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Temperature activated ionic conductivity in gallium and indium phthalocyanines

Sait Eren San^{a,*}, Mustafa Okutan^a, Tebello Nyokong^b, Mahmut Durmuş^c, Birol Ozturk^d

^a Organic Electronics Group, Department of Physics, Gebze Institute of Technology, Gebze 41400, Kocaeli, Turkey

^b Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

^c Department of Chemistry, Gebze Institute of Technology, Gebze 41400, Turkey

^d Department of Physics, Syracuse University, Syracuse, NY 13244, USA

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1. Introduction

Metallophthalocyanines (MPcs), a family of aromatic macrocycles based on an extensive delocalized $18-\pi$ electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific research. There is a growing interest in the use of phthalocyanines (Pcs) in a variety of applications, including non-linear optics [1], semiconductor devices [2], Langmuir–Blodgett films [3], electrochromic display devices [4], liquid crystals [5] and as photosensitizers in photodynamic therapy (PDT) [6]. For non-linear optical applications, MPcs have advantages over the currently used inorganic compounds due to their small dielectric constants [7], fast response times, ease of processability into optical components and their lower cost [1,7]. The structures of MPcs can be modulated in many ways, by changing the peripheral and non-peripheral substituents on the ring in addition to changing the central metal and the axial ligands.

Heavy metals, especially diamagnetic metals, play a major role in photosensitizing and optical limiting mechanisms because they enhance intersystem crossing through spin orbit coupling. This enhancement is desirable as it improves the probability of forming a large population in the triplet state. Axial ligands in MPcs play a key role in preventing or minimizing intermolecular interactions, which causes aggregation in solution. Aggregation can result in the fast decay of excited states. Indium and gallium are useful central metals in MPcs complexes since they are diamagnetic and are able to host axial ligands. Gallium and indium phthalocyanines

ABSTRACT

The effects of introducing gallium and indium metals into phthalocyanine molecules were investigated via temperature and frequency dependent dielectric spectroscopy. The dielectric properties of Ga(III) and In(III) phthalocyanine pellets were measured at frequencies from 1 kHz to 1 MHz in the temperature range 300–530 K. The temperature dependence of the real part of the dielectric constant suggested that these compounds exhibit semiconductor behavior. The activation energy values were calculated from the Arrhenius plots at different frequencies. A distinct transition in these plots indicated the activation of ionic conductivity at higher temperatures.

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have been reported to have good photosensitizing and optical limiting properties [1,7–11].

In the scope of this work, chlorogallium (ClGaPc) and chloroindium (ClInPc) phthalocyanine samples were examined with dielectric spectroscopy (DS). This method is shown to be a reliable tool for investigating molecular scale events and for the optimization of tailored materials [12–14]. The temperature dependence of the real part of their dielectric constants and dielectric loss were measured and analyzed. Activation energies of ClGaPc and ClInPc samples were also calculated at different frequencies. The conductivities and the activation energies of the samples increased at elevated temperatures, which were attributed to the activation of the ionic conductivity with increasing temperature.

2. Experimental

2.1. Sample preparation

2.1.1. ClGaPc

This compound was synthesized and characterized according to the method reported elsewhere [15]. Briefly, a mixture of phthalonitrile (5 g, 0.04 mol), anhydrous gallium trichloride (5.5 g, 0.03 mol), and 20 mL of quinoline (double distilled over CaH₂, deoxygenated) was refluxed for 1 h (particular attention was paid to the exclusion of water during this step). After cooling the mixture to approximately 273 K, the reaction mixture was filtered. The mixture was washed with toluene and methanol and dried at 383 K. The final solid compound had a purple color. Yield: 3.4 g (55%). Anal. Calc. for $C_{32}H_{16}N_8GaC1$: C, 62.22; H, 2.61; N, 18.14. Found: C, 62.75; H, 2.34; N, 18.89%.



^{*} Corresponding author. Tel.: +90 262 605 13 13; fax: +90 262 653 84 97. *E-mail address:* erens@gyte.edu.tr (S.E. San).

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Fig. 1. Chemical structures of gallium(III) and indium(III) phthalocyanines.

2.1.2. ClInPc

Synthesis and purification was as outlined for ClGaPc, except that anhydrous indium trichloride was employed instead of anhydrous gallium trichloride. The employed reagents were: phthalonitrile (5 g, 0.04 mol), indium(III) trichloride (6.6 g, 0.03 mol) in quinoline (20 ml). A purple colored compound was obtained. Yield: 4.1 g (62%). *Anal.* Calc. for $C_{32}H_{16}N_8$ InCl: C, 57.99; H, 2.43; N, 16.91. Found: C, 58.21; H, 2.68; N, 17.23%.

The chemical structures of the gallium(III) (CIGaPc) and indium(III) (CIInPc) phthalocyanines are shown in Fig. 1.

2.2. Electrical measurements

After the synthesis and purification processes, the ClGaPc and ClInPc samples were characterized with dielectric spectroscopy to determine their dielectric properties and activation energies. Samples were pelletized with a hydraulic press at a pressure of 10 tons. The resulting pellets had a 1 mm thickness and 13 mm diameter. A HP 4194A impedance analyzer was employed in the DS measurements. The temperature dependent dielectric response was measured at four different frequencies in the 1 kHz–1 MHz range and the rms amplitude of the instrument was set to ~495 mV. The temperature was monitored by a PT 100 resistor that was in direct thermal contact with the sample. The NOVOTHERM Temperature Control System (NTCS) enabled the monitoring of the temperature in the 300–530 K range with an accuracy >0.1 K. The duration of one frequency sweep at a fixed temperature was approximately 1 min. At each temperature point, the temperature and frequency dependent.

dence of the real and imaginary parts of the dielectric constant were recorded by the automated NTCS setup, shown in Fig. 2.

3. Results and discussion

The complex dielectric expression, $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the real part, and ε'' is the imaginary part of dielectric constant, was utilized in the analysis of the DS results. The real part of the dielectric constant was calculated from the equation $\varepsilon' = C_p d/(\varepsilon_0 A)$, where $C_{\rm p}$ is the parallel plate capacitance, d is the inter electrode distance, ε_0 is the permittivity of free space and A is the area of the sample. The dielectric loss (tan δ), also a critical parameter in DS, was derived from the ratio of the imaginary (ε') and the real (ε') parts of the dielectric constant by using $tan(\delta) = \varepsilon''/\varepsilon'$, where $\delta = 90 - \phi$ and φ is the phase angle. The dielectric loss is also known as the dissipation factor and is typically considered as a characteristic energy loss quantity. The AC conductivity is given by $\sigma = \varphi \varepsilon''$, where ω = $2\pi f$ is the angular frequency. The results of the temperature dependent ε' measurements are shown in Fig. 3. Both samples exhibited similar trends as the temperature and frequency were increased; ε' had a constant value of ~6 at low temperatures and started to increase as the temperature was further raised at frequencies of 1 kHz–1 MHz. The increase rate of ε' declined as the frequency was increased; it varied between approximately 9-59 for ClGaPc and 7.5–28.5 for ClInPc at T = 525 K for the reported frequencies. The onset temperature, where ε' started to increase, had varving values at different frequencies. As is shown in Fig. 3a, the onset temperature values were approximately 370, 410, 450 and 490 K at 1 kHz, 11.6 kHz, 132 kHz and 1 MHz, respectively for the ClGaPc sample. For the ClInPc sample (Fig. 2b), the onset temperature values were approximately 350, 390, 430 and 480 K at 1 kHz, 11.6 kHz, 132 kHz and 1 MHz, respectively. Pcs are known as functional dielectric materials, and these results suggest that they have acquired semiconductor properties with gallium and indium insertion. The increasing ε' value with the decreasing frequency is attributed to the blocking of the charge carriers at the electrodes.

Temperature scans of both samples for the dielectric loss were also recorded at 1 kHz, 11.6 kHz, 132 kHz and 1 MHz frequencies (Fig. 4). The magnitude of tan δ increased at elevated temperatures for all the frequencies used. The samples showed a significant variation in the temperature dependence of the dielectric loss (dissipation factor). The ClGaPc sample exhibited a strong intermediate peak with a constant value of 0.6 at 1 kHz, 11.6 kHz and 132 kHz



Fig. 2. Experimental set up for temperature dependent dielectric spectroscopy. PC: computer, IA: impedance analyzer, NH: novotherm heating unit, NM: novotherm microprocessor controller unit.



Fig. 3. Temperature dependence of the real part of the dielectric constant at different frequencies, (a) gallium(III) phthalocyanine, (b) indium(III) phthalocyanine pellets.

frequencies (Fig. 4a). The position of the peak moved to higher temperatures as the frequency was increased and moved out of the measured temperature range for the 1 MHz measurement. This peak appeared as a shoulder in the 1 kHz measurement of the ClIn-Pc sample and was absent in the higher frequency measurements (Fig. 4b). These results indicate the presence of dipoles in both samples; the deficiencies of the materials and imperfections lead to the formation of dipoles. The increasing temperature causes faster rotation of the dipoles, which in turn gives rise to the increasing $tan\delta$ values and the movement of the intermediate tan δ peak to higher temperatures with the increasing frequency, showing that both samples are polar [16]. The overall temperature dependent dielectric loss values of ClInPc were lower compared to those for ClGaPc for the measured temperatures and the frequencies except the 1 kHz measurement where the dielectric loss value raised to a higher value than that for the ClGaPc sample at 525 K.

Charge conduction in MPcs is known to have both electronic and ionic components [17]. There is considerable π - π' orbital overlapping between neighboring stacked MPc molecules which results in the formation of a one dimensional electronic conduction path. The metal cations also contribute to the conduction by traveling in the channels formed by the stacked MPc molecules. It is shown that, using the radius scales of synthesized Ga and In in combination with the dielectric behavior of Pcs, it is possible to evaluate the ionic transport parameters. They acquire an intrinsic impurity



Fig. 4. Temperature scans of the dielectric loss at different frequencies, (a) gallium(III) phthalocyanine, (b) indium(III) phthalocyanine pellets.

state. This phenomenon is explained by the semiconductor structure acquired by centers involved in Pcs *via* the hopping charge transport mechanism [18].

Fig. 5 shows the AC conductivity plots of the ClGaPc and ClInPc samples at different frequencies. The conductivities of both samples increased with increasing temperature and frequency, indicating that the electronic conduction is dominant in the measured range of temperatures and frequencies. The enhancement of the conductivity with increasing frequency suggests that the hopping mechanism is effective in electronic charge transport in both samples at all temperatures. Each curve in Fig. 4a and b had two distinctive regions (I and II) corresponding to different activation energies, satisfying an Arrhenius law of the form:

$$\sigma = \sigma_0[\exp(-E_{\rm I}/(kT)) + \exp(-E_{\rm II}/(kT))] \tag{1}$$

where σ_0 is the pre-exponential factor, E_1 and E_{II} are the activation energies in units of electron volt (eV) and k is the Boltzmann constant. E_1 and E_{II} were calculated from the slopes of $\ln(\sigma)$ versus 1000/T (K⁻¹) plots, shown in Fig. 5. The transition from region I to region II occurs at 388 and 368 K for ClGaPc and ClInPc samples, respectively. The frequency dependent activation energy values in these regions are listed in Table 1. The activation energies of both samples are proportional to the frequency at higher temperatures and inversely proportional at lower temperatures. These results can be understood in terms of the varying contribution of the ionic component to the conductivity at increasing temperatures. The acti-



Fig. 5. Arrhenius plots of the AC conductivity for the (a) ClGaPc and (b) ClInPc samples at different frequencies.

vation energy declines with the increasing frequency in region II, suggesting that electronic charge transport is the dominant component in the conductivity at lower temperatures. As the samples reach the transition temperatures, the ionic conductivity is activated through the dissociation of the metallic cations from their host molecules (region I). Cationic species start to flow in the channels formed by the stacking of MPc molecules. The ionic component contribution enhances the increase rate of conductivity in region I along with the further enhanced electronic transport at higher temperatures. There is a decline in the increase rate of the ClInPc sample conductivity at lower frequencies associated with the higher dielectric loss, as shown in Fig. 3, for those frequencies at higher temperatures. A second effect that is more general to both samples at all frequencies in this region is the increase in the activation energy with the increasing frequency. This effect is attributed to the slower response of the ionic conductivity mechanism to the higher frequency fields at temperatures closer to the transition point. A quantitative analysis may provide specific information about the contributions of ionic and electronic components to the conductivity at varying temperatures and frequencies by using Nyquist diagrams and by defining appropriate equivalent circuits [17]. However, such analysis is beyond the scope of this paper and will not be presented here.

Table 1

ſemi	perature and	l frequency	/ dependencies	of activation	energies o	f ClGaPc and ClInP	c.

E (eV)	ClGaPc		ClInPc	
	Region I	Region II	Region I	Region II
	(388–530) K	(304–388) K	(368–530) K	(304–368) K
1 kHz	0.55216	0.35806	0.36724	0.47241
11.6 kHz	0.56965	0.35369	0.41145	0.43099
132 kHz	0.73686	0.12245	0.49863	0.17008
1 MHz	0.85373	0.07845	0.56793	0.09303

There are many serious works revealing the current advances in phthalocyanines as newsworthy and living materials in technology [19–24]. Our attempts to exploit DS for the characterization of these functional materials are presented in this work.

4. Conclusions

Temperature dependent dielectric properties of ClGaPc and ClInPc compounds were analyzed to determine the dielectric properties of these Pc complexes after the insertion of gallium and indium metals. Ga and In embedded Pcs showed the standard temperature dependence characteristics of conventional semiconductors. The temperature dependence of the conductivities of both samples exhibited Arrhenius behavior. Our results suggest that the ionic conductivity is activated at elevated temperatures in both samples. A detailed analysis of the dielectric properties of hybrid Pcs with gallium and indium metals was performed for the first time in the scope of this work. These metal embedded Pcs can be utilized as building blocks in a variety of semiconductor based new applications, such as solar cells and OLEDs. Our results can be exploited in the design of these new devices, which could be of critical importance in electronics.

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