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Ac electrical parameters of Al-ZnPc-Al organic semiconducting films

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Abstract: The ac electrical parameters of thermally evaporated zinc phthalocyanine, ZnPc, semiconducting thin films was measured in the temperature range of 180 – 390 K and frequency between 0.1 and 20 kHz. Aluminum electrode contacts were utilized to sandwich the organic ZnPc semiconducting films. Capacitance and loss tangent decreased rapidly with frequency at high temperatures, but at lower temperatures a weak variation is observed. An equivalent circuit model assuming ohmic contacts could qualitatively and successfully explains capacitance and loss tangent behavior.

The ac conductivity showed strong dependence on both temperature and frequency depending on the relevant temperature and frequency range under consideration. Ac conductivity σ (ω) is found to vary with ω, as ω^s with the index s $\leq$ 1.35 suggesting a dominant hopping conduction process at low temperatures (< 250 K) and high frequency. The conductivity of some samples did not increase monotonically with temperature. This behavior was attributed to oxygen exhaustion of the sample as its temperature is increased. The ac conductivity behavior at low temperatures of ZnPc films could be described well by Elliott model assuming hopping of charge carriers between localized sites.

Keywords: Thermal evaporation, organic semiconductor, capacitance, conductivity, ZnPc
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1 Introduction

The importance of emphasized studies on metal- or metal-free phthalocyanine (Pc) compounds as a result of recent investigations showing growing significance of these composites that could be employed in technological applications (gas sensors, solar cells, semiconductors...etc) and even in some medical applications as a novel compound that could be employed in photodynamic therapy [1–5]. Besides, phthalocyanine compounds are chemically stable having dense colors suitable to be employed as dyes and pigments in textile and paint industries. Phthalocyanines are thermally stable aromatic organic compounds having semiconducting behaviors. They could be found in several crystalline polymorphs, including primarily the α-, β-, and γ-structure. There are more than 70 different phthalocyanine complexes that can be fabricated by replacing the two hydrogen atoms at the center of the molecular structure of the metal-free phthalocyanine, H_2Pc, molecule [6]. A schematic representation of ZnPc molecule is displayed in Fig. 1.

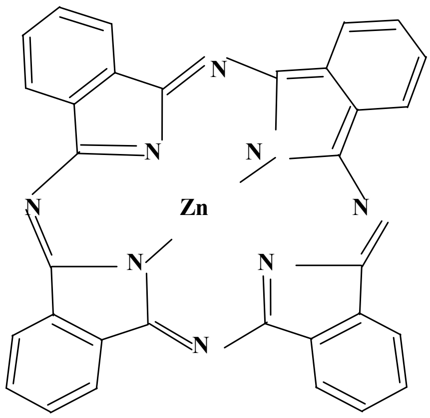

Fig. 1 A schematic diagram of the organic ZnPc molecule.

The ac electrical properties of phthalocyanine complexes (CuPc, ZnPc, CoPc, H_2Pc. . .) have attracted several research groups in the last decades [7–14]. In addition, the technological applications of these compounds have also received the attention of many more research groups. In a comprehensive study on controlled p-doping of pigment layers, Pfeiffer et al. [15] concluded that doping has the potential of both reducing the series resistance and increasing the photo-voltage of organic cell in doped ZnPc donor-acceptor hetero-junctions. Moreover, Gao and Kahn [16] intensively investigated the electronic structure and current injections in p-doped ZnPc films. More recently, many groups focused their attention in gas sensing devices using organic phthalocyanine compounds such as NiPc, ZnPc, CuPc and CoPc [17–19]. Besides, CuPc was employed as a buffer zone in manufacturing a white organic light emitting diode [20], while PtPc solution was utilized to generate various types of switching devices [21]. The effect of oxygen on the photovoltaic properties of organic solar cells consisting of ZnPc was thoroughly investigated by Kerp and van Faassen [22]. They observed a noticeable increment in the short-circuit current when increasing the partial O_2 pressure.

Recently, the ability of using ZnPc thin layers as gas sensing devices was examined thoroughly by studying the effect of gases, either oxidizing (O_2 and NO_2) or reducing (H_2 and NH_3) gases, on the electrical conductivity of the sample [23, 24]. Moreover, Gao and coworkers [25] synthesized tetra-trifluoroethoxyl zinc phthalocyanine (an organic compound that can be dissolved in most organic solvents) that has the potential to be employed in photodynamic therapy of cancer. In addition, ZnPc was employed in some medical application due to its selective binding to tumor-selective antibodies, and it has been used in the synthesis of a novel compound applicable in photodynamic therapy [5]. High-resolution electron transmission spectroscopy (HRTEM) and digital processing were utilized to determine the structural of atomic and electronic distribution [26]. The type of ordering and the effects on the corresponding frontiers orbital and the electrostatic potential could be identified from such study.

The ac and dc electrical characterizations of the organic semiconducting ZnPc films have attracted several groups in the past few years. Saleh et al. [4] measured the IV characteristics (dc measurements) of ZnPc over a wide range of temperature. In addition, the dependence of ac electrical parameters (conductivity, capacitance and loss tangent) on frequency and temperature of Au-ZnPc-Au films was thoroughly investigated by Saleh and co-workers [10]. The conductivity, capacitance and loss tangent were found to be strongly dependent on frequency and temperature. Also, a partial transformation from the α-form to β-form was observed at temperature in excess of 430 °C. Abdel-Malik and co-workers [27] measured ohmic and space charge limited currents in beta-phase ZnPc single crystals as a function of temperature, and deduced the depth and concentration of localized trapping levels. Boudjema et al. [28] have related the electrical properties of ZnPc and NiPc thin films, when using rectifying electrodes, to an equivalent-circuit model, which divides the material into surface, space-charge and bulk regions. Oxygen doping in ZnPc thin films has been studied by Twarowski [29] who suggested that oxygen molecules diffuse into the films and act as acceptors. In addition, Twarowski studied the Schottky barrier capacitance in α and β phases of ZnPc as a function of temperature, frequency and film thickness. He observed a decrease in the space-charge density as the temperature is lowered. The model proposed by Twarowski to explain this phenomenon suggested two sites for the dopant, and only one of them is active in generating charge, so that by lowering the temperature, the active site will be depopulated.

Collins and Mohammed [30] made an intensive study of the dark conductivity of ZnPc as a function of the material purity, crystal phase, and temperature. They also studied the sensitivity of ZnPc to gases such as air, O_2, N_2, Ar, and NH_3. The α-form of ZnPc was found to grow in randomly oriented micro-crystallites, but the β-phase showed oriented needle-like crystals. The electrical and structural properties of ZnPc strongly depend on the material purity. Like other phthalocyanines, the conductivity of both α- and β-ZnPc was found to be critically dependent on the presence of O_2. The sensitivity to other gases differed between the two phases, but in both cases the presence of NH_3 caused a large dark conductivity decrease. The conductivity of β-ZnPc was found to be higher than that of α-phase, in contrast to the results found by Saleh et al. [10]. The contradiction in the results may be accredited to the purity of the material and to oxygen content in the samples. Conductivity of phthalocyanines generally depends on hole concentration and the decrease in conductivity during a phase transition is being caused by inhibition of the carriers from transferring to the electrode due to temporarily thermal diffusion of constituent atoms [31].

In the present work we report on the ac electrical properties (conductivity, capacitance and loss tangent) of semiconducting ZnPc thin films with Al electrodes. The study covered the frequency range from 0.1 to 20 kHz and temperature from 180 to 390 K. We will discuss the results according to available models, hoping the study will give better understanding of the electrical properties of ZnPc in particular, and to other metal-phthalocyanines in general.

2 Experimental

Three-layered sandwich structures of Al-ZnPc-Al thin film samples were deposited onto a previously thoroughly cleaned Corning glass substrate. ZnPc (of purity 97.5 %) films were deposited by thermal evaporation technique using Edwards (12E6/1126) coating unit. As the chamber pressure approached a value of approximately 10^{-3} Pa, deposition was initiated at low rates to keep pressure as low as possible. The Al-electrode layers were evaporated using a tungsten filament while a molybdenum boat was utilized to evaporate zinc phthalocyanine layer.

The fabrication of the sandwich structures took place without breaking the vacuum using a sequential masking system. Eight bottom electrode fingers of aluminum were deposited onto the substrate at a rate of about 1 nm/s. The phthalocyanine layer was then deposited at rate of about 0.5 nm/s, and finally the third Al-layer was then deposited firstly at lower deposition rate to avoid any thermal damage to the underlying ZnPc films. The active area of each cell sample was 1.2×10^{-5} m^2. Deposition rates and film thicknesses were monitored using a conventional quartz crystal; accurate film thicknesses were determined after deposition using a Planer Surfometer (SF 200) stylus instrument. All measurements reported in the present work were performed on films of thickness of about 0.6 to 1 μm.

The ac electrical measurements were made in a subsidiary vacuum system at pressure of about 10^{-3} Pa. Sample temperatures were measured using a chromel-alumel thermocouple attached to a Fluke K/J digital thermometer. The sample temperature was varied and stabilized by controlling the heating and cooling rates. Capacitance, loss tangent and conductance were measured in the frequency range 0.1 to 20 kHz and temperature between 180 – 390 K using a Hewlett-Packard (4276A) LCZ meter equipped with a four-terminal test fixture.

3 Results and discussion

3.1 Capacitance and loss tangent

In this section the capacitance and loss tangent dependence on frequency and temperature is presented and discussed.

3.1.1 Frequency dependence

Capacitance, C, and loss tangent, tan δ, were systematically measured in the frequency range from 0.1 – 20 kHz for various samples at different fixed temperatures. The dependence of capacitance on frequency is displayed in Fig. 2A, while Fig. 2B demonstrates the loss tangent dependence on frequency. As could be noticed from Fig. 2A, at low frequencies (< 1 kHz) and temperatures above room temperatures, C is strongly frequency dependent, while at higher frequencies and T < 300 K, a weak dependence is observed and C approaches a constant value. Similarly, tan δ is frequency and temperature dependent as could be seen in Fig. 2B. At low frequencies and all temperatures, a strong dependence is observed, while at higher frequencies a moderate dependence is apparent. Such behavior have been found previously in other phthalocyanine thin films like for example CuPc [7], Au-ZnPc-Au [10], CoPc [11], H_2Pc [12] and in FePc [32], and also in CoPc pellets [13]. In addition, some non-organic compounds like ZnO [33], ZnS [34] and CeO_2 [35] showed resembling behavior.

Qualitatively, this behavior of phthalocyanine compounds had been successfully explained in terms of equivalent circuit model proposed by Goswami and Goswami for ZnS films [34]. This model assumes that the system does not include Schottky barriers at the contacts. This equivalent circuit model assumes that the dielectric medium could be satisfactorily modeled by an inherent capacitive element C, unaffected by both the frequency and temperature, in parallel with a discrete resistive element R due to the dielectric film. The resistive element is presumed to be temperature dependent component specified by the following equation:

$$R = R_o \exp\left(\frac{\Delta E}{k_B T}\right) \tag{1}$$

where R_o is a constant and ΔE is the activation energy. A constant series resistance r_o due to wire leads is also connected in series with the parallel RC combination. The measured series capacitance C_s, and the series resistance R_s are given by:

$$C_s = C + \frac{1}{\omega^2 R^2 C} = \frac{1 + \omega^2 R^2 C^2}{\omega^2 R^2 C} = (1 + D^2)C \tag{2}$$

$$R_s = r_o + \frac{(1/\omega RC)^2 R}{[1 + (1/\omega RC)^2]} = r_o + \frac{D^2}{1 + D^2} R \tag{3}$$

where D = $1/\omega$RC and ω is the angular frequency. The loss tangent, tan δ, due to power dissipation in the sample is given by $\omega C_s R_s$, and therefore:

$$\tan\delta = \frac{R + r_o}{\omega C R^2} + \omega r_o C = D\left(\frac{R + r_o}{R}\right) + \omega r_o C \tag{4}$$

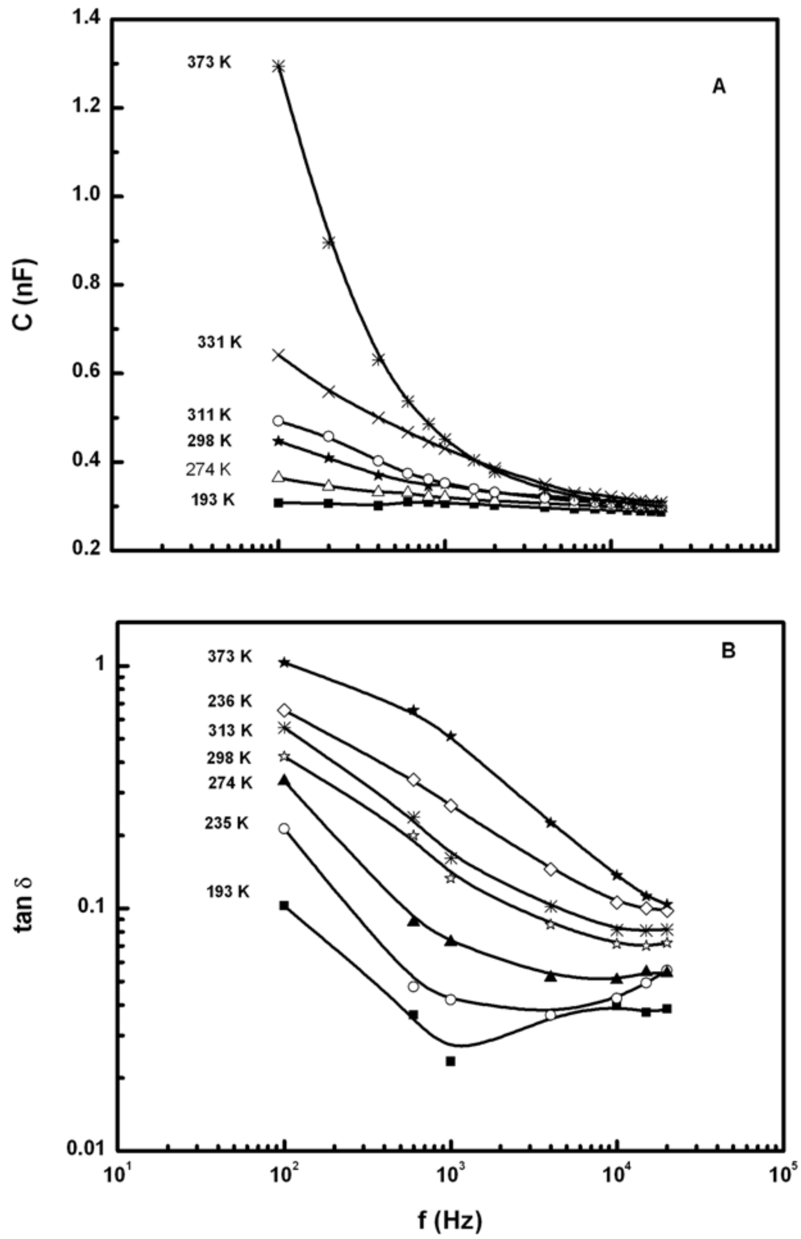

Fig. 2 Dependence of: A) capacitance and, B) loss tangent on frequency of organic ZnPc films at different fixed temperatures.

According to eq. (2), C_s should approach a constant value C at high frequency for all temperatures as observed in Fig. 2A. In addition, the measured values of tan δ in the present study are in good qualitative agreement with the model. **The ω^{-1} term on the right hand side of Eq. (4) dominates at low frequencies while the ω term dominates at higher frequencies. We therefore expect a low frequency and**

high frequency regions separated by a minimum given by:

$$\omega_{\min} = \sqrt{\frac{1}{r_o R C^2}} \quad (5)$$

As could be seen clearly in Fig. 2B, a minimum and an indication of minimum is observed at low temperatures and moderate frequencies. **A minimum value is clearly exhibited for the 193, 253 and 274 K-curves. The position of the minimum of tan δ as predicted by Eq. (5) is qualitatively observed, in that the minimum for the 193 K is at lower frequency than those for 253 K and 274 K**. Nevertheless, no minimum was observed in tan δ for some other phthalocyanine samples as CuPc [7], ZnPc [10], CoPc [11], H_2Pc [12] and FePc [32], while in MoPc [8] a broad minimum was observed followed by maximum at about 1.9×10^5 Hz. Moreover, a minimum was observed in non-organic materials such as ZnO [33], ZnS [34] and AlN_x [36]. The minimum was broad in the case of ZnO as it only appeared at temperatures below 320 K, while in ZnS a sharper minimum was detected.

3.1.2 Temperature dependence

To look more closely to the temperature dependence of capacitance and loss tangent, the capacitance and loss tangent were measured for several samples in the temperature range from 180 – 390 K at different fixed frequencies. Fig. 3 displays the variation of capacitance (A) and loss tangent (B) with temperature at various constant frequencies. The novel feature of the present study is that the capacitance and loss tangent of Al-ZnPc-Al appear to show a steady variation with temperature above 270 K. Similar performance was observed in this laboratory for other metal-phthalocyanines such as in a thermally evaporated CuPc [7], Au-ZnPc-Au [10], CoPc [11], and in FePc [32] thin films. Generally, both C and tan δ increase at temperatures above room temperature and low frequencies while at low temperatures and high frequencies both are almost constant. The increase in capacitance and loss tangent with increasing temperature may be ascribed to the enhanced conductivity through thermal excitation of the charge carriers. Vidadi and co-workers [37] measured the series capacitance in CuPc films using aluminum electrodes as a function of temperature and frequency and observed similar behavior. It is well known that aluminum electrode provides blocking contact (Schottky barrier) to CuPc. The results of Vidadi and co-workers were adequately explained in terms of the model proposed by Simmons et al. [38]. In this model, the structure of the thin film sample is represented in terms of a temperature-dependent resistance shunted by a fixed capacitance and in series with two capacitances corresponding to the two Schottky barriers representing the two aluminum electrodes. This model predicts a maximum in tan δ at certain frequency. In the present study, no maximum was observed in tan δ over the entire frequency range available, however, a maximum was detected in MoPc [9] thin films at about 1.9×10^5 Hz.

In some cases, the capacitance of certain ZnPc samples showed behavior slightly different than those discussed above. Fig. 4 displays the capacitance of ZnPc sample as

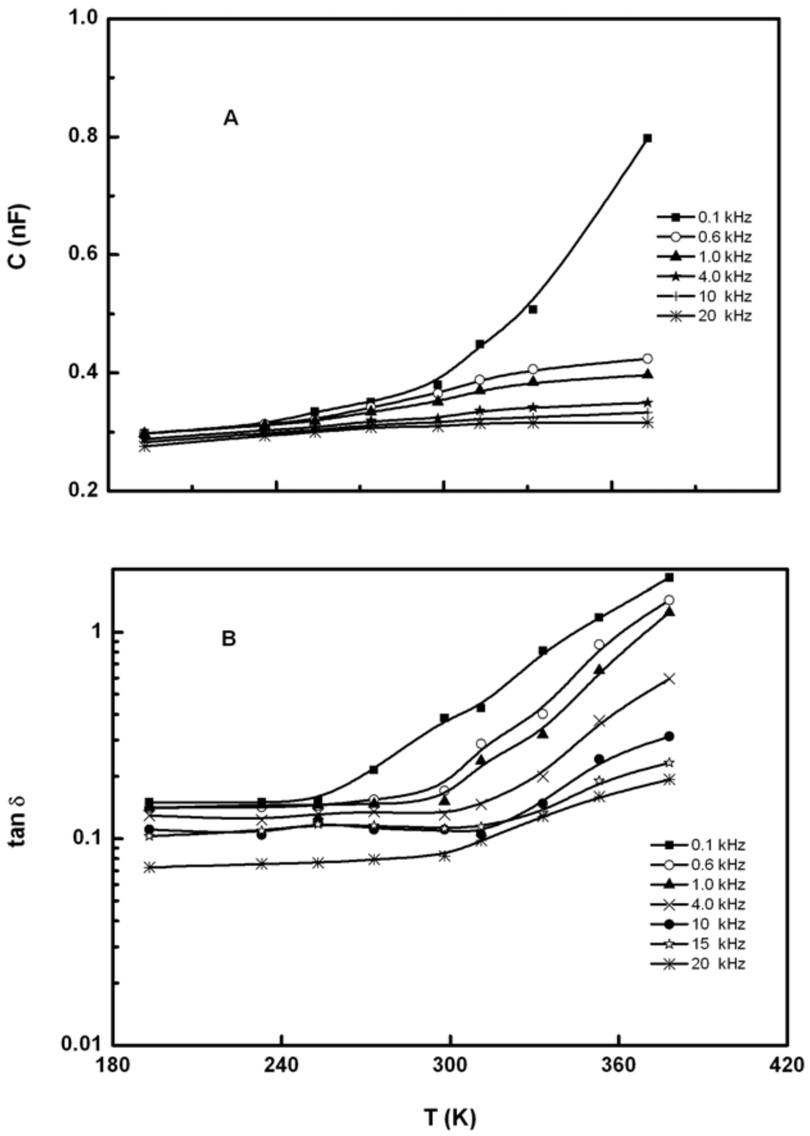

Fig. 3 Dependence of: A) capacitance and, B) loss tangent on temperature of organic ZnPc films at different fixed frequencies.

a function of frequency for various fixed temperatures. The general trend of the capacitance is the same as other samples, but at temperatures above 300 K, the capacitance decreased and then increased as the temperature is raised. Such behavior may be attributed to the excess of O_2 molecules in the sample and then desorption of O_2 as the temperature is raised. Similar behavior was also observed in H_2Pc [12] and NiPc [39]. It is well known that annealing and/or heating phthalocyanine samples to high temperature will stabilize the electrical properties due to oxygen exhaustion and structural changes. Further discussion of this phenomenon will be presented in the subsequent sections.

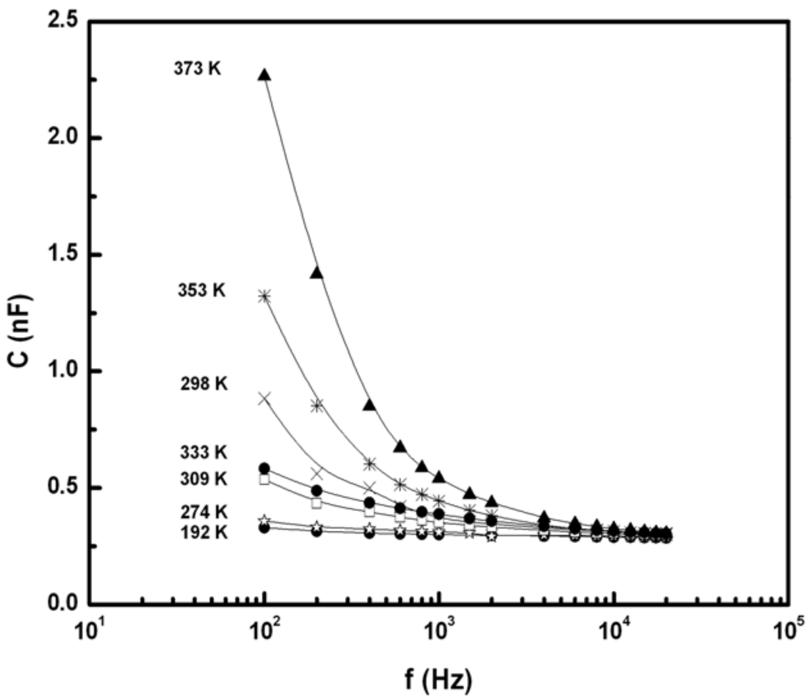

Fig. 4 The variation of capacitance with frequency at various fixed temperatures.

3.2 The ac electrical conductivity

The ac electrical conductivity of ZnPc films sandwiched between two Al-electrodes was measured as a function of temperature and frequency. The study covered a frequency range from 0.1 to 20 kHz and temperature from 180 to 390 K.

3.2.1 Variation of ac conductivity with frequency

Fig. 5 demonstrates the dependence of conductivity on frequency for two samples at different fixed temperatures on a double logarithmic scale. Generally, the conductivity increases slowly with frequency at low frequencies and very low temperatures, while the increase is stronger at higher frequencies and low temperatures. At higher temperatures, a steady but weak σ dependence on frequency is observed. In addition, a sharp conductivity drop is observed in some ZnPc samples above room temperature as could be seen in Fig. 5A, however no such drop is detected in other samples (Fig. 5B). The drop in the conductivity above 300 K may be attributed to exhaustion of excess oxygen molecules [12] and not to phase transformation that occurs around 430 K [10]. More discussion about this conductivity decrease above 300 K will follow later. The curves in Fig. 5A and B may be fitted to a relation of the form:

$$\sigma(\omega) = A\omega^s \tag{6}$$

where A is a complex constant, ω is the angular frequency and the index s is determined from the slopes of the curves. Generally, the frequency dependence of ac conductivity of other phthalocyanine compounds has similar performance [7, 9–12]. In contrary, Blagodarov et al. [40] noticed that the conductivity of metal phthalocyanine thin films was frequency independent when an external voltage was applied to the films. This behavior was ascribed to domination of the overall conductivity by the band condition component.

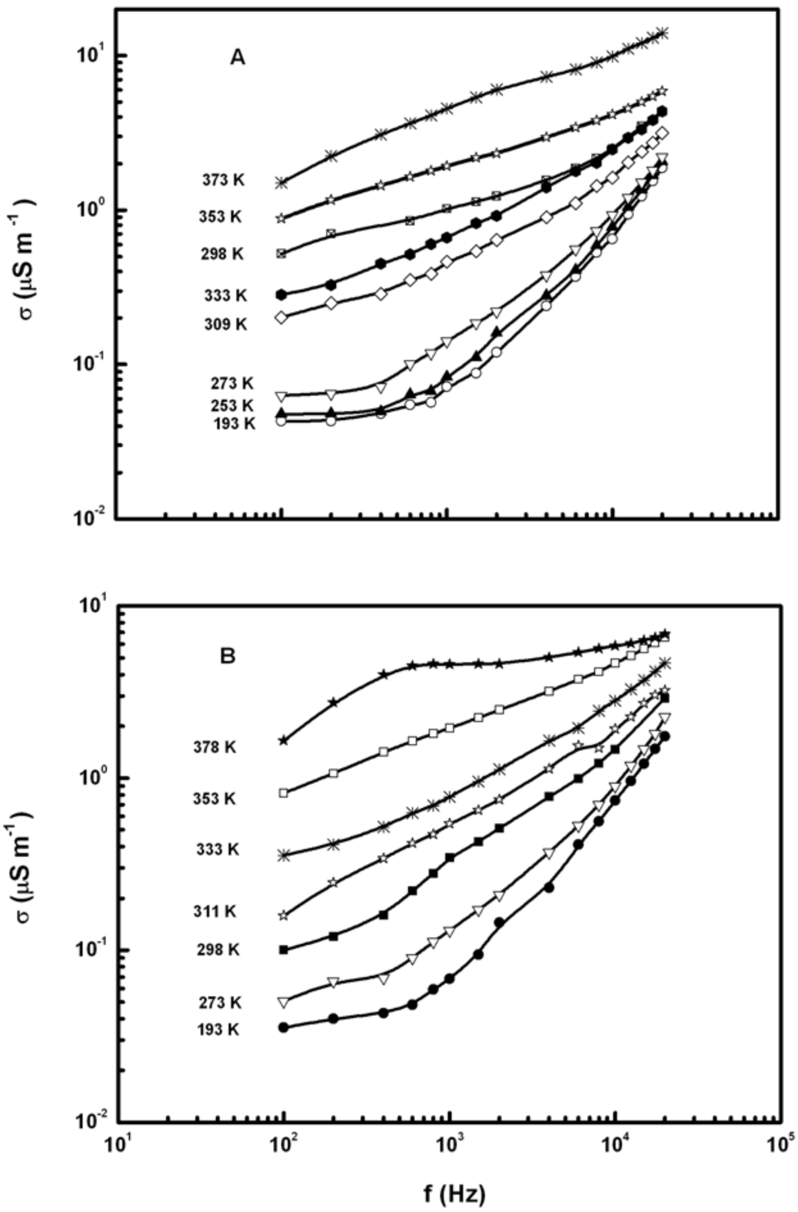

Fig. 5 Dependence of ac conductivity on frequency at different fixed temperature for: A) σ of a sample that do not monotonically increase with temperature and B) σ of a sample that do monotonically increase with temperature.

The values of the index s, as derived from the slopes of curves of Fig. 5, at different temperature and frequency ranges are listed in table 1. Such variation of s with frequency is probably related to a progressive transition between hopping regions. The highest estimated value of s = 1.34 was observed at high frequencies and low temperatures. In other studies, the index s was estimated to be less than unity as in CuPc [7], MoPc [9], ZnPc [10], CoPc [11] and H_2Pc [12] films. Generally, the present values of s qualitatively agree with the values estimated for other phthalocyanine compounds [7–12] especially at frequency greater than 0.3 kHz. Nevertheless, a maximum value of 1.75 at frequencies greater than 10^4 Hz had been observed in magnesium phthalocyanine, MgPc, films [41]. Besides, similar trend of the index s has been observed in inorganic amorphous oxide films [33, 35]. It is worth mentioning here that the expected ω^2 dependence of conductivity will correspond to two-center hopping between similar pairs of centers [41].

The measured conductivity of ZnPc in the present study and the general values of s (predominantly for f $<$ 5 kHz) appear to be consistent with a hopping process as described by the following equation proposed by Elliott [42]:

$$\sigma(\omega) = \frac{\pi^2 N^2 \varepsilon}{24} \left[\frac{8e^2}{\varepsilon W_m}\right]^6 \frac{\omega^s}{\tau^\beta} \tag{7}$$

where N is the density of localized states, ε is the permittivity, τ is the effective relaxation time, e is the electronic charge and the index s is related to β at low temperature by the relation:

$$s = 1 - \beta = 1 - \frac{6k_B T}{W_m} \tag{8}$$

where W_m is the optical barrier energy gap of the material, k_B is Boltzmann's constant, and the index β is smaller than unity.

T (K)	Frequency range (kHz) 0.1 – 0.6	0.7 – 4	5 – 20
193	0.159	0.879	1.240
273	0.285	0.736	1.223
298	0.428	0.652	0.824
311	0.535	0.521	0.665
333	0.315	0.518	0.657
353	0.389	0.351	0.452
378	0.565	0.052	0.186

Table 1 Variation of the index s with temperature and frequency range as derived from Fig. 5B.

3.2.2 Variation of ac conductivity with temperature

In the present investigation, some of the measured values of the conductivity do not increase monotonically with temperature as displayed in Fig. 5A. In order to further investigate this phenomenon, the conductivity was measured as a function of temperature at various fixed frequencies. Fig. 6 displays the variation of σ with inverse of temperature for: A) σ for a sample that do not increase monotonically with temperature, and B) σ for a sample that do increase monotonically with temperature. Fig. 6A demonstrates similar dependence as observed in metal-free phthalocyanine, H_2Pc, [12], while Fig. 6B showed analogous variation as that found in some metal-substituted phthalocyanine [7, 8, 10, 11, 32]. In general, both σ – T curves show strong frequency dependence at low temperatures associated with very small activation energy (0.02 – 0.07 eV) consistent with the hopping of charge carries between localized states [43, 44]. However, at higher temperatures both samples showed weak-frequency dependence associated with relatively high activation energy (1 – 2 eV) indicating free band conduction process of charge carriers. Activation energy (ΔE) was derived out from the slopes of the σ – T curves (Figs. 6A and B) assuming that $\sigma = \sigma_o \exp(-\Delta E/k_B T)$. The estimated values of the activation energy in the present study are higher than those reported for other metal phthalocyanine compounds [7, 10–12] and this discrepancy may be attributed to the usage of Al-electrodes that act as blocking contacts and to the structural variation and oxygen content that act as acceptors [7, 45].

The peaks appearing in the conductivity around 300-330 K as displayed in Fig. 6A are due to oxygen exhaustion out of the sample as confirmed in this laboratory. We re-measured the conductivity of H_2Pc sample that behaved the same as Al-ZnPc-Al and recycled the temperature of the sample between 228 K and 433 K [12]. Fig. 7 demonstrates the ac conductivity at 1 kHz for α-H_2Pc thin films of thickness 0.7 μm. The figure shows the conductivity for temperature increasing up to about 430 K (curve A), followed by the characteristics obtained with temperature decreasing down to about 300 K (curve B). The disappearance of the conductivity peak during the decreasing temperature measurements can be attributed to desorption of the oxygen impurities from the sample during the heating cycle. To ensure that the peak is not due to a hysteretic effect or a phase transition, the sample was cooled down to 228 K and then re-heated again to 433 K. No peak was observed in the second heating cycle, confirming the oxygen drain from the sample. Similar behavior has also been observed in dc conductivity measurements of NiPc films [39] and α-CuPc thin films [7, 45]. It is evident therefore that annealing or heating the sample to high temperature will stabilize the electrical properties due to oxygen desorption and structural changes [10, 12, 45, 46]. The difference in the conductivity between one sample and another may be associated with thickness differences, structural defects, grain boundaries and impurities. Harrison and Ludewig [45] observed similar disparity in conductivity curves and activation energies in their dc conductivity measurements of α-CuPc thin films. They associated this type of behavior to oxygen exhaustion and to a partial phase transformation from α- to β-phase. However, Abdel-Malik and Cox [47] attributed the variation of the activation energy, in NiPc single crystals, to a transition from an extrinsic to non-extrinsic conduction mechanisms in a partially compensated sample.

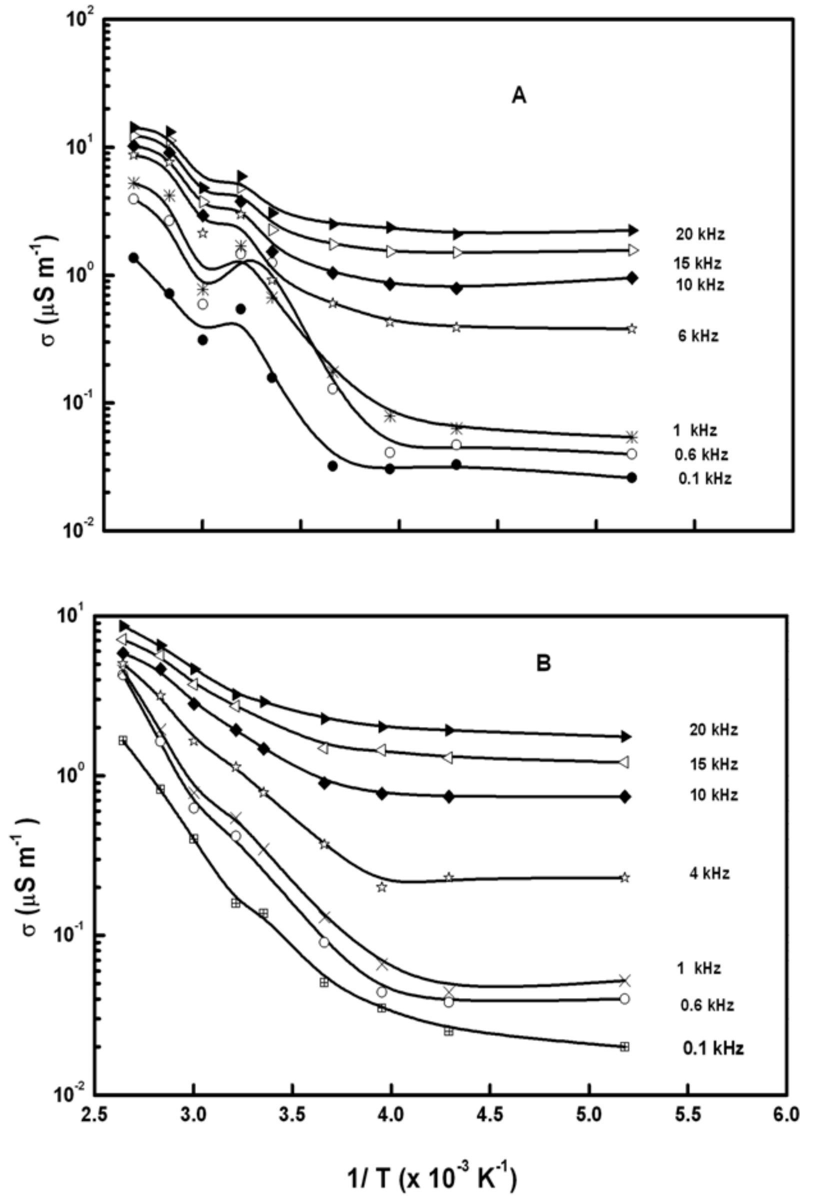

Fig. 6 Dependence of ac conductivity on temperature at different fixed frequencies for: A) σ of a sample that do not monotonically increase with temperature and, B) σ of a sample that do monotonically increase with temperature.

4 Summary and conclusions

Ac electrical properties (capacitance, loss tangent and conductivity) have been investigated for semiconducting ZnPc thin films with Al-electrodes in the frequency range of 0.1 – 20 kHz and temperature range of 180 – 390 K. It has been observed that both capacitance and loss tangent are strongly frequency and temperature dependent at tem-

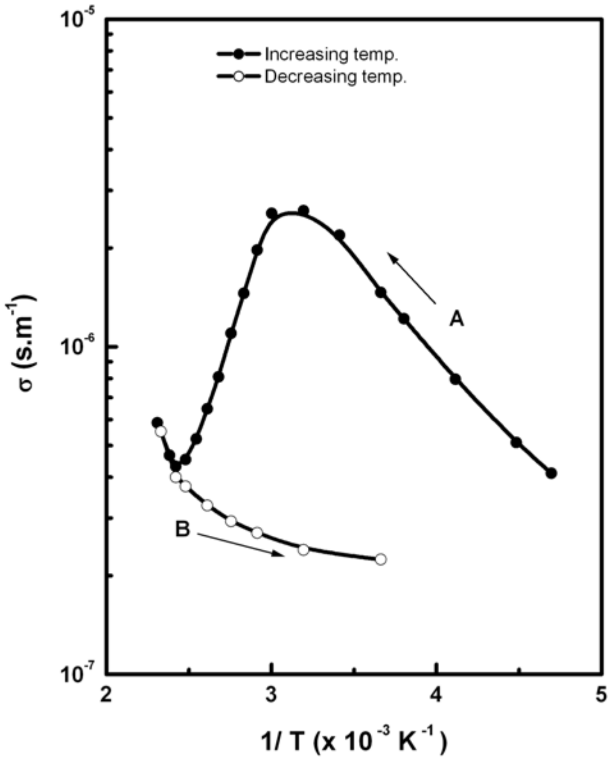

Fig. 7 Dependence of ac conductivity on inverse temperature with increasing temperature (curve A), and decreasing temperature (curve B) for H_2Pc sample at constant frequency of 1 kHz.

peratures above 300 K and frequencies below 3 kHz. However, at lower temperatures, capacitance is almost constant and the loss tangent is weakly frequency dependent. The present capacitance and loss tangent data of ZnPc could be qualitatively explained in terms of an equivalent circuit model proposed to describe the non-organic ZnS and ZnO films [34].

The ac conductivity, $\sigma(\omega)$, of semiconducting ZnPc films showed ω^s dependence with the index s < 1.35. Such behavior appears to indicate that hopping is the predominant conduction process over the frequency range studied in MoPc thin films as observed by James et al. [8]. At low temperatures and high frequencies, the observed values of s are in a reasonable agreement with those predicted by the Elliot model [42] originally proposed to explain ac behavior of amorphous materials. For higher temperatures and low frequencies, free-carrier hopping conduction is observed. At low temperatures the mean value of the activation energy derived was about 0.05 eV, while at higher temperatures an average activation energy of about 1 eV was estimated. Some samples showed a noticeable drop in conductivity above 300 K and then an increase as the temperature is raised. This behavior was attributed to oxygen exhaustion out of the sample during warming up. The present ac results of ZnPc films with Al-electrodes are consistent and in good agreement with those of other metal phthalocyanines compounds like CuPc films, ZnPc films, MoPc, CoPc, and H_2Pc films [8–12].

In conclusion, more work on ZnPc and other phthalocyanine compounds are essential to help better the understanding of such systems, but over a wider range of frequency and temperature. The investigation should include the variation of ac-electrical properties with preparation conditions, heat treatment, annealing duration, annealing atmosphere, and the effect of electrode material.

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