MODIFIED GROWTH TECHNIQUE AND CHARECTERIZATION OF SCN LIGAND BASED NLO CMTC AND MMTC SINGLE CRYSTALS

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Abstract

The crystalline behavior of a non centrosymmetric semi organic nonlinear Cadmium Mercury Thiyocyanate (CMTC) and Manganese mercury thiocyanate (MMTC) single crystal were studied under modified technique using modified Bridgeman technique in a closed wooden box in a period of 30 days. The mechanical behavior was calculated using the micro hardness measurement. The ac/dc conductivity, photoconductivity and dielectric properties of the CMTC and MMTC crystal were studied.

Keywords: Solution growth; micro hardness, CMTC, MMTC, ac /dc conductivity

1. INTRODUCTION

Nonlinear optics has been the subject of numerous investigations by both theoreticians and experiments in recent years due to the potential applications in optical processing, optical computing, optical data storage and eye and sensor protection, photolithography, underwater communications, laser displays, etc [1]. In the past several materials have been investigated for their NLO properties and organometallic complex crystals have emerged as a promising class of NLO materials due to their excellent nonlinear properties. However, poor mechanical strength, high optical absorption, the tendency for photochemical changes and mostly needle like growth habit are their limitations from the applications perspective [2].

Thiocynate (SCN) ion is a good chromophore for second-order NLO properties, it forms coordination compounds with II B divalent d^{10} ions such as Zn^{2+},Cd^{2+} ,Mn^{2+} and Hg^{2+} on the basis of the molecular engineering method and double ligand model [3]. Cadmium mercury thiocyanate (CMTC) is a good nonlinear optical material with excellent physicochemical properties and promise for applications. The CMTC crystal belongs to the $\bar{I}4$ space group with lattice parameters a =1.1487 nm and c = 0.4218 nm. Manganese mercury thiocyanate (MMTC) is a good nonlinear optical material for realizing blue-violet out by frequency doubling of laser diode radiation. It crystallizes in tetragonal system with lattice parameters of a =11.324 Å and c = 4.270 Å [4]. In MMTC, the SCN ligand is a good electron supplier, whereas, Mn^{2+} and Hg^{2+} are two strongly accepting ions. The thermal contraction occurs in the direction parallel to the a-axis where MMTC molecules are connected by the infinite three dimensional –Mn-NCS-Hg- networks [5].

CMTC and MMTC crystals are candidate material for laser diode frequency doubling to realize blue-violet output. During the growth of CMTC and MMTC, the control of multi nucleation is more tedious process. In order to obtain high optical quality single crystals for nonlinear optical applications, a systematic investigation has been carried out to improve the growth conditions in different methods. In this paper, we mainly focused the growth method using modified technique.

2. EXPERIMENTAL

CMTC was synthesized using AR grade ammonium thiocyanate, mercury chloride and cadmium chloride taken in the stoichiometric ratio 4:1:1 in deionized water at room temperature. The resultant compound was recrystallized using hot water so that the co-precipitated NH_4Cl gets dissolved. Solubility studies were carried out in the mixed solvent of 10 % Acetone with water by the gravimetric method for various temperatures. The recrystallized salt of CMTC was added in small quantity to 100 ml of mixed solvent by stirring the solution continuously. Prior to commencement, the sample was heated to 45 °C for one day. The temperature was then reduced to 40 °C. After seasoning, the beaker was kept in a wooden box and the lamps were fixed due to maintain the temperature. The MMTC single crystals were synthesized using ammonium thiocyanate, mercury chloride and manganese chloride in the stoichiometric ratio 4:1:1. All the chemicals were purchased from Merck.

Powder X-ray diffraction analysis was carried out for the identification of the crystal using X-ray diffractometer, MODEL RICH. SEIFERT, XRD 3000P with monochromatic nickel filtered CuK_α (λ = 0.15406 nm) radiation. The sample was scanned over the range 10 - 50° at the rate of one degree/minute. Microhardness study was conducted using a Vickers microhardness tester and Knoop hardness tester. The *ac* conductivity measurements were carried out using HIOKI 3532-50 LCR HITESTER in the frequency range 100 Hz to 1 MHz.

3. RESULTS AND DISCUSSION

3.1 Powder X-ray Diffraction study

The spectrum recorded at room temperature, all the observed reflections were indexed. The (*h k l*) planes satisfy the general reflection conditions of space group observed from single crystal XRD. The lattice parameters of MMTC are a = b = 11.301 Å, c = 4.269 Å .The obtained values are in good agreement with the literature values. The crystal has a = 11.4553Å c = 4.2021Å values and the calculated lattice parameter values indicate that the crystals are tetragonal.

3.2 Microhardness study

The calculated values of H_V for various loads are plotted as given in Figure 1. The graph indicates that the microhardness number increases with increasing load. By plotting log d *vs* log p, the values of work-hardening coefficient n were calculated using the least squares fit method (Figure 2). The „n‟ value was found to be 3.5 for MMTC single crystal. In the case of CMTC, the hardness number increases with applied load and "n" is found to be 2.9. According to Onitsch [6], if $n > 2$, the microhardness number H_V increases with increasing load and if $n < 2$, H_V decreases with increasing load.

The mechanical strength of the materials was studied employing the Knoop hardness tester. The calculated values of H_K for various loads are plotted as given in Figure 3. From the Knoop hardness measurements, the Young‟s modulus (E) were found to be 1.942×10^{10} Nm^{-2} for MMTC and 1.3491×10^{10} Nm^{-2} for CMTC.

3.3 Dielectric study

Dielectric properties are correlated with the electro-optic property of the crystals [7]. Figure 4 and 5 shows the variations of dielectric constant and dielectric loss of MMTC and CMTC crystals at different temperatures as a function of frequency. The dielectric constant decreases with increasing frequency and becomes almost saturated beyond 1 kHz for all temperatures. The decrease in dielectric constant of MMTC and CMTC single crystal at low frequencies may be attributed to the ependence of electronic, ionic, orientational and space charge polarizations. The space charge contribution will depend on the purity and perfection of the material and it has noticeable influence in the low frequency region. Hence, the larger values of dielectric constant exhibited by MMTC and CMTC crystals at low frequencies may be attributed to space charge polarization arising due to the crystal defects at grain boundary interfaces [8]. It can be noted that the dielectric constant for MMTC is more than that of CMTC at all temperatures and frequencies region. The very low value of dielectric constant at higher frequencies is important for extending the material applications towards photonic, electro-optic and NLO devices.

3.4 AC/DC conductivity study

Small signal *ac* impedance analysis is a powerful technique for the electrical characterization of materials. The sample was heated in the temperature range 308 - 368 K. The *ac* conductivity was calculated using the formula; $\zeta_{ac} = \omega\varepsilon_r \tan\delta\varepsilon_o$ (where ε_o is the vacuum dielectric constant) at different temperatures (Figure 6). Figure 6 shows the plot of *ac* conductivity versus 1000/T. It is evident from the graph that the conductivity increases with temperature. The activation energy for ionic migration was estimated from the graph. The line of best fit for the plot of $ln\ \zeta_{ac}T$ versus 1/T obeys Arrhenius relationship $\zeta_{ac} = \zeta_o \exp(-E_a/kT)$ where ζ_o is the pre-exponent factor, E_a the activation energy for the conduction process and k is the Boltzman constant. Therefore, the sample exhibits Arrhenius type conductivity behaviour in the temperature range of investigation. The variations activation energies with frequencies are shown in Figure 6. The activation energy is found to increase with increasing frequency. The activation energy (E_{dc}) is calculated from the slope of the graph between $ln\ \zeta_{dc}$ *versus* 1000/T (Figure 7) and it is found to be 0.049 eV and 0.036 eV for MMTC and CMTC respectively. On quenching or rapid cooling, a fraction of the vacancies freeze and the pre-exponential term includes a contribution from those frozen vacancies [9,10]

4 CONCLUSIONS

The hardness studies show the decreasing nature of hardness number with increase in load. Dielectric characterization shows low value of dielectric constant at higher frequencies for these crystals. The activation energy is determined from the plots of ac/dc conductivity. The promising crystal growth characteristics and properties of MMTC and CMTC crystals nominate it as a potential material for photonic, electro-optic and SHG device application.

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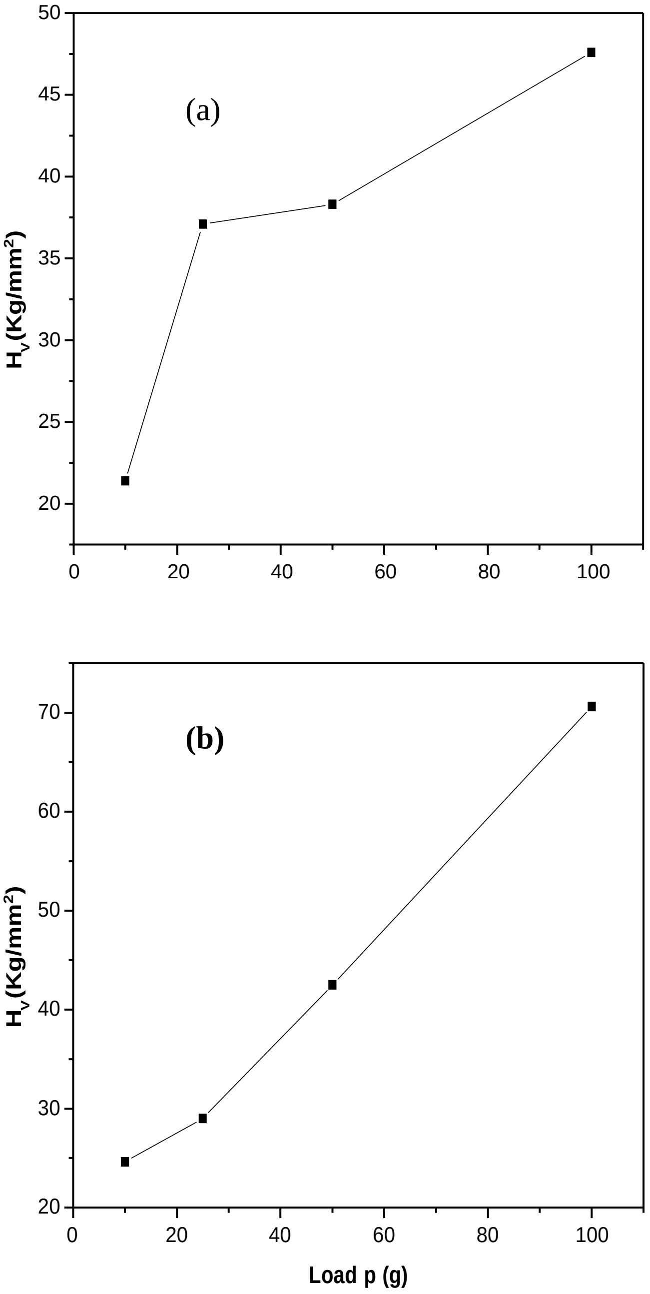


Figure 1 Vickers hardness profile of a) MMTC and b) CMTC as a function of applied load

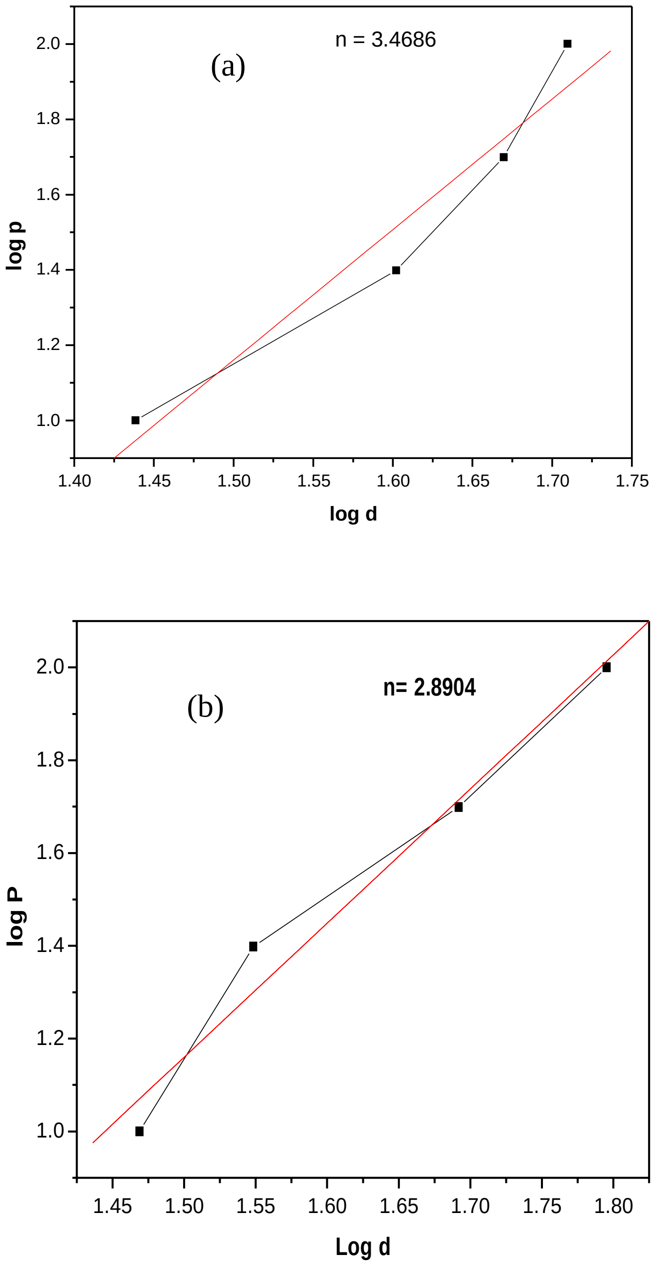


Figure 2 Plot of log d Vs log p for a) MMTC and b) CMTC single crystal

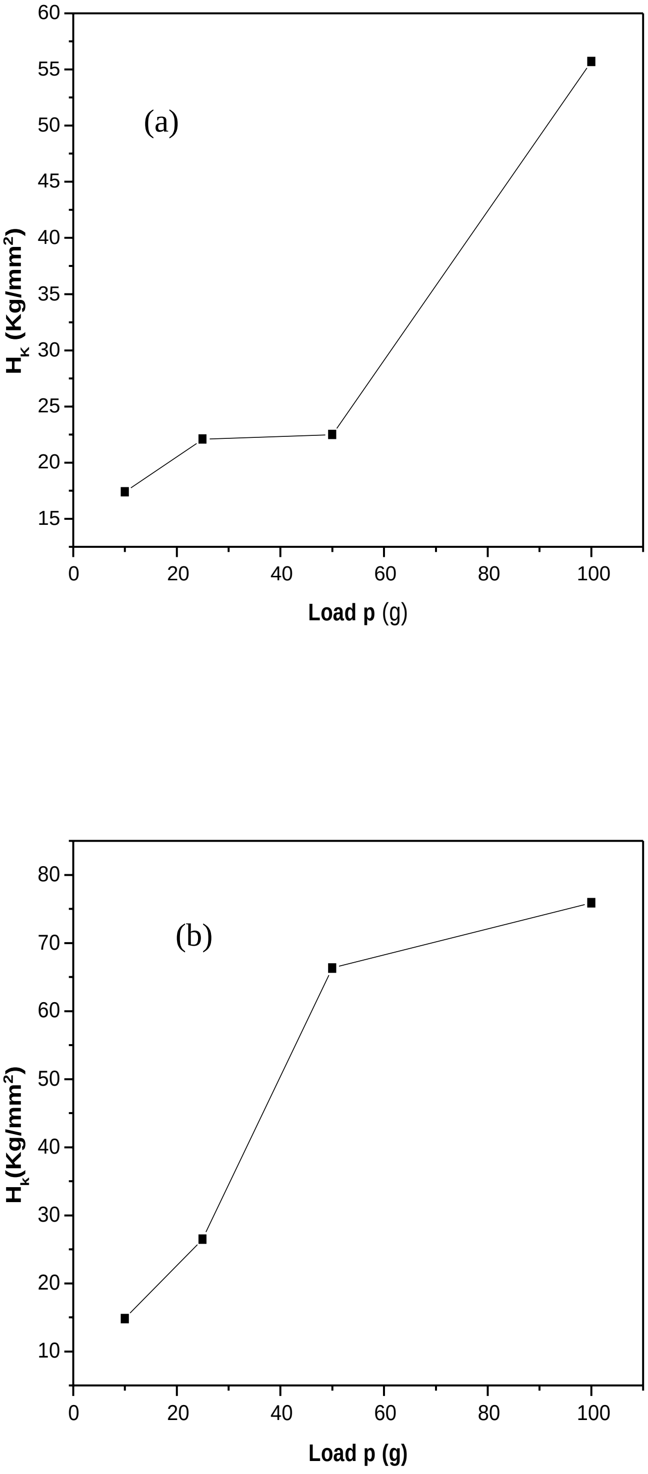
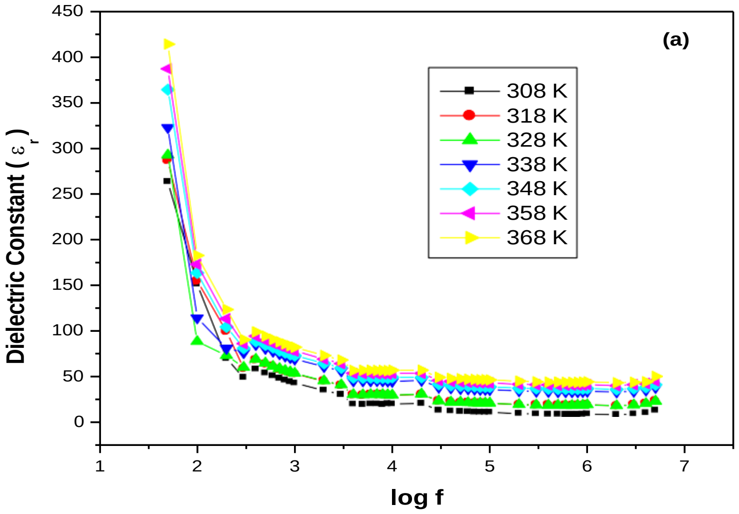


Figure 3 Variation of Knoop hardness number with applied load for (a)MMTC and (b)CMTC



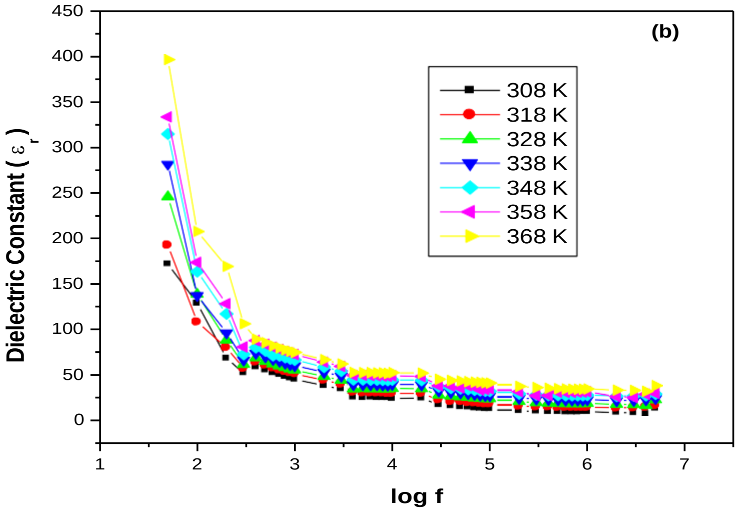


Figure 4 Variation of dielectric constant with log frequency at different temperatures for (a) MMTC and (b) CMTC single crystal

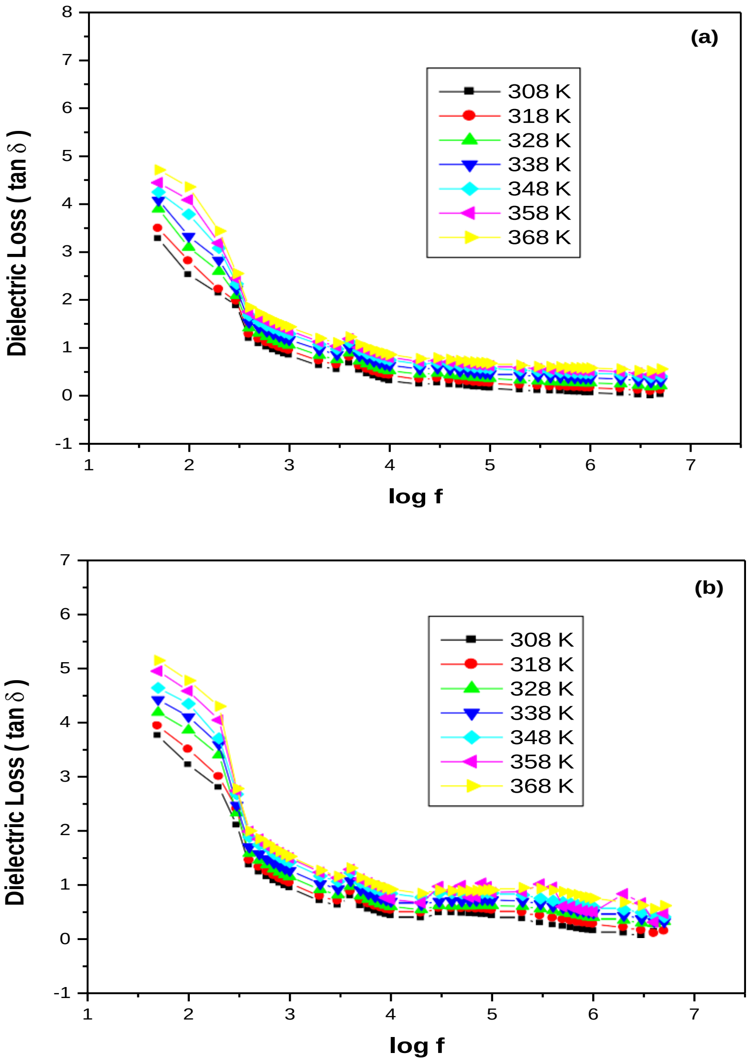


Figure 5 Variation of dielectric loss with log frequency at different temperatures for (a) MMTC and (b) CMTC single crystal

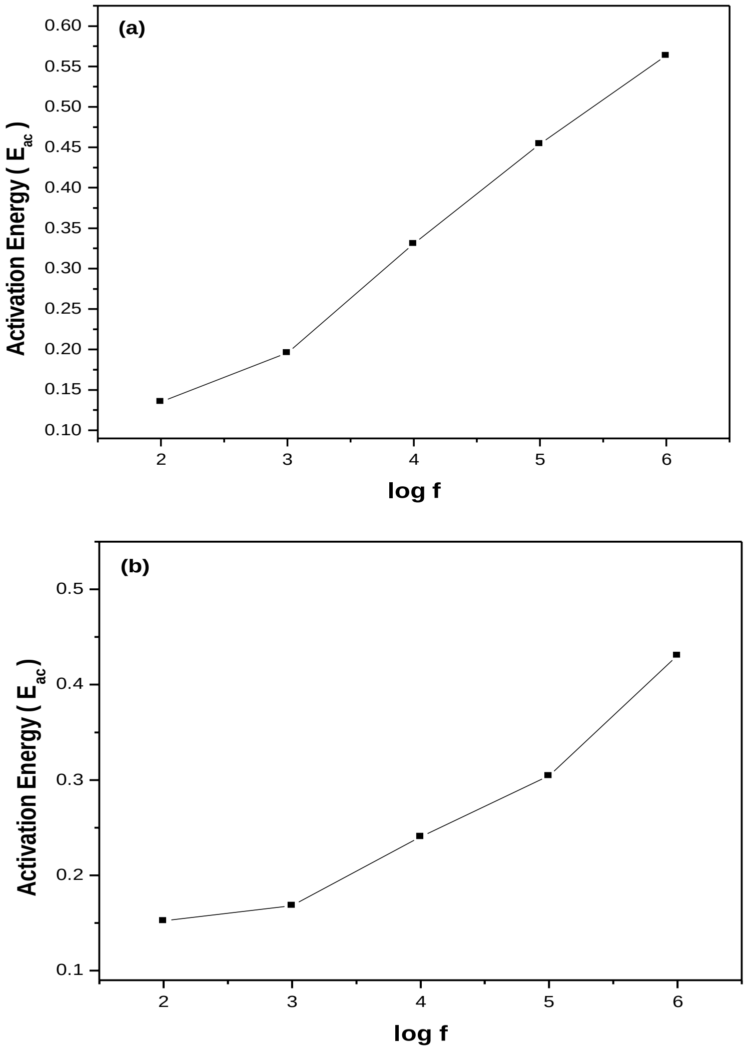


Figure 6 Plot of ln(σ_{ac})T versus 1000/T for a) MMTC and b) CMTC single crystals

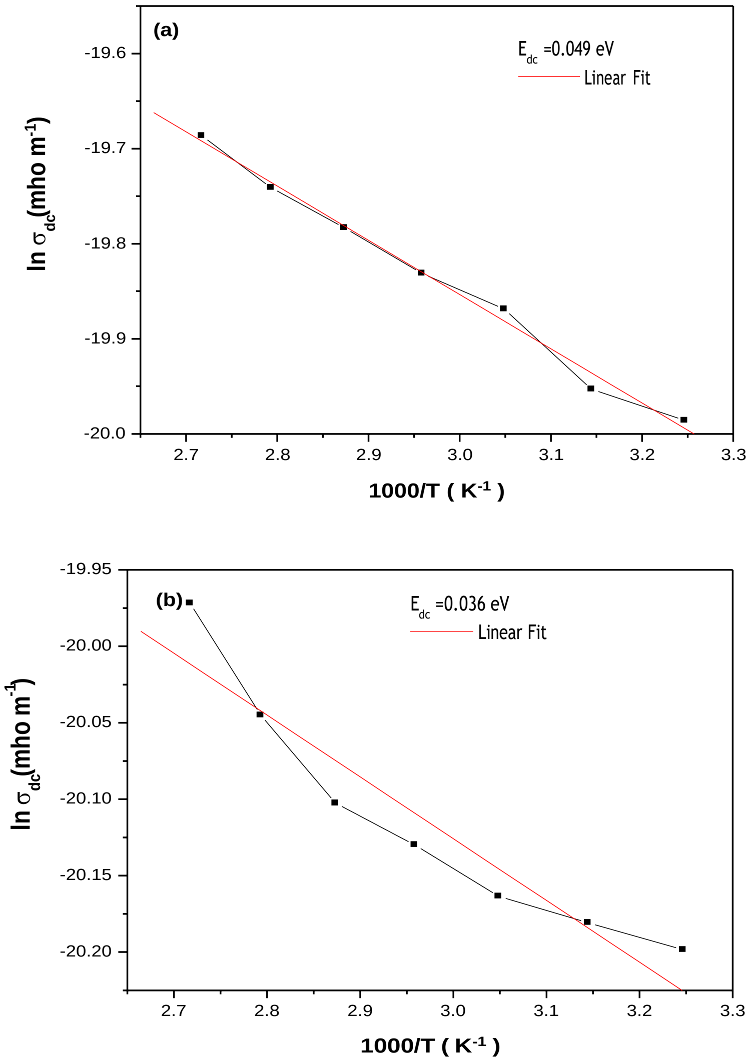


Figure 7 Plot of ln(σ_{dc})T versus 1000/T for a) MMTC and b) CMTC single crystals