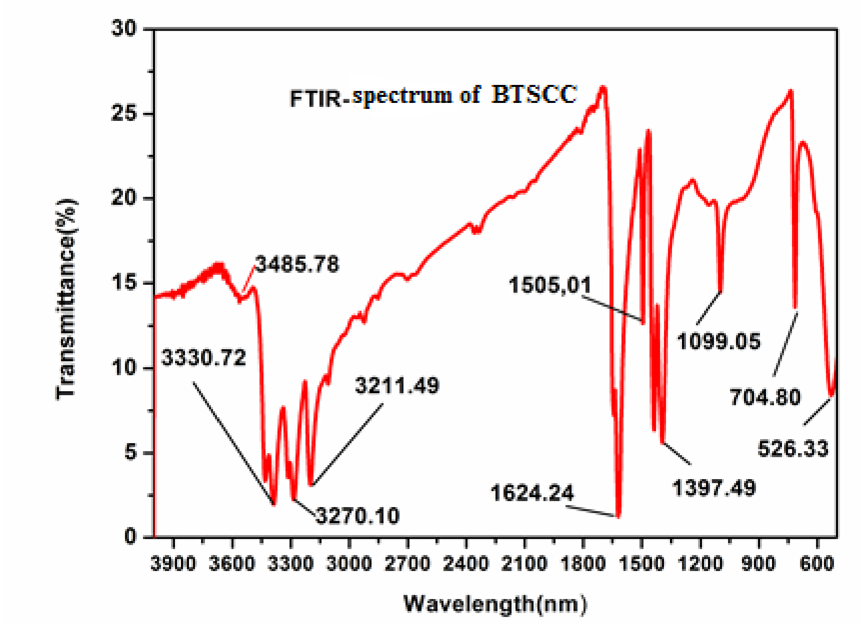

Figure 3: FTIR Spectrum of functional group assignments forBTSCC crystal

The FTIR spectra observed for the BTSCC crystal is shown in **Fig.3**. Various modes of vibrations of the functional group Assignments of BTSCC crystal by FT-IR spectroscopy and the main shiftsof the frequency bands are observed in the low frequency region is shown **Table 1**. This conforms the metal coordination tothiourea.The broad envelope observed at 3485.78 cm^{-1}, 3330.72 cm^{-1}, 3270.10 cm^{-1} and 3211.49 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of γ_s (NH_2) grouping of cadmium coordinated thiourea [**10**]. The absorption bands observed at 1505.01 $cm^{-1}$and 1624.24cm^{-1} forthiourea have been assigned to the γ_s (N-C-N) and δ_{as} (NH_2) stretching vibration of as-grown crystal. For the crystals grown in the present study, frequencies corresponding to the above vibration are found to be increased. This result can be attributed to the increase the double bond character of carbon to nitrogen bond on complex formation. The γ_s(C=S) stretching of thiourea (1397.49 cm^{-1}) is found to be shifted to lower values in the spectra observed for the grown crystals. This clearly indicates the coordination of sulfur with cadmium and sodium. On coordination through sulfur, the nature of vibration is slightly changed. γ_s(N-C-N) stretching vibration(1099.05 cm^{-1}) of thiourea is found to be shifted to higher values in the spectra clearly established that the delocalization of nitrogen lone pair electrons over carbon-sulfur bond. This is essential for the NLO property of any material [**11**]. The symmetric stretching vibration γ_s(C=S)at 704.80 cm^{-1} and the asymmetric bending vibrationδ_{as}(N-C-N) at 526.33 cm^{-1} bands of thiourea is found to be shifted to lower values in the spectra revealed that the decrease in double bond character of carbon to sulfur bond on complex formation.

Table 1: Various modes of vibrations of the functional group Assignments of BTSCC crystal by FT-IR spectroscopy. (Band positions in (cm−1).

NaCuOx crystal band position(cm^{-1})	Assignment
3485.78, 3330.72, 3270.10&3211.49	$\gamma_s(NH_2)$
1505.01	γ_s(N-C-N)
1624.24	$\delta_{as}(NH_2)$
1397.49	γ_s(C=S)
1099.05	γ_s(N-C-N)
704.80	γ_s(C=S)
526.33	δ_{as}(N-C-N)

δas; asymmetric bending; δs: symmetric bending; γs: symmetric stretching; γas: asymmetric stretching.

3.3 EDX spectrum

The EDX pattern of Na^+ doped band pure is thiourea cadmium chloride crystal was recorded (**Fig**.4) and the EDX spectrum confirmed the presence of cadmium, sodium, chlorine, nitrogen and sulphur of the as-grown sodium doped bisthioureacadmium chloride single crystals. It is observed that the atomic concentration of Na, Cd, Cl, S and N in the BTSCC crystal is calculated (**Table**2).

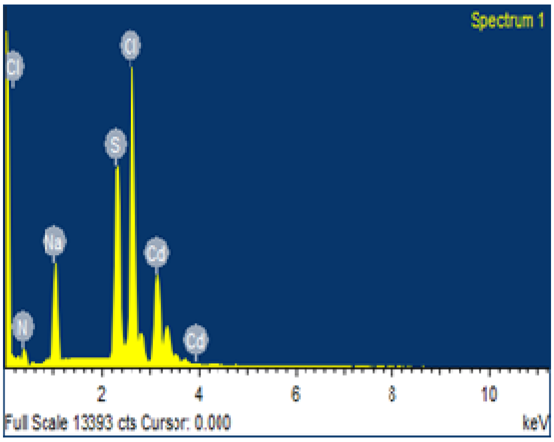

Table 2:Atomic weight percentage of BTSCC crystal

ELEMENT	WEIGHT(%)	ATOMIC(%)
NK	19.54	41.30
Na K	11.10	14.29
S K	14.75	13.66
Cl K	28.67	23.95
Cd L	25.94	6.83
TOTAL	100	100

Figure 4: EDXspectrum of BTSCC crystal

3.4 Photo luminescentspectrum (PL)

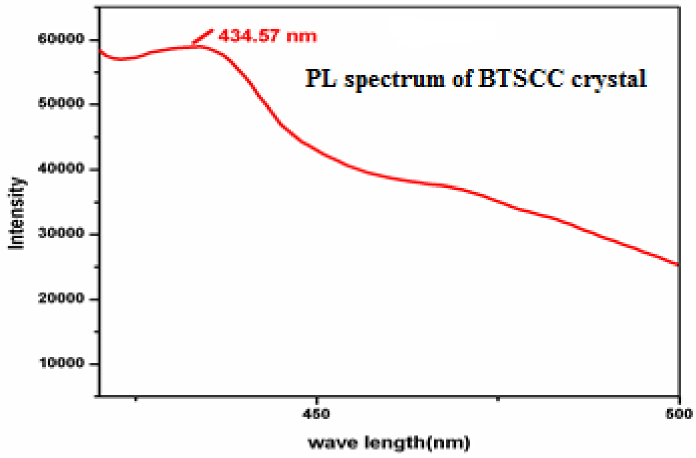

Figure 5: The PL spectrum of thiourea doped sodium cadmium chloride crystal

The PL spectrum of thiourea doped sodium cadmium chloride crystal is shown in the **Fig.5**.The observed first broad peaks at 437.57 nm of the PL emission spectrum for BTSCC crystal corresponds to the π-π* transition within the NH_2 units of the grown crystal. This indicates that they have indigo fluorescence emission. In addition to that, the sharp absorption peaks observed in the UV region are due to the absorption of UV light by the Na^+ and Cd^{2+} ions resulting to the splitting of transition of energy levels from the highest occupied orbital to the lowest unoccupied orbital [**12**].

3.5 UV spectral studies

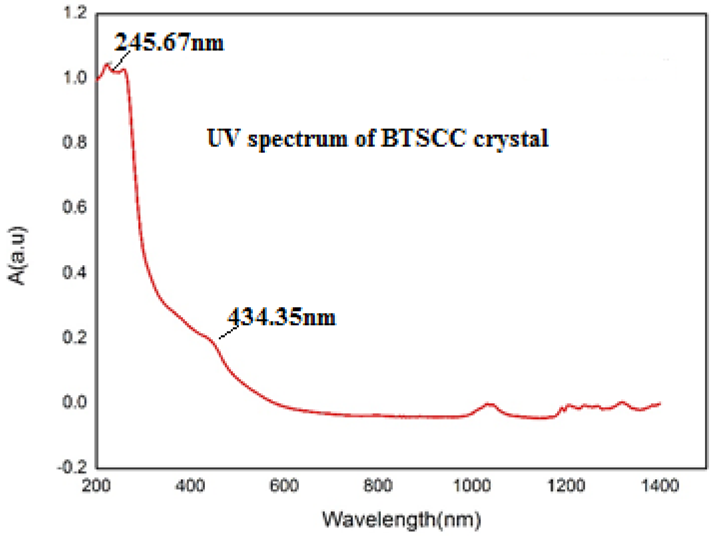

Figure 6: Observed non-linearity in the absorbance curve of BTSCC crystal.

The absorption spectrum of BTSCC crystal is shown in **Fig. 6**. From the observed non-linear UV absorption spectral curves, the lower cut-off wavelength for bisthiorea sodium copper chloride crystal was found to be 245.67 nm and 434.35 nm. It is interesting to observe a strong, intense peak around 250-450 nm which is assigned to the thioureagroup of metal halide crystal **[13]** has been reported. The recorded optical spectrum of the thiourea doped sodium cadmium chloride crystal is found to be active in the UV –Visible region having a significant absorption in the lowest cut- off wavelength of 245.67 nm and the band gap energies of the as grown samples are calculated by using the relation (1)

Band gap (E_g)=hν (1)

Where h = Planks constant = 6.626×10^{-34} Joules sec

ν= frequency of the applied uvray.The frequency of UV ray is written in termsof its wavelength by using the relation (2)

Band gap Energy (E) = h*C/λ (2)

Where C = Speed of light = 3.0×10^{8} meter/sec and λ = Cut off wavelength = 245.67×10^{-9} meters

Table 3: Calculated optical parameters of as-grown BTSCC crystal

H	C	λ (m)	$E_{g(jou)}$	$E_{g(eV)}$	**Ref. index (n)**	**Reflectance (R)**	ϵ_∞
6.63E-34	3.00E+08	2.45E-07	8.1156E-19	5.0709	1.9688	0.3263	3.876

The wide range of band gap energy combined with the lower cut-off near 250nm, makes the usefulness of these materials for laser and device applications [**14**].The relation between the refractive index (n) and the energy gap (E_g) through some modified form of T.M Moss et al., and C. RamachandraRajaa, et al., [**15, 16**] were given by the equation ,

$E_g e^n = 36.3$ (3)

This relation (3) holds true of energy gaps greater than 0 eV. The frequency or wavelength of refractive index is called dispersion. Dispersion is an important property for optical design and in the transmission of information. Further studies on the refractive index (n), dielectric constant and reflectance (R) of the crystals are calculated by using the expression (4) and (5),

$$\mathbf{R} = \left(\frac{\mathbf{n-1}}{\mathbf{n+1}}\right)^{\mathbf{2}} \quad (4)$$

$$\epsilon_\infty = n^2 \quad (5)$$

Where'ϵ_∞'represents the high-frequency dielectric constant which was determined from the relation (3).

The calculated high value of dielectric constant ,refractive index and low value of reflectance from the given **Table 3**confirmed that the grown crystal has wide transparency window and more transparent to transmit the light from 245 to 1100 nm. As a result, the title crystal has been shown to be a useful material for the nonlinear optical applications.

3.6 Solubility

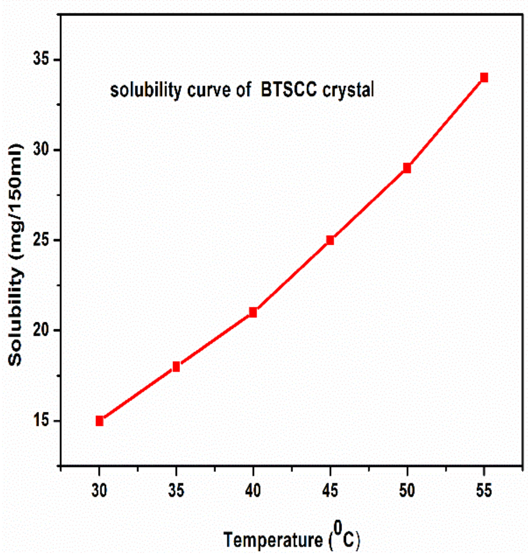

Figure 7: Solubility graph of bisthiourea sodium cadmium chloride crystal at various temperatures.

Solubility is one of the factors of better non-linear activities [**17**] of the as-grown samples was proved by solubility test using deionized warm water as a solvent. The solubility of BTSCCwas determined in the temperature range of 30 °C to 55°C. Solubility studies were carried out in a constant temperature bath (CTB) with the cryostat facility with an accuracy of +0.01 K. The solution was stirred continuously for half an hour to achieve the stabilization. After attaining the saturation, the equilibrium concentration of the solute was analysed gravimetrically. The same process was repeated and the solubility curves were observed to 15 mg / 150 ml and 35 g /150 ml for as-grown crystals for different temperatures (**Fig.7**). It is observed from the curve that the solubility is found to increase with an increase in temperature or BTSCC was due to the hydrogen bonding and the soluble nature of sodium and cadmium chloride in water. This result showed the improved solubility demands the sodium copper oxalate dihydrate crystal for further optical applications.

3.7 NLO test (SHG)

The powder second harmonic generation forBTSCC was measured using the Kurtz powdertechnique. The powder sample, with anaverage particle size of 50–75 mm was illuminatedusing a Q-switched Nd: YAG laser having awavelength of 1064nm and a pulsewidth of 8 ns.Second harmonic generation was confirmed by theemission of green radiation (l ¼ 532 nm). Thepowder SHG efficiency of BTSCC was found to be0.75 times of urea. This result was moderately high as already reported SHG efficiency of the pure BTCC crystal [**18**].

IV. Conclusions

BTSCC was synthesized and its solubility analysed in the temperature range 30-55^{0}C. The solubility curve indicates high solubility of BTZC in water with a positive solubilitytemperaturegradient.Single Crystals of BTSCC have been grown by slow evaporation technique at roomtemperature. Unit Cell parameters have been evaluated by powder crystal XRD technique. The functional groups of C=S, N-C-N, C-H and NH_2were identified by FTIR spectral studies and also the presence of theseexpected groups of elements were confirmed by EDX spectral studies. The wide band gap energy, low reflectance, high refractive index and moderate dielectric constant values were proved the good nonlinear properties of the as-grown BTSCC crystal for optical applications. Furtherthe enhanced SHG efficiency of the BTSCC crystal confirmed that it is potential candidate for non-linear optical applications.

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