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Impedance analysis of bimetallic thiocyanate ligand based single crystals of $MnHg(SCN)_4$ and $CdHg(SCN)_4$

R. Josephine Usha*, J. Arul Martin Mani and V. Joseph

Department of Physics, Loyola College, Chennai, Tamil Nadu, India

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ABSTRACT

Single crystal of manganese mercury thiocyanate (MMTC) and cadmium mercury thiocyanate (CMTC) were grown by slow evaporation technique. The conditions for the growth were optimized. The cell parameters of the grown crystals were confirmed by using single crystal X-ray Diffraction. The grown crystals have high NLO efficiency compared to KDP and urea. The optical properties were studied by using UV-Vis spectroscopy. The optical band gap energy values of MMTC and CMTC crystals were reported. The measurement of complex impedance response to small ac signals was carried out in the frequency range of 20 Hz to 1MHz at different temperatures. The activation energy has been calculated using Arrhenius plot as a function of temperature.

Keywords: crystal growth, NLO, impedance, activation energy.

INTRODUCTION

Due to unique properties, the nonlinear optical (NLO) single crystals have promising applications in the area of photonics such as highspeed information processing, frequency conversion, optical communication, high optical disk data storage, etc. Among the different varieties of NLO materials investigated, the recent interest has been mainly focused on organometallic compounds due to the unique charge transfer capability associated with charge transfer transitions either from metal to ligand or ligand to metal. According to the idea of "combining the inorganic distorted polyhedran with asymmetric conjugate organic molecules", organometallic materials have been attracting a great deal of attention in the nonlinear optical field [1]. These NLO metal complexes exhibit donar - (- conjugate bridge) and acceptor - (D- -A) structures. The most striking features are; the -N=C=S bridges which connect the center atoms of the infinite three dimensional -A-N=C=S-B- networks. An organic ligand is usually more dominant in the NLO effect. The metal ligand bonding in organometallics give rise to large molecular hyperpolarizabilities due to the transfer of electron density between the metal atom and the conjucated ligand systems [2,3]. Ligands like thiourea (tu) and thiocyanate (SCN) with S and N donars are capable of combining with metal to form stable complexes through coordinated bonds. The crystals formed with SCN ligand have shown a relatively higher SHG effect than those crystals formed with the other organic ligands. Due to the potential role in the second order nonlinear optical (SONLO) application, bimetallic thiocyanate complex with general formula: AB (SCN) where [A=Mn,Cd,Zn; B=Hg,Cd] have been widely investigated. This class of materials is reported to be potential candidates for the generation of blue – violet light by doubling the frequency of semiconductor diode laser [4].

In recent years, the more detailed preparation, structure, thermal, electrical and SONLO properties of these compounds have already been reported. The surface features like scanning electron microscopy (SEM), etching and atomic force microscopy (AFM) studies were reported by Rajesh Kumar et al [5]. Impedance spectroscopy (IS) is a highly practical tool to investigate the electrical properties of the solid. This article deals with our attempts to investigate *ac* electrical property of crystals manganese mercury thiocyanate (MMTC) and cadmium mercury thiocyanate (CMTC). Survey of literature indicates that these systems have not been investigated by complex impedance spectroscopy. Impedance (Z) is a more general concept than resistance because it takes phase differences into account. In *ac*., the resistance R, is replaced by the impedance, Z, which is the sum of resistance and reactance. It can be written as

$$Z = Z' + Z''$$

Where Z’ is the real part and Z” is the imaginary part of Z [6]. Generally, Z is frequency dependent. The impedance (admittance) plots consist of two arcs, one due to the bulk of the sample (single crystal) / grains themselves (polycrystalline) and the other due to electrodes. An additional arc can also be there due to grain boundaries. In this work we have investigated the growth and electrical properties of two well known organometallic NLO crystals of $MnHg(SCN)_4$ (MMTC) and $CdHg(SCN)_4$ (CMTC). The crystals are also subjected to single crystal XRD, optical absorption and SHG test.

MATERIALS AND METHODS

2.1. Synthesis and crystal growth

Manganese mercury thiocyanate ($MnHg(SCN)_4$) was synthesized by taking ammonium thiocyanate, mercury chloride and manganese chloride in the ratio of 4:1 and cadmium mercury thiocyanate ($CdHg(SCN)_4$) was synthesized by taking ammonium thiocyanate, mercury chloride and cadmium chloride in the same ratio of 4:1. The starting materials were of analytical reagent grade and used as purchased. The raw materials used in these studies were synthesized in deionized water at room temperature based on the following reactions:

(i) For manganese mercury thiocyanate,

$$4NH_4SCN+MnCl_2+HgCl_2 \rightarrow MnHg(SCN)_4+4NH_4Cl$$

(ii) For cadmium mercury thiocyanate,

$$4NH_4SCN+CdCl_2+HgCl_2 \rightarrow CdHg(SCN)_4+4NH_4Cl$$

The purity of the material can be enhanced by repeated recrystallization (typically 2 to 3 times).

A known weight of recrystallized powder sample of MMTC single crystal was dissolved in deionized water. The solution was constantly stirred for 24 hours to overcome the concentration gradient in the crystallizer. The pH value played a definite role in the crystallization process [7]. The optimum pH value for MMTC was 2.8. The saturated solution was taken in a crystallizing vessel and covered with perforated sheet to initiate slow evaporation at room temperature. Seed crystals were formed due to spontaneous nucleation in the supersaturated solution. Optically clear and defect free seed crystals with perfect shapes were chosen for further growth. The seed was suspended in the supersaturated mother solution. This solution was allowed to evaporate at a constant temperature of 305K by covering the vessel with a perforated lid. Good quality crystals of dimension up to 14 x 12 x 11 mm^3 were harvested in a period of 50 to 60 days.

For CMTC, ammonium thiocyanate, mercury chloride and cadmium chloride were first dissolved in deionized water and stirred separately. White colour precipitate was observed when these three solutions were mixed together [8]. To avoid this, the mixture of acetone and water solvent were used. High purity CMTC was synthesized using the acetone and water solvent in the ratio of 3:1. The solution was covered with air-tight sheet and stirred for a few hours. After vigorous stirring, the pH of the solution was adjusted to 2.5 by adding diluted HCl. The supersaturated solution was kept in a constant temperature bath and crystal of dimension up to 11 x 2 x 1 mm^3 was obtained in a period of 20 to 30 days. The photograph of MMTC and CMTC crystals is shown in Figures (1a), (2b) respectively. It is clearly evident from these photographs that CMTC exhibits needle morphology and MMTC possesses prismatic shape.

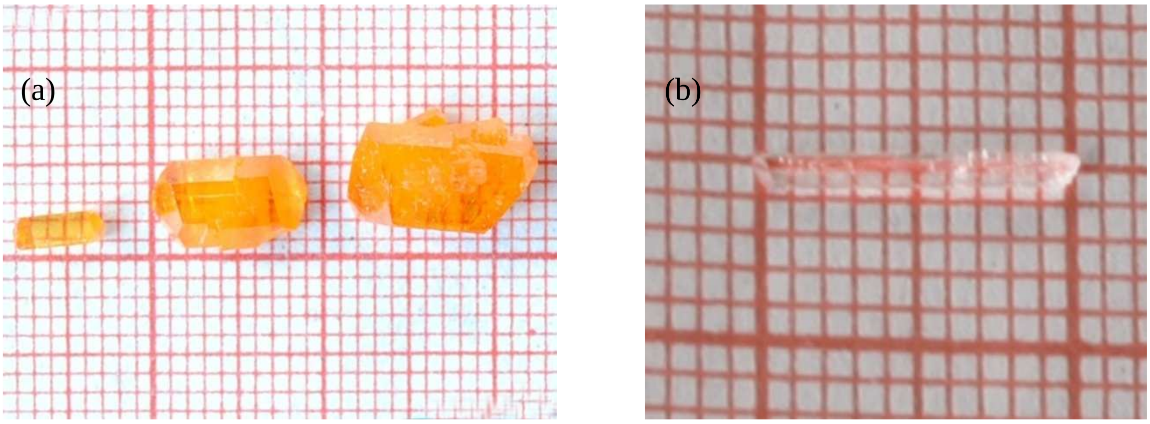

Fig. 1. Photogrph of grown crystals a) MMTC b) CMTC

RESULTS AND DISCUSSION

3.1. Single Crystal XRD

The cell parameters of the grown MMTC and CMTC single crystals were determined using Enraf-Nonius CAD4-MV31 single crystal X-ray diffractometer. The crystal data are presented in Table 1.

Table 1. Single crystal XRD data for MMTC and CMTC

Crystal	MMTC	CMTC
Empirical formula	$MnHg(SCN)_4$	$CdHg(SCN))_4$
Crystal system	Tetragonal	Tetragonal
Space group	$I\bar{4}$	$I\bar{4}$
a= b (Å)	11.274	11.57
c (Å)	4.25	4.25
α = β = γ (deg)	90	90
Volume $(Å)^3$	542	569

3. 2. SHG Measurement

Kurtz and Perry powder SHG test is extremely useful for initial testing of materials for second harmonic generation. The microcrystalline materials of urea and KDP were used for comparison. The fundamental beam of 1064 nm from Q-switched Nd:YAG laser was used to test the SHG efficiency of the samples. The SHG signal generated in the sample was confirmed from emission of green radiation from the sample [9]. When a laser input of 2.3 mJ was passed through MMTC, the SHG efficiency was determined 7 times greater than urea and 71 times than KDP. Using an incident beam of laser power of 1.8 mJ, the SHG efficiency of CMTC was found to be 11 times than urea and 106 times than KDP which is suitable for NLO devices when compared to MMTC single crystal.

3. 3. Optical absorption study

The recorded optical absorption spectra of MMTC and CMTC single crystals are shown in Figures (2a) and (2b). The UV cut-off wavelength of MMTC is seen at 235 nm while for CMTC it is around 243 nm. It is well known that an efficient NLO crystal has an optical transparency and lower cut-off wavelength between 200 and 400 nm.

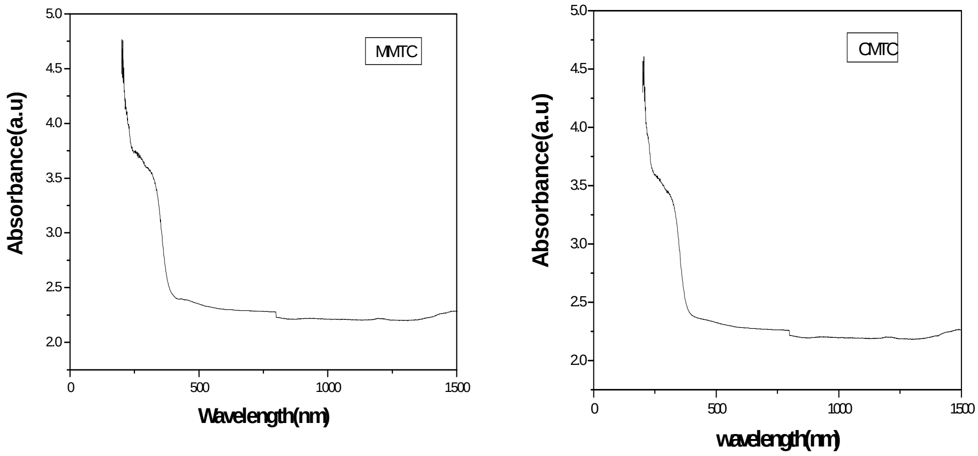

Fig. 2. Optical absorption spectrum 2a) MMTC and 2b) CMTC

The direct optical band gap values of MMTC and CMTC have been calculated from Tauc relation which is given by,

$$(\alpha h\nu) = A\,(h\nu - E_g)^n$$

where α - absorption coefficient, hν - photon energy(eV), E_g - energy band gap(eV), n - ½ (for direct transitions). A graph is plotted between $(\alpha h\nu)^2$ along y axis and hν along x axis. The extrapolation of the straight line when $(\alpha h\nu)^2 = 0$ gives the value of the energy band gap of the material [10]. From the Figure (3), the band gap values of 3.2 eV and 2.6 eV were obtained for MMTC and CMTC respectively. Thus, the present study confirms the relatively better optical quality of MMTC crystal when compared with CMTC crystal.

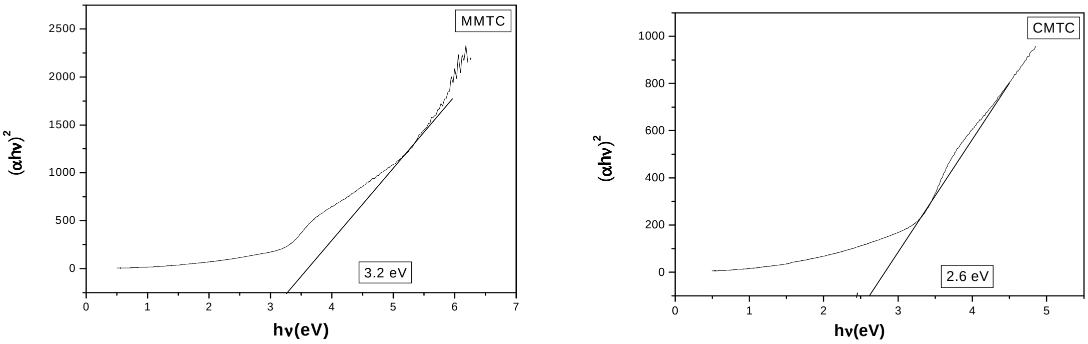

Fig. 3. Tauc's plot of MMTC and CMTC

3. 4. Impedance Spectroscopy

The grown crystals were powdered and then made as pellets for impedance spectroscopy studies. The thicknesses of the samples were 0.9 mm and 0.8 mm respectively. To study the electrical properties of the samples, the flat surfaces of the pellets were coated with silver paint and dried completely before perform the experiments [11]. In the present case, electrical measurements were performed using an impedance analyzer HT 4284A precision LCR meter from 20Hz to 1MHz. All the electrical measurements of the crystals were carried out at two different temperatures (298 and 333K).

The *ac* conductivity study using complex impedance spectroscopy is performed to characterize the bulk resistance of the crystalline material. The complex impedance spectra for the grown crystals are shown in Figures (4 and 5). It was plotted in the complex plane represented by the real part versus imaginary part (cole-cole plot) [12,13]. Due to the high frequency limitation of the used impedance analyzer, incomplete semicircles were obtained at low temperatures. Some of the semi circles are incomplete, because the resistivity of the crystal is very large at low temperatures [14]. The diameter of the arc and bulk resistance will be decreased with increasing temperature. The electrical conductivity is proportional to temperature. It indicates that the mobile ion has surface electrode effect at higher temperature. The *ac* conductivity of the grown crystals is determined from the real part of the impedance using the relation,

$$\sigma_{ac} = t/R_bA$$

where t is the thickness of the sample, A is the area of the face in contact with the electrode and R_b is the bulk resistance which is found from the graph [15]. The calculated *ac* conductivity of MMTC single crystal at the temperatures 298 K and 333 K are 6.42 $\times 10^{-5}$ and 4.33 $\times 10^{-4}$ (Scm^{-1}).

In the case of CMTC, the calculated *ac* conductivity values are 1.25 $\times$ 10^{-6}, 1.74 $\times$ 10^{-5} (Scm^{-1}). The conductivity of the MMTC single crystal is atleast 10 fold higher than CMTC crystal. Figure (6) shows the Arrhenius plot for MMTC and CMTC samples. The Arrhenius equation is given by,

$$\sigma = \sigma_0 \exp(-E_a / k_B T)$$

where E_a is the activation energy, k_B is the Boltzmann constant [16]. The ac conductivity shows a linear Arrhenius behavior indicating that the charge carriers are band conduction electrons. The calculated activation energies of MMTC and CMTC crystals are 1.85 eV and 0.48 eV.

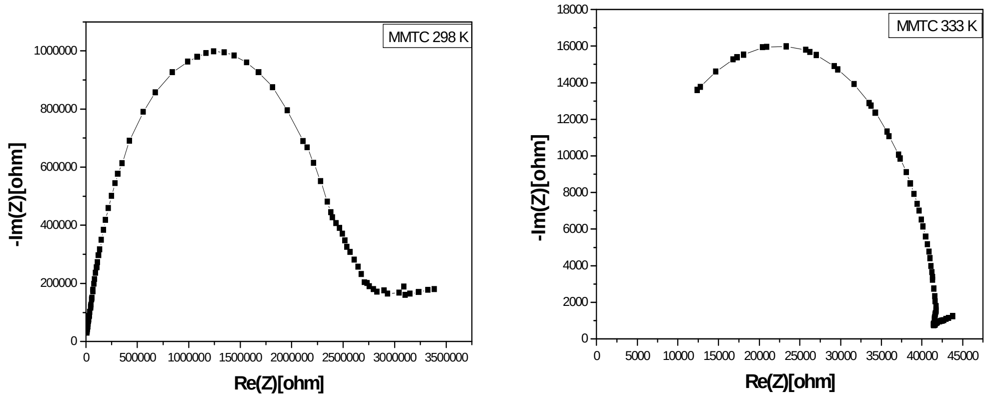

Fig. 4. *ac* conductivity of MMTC at 298K and 333K

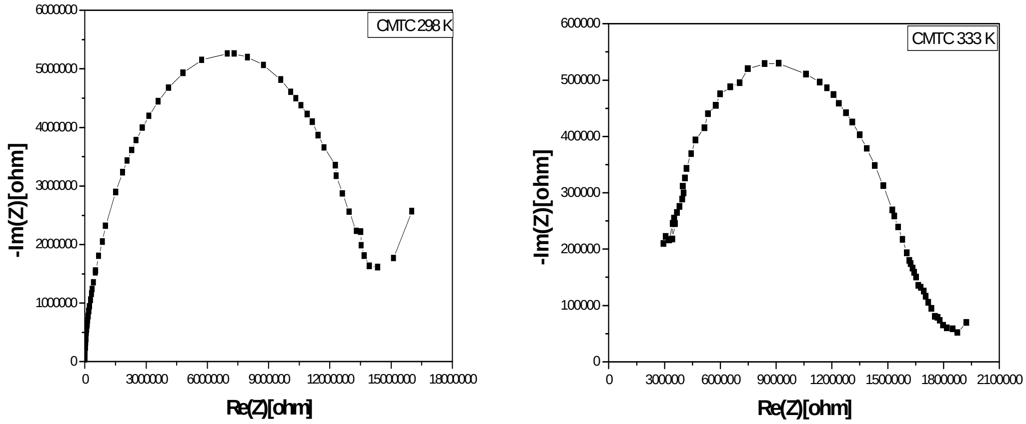

Fig. 5. *ac* conductivity of CMTC at 298K and 333K

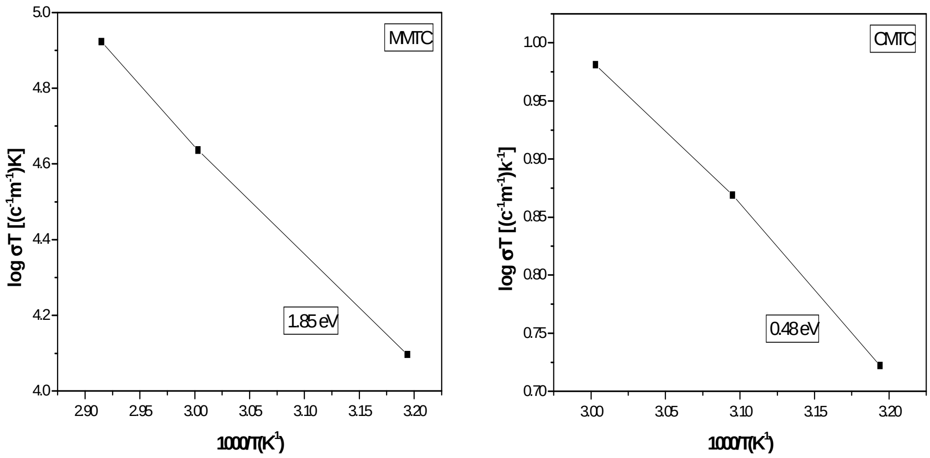

Fig. 6. Arrhenious plot of MMTC and CMTC

CONCLUSION

Single crystal of bimetallic thiocyanates of MMTC and CMTC were grown from slow evaporation technique. Tetragonal crystal structure was confirmed by single crystal XRD analysis. NLO study confirms the suitability of the material for SHG applications. The UV cut-off wavelength and band gap energy are reported. The electrical conductivity of the bimetallic complexes of MMTC and CMTC is found to increase with temperature and this is an important property for these materials in the construction of photonic and NLO devices. The activation energies of MMTC and CMTC have been identified.

REFERENCES

[1] X. Q. Wang, D. Xu, M. K. Lu, D. R Yuan, S. X. Xu, *Materials Research Bulletin* 36 (**2001**) 879-887.
[2] X. Q. wang, D. Xu, M. K. Lu, D. R. Yuan, J. Huang, G. W. Lu, G. H. Zhang, S.Y. Guo, H. X. Ning, X. L. Duan, Y. Chen, Y. Q. Zhou, *optical Materials* 23 (**2003**) 335-341.
[3] X. Q. Wang, X.F. Cheng, S. J. Zhang, D.Xu, G. H. Zhang, Z. H. Sun, F. P. Yu, X. J. Liu, W. L. Liu, C. L. Chen, *Physica B* 405 (**2010**) 1071-1080.
[4] Xitao Liu , Xiniang Wang, Zhihua Sun, Xiaojing Lin, Guanghui Zhang, Dong Xu, *Journal of crystal growth* 317(**2011**) 92-97.
[5] T. Rajesh Kumar, R. Jeyasekaran, S. M. Ravikumar, M. Vimalan, P. Sagayaraj, *Applied surface science* 257 (**2010**) 1684-1691.
[6] R. Padma Suvarna, K. Raghavendra Rao and K. Subbarangaiah *Bull. Mater. Sci*., 25 (**2002**) 647-651.
[7] G. P. Joseph, I. Korah, K. Raja Rajan, P. C. Thomas, M. Vimalan, J. Madhavan and P. Sagayaraj, *Crystal Research Technology* 42 (**2007**) 295-299.
[8] C. M. Raghavan, R. Pradeepkumar, G. Bhagvanarayanan, R. Jayavel, *Journal of crystal growth* 311 (**2009**) 3174-3178.
[9] P. Sagayaraj, Ginson. P. Joseph, *Journal of material science: Mater electron* 20 (**2009**) s390-s394.
[10] I. Vetha Potheher, K. Rajarajan, M. Vimalan, S. Tamil Selvan, R. Jeyasekaran, P.Sagayaraj, *Physica B* 406(**2011**) 3210-3214.
[11] R. Thangavel, V. Sabarinathan, S. Ramasamy, J. Kumar, *Materials Letters* 61(**2007**) 4090-4093.
[12] B. Milton Boaz, S. Mary Navis Priya, J. Mary Linet, P. Martin Deva Prasath, S. Jerome Das, *Optical Materials* 29 (**2007**) 827-832.
[13] S. Narendar Reddy, A. Sadananda chary, T. Chiranjivi, Solid State Ionics 42 (**1990**) 101-107.
[14] R. H. Chen, Chen-Chen Yen, C. S. Shern, T. Fukami, *Solid state Ionics* 177(**2006**) 2857-2864.
[15] R. Jerald Vijay, N. Melikechi, T.Rajesh Kumar, Joe G. M. Jesudurai, P. Sagayaraj, *Journal of crystal growth* 312 (**2010**)420-425.
[16] C.V. Kannan, S. Ganesamoorthy, D. Rajesh, R. Jayavel, H. Kimura, *Solid State Communication* 136 (**2005**) 215-219.