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AC conductivity and dielectric measurements of bulk magnesium phthalocyanine (MgPc)

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ABSTRACT

The AC conductivity, $\sigma_{ac}(\omega)$ for bulk magnesium phthalocyanine (MgPc) in the form of compressed pellet in the frequency range of 1–500 kHz and in a temperature range of 303–443 K with evaporated ohmic Au electrodes have been investigated. The frequency dependence of the impedance spectra plotted in the complex plane shows semicircles. The Cole–Cole diagrams have been used to determine the DC conductivity. The AC conductivity, $\sigma_{ac}(\omega)$, is found to vary as ω^s in the frequency range of 1–500 kHz. At high range of frequency, $s < 1$ and it decreases with increasing the temperature. The variation of s with temperature suggests that the AC conduction is due to the correlated barrier hopping (CBH). The dielectric constant, ε', and dielectric loss, ε'', for bulk MgPc were decreased with increasing frequency and increased with increasing temperature.

1. Introduction

Organic semiconductors are of steadily growing interest as active components in electronics and optoelectronics. Due to their flexibility, low cost and ease of production they represent a valid alternative to conventional inorganic semiconductor technology in a number of applications, such as flat panel displays and illumination, plastic integrated circuits and solar energy conversion although first commercial applications of this technology are being realized nowadays, there still the need for a deeper scientific understanding in order to achieve optimum device performance [1].

Phthalocyanines represent a large family of heterocyclic conjugated molecules with high chemical stability. The study of these compounds is very essential to understand the behaviour of their electronic physical properties under various conditions: such as changes in temperature, pressure, frequency, ambient gases, etc. [2]. The electronic properties of metal phthalocyanine compounds (MPc's) have received increasing attention because of their importance as prototype semiconductors and their uses in technological applications such as generate various types of switching devices [3]. MPc's although there is evidence that they may exhibit suitable properties for numerous applications [4].

Dielectric relaxation studies are important to understand the nature and the origin of dielectric losses, which, in turn, may be useful in the determination of structure and defects in solids. The magnitude of geometric and measured capacitance may differ if the electric field at the metal insulator interface varies with the insulator over the region. AC conductivity and dielectric measurements of metal phthalocyanine were the subject of several investigations in the last decades [5–11]. The data were analyzed within the frame of the 'universal' power law $\sigma \propto \omega^s$.

In the present work, AC conductivity, dielectric constant and dielectric loss measurements were performed for MgPc in bulk form. The temperature and frequency dependence of the electrical conductivity, the dielectric constants for MgPc were investigated and the results were analyzed to determine some related parameters and to suggest predict the operating electronic conduction mechanisms.

2. Experimental techniques

The powder of magnesium phthalocyanine (MgPc) 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 $\sim 1.96 \times 10^8$ N/m^2 in the form of a pellet 1.1×10^{-2} m diameter and thickness of 0.71×10^{-3} m. MgPc pellet was sandwiched between two evaporated Au film electrodes to be ohmic contacts to the sample [12]. The electrical contacts were equipped with copper wires, which applied to the metal electrodes of the pellet by using conductive silver past.

A programmable automatic RLC bridge, model Hioki 3532 Hitester, was used for the AC measurements. The sample was placed in a holder specially designed to minimize stray capacitance. The range of frequencies was 1–500 kHz. The temperature of the sample was measured by a thermocouple over a temperature range 303–443 K. For the sample under investigation, the impedance, Z, the capacitance, C, and the phase angle, φ, were measured. The total conductivity $\sigma_t(\omega)$ was calculated from the following equation: $\sigma_t(\omega) = d/ZA_0$, where d is the thickness of the sample and A_0 is the cross-sectional area. The AC conductivity $\sigma_{ac}(\omega)$ was calculated by using the relation: $\sigma_t(\omega) = \sigma_{ac}(\omega) + \sigma_{dc}$. The dielectric constant, ε_1, was calculated from the equation: $\varepsilon' = dC/A_0\varepsilon_0$, where ε_0 is the permittivity of free space. The dielectric loss, ε'', was calculated from the equation: $\varepsilon'' = \varepsilon' \tan\delta$, where $\delta = 90 - \varphi$.

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3. Results and discussion

Analysis of dielectric properties as functions of frequency is generally known as impedance spectroscopy, and dielectric relaxation spectroscopy or, more appropriately, AC spectroscopy.

Certain dielectric quantities or functions are employed more often than others depending on the particular field of application. The complex dielectric constant ε^* complex impedance Z^*, and complex conductivity σ^* which are used to calculate the corresponding time constants for the relaxation models of Cole–Cole and ideal conduction, and the dissipation factor or loss tangent, $\tan\delta$, is often used to characterize the dielectric loss of a material, which is given by [13]

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{Z'}{Z''} \tag{1}$$

where ε' and Z' are the real parts of the dielectric constant and impedance, respectively, and ε'', Z'' are the imaginary parts.

The functions used to describe the frequency-dependent properties of material can be expressed in terms of ε^* as [14]

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \tag{2}$$

and

$$Z^* = Z' - iZ'' = \frac{1}{i\omega C_0 \varepsilon^*} \tag{3}$$

$$Z' = Z\cos\varphi \quad \text{and} \quad Z'' = Z\sin\varphi$$

where $i = \sqrt{-1}$, and the geometrical capacitance C_0 for a disc area A_0, and thickness d is given in terms of the vacuum permittivity ε_0, by the relation

$$C_0 = \frac{\varepsilon_0 A_0}{d}. \tag{4}$$

Fig. 1 shows the relation between the imaginary part of the electrical impedance Z'' and its real part Z' as simply various temperatures. The complex impedance spectra of MgPc related to the frequency of the applied sinusoidal voltage for different temperatures in the range 303–443 K.

Since the Au electrodes are ohmic contact they do not give rise to Schottky barrier and are thus represented in the model by a small series resistance, r. The dielectric layer is represented by a frequency-independent capacitive element C' in parallel with a temperature-dependent resistive element R; and this leads to the establishment of the relations [15]

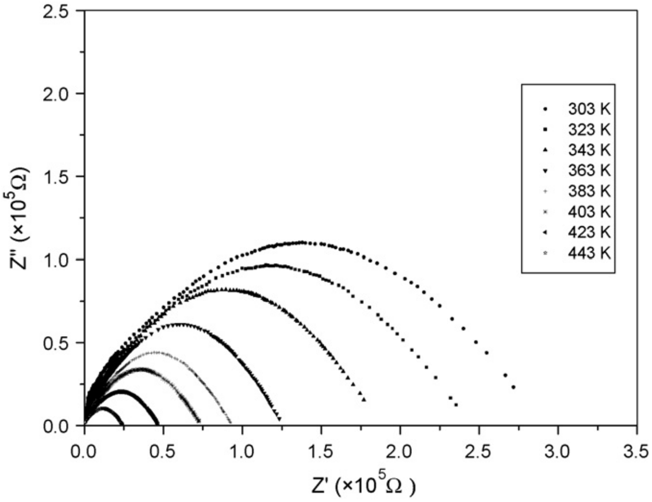

Fig. 1. Complex impedance spectra of MgPc for a range of temperatures.

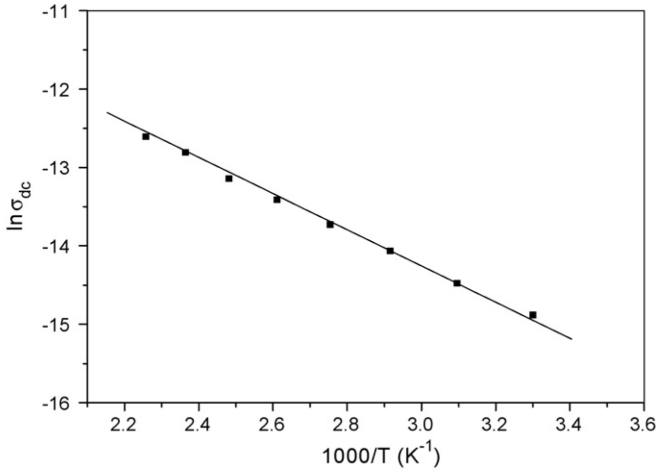

Fig. 2. Temperature dependence of DC conductivity of MgPc.

$$Z' = r + \frac{R}{1 + \omega^2 C'^2 R^2} \tag{5}$$

$$Z'' = \frac{i\omega C' R}{1 + \omega^2 C'^2 R^2} \tag{6}$$

It is clear that Z' depends on the applied frequency and its equal to $(r + R)$ at zero frequency (DC) and only on (r) at higher frequencies.

The temperature dependence of the model can be considered represented via a thermally activated process, following the formula:

$$R = R_0 \exp\left(\frac{\Delta E}{kT}\right) \tag{7}$$

where R_0 is a constant and ΔE is the activation energy.

The resistance R could be obtained from the intersection of the low-frequency semicircles with the Z'-axis. The calculated value could be employed to shed light on the variation of the DC conductivity σ_{dc} of MgPc with temperature. Fig. 2 shows a plot of $\ln\sigma_{dc}$ versus $1/T$ the slope of this curve gives $\Delta E = 0.20 \pm 0.01$ eV, while the intercept gives $\sigma_0 = 6.57 \times 10^{-4}$ S m^{-1}.

The experimental data can be analyzed using the following relation [16]:

$$\sigma = \sigma_{00} \exp\left(-\frac{T_0}{T}\right)^{1/4}, \tag{8}$$

where T_0 is the characteristic temperature ($T_0 = 2.1[\alpha^3/k_B N(E_F)]^{1/4}$). The corresponding T_0 has been evaluated from the straight line relating slope of $\ln(\sigma_{dc} T^{(1/2)})$ with $T^{(-1/4)}$ given in Fig. 3. The value of T_0 was found to be 1.71×10^8 K. In addition, the density of localized states at Fermi level, $N(E_F)$, calculated by taking a constant value of the exponential decay parameter of localized states wave functions, α^{-1} (10^{-7} cm) in the relation and found to be 1.32×10^{18} eV^{-1} cm^{-3}.

Fig. 4 shows the AC conductivity $\sigma_{ac}(\omega)$ as a function of reciprocal temperature at different frequencies. From the figure, $\sigma_{ac}(\omega)$ increases linearly by increasing temperature. This indicates that the AC conductivity which asiginates from different localized states in the gap [17] is a thermally activated process. The temperature dependence of $\sigma_{ac}(\omega)$ is represented by

$$\sigma_{ac}(\omega) = \sigma_0' \exp\left(-\frac{\Delta E_{ac}}{kT}\right), \tag{9}$$

where σ_0' is a constant and ΔE_{ac} is the activation energy for conduction. The obtained values of the AC activation energy for different frequencies are almost between 0.16 eV at 1 kHz and 0.06 eV at 500 kHz.

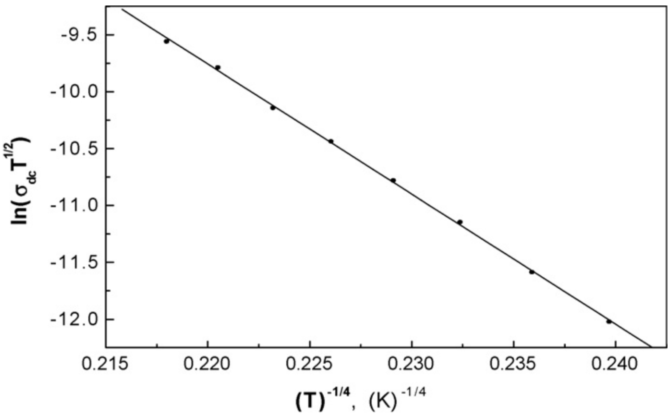

Fig. 3. plots of $\ln(\sigma_{dc}T^{(1/2)})$ versus $T^{(-1/4)}$ for MgPc.

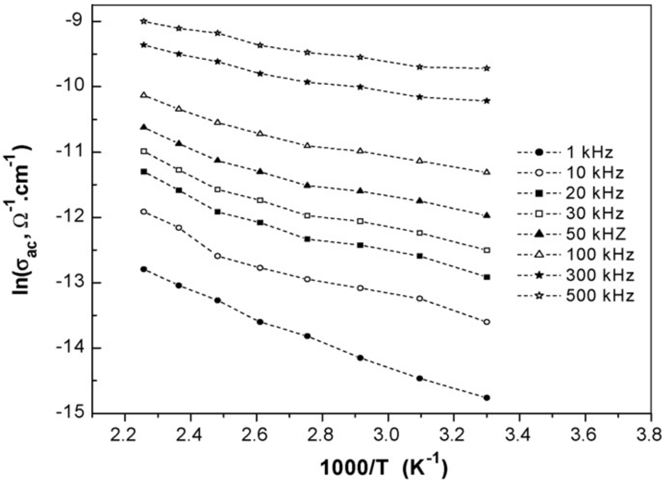

Fig. 4. Variation of AC conductivity, $\sigma_{ac}(\omega)$, with temperature at different frequencies for MgPc.

Fig. 5 shows the dependence of AC conductivity, σ_{ac}, on frequency, ω (1–500 kHz) at different temperatures in the range of 303–443 K. It is clear from this figure that σ_{ac} increases with increasing frequency. A similar behaviour has been observed in H_2Pc [2] and CuPc [18] thin films.

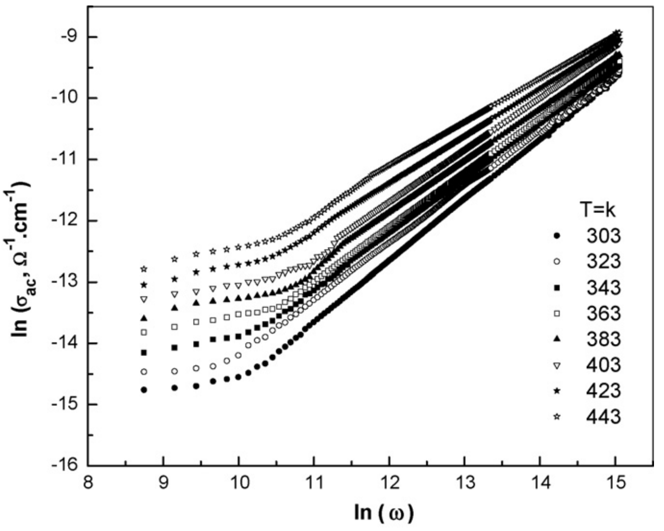

Fig. 5. Frequency dependence of AC conductivity $\sigma_{ac}(\omega)$ of MgPc at various temperatures.

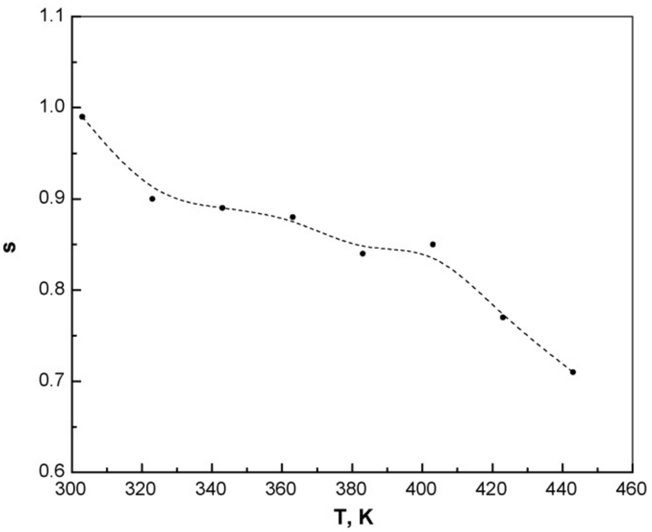

Fig. 6. Variation of the exponent *s* with temperature.

The conductivity obeys the power law [19]

$$\sigma_{ac}(\omega) = A\omega^{s} \tag{10}$$

where *A* is a constant independent on temperature, ω the angular frequency, $\omega = 2\pi f$, and *s* is the frequency exponent.

The frequency exponent, *s*, can be calculated from the slope of the straight lines in Fig. 5. At high frequencies the exponent *s* decreases from 0.99 at 300 K to 0.71 at 443 K as shown in Fig. 6.

The temperature dependence of *s* seems to be very complex so the various theoretical models [20–22] for AC conductivity were suggested to explain the experimental observations of complex systems.

It was found that the appropriate theoretical model, which can describe the function $\sigma_{ac}(\omega)$ in the present work is the correlated barrier hopping (CBH) model [21], in which the charge carrier hops to the equivalent sites over the potential barrier separating them. The inclusion of Coulomb interaction between the individual barriers reduces the barrier height.

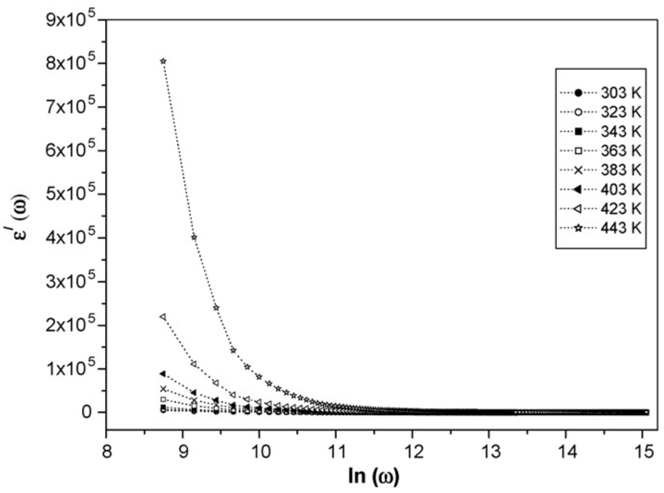

Fig. 7. Variation of the dielectric constant $\varepsilon'(\omega)$ with frequencies at different temperatures for MgPc.

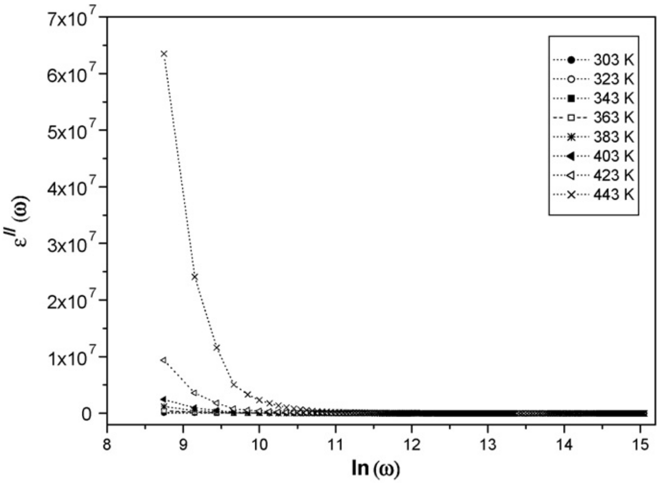

Fig. 8. Variation of the dielectric loss $\varepsilon''(\omega)$ with frequencies at different temperatures for MgPc.

The $\sigma_{\rm ac}(\omega, T)$ conductivity in the CBH model to a first approximation it taken as [21]:

$$\sigma_{\rm ac}(\omega, T) = \frac{\pi^2[N(E_{\rm F})]^2\varepsilon}{24}\left(\frac{8e^2}{\varepsilon W_{\rm M}}\right)^6 \frac{\omega^s}{\tau_0^{1-s}}, \tag{11}$$

where ε is the dielectric constant of the investigated material, e the electronic charge and τ_0 is the effective relaxation time. According to Ref. [21], τ_0 is expected to have a value of the order of an inverse phonon frequency (=10^{-13} s) and, $W_{\rm M}$ is the maximum barrier height over which the electrons hops. Generally, the experimental value of $W_{\rm M}$ is equal or less than $E_{\rm g}$ of the material of the investigated film depending on its structure parameters average grain size and orientation, defect distribution, phase content, and charge density. None of these factors was entered into the CBH model derived originally for uniform homogeneous non-crystalline insulators. Therefore, the experimental value of s can be any value <1 [23]. The importance of frequency-dependent loss measurements in illuminating the physics of amorphous semiconductors arises because the AC conductivity is often dominated by electron states deep within the energy gap, in the region of the Fermi level. The frequency dependence of the dielectric constant $\varepsilon'(\omega)$ is plotted at different temperature is shown in Fig. 7. It is clear from this figure that $\varepsilon'(\omega)$ remains almost constant with temperature till 360 K then it increases by increasing temperature; the rate of increase being different at different frequencies. The increase is higher at lower frequencies, therefore, $\varepsilon'(\omega)$ exhibit strong temperature dependence at higher temperature and lower frequencies.

The observed behaviour revealed that the MgPc exists in the form of molecular dipoles which remain frozen at low temperature (cannot be oriented), while at high temperature the dipoles can rotate freely as suggested by Srivastava et al. [24], and increase the orientation polarization and hence increase $\varepsilon'(\omega)$. It is clear from this figure that $\varepsilon'(\omega)$ decreases by increasing frequency at higher temperature, this variation is small at lower temperatures. The decrease of $\varepsilon'(\omega)$ with frequency can be explained as follows; at low frequencies the dielectric constant $\varepsilon'(\omega)$ for polar material is due to the contribution of multi-component of polarizability, deformational polarization (electronic and ionic polarization) and relaxation polarization (orientational and interfacial polarization) [25]. When the frequency is increased, the dipoles will no longer be able to rotate sufficiently rapidly, so that their oscillations begin to lag behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation polarization stopped, so $\varepsilon'(\omega)$ decreases at higher frequencies approaching a constant value due to the interfacial or space charge polarization only.

The frequency dependence of the dielectric constant $\varepsilon''(\omega)$ is plotted at different temperatures is shown in Fig. 8. It is observed from the figure that $\varepsilon''(\omega)$ is found to decrease by increasing frequency and remains almost constant by increasing temperature till 360 K then it increases with increasing temperature; the rate of increase being different at different frequencies. The increase is higher at lower frequencies, therefore, $\varepsilon''(\omega)$ exhibit strong temperature dependence at higher temperatures and lower frequencies. As the temperature increases, the electrical conduction losses increase which increases the value of the dielectric loss $\varepsilon''(\omega)$.

4. Conclusion

AC conductivity $\sigma_{\rm ac}(\omega)$of bulk MgPc, with evaporated ohmic Au electrodes was measured as a function of frequency and temperature. The Cole–Cole diagrams were used to determine the DC conductivity which was explained according to the VRH mechanism. The AC conductivity $\sigma_{\rm ac}(\omega)$ was found to vary with ω^s in the frequency range of 1–500 kHz. At high range of frequencies the frequency exponent, s, was ∼ equal to unity and decreased with increasing temperature indicating that conduction is due to the correlated barrier hopping (CBH) mechanism. The temperature dependence of $\sigma_{\rm ac}(\omega)$ showed a linear increase by increasing temperature. The calculated AC activation energy was found to decrease by increasing frequency. This may be indicated that the AC conductivity is a thermally activated process from different localized states in the gap. The dielectric constant, ε' was found to decrease by increasing frequency and increase with increasing temperature. The dielectric loss, ε'', was also found to be decreased by increasing frequency and increase by increasing temperature. Also, such behaviour revealed that the bulk MgPc sample exists in the form of molecular dipoles.

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