Synthesis and Characterization of Cerium Urea Thiourea Chloride Single Crystal Developed By Slow Evaporation Method

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Abstract : A single crystal of cerium doped urea thioureahasbeen grown successfully from its aqueous solution. The grown crystals have been subjected to X-ray diffraction studies to identify the morphology and structure. The DTA studies showed the thermal properties of the crystals. The functional group of the grown crystals was found by UV - Visible double beam spectra, FT-IR analysis, NMR and XRD studies.
*KEYWORDS : Urea, Thiourea, Cerium chloride, **Cerium urea thiourea chloride** (CeTUC), X-Ray diffraction, UV-Vis, FT-IR, NMR, TGA, NLO and micro hardness.*

I.   Introduction

Generation of nonlinear optical materials has a significant impact on laser technology, optical communication and optical storage technology [1, 2]. High-performance electro-optic switching elements for telecommunications and optical information processing are based on materials with high nonlinear optical properties. The search for new frequency conversion materials in recent years has concentrated on semi-organic complexes. The metal-organic materials have the potential for combining the high optical nonlinearity and flexibility of organics with temporal, thermal stability and excellent transmittance of inorganics [3-10].

Recently, the metal complexes of thiourea are being explored. Among the semi-organic NLO materials, metal complexes of thiourea received much attention as they have low UV cut-off wavelength and possess better nonlinearity than KDP. They have higher values of laser damage threshold and can be used in frequency doubling and laser fusion experiments [4-15]. In this paper, we are presenting a preliminary report on the growth and characterization of semi-organic single crystals, urea thiourea cerium chloride(CeTUC) by slow evaporation technique.

II. Experimental method

2.1 SYNTHESIS

1.2g of urea,8g ofthiourea and4.2g ofcerium chloride were dissolved in 30 ml of double distilled water. The solution was thoroughly mixed using a magnetic stirrer. A crystalline substance was formed. The Urea Thiourea Cerium chloride solution was prepared in water and maintained at $30^{o}C$ with continuous stirring to ensure homogeneous temperature and concentration. The solution was kept at $30^{o}C$ for fifteen days in order to get hard thiourea and urea doped single crystal.

Crystal growth large single crystals can be grown from slow evaporation solution growth. Single crystals of Cerium urea thiourea are grown by slow evaporation of the saturated aqueous solution at room temperature. Good quality single crystals were grown within fifteen days.

$$CeCl_3 + NH_2CONH_2 + NH_2CSNH_2 \longrightarrow CeCl.NHCSNH_2. NHCONH_2 + 2HCl$$
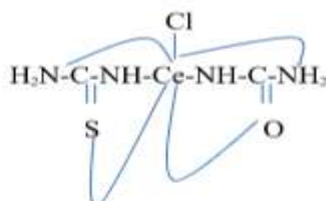
Molecular structure of CeTUC

Fig.1- Shape of CeTUC

2.2 UV-VIS SPECTRAL ANALYSIS

The optical transmittance range and transparency cut-off wavelength are the main requirements for device applications.

2.3 THERMAL ANALYSIS

Thermo Gravimetric Analysis (TGA) givesthe information regarding the phase transition and different stages of decomposition of the crystal system.

2.4 FT-IR SPECTRAL ANALYSIS

FT-IR Spectroscopic studies were effectively used to identify the functional groups present in the synthesized compound and to determine the molecular structure.

2.5 NMR

^{1}H NMR CHEMICAL SHIFTS

Molecular structure of the grown crystal was investigated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrums indicate the presence of different proton environments in the title crystal.

^{13}C NMR CHEMICAL SHIFTS

^{13}C NMR spectrum arises in the same way as in the proton NMR spectrum. Each carbon nucleus has its own electronic environment, different from the environment of other, non-equivalent nuclei; it feels a different magnetic field, and absorbs at different applied fields strength.

III. Results And Discussion

3.1. X-RAY DIFFRACTION ANALYSIS

Single crystal X-ray diffraction study was performed for the grown CeTUC crystal. It was found that CeTUC crystal belongs to orthorhombic system ($\alpha = \beta = \gamma = 90°$). Lattice parameter values of CeTUC are compared with reported TU in Table 1. In the case of doped sample, a slight variation in the cell parameters is observed, which may be due to the incorporation of urea and thiourea ligands. This analysis revealed that the induction of urea and thiourea ligand in the CeTUC crystal does not change the crystal system though there is a small change in the lattice parameters. The powder sample of CeTUC was scanned over the range 10-80° at a rate of 1° per minute and the powder X-ray diffraction patterns were indexed using Check cell software (Fig. 2).The Lattice parameter (a) was calculated by selecting the (102) plane using the formula [2],

$$Sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

Sample	System	2θ(degree)	FWHM	hkl	Lattice parameter (Å)	
					Calculated	Reference
TU	Orthorhombic	23.25	0.16	200	7.644	7.644
		20.81	0.16	020	8.527	8.559
		32.57	0.24	002	5.493	5.492

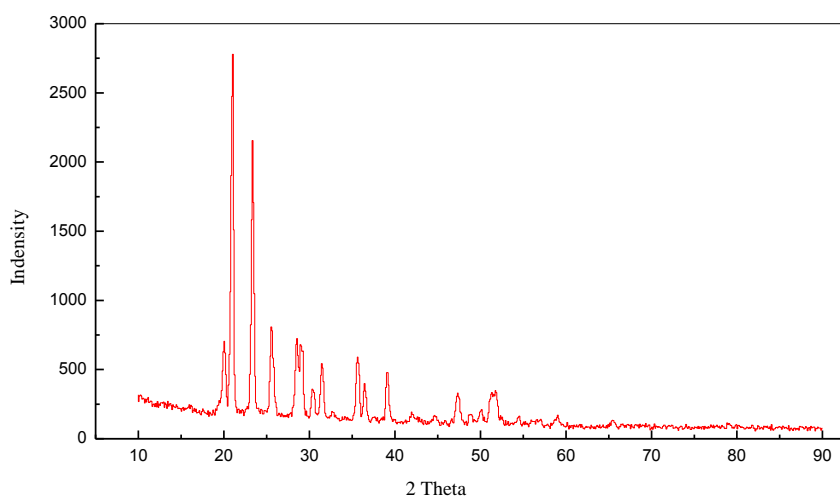| Sample	System	2θ(degree)	FWHM	hkl	Lattice parameter (Å)	
					Calculated	Reference
CeTUC	Orthorhombic	21.017	0.3718	200	4.2235	4.224
		23.395	0.3491	020	3.7993	3.805
		25.644	0.4347	002	3.4709	3.456

Fig.2- XRD pattern of CeTUC

3.2. FOURIER TRANSFORMS INFRARED SPECTROSCOPY

The FTIR spectra of Cerium urea thiourea grown crystals are shown in figure3. In the higher wavelength region, the peak at 3560 cm^{-1} is assigned to C-H, N-H stretching vibration. The region3558 cm^{-1} and 3320 cm^{-1} with strong intensity represents N-H stretching mode. The broad envelope positioned in between 3320 cm^{-1} and 2515 cm^{-1} corresponds to the symmetric and asymmetric stretching modes of NH$_2$ group. Combinational overtones extend to the bands from 2500 cm^{-1}.The peak at 1650 cm^{-1} indicating the C=O stretching mode of vibration. The NH$_2$ bending vibrations occur at 1578, 1572 and 814 cm^{-1}. The peak at 1530 cm^{-1} is due to NH$_2$ bending vibration. The peaks at 1430-1410 cm^{-1} corresponds to the C=S stretching. The C-C stretching mode of vibration occurs in 1420 cm^{-1} peak. The peak at 1205 cm^{-1} gives rise to C-N stretching mode of vibration. The spectra show absorption bands in the region of 1135 cm^{-1} and 1054 cm^{-1} which are due to in-plane C-H bending vibration. The band 1080 cm^{-1} signifies the N-H symmetric bending. The bands at 860 cm^{-1} and 790cm^{-1} revealed that C-N deformation mode. The ring deformation occursat the peak of815 cm^{-1}. C=O deformation is identified by the band at 640 cm^{-1}. C-H out-of plane bending peaks obtained at 660 cm^{-1} and 688 cm^{-1}. The bands 710, 680-620cm^{-1} represents C-C deformation and the presence of chloride. The absorption bands in the region of 480-420 cm^{-1} are due to N-C stretching vibration. The assignments confirm the presence of various functional groups present in the material. Our investigations were well compared with earlier reports [10-19].
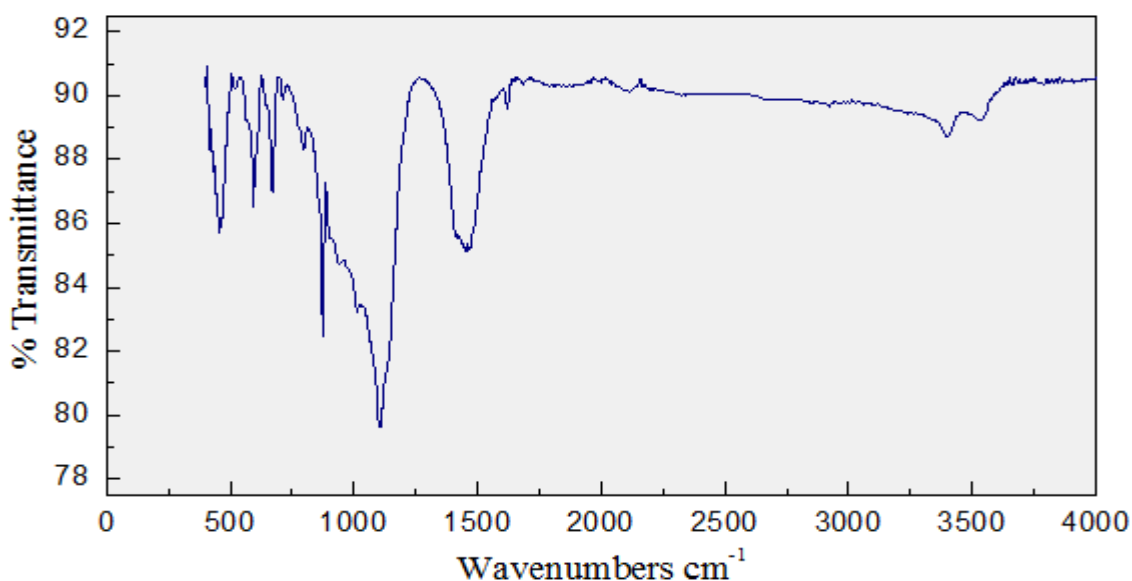

Fig.3- FT-IR spectrum of CeTUC

Table. 1-IR Spectrum data's

Crystal	Wavenumber (cm⁻¹)	Band Assignment
CeNTU single Crystal	3500	C-H, N-H
	3500 and 3123	N-H
	3490 and 2711	NH_2
	2995 - 3000	C-H
	1750	-C=O
	1420 - 1470	-C=S
	1350	-C-C-
	1215	-C-N-

3.3 UV- VISIBLE STUDIES

The UV-Visible spectrum of the single crystal CeTUC indicateslow absorption in the entire visible and near infrared region of the crystals. This is a desirable property for NLO applications since a wider optical transparency in these regions enhances the frequency conversion efficiency in the corresponding wavelengths.

The cuts off wavelengths of CeTUC single crystal were found to be 308 nm, 520 nm and 934 nm respectively. The optical transmittance in the entire visible region and the cut off wavelength (λ_{cut}) was observed as this is due to π-π* transition in the compounds. The band gap energy ($E_g = hc/\lambda$) was found to be 8.14eV for pure and Cerium urea thiourea crystals.The large transmission in the entire visible region and short cut off wavelength enables it to be a potential material for second and third harmonic generation.[20-27]

Crystal	Wavelength (nm)	% Transmittance
CeTUC	308	87.9
	520	118.4
	934	121.4

3.4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (NMR)

NMR spectrum of CeTUC was recorded using FT-NMR spectrometer. CeTUC crystal was powdered and dissolved in deuterated Dimethyl Sulfoxide (DMSO). FT-NMR spectrum recorded for CeTUC is shown in figure 4. A chemical shift at 7.027– 7.093ppm is due to =C-NH proton. The chemical shift at 7.02 ppm is assigned to =C-NH proton. Chemical shift at 2.508 ppm is due to –C=O. A chemical shift at 1.35 ppm is due to =C- proton [12]. The chemical shift at 7.093 is due to H–N-C=O. A chemical shift at 3.50 is due to –C=S. The above values confirm the structure of CeTUC.
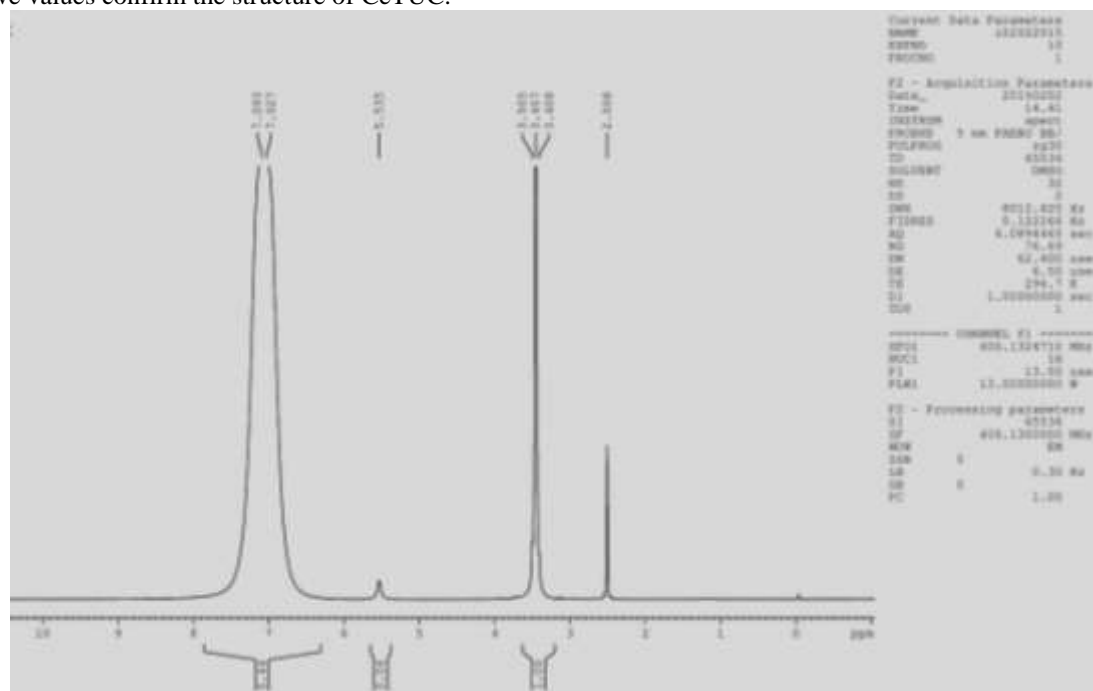

Fig.4- NMR spectrum of CeTUC

3.5 THERMAL ANALYSIS

TGA analysis of the CeTUC crystal was carried out in the temperature range 10- 900°C. The recorded thermogram is shown in Fig. 5. From TGA curve it is observed that the weight loss starts from 70°C. There is 13.5 % weight loss between 70 to 80°C. This weight loss is due to the liberation of HCl molecule. There is 7.7 % weight loss between 340°C to 380°C. This weight loss is due to the liberation of NH_3. There is 12.72 % weight loss between 565°C and 670°C. This weight loss is due to the liberation of CO. There is 17.7 % weight loss at 830°C. This weight loss is due to the liberation of H_2S. This endothermic event is in good agreement with the TGA trace [21].
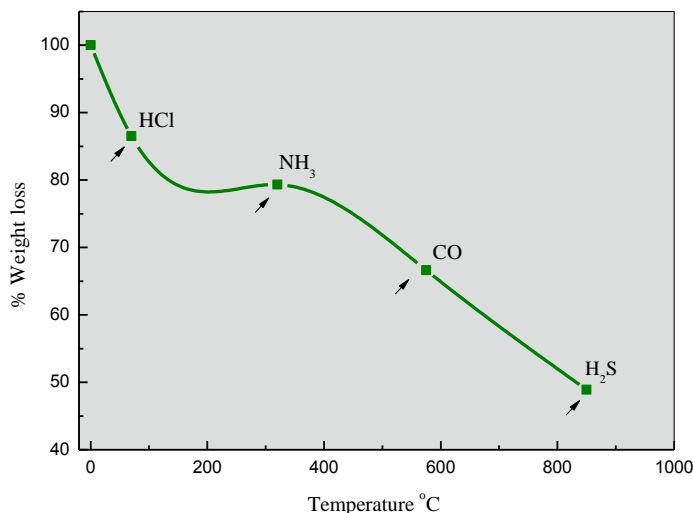

Fig. 5. Thermogravimetric analysis for the determining the weight loss

3.6 MICRO HARDNESS STUDIES

Hardness of the material is a measure of resistance that offers to deformation. The transparent polished crystal free from cracks was selected for hardness measurements. The indentations were made on the flat surface with the load ranging from 10 to 100 g using Shimadzu make-model-HMV-2 fitted with Vicker's pyramidal indenter and attached to an incident light microscope. The indentation time was kept as 5s for all the loads. The Vicker's hardness (Hv) was calculated from the relation [21],

$$Hv = \frac{1.8544P}{d^2} P/d^2 \ kg/mm^2$$

Where, P is the applied load and d the average length of the diagonal of the indentation mark. With P in g and d in µm, the units of Hv turned out to be kg/mm². The variation of micro hardness with applied load for the prominent (102) plane of the CeTUC crystal is shown in Fig. 6. It is found that the hardness values increases with the increase of the applied load. This behaviour of increasing micro hardness with the load known as reverse indentation size effect (RISE) [21], which is also attributed due to existence of distorted zone near crystal medium interface, effect of vibrations, specimen chipping etc., and the plastic deformation is dominant. At low loads or strains, plastic deformation of crystals mainly involves the nucleation of dislocations along a particular slip system. The RISE effect can be qualitatively explained on the basis of the depth of penetration of the indenter [21]. At small loads, the indenter penetrates only the surface layers and therefore, the effect is shown sharply at the early stages. When the applied load increases, the penetration depth also increases and the overall effect must be due to the surface and inner layers. When only one slip system is active during plastic deformation at low loads, the number of active parallel glide planes during indentation is low. Therefore the nucleating dislocations rapidly propagate into the material without experiencing substantial mutual interaction stress between them. Consequently in this stage, indentation depth increases proportionally with applied pressure.
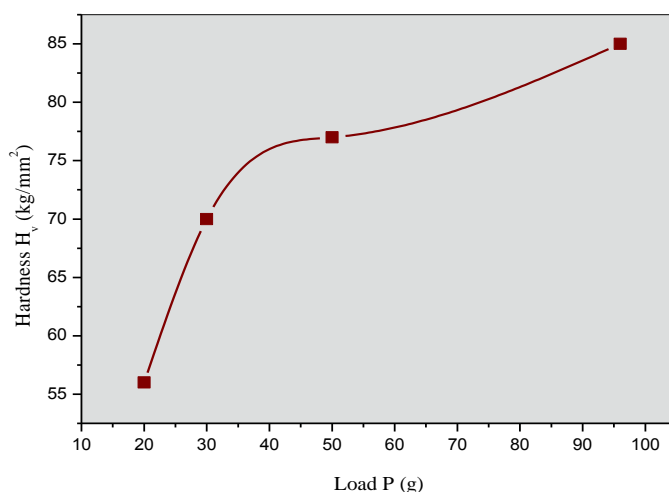
Fig. 7 : Variation of hardness number with load

3.7 NLO STUDIES

The second harmonic signal, generated in the crystals was confirmed from the emission of yellow radiation by the crystals. The NLO SHG values of the CeTUC single crystals were determined and compared to the reported SHG value of pure KDP [21, 27].

Crystal	Second harmonic signal output (mJ)	SHG efficiency (compared to SHG efficiency of pure KDP)
CeTUC	5.7	2.2

IV. Conclusions

The good quality single crystals ofCeriumurea thiourea are successfully grown by slow evaporation method at room temperature.The UV-Vis spectra showed that the crystals had a wide optical window, no absorbance and good optical transmittance in the entire visible region.FT -IR analysis confirmed the presence of functional groups in the grown crystals.TGA thermogram revealed the thermal stability of the materials.The powder X-Ray diffraction study confirms the lattice parameter values. The good optical quality and their suitability for NLO applications. Kurtz-Perry powder SHG test was employed to determine the SHG efficiency of the samples and the values were compared to the reported SHG efficiency of pure KDP.

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