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# Impact of Organic Entity on Structural and Optical Characteristics of Cadmium Thiourea Acetate Crystals for Nonlinear Optical Applications

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## Abstract

In this study, L-Methionine, an organic ligand, was introduced into cadmium thiourea acetate (CTA) crystals to investigate its impact on the structural and optical properties of the CTA crystals. Single crystals of L-Methionine doped CTA, were synthesized using a slow solvent evaporation technique from an aqueous solution. The crystallographic parameters were determined using powder X-ray diffraction. The functional groups present in the grown crystals were identified through Fourier Transform Infrared (FT-IR) spectroscopy. The effect of L-Methionine on the optical transmittance of the crystals was studied over the wavelength range of 200-900 nm using UV-visible spectroscopy. The data obtained from the transmittance measurements were then used to evaluate key optical constants of the grown crystals.

**Keywords:** Crystal growth, Single Crystal, Structural studies, Optical studies.

## 1. Introduction

Hybrid materials with outstanding non-linear optical (NLO) properties have been increasingly explored over the years due to their extensive applications in creating devices essential for optical signal processing, laser fusion, ultrafast laser systems, optoelectronics, and NLO-assisted photonic devices [1]. Recently, the crystals of the thiourea metal complex family have garnered significant attention. This is due to their organo-metallic bonds, which enhance non-linearity, laser damage thresholds, electronic properties, and mechanical and thermal stability [2]. Among these, cadmium thiourea acetate is a promising NLO crystal, known for its distinctive structural, optical, electrical, mechanical, and thermal properties, attracting extensive research [3-5].

Researchers have optimized the characteristics of CTA crystals by introducing various dopants, including amino acids like L-valine, L-proline, glycine, L-alanine, urea, and different metals

[6-10]. Studies reveals that amino acid dopants significantly improve crystal quality, optical transmittance, second harmonic generation (SHG) efficiency, mechanical strength, and dielectric properties. This is attributed to the presence of donor $NH_2+$ and acceptor COOH groups in amino acids, which facilitate intermolecular charge transfer. Moreover, amino acids typically feature chiral carbon atoms and crystallize in non-centrosymmetric space groups, enhancing their optical properties [11].

L-Methionine, a nonpolar sulfur-containing amino acid (IUPAC name: α-amino-β-methyl mercaptobutyrate), is particularly interesting due to its extensive hydrogen bonding network and chiral centres, making it an excellent candidate for improving the optical characteristics of materials [12]. Despite these advantages, no research has yet examined the effects of L-Methionine doping on the properties of CTA crystals. This study aims to fill that gap by investigating how L-Methionine influences the structural and optical of CTA crystals.

## 2. Experimental Procedure

### 2.1 Material synthesis and crystal growth

To synthesize the pure cadmium thiourea acetate (CTA) crystal complex, cadmium acetate and thiourea salts, sourced from Merck, were dissolved in double-distilled water in a 1:2 molar ratio. The chemical reaction for this synthesis is depicted below:

$$2[CS(NH_2)_2] + Cd\,(C_2H_30_2)_2 \longrightarrow Cd\,[CS(NH_2)_2]_2(C_2H_3O_2)_2$$

**Fig.1 Photograph of LM - CTA**

To ensure the purity of the CTA metal complex, it underwent repeated recrystallization. The purified CTA salt was then dissolved in deionized water to create a supersaturated solution. To this solution, precisely 0.3 mole% of L-Methionine was added while stirring continuously for 5 hours to ensure uniform doping throughout the CTA aqueous solution. This doped solution was then filtered using No.1 Whatman filter paper and transferred to a clean beaker for slow evaporation at room temperature (36°C). The purity of the 0.3 LM-CTA was further enhanced through successive recrystallization. High-quality, transparent crystals of L-Methionine doped CTA were successfully grown over 4 weeks, as shown in Fig.1.

## 3. Results and discussions

### 3.1. Powder XRD analysis

The sharpness of the PXRD pattern provides insights into the crystalline nature, the presence of defects, and grain boundaries within a material [13-14]. For the L-Methionine doped CTA crystal, PXRD analysis was conducted over a 2θ range of 10-70° using a Bruker advanced D8 powder X-ray diffractometer. The resulting PXRD pattern for the L-Methionine CTA crystal is displayed in Fig. 2. The prominent diffraction peaks were indexed using PowderX software. The analysis indicates that the LM-Methionine doped CTA crystal exhibits a similar orthorhombic crystal structure to that of the pure CTA crystal.

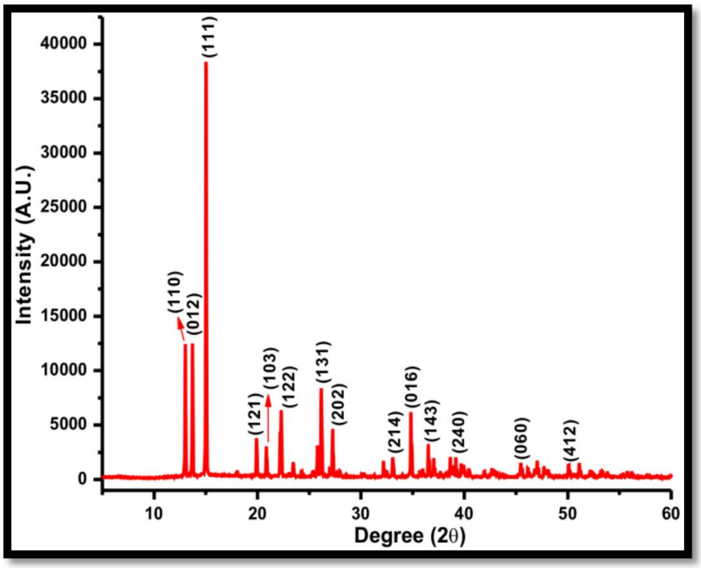

**Fig. 2. Powder XRD of M-CTA**

**Table 1. XRD data**

| Crystal | Structure | Volume (Å)$^3$ | Cell parameters (Å) |
|---|---|---|---|
| CTA | Orthorhombic | 508.80 | a = 7.56, b = 11.87,<br>c = 5.67 |
| LM-CTA | Orthorhombic | 512.38 | a = 7.58, b = 11.88,<br>c = 5.69 |

The evaluated unit cell parameters are listed in Table 1 and are consistent with previously reported values for similar crystals [15]. Additionally, the sharp diffraction peaks observed in the PXRD pattern of the L-Methionine CTA crystal suggest excellent crystallinity and fewer grain boundaries [16].

### 3.2. Fourier Transform Infrared (FT-IR) Analysis

FT-IR spectroscopy is instrumental identifying coordination sites, the nature of metal-ligand bonding, and elucidating the structures of coordination compounds. For the grown crystals, FT-IR spectral analysis was performed using a Bruker α-ATR spectrophotometer within the 600-4000 cm$^{-1}$ range. The recorded spectrum is displayed in Fig.3. Table 1 lists the observed vibrational frequencies and their assignments for both pure and doped CTA crystals.

In the pure CTA crystal, characteristic transmittance peaks were observed at 671.72 cm$^{-1}$, 725.23 cm$^{-1}$, 789.46 cm$^{-1}$, 942.63 cm$^{-1}$, 1110.50 cm$^{-1}$, 1412.02 cm$^{-1}$, 1495.11 cm$^{-1}$, 1628.48 cm$^{-1}$, 1667.34 cm$^{-1}$, 3306.14 cm$^{-1}$, and 3431 cm$^{-1}$ [17]. Specific peaks include 666.92 cm$^{-1}$, attributed to C-C bond deformation in thiourea, and C=S stretching at 720.70 cm$^{-1}$ and 778.51 cm$^{-1}$. Additional peaks were observed at 942.63 cm$^{-1}$ and 11103.81 cm$^{-1}$, corresponding to C-H deformation and N-C-N stretching, respectively.

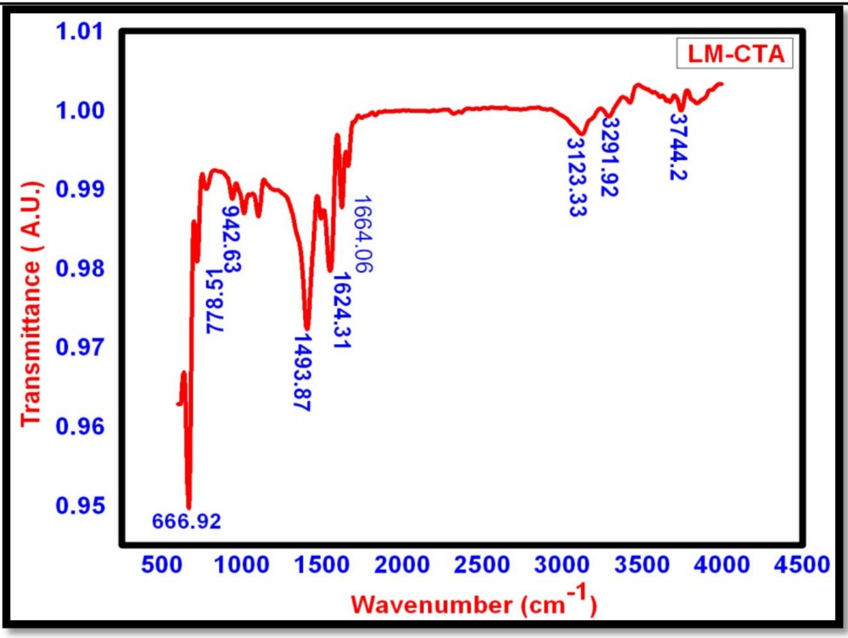

Fig. 3. FTIR Spectrum of LM-CTA

The C=S stretching was noted at 1407.17 cm⁻¹, and the COO⁻ stretching associated with the acetate ion appeared at 1493.87 cm⁻¹. $NH_2$ bending was identified at 1624.31 cm⁻¹, and the C=O stretching was confirmed by a peak at 1664.06 cm⁻¹. Peaks at 3291.92 cm⁻¹ and between 3744.22 cm⁻¹ and 3839.57 cm⁻¹ indicate $NH_2$ deformation and N-H stretching, respectively. These observed shifts in functional frequencies indicate the successful incorporation of the L-Methionine dopant into the CTA crystal structure.

**Table 1. Observed IR frequencies (cm$^{-1}$) of pure CTA and LM - CTA**

| Pure CTA | Doped CTA | Assignment |
|---|---|---|
| 671.72 | 666.92 | C-C Deformation of Thiourea |
| 725.23 | 720.70 | C= S Stretching Vibration |
| 789.46 | 7785.51 | C= S Stretching Vibration |
| 942.63 | 942.63 | C-H deformation |
| 1110.50 | 1103.81 | N-C-N Stretching |
| 1412.02 | 1407.17 | C=S Stretching |
| 1495.11 | 1493.87 | COO Stretching |
| 1628.48 | 1624.31 | $NH_2$ Bending |
| 1667.34 | 1664.06 | C=O Stretching |

| | | |
|---|---|---|
| 3306.14 | 3291.92 | $NH_2$ Deformation |
| 3431 | 3673.09 -3744.2 | NH Stretching |

### 3.3 UV-visible Study

Analysing optical transmittance is crucial to determine a crystal's suitability for various optical device applications. In this study, the linear optical properties of the pure and L-Methionine doped CTA crystals (each with a thickness of 1.5 mm) were examined using UV-visible spectroscopy. The transmittance spectrum was measured for the range of 200-900 nm using a Shimadzu UV-2450 spectrophotometer, and the results are displayed in Fig. 4. It is important to note that the transmittance of a single crystal can be influenced by both extrinsic factors such as structural defects, impurities, and crystal orientation, and intrinsic factors like optical density, electron transitions, and light-responsive optical units [18-20]. In this analysis, it was found that the grown crystals exhibit an optical cutoff at lower wavelengths. The maximum transmittance recorded for pure CTA was 45%, while the LM-CTA doped crystals achieved a significantly higher maximum transmittance of 85% across the visible spectrum. This indicates a substantial 40% increase in transmittance due to the doping with L-Methionine.

The transmittance of a crystal is determined by optically active building units, orientation along specific planes, and the density of defect centres. Defect centres can cause light loss within the crystal medium, leading to diminished optical signals [21-23]. The enhanced transmittance observed in the LM-CTA crystals suggests a reduction in defects due to the incorporation of L-Methionine into the crystal structure. As a result, the LM-CTA crystals, with their superior optical quality, are well-suited for applications such as UV-tunable lasers and generating harmonic signals at 1064 nm [24-25]. Additionally, the band gap of the LM-CTA crystal was estimated by plotting $(\alpha h\nu)^2$ against photon energy ($h\nu$) at room temperature. As shown in Fig. 5, the band gap (Eg) was determined to be 4.33 eV. This wide optical band gap in the visible region makes the doped CTA crystal a promising candidate for optoelectronic applications [26].

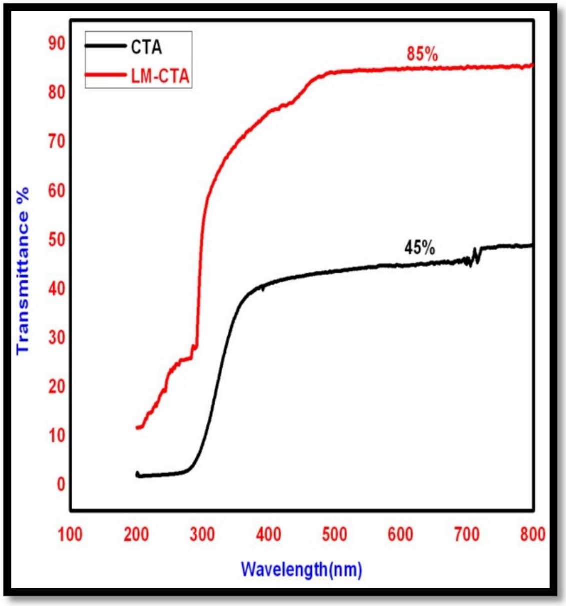

**Fig. 4 Transmittance Spectrum**

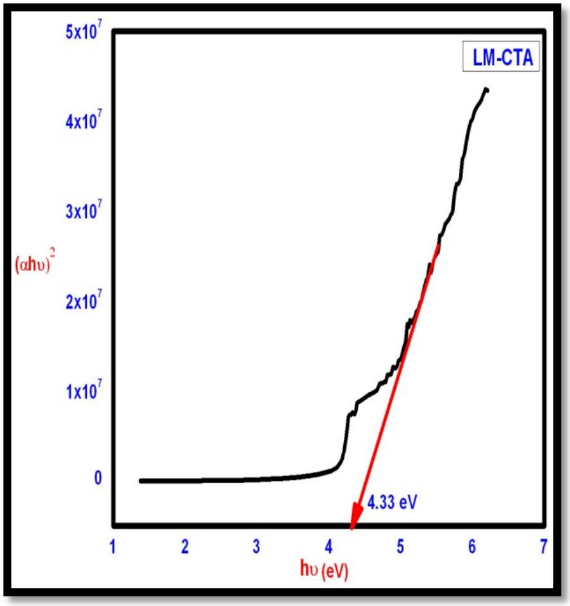

**Fig. 5 $(\alpha\hbar\nu)^2$ vs $\hbar\nu$**

A detailed study of optical parameters is essential for evaluating the optical quality of a crystal, which is crucial for its application in processing, tuning, calibrating, and designing technological devices [27]. This study explored how L-Methionine doping affects the optical properties of CTA crystals, including optical conductivity, extinction coefficient (k), refractive index (n), and reflectance (R).

The relationship between optical conductivity and photon energy, as shown in Fig. 6, indicates that optical conductivity increases with higher photon energy. This suggests that the doped crystal responds well to light, enhancing its potential for optoelectronic applications. The variations of the extinction coefficient, refractive index, and reflectance with wavelength are depicted in Fig. 7, 8 and 9 respectively. The extinction coefficient for the L-Methionine doped CTA crystal decreases with increasing wavelength, which is characteristic of semiconducting materials [28]. This reduction in the extinction coefficient at higher wavelengths implies lower optical losses, making the doped crystal more efficient for applications requiring high optical clarity and minimal signal degradation.

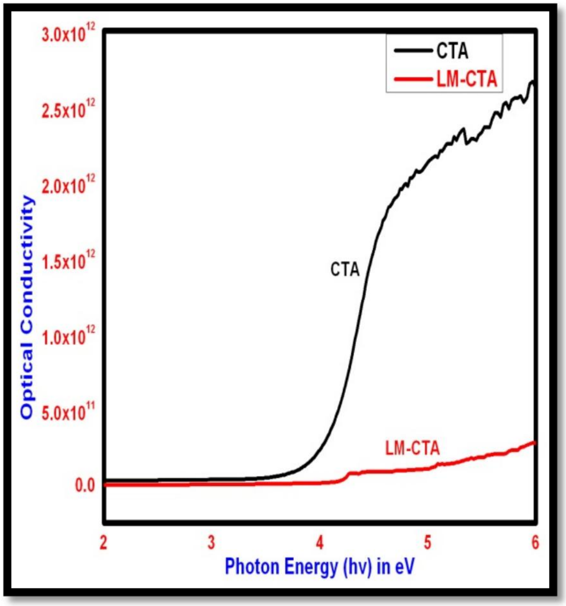

Fig. 6 Optical Conductivity

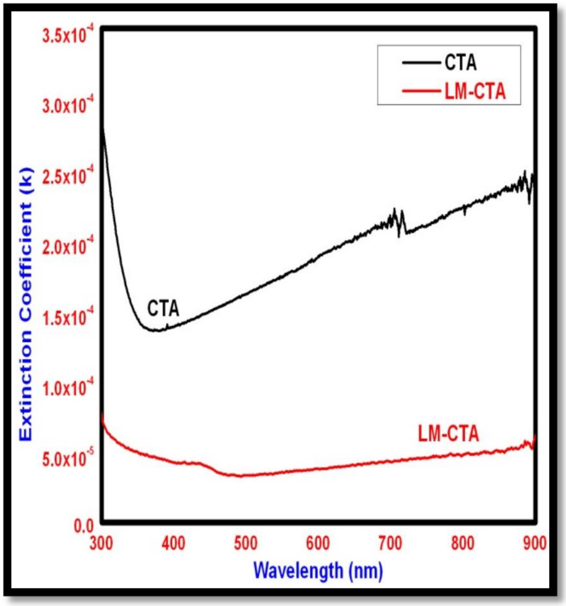

Fig. 7 Extinction Coefficient

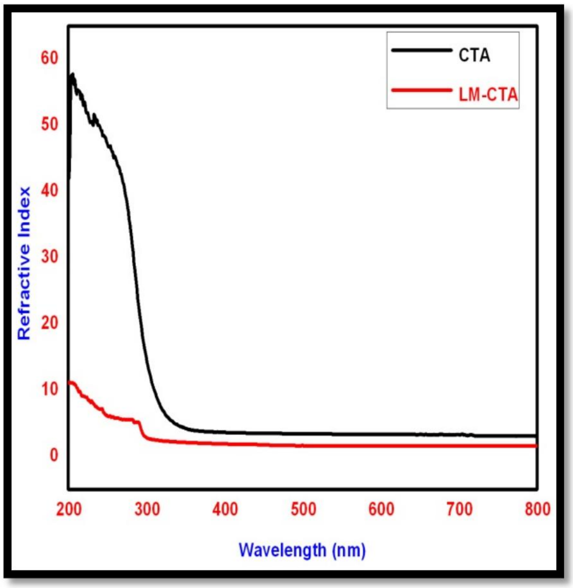

Fig. 8 Refractive Index.

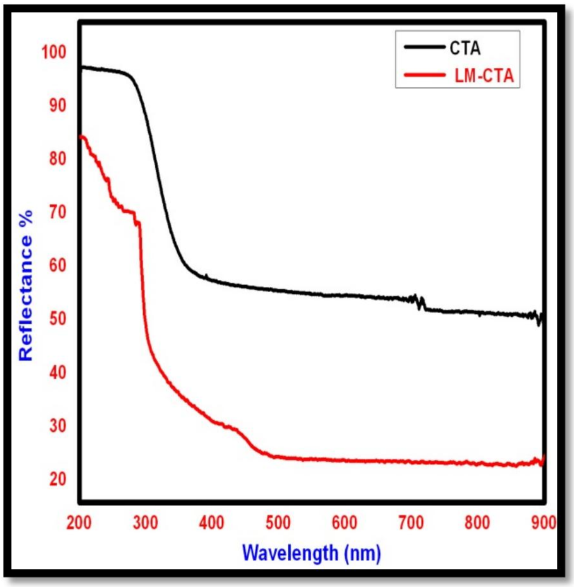

Fig. 9 Reflectance.

The refractive index, calculated using the formula reported by Bakr et al. [28], was determined to be 1.6 at a wavelength of 360 nm. Materials with lower refractive indices and reflectance are highly desirable for calibrating optical filters, reflectors, and resonators. Additionally, materials with lower refractive indices find extensive applications in holographic data storage devices and as external coating materials for solar thermal devices [29]. Therefore, the LM-CTA crystal is recommended as a promising optical material compared to pure CTA for advanced nonlinear optical (NLO) applications.

## 4. Conclusions

In the current study, high-quality pure and LM-CTA crystals were grown using the slow solvent evaporation technique. Analysis using PXRD confirmed the crystals' orthorhombic structure with slight variations in cell parameters. FT-IR analysis identified the functional groups present in the crystals. UV-visible studies indicated that the LM-CTA crystal exhibits an optical transmittance of 85%, indicating a 40% improvement compared to pure CTA. The grown crystal possesses a high optical band gap of 4.33 eV, leading to enhanced optical conductivity, lower extinction coefficient, reduced refractive index, and reflectance compared to pure CTA crystals, making it suitable for various nonlinear optical applications.

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