AC Conductivity and Dielectric Measurements of Bulk Cobalt Phthalocyanine (CoPc)

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Abstract: Cobalt phthalocyanine (CoPc) was prepared as a compressed pellet with evaporated ohmic gold (Au) electrodes. AC conductivity and dielectric measurements were performed as a function of both frequency (10^2 – 10^6 Hz) and temperature (298 – 407 K). The ac conductivity showed ω^s dependence, where ω is the angular frequency and s is a frequency exponent. The behaviour of ac conductivity was interpreted by the correlated barrier hopping (CBH) model. Dielectric constant and dielectric loss were found to decrease by increasing frequency and increase by increasing temperature.

Key words: Cobalt phthalocyanine (CoPc), AC conductivity, dielectric properties.

INTRODUCTION

Organic semiconductors have become very attractive to replace inorganic semiconductors in the development of lightweights and inexpensive light-electricity conversion devices (Saad, E.A.I., 2005). It has many applications in organic devices, such as organic light emitting diodes (Blochwitz, J. et al., 1998 and Liew, Y.F. et al., 2004), rectifiers (Anderson, T.L. et al., 1993), organic switches (Xue, J. et al., 2003) and memory devices (Tondelier, D. et al., 2004 and Park, Y.G. et al., 2002). Phthalocyanines are large macrocyclic molecules with applications in the fields of conductive polymers, chemical sensors, electrochromism, etc., due to their low cost facilenes of large-scale preparation, as well as chemical and thermal stability (Chen, P.Y. et al., 2001). Therefore, the study of these compounds is very essential to understand the behavior of their electronic physical properties under various conditions such as changes in temperature, pressure, frequency, ambient gases, etc. (El-Nahass, M.M. et al., 2003). Such understanding is essential for improving the quality and performance of electronic devices. Electrical impedance analysis has proved to be a powerful technique for identifying and characterizing the charge transport phenomenon in various materials (Anthopoulos, T.D. et al., 2003). AC measurements yield information which can be used to determine whether the intrinsic conduction process can be described by the hopping model or band theory, under particular operating conditions (Azim-araghi, M.E. et al., 1996). In short both dielectric and ac conductivity phenomena yields information about the mechanism of conduction (Kalugasalam, P. et al., 2009).

The aim of the present work is to study the ac conductivity and dielectric behaviour of cobalt phthalocyanine (CoPc) in bulk form over the frequency range of 10^2-10^6 Hz and temperature range of 298–407 K.

Experimental Procedure:

The powder of cobalt phthalocyanine (CoPc) was obtained from Kodak Company, UK. It was thoroughly grounded in a mortar to obtain very fine particles, and then it was compressed under a pressure of about 2×10^7 N/m^2 in the form of a compressed pellet. The resulting pellet has a thickness, d, of 0.95 × 10^-3 m and a diameter of 1.1×10^-2 m. Then, the pellet was coated with an evaporated gold film (Au) to serve as ohmic electrodes. The impedance, Z, capacitance, C, and the phase angle, φ were measured directly by a programmable automatic RLC bridge (model Hioki 3532 Hitester) over the frequency range 10^2-10^6 Hz. The temperature of the pellet was measured using a thermocouple over the temperature range 298 – 407 K. AC conductivity σ_{ac}(ω) of CoPc pellet is determined using the following relation:

σ_{ac}(ω) = σ_{dc} + σ_{ac}(ω) \tag{1}

RESULT AND DISCUSSION

AC Conductivity:

Frequency Dependence:

It is well established that the dependence of conductivity, \(σ_{ac}(ω)\), on the angular frequency, \(ω=2πf\), for many materials including glasses, organic, polymer and crystal materials, takes the following form:

\[σ_{ac}(ω) = σ_{dc} + \sigma_{ac}(ω)\]
where \( \sigma_{dc} \) is the dc conductivity and is supposed to be independent on frequency. While the ac conductivity, \( \sigma_{ac}(\omega) \), is frequency dependent. The variation of \( \sigma_{ac}(\omega) \) as a function of frequency at different temperatures for the compressed pellet is shown in Fig. 1. The ac conductivity can be determined by subtracting the dc conductivity values, which obtained from extrapolating the experimental data of the total conductivity at low frequencies up to zero frequency at each temperature, from the values of the total conductivity according to Eq. 1. Figure 2 shows the frequency dependence of \( \sigma_{ac}(\omega) \) of CoPc at various temperatures. As observed from the figure, that \( \sigma_{ac}(\omega) \) increases by increasing the frequency. The dependence of \( \sigma_{ac}(\omega) \) on frequency can be expressed by the following relation (Ghosh, A., 1990 and Elliott, S.R., 1977):

\[
\sigma_{ac} = A \omega^s
\]  

(2)

Fig. 1: Frequency dependence of \( \sigma_{tot}(\omega) \) for CoPc at different temperatures.

where \( A \) is a constant depend on temperature and \( (s) \) is the frequency exponent. The values of frequency exponent \( (s) \) were determined from the slope of the linear parts in Fig. 2 for different temperatures and were listed in Table 1. From such table, the calculated values of \( s \) showed a decrease with the increase in temperature. This behaviour is associated with a hopping process for the charge carriers between localized sites separated by barrier height (Yaghmour, S.J., 2010). So, the frequency dependence of \( \sigma_{ac}(\omega) \) can be explained in terms of correlated barrier hopping (CBH) model and it is given by the following expression (Farid, A.M. et al., 2002):

\[
\sigma_{ac}(\omega) = (\pi N^2 \epsilon^*/24) (8e^2\epsilon^*/W_{0d})^6 (\omega^s/\tau^6)
\]  

(3)

Fig. 2: Frequency dependence of \( \sigma_{ac}(\omega) \) for CoPc at different temperatures.

<table>
<thead>
<tr>
<th>( T (K) )</th>
<th>( S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.947</td>
</tr>
<tr>
<td>328</td>
<td>0.876</td>
</tr>
<tr>
<td>357</td>
<td>0.859</td>
</tr>
<tr>
<td>365</td>
<td>0.822</td>
</tr>
<tr>
<td>395</td>
<td>0.777</td>
</tr>
<tr>
<td>407</td>
<td>0.762</td>
</tr>
</tbody>
</table>
where \( N \) is the density of localized states, \( \varepsilon \) is the permittivity of material, \( e \) is the electronic charge, \( W_M \) is the maximum barrier height of the material under investigation, \( \tau \) is the effective relaxation time and the exponent \( s \) is related to \( W_M \) at low temperature by the relation:

\[
s = 1 - \beta = 1 - (6k_B T/W_M)
\]  

(4)

where \( k_B \) is Boltzmann’s constant.

**Temperature Dependence:**

The temperature dependence of \( \sigma_{ac} \) for CoPc pellet is shown in Fig. 3 for different frequencies. It is clear from the figure that \( \sigma_{ac}(\omega) \) decreases linearly with the reciprocal of temperature. This suggested that \( \sigma_{ac}(\omega) \) is a thermally activated process from different localized states in the gap (Farid A.M. et al. 2002). The ac conductivity as a function of temperature at constant frequency expressed as (El-Shabasy, M. et al., 1996):

\[
\sigma_{ac} = \sigma_0 \exp (-\Delta E_{ac}/k_B T)
\]  

(5)

Fig. 3: Temperature dependence of \( \sigma_{ac}(\omega) \) for CoPc at different frequencies.

where \( \sigma_0 \) is a constant and \( \Delta E_{ac} \) is the activation energy for conduction. The activation energy for conduction was calculated for different frequencies and listed in Table 2. It can be seen that \( \Delta E_{ac} \) tends to decrease with the increase in frequency. Such behaviour can be attributed to the contribution of the frequency of the applied field to the conduction mechanism, which confirms the hopping conduction to the dominant mechanism (Farid, A.M. et al., 2002).

<table>
<thead>
<tr>
<th>( f ) (KHz)</th>
<th>( \Delta E_{ac} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.165</td>
</tr>
<tr>
<td>1</td>
<td>0.154</td>
</tr>
<tr>
<td>8</td>
<td>0.142</td>
</tr>
<tr>
<td>50</td>
<td>0.132</td>
</tr>
<tr>
<td>100</td>
<td>0.113</td>
</tr>
<tr>
<td>500</td>
<td>0.087</td>
</tr>
</tbody>
</table>

Table 2: Values of \( \Delta E_{ac} \) at different frequencies.

**Dielectric Properties:**

**Dielectric Constants:**

Many dielectric functions, as the complex dielectric constant, \( \varepsilon^* \), have been used to described the frequency-dependent properties of materials. This function can \( e \) expressed as (Cao, W. et al., 1990 and Jonscher, A.K., 1983):

\[
\varepsilon^* = \varepsilon' - i \varepsilon''
\]  

(6)

where \( i = \sqrt{-1} \), \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the complex dielectric constant, respectively. Fig. (4 and 5) show the frequency dependence of the dielectric constant, \( \varepsilon' \), and the dielectric loss, \( \varepsilon'' \), of CoPc pellet at different temperatures. Both of \( \varepsilon' \) and \( \varepsilon'' \) decrease by increasing frequency and increase by increasing temperature. At low frequencies and high temperatures, the rate of decreasing of both \( \varepsilon' \) and \( \varepsilon'' \) as compared with that at higher frequency.
Electric Modulus:

Electrical modulus formalism has been introduced due to its special advantage of suppressing the electrode polarization effects (Ponpandian, N. et al., 2002). The complex electric modulus (M*) is derived from the complex permittivity, according to the relationship

$$ M^* = \frac{1}{\varepsilon^*} = M' + i M'' $$

The real and imaginary parts of the electric modulus (M' and M'', respectively) can be calculated from $\varepsilon'$ and $\varepsilon''$ as follows (Ram, M.K. et al., 1998):

$$ M' = \varepsilon'/[(\varepsilon')^2 + (\varepsilon'')^2], \quad M'' = \varepsilon''/[(\varepsilon')^2 + (\varepsilon'')^2] $$

The modulus representations of dielectric process give some idea of relation of dipoles that exists in different environments, independent of the strong effect of dc conductivity, which often mask the actual dielectric relaxation processes, actives in this type of system (Soares, B.G. et al., 2006). The frequency dependence of M' and M'' are shown in Figs. 6 and 7 at different temperatures, respectively. M' shows an increase with the increase in frequency at constant temperature and a decrease with the increase in temperature at constant frequency. M'' exhibits peaks for various temperatures, where the peak position is shifted towards higher frequencies with the increase in temperature. The presence of such relaxation peaks in the M'' plots indicate that the sample under investigation is ionic conductor (Khiar, A.S.A. et al., 2006). The position of the characteristic relaxation frequency, $\omega_m$, in plots of M'' depends upon the conductivity relaxation time, $\tau_m = \omega_m^{-1}$. Thus the temperature dependence of the characteristic relaxation time can be estimated from plots of $\ln\omega_m$ vs 1000/T as shown in Fig.8, which satisfies Arrhenius law ($\omega = \omega_0 \exp(-E_\omega/k_BT)$). The value of the activation energy of the relaxation processes, $E_\omega$, is found to be 0.019 eV.
Fig. 6: Frequency dependence of real electric modulus, $M'$, for CoPc at different temperatures.

Fig. 7: Frequency dependence of imaginary electric modulus, $M''$, for CoPc at different temperatures.

Fig. 8: Plot of $\ln \omega_m$ verse $1000/T$ for CoPc.

**Conclusion:**

AC conductivity, $\sigma_{ac}(\omega)$, of CoPc in bulk form was found to vary as $\omega^s$ in the frequency range of $10^2$-$5\times10^5$ Hz. The behaviour of $\sigma_{ac}(\omega)$ was interpreted by the correlated barrier hopping (CBH) model. The temperature dependence of $\sigma_{ac}(\omega)$ showed a linear dependence. The calculated ac activation energy was found to decrease by increasing frequency. Both of dielectric constants, $\varepsilon'$, and dielectric loss, $\varepsilon''$, were found to decrease by increasing frequency at constant temperature and increase by increasing temperature at constant frequency. Studies of frequency dependence of electric modulus formalism showed that the imaginary parts of the electric modulus, $M''$, exhibits peaks for various temperatures. The temperature dependence of the characteristic relaxation time can be estimated from Arrhenius law.

**REFERENCES**


