Growth, optical, electrical and photoconductivity studies of a novel nonlinear optical single crystal: Mercury cadmium chloride thiocyanate

S.M. Ravi Kumar*, S. Selvakumar, P. Sagayaraj and A.Anbarasi

1PG & Research Dept.of Physics, Govt. Arts College, Thiruvannamalai - 606 603, India
2Department of Physics, Govt. College, Nandanam, Chennai – 600 035, India
3Department of Physics, Loyola College, Chennai – 600 034, India
4Department of Physics, Periyar Arts College, Cuddalore- 607 001, India

*Email: smravi78@rediffmail.com Mobile: 09884473709

Abstract SCN ligand based organometallic non-linear optical mercury cadmium chloride thiocyanate (MCCTC) crystals are grown from water plus methanol mixed solvent by slow evaporation technique. The grown crystals are confirmed by single crystal X-ray diffraction analysis which reveals that the MCCTC belongs to rhombohedral system with R3c space group. MCCTC exhibits a SHG efficiency which is nearly 17 times more than that of KDP. The dielectric constant, dielectric loss measurements of the sample have been carried out for different frequencies (100 Hz to 5 MHz) and, temperatures (308 to 388 K) and the results are discussed. Photoconductivity study confirms that the title compound possesses negative photoconducting nature. The surface morphology of MCCTC was also investigated.

Keywords: Solution growth; Characterization; NLO material; X-ray diffraction

1. Introduction

Nonlinear optics (NLO) has emerged as one of the most attractive fields of current research in view of its vital applications in areas like optical modulation, optical switching, optical logic, frequency shifting and optical data storage for developing technologies in telecommunications and signal processing. Materials with large second order nonlinear optical (SONLO) properties, short transparency cut off wavelengths and stable physicochemical performance are needed to realize many of these applications [1,2]. In this connection, attempts have been made by researchers to develop new organometallic compounds (which contain at least one direct M-C bond between metal and organic ligands) and coordination compounds (in which the metal and the ligands are connected through M-O, M-N, M-S or M-P bonds), these compounds combine the features of both inorganic and organic compounds. Organometallic and coordination compounds offer a variety of molecular structures by changing the metals, ligands, coordination numbers and so on. In metal thiocyanate complexes, the thiocyanate (SCN) plays a crucial role in combining the versatile ambidentate ligand with two donor atoms. Being a ligand with potential S and N donors, thiocyanate (SCN) ion is of interest not only due to the structural chemistry of its multifunction coordination modes, but also because of the formation of complexes with NLO activities [3-7]. Metallic thiocyanates and their derivatives are such potentially useful candidates among the organometallic systems because all of them contain \( \text{–S=C=N–} \) bridges, which connect with metal atoms, forming infinite two dimensional or three dimensional networks. The infinite networks confer a relatively large polarization, which induces relatively large macroscopic nonlinearities in these materials and the same has been proved recently by few research groups [8-10]. Mercury cadmium chloride thiocyanate (MCCTC) is one such potentially useful SONLO crystals with an empirical formula \( \text{Hg}_2\text{CdCl}_2(\text{SCN})_6 \). In the earlier works, MCCTC was grown from methanol by slow evaporation; unfortunately, the reported size of the crystal was very small. Hence, the present work addresses the key issue of growing bulk size crystal from a mixed solvent (methanol plus water) by slow evaporation technique. The grown crystal has been confirmed by single crystal XRD. The dielectric, photoconductivity and surface morphology studies are investigated and reported. The nonlinear optical property of the single crystal has been confirmed by SHG test.
2. Experimental procedure

2.1 Synthesis

The starting materials were analytical reagent grade (purity >98.0%) and used as purchased. Appropriate amounts of mercury thiocyanate and cadmium chloride taken in the molar ratio of 3:1 were dissolved in methanol solvent to synthesis MCCTC. The chemical equation is as follows.

\[ 3(Hg(SCN)_2) + CdCl_2 \rightarrow Hg_3CdCl_6(SCN)_6 \]

The synthesized salt was further purified by repeating the crystallization experiment twice or thrice.

2.2 Crystal Growth

The saturated solution of MCCTC was prepared in methanol plus water mixed solvent at room temperature and stirred well to enable homogeniation of the solution. The seed crystals were prepared by the conventional isothermal evaporation method. Good quality seed was chosen and then kept suspended into the supersaturated solution. MCCTC crystal was grown by slow evaporation method at 303 K. Crystal having dimensions up to 10 x 4 x 2 mm\(^3\) (Figure 1) was harvested in a period of 35-40 days.

![Figure 1. Photograph of as grown crystal of MCCTC.](image)

3. Results and discussion

3.1 X-ray diffraction (XRD) analysis

The lattice parameter values of MCCTC from single crystal XRD are determined as \(a = 11.184 \text{ Å} \), \(b = 11.191 \text{ Å} \) and \(c = 59.908 \text{ Å} \). The values of unit cell volume (\(V\)) and density (\(D\)) are 6493.2 Å\(^3\) and 3.47 g/cm\(^3\) respectively. The XRD data is in good agreement with reported value [11], and thus confirm the grown crystal.

3.2 Nonlinear optical (NLO) study

The nonlinear optical property of MCCTC was evaluated by the Kurtz and Perry powder technique [12] and microcrystalline powder of KDP was taken as the reference material. For a laser input pulse of 5.6 mJ, the second harmonic signal of 160 mV and 2.7 V were obtained through KDP and MCCTC respectively and thus confirming its second harmonic efficiency to be 17 times that of KDP.

3.3 Dielectric constant and dielectric loss measurements

Dielectric constant and dielectric loss of the sample have been measured for different frequencies (100 Hz to 5 MHz) at different temperatures (308 to 388 K). Figures 2 and 3 show the variations of dielectric constant and dielectric loss respectively as a function of frequency at different temperatures. It is observed from figure 2 that the dielectric constant (at 308 K) decreases with increase in frequency from 100 Hz to 10 kHz and then attains a constant value of 28.61. The same trend is observed for other temperatures too. It is also observed that the value of dielectric constant increases with temperature. Such variations at higher temperature may be attributed to the blocking of charge carriers at the electrodes [13]. The decrease of dielectric constant at low frequency region may be due to space charge polarization. Figure 3 indicates that as the frequency increases, the dielectric loss decreases exponentially and then attains a lower value of 0.049 at 308 K. The low value of dielectric loss confirms the lesser level of defects present in the grown sample.
3.4 Photoconductivity study

Photoconductivity measurements were made using the Keithley 485 picoammeter. The dark current was recorded by keeping the sample unexposed to any radiation. The experiment was performed at room temperature (303 K). The applied field was varied from 0 to 2500 V/cm. The variations of photo current ($I_p$) and dark current ($I_d$) with applied field are shown in Figure 4. It is observed from the plot that the dark current is always higher than the photo current for different applied field. Thus, MCCTC crystal is found to exhibit negative photoconductivity. The negative photoconductivity exhibited by the sample may be due to the reduction in the number of charge carriers in the presence of radiation [14].

3.5 SEM analysis

The SEM micrographs of MCCTC were taken at room temperature (303 K) with different magnification (x500 and x5000). The micrographs are shown in Figures 5 and 6. The surface appears smooth though it has well defined microcrystals on the surface. The formation of needle shaped microcrystals is clearly evident in figure 6 with higher magnification.
4. Conclusion
Optically clear single crystal of MCCTC was successfully obtained by slow evaporation method. Single crystal XRD study confirms the rhombohedral structure. The dielectric study revealed that the crystal has low dielectric constant and low dielectric loss in the high frequency region. The negative photoconducting nature of MCCTC crystal is confirmed by photoconductivity studies. The surface morphology was analyzed.

5. References
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