

# Dielectric characterization of semiconducting ZnPc films sandwiched between Gold or Aluminum electrodes

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**Abstract** The dependencies of complex dielectric functions (the dielectric constant,  $\varepsilon_1$ , and the dielectric loss,  $\varepsilon_2$ ), on frequency and temperature of zinc phthalocyanine (ZnPc) thin films sandwiched between either gold or aluminum Ohmic-electrode contacts have been investigated in the temperature range of 93–470 K and frequency range 0.1–20 kHz. It is found that both values of  $\varepsilon_1$  and  $\varepsilon_2$  decrease with increasing frequency and increase with decreasing temperature. The rate of change depends greatly on the temperature and frequency ranges under consideration. Around room temperature, neither  $\varepsilon_1$  nor  $\varepsilon_2$  show any appreciable change through the whole range of frequencies. Thus, the dielectric dispersion is found to include of both dipolar and interfacial polarizations. The dependencies of both dielectric functions on frequency at different temperatures were found to follow a universal power law of the form  $\omega^n$ , where the index  $0 < n \leq -1$ . This indicates that the correlated barrier hopping (CBH) model is a suitable mechanism to describe the dielectric behavior in ZnPc films. Furthermore, the results of the dielectric response indicate that polarization in these films could be in the form of non-Debye polarization. However, the Debye polarization can be traced below room temperature. The obtained results of the relaxation-time,  $\tau$ , dependency on temperature have shown that a thermally-activated process may be dominated in ZnPc thin films conduction at high temperatures. Partial phase transition (from

$\alpha$ - to  $\beta$ -phase) has been observed around 400 K in molecular relaxation-time,  $\tau$ , and optical dielectric constant,  $\varepsilon_\infty$ . Arrhenius behavior has been observed for all the dielectric loss and conductivity relaxation-times above room temperature and their activation energies are explained and reported. The optical dielectric constant  $\varepsilon_\infty$  was found to increase with temperature.

## 1 Introduction

Organic semiconductor compounds, such as phthalocyanine (Pc), have become increasingly attractive to replace inorganic semiconductor compounds in the development of lightweight and inexpensive electric-conversion devices [1]. Accordingly, this class of material has been used extensively in different fields of science, industry, and technology. These organic-compound devices have many applications, such as gas sensors [2], thin film transistors [3], organic light emitting diodes [4], rectifiers [5], organic switches [6], memory devices, and photovoltaic cells [7–9]. Recently, Pc compounds are employed in biological, biophysical and biomedical applications, nanoparticles, and in the synthesis of a novel compound applicable in photodynamic therapy of cancer [10–12]. Traditionally, phthalocyanine compounds have been employed intensively as dyes and pigments in the textile and paint industries due to their intense colors, and their high thermal and chemical stability properties.

The metal-phthalocyanine compounds (about 70 complexes), as zinc phthalocyanine (ZnPc), have proven to be highly conjugated systems, and they incorporate a typical prototype of organic semiconductors. ZnPc compounds have been fabricated in many forms as thin films [13, 14], bulk pellets [15], and single crystals [16], to investigate their different properties. During the past three decades, several

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experimental as well as theoretical investigations [17–19] have been performed by physicists and chemists to explore the crystal structure, bulk, and amorphous properties of various phthalocyanine compounds [17–20]. Measurements of electrical conductivity were aimed at understanding conduction processes and at obtaining information about the defect states in semiconductors [21, 22]. It was found that electronic conduction is dominated by charge carrier hopping for all applied voltages and temperatures below 250 K [13, 14, 17, 18]. At higher temperatures and voltages just below 2 V, conduction was found to be Ohmic; while at higher voltages (above 2 V), a space-charge limited conduction (SCLC) process was observed [23].

The ac analysis technique has been widely used to study the dielectric behavior of crystalline, polycrystalline, and amorphous materials [13, 14, 24–26]. The ac-conductivity,  $\sigma(\omega)$ , dependency on angular frequency  $\omega$ , was found to follow Jonscher's universal power law of the form  $\omega^s$ , where the index  $s \leq 1$  [13, 14, 17, 18]. A considerable decrease in conductivity at all frequencies is observed in the temperature range 400–500 K particularly at temperatures above 430 K. This decrease was attributed to a possible partial  $\alpha$ -to  $\beta$ -phase transition [13, 14, 27, 28]. The dielectric study at low frequency range is particularly interesting in polymer systems due to their nature of having long chains and high molecular weight. It is well known that most of the properties, such as dielectric constant and elastic compliance, in polymeric materials are dispersive even at low frequencies, reflecting relatively high activation energies for the motion of molecular units and chain segments [29].

Theoretically, dielectric relaxation spectroscopy (DRS) can probe the interaction of a macroscopic sample with a time-dependent electric field. The resulting polarization of the material that responds to the electric field can be expressed by the frequency-dependent complex permittivity,  $\varepsilon^*(= \varepsilon_1 - i\varepsilon_2)$ , the ac-conductivity,  $\sigma_{ac}$ , or the complex impedance,  $Z^*$ , spectrum. The complex dielectric constant of a material is determined by electronic, ionic, dipolar, and space-charge polarization [30]. The space charge contribution depends on the purity and the perfection of dielectric samples. Generally, its influence is negligible at very low temperatures and noticeable in the low frequency region [31]. Therefore, the presence of any dielectric relaxation corresponds to one or more of the microscopic polarization mechanisms. Each relaxation process may be characterized by a relaxation-time, which describes the time-decay of its polarization in the presence of a periodic field. The dielectric relaxation, which is due to a number of different polarization mechanisms, could be attained using DRS analysis [32]. Accordingly, dielectric relaxation studies are very important for understanding the nature and the origin of dielectric losses, which in turn may be useful in the determination of structural defects in solids [5].

The present study aims to investigate the dielectric properties of ZnPc thin films sandwiched between two Ohmic electrodes, i.e., Au or Al-electrodes. The measurements are performed in the temperature range of 93–470 K with a frequency between 0.10 and 20 kHz.

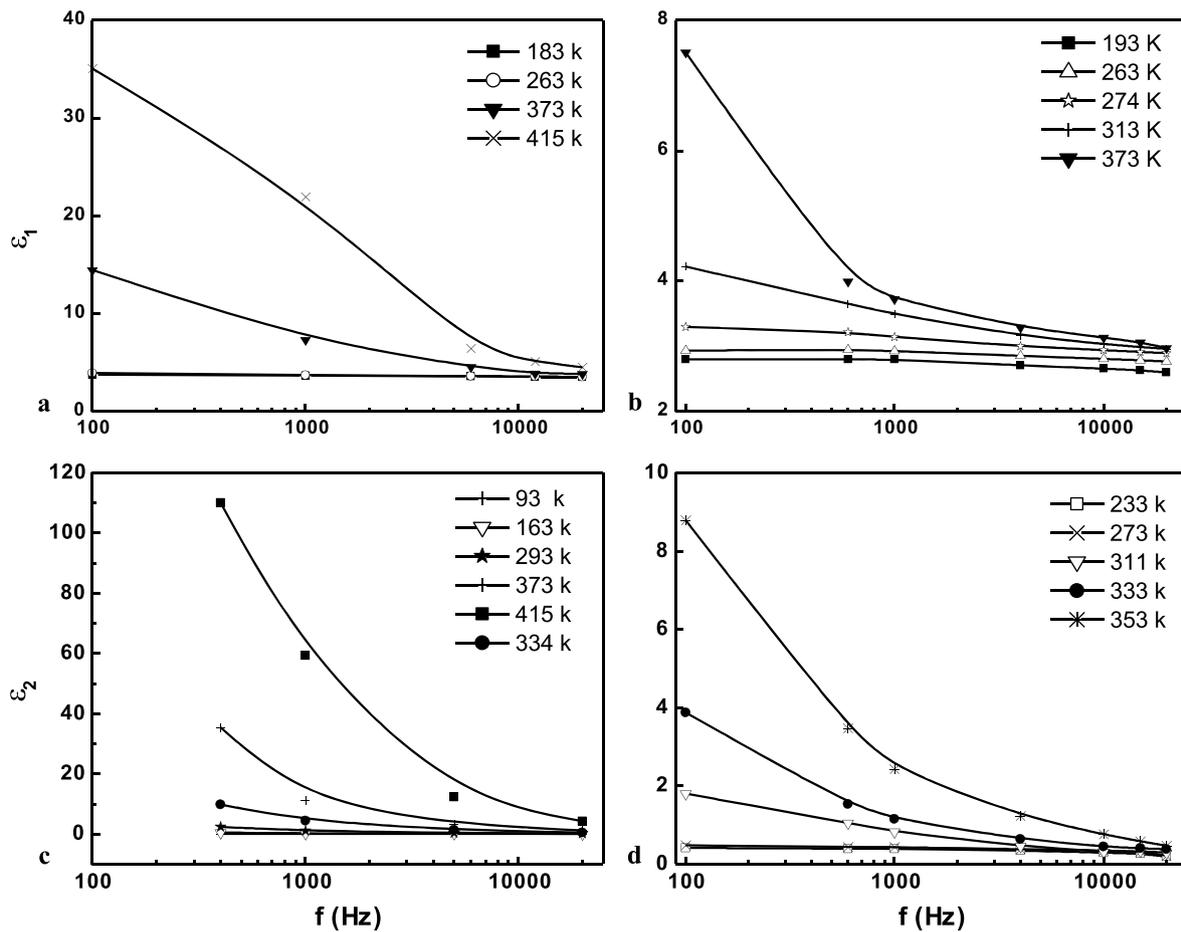
## 2 Experimental procedure

The ZnPc powder obtained from Fluka AG, with a purity of about ~97 % was used to prepare samples in the form of Au-ZnPc-Au and Al-ZnPc-Al sandwich films. ZnPc thin films with different thicknesses were prepared by the thermal evaporation technique using Edward's coating unit [17, 18]. A typical sample of ZnPc thin film has an active area of  $12 \mu\text{m}^2$  and a thickness range of 0.5–1.7  $\mu\text{m}$ . The experimental procedure can be summarized as follows: The surface electrode was evaporated from a molybdenum boat onto pre-cleaned corning glass substrates. Then the ZnPc film was deposited, and the second electrode was deposited at low rates in order to avoid damage of the surface of ZnPc film. During all stages of depositions, the evaporation rate and film thickness were continuously monitored by a Maxtek quartz crystal unit. The ZnPc thin films with different electrode materials (Au or Al) were thermally evaporated at a pressure of approximately  $10^{-3}$  Pa onto the substrate that was held at room temperature. The fabrication of the sandwiched film structure took place without breaking the vacuum, using a home-made sequential masking system [33].

The ac electrical measurements were performed at a pressure of less than  $\sim 10^{-3}$  Pa in subsidiary vacuum chamber, designed to minimize both stray capacitance and ambient gases [33]. A homemade liquid nitrogen cryostat was used for electrical measurements. The temperature of the sample was measured by a calibrated chromel-alumel thermocouple over a temperature range 90–470 K. The thermocouple was connected in series with an automatic relay and a digital temperature thermometer, which allowed controlling the temperature automatically with an accuracy of  $\pm 1$  K. Stabilized power supply incorporated with a digital electrometer was connected to the sample via short leads, and then measurements were recorded by a microprocessor. Capacitance, loss tangent, and conductance were measured in the frequency range 0.1 to 20 kHz and temperature range 90–470 K using a Hewlett-Packard LCZ meter equipped with a four-terminal test fixture. More details on the sample preparation and ac-measurements can be found elsewhere [13, 14, 17, 18].

## 3 Results and discussion

The dielectric functions (dielectric constant,  $\varepsilon_1$ , and the dielectric loss,  $\varepsilon_2$ ) are calculated from the measured ca-



**Fig. 1** Dependence of  $\varepsilon_1$  and  $\varepsilon_2$  on frequency at different temperatures for Au-ZnPc-Au sample (a and c) and Al-ZnPc-Al sample (b and d), respectively

capacitance between the electrodes and the loss tangent  $\tan \delta$  [17, 18]. The dielectric constant,  $\varepsilon_1$ , is calculated from the measured capacitance data using the equation:

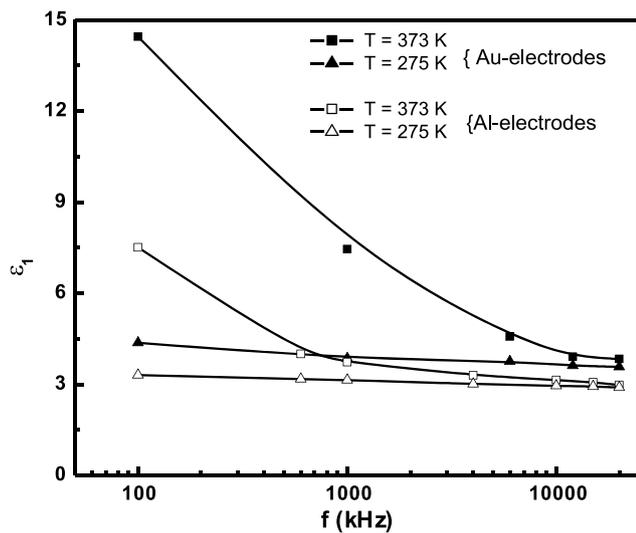
$$\varepsilon_1 = \frac{Cd}{\varepsilon_0 A} \quad (1)$$

where  $C$  is the dielectric capacitance,  $A$  is the effective area of the film,  $d$  is the film thickness, and  $\varepsilon_0$  is the permittivity of free space. Additionally, the dissipation factor or loss tangent,  $\tan \delta$ , is used to calculate the material dielectric loss,  $\varepsilon_2$ , according to the following relation [31]:

$$\varepsilon_2 = \varepsilon_1 \tan \delta \quad (2)$$

The derived values of,  $\varepsilon_1$  and  $\varepsilon_2$ , as a function of frequency at different fixed temperatures for both Au-ZnPc-Au, and Al-ZnPc-Al thin film samples are displayed in Fig. 1. Figure 1a (or c), and b (or d) show the variation of  $\varepsilon_1$  (or  $\varepsilon_2$ ) with frequency for Au- and Al-electrodes, respectively. Both functions of  $\varepsilon_1$  and  $\varepsilon_2$  are strongly dependent on frequency and temperature. Such variation depends on the temperature and the frequency range of interest. Below room temperature,  $\varepsilon_1$  and  $\varepsilon_2$  variation with temperature is weak and their

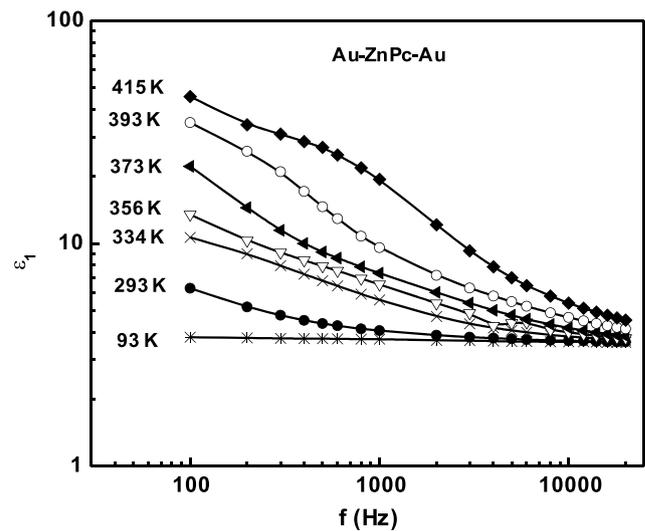
corresponding values are almost constant over all frequency-ranges of this study. However, as the temperature increases,  $\varepsilon_1$  and  $\varepsilon_2$  variation with temperature is very strong at low frequencies, while at higher frequencies, both  $\varepsilon_1$  and  $\varepsilon_2$  saturates to a constant value. Qualitatively speaking, the behavior of the ZnPc-sample sandwiched between Au- or Al-electrode is found to have the same trend over the entire temperature range of study and a considerable frequency dependency of both  $\varepsilon_1$  and  $\varepsilon_2$  values have been observed. For both electrodes, a high degree of dispersion in the dielectric functions,  $\varepsilon_1$  and  $\varepsilon_2$ , is observed at low frequencies. Both of  $\varepsilon_1$  and  $\varepsilon_2$ , show strong frequency dependency and fast large variations below about 10 kHz particularly at high temperatures, while above this frequency and for all temperatures, the variation of dielectric functions slows down and eventually becomes almost constant at high frequencies. Other researchers observe similar frequency and temperature behavior of  $\varepsilon_1$  and  $\varepsilon_2$  in CuPc, FePc, MgPc, H<sub>2</sub>Pc, and ZnPc [15, 23, 34]. No loss peak in the dielectric loss function,  $\varepsilon_2$ , is observed over the entire current frequency range of interest. This type of behavior is particularly inter-



**Fig. 2** The variation of  $\varepsilon_1$  with frequency at 275 K and 373 K for ZnPc sample with Au-electrodes (solid symbols) and ZnPc sample with Al-electrodes (open symbols)

esting, since most dielectric properties in polymeric materials are dispersive at low frequencies, reflecting relatively high activation energies for the motion of molecular units and chain segments [35]. The behavior of dielectric functions can be interpreted as follows: In the low frequency region, all types of polarizations (electronic, orientation, space charge polarizations, etc.) are expected to be present. As the frequency increases, the overall polarization decreases, and at higher frequencies the dielectric functions become almost frequency independent. Accordingly, the high values of  $\varepsilon_1$  observed at low frequencies and high temperatures may be attributed to the formation of space charge layers created at the electrode sample interface due to the ionic migration [21, 22, 25, 26, 36]. Nobre and Lanfredi [36] attributed the dispersions to the presence of atomic defects, which give the structure great flexibility and capacity to form solid solutions. Furthermore, this type of dispersion behavior is generally observed in dielectrics whereas a conduction hopping-type mechanism is present [23, 25, 26].

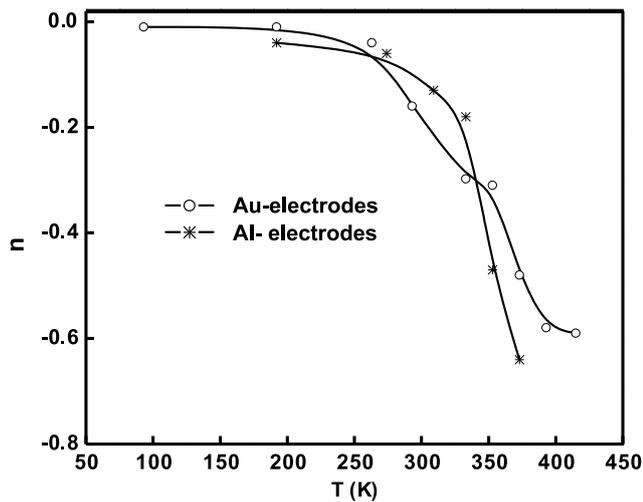
As could be seen from Fig. 1, the calculated dielectric functions,  $\varepsilon_1$  and  $\varepsilon_2$ , values of the Au-electrodes sample are higher than those of Al-electrodes at a specific temperature. In Fig. 2, the data of  $\varepsilon_1$  as a function of frequency are replotted at two specific temperatures: 275 K and 373 K. At a temperature of 275 K, the values of  $\varepsilon_1$  for Au-ZnPc-Au thin film sample are slightly higher than those of the Al-ZnPc-Al sample. This disparity of  $\varepsilon_1$  values might be attributed to packing density of the sample, impurity concentration, and thickness variation [37]. However, as the temperature is increased to 373 K, the variations of  $\varepsilon_1$  values become more pronounced especially in the low frequency region. When the temperature is raised up, more and more charges are injected from the electrode material to the in-



**Fig. 3** The variation of the real part of the dielectric function,  $\varepsilon_1$ , with angular frequency,  $\omega$ , for Au-ZnPc-Au sample plotted on a log-log scale

terface between the electrode and the ZnPc sample forming a space-charge layer. Such a layer will certainly affect the value of  $\varepsilon_1$  due to variation of charge ejection between Au- and Al-electrode [13, 14, 17, 18, 23]. Another interesting observation is that at a higher frequency,  $\varepsilon_1$  of the Au-ZnPc-Au sample saturates to a constant value while  $\varepsilon_1$  of Al-ZnPc-Al saturates to a different constant value. This behavior might be accredited to the fact that at high temperatures the jump frequency of the mobile ion is large and it matches with the frequency of the applied electric field at resonance [25, 26, 35].

The observed logarithmic variations of the dielectric function,  $\varepsilon_1$ , with angular frequency,  $\omega$ , are exhibited in Fig. 3. As it can be seen from the figure, the general behavior of such variations is not linear over the whole frequency range, but an approximately linear behavior can be seen over certain frequency ranges. Strictly speaking, a linear behavior can be traced during the frequency ranges: 0.1–1 kHz, 1.5–9 kHz, 10–15 kHz, and above 15 kHz. This is an indication of a non-Debye type of behavior, where more than one relaxation-time can be attained [38]. Such behavior indicates that more than one conduction mechanisms are involved in the conduction processes in ZnPc films sandwiched between metal-electrodes. The dispersion behavior in  $\varepsilon_1(\omega)$  can be explained in terms of the ion diffusion and polarization model [25, 26, 39, 40]. The increase of  $\varepsilon_1(\omega)$  in the low frequency zone can be attributed to the contribution from polarization of charges. In this frequency region, the ions jump along the field direction and pile up at sites with a high free energy barrier in the field direction after successfully hopping sites with a low free energy barrier. This charge-piling leads to a net polarization of the ionic medium and hence a large contribution to the low frequency value of  $\varepsilon_1(\omega)$ .



**Fig. 4** Dependence of the power index,  $n$ , on temperature for ZnPc sample with Au-electrodes (*open circles*) and Al-electrodes (*stars*)

At high frequencies, the periodic reversal of the field takes place so rapidly that there are no excess ion jumping along the field direction, and hence fast change of  $\varepsilon_1$  are expected. The value of  $\varepsilon_1(\omega)$  remains nearly constant at high frequencies, which is probably the result of a rapid polarization process with no ionic movement contribution due to the rapid field oscillations. At such high frequencies, ions can only oscillate without reaching the sample electrode interface [41].

The variation in  $\varepsilon_1(\omega)$  with frequency could be described quantitatively by a law having the form [23, 25, 26, 34, 39, 40]:

$$\varepsilon_1(\omega) = A\omega^n \quad (3)$$

where  $A$  is a constant depending on temperature, and  $n$  is a temperature-dependent exponent assuming negative values ( $n < 0$ ). Figure 4 displays the variation of the exponent  $n$  on temperature for ZnPc samples with either Au- or Al-electrodes. At low temperatures, the index  $n$  is weakly temperature dependent, however, as the temperature increases; the temperature dependency is more prominent. As the temperature increases above 370 K,  $n$  seems to saturate to a constant value of about  $-0.65$  as clearly observed in Au-electrodes. Such frequency-dependency behavior of  $\varepsilon_1$  has been observed in other phthalocyanine compounds like: CoPc pellets [42], MgPc [15], ZnPc [17, 18, 23, 27, 34] and also in some inorganic amorphous compounds and glasses [31, 41, 43–46]. Several theoretical models based on the relaxation caused by the hopping or tunneling of electrons between equilibrium sites have been developed to explain the frequency and temperature-dependence of the frequency exponent,  $n$ , [21–23, 25, 26, 34]. The ac-conduction in many compounds was found to follow the so-called correlated barrier hopping model (CBH) proposed by S.R. Elliott [21, 22]. According to this model, the ac-conductivity

**Table 1** The derived maximum barrier height,  $W_m$ , values for Au-ZnPc-Au and Al-ZnPc-Al thin film

Frequency range (kHz)					T(K)
Au-electrodes			Al-electrodes		
8–20	1–8	0.1–1	5–20	0.5–4.5	
0.401	0.405	0.411			93
0.301	0.216	0.135			163
				0.832	193
				0.543	273
0.281	0.230	0.214	0.857	0.441	295
			0.488	0.335	310
0.221	0.220	0.227	0.507	0.357	333
			0.332	0.281	353
0.227	0.227	0.227	0.236	0.206	375
0.257	0.275	0.257			393
0.262	0.262	0.272			415

is directly proportional to angular frequency  $\{\sigma(\omega) \propto \omega^s\}$  and the charge carrier hops between sites over the potential barrier separating them and the value of exponent  $s$  is predicted to increase toward unity as the temperature tends to approach absolute zero. Many research reports showing evolving hopping models reported values of less than unity for the frequency-power index  $s$  [13–15, 17, 18, 21–23, 27, 42–46]. As it can be seen from Fig. 4, at low temperatures, the value of  $n$  is almost constant, and this indicates a charge hopping mechanism is dominant [13, 14, 17, 18, 23, 27]. Accordingly, the CBH model is suitable to describe the  $\varepsilon_1$  {or  $\sigma(\omega)$ } dependency on temperature for ZnPc thin films sandwiched by Au- or Al-electrodes. In the correlated barrier hopping, CBH, model, the ac-conductivity frequency-exponent,  $s$ , could be approximated to first order by a relation of the form [13, 14, 17, 18, 23, 34, 46–48]:

$$s = 1 - \frac{6k_B T}{W_m} \quad (4)$$

where  $W_m$  is maximum barrier height of ZnPc films,  $T$  is the absolute temperature and  $k_B$  is the Boltzmann's constant. The derived values of index  $s$  from the slopes of curves of  $\ln \sigma$  versus  $\omega$  strongly suggest that a hopping conduction mechanism was dominant at low temperatures and all frequencies, while at higher temperatures, thermally-activated band conduction process is evident [13, 14, 17, 18].

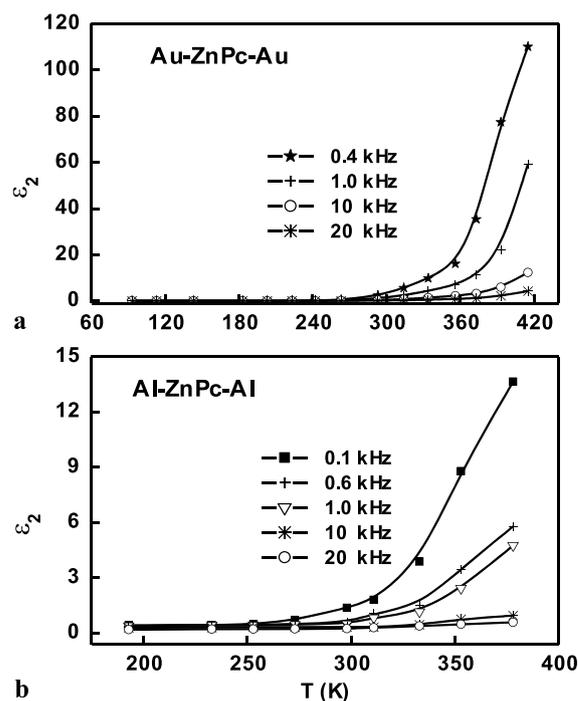
Equation (4) was employed to estimate the values of the barrier height width,  $W_m$ , for ZnPc films sandwiched between Au- or Al-electrodes. The values are tabulated in Table 1. As can be noticed from the table,  $W_m$  is strongly temperature and frequency dependent. The variation of the values of  $W_m$  for ZnPc with Au-electrodes and those for Al-electrodes is partially due to electrode material and the resulting interface between the electrodes and ZnPc films. In addition, impurity concentration, packing fraction and

charge piling within the sample have also great effect in  $W_m$  values. It is worth mentioning here that in some cases a very thin oxide layer ( $\text{Al}_2\text{O}_3$ ) formed between Al-electrode and Pc film [13, 14, 23, 49, 50]. The obtained results of the barrier height,  $W_m$ , are in a good agreement with the ZnPc results [23, 49].

The dielectric loss, ( $\varepsilon_2 = \varepsilon_1 \tan \delta$ ), exhibits similar behavior as that of  $\varepsilon_1(\omega)$  and no loss peak in the frequency range 0.1–20 kHz is observed (Fig. 1b & d) as in  $\text{H}_2\text{Pc}$  [34]. At low frequencies, values of  $\varepsilon_2$  are found to be much higher than its values at higher frequencies and at specific temperatures. Similar results are observed in ZnPc, FePc, CuPc, and PbPc thin films [15, 21, 22, 34, 49–51]. An upward trend in  $\varepsilon_2(\omega)$  at low frequencies (lower than 0.1 kHz) is attributed to dc conductivity with electrode polarization, i.e., the conduction loss is predominate. As  $\varepsilon_2$  describe the electromagnetic wave absorption, its general behavior can be interpreted on the basis of wave absorption. This can be explained as follows: Energies of incident waves are absorbed during the electron excitation from the valence to the conduction band. Therefore, under the influence of the field, ions move through the network, and thus generate conduction losses. At lower temperatures and higher frequencies, the capacity for mobility decreases, and consequently the conduction losses decreases [52, 53]. Therefore, the dielectric loss behavior at lower temperatures is mainly attributed to thermally activated relaxation of freely rotating dipoles, where thermal energy is the only type of relaxation. At higher temperatures and lower frequencies, it is due to electrical conduction with the hopping motion of ions [54]. At lower frequencies, ions hop easily out of the sites with low free energy barriers in the electric field direction and tend to accumulate at sites with high free energy barriers. This leads to a net polarization of the ionic medium and gives higher dielectric constant values [55]. However, at a high frequency, the charge carriers will no longer be able to rotate rapidly enough, so their oscillation will begin to lay behind this field resulting in a decrease of dielectric constant [55]. This is an indication that conduction loss is predominate and an analysis of the obtained data for the dielectric loss dependence on frequency, shows that  $\varepsilon_2$  should follow a power law of the form:

$$\varepsilon_2 = B\omega^m \quad (5)$$

where  $B$  is a temperature-dependent constant and  $m$  is a frequency-power index. The power index  $m$  is a temperature dependent, which could be derived from the slopes of the straight lines of  $\log \varepsilon_2$  vs.  $\log \omega$ . Negative values of  $m$  were obtained (between 0 to  $-1$ ) for all inspected samples over the frequency-temperature range of interest. Such behavior in  $\varepsilon_2$  has been previously observed in other phthalocyanine thin films like ZnPc [23] and CoPc pellets [42, 58]. This type of dependence is in good agreement with the Giuntini et

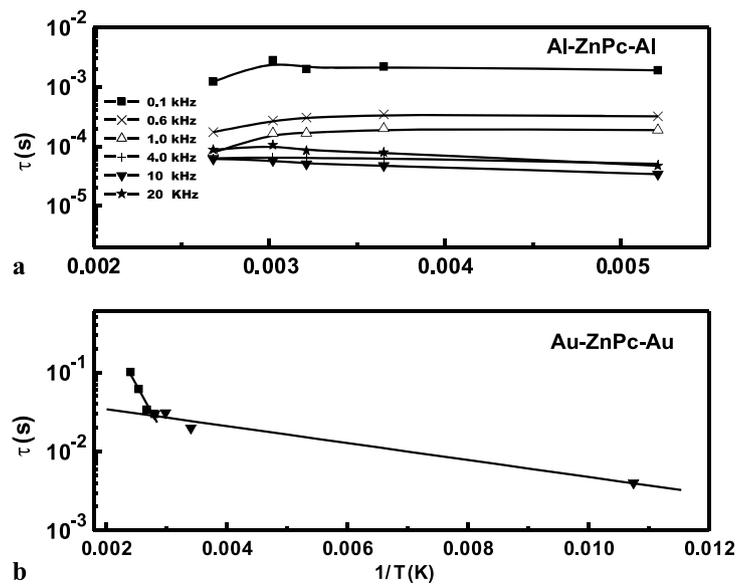


**Fig. 5** Dependence of the dielectric loss function,  $\varepsilon_2$ , on temperature at different fixed frequencies for ZnPc sample with either Au- or Al-electrodes

al. model for describing dielectric behavior of chalcogenide glasses [57, 58].

The dependencies of dielectric functions on temperature are also important tools to examine the normal or relaxing of the dielectric behavior of the medium. Figure 5a (or 5b) demonstrates the variation of  $\varepsilon_1$  (or  $\varepsilon_2$ ) on temperature at different constant frequencies for Au-ZnPc-Au and Al-ZnPc-Al sample, respectively. As can be seen from Fig. 5, the dielectric functions are almost constant below 250 K, and then, they start increasing steadily with increasing temperature. At higher temperatures and low frequencies, the increase in  $\varepsilon_1$  (or  $\varepsilon_2$ ) is very rapid with no observed loss peak at any temperature. This behavior is typically observed in polar dielectrics in which the orientation of dipoles is facilitated with rising temperature, and thereby the dielectric constant is increased [38]. Similar behavior of the dielectric function was observed in other organic metal-phthalocyanine compounds [13–15, 23, 42, 48, 49]. The observed behaviors of  $\varepsilon_1$  and  $\varepsilon_2$  on temperature may be attributed to the enhanced conductivity through the thermal excitation of the charge carriers. At low temperatures, the contribution of electronic and ionic components to the total polarizability will be small. As the temperature is increased, the electronic and ionic polarizability start to increase. The increase of dielectric functions is due to several factors as: charge accumulation, impurity concentration, electrode type, and bonding defects generated in the film network. The produced defects thus create easy path-

**Fig. 6** Dependence of relaxation time on inverse of temperature: **a**; for Al-ZnPc-Al sample at different fixed frequencies, and **b**; for Au-ZnPc-Au sample at a fixed frequency



ways for the migration of charges that would build up space charge polarization and facilitate an increase in the dielectric parameters [39, 40]. In some cases, the Al-electrode gives blocking contact (Schottky barrier to ZnPc), while the Au-electrode provides Ohmic contact [17, 18, 41]. Such behavior greatly affects the conductivity of the sample, hence the dielectric properties. It is worth mentioning that the electrical properties in many compounds, such as phthalocyanines, are significantly affected by the preparation conditions and the presence of impurities such as  $O_2$  [13, 14, 41, 49]. Consequently, heating as well as annealing samples at high temperatures stabilize the electrical properties due to oxygen desorption and structural modifications [4, 13, 14, 17, 18].

The general dependence of dielectric functions on temperature may be represented for temperatures above 290 K by an empirical relation of the form [29, 59, 60]

$$\varepsilon \approx A e^{-B \frac{T}{T_0}} \sinh\left(-B \frac{T}{T_0}\right) \quad (6)$$

where  $A$ ,  $B$  are frequency-dependent constants, and  $T_0$  is a characteristic temperature. The dependence of  $\varepsilon_2(\omega)$  on temperature is characterized by no dielectric loss peak at any temperature; this makes the determination of characteristic frequency  $\omega_m$  for the dielectric loss is not possible according to Hunt's model [59, 60]. However, it can be approximated from Fig. 5b by picking up a certain fixed value of  $\varepsilon_2(\omega)$  and by moving up with increasing temperatures. Then the frequency belonging to each temperature curve is estimated by making a projection on the frequency axis. For instance, at a certain value of  $\varepsilon_2(\omega)$  {for example, taking  $\varepsilon_2(\omega) = 0.5$ }, the corresponding frequency values at different temperatures could be determined from Fig. 5. The ob-

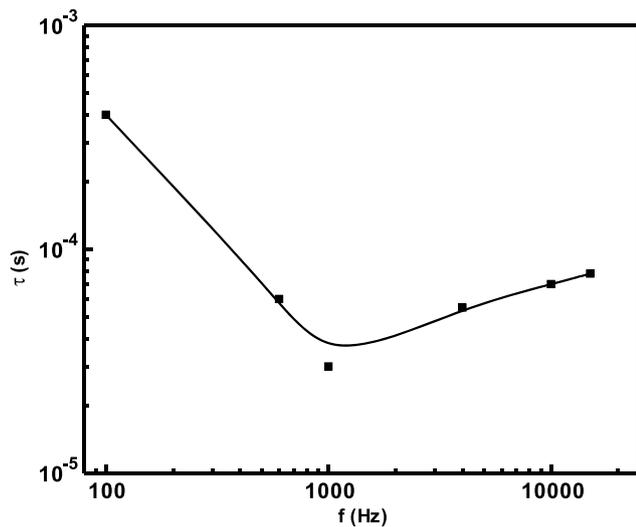
served variation of angular frequency,  $\omega$ , with temperature may follow an Arrhenius relation of from [15, 29, 59, 60]:

$$\omega = \omega_0 e^{-\frac{E_\tau}{k_B T}} \quad (7)$$

where  $E_\tau$  is the activation energy for dielectric loss and  $k_B$  is Boltzmann's constant. The activation energy,  $E_\tau$ , of dielectric loss was calculated from the slopes of the least square fit of the data. It is worth mentioning here that the Arrhenius law is valid for both low and above the characteristic frequency  $\omega_m$  in general. The average (or the most probable) spread of relaxation-time,  $\tau$ , can be extracted from the angular frequency value  $\tau = 2\pi/\omega$ . The reciprocal temperature dependence of  $\tau$  satisfies the Arrhenius relation represented by [23, 43, 54]:

$$\tau = \tau_\infty e^{-\frac{E_\tau}{k_B T}} \quad (8)$$

where  $\tau_\infty$  is the relaxation-time at infinite (very high) frequency. The calculated relaxation-time values of Al-ZnPc-Al films are plotted against the inverse of temperature,  $T$ , (on a semi-log plot) for different frequencies are demonstrated in Fig. 6a. Almost a linear relation between the relaxation time and  $1/T$  is observed at low temperatures and it decreases as frequency is increased (except at  $f = 15$  kHz). The relaxation-time increases with decreasing temperature up to 330 K, and after that the dependence is almost linear. The Arrhenius temperature dependence of the conductivity is indicative of a process with activation energy such as ionic diffusion. Accordingly, the temperature dependence of  $\tau$  in a thermally-activated process is generally described by Eq. (8) [15, 23]. Two linear relations between  $\ln \tau$  and  $1/T$  are clearly revealed in Fig. 6a. These two lines are evidence for the transition in ZnPc films from one conduction process (hopping) to temperature-activated band one. Additionally, a partial  $\alpha$ -phase to  $\beta$ -phase transition may affect



**Fig. 7** Dependence of the characteristic time,  $\tau_{\infty}$ , on frequency for Al-ZnPc-Al sample

the relaxation time due to structural change from tetragonal to the monoclinic hence affecting the dipole dimension and orientation [17, 18, 55].

Alternatively, the relaxation time,  $\tau$ , for Au-Zn-Pc sample was calculated from the values of  $\varepsilon_1$ ,  $\varepsilon_2$  at different temperatures using the following relation [23, 61].

$$\tau = \frac{\varepsilon_2}{\omega(\varepsilon_1 - \varepsilon_{\infty})} \quad (9)$$

where  $\varepsilon_{\infty}$  is the optical dielectric constant at very high (infinite) temperature. The optical dielectric constant,  $\varepsilon_{\infty}$ , was determined from extrapolating  $\varepsilon_1 - f$  curves (Fig. 1) at different constant temperatures [34]. The dependence of relaxation time on temperature for Au-ZnPc-Au sample at a fixed frequency is displayed in Fig. 6b. In this sample, the temperature variation was extended between 90 and 450 K. Two regions are obviously observed: one at low temperatures ( $T < 300$  K) where a hopping conduction process is dominant, and the other at higher temperature where a temperature-activated process is prevailing.

Using the least square fitting technique, the activation energy,  $E_{\tau}$ , and  $\tau_{\infty}$  for ZnPc-thin film sample could be estimated from the slope and intercept of  $\ln \tau$  versus  $1/T$  curves of Fig. 6a. The calculated values of  $\tau_{\infty}$  for all frequencies and  $E_{\tau}$  at 0.6 kHz (for the Al-ZnPc-Al sample) were found to be about  $2 \times 10^{-5}$  s and 0.024 eV. The small value of activation energy is a confirmation of electron-hopping process is dominant [15, 17, 18, 21–23, 45]. The activation energy and relaxation times values are in good agreement with those found by other researchers [15, 17, 18, 23, 34].

The calculated values of  $\tau_{\infty}$  from Fig. 6a and their frequency dependencies are represented in Fig. 7. It is clear that  $\tau_{\infty}$  has strong frequency dependence below about  $\sim 1$  kHz, however, above this frequency the dependence is weak and

seems to saturate to a constant value above 20 kHz. It is vital to extend the future experimental work up to 500 kHz. The decrease of  $\tau_{\infty}$  with frequency could be explained on the basis of absorption wave phenomenon. At lower frequencies, the mobility of the charge carrier is large and the relaxation-time decreases with increasing frequency; while at higher frequencies, the capacity of charge mobility is reduced, and hence relaxation-time increases slowly as frequency increases [55, 56].

#### 4 Summary and conclusions

The dielectric properties of zinc phthalocyanine, ZnPc, thin films sandwiched between two metallic electrodes, (Au or Al) have been investigated. The temperature and frequency dependence of the dielectric function is greatly influenced by the temperature and frequency range of interest. Both  $\varepsilon_1$  and  $\varepsilon_2$  are decreasing with increasing frequency and increasing with increasing temperature. The rate of the increase by rising temperature is faster at higher temperatures and the rate of decrease by increasing frequency is faster at lower frequencies. The frequency dependence of dielectric functions can be explained by polarization models. At low temperatures, the charge carriers which in most cases have lower thermal energy cannot orient themselves with respect to the direction of the applied field; therefore, their contribution to the polarization and to the real part of the dielectric constant is weak. As the temperature increases gradually, more and more of the bound charge carriers are excited, hence their response to the change in the external field more easily. This in turn enhances their contribution to the polarization, leading to an increase of the real part of the dielectric constant. The high values of the dielectric constant in the present study may be attributed to the increase in space charge polarization process and also to an impurity concentration in the sample. The rapid increment of  $\varepsilon_2$  at relatively high temperatures can be explained in terms of the conduction losses [62].

The variation of the frequency exponent,  $n$  ( $\varepsilon = \omega^n$ ), with temperature for ZnPc thin films indicates that  $n$  increases with decreasing temperature and approaches about  $-0.65$  above 300 K. This result implies that correlated barrier hopping (CBH) model is the most suitable model to describe the dielectric functions dependencies for ZnPc thin films in this temperature range.

The results of the dielectric response indicate that polarization in the sample could be in the form of non-Debye-polarization. The relaxation-time is calculated from Arrhenius plots and dielectric functions  $\varepsilon_1$ , and  $\varepsilon_2$ . The temperature dependence of relaxation-time can be expressed by a thermally-activated process. A relaxation-time of the order of 0.1 ms was estimated in the temperature range between

300 and 400 K. The prevailing conduction mechanism under ac field was found to be electronic hopping at low temperatures and thermally-activated one at higher temperatures. At temperature above 393 K, a partial change of phase from  $\alpha$ -phase to  $\beta$ -phase begins to occur [23, 50].

In conclusion, this study clearly shows that electrode type affects the dielectric behavior of ZnPc quantitatively, but not qualitatively when electrodes provide Ohmic conduction. This study can be extended to fully gain more insight on relaxation-time of phthalocyanine-compound systems using Cole-Cole technique. The proposed investigation should cover a wider frequency- and temperature-range and use other metallic electrode materials such as In, Ag, and Cu. The charge injection from the electrode material to the phthalocyanine compound will greatly influence the dielectric performance. Additionally, other ZnPc phases (such as  $\alpha$ -,  $\beta$ -, and  $\gamma$ -phase) should be addressed to fully understand the dielectric properties for these important and promising organic compounds.

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