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Dielectric and Conductivity Studies on Cobalt Phthalocyanine Tetramers

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ABSTRACT: Electrically conductive organic and metal-organic polymers are of great interest and they have applications in electronic, optical, photonic, photoelectric, electrochemical, and dielectric devices. Tetrameric cobalt phthalocyanine was prepared by conventional chemical method. The dielectric permittivity of the tetrameric cobalt phthalocyanine sample was evaluated from the observed capacitance values in the frequency range 100 KHz to 5 MHz and in the temperature range of 300 to 383°K. It is found that the system obeys the Maxwell Wagner relaxation of space charge phenomenon. Further, from the permittivity studies AC conductivity was evaluated. The values of AC conduc-

tivity and DC conductivity were compared. Activation energy was calculated. To understand the conduction mechanism Mott's variable range hopping model was applied to the system. The $T^{-1/4}$ behavior of the DC conductivity along with the values of Mott's Temperature (T_0), density of states at the Fermi energy $N(E_F)$, and range of hopping R and hopping energy W indicate that the transport of charge carriers are by three-dimensional variable range hopping. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2529–2535, 2004

Key words: dielectric properties; conjugated polymers; tetramers; AC and DC conductivities; conduction mechanism

INTRODUCTION

Phthalocyanines and their polymers are well known for their unique photoconducting and semiconducting properties.^{1–7} Though the discovery of these materials is accidental, the phthalocyanine ring is a good ligand and every element in the periodic table, including nonmetallic elements such as silicon and phosphorous, form a complex with phthalocyanine ring.^{1,5,8} Materials based on phthalocyanines have been of particular significance in many fields concerning energy conversion (photovoltaic and solar cells), electrophotography, photosensitizers, gas sensors, rectifying devices, electrochromism, optical data storage, LB films, liquid crystals, and nonlinear optics.^{9,10} The electrical properties of polymeric phthalocyanine are of interest because of their conjugated structure and stability against light, heat, moisture, and air. Hence polymeric phthalocyanines are suitable candidates for use as environmentally stable electrically conductive materials.^{11–14} Polymeric metallophthalocyanines of copper (Cu), nickel (Ni), and cobalt (Co) possess large extended conjugated structures and exhibit high conductivity.^{12,15,16} Among them, tetrameric cobalt phthalocyanine exhibits greater conductivity than the nickel and copper phthalocyanine tetramers.¹² Hopping or

tunneling conduction mechanism is the usual transport of charge carriers found in conducting polymers.

To understand the semiconducting and dielectric properties of tetrameric cobalt phthalocyanine compound, a systematic investigation on these properties and their variation with temperature and frequency is attempted in this paper. The mechanism of electrical conduction is explained using Mott's variable range hopping model.

EXPERIMENT

Preparation of cobalt phthalocyanine tetramer

Tetramer of cobalt phthalocyanine was prepared, purified, and characterized by the methods reported earlier.^{17,18} In this method, cobalt sulfate, pyromellitic dianhydride, excess urea, ammonium chloride, and ammonium molybdate were ground well and heated at 180°C in nitrobenzene media for 12 h. The reaction mixture was then cooled and washed with methanol several times to remove nitrobenzene. The crude product was further boiled with 2N sodium hydroxide containing sodium chloride and filtered. The residue was acidified with hydrochloric acid and washed several times and dried to obtain phthalocyanine tetramer. The structure of tetrameric cobalt phthalocyanine is shown in Figure 1.

Elemental analysis

Elemental analysis was carried out in a Perkin–Elmer 2400 elemental analyser, which uses a combustion

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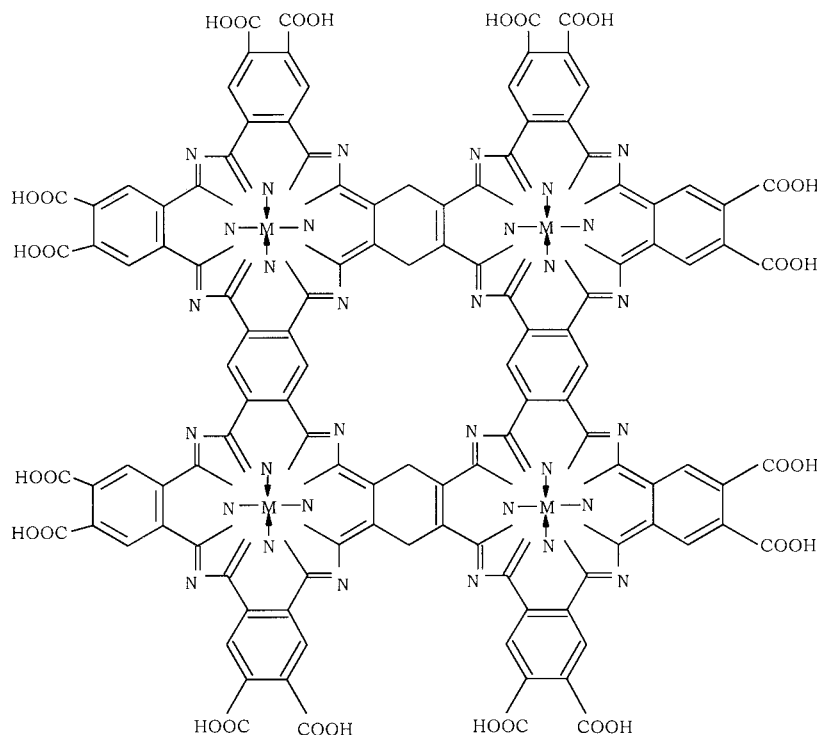


Figure 1 Structure of metallophthalocyanine tetramer [M-Cobalt].

method to convert the measured elements (C, H, and N) to simple gases. These gases were then measured as a function of thermal conductivity. The metal content of the compound was estimated by decomposing a known weight of the material with concentrated sulfuric acid and the estimation of this solution was carried out by atomic absorption spectroscopy.

The elemental analysis values of carboxyl-terminated tetramer are shown in Table I. The values of carboxyl-terminated tetramer in Table I were calculated based on the structure given in Figure 1. Since the carboxyl-terminated tetramer contains bound water molecules it does not give one-to-one agreement with the calculated and observed elemental analysis values. The purity of the compound was reconfirmed by the following method.¹²

The carboxyl-terminated tetramer (1.0 g) was thoroughly ground to a powder and refluxed in boiling

acetic anhydride (20 mL) for 36 h. The reaction mixture was cooled and filtered. The residue obtained was washed with chloroform and dried in a vacuum oven (1 mmHg) at 373°K for 5 h. The presence of anhydride was confirmed by characteristic infrared (IR) peaks at 1,830 and 1,720 cm^{-1} . The elemental analysis of anhydride terminated tetramer given in Table I agree fairly well with the calculated values indicating the purity of the product.

Dielectric permittivity measurements

The tetrameric cobalt phthalocyanine powder samples were pressed in the form of pellets of 10-mm diam and thickness ranging from 1 to 3 mm. The permittivity studies were carried out on these pellet samples using a homemade dielectric cell and an HP 4285A LCR meter in the frequency range 100 KHz to 5 MHz from

TABLE I
Elemental Analysis of Carboxyl-Terminated Cobalt Phthalocyanine Tetramer and Anhydride-Terminated Cobalt Phthalocyanine Tetramer

Molecular formula of repeat unit		Elemental analysis (wt%)			
		C	H	N	Co
Carboxyl terminated tetramer [C ₁₂₀ H ₄₀ N ₃₂ O ₃₂ Co ₄ · 8H ₂ O]	Calculated	51.0	2.0	15.88	8.35
	Observed	44.0	1.96	14.90	8.20
Anhydride terminated tetramer [C ₁₂₀ H ₂₄ N ₃₂ O ₂₄ Co ₄]	Calculated	56.89	0.95	17.69	9.30
	Observed	54.86	1.52	17.63	9.20

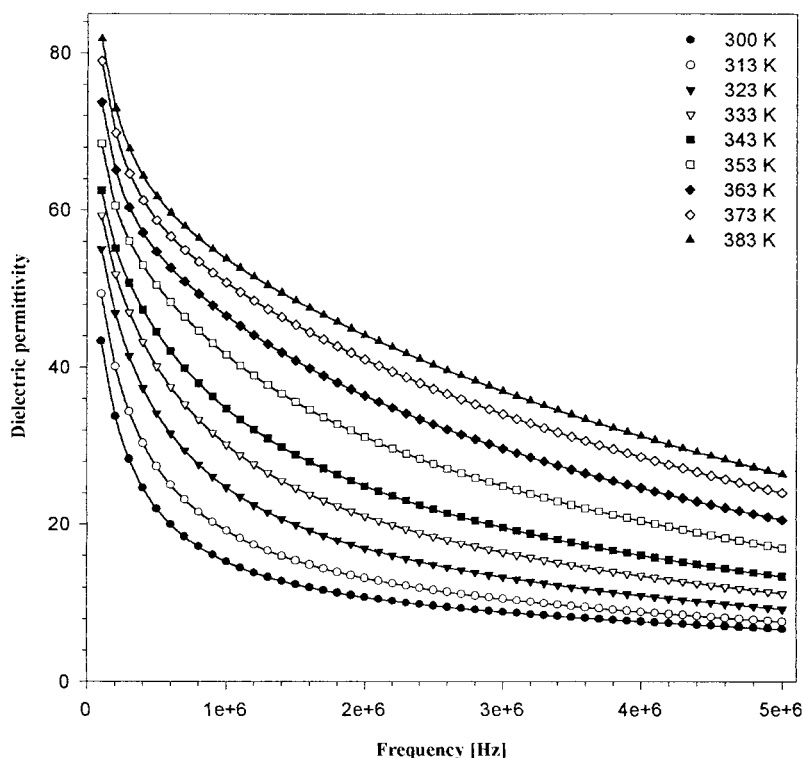


Figure 2 Dielectric permittivity of CoPc tetramer at different temperatures.

room temperature (300°K) to 383°K under dynamic vacuum (10^{-2} Torr). The cell was standardized using standard Teflon samples and the lead and fringe capacitances were estimated. The LCR meter was interfaced via a PC and the dielectric measurements were carried out by using a package based on virtual instrumentation (VI) commonly known as LabVIEW. From the measured values of dielectric permittivity and the dielectric loss factor the AC conductivity was calculated.

DC conductivity measurements

Electrical conductivity measurement was carried out on the pellets of tetrameric cobalt phthalocyanine using a Keithley 487 Picoammeter and a conductivity cell under high vacuum (10^{-5} Torr) in the temperature range 90–300°K by employing a two-probe technique.

RESULTS AND DISCUSSION

The dielectric studies of the cobalt phthalocyanine tetramer samples were calculated using the relation

$$C = \frac{\epsilon_0 \epsilon_r A}{d} \quad (1)$$

where C is the capacitance of the sample, A is the surface area of the sample, ϵ_0 is the permittivity of air, and ϵ_r is the dielectric permittivity of the sample

The characteristic dependence of dielectric permittivity ϵ with frequency for different temperatures was plotted and is shown in Figure 2. The dielectric permittivity shows a constant increase with temperature but a decrease with frequency.

Normally, metallophthalocyanine tetramers are highly conjugated and have a large planar structure. The π electrons are completely delocalized over the entire molecule. If the applied field is increased the probability of tunneling of electrons between molecules is also increased causing high dielectric permittivity and dielectric loss.¹⁴ The decrease of dielectric permittivity with increase in frequency can be explained using Koop's phenomenological theory.¹⁹ According to this theory the dielectric structure is considered as an inhomogeneous medium of two layers of Maxwell Wagner type.¹⁴

The variation of $\tan\delta$ with frequency for different temperatures is shown in Figure 3, in which $\tan\delta$ shows a loss peak characterized by a relaxation frequency for all temperatures. After the loss factor reaches maximum it decreases almost linearly at lower temperatures and there is not much variation at higher temperatures. Also from the figure it is observed that, when temperature increases, the value of maximum

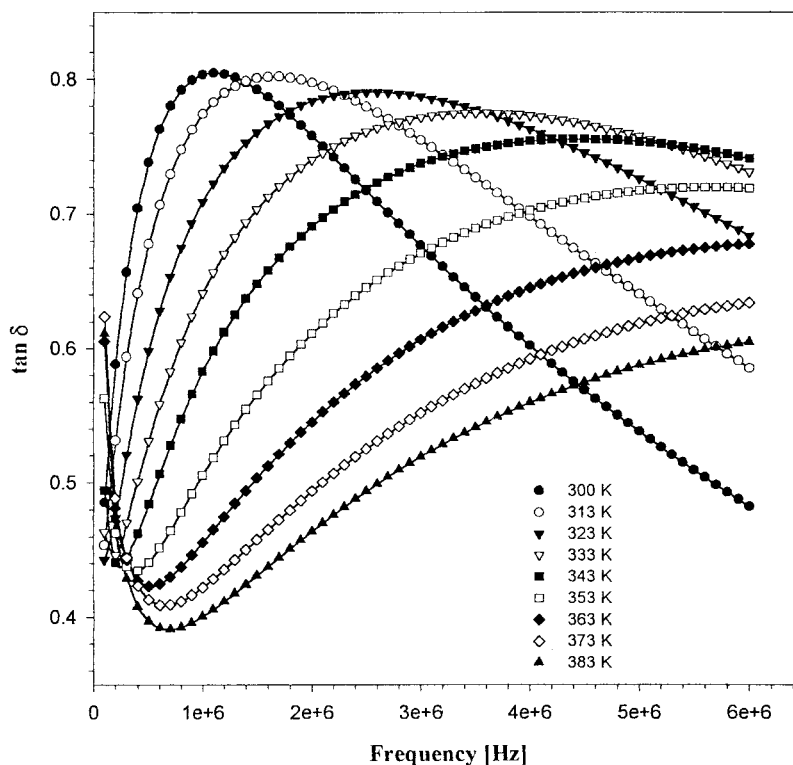


Figure 3 Dielectric loss versus frequency of CoPc tetramer at different temperatures.

dielectric loss shifts toward higher frequency. Here $\tan\delta$ depends on both frequency and temperature.

The frequency versus AC conductivity graph was plotted for different temperatures and is depicted in Figure 4. From the figure, it is seen that the value of AC conductivity does not show much variation at lower frequencies both at room temperature and at higher temperatures. That is, there is no appreciable variation of AC conductivity with temperature at lower frequencies (≈ 100 KHz); above 100 KHz it shows a rapid increase with frequency. This is in accordance with the theory of AC conduction in amorphous materials, which predicts that, for polaron transport or other hopping modes, the AC conductivity will increase monotonically with increased frequency of the applied field.²⁰ The AC conductivity, dielectric permittivity, and dielectric loss can be related by the following equation

$$\sigma_{AC} = 2\pi\epsilon_0\epsilon_r f \tan\delta \quad (2)$$

where ϵ_0 is the permittivity of air, ϵ_r is the dielectric permittivity of the sample, f is the frequency, and $\tan\delta$ is the dielectric loss.

The variation pattern of AC conductivity with frequency for different temperatures is shown in Figure 4 and indicates that the AC conductivity increases with temperature as the frequency increases. This is because, as the temperature increases, the mobility of

charge carriers also increases. When frequency increases the dielectric permittivity decreases (Fig. 2), $\tan\delta$ is also found to increase with increase of frequency. However, the rate of decrease of dielectric permittivity with frequency is lower than the rate of increase of loss factor with frequency and hence there is a net increase of AC conductivity with increase of both frequency as well as temperature.

The DC conductivity (σ_{DC}) in the region 90 to 300°K was calculated and plotted and is shown in Figure 5. Activation energy of the sample was calculated using the relation

$$\sigma_{DC} = \sigma_0 \exp(E_A/KT) \quad (3)$$

The DC conductivity of tetrameric cobalt phthalocyanine at room temperature is of the order of 10^{-3} S/cm and the activation energy is 0.12 eV. In general, in phthalocyanine the electrical conductivity is associated with mobile π electrons of the phthalocyanine ring and the conductivity is due to thermal excitation of π electrons from the highest filled to lowest empty π orbitals. This energy difference between these two levels for monomeric phthalocyanine is 1.5 to 1.7 eV.²¹ The presence of extended structure in a polymer reduces the bandgap, which governs the intrinsic electrical properties.¹² In polymeric phthalocyanine because of the extended conjugated structure the energy values are much lower as seen by our measurements.

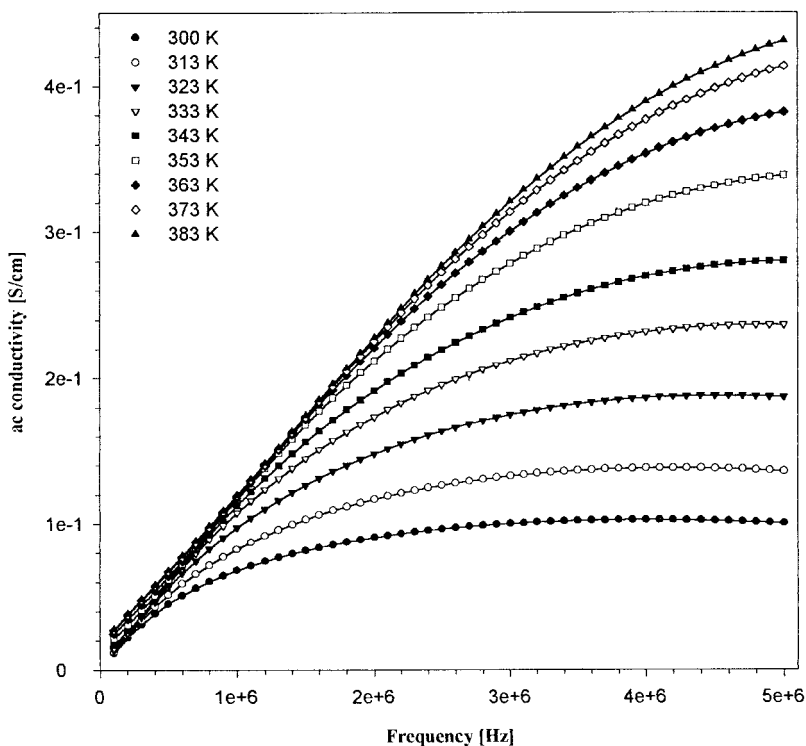


Figure 4 AC conductivity of CoPc tetramer with frequency at different temperatures.

The DC conductivity values obtained for the tetramer are $\approx 10^{-3}$ S/cm, which is much higher than that of monomeric phthalocyanine (10^{-10} S/cm). It is found

that the AC conductivity is higher than that of DC conductivity. If the charge transport is due to hopping, the AC conductivity will be higher than the DC con-

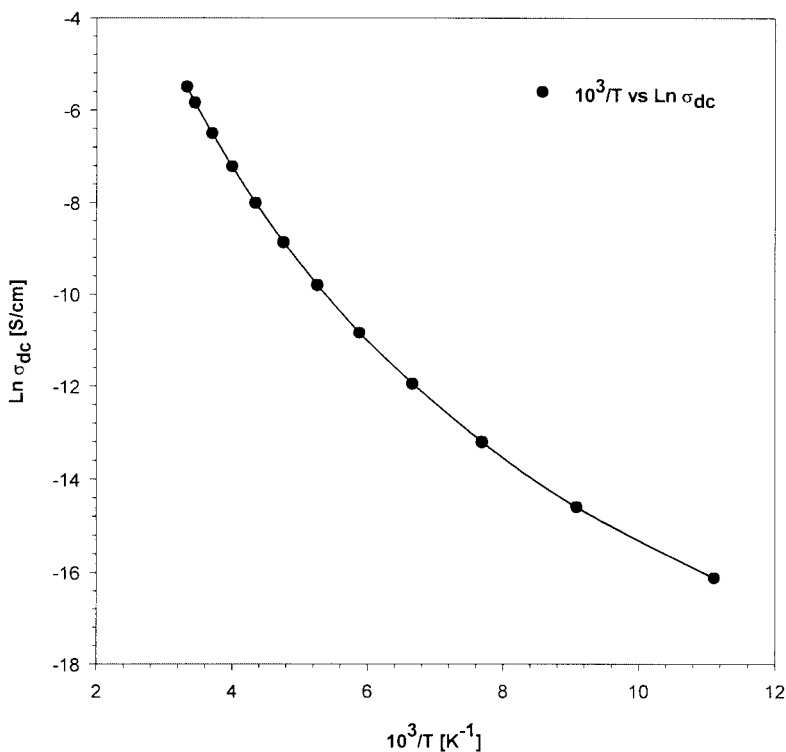


Figure 5 Temperature dependence of DC conductivity of CoPc tetramer.

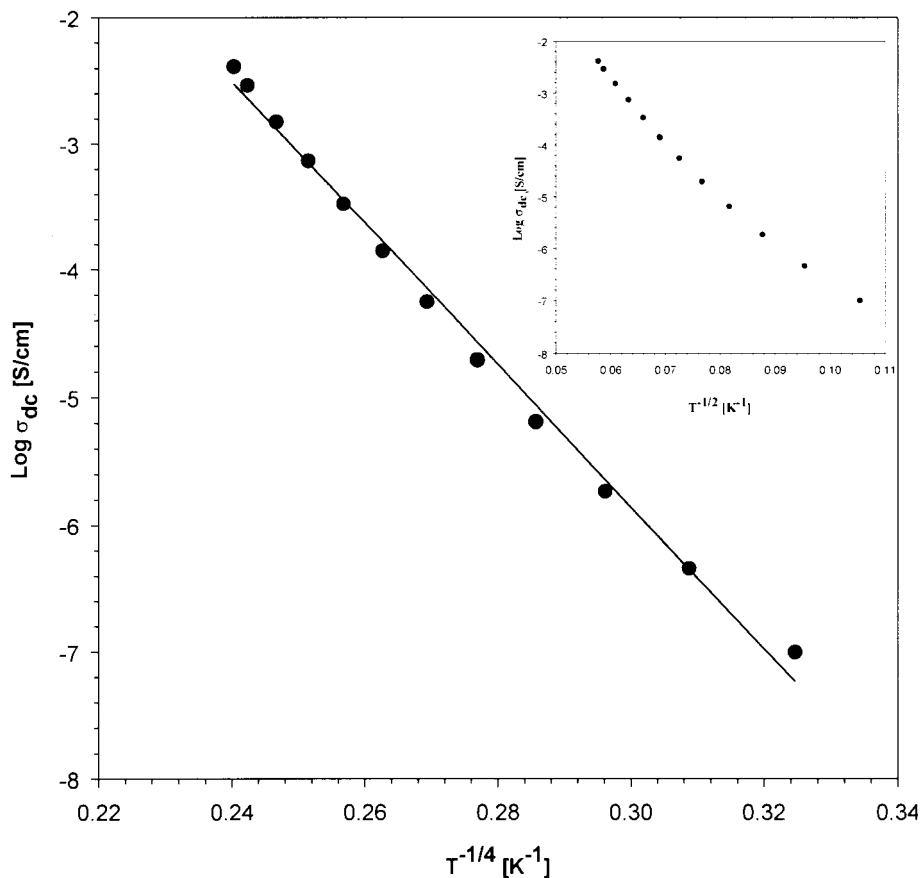


Figure 6 Plot of $\log \sigma_{DC}$ as a function of $T^{-1/4}$. (Inset) $\log \sigma_{DC}$ as a function of $T^{-1/2}$.

ductivity.²² This proves that hopping type of charge transport occurs in the tetrameric cobalt phthalocyanine. In the case of DC conduction, charge carriers have to cross the entire sample and, if the hopping sites are randomly distributed, the current path will inevitably include some long distance hops, which have a very small hopping probability. At high frequencies, hopping mainly occurs between close neighbors, because the field is reversed before the long distance hop.

To understand the conduction mechanism in these conjugated systems a Mott's variable range hopping model is used.²³ According to this model, in a disordered material when the charge carriers are localized due to random electric fields, instead of band conduction, charge transport takes place via phonon-assisted hopping between localized states. Since the localized

states have quantized energies extending over a certain range, activation energy is required for each hop.

The mechanism is based upon the idea that carriers tend to hop larger distances to sites, which lie energetically closer than to their neighbors.

According to the Mott's variable range hopping model, the DC conductivity in three dimensions can be expressed as

$$\sigma_{DC} = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right] \quad (4)$$

where T is the temperature and T_0 is the Mott's Characteristic temperature and is given by

$$T_0 = \frac{\lambda \alpha^3}{KN(E_F)} \quad (5)$$

TABLE II
Mott Temperature, Density of States at the Fermi Energy, Range of Hopping and Energy for Hopping of Tetrameric Cobalt Phthalocyanine

Sample	Mott temperature T_0 (°K)	$N(E_F)$ ($\text{cm}^{-3} \text{eV}^{-1}$)	R_{hop} (Å) (100°K)	W_{hop} (eV) (100°K)
Tetrameric cobalt phthalocyanine	9.68×10^6	2.17×10^{22}	3.20	0.15

Where $\lambda \approx 18.1$ is a dimensionless constant,²⁴ α is the inverse rate of fall of the wave function,²⁵ K is the Boltzmann constant and $N(E_F)$ is the density of states at the Fermi energy.

The range of hopping R ²⁶ and the energy for hopping W in three-dimensional variable range hopping are expressed as

$$R = \left[\frac{9}{8} \pi \alpha K T N(E_F) \right]^{\frac{1}{4}} \quad (6)$$

and

$$W = K(T_0 T^3)^{\frac{1}{4}} \quad (7)$$

Log σ versus $T^{-1/4}$ gives best fit as seen in Figure 6. Figure 6, inset, indicates that Log σ versus $T^{-1/2}$ does not result in a perfect fit. The value of Mott's Characteristic temperature T_0 has been calculated from the graph log σ versus $T^{-1/4}$ (Figure 6) and is found to be 9.68×10^6 K. From Equations (5–7) the value of $N(E_F)$, R , and W were calculated at 100°K and the values cited (Table II) are estimated after assuming a reasonable value for $\alpha = 1 \text{ \AA}$. Table II depicts the Mott temperature and its parameters for tetrameric cobalt phthalocyanine. Low values obtained for the mobility indicates that the electronic states are localized, in accordance with the hopping mechanism.

The temperature dependence of DC conductivity has been studied and is found to follow the three-dimensional variable range hopping. From the above discussions it is seen that the best fit to the DC conductivity can be achieved with a $T^{-1/4}$ behavior and the values of T_0 , $N(E_F)$, R , and W can be found by assuming that the conduction is three dimensional and follows the variable range hopping model. To enhance the conductivity of phthalocyanine, they can be modified either by thermal or chemical treatment.^{27,28}

CONCLUSION

The variation of dielectric permittivity of tetrameric cobalt phthalocyanine with temperature and frequency has been studied and it is found that the dielectric permittivity values increase from 43 to 81 at 100 KHz in the temperature range of 300 to 383°K. But the dielectric permittivity decreases when frequency increases from 100 KHz to 5 MHz and the values remain constant at very high frequencies. The activation energy for electrical conductivity is found to be 0.12 eV and the conduction behavior is found to fit the three-dimensional variable range hopping model with

the values of 9.687×10^6 K, $2.168 \times 10^{22} \text{ cm}^{-3} \text{ eV}^{-1}$, 3.20 \AA , and 0.15 eV for Mott temperature T_0 , density of states at the Fermi energy $N(E_F)$, range of hopping R , and hopping energy W at 100°K, respectively.

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