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Growth, Optical and Thermal properties of MFCTC single crystal

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Abstract: Single crystal of bis mercury ferric chloride tetra thiocyanate [$Hg_2FeCl_3(SCN)_4$; (MFCTC)] was grown from ethanol-water (3:1) mixed solvent using slow evaporation solvent technique (SEST). The cell parameters of the grown crystal were confirmed by single crystal XRD. The presence of functional groups and coordination of transition metal ions with the SCN ligand is well identified using FT-IR spectral profile. The UV-Vis-NIR study revealed the ultraviolet cut-off wavelength of MFCTC in ethanol as 338 nm. The dielectric constant and dielectric loss of the sample were studied as a function of frequency and temperature. The thermal stability and thermal decomposition of MFCTC were analyzed by using TG-DTA and DSC, which show that the sample is thermally stable up to 234.31°C which is comparatively far better than the thermal stability of $Hg_3CdCl_2(SCN)_6$; (171.3°C). The nonlinear optical efficiency of the grown crystal was estimated by Kurtz powder method and the result proves that MFCTC is found to be superior to KDP.
Keywords: Solution growth, X-ray diffraction, Dielectric, Thermal studies and NLO materials.

1. Introduction

Non linear optics plays a key role in the field of telecommunication, optical computing, optical information and optical data storage. New nonlinear optical (NLO) frequency conversion materials have a significant impact on laser technology [1,2]. Bismercury ferric chloride thiocyanate (MFCTC) is one such potentially useful SONLO crystals with an empirical formula $Hg_2FeCl_3(SCN)_4$. In the earlier work MFCTC was grown form ethanol-water (3:1) mixed solvent using slow evaporation solvent technique (SEST). The dimensions of crystal size 8mm×4mm×4mm were achieved and its various physical properties were measured and published already [3]. As a continuation of this work, the crystal growth and physicothermala property including IR spectral and thermal characterization and optical transparency of MFCTC is compared with MCCTC investigated in our present paper.

2. Experimental procedure

2.1. Synthesis

The synthesis of MFCTC has been carried out according to the following equation.

$2\ Hg(SCN)_2 + FeCl_3 \rightarrow Hg_2FeCl_3(SCN)_4$

2.2. Crystal growth

The saturated solution of MFCTC was prepared in ethanol-water mixed solvent at room temperature and vigorously stirred of hours. The filtered solution is kept in a beaker and then covered with uniformly perforated transparent sheet and allowed the solution to slowly evaporate under room temperature. MFCTC crystal was grown by slow evaporation method at 303K. Crystal having dimensions up to 8mm×4mm×4mm was harvested in period of 20 to 30 days.

3. Results and discussion

Single crystal X-ray diffraction studies

XRD data of MFCTC indicates that it belongs to monoclinic system with the space group $P2_1$. The cell parameters are found to bea = 16.524Å, b=8.346 Å and c =6.412 Å,V= 884.27 $Å^3$.The XRD data of the present work is in good agreement with the reported work[3].

FT-IR analysis

The FT-IR spectra of MFCTC and NH_4SCN were recorded in the range 4000-400cm^{-1} using Bruker IFS-66V spectrometer. The major frequency components involved in MFCTC along with $NH_4SCN$are listed in Table1. The functional groups of MFCTC were also well identified and compared with Mercury cadmium chloride thiocyanate (MCCTC) and NH_4SCN. The CN stretching frequency observed as strong peaks at 2117 and 2135 cm-1 is actually shifted from the stretching frequency (2048.99 cm-1) of free radical thiocyanate ion. The shift in frequency may be attributed to the coordination of S of SCN with the Hg ion as per Hard Soft Acid Base concept. The above facts clearly establish the incorporation of thiocyanate ligand (SCN) in MFCTC [1].

SHG studies

The NLO efficiency of MFCTC crystal was evaluated by the Kurtz and Perry powder technique using a Q-switched mode locked Nd^{3+} : YAG laser emitting 1.064µm, 8 –ns laser pulses with spot radius of 1mm. Microcrystalline materials of KDP and urea were used for comparison with MFCTC while performing the SHG study. For a laser input pulse of 2.48mJ, the second-harmonic signals 22, 130, and 46mW were obtained through KDP, urea and MFCTC samples, respectively. Hence, it is observed that the SHG efficiency of MFCTC is superior to KDP.

Optical absorption studies

The UV-Vis-NIR study of the grown crystal was done using varian carry 5E spectrometer shown in figure. The size of the crystal obtained was not sufficient to perform optical studies in crystal form to the uv absorption spectra were taken for the solution of ethanol. The transparency cut off occurs at 338nm and transparency wavelength fairly smooth compared to MCCTC as shown in Fig.1.

Dielectric studies

Single crystal of MFCTC with polished surface was taken for measurement of dielectric constant and dielectric loss by HIOKI 3532 – 50 HISTESTER LCR meter with a conventional four terminal sample holder. The measurement was carried out for the frequency ranging from 1KHZ to 5KHZ at different temperature. The dielectric constant and dielectric loss were calculated for varying frequencies under different temperature slots form 303K to 363K and plotted. From the plot is observed that both dielectric constant and dielectric loss decrease with increase in frequencies.

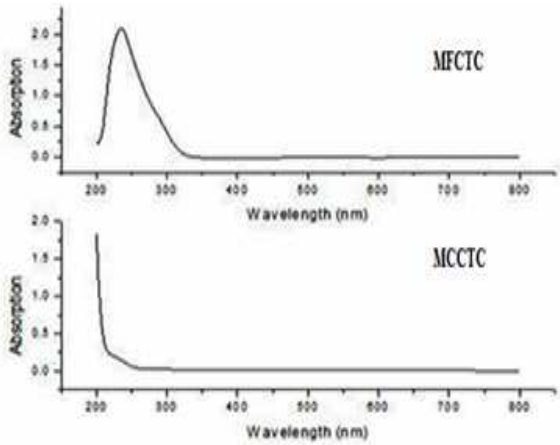

Figure 1. UV-Vis-NIR spectrum of MFCTC in comparison with MCCTC

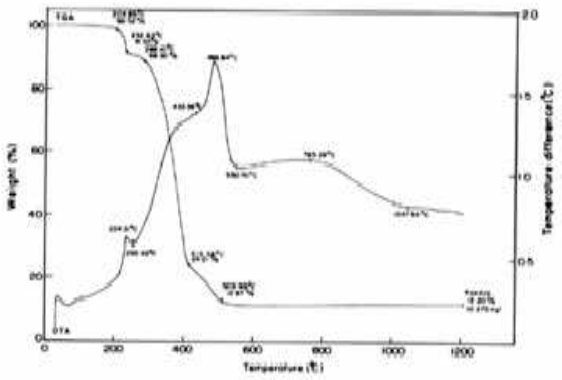

Figure 2. TGA-DTA profile of MFCTC

Thermal studies

Thermal properties of MFCTC single crystal were studied by thermogravimetric analysis (TGA) using SDT Q600 simultaneous thermal analyzerand TG- DTA analysis of MFCTC sample was carried out from room temperature to 1200°C in Nitrogen atmosphere at heating rate 20°C/ min. The TGA and DTA curves of MFCTC are shown in Fig 2. TGA curves shows that there are three major steps in weight loss. The first decomposition occurs about 234.31°C. From TGA- DTA analysis, it is clearly understood that the title compound is thermally stable up to 234.31°C.

Conclusion

MFCTC single crystal were grown form 3:1 ratio ethanol-water mixed solvent by the solvent evaporation method. The grown crystal of MFCTC was confirmed by single crystal XRD. The functional groups of resulting compound were well-identified using FT-IR spectroscopic analysis. The optical studies revealed that the UV cut off wavelength lies at 338 nm and the sample possesses broad optical transparency from 338nm to 1200nm in ethanol solution. The thermal analysis established that the sample is thermally stable up to 234.31°C which is superior to the thermal stability of MCCTC (171.3°C) The dielectric studies revealed that the sample exhibits low dielectric constant and dielectric loss at higher frequencies. The second harmonic conversion efficiency of MFCTC is found for be better than KDP.

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