AC ELECTRICAL CONDUCTIVITY OF PHALOCYANINA
TO ALUMINUM CHLORIDE

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ABSTRACT

Ac conductivity in the frequency range of 5×10^3 to 5×10^3 Hz of Phthalocyaninato Aluminum Chloride (PcAlCl) was measured, which consists of frequency dependent and independent parts. The Dc conductivity is attributed to the charge carrier's transition, between valance and conduction bands, while the Ac conductivity is due to hopping of charge carriers, between the localized sites around Femi level which is an indication of degree of imperfection around Fermi level in the crystal lattice.The number of the hopping sites were estimated, using Webb and William relation $4.7 \times 10^{20} eV^{-1} cm^{-3}$.

KEYWORDS: Phthalocyaninato Aluminum Chloride, Ac And Dc Electrical Conductivity

INTRODUCTION

Studies of temperature dependence of the electrical conductivity of some compounds, show an agreement with Arrhenius behavior, which may be explained as the result of the presence of states, in the band gap (around Femi level)[1,2].

AC conductivity measurements assumed the existence of localized sites, between which electrons may hope. In response to the alternating field. The hoping conduction is frequency dependent ($\sigma\alpha\omega^n$), where ωis the angular frequency. The sample which show significant crystal imperfections or disorder, show a significant frequency dependent conductivity in addition to the frequency independent. Which make an assumption of both hole and electron mobilities and their temperature dependence.

Such behavior has been found in many compounds, such as, TCNQ complex salts,

Phthalocyanines and polymers[3, 4,5].

In This work, phthalocyaninato Aluminum chloride (PcAlCl) was prepared, and its dc and ac electrical conductivity were studied.

Synthesis of Phthalocyaninato Aluminum Chloride (PcAlCl)

A mixture of 5.59 g (0.04 mole) of phthalicunhydride, 1.19 g(0.01 mole) of unhydrous aluminum try chloride, 10 g of urea and 0.01 g of ammonium molybdate in nitrobenzene were refluxed for six hours, with mechanical stirring. The reaction mixture was then cooled and filtered. The solid precipitate was refluxed with water for 15 minutes, cooled and filtered. The same procedure was done with acetone, hexane, chloroform and carbon tetrachloride, to remove the impurities[6]. The final blue solid precipitate was dried at 110 ^{0}C. The yield was 3.1 g (61%), don't melt till 230 ^{0}C. The reaction question is shown in figure 1. CHN analysis for the final product ($C_{32}H_{16}N_8AlCl$) shows: Calculated:
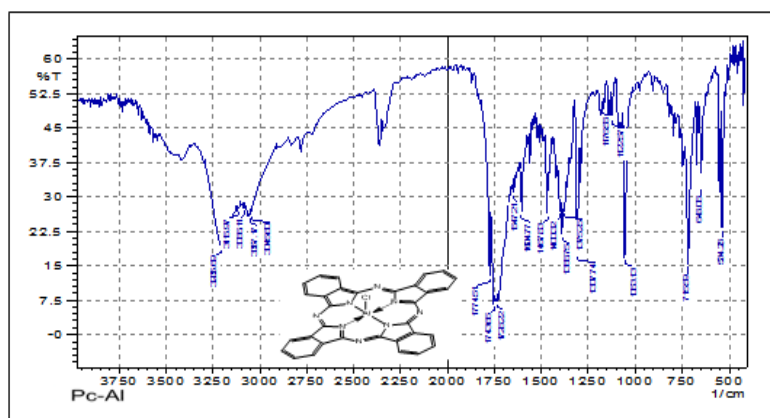
C(70.13%), H(2.78%), N(19.49%); Found: C(69.01%), H(2.21%), N(18.32%).
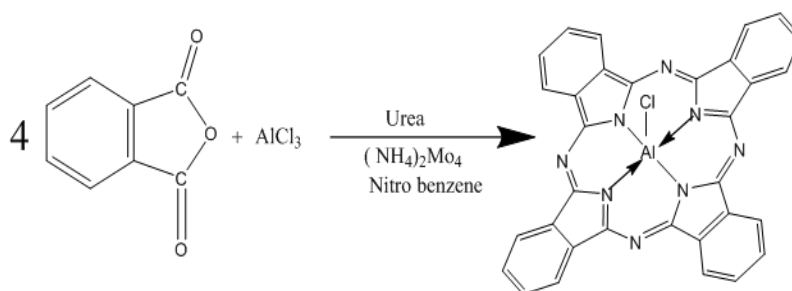
Figure 1: Preparation of PcAlCl

RESULTS AND DISCUSSIONS

IR: The disappearance of the carbonyl group at 1700 cm^{-1} and the presence of the aromatic at 3151 and C=N at 1646 cm^{-1}are the most characteristic IRspectrum[7]of PcAlCl. Figure 3.

Figure 2: The IR spectrum of PcAlCl

The electronic spectrum: The electronic spectrum of the complexes, PcAlCl, shows the characteristic (Soret band) at 354 nm and, due to, π-π* and n-π* transitions, and Q band at 673 nm, which is due to, π-π* and weak d-d transition of the central metal atom, hidden inside the Q-band [1, 7, 8], with an extinction coefficient (ε) 1.2×10^4L.mol^{-1}.cm^{-1}. The solvent DMF was used to prevent or reduce aggregation, of the complex molecules.
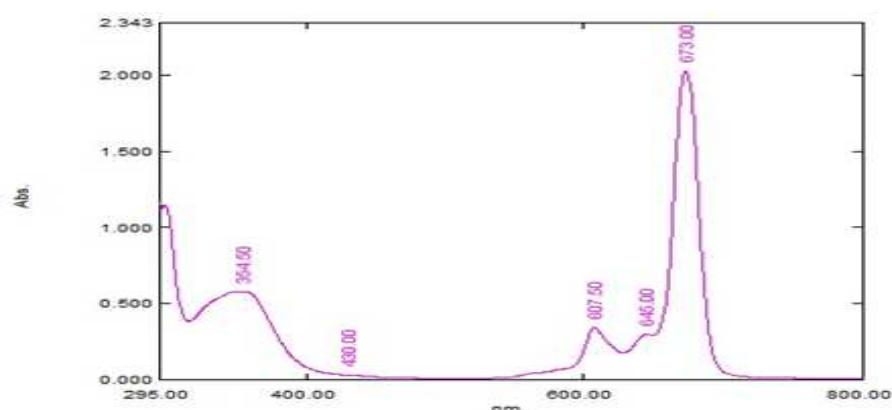
Figure 3: The Electronic Spectrum of PcAlCl

ELECTRICAL PROPERTIES

Preparation of the samples: The samples were casted as sandwich cells, on fluorine doped tin oxide (FTO) glass substrate, which is conducting from one side with 1 cm^2 surface area. The thickness of the casted film is 0.5 mm and then, the cell constant is 10^{-2} cm^{-1}. The sample cell was put in cryostat, which is supplied with variable heating element and cell electrode holder and voltage supply. The cryostat is connected to voltmeter and ammeter[8], to measure the voltage and the current. The temperature was measured using copper-constantan thermocouple, placed near the sample. The dc electrical conductivity measurement were carried out in the temperature range of (303- 393) K and at 3 volts. The Ac electrical measurement were measured in the frequency range of (5 -50) KHz and temperature range of (303 – 393) K.
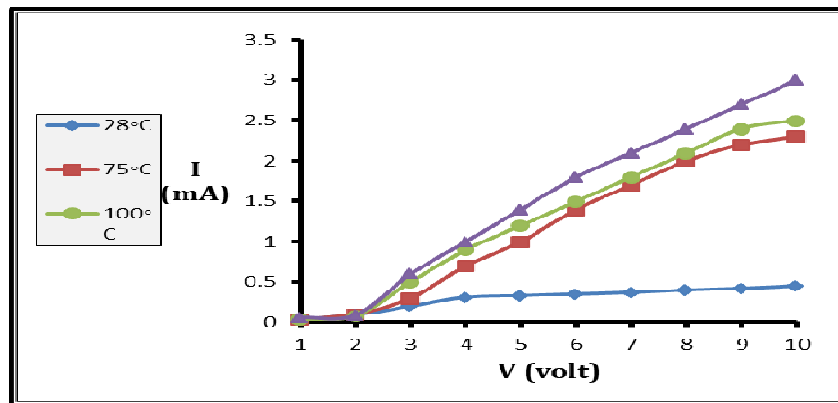
Figure 4: I/V curve at Different Temperatures forPcAlCl

Figure 5, shows the I/V curve for the complex (PcAlCl), at 30 ^{0}C, voltage range is 0-10 volts. It shows anohmic relation, especially at lower voltages, where there is no space charge limited current.

Figure 6, shows the relation between log conductivity (logσ) and log angular frequency (log ω), at different temperatures for the complex, where ω is the angular frequency (2πf), and f is in Hertz. The figure shows the increase of ac conductivity, with frequency and temperature[4].

Figure 7, shows the variation of log conductivity with inverse temperature at different frequencies, for both dc conductivities at different frequencies. It shows that, the measured ac conductivity is higher than dc conductivity and dc conductivity is approaching the ac conductivity, at lower frequency. The ac conductivity increases with increasing temperature and frequency.

The measurement shows that, the measured conductivity ($σ_T$) contains ac and dc conductivities [3, 9].

$$σT = σdc + σω$$

Where $σ_ω = ω^n$ (varies with frequency, n is constant), and $σ_{dc}$ follows Arrhenius equation, $σ_{dc} = σ_0 e^{-\frac{ΔE}{kT}}$

Figure 8, shows the variation of log Capacitance (logC) in pF, with log ω in Hertz. The figure shows the increase of the capacitance, with temperature and decreases with frequency, which tend to approach common value.

Figure 9, shows the variation of log ($C_∞$ –C), with ln ω at different temperature, according to Kramer Kronigrelation [3, 10]. $C = C_∞ + A ω^{n-1}$

Where, C is the capacitance at any frequency and C∞ is the capacitance at infinity (which means at common value of capacities), which is assumed to be at 10^5 Hz. A and n are constants.

Using Mott and Davis equation [11, 12].

$$\sigma_\omega = \frac{4\pi}{3}(\ln 2)e^2 kTN(E_F)^2 \alpha^{-5}[\ln\frac{\vartheta_{ph}}{\omega}]^4\omega$$

N (E_F), the number of energy states around Fermi level, is estimated to be 4.7×10^{20} eV^{-1} cm^{-3}, where charge of electron is 4.8×10^{-10}esu, k is8.617×10^{-5} eV/K, T is taken as 303 K, α is the reciprocal interplanner spacing, which is calculated from X-ray diffraction (Figure 10, 2Θ=25^0). ϑ_{ph} is the phonon frequency taken as 10^{12} Hz [3, 5] and ω is taken as 5 kHz.

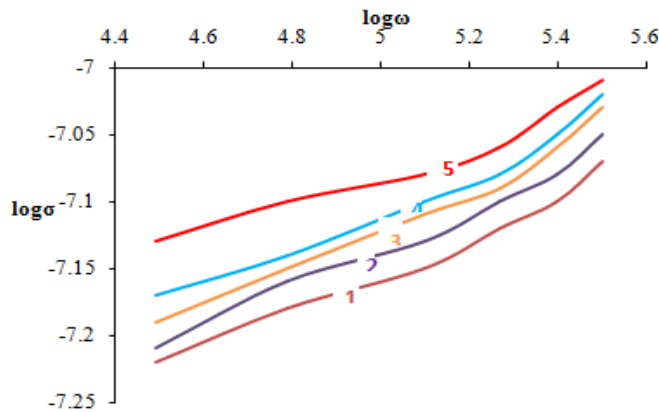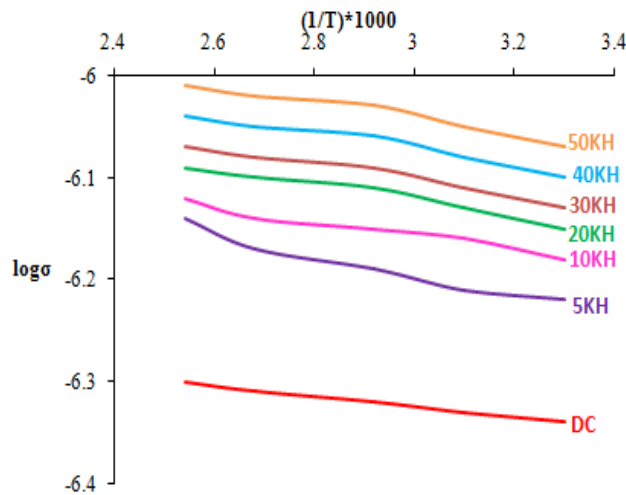**Figure 5: Relation between log σ and log ω at Different Temperatures, for PcAlCl**

Figure 6

Figure 6: The relation between log σ and reciprocal temperature for the frequency independent part (dc conductivity (1) and for frequency dependent part (ac conductivity at different frequencies (2-5, 3-10, 4-20, 5-30, 6-40, 7-50)) KHz.
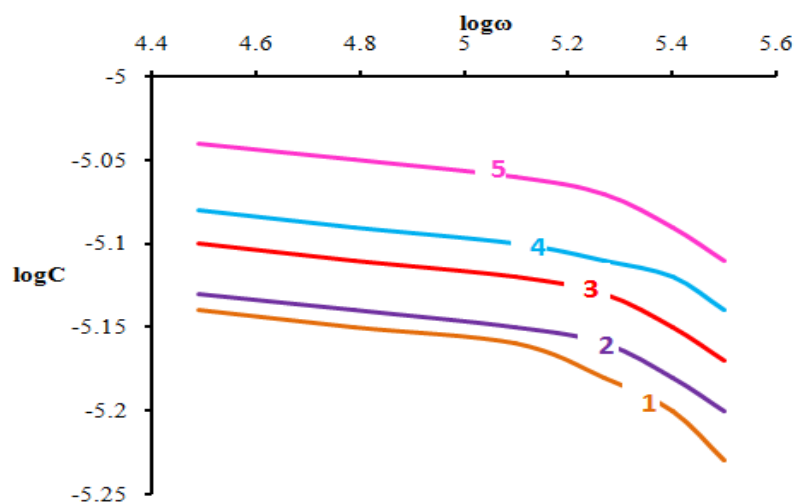
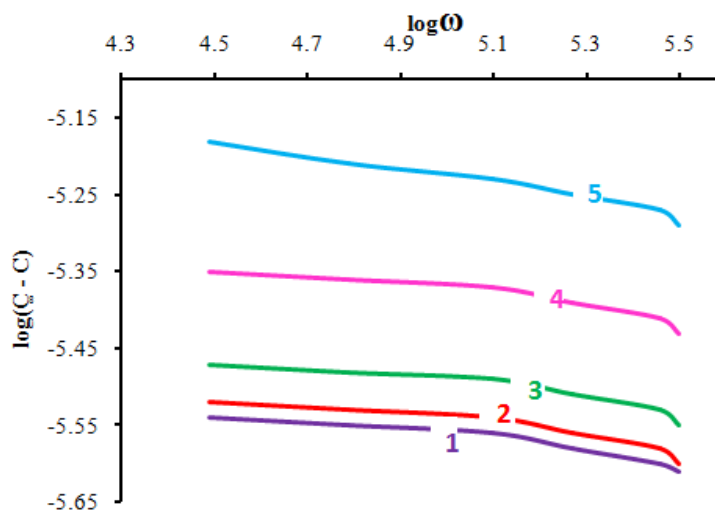**Figure 7: The Relation Between log C and log ω at Different Temperatures for(PcAlCl)**

Figure 8: The Relation Between log(C00 – c) and log ω at Different Temperatures, forPcAlCl

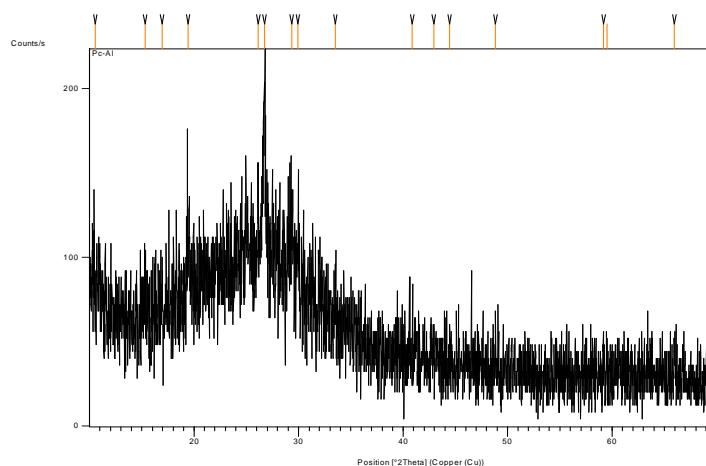**Figure 9: The X-Ray Diffraction of PcAlCl**

CONCLUSIONS

Thin film of PcAlCl act as semiconductor. Ac conductivity increases with frequency and temperature, and its Capacitance decreases with both Frequency and Temperature. The number of energy states around Fermi level is estimated to be $9.6 \times 10^{19} \text{eV}^{-1} \text{cm}^{-3}$

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