Synthesis, structural, optical, thermal and dielectric aspects of a semiorganic nonlinear optical crystal by solution growth technique

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Single crystals of cadmium thiourea fluoride [Cd $(H_2NCSNH_2)_2$] F_2, abbreviated as CTF, was grown by slow evaporation and slow cooling process at an optimized pH of 4.0. The lattice parameters of the grown crystal were determined by X-ray diffraction studies and the crystallanity of the material was confirmed by powder X-ray diffraction. The presence of functional groups and the coordination of metal ions to thiourea were confirmed by FTIR and Raman spectroscopy analyses. The range of optical transmission was determined by recording UV-Vis-NIR spectrum. Thermal stability of the CTF crystal was determined from TG-DTA curves, which indicate that the material is stable up to 225°C. The non-linear nature of the crystal was confirmed by SHG test. Studies of dielectric properties (dielectric constant and dielectric loss) both as function of frequencies (100 Hz to 5 MHz) for varying temperatures in the range 308-368K suggest good candidate for electro optic modulators.

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1. Introduction

The search for new frequency conversion materials over the past decade has concentrated primarily on organic compounds [1,2]. However, the implementation of single crystal, organic materials in practical device applications has been impeded by their often inadequate transparency, poor optical quality and low laser damage threshold. Inorganic crystals have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities because of the lack of Л – electron delocalization. Hence recent search is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness for device fabrication [3,4]. Metal complexes of thiourea, commonly called semiorganics, include the advantages of both organic and inorganic part of the complex. In recent years, a number of semi-organic complex products of thiourea have attracted great interest because these metal-organic complexes combine the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics [5,6]. Thiourea with its resonance structure, has been thoroughly investigated by previous workers [7]. It is a material with more than 700 structures and also interesting inorganic matrix modifier due to its large dipole moment [8] and its ability to form an extensive network of hydrogen bonds and its complexes with transition metals exhibit interesting properties. Also metals with d^{10} configuration like zinc, cadmium, mercury readily combine with thiourea resulting in stable compounds with high optical nonlinearity and good physiochemical behavior [9]. In general, crystals of the type M $[TU]_2[X]_2$, where M=Cd, Co, Hg, Pb, Ti or Zn, TU is thiourea and X is halogen, have been found to exhibit good NLO properties. Many metal complexes of thiourea and thiourea analogs have been investigated and reported the vibrational spectra of bis-thiourea complexes [10-15]. A variety of crystals of this class has been grown by several groups [16-26]. Till now a detailed analysis of vibrational frequencies, IR and Raman spectra of CTF have not been reported. In this paper, first time we report the powder X-ray diffraction, optical, FT-IR, FT-RAMAN spectroscopy and nonlinear properties for the title molecule cadmium thiourea fluoride (CTF).

2. Experimental

2.1 Synthesis and crystal growth

Raw material for the growth of CTF was synthesized by mixing aqueous solutions of cadmium fluoride and thiourea in the ratio of 1:2.

Preparation of CTF was prepared according to the following chemical reaction

$$CdF_2 + 2(H_2NCSNH_2) \rightarrow [Cd(H_2NCSNH_2)_2]F_2$$

Since thiourea has the coordination capacity to form different phases of metal-thiourea complexes, the mixtures of the reactants had to be stirred well to avoid co-precipitation of multiple phases. The product was purified by repeated recrystallization before it is used for the crystal growth. CTF crystals were grown from aqueous solution by slow evaporation technique. The grown crystals are shown in Fig. 1(a). Saturated aqueous solution of 200 ml of cadmium fluoride and thiourea in the ratio of 1:2 was taken in a crystallizing vessel with perforated covers and placed in a constant temperature bath controlled to an accuracy of ± 0.01 ºC. The temperature of the bath was lowered at the rate of 0.1 ºC/day. Bulk transparent single crystals with dimensions up to 2.8 × 1.5 x 1.4 cm^3 with well-defined morphology were harvested after a typical growth period of 20 days. One of the grown bulk transparent single crystals is shown in Fig. 1 (b).

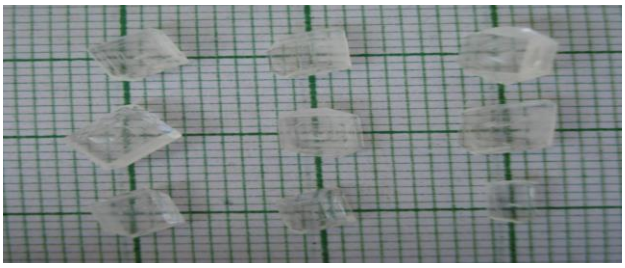

Fig. 1(a). Photograph of a grown of CTF single crystals by slow evaporation technique.

Fig. 1(b). Photograph of a grown of CTF single crystal by slow cooling technique.

3. Characterization

3.1. Single crystal XRD

To confirm the identity of the synthesized salt, crystal X-ray diffraction studies have been carried out to find the unit cell parameters and cell volume from Enraf Norius CAD4 diffractometer with MoKα (λ = 0.7107Å). It is observed that the CTF crystals belongs to triclinic system with centrosymmetric space group P-1 and the corresponding cell parameters are a = 8.75 Å, b =9.07 Å, c= 9.76 Å, with α=91.69°, β=110.50°, γ=95.49°. The calculated cell volume is 721 Å^3. The crystallinity of CTF single crystal was confirmed by the powder X-ray diffraction study and diffraction peaks are indexed (Fig. 2) from crystal structure parameters obtained in the present study.

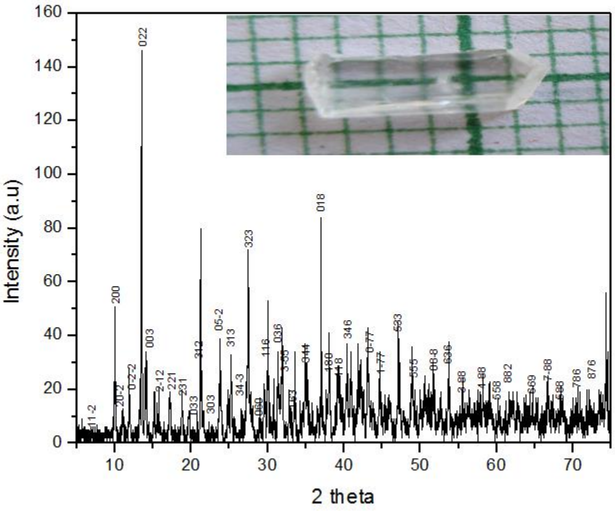

Fig. 2. Powder diffraction pattern of CTF single crystal and the photograph of CTF grown by slow evaporation is shown as inset.

3.2 Vibrational spectral analyses

FT-IR and Raman spectral studies were effectively used to identify the functional groups present in the synthesized compound and to determine the molecular structure as well to confirm the structure of the molecule. To analyze qualitatively the presence of the functional groups in CTF crystal, FTIR and Raman spectra were recorded using BRUKER 1FS66V spectrophotometer by KBr pellet technique in the region 4000-400 cm^{-1} and FT-Raman spectrum of CTF has been recorded using Nd:YAG laser which has excitation wavelength in the region 4000–100 cm^{-1} on the same spectrophotometer equipped with FRA 106 FT-Raman module accessory. The recorded FTIR and FT-Raman spectra of CTF are shown in Fig. 3 and Fig. 4 respectively. A number of reports are available on the IR absorption studies of thiourea [27, 28]. When it was compared with those spectra of thiourea [29-31], shifts in the peaks were observed. The NH stretching vibrational bands observed at 3394 and 3175 cm^{-1} produces fine structure in the lower energy region. The bonds of thiourea were not shifted to lower frequencies on the formation of cadmium thiourea complex which indicates nitrogen to cadmium bonds are not present in the coordination compounds. The actual shift in the NCH bending vibrational band observed in Raman spectrum at 712 cm^{-1} confirms and this substantial shift in this region proves that nitrogen to cadmium bond has not formed in the compound. In the complex, there are two possibilities by which the coordination of cadmium with thiourea can occur. The coordination with cadmium may occur either through nitrogen or through sulfur of thiourea [32]. Most of the metals form complex through sulfur [33]. The study of the spectra of CTF shows a shift in frequency band in the low frequency region.

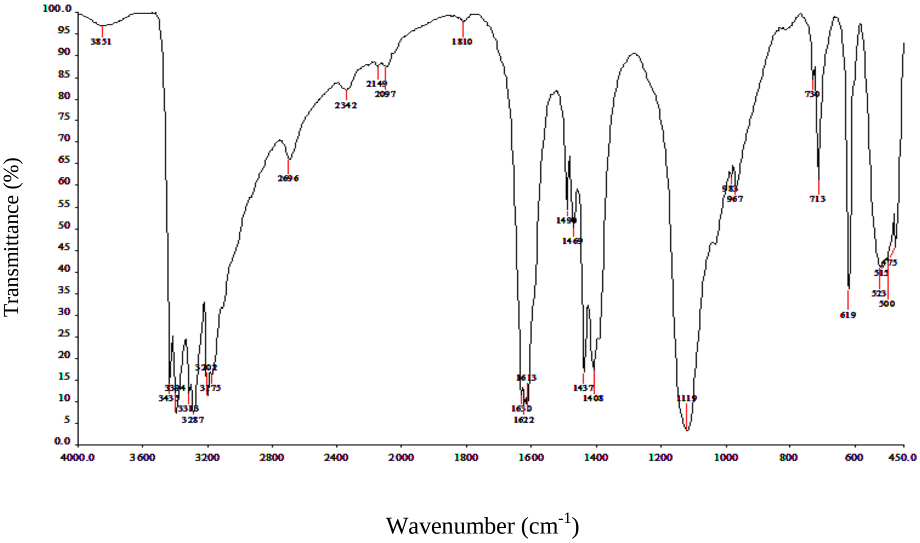

Fig. 3. FT-IR Spectrum of CTF.

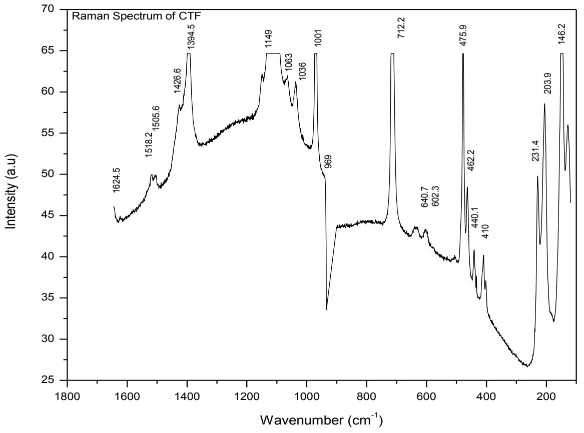

Fig. 4. RAMAN Spectrum of CTF.

Raman scattering is a versatile non-destructive tool for characterization of crystalline materials. It is effectively used to identify functional groups to help determining the molecular structure of synthesized complexes and it can also be used in conformational analysis of samples. The shift in the frequency are noted with the help of FT-Raman spectra in the finger print region, thereby the assignment of functional modes of vibrations presence have been confirmed. The symmetric and antisymmetric C=S stretching vibrations in thiourea at 740cm^{-1} and 1470 cm^{-1} were shifted to 713 and 1408 cm^{-1} for CTF crystal respectively because of the addition of metal ion in the complex. Further, the sharp peak in FT-Raman is assigned to C=S stretching supports the actual shift thereby the metal ion in the complex is confirmed.

The absorption band on N-H stretch falls in the region 3000-3400 in the spectrum of thiourea were not shifted to lower frequencies on the formation of metal thiourea complex in the grown CTF crystal. This indicates that nitrogen to metal bonds is absent and the bonding must be between sulphur and metal. This increase in wavenumber may be due to the stronger double bond character of the carbon to nitrogen bond on complex formation. The peaks between 1700 and 2700 cm^{-1} were due to overtones and combination bands. The band observed at 1490 cm^{-1} for CTF corresponds to the 1470 cm^{-1} band of thiourea assigned to NCN bending vibration. The weak band at 1505 cm^{-1} at FT-Raman is assigned to NCN bending vibration. The appearance of band at 1408 cm^{-1} for CTF single crystal against the absorption of pure thiourea at 1414 cm^{-1} confirms the formation of coordination. Increase of C-N and decrease of C-S stretching frequencies show the complex formation of metal ion. The carbon fluorine stretching band appears in the range 1000 – 1300 cm^{-1} and it is the strongest bond in fluoroalkenes. In the present study the sharpest band appeared at 1119 cm^{-1}in FT-IR is assigned to CF stretching mode and it is very well complemented in FT-Raman band at 1149 cm^{-1}, thereby to confirm the metal bond in the crystal [34]. In the low frequency region, called finger print region, two peaks appeared at 983 cm^{-1} and 713 cm^{-1} in FT-IR and sharp peak at 969 and 712 cm^{-1} in FT-Raman are assigned for metal complex compared to 1089 cm^{-1} and 730 cm^{-1} peaks of thiourea. Based on the shift in the peak positions of NH_2 grouping, the bonding of thiourea with cadmium fluoride is very well established. The characteristic vibrations of CTF have been compared with those of thiourea and the shift observed may be attributed to the formation of cadmium thiourea fluoride. Also the spectrum of CTF crystal largely differs from that of spectrum of thiourea crystal [28-30] the formation of cadmium thiourea fluoride is once again confirmed. The characteristic vibrational wavenumbers are assigned in the Table 1.

Table 1. Comparison of fundamental vibrational modes of THIOUREA and CTF.

Thiourea cm^{-1}	CTF crystal		Assignments
	FT-IR	**FT-Raman**	
3376	3363		--
3280	3287		υ_{as} (NH_2)
3167	3175		υ_s (NH_2)
1627	1622	1624 (w)	υ_s (NH_2)
1471	1490	1505 (w)	δ (NH_2)
-	1119 (s)	1149	υ (N-C-N)
989	983	969 (s)	υ_s (CF)
740	713	712 (s)	ρ (NH_2)
	616	640 (w)	υ (C=S)
494	500	475 (s)	δ (N-C-N)
469	-----		δ (N-C-N)

υ-stretching, ρ-rocking, δ-bending, υ_{as}–asymmetric stretching, υ_s-symmetric stretching

3.3 Optical absorption and NLO studies

Optical transmission spectrum gives valuable information about structure of the molecule because the absorption of UV and visible light involves the promotion of electron in σ and π orbital from the ground state to higher energy state. The optical transmittance range and transparency cut-off wavelength are the main requirements for device application. The optical absorption spectra of CTF crystals were recorded by Shimadzu UV-1061 UV–Vis spectrophotometer in the wavelength range 200-100 nm with high resolution**.** The CTF crystal has UV cut-off wavelength at 310 nm [Fig. 5a] attest the usefulness of the material for blue light emission and hence in optoelectronic field and non-linear optical applications [35]. The observed band beyond cut-off value confirms certain overtones and obsorbance due to electronic transition. And thereafter the transmission becomes almost constant and there is no change in transmission in the entire visible region up to 800 nm [Fig. 5b], these materials can find applications as windows in spectral instruments in that region and for optical fabrications [36].

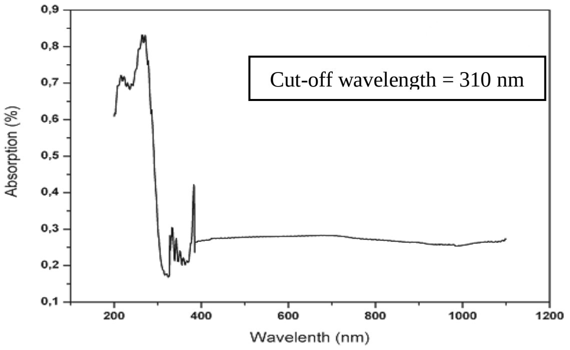

Fig. 5(a). Absorbance spectrum of CTF.

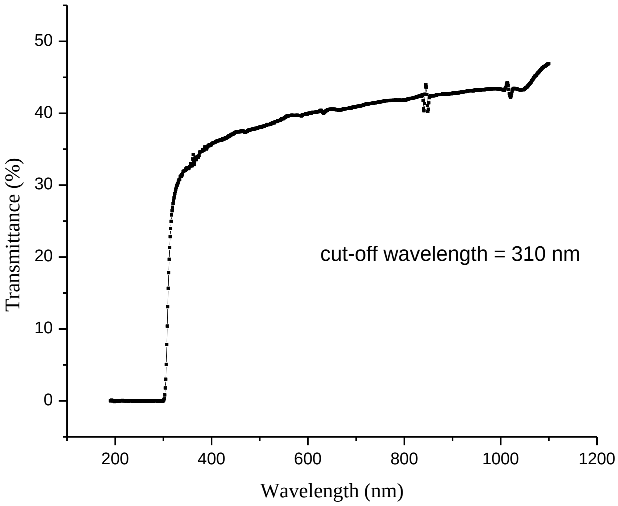

Fig. 5(b). Transmission spectrum of CTF.

The second harmonic generation (SHG) efficiency of CTF was determined by a modified version of the powder technique developed by Kurtz and Perry [37]. The crystal was ground into a homogeneous powder of particle size (100-150 μm) and densely packed between two transparent glass slides. A Q-switched Nd: YAG laser beam of wavelength 1064 nm (pulse width 8 ns, energy 5.5mJ/s) was allowed to strike the sample cell normally. The SHG output (532 nm) is finally detected by a photomultiplier tube and displayed on the oscilloscope. The second harmonic generations was confirmed by the emission of green radiation (532 nm) [38-41].

3.4 Thermal analysis

The thermal characterization was determined by thermo gravimetric analysis and differential thermal analysis using a NETZSCH STA 409 C/CD and NETZSCH DSC 204 thermal analyzer in a nitrogen atmosphere. The sample was kept in nitrogen atmosphere in the temperature range 25ºC-800ºC with a heating rate of 27ºC min^{-1}. The TGA thermogram of the CTF crystal is shown in Fig. 6. It is seen from the derivatogram of thiourea complex of cadmium halide that there is a major weight loss starting at 225°C before the start of the decomposition, illustrates the absence of physically adsorbed or lattice water in the crystal. Also in the derivatogram of DTA, a sharp endothermic peak at 225°C indicates the melting of the material. Further heating above 225°C results in the thermolysis substances, probably H_2S, CO_2, NH_3, CH_4, and CO molecule. The next stage of decomposition corresponds to the decomposition of residue i.e cadmium sulphide being the final product and since F is not directly bonded to cadmium ion which is confirmed by vibrational analyses, and also being highly electronegative combines with H favors the formation of HF on decomposition. The resulting fluorocarbons are not oxidized by air oxygen and are low-volatile [42]. Thus from thermal analyses, it is seen that the compound crystal can be utilized for device applications up to 225°C possible application in lasers, where the crystal is required to withstand high temperatures [43].

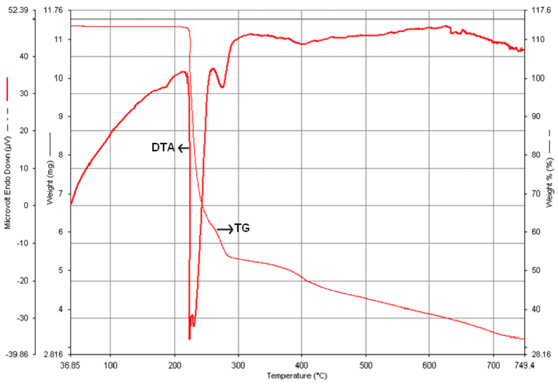

Fig. 6. TG & DTA Curves of CTF single crystal.

3.5 Dielectric studies

The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. Hence, the grown CTF single crystal was subjected to dielectric studies using HP 4275 Multi frequency LCR meter. A sample of dimensions 7.00 × 6.00 × 3.00 mm^3 was placed between the two copper electrodes and thus a parallel plate capacitor was formed. The capacitance on the sample was measured by varying the frequency from 100 Hz to 5 MHz. Dielectric constant ($\acute{\varepsilon}$) and dielectric loss of CTF single crystal was determined as a function of frequency, in the temperature range from 35° to 95°C. The dielectric constant $\acute{\varepsilon}$ was calculated using the relation $\acute{\varepsilon} = Cd/\varepsilon_0 A$ Where C is the capacitance, d is the thickness of the crystal, ε_0 is the vacuum dielectric constant and A is the area of the crystal. The dielectric loss was calculated using the relation $\varepsilon = \acute{\varepsilon} D$ Where D is the dissipation factor. Fig. 7a shows the plot of dielectric constant ($\acute{\varepsilon}$) versus applied frequency. The maximum dielectric constant (238) appeared in the lower-frequency region (100 Hz) and lowest value (50) in the high frequency (5 MHz). The contributions of all the four polarizations such as electronic, ionic, orientation and space charge are predominant in the lower frequency region [44]. This implies that the CTF single crystal exhibits normal dielectric behaviour. In normal dielectric behaviour, the dielectric constant decreases with increasing frequency and reaches a constant value, depending on the fact that beyond a certain frequency of the electric field, the dipole does not follow the alternating field. The crystals with high dielectric constant lead to power dissipation [45]. The material having low dielectric constant will have less number of dipoles per unit volume. As a result it will have minimum losses as compared to the material having high dielectric constant [46-47]. Therefore, CTF may be used for high speed electro optic modulations. The dielectric loss (ε) as a function of frequency at different temperatures is shown in Fig. 7b. The dielectric loss decreases with frequency exponentially and increases with temperature. It suggests that the dielectric loss strongly depends on the frequency of the applied field which is similar to the dielectric constant in the ionic system [48-49].

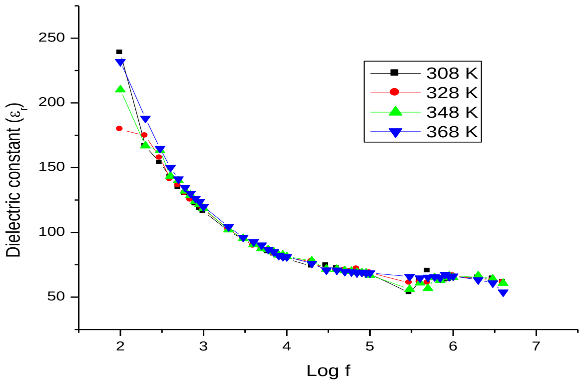

Fig. 7. (a) Variation of dielectric constant with frequency of the applied electric field.

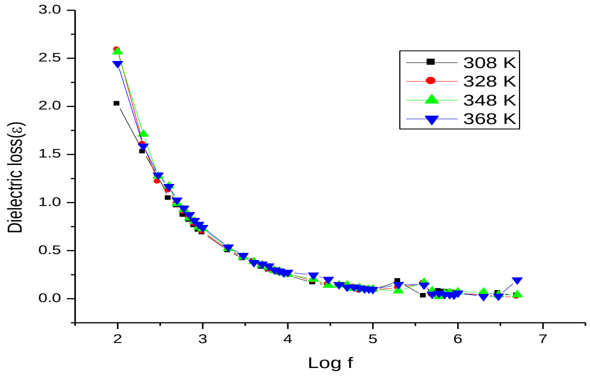

Fig. 7. (b) Variation of dielectric loss with frequency of the applied electric field.

4. Conclusions

In the present investigation, single crystals of cadmium thoiurea fluoride (CTF) was successfully grown using deionized water as solvent by slow evaporation and slow cooling technique. Its structural and spectral studies were carried out using single crystal X-ray diffraction, FT-IR and FT-Raman analysis. Crystallographic data indicate that the CTF crystallize under triclinic structure. Vibrational analysis confirmed the coordination of metal halide with thiourea in the crystal lattice. CTF possesses a wide transparency range with UV cut-wavelength at 310 nm and can find application in optical devices. The thermal studies confirm that the crystal structure is stable up to 225°C which is higher than the reported thiourea complexes, indicates its suitability for application in lasers field. NLO behavior of the CTF crystal has been observed by Kurtz-Perry powder technique. The dielectric constant and dielectric loss of the crystal studies for a wide range of frequencies suggest that the grown crystal is free from defects. Thus cadmium thiourea fluoride is potential candidate for nonlinear optical applications.

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