International Journal of Current Science Research
www.drbgrpublications.in

Volume: 2; Issue: 2; February-2016; pp 308-315. ISSN: 2454-5422

GROWTH AND CHARACTERIZATION OF COBALT DOPED TRIMETALLIC THIOCYANATE

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Abstract

Crystals are essential for a variety of scientific and commercial purposes. Modern solid-state electronics is based on Crystal growth revolution. Some metallic thiocynate complexes exhibit excellent nonlinear opitical properties single crystals of one such materials Cobalt Zinc cadmiumand mercury thiocynate. CoZncd Hg $(SCN)_4$ have been grown in silica gel with gel technique by the process of diffusions and the optimum growth condition has been studied. Crystals of 5mm length have been obtained. EDAX analysis was performed and the relative elemental composition and weight percentage present in the crystal are determined. The tetragonal structure of grown crystal was confirmed by single crystal X-ray diffraction. The presence of various functional groups was identified by FTIR analysis.TG/DTA analysis have shown that the thermal decomposition of grown crystal in multi-step process.

Keywords: Gel growth, EDAX, X-ray diffraction, FTIR, TG/DTA.

Introduction

Recently, non linear optical materials capable of frequency conversion are gaining much importance for many applications such as optical computing, Laser sensing, photonic devices, optical memories, optical switches, etc. (Xinqiang Wang *et al* 2003). Organic materials posses good non linear properties whereas, lack in mechanical and thermal stability mechanical and thermal stabilities are found to be high for inorganic crystals. Hence, Semi-organic crystals with combined properties of organic and inorganic Crystal have attracted the attention of researchers. Trimetallic thiocynates are semi- organic compounds with chemical formula ABCD $(SCN)_4$. The bimetallic thiocynate (ZMTC), cadmium mercury thiocynate

(CMTC) and cobalt mercury (CMTC) are found to have good characteristics such as crystallization, high thermal stability (Z Blank 1973). Both ZMTC and CMTC are second order nonlinear optical materials by converting 1064 nm radiation (Bergman 170). For the growth of single crystal of Cobalt doped Zinc, cadmium, mercury thiocynate (ZCMTC), the gel technique become much more important because of there low stability in any solvent. Growth of Co doped ZCMTC crystals in gel had been reported. (Blank 1973, NishaSanthaKumari 2007) and from aqueous solution (X Q Wang D *et al* 2002).

This paper discuss the optimum condition for the growth of single crystals of Cobalt doped ZCMTC in silica gel using the reagents Cobalt chloride, Zinc chloride, cadmium chloride, mercury (II) chloride, and ammonium thiocynate. Coloured crystals of Cobalt doped ZCMTC of length 2 to 5 mm have been obtained. There is no change in the colour of the crystal after recovering from the gel. The spectral analysis has been carried out to identify the functional group of the gel grown crystals. The report of our work is presented and discussed here.

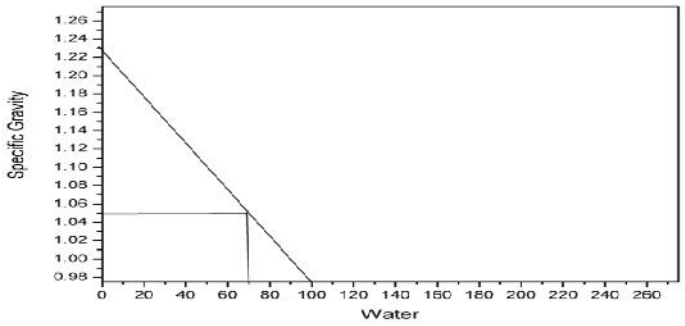
Experimental Procedure

Growth of single crystals of ZCMTC was carried out in silica gel by the single diffusion method in a highly acidic medium of pH 3. The reaction between Cobalt chloride, Zinc chloride, cadmium chloride, mercury (II) chloride and ammonium thiocynate in gel medium resulted in the growth of single crystals of Cobalt doped ZCMTC.

$$CoCl_2 + ZnCl_2 + CdCl_2 + HgCl_2 + 4NH(SCN) \longrightarrow CoZnCdHg(SCN) + 4NH_4Cl$$

Mercury chloride and ammonium thiocynate together were taken as the inner reagent Cobalt chloride, Zinc chloride and cadmium chloride was added on to the top of the gel as an outer reagent.

Stock solution of sodium Meta silicate was prepared by adding 48.8 g of sodium Meta silicate was dissolved in 100ml of distilled water and then determined the specific gravity as 1.23g/cc. Then plot a graph volume of water Vs specific gravity. By using the graph prepared sodium Meta silicate of specific gravity 1.05 by adding 77 ml distilled water with 23 ml stock solution (sodium Meta silicate solution of 1.23 g/cc).



20ml of above solution was taken and added with 15ml excelar grade glacial acetic acid. The pH of the above solution was kept 3.Aqueous solution of $Hgcl_2$(0.5M) was prepared and 32ml of it is added to the above solution of pH 3 with 16ml of 4M aqueous solution of NH_4(SCN) and allowed for gelling in the test tube of length 15 cm and diameter 1.4cm. To solution free from dust and impurities care was taken to cover the test tube. After gelenation it was left undisturbed for another 48h for ageing of the gel. Then aqueous solution of 5ml $CoCl_2$ (0.5M), aqueous solution of 5ml $ZnCl_2$ (0.5M) and aqueous solution of 5ml $CdCl_2$ (1M) were added gently to the top of the gel. After a week the colorless needle shape crystals were grown at the interface. The grown crystals are shown in fig (1) a and b.

Fig 1(a)

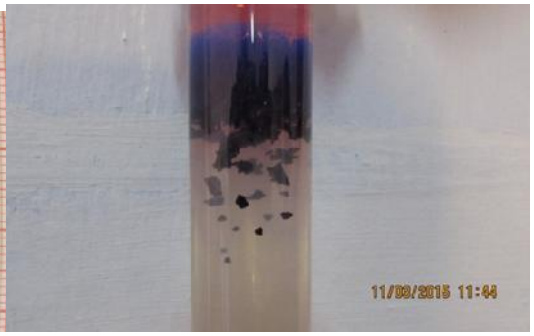


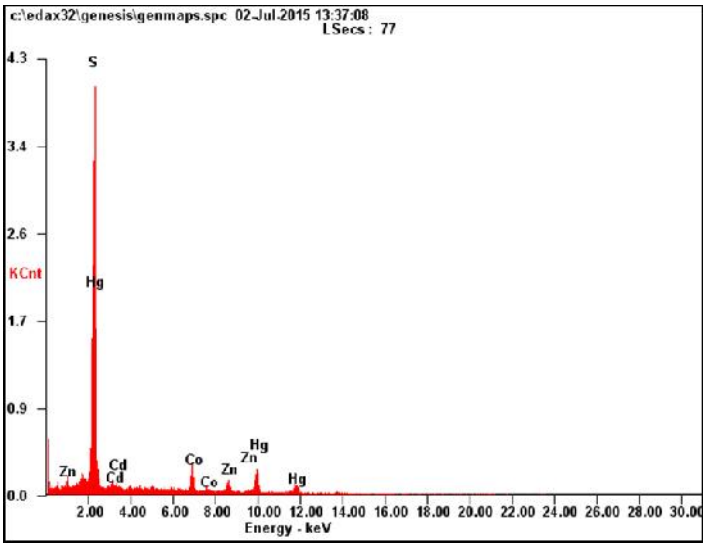
Fig 1(b)

Gel Solution	**Specific gravity**	**Addition of acid**	**pH**	**Inner reagent**	**Outer reagent**	**Nature of crystal**
77ml distilled water +23ml stack solution	1.05	15ml acidic acid exclear grade	3	32ml 0.5M$HgCl_2$+16ml 4M NH_4SCN	5ml 0.5M $ZnCl_2$+5ml 1M $CdCl_2$	Crystals of size 4mm

Characterization

EDAX analyses

EDAX facility available at Indian Institute of Tecnology, (SAIF) Chennai, was used to record the confirmation of all three metal ions that are present in the complex. Energy dispersive x-ray spectroscopy for cobalt doped ZCMTC crystal was carried out using Quanta 200 FEG scanning electron microscope.EDAX spectra of all grown crystal was shown in the fig (3.1)



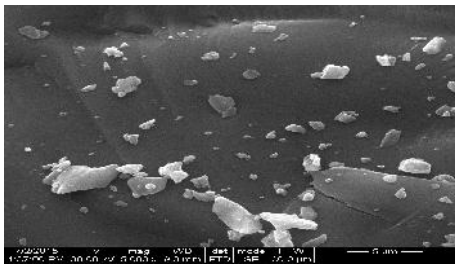
Fig(3.1).EDAX spectra showing peaks corresponding to metal constituents in co doped ZCMTC crystal.

The relative elemental composition and weight percentage were directly computed with software. The analysis was repeated at four different location of sample and the mean response of the each elements detected in the sample was calculated. The peak in fig(3.1) are identified to those of cobalt(Co^{+}), zinc(Zn^{+}), cadmium(Cd^{+}), mercury(Hg^{+}) which confirm the doping (NishaSanthaKumari & Kalainathan 2009, Jagdish & Rajesh 2012). The approximate concentration, atomic weight is shown below

Element	Wt%	At%
S	37.56	70.39
Cd	04.89	02.61
Co	09.23	09.41
Zn	05.01	04.61
Hg	43.31	12.98

Scanning Electron Microscope (SEM)

The SEM image of grown cobalt doped ZCMTC crystal was given below in fig(3.2).



Fig(3.2) SEM image of Co doped ZCMTC crystals

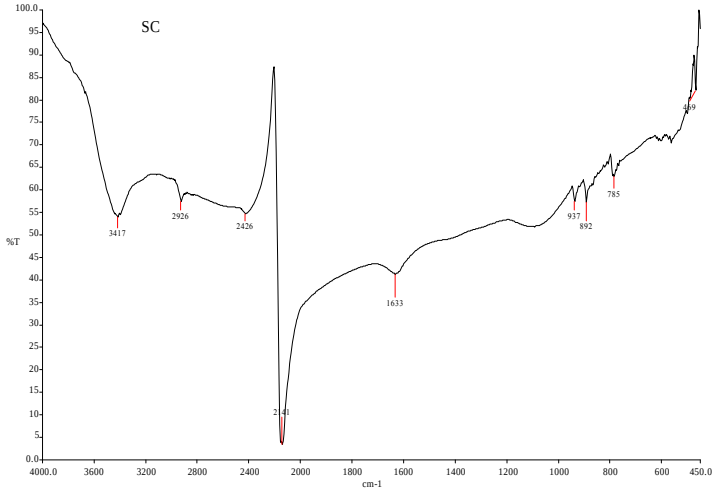
Single crystal XRD

The Co doped ZCMTC crystals were subjected to single crystal x-ray diffraction to Obtain the unit cell parameter and to conform the crystallinity of grown crystals, using single crystal diffractometer. The lattice parameter obtained are a=b=11.17 Å,C=4.46 Å,$\alpha=\beta=\gamma=90^0$ the unit cell volume V=554 $Å^3$**.**The ZCMTC crystals belongs to tetragonal crystallographic system.

Fourier transform infrared and transmission:

FTIR Spectrum of ZCMTC crystal was recorded using PerkinElmer FTIR spectrometer. The instrument scanning range is MIR 450-4000cm^{-1} and its resolution is of 1.0 cm^{-1}. The significant peak noted above 2100 cm^{-1} in all the present trimetallic crystal systems, reveals the coordination of thiocyanate group with the metal ions of the crystal system (Vijayabhaskaran & Ramachandra Raja 2012, Jagdish & Rajesh 2012). FTIR Spectrum of Co doped ZCMTC crystal was recorded using PerkinElmer FTIR spectrometer. The instrument scanning range is MIR 450-4000cm^{-1} and its resolution is of 1.0 cm^{-1}. Fig(3.3) shows the FTIR spectrum and table (3.1) gives the spectral data.

The intense peak at 2141cm^{-1} Corresponds to CN stretching vibration (γ_{cn}).The peak observed at 785cm^{-1} is due to the Cs stretching (γ_{cs}). The absorption peak at 469 cm^{-1} are assigned to SCN bending vibration (δ_{NCS}) while those at 892 and 937cm^{-1} correspond to 2 δNCS.



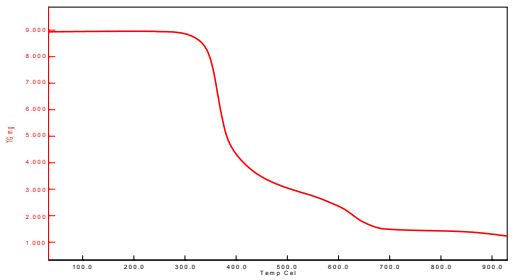
Fig(2)

Assignment	**Wave number (Cm^{-1})**
γ_{CN}	2141
γ_{cs}	785
δ_{NCS}	469
$2\ \delta_{NCS}$	892,937

Table 4.1: FTIR spectral data of ZCMTC

Thermogravimetric and Differential thermal analysis

TGA, DTA and DSC are very well known thermal charaterization methods to explore the thermal properties of chemical compounds (NishaSanthaKumari & Kalainathan 2009, Jagdish & Rajesh 2012).To study the thermal stability of the crystal, thermogravimertric and differential thermal (TG/DTA) analyses were carriedout in nitrogen atmosphere. Fig(3.4) shows the TG/DTA curve of cobalt doped ZCMTC crystal.



Fig(3.4) TG/DT1A curve of Co doped ZCMTC

Gel grown cobalt doped ZCMTC crystals are thermally stable upto 305ºC and decomposition starts only at 305 ºC. The TG curve shows three steps. The loss of mass in first step (305 ºC to 375 ºC) implies breakdown of the three dimensional steric structure with the evaluation of one CS_2 (carbon disulphide), $1/2N_2$ (nitrogen) gas,$3/2(CN)_2$ (cyanogen). The mass loss on second step (375 ºC and 535 ºC) corresponds to the evaluation of sublimation Hg. The third step extends upto 930 ºC .The mass loss on third step corresponds to it may be assumed to the loss of the fraction of Cd and S (Jagdish, N.P. Rajesh 2012). The observed results are also supported by the previous literature reports(X Q Wang D *et al* 2003).

Conclusion

From the above study, it is concluded that ZCMTC single crystals can be obtained by the gel technique in a highly acidic gel medium. The reagents required in this case are Cobalt chloride, Zinc chloride, cadmium chloride, mercury (II) chloride and ammonium thiocynate. EDAX analysis was performed and the relative elemental composition ana weight percentage present in the crystal are determined. The tetragonal structure of grown crystal was confirmed by single crystal X-ray diffraction. The presence of various functional groups was identified by FTIR analysis.TG/DTA analysis have shown that the thermal decomposition of grown crystal in multi-step process.

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