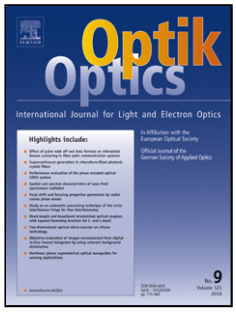

Title: Synthesis, growth and optical studies of novel organometallic NLO crystal: Calcium bis-thiourea chloride

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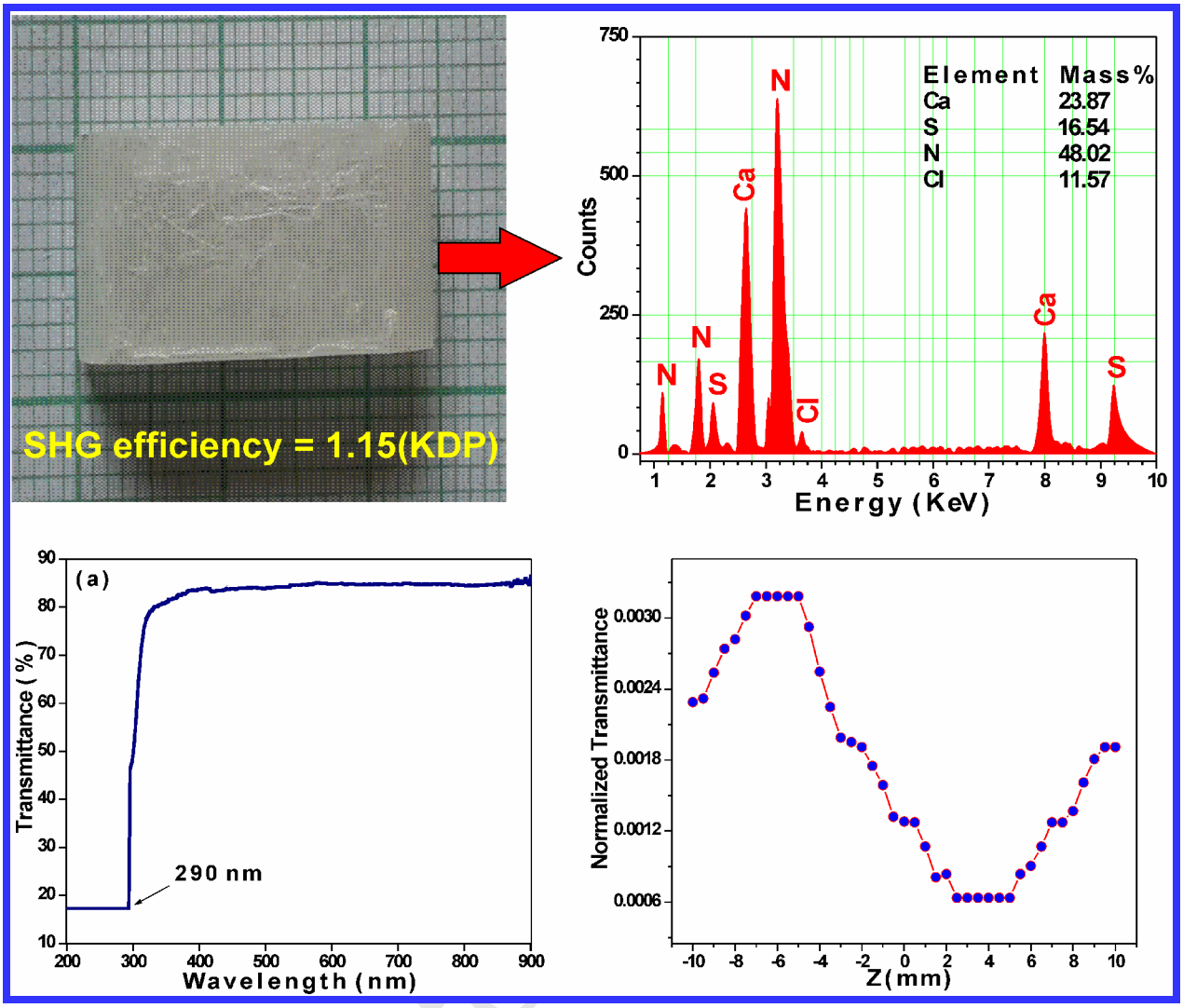
HIGHLIGHTS

- A novel organometallic crystal calcium bis-thiourea chloride (CBTC) is grown
- CBTC complex formation has been confirmed from EDX and FT-IR analysis
- CBTC crystal is optically transparent upto 82% and its band gap is 4.2 eV
- SHG efficiency of CBTC crystal is 1.15 times higher than KDP crystal
- Z-scan study identified the self-defocusing nature of CBTC crystal

Graphical Abstract



Synthesis, growth and optical studies of novel organometallic NLO crystal: calcium bis-thiourea chloride

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Abstract

A novel organometallic crystal calcium bis-thiourea chloride (CBTC) has been synthesized and confirmed by means of EDX and FT-IR analysis. The (25×9×10) mm^3 CBTC crystal has been grown from aqueous solution by slow solution evaporation technique. The UV-visible spectral study has been carried in the range of 200-900 nm to assess the optical transparency of CBTC crystal. The optical constants such as band gap, optical conductivity, refractive index and reflectance of grown crystal have been evaluated using the transmittance data. The color centered fluorescence behavior of grown crystal has been explored in visible region. The Z-scan technique has been employed to determine the negative third order nonlinear refraction behavior of CBTC crystal. The magnitude of third order nonlinear refraction (n_2), nonlinear susceptibility (χ^3), nonlinear absorption (β) and FOM of grown crystal has been calculated using the Z-scan data. The χ^3 of magnitude 3.56×10^{-5} esu confirms the strong polarizing nature of CBTC crystal. The kurtz-perry test confirmed the SHG efficiency of CBTC crystal is 1.15 times higher than KDP crystal material.

Keywords: Crystal growth, Optical studies, SHG, Z-scan technique, Nonlinear optical materials

1. Introduction

In past decade, growth and designing of new organic, inorganic and semi-organic nonlinear optical (NLO) crystal has been emphasized due to their everlasting demand for applications in photonics, electro-optic modulation, optical data processing and retrieving systems, optical limiting, laser frequency conversion and

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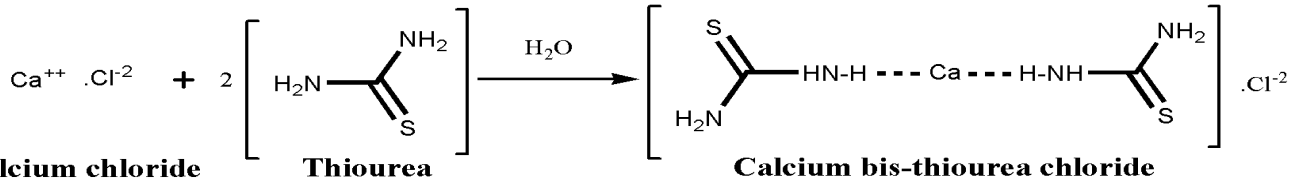
optical switching devices [1]. Immense attention has been aimed to develop the organometallic complex crystals which offer potential features like high laser damage threshold, low dielectrics, better nonlinear efficiency, low angular sensitivity and high structural stability [2-3]. Thiourea is evidently considered as a model organic material which possesses large dipole moment and huge capability to form metal ligand bond through strong and wide -H bonding network [4]. On the other hand the inorganic metals easily co-ordinates with thiourea and acquire the accentric symmetrical orientation, which is the prime requirement to obtain high optical transparency and sufficiently large nonlinear response from the crystal system [5]. The well known NLO thiourea based organometallic crystals reported in literature are thiourea urea magnesium chloride (TUMC), potassium thiourea bromide (PTB), bis-thiourea cadmium acetate (BTCA), copper thiourea chloride (CTC), bis-thiourea zinc acetate (BTZA), zinc thiourea chloride (ZTC), bis-thiourea cadmium chloride (BTCC), bis-thiourea cadmium formate (BTCF), potassium thiourea thiocyanide (PTT) and urea thiourea cadmium sulphate (UTCS) [1-9]. The superior linear and nonlinear optical properties of organometallic crystals hold very crucial role in order to achieve long term performance, reproducibility and reliability of optical devices. Hence, present manuscript successfully attempts to synthesis, grow and study the optical behavior of novel NLO crystal calcium bis-thiourea chloride (CBTC). The CBTC crystal has been characterized by EDX, FT-IR, UV-visible, Kurtz-perry test and Z-scan analysis.

2. Experimental

The salt of CBTC was synthesized by dissolving fused calcium chloride and thiourea in double distilled deionized water and the reaction mechanism for formation of CBTC complex is shown below,



The aqueous mixture was allowed to react for eight hours to avoid the co-precipitation and obtain the homogeneous solution of CBTC complex. The solution was gradually filtered in a rinsed beaker using the Whatman filter paper and kept for slow evaporation at room temperature. The CBTC crystal grown by

employing isothermal solution evaporation technique was harvested within the period of 20 days and the well faced as grown single CBTC crystal of dimension (25×9×10) mm^3 is shown in Fig. 1. As optical devices require the high purity materials the synthesized CBTC salt was successively recrystallised to eliminate the crystalline impurities and obtain good quality CBTC crystal.

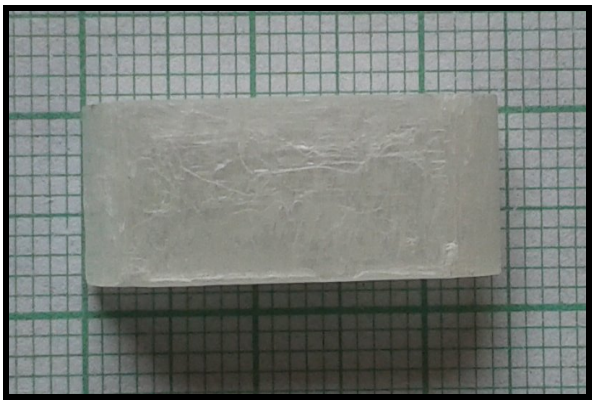


Fig. 1. Photograph of CBTC crystal

3. Results and discussion

3.1. Spectral studies

3.1.1. Elemental analysis

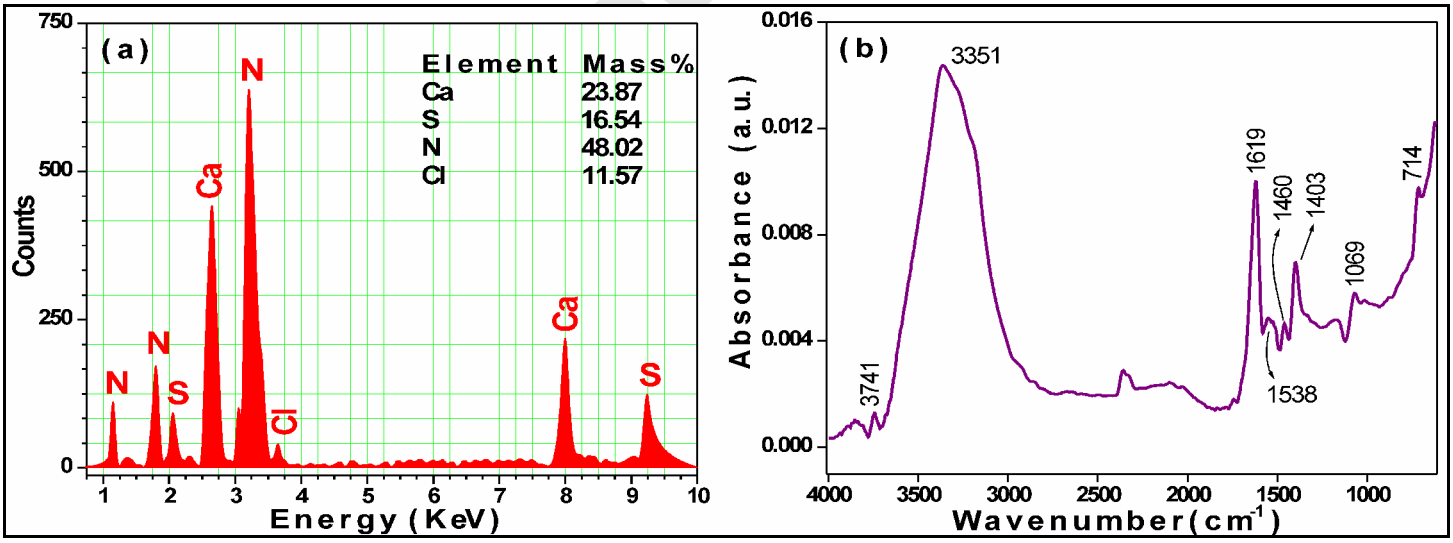


Fig. 2. a) EDX spectrum, b) FT-IR spectrum of CBTC crystal

The qualitative elemental detection of CBTC crystal has been performed by means of energy dispersive X-ray (EDX) analysis using the HITACHI S4700 instrument. In order to confirm the co-ordination of thiourea with calcium metal ion and determine its composition, the single CBTC crystal was powdered and the EDX

spectrum of powdered sample was recorded in the energy range of 0.1 to 10 KeV. The EDX spectrum is shown in Fig. 2a and the energy peaks observed in the spectrum confirmed the inhabitance of calcium (Ca) in crystal with the mass% of 23.87 along with other expected elements; nitrogen (N), sulphur (S) and chlorine (Cl).

3.1.2. Fourier transform infrared (FT-IR) analysis

The functional groups of grown crystal were qualitatively identified by recording the FT-IR spectrum using the spectrophotometer (Bruker-ATR) in the range of 600-4000 cm^{-1}. The absorption FT-IR spectrum of CBTC crystal is shown in Fig. 2b. The absorption peaks observed at 714 cm^{-1} corresponds to the C-Cl co-ordinated stretching vibration. The peak observed at wavenumber 1403 cm^{-1} corresponds to the C=S bond stretching vibration associated with metal co-ordinated thiourea. The N-C-N bond stretching vibrations are observed at wavenumber 1069 and 1460 cm^{-1}. The stretching vibration of C-N bond is attributed at 1538 cm^{-1}. The absorption peak at 1619 cm^{-1} is attributed to the NH_2 bending vibration. The prominent shift in vibrational frequencies of thiourea discussed in table 1 clearly indicates the co-ordination of calcium ion with thiourea [3].

Table. 1.

Functional groups of thiourea and CBTC crystal

Wavenumber (cm^{-1})		Assignments
Thiourea	CBTC	
730	714	C-Cl stretching
1083	1069	N-C-N stretching
1417	1403	C=S stretching
1470	1460	N-C-N stretching
	1538	C-N stretching
1625	1619	NH_2 bending

3.2. UV-visible spectral analysis

3.2.1. Optical transmittance and absorbance

In order to determine the operative transparency range of CBTC crystal (2 mm thickness) the UV-visible

transmittance (Fig. 3a) and absorbance (Fig. 3b) spectrum has been recorded in the range of 200-900 nm. The transmittance spectrum reveals that the grown crystal is optically transparent upto 82% and it is uniform over the entire range of visible region which is an assertive quality of material to inherit the NLO behavior. The uniform transparency indicates that the CBTC crystal system has high optical homogeneity and less crystalline (point and line) defects which significantly avoid the scattering of light [10]. The transmittance cut-off of CBTC crystal is found to be at 290 nm which is evident in both transmittance and absorbance spectrum. The sharp fall of transmittance in lower wavelength range is attributed to active n to π* transition associated with the nitro group of thiourea. The considerably wide operative range, high transparency window and least absorbance facilitate the use of CBTC crystal for UV-tunable lasers as well as transmission of blue and green harmonic frequencies of Nd:YAG laser operating at 1064 nm.

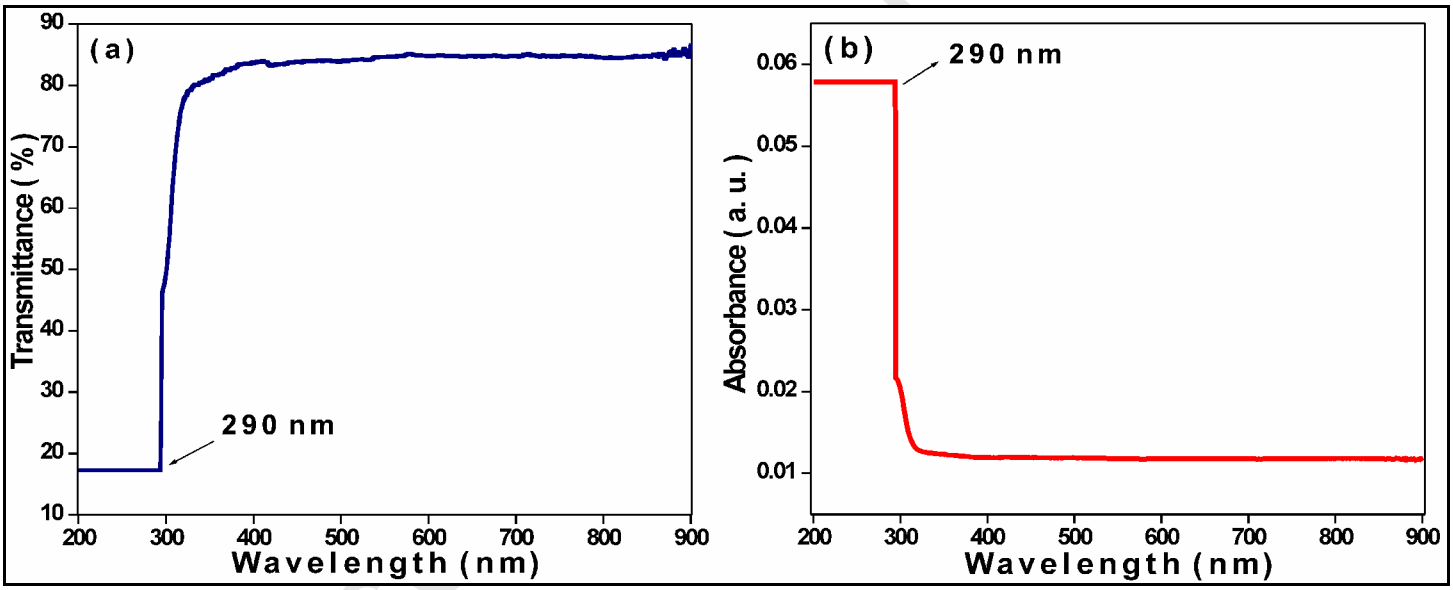


Fig. 3. a) UV-visible transmittance spectrum, b) UV-visible absorbance spectrum

3.2.2. Determination of optical constants

The detail information of optical constants of material plays significant role to tailor the technological components as per the application requirement. One of the most vital optical constant is band gap. The Tauc's extrapolation plot (Fig. 4a) drawn using the relation ($\alpha h\nu = A(h\nu - E_g)$ clearly evidences the dependence of absorption coefficient (α) on incident photon energy (hν) which helps to determine the optical band gap (E_g) of the material. The optical band gap of CBTC crystal is found to be 4.2 eV. The wide band gap suggests the

suitability of CBTC crystal for optoelectronics applications [11]. The photonic response of optical conductivity is plotted in Fig. 4b. The increasing trend of optical conductivity ($\sigma_{op} = \alpha nC/4\pi$) of CBTC crystal with a magnitude of 10^{12} $S^{-1}$is an advantageous factor for signaling and computing the ultrafast optical data [12].

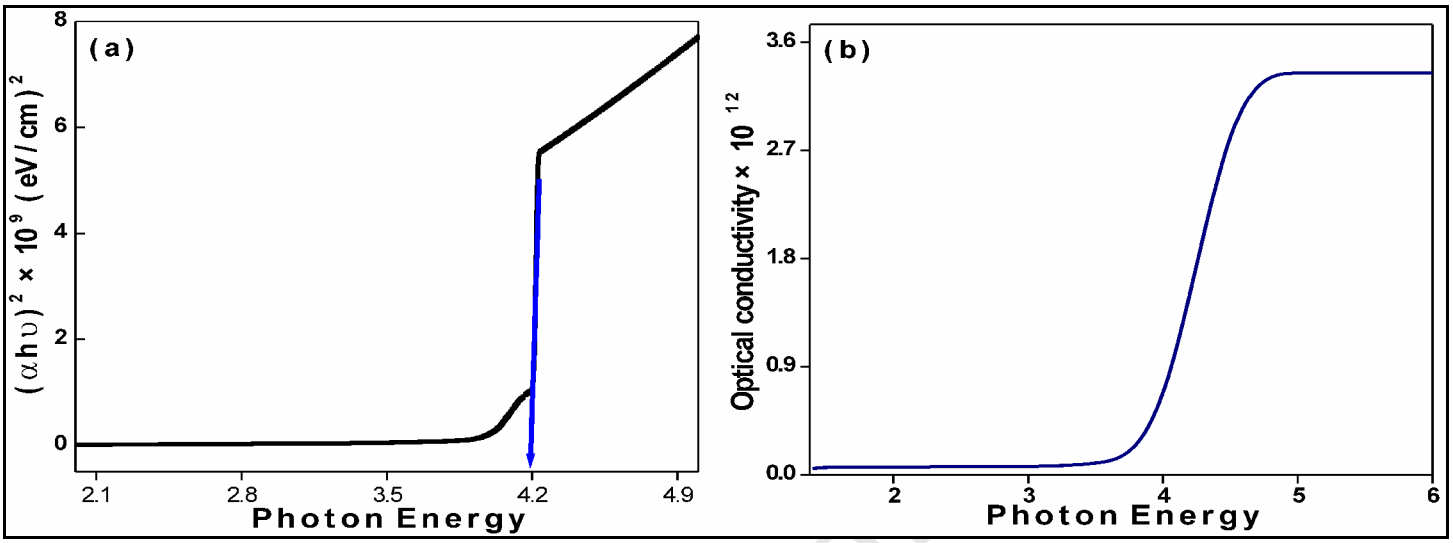


Fig. 4. a) Tauc's plot, b) Plot of optical conductivity

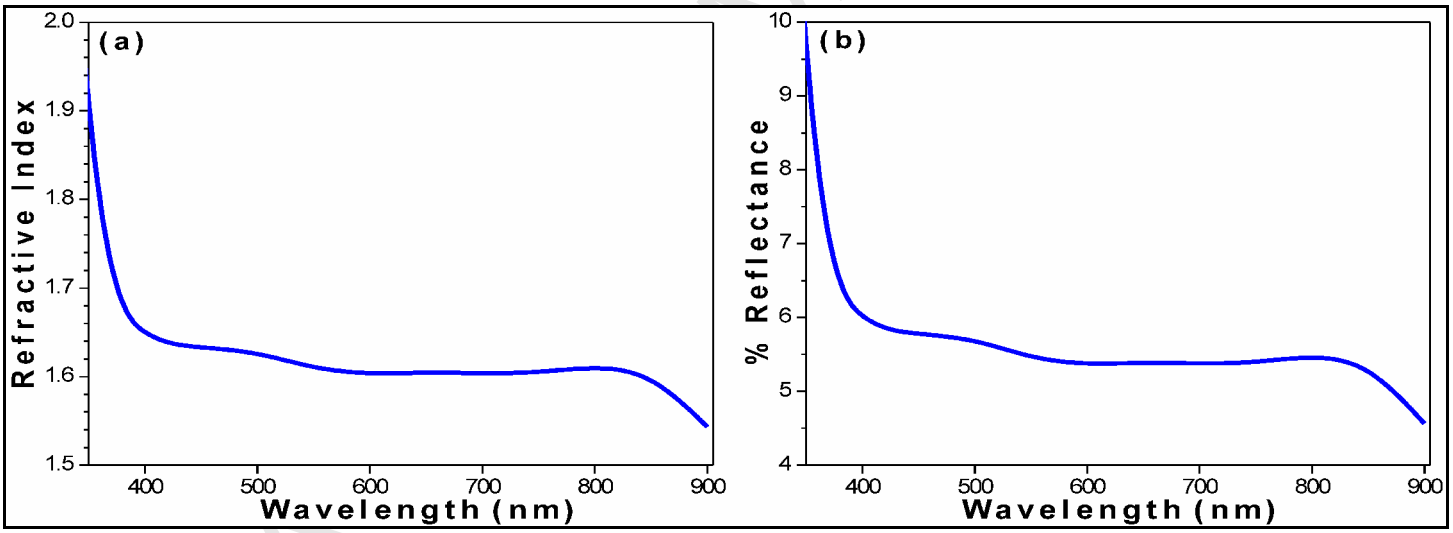


Fig. 5. Plot of wavelength dependent a) Refractive index and b) Reflectance

The refractive index and reflectance of CBTC crystal has been calculated using the fundamental equations [13] and the corresponding plots are shown in Fig. 5a and 5b respectively. The magnitude of refractive index and reflectance is sufficiently lower in visible region which is an essential parameter for calibrating the optical components such as filters, resonators and reflectors [14]. The photo-refractive materials also find wide applications in storing and processing the holographic data. The higher optical homogeneity, high optical

transparency, low refractive index and low reflectance of CBTC crystal could serve better for fabricating electro-optic modulators and photonic devices [15].

3.3. Fluorescence studies

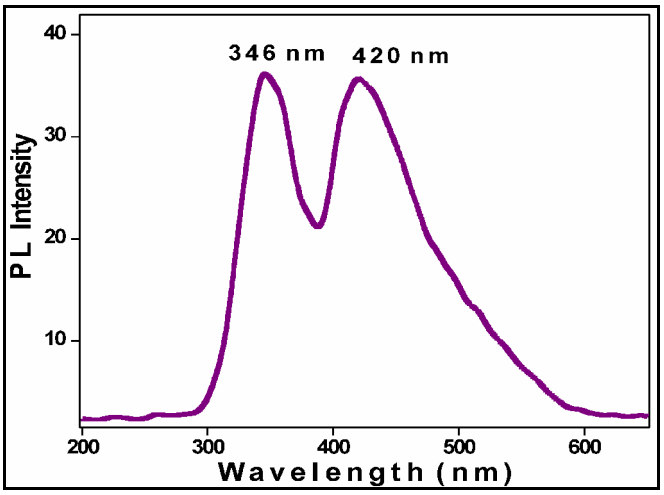


Fig. 6. Fluorescence emission spectrum

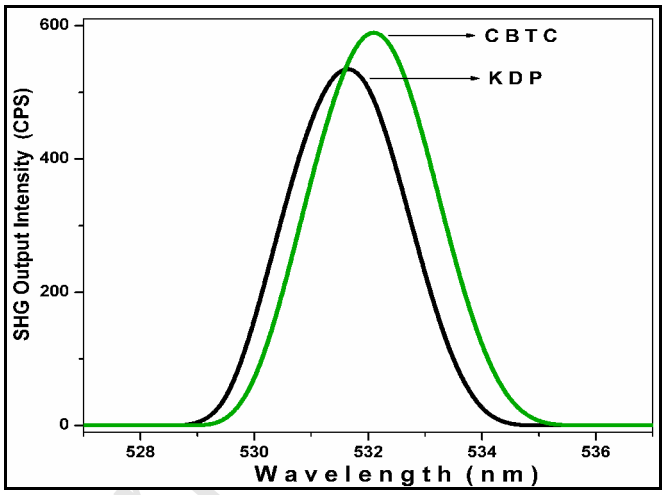


Fig. 7. Plot of SHG output intensity

The analysis of emission (EM) spectrum of photo-excited material gives an imprint of intrinsic impurities, electronic transition states and information related to the surface disorders and roughness of materials [16]. The photoluminescence (PL) intensity majorly depends on the excitation energy as well as on the intensity of the incident beam. In present analysis the CBTC crystal has been photo-excited with an excitation wavelength of 350 nm (i.e. 3.54 eV) and the EM spectrum was recorded with no delay in the range of 200 to 650 nm using F-7000 FL spectrophotometer (EM slit width = 1 nm, scan speed = 240 nm/min, response time = 0.1S). The EM spectrum shown in Fig. 6 reveals that CBTC crystal has strong violet emission with two measure peaks centered at 346 nm and 420 nm and the corresponding energies are 3.58 eV and 2.95 eV. The distinctive nature of PL peaks indicates that the CBTC crystal has good optical quality which is stringent requirement for material to be NLO active [12]. The CBTC crystal with prominent violet emission could be used as a reference material for element detection in the field of biotechnological, chemical and medical applications [17].

3.4. Nonlinear optical studies

3.4.1. Kurtz-perry powder test

In order to determine the effective frequency doubling behavior of the CBTC crystal the kurtz-perry powder

SHG test [18] has been carried out using the Q-switched Nd:YAG laser (1064 nm, 10 Hz, 6 ns) delivering the input energy of 5.4 μJ/pulse. The KDP and CBTC crystals were finely grounded to microgranules of uniform size and the individual sample was multishot by a polarized gaussian beam of Nd:YAG laser. The output signals were colliminated through the array of photomultiplier tube to record the output SHG intensity of the sample. The emission of sharp green light from the crystalline powder confirmed the second order NLO behavior of CBTC crystal and the output SHG intensities are plotted in Fig. 7. The enhanced SHG efficiency of CBTC crystal is found to be 1.15 times that of KDP material. This confirms that the organometallic bond substantially tunes the CBTC crystal to accentric structural orientation and anharmonic electronic distribution which favor easy photoinduced charge transfer through donor-acceptor chromospheres. The SHG efficiency of CBTC crystal is significantly higher as compared to other organometallic crystals namely; TUMC [1], UTCS [9], BTCA [19] and BTZC [20].

3.4.2. Third order nonlinear optical (TONLO) studies

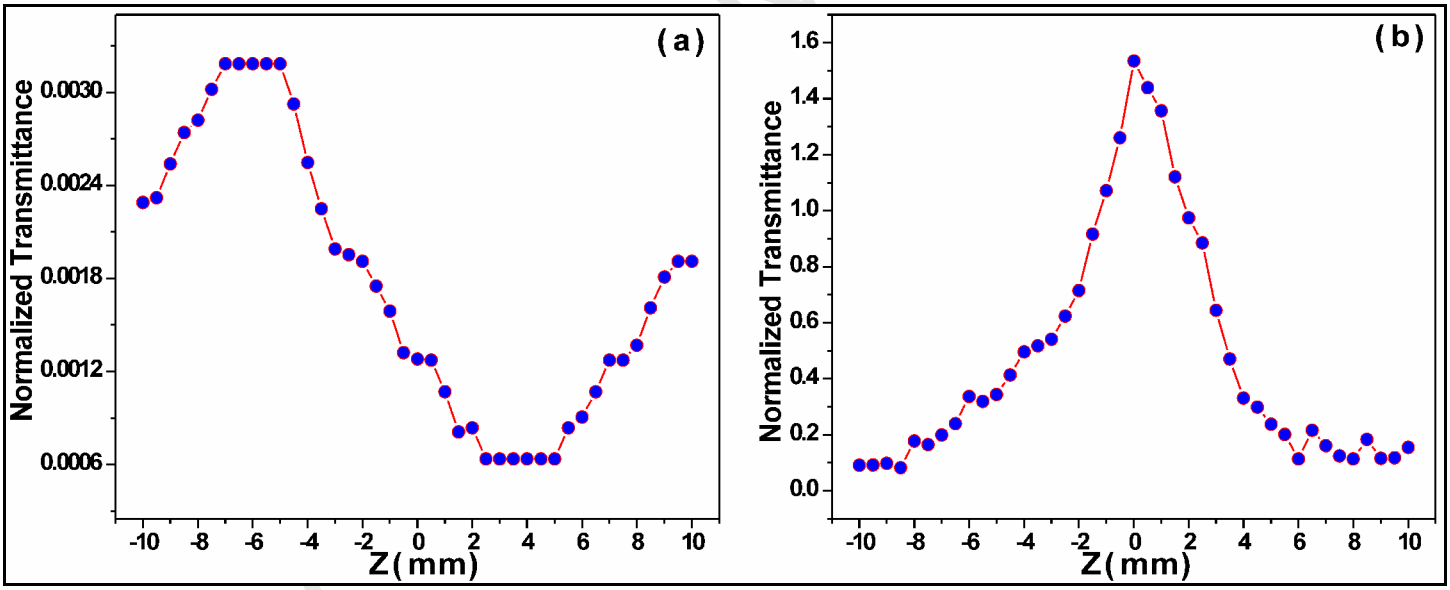


Fig. 8. a) Close and b) Open aperture Z-scan transmittance

The Z-scan analysis is an influential laser assisted sensitive technique to examine the TONLO behavior of material systems at nano-, pico- and femto-second time scale [21]. In present study, the path dependent transmittance profile offered by CBTC crystal (1 mm) in close and open aperture Z-scan configuration (detailed in table. 2) has been investigated using the He-Ne laser. The filtered beam of laser was normally irradiated

through a convex lens on the crystal surface and the Z position of crystal was gradually changed along the beam focused path. The transmittance through the crystal corresponding to change in Z position of crystal has been traced through the photo detector placed at far field. The closed aperture Z-scan curve shown in Fig. 8a evidences the self-defocusing (negative nonlinear refraction (n_2)) tendency of crystal as transmittance follows the peak to valley phase shift about the focus. The self-defocusing materials hold wide demand for protection of night vision optical sensors [22]. The phase shift about the focus is a crucial phenomenon which is evolved due to the localized absorption and the optical energy distribution along the crystal surface induced by the highly repetitive rate of incident optical field [23]. The peak to valley transmission (ΔT_{p-v}) can be expressed in phase shift as,

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}\left|\Delta\phi\right| \quad (1)$$

where S = [1-exp ($-2r_a^2/\omega_a^2$)] is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam waist radius in front of aperture. The n_2 of CBTC crystal has been determined using the relation,

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \quad (2)$$

where $K = 2\pi / \lambda$, $I_0 = 2P/\pi\omega_a^2$, is the incident irradiance intensity of beam at the focus (Z=0), the effective thickness of the sample $L_{eff} = [1\text{-exp }(-\alpha L)]/\alpha$, depends on linear absorption coefficient (α) and L thickness of the sample. The open aperture Z-scan curve depicted in Fig. 8b has been analyzed to quantify the nonlinear absorption coefficient (β) of CBTC crystal. It reveals that the transmittance of crystal gains maximum value at the focus which verifies the presence of saturable absorption (SA) [24]. The dominance of ground state linear absorption coefficient over the excited state absorption is the primary factor responsible for SA effect [25]; which is also observed in case of CBTC crystal. The β value has been estimated using equation,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \quad (3)$$

where ΔT is the one valley value obtained in open aperture Z-scan curve. The magnitude of β is found to be

1.08×10^{-5} cm/W for grown crystal. The χ^3 of the material can be determined by evaluating the following equations,

$$\mathrm{Re}\,\chi^{(3)}(esu) = 10^{-4}(\varepsilon_0 C^2 n_0^2 n_2)/\pi(cm^2/W) \quad (4)$$

$$\mathrm{Im}\,\chi^{(3)}(esu) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)/4\pi^2(cm/W) \quad (5)$$

$$\chi^3 = \sqrt{(\mathrm{Re}\,\chi^3)^2 + (\mathrm{Im}\,\chi^3)^2} \quad (6)$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. The higher χ^3 value of CBTC crystal indicates the strong polarizing nature of CBTC crystal [26]. The high polarizability is predominant in materials showing large optically induced π-electrons delocalization [27] which might have been observed in CBTC crystal due to increased charge transfer through wide network of thiourea-metal ligand linkage. The superior magnitude of n_2 and χ^3 of CBTC crystal are systematically compared in table 3 [28-29]. Thus, CBTC crystal could be a potential TONLO material for night vision sensors and optical power limiting devices.

Table. 2.

Optical resolution of Z-scan setup

Parameters and notations	Details
Laser wavelength (λ)	632.8 nm
Laser power (P)	10 mW
Lens focal length (f)	20 cm
Optical path distance (Z)	113 cm
Beam waist radius (ω_a)	1 mm
Aperture radius (r_a)	15 mm
Incident intensity at the focus (I_o)	2.3375 KW/m^2

Table. 3.

Nonlinear refraction and cubic susceptibility of CBTC and other thiourea-metal complex crystals

Parameter	CBTC	BTZA	α-$LiIO_3$	BTZB	BTZC	ZTS	BTCF
n_2 cm^2/W	-9.02×10^{-11}	-2.11×10^{-6}	5.46×10^{-7}	-5.41×10^{-8}	-6.64×10^{-8}	-5.22×10^{-8}	-9×10^{-13}
χ^3 esu	3.56×10^{-5}	1.67×10^{-6}	1.63×10^{-3}	3.05×10^{-6}	3.6×10^{-6}	3.5×10^{-6}	1.38×10^{-8}
Reference	Present	[5]	[24]	[28]	[28]	[28]	[29]

4. Conclusions

Single CBTC crystal was successfully grown by slow solution evaporation technique. The detected Ca ion in EDX analysis and identified functional groups in FT-IR spectrum confirmed the formation of new organometallic CBTC crystal. The UV-visible study explored the high optical transparency, low absorption, large transmission range, wide optical band gap and superior optical homogeneity of CBTC crystal in entire visible spectrum. The CBTC crystal showed violet fluorescent emission with two prominent peaks centered at 2.95 eV and 3.58 eV. In Kurtz-perry test, the SHG efficiency of CBTC crystal is found to be 1.15 times that of KDP crystal. The closed aperture Z-scan analysis confirmed the negative NLR behavior and the saturable absorption observed in open aperture configuration is due to the dominance of ground state linear absorption in CBTC crystal. The nonlinear absorption coefficient of CBTC crystal is found to be 1.08×10^{-5} cm/W. The CBTC crystal possesses χ^3 of order 10^{-5} esu which confirmed the profound charge mobilizing nature through the thiourea-metal ligand bond linkage. All above studies infer that CBTC crystal is an outstanding NLO material which pronounces its effective utility for designing electro-optic modulators, UV-tunable lasers, night vision sensors, photonics and optical limiting devices.

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Table. 3.

Nonlinear refraction and cubic susceptibility of CBTC and other thiourea-metal complex crystals

Parameter	CBTC	BTZA	α-$LiIO_3$	BTZB	BTZC	ZTS	BTCF
n_2 cm^2/W	-9.02×10^{-11}	-2.11×10^{-6}	5.46×10^{-7}	-5.41×10^{-8}	-6.64×10^{-8}	-5.22×10^{-8}	-9×10^{-13}
χ^3 esu	3.56×10^{-5}	1.67×10^{-6}	1.63×10^{-3}	3.05×10^{-6}	3.6×10^{-6}	3.5×10^{-6}	1.38×10^{-8}
Reference	Present	[5]	[24]	[28]	[28]	[28]	[29]