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Synthesis and characterization of a novel non-linear optical crystal Cadmium mercury thiocyanate glycol monomethyl ether

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ABSTRACT: *Non-linear optical single crystals of cadmium mercury thiocyanate glycol monomethyl ether CMTG were conveniently grown from a mixed solvent of glycol monomethyl ether and water by slow evaporation method. The good quality single crystal has been harvested in a period of 60-65 days. The crystal structure and morphology were confirmed by single crystal X-ray diffraction analysis. Presence of functional groups and coordination of glycol monomethyl ether and thiocyanate in the CMTG compound were confirmed by FTIR analysis. Thermal stability and decomposition process were studied by means of thermogravimetric analysis and differential thermal analysis. Dielectric measurements on CMTG single crystal was carried out for various frequencies at room temperature. The relative second harmonic generation efficiency of CMTG crystal has been tested by Kurtz-Perry powder technique. The optical studies has been carried out and found that the tendency of transmission observed from the specimen with respect to wavelength of light is practically more suitable for opto-electronic applications.*

Keywords: *Organometallic, synthesis, structure, solvent evaporation method, second harmonic generation, Dielectric constant.*

I. INTRODUCTION

The emergences of new materials with superior quality are often responsible for major advantages in new technologies. In recent years much attention has been paid to the research of novel, high-quality nonlinear optical (NLO) crystals. In opto-electonic technologies and communication, fibre optics plays a vital role. The organometallic and coordination complex crystals combine the advantages of both organic and inorganic crystals. Compared to organic crystals, the inorganic crystals have good physicochemical stabilities, short UV cut off wavelength and large second order non linearities. Recently, it is found that transition metal, inorganic compounds and coordination complex have emerged as extremely promising building block for opto-electronic materials. In the present trend, thiocyanate group of materials are gaining attention due to their good second order non-linearity. Cadmium mercury thiocyanate glycol monomethyl ether (CMTG) is a complex NLO crystal which belongs to orthorhombic crystal system with noncentro symmetric space group Pca21. In the present investigation, the growth of CMTG has been achieved by slow solvent evaporation technique. The growth of relatively larger size of dimensions 14x7x3mm^3 have been reported here. The grown crystals were characterized by XRD, NLO test, FTIR, optical absorption studies, dielectric studies, thermal analysis and photoconductivity studies. The non-linear optical property of the single crystal has been confirmed by Second harmonic generation.

II. EXPERIMENTAL DETAILS

Starting materials used were analytical reagent grade of purity 98%. CMTC crystal is synthesized by taking the raw materials in the proper stoichiometric ratios and then dissolved in de-ionized water. The growth and preparation have been carried out in aqueous solution to give the following reaction.

$$4KSCN+CdCl_2+HgCl_2\text{--------}>CdHg(SCN)_4+KCl$$

Single crystals of CMTG were grown by dissolving the CMTC in glycol monomethyl ether taken with water in the ratio (2:1) as a ligand. The solution was vigorously stirred for about 7 hours and then filtered. The filtered solution was kept for nucleation. The solution was allowed to evaporate in room temperature. The chemical reaction is as follows: $CdHg(SCN)_4+CH_3OC_2H_5O\text{----------}> CdHg(SCN)_4(CH_3OC_2H_5O)$. Single crystals of CMTG were grown within a period of 60-65 days of dimensions up to 14x7x3 mm^3 by slow evaporation technique. The grown crystals exhibits hygroscopic nature. In order to avoid the loss of optical transparency the crystals were kept in a dark place.

Photograph of as grown CMTG single crystal

The functional groups present in the title compound have been identified by Bruker IFS 66V model FTIR spectrometer using KBr pellet technique in the region 450-4000cm^{-1}. The single crystal X-ray diffraction analysis were carried using Enraf Nonius CAD4 single crystal X-ray diffractometer. The lattice parameters and cell volume were determined. The optical absorption spectrum was recorded in the wavelength range 250-1000 nm using Varian Cary 5E spectrophotometer. The dielectric constant of the sample was measured at room temperature using HIOKI 3532 50 LCR HITESTER in the frequency region 50Hz-5MHz. The measurements of dark current and photocurrent were done using a picoammeter. The crystal sample is well polished and surfaces are cleaned with acetone. This is attached to a microscope slide and two electrodes of thin copper wire are fixed on to the specimen at some distance using silver paint. A d.c power supply, a Keithley 485 picoammeter and the prepared sample are connected in series. The applied field is increased in steps of 5V. The sample is covered with a black cloth to avoid exposure to any radiation and the dark current is measured. To measure the photoconductivity, light from a 100W halogen lamp is focussed on to the sample. The required current is noted for varying applied fields. The second harmonic generation test was made using Kurtz and Perry technique.

III. RESULTS AND DISCUSSIONS

A. Single Crystal X ray diffraction:

The grown crystals of CMTG were subjected to single crystal X ray diffraction studies using ENRAF NONIUS CAD4-F diffractometer. The structure was solved by the direct method and refined by full matrix least square technique using the SHELXL program. The X-ray diffraction studies confirm that the grown crystals of CMTG belongs to orthorhombic crystal system with noncentro symmetric space group Pca21. The cell parameter values are a=8.41Å, b=8.63Å, c=26.75Å, α=90˚, β=90˚, ϒ=90˚,V=1997.9154 Å^3 respectively. The XRD data of the sample coincides with the reported work (Shiyi Guo et al 200b).

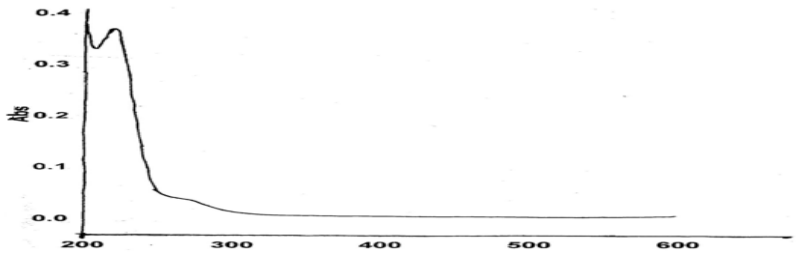
B. Kurtz powder technique:

Non linear optical property of the sample was tested by Kurtz and Perry technique and the efficiency of the sample was compared with microcrystalline powder of KDP and urea as the reference material. A Q-switched mode locked Nd:YAG laser

operates at the fundamental wavelength of 1.64um, generating 6mJ/pulse. In the present investigation the laser pulse of 8ns with spot radius of 1mm was used. The input laser beam was passed through the Infrared reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of 0.154mm. When a laser beam of 6.2mJ was passed through the sample, second harmonic signal of 532nm were generated and the output voltage of 160mV, 960mV and 2784mV were obtained from KDP, urea and CMTG respectively. The experimental data shows that the second harmonic efficiency of the sample was nearly 7 times than that of KDP crystal.

C. UV Vis NIR study:

The optical absorption spectral analysis for CMTG was carried out and the absorption spectrum was recorded using Varian Cary 5E Spectrophotometer where the absorbance is monitored from longer to shorter wavelength, the absorption is found to be less in the entire visible region of the spectrum. This is the most desirable property of the materials possessing NLO activity. The crystal is highly transparent in the entire UV visible region. The UV cut off wavelength was found to be 236nm. This crystal can be used for UV tunable laser and SHG device applications effectively. The recorded spectrum is shown in fig 1.



Wavelength (nm) Fig1. UV CMTG crystal

D. FTIR spectral analysis

FTIR (Fourier Transformation Infrared) spectroscopy is one of the most reliable methods for identification and characterization of organometallic compounds. The powder form of CMTG was mixed with KBr to form pellets for obtaining optical transmission spectrum. The various functional groups present in CMTG were identified and confirmed by recording the Fourier Transform Infra Red spectrum in the range 4000-400cm-^{1} using AVATAR 330 FTIR spectrometer. FTIR spectrum of CMTG is presented in fig 2. From the spectrum it is observed that the intense sharp peak at 2102 cm-1 is assigned to CN vibrations. The CS vibration is observed to produce a less intense peak at 714cm-1. The peaks at 508cm-1, 929cm-1 are due to the bending modes of NCS. In the higher region, OH vibrations of H_2O produce more intense broad band at 3588cm-1. The stretching mode of water is seen at 1610cm-1. The assignment of the main characterisitic IR band frequency is in good agreement with literature. The stretching and bending modes of CH3 are found shifted from the frequencies of free GME. Therefore the molecular structure of GME in the title compound is different from that of the free GME due to the fact that the GME molecule combines with Cd as a monodentate ligand through the O atom. Table1. shows the IR band frequencies observed for CMTG.

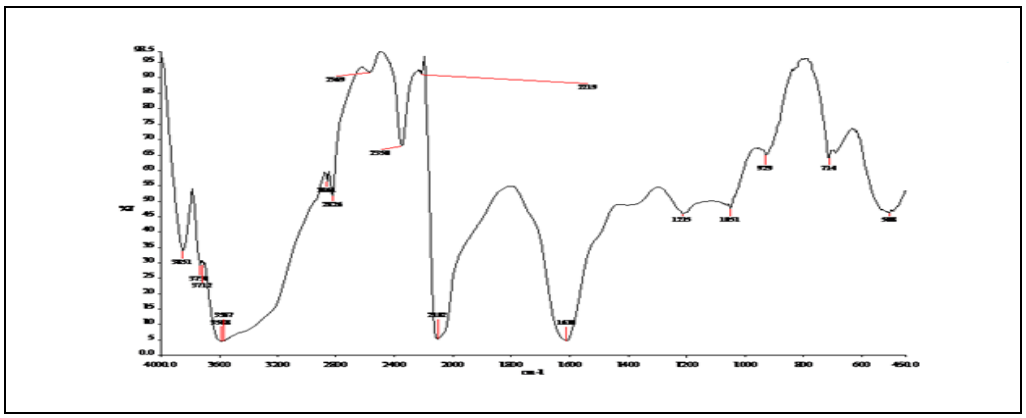


Fig2. FTIR spectrum of CMTG

Band frequencies for CMTG crystals (cm^{-1})	Assignment
2102	CN stretching
714	CS vibration
508	NCS bending
929	NCS bending
3588	OH vibration
1610	H_2O stretching
900	C- H bending

Table1. Assignment of IR band frequencies of CMTG

E. Dielectric studies:

The exponential decrease of dielectric loss with frequency is shown in fig3. From the curve it is observed that the dielectric constant and dielectric loss decreases slowly with increasing frequency and attains saturation at higher frequencies. The low dielectric constant value of the crystal at high frequency is attributed to space charge polarization (Rao et al 1965). The low dielectric loss was consistent with nearly constant level of dielectric constant over wide frequency range. Fig 4. shows the variation of dielectric constant as a function of

log frequency. The low values of dielectric loss indicate that the grown crystal contains minimum defects present in the crystal. As the frequency increases, a point will be reached where the space charge cannot sustain with external field and hence polarization decreases giving rise to diminishing values of dielectric constant.

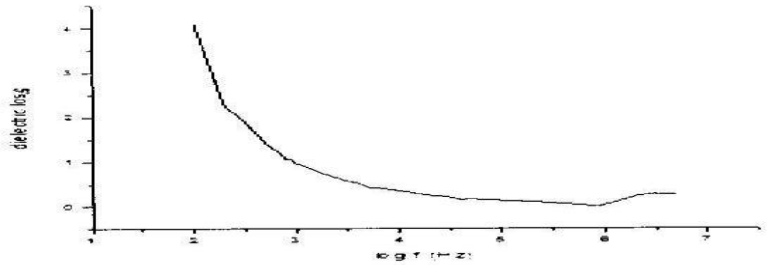


Fig 3. Dielectric loss vs log of Frequency

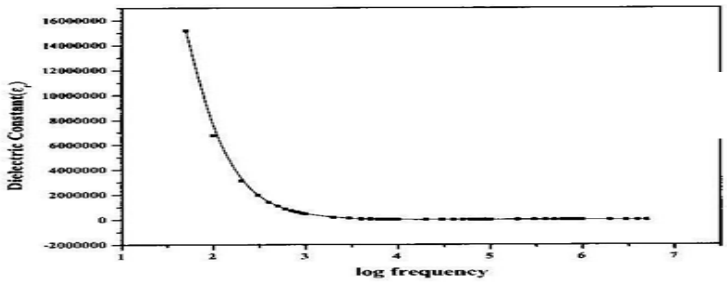


Fig4. Dielectric constant vs log of frequency

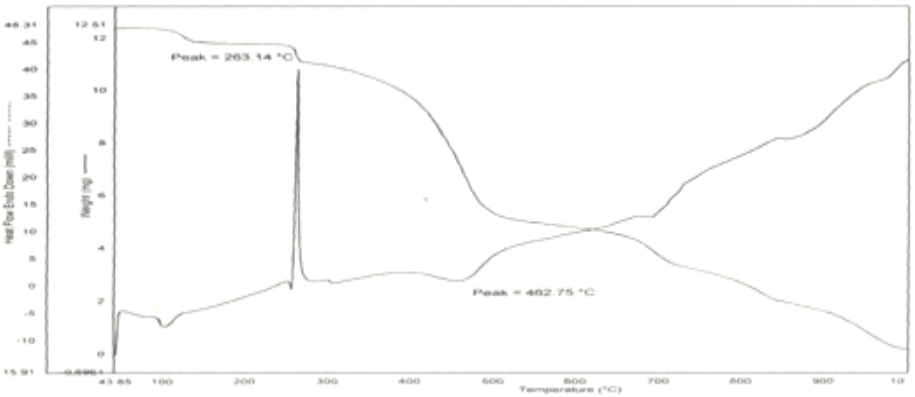


Fig 5. TG-DTA traces of CMTG single crystal

F. Thermal Analysis:

The thermal stability of CMTG has been studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) using NETZSCH STA 409C instrument under nitrogen atmosphere with a heating rate of 20℃/min. From the TGA curve the percentage of weight loss with temperature can be determined. The DSC technique involves the measurement of temperature difference between the sample and an inert reference material, as both are subjected to simultaneous and identical temperature program. The origin of the temperature difference in the sample lies in the energy difference between the products and reactants or between the two phases of the substance. This energy difference is manifested as enthalpic changes-either exothermic or endothermic. The thermal effects are observed as peaks whose sequence, sign, magnitude and shape reflect the physical or chemical changes taking place. The DTA method is applicable to all the studies listed for TGA and also to phase transitions including polymerization, phase equilibria and chemical reactions. The TGA trace of CMTG reveals the different stages of decomposition of the sample. The DTA peak observed at 263.14 ℃ confirms the decomposition of the three dimensional steric structure of CMTG which is also confirmed by the sharp peak obtained at 264.17 ℃ in the DSC curve. It is worth mentioning that this value coincides well with the recorded TGA value. The TGA-DTA trace is shown in fig5. and DSC curve in fig 6. respectively.(I.Vetha Potheher,2007)

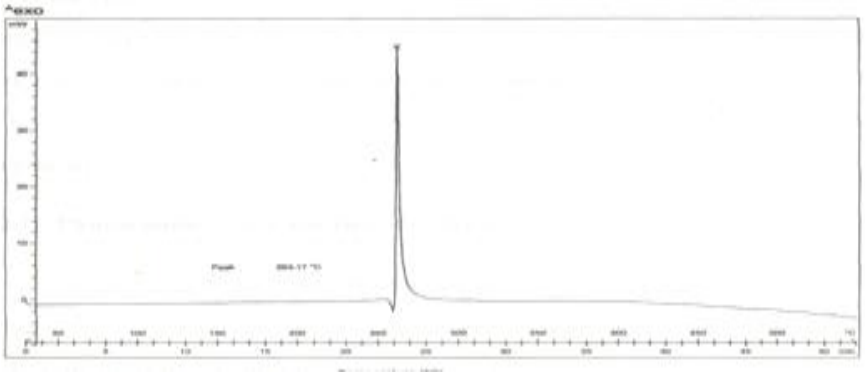


Fig 6. DSC traces of cmtg single crystal

G. Photoconductivity studies:

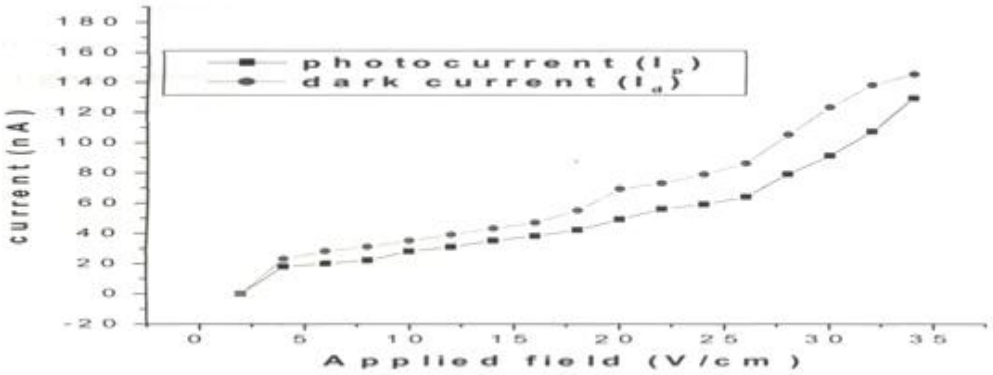


Fig7. Field dependent photoconductivity of CMTG single crystal.

Fig7. shows the variation of both dark current and photocurrent with applied field at different levels of illumination. The required current is noted for varying applied field . It is seen from the plots that both dark current and photocurrent of the sample increase linearly with the applied field. The dark current is seen to be higher than that of photocurrent for the same applied field, which is termed as 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. The decrease in mobile charge carriers during negative photoconductivity can be explained by Stockmann model also.

IV. CONCLUSION

Single crystals of CMTG are grown in GME-water mixed solvent by slow evaporation method in a constant temperature bath. Single crystal X-ray diffraction analysis shows the crystal belongs to orthorhombic system. Functional groups were analyzed by using FTIR analysis, which have revealed the characteristic vibration modes of CMTG crystal. The optical property of the grown crystal was studied by UV-Vis NIR spectroscopy and UV cut off wavelength was found to be 236 nm. The TGA-DTA and DSC analysis under nitrogen atmosphere reveal that CMTG crystal was stable up to 263.14 ℃ and 264.17 ˚C respectively. The second harmonic generation efficiency by Kurtz-Perry powder technique reveals that the crystal was 7 times that of KDP. The dielectric study suggests that CMTG has low value of dielectric permittivity which explains its high SHG efficiency. The photoconductivity study confirms the negative photoconductivity nature of the sample.

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REFERENCES

[1]. Blank Z,J. (1973) Crystal growth Vol 18, pp281-288.
[2]. Brice J.C (1973) Wiley New York.

[3]. Bube R.H (1981) Photoconductivity studies, Wiley Interscience NewYork.[4]. Buckley H.E (1951) Crystal growth, John Wiley and Sons, New York.[5]. Duan X.L, Yuan D.R Zhong Z W et al., J Crystal Growth, 223 (2001) 432.[6]. Duan X L, Yuan D R, Wang X Q et al., J Crystal Res Technology, 37(2002) 1066.[7]. Topacli C and Topacli A,J molecular Structure, 644 (2003) 145.[8]. Wang X Q, Xu D, Lu M K, et al., J Crystal Growth, 224 (2001) 284.[9]. Pandi S and Jayaraman D, Matter Chem Phy 71(2001) 314.[10]. Kurtz S K and Perry T T, J Appl Phy, 39 (1968) 3798.[11]. Joshi V N, Photoconductivity, (Marcel Dekker, New York), 1990.[12]. Tian Y P, Duan C Y, Zhao C Y et al., Inorg Chem 36 (1997) 1247.[13]. P. Sagayaraj, Ginson P. Joseph, Journal of Material Science: Materials in Electronics,January 2009, Volume 20, issue 1 Supplement, pp 390-394.[14]. P. Nisha Shantha Kumari, S. Kalainathan, G. Bhagavanarayanna Crystal Research and Technology, Volume 43, Issue 3, pages 276-281, March 2008.