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Evaluation of the Structural, Optical, Thermal, Mechanical and NLO properties of Cadmium Chloride incorporated Thiosemicarbazide crystal- A Potential material for optical and Second harmonic generation applications

J. Thomas Joseph Prakash*, J. Martin Sam Gnanaraj
PG and Research Department of Physics, H.H. The Rajah's College
(Affiliated to Bharathidasan University) Pudukkottai -1, Tamilnadu, India

Abstract*— Conventional Slow evaporation solution growth technique was employed to grow crystals of Group 12 metal halide incorporated thiosemicarbazide. The grown material was subjected to various characterizations studies in order to test its suitability in NLO device fabrications below its melting point. The optical properties were examined by UV Visible NIR spectral studies. The melting point and the other thermal parameters were obtained from the TG/DTA thermogram. The obtained results show that the title material is a very effective candidate possessing excellent NLO properties.

***Index Terms*— NLO, Optical assessesment, Single crystal XRD, TG/DTA.**

I. INTRODUCTION

In recent years there has been considerable interest on the synthesis of semiorganic nonlinear optical materials with good second-order nonlinearities having potent application in telecommunication, optical computing and optical data storage devices [1]. Poor mechanical, thermal properties, damage during processing, difficulty in growing large size for device application of the organic NLO crystals paved the way for exploring a new class of materials known as the semiorganic materials. Semiorganic crystals have good thermal, mechanical properties and large nonlinear coefficient [2, 3].

Since the theory of double-radical model (organic conjugated molecular groups are included in the distorted polyhedron of coordination complex) was brought up in 1987 metal–organic coordination compounds as NLO materials have attracted much more attention for their considerable high NLO coefficients (contrast to inorganic materials), stable physico-chemical properties and better mechanical intension (contrast to organic materials). With the guidance of this theory, many metal–organic coordination materials with good NLO effect have been designed and synthesized [4-10]. The metal–organic coordination complexes can also provide the following advantages: (i) an enhancement of the physico-chemical stability, (ii) the breaking up of the centro-symmetry of the ligand in the crystal, and (iii) an increase in NLO intensity, via metal–ligand bridging interactions. The central metal ion (together with its hybrid electronic orbital) not only offers a certain anisotropic field to keep the NLO active chromopher ligands in a favorable acentric arrangement but also involved in the NLO processes. In this respect thiosemicarbazide and its derivatives are interesting materials for SHG generation. Synthesis of Thiosemicarbazide cadmium chloride monohydrate crystals was already reported by A. Sankar et. al., [11] and P. Maadeswaran et. al., [12] In the present work, the synthesis and growth of Cadmium thiosemicarbazide chloride crystals are reported. Further the Photoluminescence was measured in the visible region.

II. CRYSTAL GROWTH

Cadmium thiosemicarbazide chloride was synthesized by dissolving commercially available Cadmium chloride (Merck, AR) and Thiosemicarbazide (SRL, AR) in equimolar ratio. The reactants were dissolved separately in deionized water of 18.2 MΩ resistivity and stirred well. After two hours, Cadmium Chloride solution was poured

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slowly into the solution containing thiosemicarbazide. In order to avoid the precipitation of multiple phases, the thiosemicarbazide solution was maintained at 80 °C. The reactant mixture was agitated thoroughly for 8 hours so as to homogenize the solute particles. The solution was evaporated in dryness at room temperature. The purity of the synthesized salt was increased by repeated recrystallization. Recrystallized salt was used for the crystal growth of CTSC crystals. Transparent crystals are obtained after a span of 20 days. The grown CTSC crystals are shown in the Fig. 1.

III. SINGLE CRYSTAL X-RAY DIFFRACTION

ENRAF NONIUS CAD4 X-Ray diffractometer equipped with MoKα radiation was employed to estimate the unit cell parameters of the CTSC crystal. The analysis was carried out at room temperature. The structure was solved by direct method and refined by full matrix least squares technique using SHELXL program. From the single crystal XRD results it was concluded that CTSC crystallizes in monoclinic system with the space group Cc. The estimated lattice parameter values are a= 10.108 Å, b= 13.917 Å, c= 6.88 Å, α= β= 90.58°, γ= 125.86° and V= 967.830 $Å^3$. The obtained lattice parameters agree very well with the reported values [11].

IV. POWDER X- RAY DIFFRACTION

The powder XRD data were collected for the grown crystals using JEOL (JDX-8030) X-Ray diffractometer equipped with CuKα radiation. The wavelength of the radiation used was 1.5406 Å. The sample was scanned at 25 °C in step scans with the scan rate and step size of 2°C/min and 0.1 respectively within the range of 10° to 75°. The high crystalline nature of the sample was well revealed by the prominent peak at specific 2θ angle. The powder XRD pattern of CTSC crystal is shown in Fig. 2. The XRD data for CTSC crystals are shown in Table 1. The peaks observed in the XRD pattern were indexed by JCPDS software.

V. FOURIER TRANSFORM INFRARED SPECTRAL ANALYSIS

The FTIR analysis was carried out using PERKIN ELMER FTIR spectrometer by KBr pellet technique for deducing the presence of functional groups and the coordination of Thiosemicarbazide and Cadmium Chloride. The spectrum was recorded within the range of 400 cm^{-1} to 4000 cm^{-1}. The recorded FTIR spectrum is shown in Figure 3. The broad peak positioned at 3184 cm^{-1} corresponds to O-H stretching vibration. The absorption bands at 1684 cm^{-1} is attributed to asymmetric stretching band of NH^{3+}, 1456 cm^{-1} to symmetric stretching band of NH^{3+}, 1374 cm^{-1} to C=S stretching vibration, 1075 cm^{-1} to C-N stretching vibration. The narrow bands at 674 cm^{-1} and 750 cm^{-1} are due to the vibrations of Cl^- of ν_1, ν_2 respectively. The peak at 1200 cm^{-1} and 1617 cm^{-1} are attributed to C=S and N-C-N stretching respectively. The obtained values coincide with the reported FTIR transmission peaks [11,12].

VI. LINEAR OPTICAL ASSESSESMENT

The nature of CTSC crystals and the optical parameters such as percentage of transmission, optical band gap are obtained from the UV visible NIR spectral analysis. Transmission spectral analysis is important for any NLO material because a NLO material can be of practical use only if it has wide transparency window. The optical characterization of CTSC crystal was carried with the help of a LAMBDA 35 UV Visible spectrophotometer. The transmission spectrum was traced within the range of 190 to 1100 nm. For achieving this, a sample of 2 mm thick was used. Figure 4 shows the transmission spectrum of CTSC single crystal.

The optical absorption coefficient was calculated using the relation

$$\alpha = (2.303 \times \log(1/T))/d \quad \text{---------- (1)}$$

Where T is the transmittance, d is the thickness of the crystal [13].
The energy dependence of the absorption coefficient suggests the occurrence of the direct band gap and hence it obeys the relation

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad \text{----------(2)}$$

Where E_g is the optical band gap, A is a constant. $(\alpha h\nu)^2$ vs. hν is the fundamental absorption region which is plotted in the Figure 5. E_g is evaluated by the extrapolation of the linear part. The band gap was found to be 3.8 eV. From the recorded spectra, the band gap of CTSC crystal was calculated and the variation of $(\alpha h\nu)^2$ vs. hν was studied using tauc's plot (Figure 5).

Also from the transmission spectra it is known that the sample has a lower cut off wavelength at 290 nm. The crystal possesses a wide transparency window in the entire visible light region, with a transmittance percentage of 45% which confirms the suitability of the title compound in NLO device applications. Since the lower cut off is

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observed at 290 nm it can be concluded that transparent well shaped CTSC crystals can be used in optical filter applications.

VII. PHOTOLUMINESCENCE ANALYSIS

The excitation and emission spectra of CTSC crystals was recorded using the Cary Eclipse spectroflurometer. The sample was excited at 290 nm. The emission spectrum was measured in the range of 300 to 400 nm. The emission peak at 394 nm was observed in the emission spectrum. The results indicate that the CTSC crystals have UV emission which is confirmed in the linear optical assessment. The band gap energy was calculated using the formula

$$\mathbf{Eg= hc/\lambda e}$$

Where h, c and e are constant λ is the wavelength of fluorescence. The band gap energy was found to be 3.8 eV for CTSC crystal. The excitation and emission spectrum of CTSC crystal is shown in Figure 6.

VIII. THERMAL ANALYSIS

The thermal stability of the CTSC crystal was checked by subjecting the sample to TG/DTA analysis in a closed chamber with controlled nitrogen flow atmosphere. The thermal stability of the sample was assessed within the range of 50°C to 900°C at a heating rate of 20K/min. The TG and DTA thermogram of CTSC crystals are shown in Figure 7.

From the TG/DTA thermogram (Figure 7), it is observed that the sharp weight loss around 147 °C is due to the absorption of water in the crystal. This result coincides with the DTA curve that the material is stable up to 147°C which corresponds to the melting point of the sample. After that a sharp endothermic transition begins in the material and the material decomposes around 290°C. The sharpness of the peak indicates the crystalline nature of the material. At various stages elements like sulphur, nitrogen present in the NH group are liberated in the gaseous state. It can be inferred that the material can be used for fabrication in NLO devices below its melting point.

IX. MECHANICAL STABILITY ANALYSIS

The mechanical stability of the CTSC crystals were analysed by the Vicker's microhardness test which was performed using the Vicker's microhardness tester fitted with a diamond indenter. The well polished, flat faced crystals were used in the evaluation. The hardness test was performed for the loads varying from 25g to 100g and the stability of the crystals towards the external stresses was observed. Also the indentation time was kept constant (10 seconds). The Vicker's microhardness value was obtained from the relation,

$$\mathbf{H_v = (1.8544 \times P)/d^2\ kg/mm^2}$$

Where H_v is the Vicker's hardness number in kg/mm^2, P is the applied load in kg, d is the average diagonal length of the indentation mark in mm.

A graph was plotted between the Vicker's hardness number (H_v) and applied load P (Figure 8) and it was observed that the crystals are quite stable up to 100 g. The work hardening coefficient was calculated by plotting the graph between log p vs log d (Figure 9) and the slope of which gives the Meyer's index according to the relation [14],

$$\mathbf{P= K_1 d^n}$$

It was found from the graph that the title material, Cadmium Thiosemicarbazide chloride comes under the category of soft materials.

X. SECOND HARMONIC GENERATION TEST

The Second Harmonic Generation efficiency of the CTSC crystals were tested by Kurtz and Perry experimental setup [15]. The grown single crystal of CTSC was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and was illuminated using Spectra Physics Quanta Ray DHS2. Nd:YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repetition rate 10 Hz. The second harmonics signal, generated in the crystal was confirmed from the emission of green radiation by the crystal. A finely powdered sample of potassium dihydrogen orthophosphate was used as a reference material in the present measurement. The SHG radiation of 532nm green light was collected by a photomultiplier tube (PMT-Philips Photonics-Triax-550) to collect only the 532nm radiation. The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052B). The input laser energy incident on the powdered sample was chosen to be 0.68 J. Powder SHG efficiency obtained for CTSC monohydrate is about 1.9 times that of potassium dihydrogen orthophosphate crystal.

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Volume 3, Issue 4, July 2014

XI. HELPFUL HINTS

A. FIGURES

Fig 1 as grown CTSC crystals

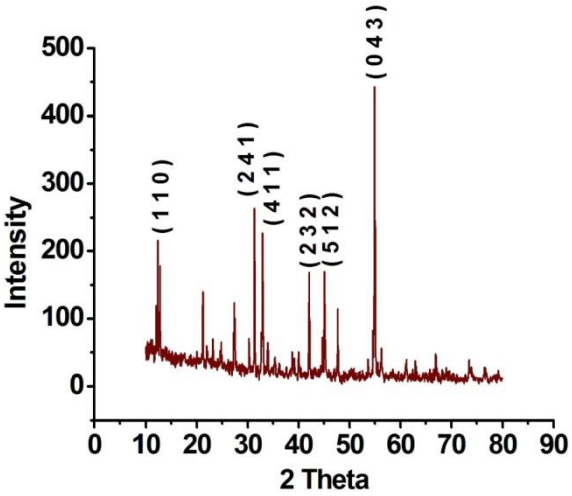

Fig 2 Powder XRD pattern of CTSC crystals

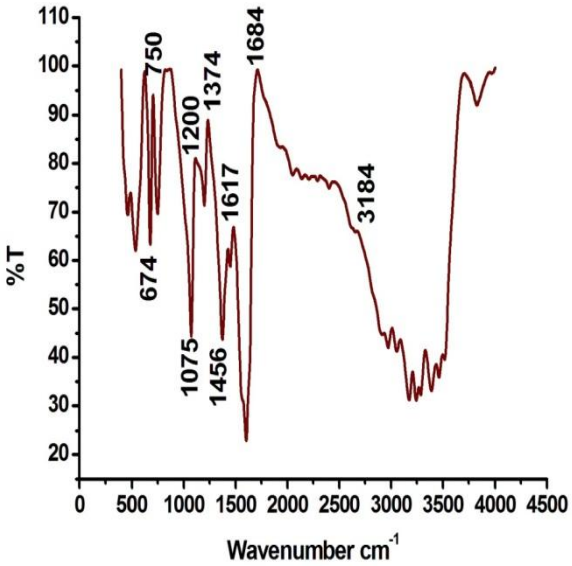

Fig 3 FTIR Transmission spectrum of CTSC crystals

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Volume 3, Issue 4, July 2014

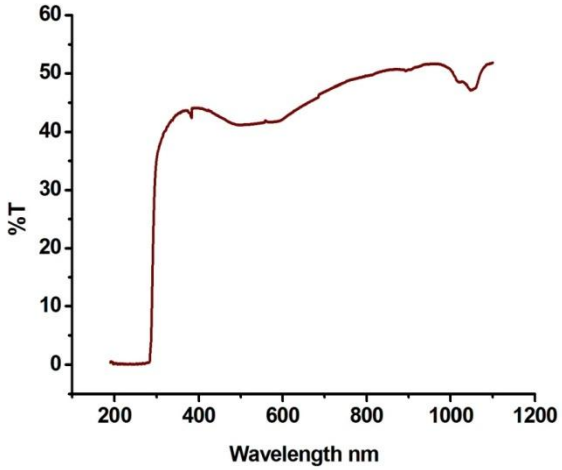

Fig 4 Optical Transmission spectrum of CTSC crystals

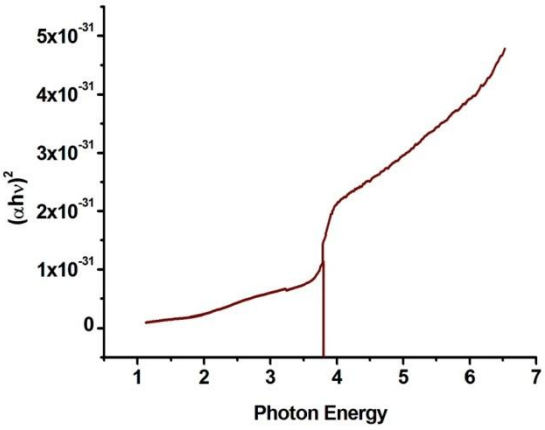

Fig 5 Tauc's plot for CTSC crystals

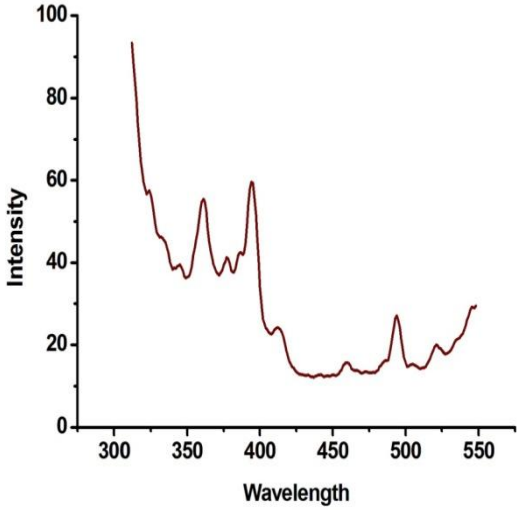

Fig 6 PL spectrum of CTSC crystal

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Volume 3, Issue 4, July 2014

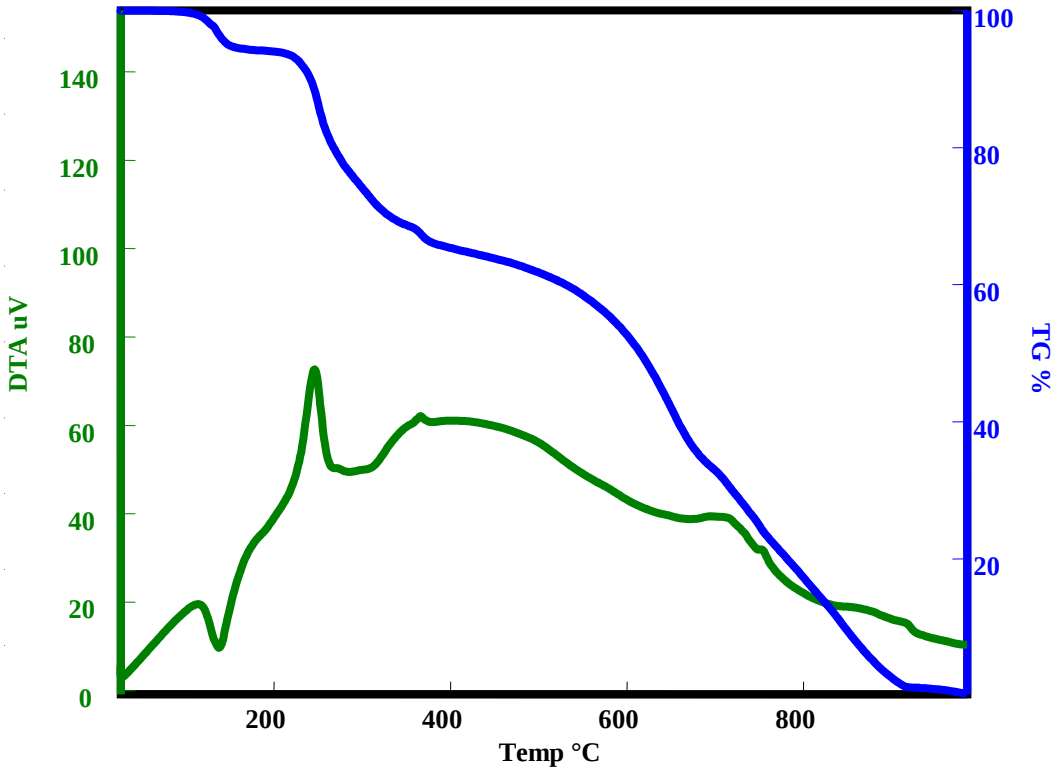

Fig 7 TG/DTA thermogram of CTSC crystal

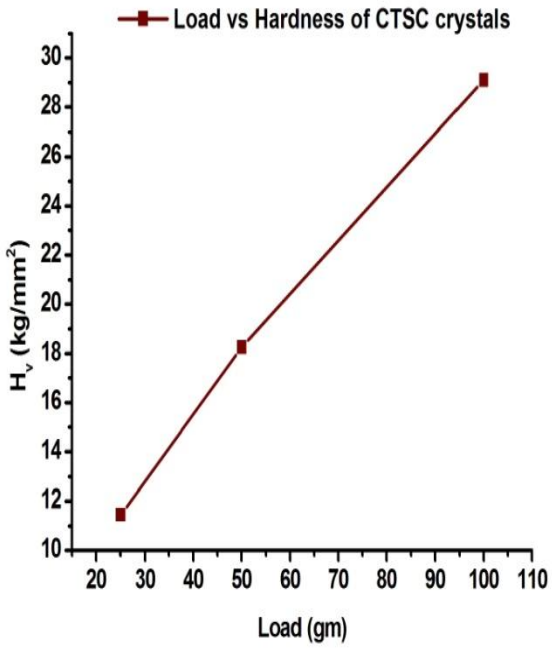

Fig 8 Load Vs Hardness

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International Journal of Engineering Science and Innovative Technology (IJESIT)
Volume 3, Issue 4, July 2014

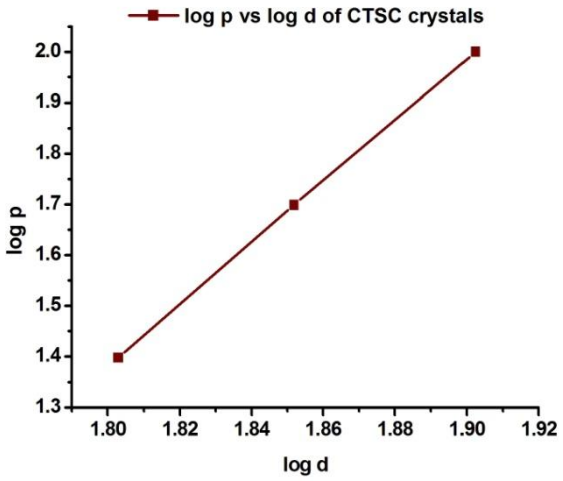

Fig 9 log p vs log d

B. TABLES

Table 1 Powder XRD data of CTSC crystals

2θ	Experimental d spacing value	h	k	l
0.10	7.1613	1	1	0
0.088	2.853	2	4	1
0.09	2.717	4	1	1
0.11	2.146	2	3	2
0.06	2.009	5	1	2
0.10	1.670	0	4	3

XII. CONCLUSION

Cadmium chloride incorporated Thiosemicarbazide crystals were grown by Slow Evaporation solution growth technique. The grown crystals were subjected to single crystal X-Ray diffraction for the estimation of the lattice parameters and it was found that the title compound crystallizes in monoclinic system with Cc space group. The spectral properties were deduced by the FTIR spectral analysis. The UV Vis NIR spectral analysis provides the information regarding the optical parameters of the sample. It was found that the title compound possesses a wide transparency window with a lower cut off falling within the visible light region < 300 nm which was confirmed in the excitation spectrum of the Luminescence analysis. Hence it can be concluded that the title material exhibits NLO property. The melting point and the thermal stability were checked by the TG/DTA analysis. The mechanical stability was evaluated by the Vicker's microhardness test and the results suggest that CTSC crystals belong to the category of soft materials. NLO studies confirm that CTSC crystals are eligible candidates in NLO applications.

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Volume 3, Issue 4, July 2014

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