Crystal growth, surface morphology, mechanical and thermal properties of UV- nonlinear optical crystal: Mercury cadmium chloride thiocyanate (MCCTC) single crystal

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Abstract: Single crystal of mercury cadmium chloride thiocyanate (MCCTC) was grown by slow evaporation solvent method at ambient temperature (SEST) with a dimension of 10x5x5 mm³. The grown single-crystal’s structure and lattice constant, density and volume were estimated by using single-crystal X-ray diffraction studies. Additionally, the chemical etching and atomic force microscopy (AFM) analysis were used to investigate reverse growth and surface morphology. Moreover, the mechanical properties such as, hardness number, yield strength, Mayer index number, and stiffness constant were calculated by Vickers’s micro-hardness measurement. The thermal stability of grown single is stable up to 171 °C observed from TG-DSC, which reveals that the sample posses low thermal stability compared to other organometallic thiocyanate families of single crystals like MMTC(381 °C), MFCTC (241 °C) and ACCTC (247 °C). The non-linear optical study of second harmonic generation efficiency for MCCTC single crystal is 17 times superior to Urea.

1. Introduction

Recently, in the past two decays, the nonlinear optical (NLO) thiocyanate based crystalline materials plays a crucial role in the field of photonics device fabrication [1-3]. Based on the above results to achieve the appropriate single-crystalline materials with superior NLO effectiveness, the accomplishment of non-centrosymmetry in crystals play a crucial role, which can be sorted out by the selection of finest chromophore like thiocyanate (SCN). The well known bimetallic SCN crystalline family MHg₃(SCN)n (M=Fe²⁺,Mn²⁺,Cd²⁺) have good nonlinear optical properties. The halogen-based bimetallic thiocyanate single crystals Hg₅CdCl₆(SCN)n and Hg₅CdBr₄(SCN)n have suggested a new engineering pathway to achieve the effectiveness of UV-NLO crystals with a wider optical transparency [4,5]. In the present work we aimed to synthesis and a non-centro symmetric single
crystal of MCCTC grown by slow solvent evaporation method and ambient temperature. The detailed crystal surface characterization is not reported elsewhere. The basic crystal structure and physicochemical properties reported on earlier researchers [6-8]. In the recent investigation, efforts were made on halogen based bimetallic-thiocyanate single crystal of MCCTC which was grown from ethanol solution. In the grown crystal surface morphology, chemical etching and solubility were studied. From the solubility studies we observed the title compound of MCCTC is poorly soluble in water, low soluble in methanol, sparingly soluble in ethanol and fully soluble in acetone. The acetone has high evaporation rate, hence it is very difficult to use as a solvent for title compound. Moreover, the physicochemical properties like thermal and mechanical stability of the grown crystal were measured by TG-DSC and Vickers’s hardness measurement, respectively.

2. Materials and methods

High-purity MCCTC single crystal was synthesized by the following process. The Hg(SCN)$_2$ and CdCl$_2$ were taken in a 3:1 molar ratio. The cadmium chloride and mercury thiocyanate were dissolved in ethanol. To avoid co-precipitation when adding these two compounds by increasing the temperature above room temperature and should not exceed above 40 °C. Hence, the co-precipitated was completely removed in the first step by the frequent re-crystallization method. The MCCTC crystalline compound was synthesized by following chemical reactions. The repeated crystallization process we got good quality of single-crystal with the dimension of 10×5×5 mm$^3$ (figure 1) after 45 days by employed slow solvent evaporation method at ambient temperature.

$$3\text{[Hg(SCN)$_2$]} + \text{[CdCl$_2$]} \rightarrow \text{[Hg}_3\text{CdCl$_2$(SCN)$_6$]}$$

The solubility is an important factor for crystal growth technique [9]. From the solubility studies, the title compound of MCCTC is poorly soluble in deionised water and low soluble in methanol and sparingly soluble in ethanol. Hence, it is difficult to grow bulk size by the slow solvent evaporation method. The figure 2 depicts the solubility of MCCTC solvent versus different temperatures.

![Figure 1. Photograph of MCCTC single crystal](image1.png)  
![Figure 2. Solubility curves of MCCTC](image2.png)

3. Results and discussions

3.1 Single crystal X-ray diffraction analysis

The lattice cell parameters of grown MCCTC single crystal was confirmed by single crystal X-ray diffractometer using ENRAF NONIUS CAD-4F single crystal X-ray diffractometer with MoK$_\alpha$ radiation ($\lambda = 0.7710$ Å). The cell parameters thus obtained by the single crystal XRD are given in Table.1. The calculated values were well matched with the earlier reported values [10].
3.2. Chemical etching analysis
In a reverse growth rate, MCCTC single crystal was observed by chemical etching studies. The crystal plane (110) face of MCCTC single crystal using water is an etchant, to inspect the crystal growth mechanism and surface features [11]. The rock etch pits were observed when MCCTC single was etched with water for 20 and 30 s. There was no shifting in etch pits with changing etching periods (30-50s). Figure 3 depicts the etch pattern of MCCTC single crystal.

![Figure 3](image)

3.3 TEM – SAED and SEM – EDAX analysis
The selected area electron diffraction (SAED) pattern of MCCTC single crystal is shown in figure 4 performed using TEM. From the SAED pattern, we observed that in the title compound of MCCTC single crystal the constituent atoms were arranged in a regular periodic arrangement throughout the crystal, in a 3-D pattern. From SAED pattern, reciprocal lattice point reveals that grown crystal of MCCTC has high crystalline nature. Additionally, the FESEM-EDAX pattern (figure 5) is used to confirm the presence of elements in MCCTC single crystal, particularly the heavy elements Cd, and Hg. Additionally, thiocyanate (SCN) and the presence of halogens (Cl) in the MCCTC single crystal.

| Table 1 XRD data of MCCTC single crystal |
|------------------------------------------|
| Empirical formula                        | Hg₃CdCl₃(SCN)₆ |
| Crystal system                           | Rhombohedra   |
| Space group                              | R3c           |
| Lattice parameters                       | a = 11.2066 Å, 11.2066 Å, and c = 53.0112 Å, b = 11.2066 Å, c = 53.0112 Å |
| Volume (V)                               | 6657.5 Å³     |
| Z                                         | 12            |
| M₀                                        | 1133.55       |
| Wavelength                               | 0.5608 Å      |
| Temperature                              | 296K          |
| Dₓ                                        | 3.47          |
3.4 Atomic force microscopic analysis.

The surface properties of grown single crystal of MCCTC were analyzed with micrometer resolution. Good quality with the well smooth plane (110) was taken and the results were measured by Agilent-Pico-LE scanning probe microscope (SPM) AFM/MFM and WSxM 5.0 develop 9.1 software. A cantilever method is used to analyze the surface properties of grown single-crystal MCCTC. Figure 6a Shows the AFM images trace on the well smooth and plat surface of MCCTC for different magnifications using micro-fabricated cantilever. The spring constant and resonance frequency of the cantilever is measured to be 0.2 Nm$^{-1}$ and 22 kHz respectively. From the results, we observed from the 3D image (figure 6b) the MCCTC crystal posse's valleys and hillocks. The result reveals that the crystal surface has a large number of valleys and hillocks image drastically affects the average roughness (Ra) and root mean square (RMS = 0.6338 µm values [12-14]. The measured R$_a$ = 0.4417 µm values, maximum height (H$_{Max}$) and surface skewness (R$_{sk}$) are listed in Table 2.
Table 2

| S.No | Parameters                          | MCCTC  |
|------|------------------------------------|--------|
| 1    | Root Mean Square (RMS) in µm       | 0.6338 |
| 2    | Rough average ($R_{av}$) in µm     | 0.4417 |
| 3    | Maximum height ($H_{Max}$) in µm   | 3.2965 |
| 4    | Average height ($H_{av}$) in µm    | 1.6343 |
| 5    | Surface skewness ($S_{ss}$) in µm  | 0.2610 |
| 6    | Surface kurtosis ($S_{ks}$) µm     | 4.2400 |
| 7    | Plane off-set ($P_{off-set}$) in µm| -0.0211|
| 8    | Ironed surface ($I_s$) (µm$^2$)    | 1273.71|

3.5 Thermal studies

The TG-DSC measurements of MCCTC have been carried out in the thermal analyzer and NETZSCH DSC 204 differential scanning calorimeter. The MCCTC exhibits endotherms for the melting/decomposition between 90 °C and 175 °C in the DSC graph. A broad but weak endothermic peak, observed between 90 and 160 °C indicates the volatilization of absorbed re-crystallization solvent of ethanol. However, a sharp and well-defined endothermic peak observed at DSC profile at 171 °C is shown in figure 7, represent a phase change from Hg$_3$CdCl$_2$(SCN)$_6$ (MCCTC) to CdHg(SCN)$_4$ (CMTC) in addition to the other decomposition fragments. An endothermic peak at 256 °C highlights the decomposition of CdHg(SCN)$_4$ into its fragments such as CdS, HgS, dicyanogen and nitrogen. The weight loss of about 63.6 %, observed in the temperature ranging from 400 °C to 620 °C, may be due to the decomposition of three times of mercury sulfide (HgS), which is also confirmed by a TG peak at 491 °C. The residue observed in the TG trace at about 620 °C might be CdS whose weight loss is in good agreement with the calculated value (13.17 %). The possible and expected thermal decomposition reactions and phase change may be represented as

$$Hg_3CdCl_2(SCN)_6 \rightarrow CdHg(SCN)_4 + Hg(SCN)_2 + 2Cl$$

$$Hg(SCN)_2 \rightarrow 2HgS + (CN)_2$$

$$CdHg(SCN)_4 \rightarrow CdS + HgS + CS_2 + \frac{3}{2}(CN)_2 + \frac{1}{2}(N_2)$$

It is significant to mention that the thermal stability of MCCTC (171 °C) is superior to the other organometallic coordination complex crystals [15-17].

3.6 Vickers’s hardness studies

The Vickers’s microhardness measurements were carried out on the grown crystals of MCCTC to estimate the mechanical properties by using Reichert MD400E ultra microhardness tester. A single crystal of MCCTC is polished and the load is applied on the dominant faces (110) from 10 to 100 g for a constant indentation period of 10 s. The Vickers hardness number ($H_v$) of MCCTC crystals are estimated for different loads. A plot drawn between the hardness value ($H_v$) and corresponding load (P) is shown in Figure 8a. It is seen from Figure 8a that the Vickers’s hardness number ($H_v$) turn-down with the raise of load. From the result, it indicates that the microhardness of MCCTC is lower than that of the other organometallic materials like TMTM, CMTC, CMTD and MMTC.
The Mayer’s index number is calculated from Meyer’s law. In order to calculate the value of ‘n’, the graph is plotted against log P versus log d inset figure 8a, gives straight line; the shape of this straight line gives the value of ‘n’. The calculated value of ‘n’ is 1.70, belongs to the soft material category. Additionally, the important parameter yield strength was calculated by using the relation \( \sigma_y = (H_v/3) \) (when \( n < 2 \)). The variation of yield strength is shown as an inset in figure 8b. The stiffness constant at various loads have been calculated by using Wooster’s empirical formula \( C_{11} = H_v^{7/4} \) and is shown in inset figure 8b. From the plot, it shows the stiffness constant decreases with the increase of load. The calculated elastic stiffness constant (\( C_{11} \)) for different loads is given in Table 3. The variation of hardness with various planes shows the anisotropic nature of MCCTC single crystal [18-20].

![Figure 7. TG-DSC trace of MCCTC](image)

**Figure 7.** TG-DSC trace of MCCTC

![Figure 8.](image)

**Figure 8.a)** Vickers’s hardness number **b)** Stiffness constant and Yield strength (inset graph)
### Table 3. The various hardness parameters of grown crystal MCCTC

| S.No | Load (P) in g | Vicker’s Hardness (Hv) in kg/mm² | Stiffness constant C11 = (Hv^7/4) | Yield Strength (when n < 2) in Pa |
|------|--------------|---------------------------------|-----------------------------------|---------------------------------|
| 1    | 10           | 93.5864                         | 2.9594 × 10^{12}                 | 3.1955 × 10^7                  |
| 2    | 25           | 68.1404                         | 2.1547 × 10^{12}                 | 2.2713 × 10^7                  |
| 3    | 50           | 37.3658                         | 1.1816 × 10^{12}                 | 1.2455 × 10^7                  |
| 4    | 100          | 3.88713                         | 1.2292 × 10^{12}                 | 1.0295 × 10^7                  |

3.7 Second harmonic generation measurement

When a laser input of 6mJ/pulse is passed through MCCTC, the second harmonic signal green light (532 nm) is produced. The output power from the MCCTC crystal is compared to that of other organometallic crystals compounds such as FMTC, TMTM, MMTC and CLTC [21-23]. It is noteworthy to mention that, the title compound of MCCTC promising materials for frequency conversion material, laser display, and photonic device fabrication devices.

4. Conclusion

In the present investigation, a single crystal of MCCTC is grown by slow evaporation solvent technique. The solubility study shows that the ethanol is preferable comparable to other organic solvents. Grown single crystal of MCCTC crystal parameter and arrangement of atoms were confirmed by single crystal X-ray diffractometer and HRTEM-SAED pattern. Additionally, the presence of Hg, Cd, SCN and halogen (Cl) were confirmed by FE-EDAX analyzer. The important surface features were estimated by atomic force microscopy studies. Moreover, the thermal stability of the title compound of MCCTC is stable up to 171 °C. The Vickers hardness measurement is used to calculate the mechanical properties of the grown crystal. From the second harmonic generation efficiency of MCCTC is very much higher than that of the other organometallic thiocyanate family like MMTC, CMTC, TMTM, ACCTC, FMTC and CLTC as well as the conventional laser materials such as LAP, KDP and Urea.

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