

EFFECT OF PHASE CHANGE ON DIELECTRIC PROPERTIES OF ZINC PHTHALOCYANINE THIN FILMS

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The dielectric constant ϵ' , and dielectric loss ϵ'' , of zinc phthalocyanine (ZnPc) thin films, are investigated in the frequency range 1–100 kHz and within the temperature range 293 – 415 K. Both the dielectric constant ϵ' and dielectric loss ϵ'' were found to increase with temperature and decrease with frequency. The Cole – Cole plots have been used to determine the molecular relaxation time τ . Results reveal that the temperature-dependence of τ is a thermally activated process. The optical dielectric constant ϵ'_{∞} was found to increase with temperature. The frequency dependence of the impedance spectra plotted in the complex plane shows semicircles. The system could be represented by an equivalent circuit of a bulk resistance in series with a parallel surface resistance-capacitance combination. Transition in ZnPc films from the α -phase to the β -phase has been observed at ~ 390 K, in molecular relaxation time τ , optical dielectric constant ϵ'_{∞} , and dc conductivity σ_{dc} .

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1. Introduction

Organic semiconductors have recently become very attractive to replace inorganic semiconductors in the development of large area, lightweight, and inexpensive light-electricity conversion devices. It has many applications in organic devices, such as organic light emitting diodes (OLED) [1-3], rectifiers [4,5], organic switches [6], and memory devices [7,8]. Particular interest has been paid in phthalocyanine compounds, on account of their ease of preparation, thermal and chemical stability, electrical, and optical properties [9]. Phthalocyanines are commonly used or proposed for a variety of organic electronic devices like photovoltaic cells [10-14], image pick-up tubes [15], gas sensors [16-18], and transistors [19,20].

The AC analysis technique has been widely used, since the early days of Cole and Cole [21], to study the dielectric behavior of crystalline, polycrystalline, and amorphous materials [22,23]. On using the frequency-dependent measurements, the contributions of the bulk material, the grain-boundaries, and electrode effects can easily be separated if their time constants are different enough to allow separation [24].

On using the AC analysis technique, the dielectric relaxation which is due to a number of different polarization mechanisms could be observed [25]. The presence of any dielectric relaxation then corresponds to one or more of the possible polarization mechanisms that occur on a microscopic scale. Each relaxation process may be characterized by a relaxation time which describes the decay with time of its polarization in a periodic field. On the other hand, certain dielectric quantities are employed more often than others, depending on the particular field of application.

In the present work, we report our investigations on the dielectric properties of zinc phthalocyanine (ZnPc) thin films. The dielectric measurements have been performed using the Cole – Cole plots [21] in the frequency and temperature ranges 1-100 kHz and 293 – 415 K, respectively.

2. Experimental procedure

Zinc phthalocyanine (ZnPc) powder, from Fluka AG Chemische Fabrik CH. 9470 Buchs, Switzerland, had been used to prepare samples in the form of Au-ZnPc-Au sandwich films under

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vacuum. ZnPc films have an active area of $(10-12) \times 10^{-6} \text{ m}^2$ and thickness of $1.5-2 \text{ }\mu\text{m}$. The Au bottom electrodes were evaporated from a molybdenum boat at a deposition rate $5 \text{ }\text{\AA}/\text{s}$ onto Corning 7059 cleaned substrates. ZnPc was evaporated at a deposition rate $10 \text{ }\text{\AA}/\text{s}$. The surface electrodes were evaporated at a deposition rate $1 \text{ }\text{\AA}/\text{s}$ in order to avoid damage of the surface of ZnPc film. The samples were prepared without breaking vacuum at a pressure $\sim 10^{-5} \text{ Torr}$, while the glass substrates were at room temperature.

To investigate the dielectric constant, dielectric loss, and impedance, an RLC meter of type PM 6304 was used. The sample was placed in an evacuated chamber, at a pressure of $\sim 10^{-3} \text{ Torr}$, designed to minimize both stray capacitance and ambient gases effects. The range of frequencies was $1 - 100 \text{ kHz}$. The temperature of the sample was measured by a calibrated K-type thermocouple over a temperature range $293 - 415 \text{ K}$. The thermocouple was connected in series with an automatic relay and a digital temperature indicator which allowed to control the temperature automatically with an accuracy of $\pm 1\text{K}$.

3. Results and discussion

Many dielectric functions, as the complex dielectric constant ϵ^* , and complex impedance Z^* , have been used to describe the frequency-dependent properties of materials. These functions may be expressed as [25-29],

$$\epsilon^* = \epsilon' - i \epsilon'' \quad (1)$$

$$Z^* = Z' - i Z'' \quad (2)$$

where $i = \sqrt{-1}$, and ϵ' , ϵ'' , Z' , and Z'' are the real and imaginary parts of the complex dielectric constant, and complex impedance, respectively.

The dielectric constant ϵ' is given by the relation C/C_0 , where C is the measured capacitance, and C_0 is the geometrical capacitance which is given for a film by the vacuum permittivity ϵ_0 , area A , and thickness t , in the relation,

$$C_0 = \epsilon_0 A / t \quad (3)$$

The dissipation factor or loss tangent, $\tan \delta$, is often used to characterize the dielectric loss of a material, which is given by

$$\tan \delta = \epsilon'' / \epsilon' = Z'' / Z' \quad (4)$$

Figs. 1 and 2, show the frequency-dependence of the dielectric constant ϵ' , and dielectric loss ϵ'' , of ZnPc thin films, of α -form [30], at different temperatures. Both ϵ' and ϵ'' decreases with increasing frequency and increases with increasing temperature. At low frequencies and high temperatures, the rate of decreasing of both ϵ' and ϵ'' is very high, while at higher frequencies the rate slows down. At room temperature, both ϵ' and ϵ'' does not show appreciable change through the whole range of frequencies. In Fig. 2, no peaks or minima appear for the dielectric loss ϵ'' within the range of measurements, which agrees with ref. [31], for dielectric measurements of lead phthalocyanine (PbPc) thin films.

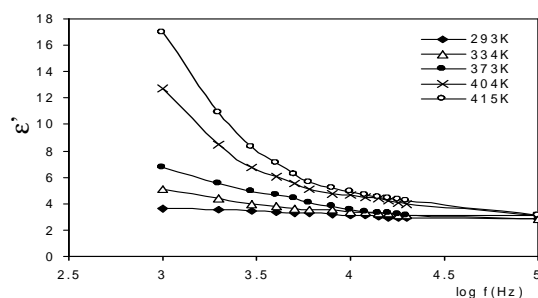


Fig. 1. Relation between $\log f$ and ϵ' .

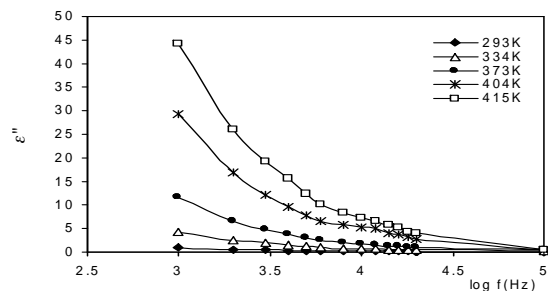


Fig. 2. Relation between $\log f$ and ϵ'' .

Figs. 3 and 4, show the temperature-dependence of the dielectric constant ϵ' , and dielectric loss ϵ'' of ZnPc thin films at constant frequencies. Both the dielectric functions increase slowly with increasing temperature, but at certain temperature the rate of increase changes and becomes higher.

At this temperature, ~393 K, a change of phase from α -phase to β -phase begin to occur. A change of phase, from α to β phase, was also observed in metal-free phthalocyanine (H₂Pc) thin films to occur at ~300 K for capacitance measurements in ref [32]. The broad peaks, observed with CuPc pellets [33], which was attributed to adsorbed oxygen molecules that tend to be desorbed at higher temperatures, was not observed here.

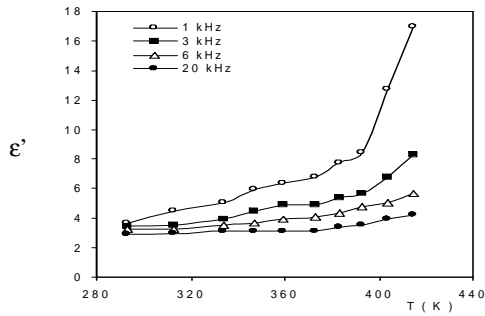


Fig. 3. Relation between ϵ' and T(K).

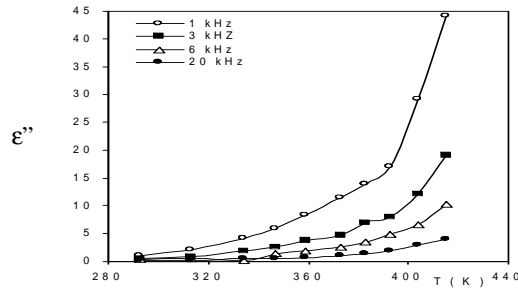


Fig. 4. Relation between ϵ'' and T(K).

The Cole-Cole diagrams $\epsilon''(\epsilon')$ of ZnPc thin films are shown at several temperatures in Fig. 5. ϵ'' vanishes upon approaching both high and zero frequencies. A semicircle is obtained for each temperature. The centers of the semicircles lie below the abscissa axes by an angle α . This confirms that there exists a distribution of relaxation times in ZnPc. The analysis of the results could reveal several parameters such as the macroscopic relaxation time τ_0 , the molecular relaxation time τ , the activation energy for relaxation E_0 , and the distribution parameter α [21,23,28].

The macroscopic relaxation time τ_0 can be evaluated using the relation [21]:

$$\frac{U}{V} = (\omega \tau_0)^{1-\alpha} \tag{5}$$

where U is the distance on the Cole-Cole diagram between the static dielectric constant ϵ'_0 ($\omega = 0$) and the experimental point, V is the distance between that point and the optical dielectric constant ϵ'_∞ (high ω), and ω is the angular frequency. The symbols α , U, and V are shown in Fig. 5. The value of τ_0 was found to decrease with temperature.

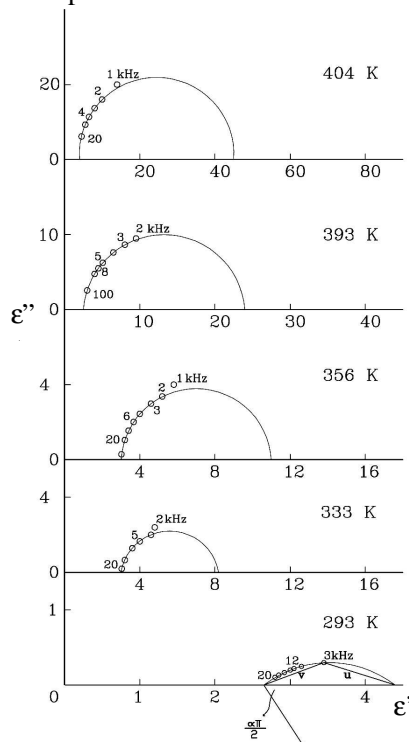


Fig. 5. The Cole-Cole diagrams of ZnPc for a range of temperatures. The frequencies are in kHz.

The molecular relaxation time τ could be evaluated from [28]:

$$\tau = \frac{2\epsilon'_0 + \epsilon'_\infty}{3\epsilon'_0} \tau_0 \quad (6)$$

The temperature-dependence of τ is a thermally activated process, described by [29,34,35],

$$\tau = \tau_\infty \exp(-E_0 / kT) \quad (7)$$

where τ_∞ is the relaxation time at infinite temperature, E_0 is the activation energy for relaxation, while τ represents the average or most probable value of a spread of relaxation times.

Fig. 6 shows the relaxation time τ for ZnPc thin films plotted against the reciprocal of temperature, and clearly shows two linear relations between $\ln \tau$ and $1/T$. These two lines are evidence for the transition in ZnPc films from α phase to β phase observed to occur at ~ 390 K. The calculated values of τ_∞ and E_0 were found to be 2×10^{-8} s and 0.12 eV for α phase, and 1.18×10^{-10} s and 0.3 eV for β phase respectively. It is observed that, the activation energy E_0 is higher for β phase than that for α phase, since the β phase is the more stable phase [36].

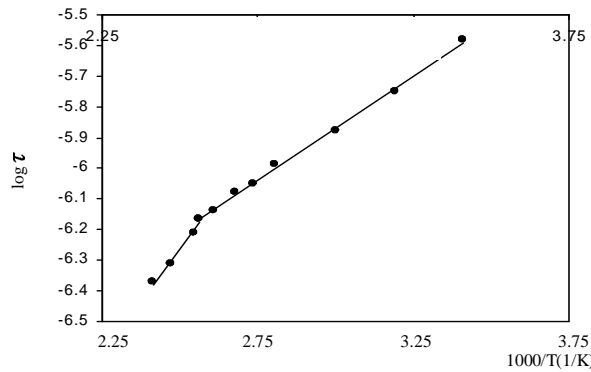


Fig. 6. Relation between $1000/T$ and $\log \tau$.

The variation of the optical dielectric constant ϵ'_∞ with temperature, calculated from Fig. 5, is represented in Fig. 7. It is clear that ϵ'_∞ increases slowly with temperature until ~ 390 K, where ϵ'_∞ increases quickly with temperature. Transition in ZnPc films from α phase to β phase begin to occur at ~ 390 K. Complete transitions in ZnPc films from α to β phase have been observed to occur at ~ 300 °C in refs. [30,36], where the films transform completely from the tetragonal to the monoclinic structure. The increase of ϵ'_∞ with temperature could be related to the well-known phenomenon that the polarization increases with temperature, which was found to be valid for a wide range of materials [22, 33,37].

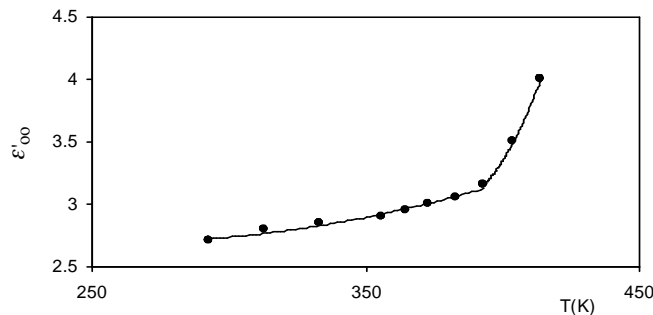


Fig. 7. Relation between ϵ'_∞ and $\log T(K)$.

Figs. 8 and 9 show the frequency dependence of the real and imaginary parts Z' , Z'' , of the complex impedance at different temperatures. The real part decreases with increasing both frequency and temperature, while the imaginary part decreases with increasing frequency and increases with

increasing temperature. However, at ≥ 390 K, the imaginary part Z'' at the low frequency range, began to decrease, and become lower than that at < 390 K, due to the phase transition at this temperature.

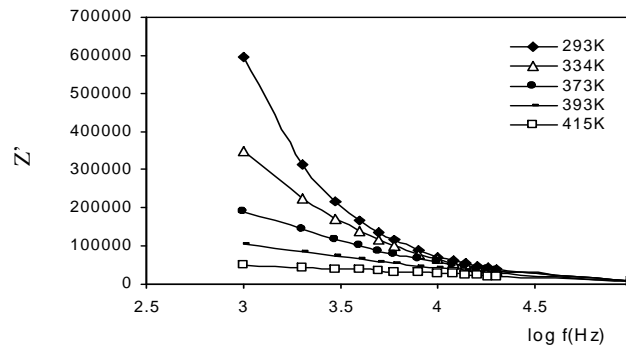


Fig. 8. Relation between $\log f$ and Z' .

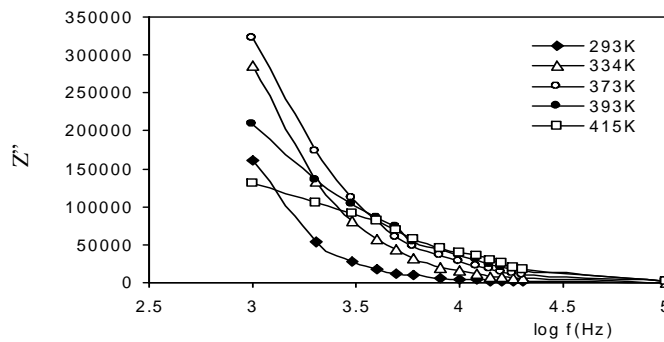


Fig. 9. Relation between $\log f$ and Z'' .

The imaginary part of the electrical impedance Z'' is plotted versus its real part Z' for various temperatures. Typical complex impedance spectra of ZnPc thin films related to the applied sinusoidal voltage for the temperature range 293 – 415 K are shown in Fig.10. The plots become progressively more circular as the temperature increases.

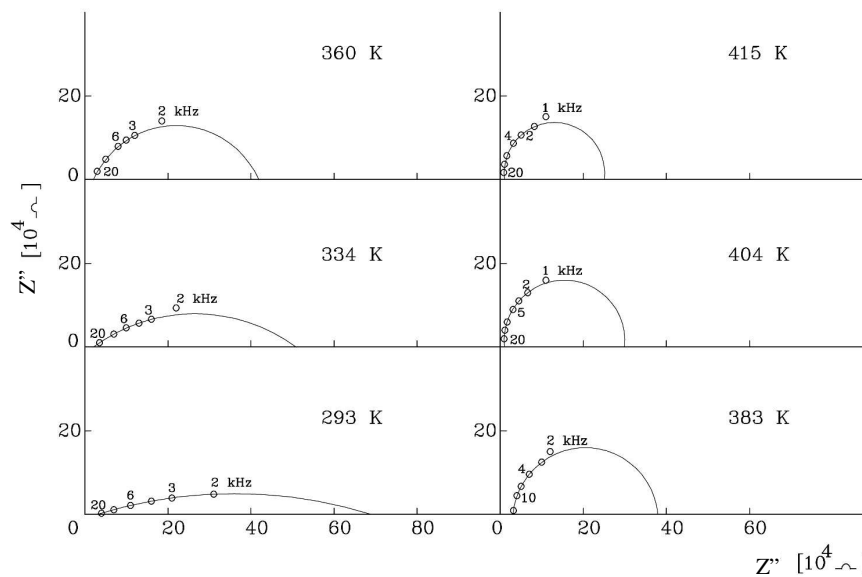


Fig. 10. Complex impedance spectra of ZnPc for a range of temperatures. The frequencies are in kHz.

The frequency dependence of both Z' and Z'' permits separation of the resistance of the grain bulk R_b from that of the surface R_s [26]. The classical semicircular form shown in Fig.10, leads to an equivalent circuit for ZnPc comprising R_b in series with parallel $R_s - C_s$ combination [27], where C_s is the capacitance of the measured sample. This leads to the established relations

$$Z' = R_b + R_s / [1 + (\omega C_s R_s)^2] \quad (8)$$

$$Z'' = i \omega C_s R_s^2 / [1 + (\omega C_s R_s)^2] \quad (9)$$

Z'' vanishes upon approaching both zero and high frequencies, whereas Z' varies throughout the applied frequency, and is equal to $(R_b + R_s)$ at zero frequency (dc), and only R_b at higher frequency. Therefore, the complex semicircle $Z''(Z')$ impedance diagram would reflect R_b at high frequencies, whereas contribution of R_s increases upon shifting to the zero frequency (dc).

It is seen from Fig.10, that the grain bulk resistance R_b is nearly constant, in the α -phase, while it decreases as the temperature increases in the β -phase. However, the grain surface resistance R_s is dependent on temperature in both phases, and decreases as the temperature increases. The temperature dependence of the surface resistance R_s is represented via a thermally - activated process, with the formula

$$R_s = R_o \exp. (\Delta E / k T) \quad (10)$$

where R_o is a constant and ΔE is the activation energy for dc conduction.

The resistance R_s could be used to evaluate the dc conductivity, using the known relationship,

$$\sigma_{dc} = \sigma_o \exp. (- \Delta E / kT) \quad (11)$$

Fig.11 shows a plot of $\log \sigma_{dc}$ versus $1/T$. The linear relationship of Fig. 11, reveals two straight lines. The first line (lower temperatures), resembles the α -phase, while the second line, beginning nearly at 390 K, resembles the β -phase. The slope of these lines gives $\Delta E = 0.046$ eV, and $\sigma_o = 2.24 \times 10^{-6} \text{ Sm}^{-1}$, for the α -phase, and $\Delta E = 0.11$ eV, and $\sigma_o = 1.45 \times 10^{-5} \text{ Sm}^{-1}$, for the β -phase. The β -phase shows higher activation energy than the α -phase, since the β -phase is less conductive than the α -phase [36]. It is seen that the activation energies for conduction process is lower than the activation energies for relaxation process. This may be attributed to the existence of impurities and defects in the organic material [9,10].

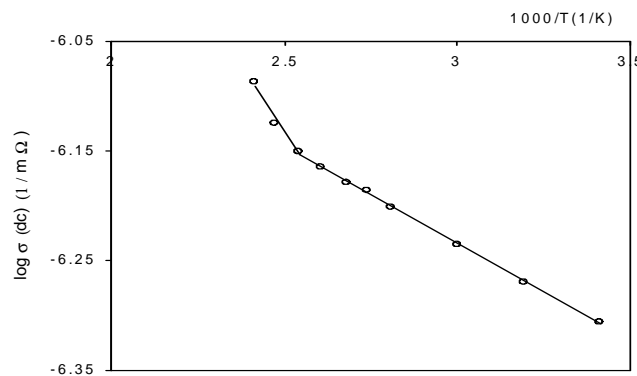


Fig. 11. Relation between $\log \sigma(\text{dc})$ and $1000/T$.

4. Summary and conclusion

We have used the AC complex impedance technique to study the dielectric properties of Zinc phthalocyanine sandwiched thin films, Au-ZnPc-Au, in the frequency range 1-100 kHz and at temperature range 293-415 K. The temperature dependence of molecular relaxation time can be

expressed by a thermally activated process. Transitions in ZnPc films from α - phase to β -phase have been observed in molecular relaxation time τ , optical dielectric constant, ϵ_{∞} and dc conductivity σ_{dc} to occur at ~ 390 K. The β -phase always shows higher activation energy than the α - phase, which confirms that β phase is more stable than the α - phase.

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