

Study on Structural and Dielectrical Properties of some Chloroquinoxaline Derivatives

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Abstract

The structural, thermal and electrical properties of three chloroquinoxaline derivatives are investigated by X-ray diffraction (XRD) and differential scanning calorimetric (DSC) techniques. It is found that the chemical composition affected the structure and thermal stability of each derivative. The dielectric properties of the three derivatives are investigated in the frequency range 100 Hz - 5MHz and in the temperature range 300 - 470 K. The behaviors of the real and imaginary parts of the dielectric constant is investigated. Also, the AC conductivity as a function of both temperature and frequency is studied. The charge carrier's conduction mechanism is found to follow the quantum mechanical tunneling (QMT) model. The complex bulk modulus is also investigated.

Keywords: Dielectric properties; Conductivity; Bulk modulus.

Introduction

The organic substances are classified as polymer, monomer and organic compounds. The investigation of these classes of materials has created completely new scientific concepts and potential for their application of perspective in molecular electronics. They mostly contained an extended π -electron system which can be transformed from a semiconducting state to a conducting state [1]. As active components in electronics and optoelectronics applications, they are of increasing interest. Since they are versatile, low cost and ease of production, they represent a valid alternative to conventional inorganic semiconductor technology in a number of applications, such as flat panel displays, organic field effect transistors, photovoltaic cells, illumination, plastic

integrated circuits and organic light-emitting diodes. Although initial commercial applications of this technology are now being realized, a deeper scientific understanding is still needed in order to achieve optimum performance of the device [2]. Owing to its uses in many technical applications. Organic compounds have gained particular attention such as: molecular switch, temperature indicator devices, temperature sensitive light filters, imaging systems and storage of energy. In this present work we introduce some chloroquinoxaline compounds which contain heterocyclic compounds with benzene ring and a pyrazine ring. Quinoxaline 1;4 dioxide provides number of applications in biology [3] and electronics [4]. It was found that the presence of functional groups and different substituted groups on the quinoxaline derivatives affected their physical properties [5]. Quinoxaline and its derivatives showed

non-linear optical behavior and can be applied in optical devices such as solar cells [6]. Quinoxaline derivatives are also thermally stable, as they begin to decompose at 200 °C [7]. In this study, the structural, and electrical properties of three newly synthesized quinoxaline derivatives in bulk form are presented. To the best of our knowledge the structural and electrical properties of these derivatives have not been investigated yet.

Experimental

Materials

The compounds under investigation in present work are three heterocyclic Chloroquinoxaline compounds namely: 8-Chloro-1-oxo-2-phenyl-1,2-dihydropyrido[3,4-b]quinoxaline 5,10-dioxide (1), (E)-6-Chloro-3-(2-(4-(dimethylamino)benzylidene)hydrazine-1-carbonyl)-2-methylquinoxaline 1,4-dioxide (2) and (E)-6-Chloro-2-(3-nitrostyryl) quinoxaline 1,4-dioxide (3). These compounds have been synthesized previously in the laboratory of the Department of Chemistry, Faculty of Science, Damietta University by Samy B. Said et al. [8]. The chemical composition of these compounds is shown in Fig. 1.

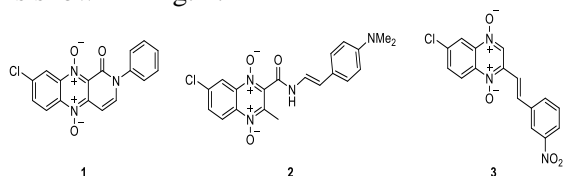


Fig.1: The molecular structural of compounds 1 ,2, and3

Measurements and Characterizations

X-ray diffraction (XRD) measurements

XRD patterns of the investigated powder samples are determined by X-ray diffractometer (Shimadzu XRD 6000). XRD measurements were performed at a scan rate of 2 degrees per second with CuK α radiation source (wavelength of 0.15406 nm), generator voltage of 40 kV, generator current of 30 mA at room temperature.

Differential scanning calorimetric (DSC).

DSC is a thermal analytical technique in which the difference in the amount of heat required to

increase the sample's temperature and the reference is measured as a function of temperature. DSC measurements are performed in the temperature range 300 – 673 K using Shimadzu DSC-50 in nitrogen atmosphere at a flow rate of 10 mL / min using the aluminum cell and a temperature increase rate of 10 ° C / min.

AC Electrical measurements.

The powder of samples 1, 2, and 3 is compressed by a hydraulic press under a pressure of 10 tons/cm² at room temperature to form pellets. The thickness and surface area of each the pellet is about (0.5 mm and 21 mm²), (0.58 mm and 25 mm²) and (23 mm and 20 mm²) for samples 1, 2 and 3, respectively. Silver paste is used to make Ohmic contacts onto the two sides of the pellets. The AC electrical measurements are performed using LCR bridge model 3522-50 HIOKI. The measurements are performed in the frequency range 100Hz – 5 MHz and in the temperature range 320 – 460 K.

Results and discussion

X-ray diffraction analysis

XRD patterns for powder compounds 1,2 and 3 are shown in Fig 2. It is noticed that compounds 1 and 2 demonstrate polycrystalline and amorphous phases due to the presence of many sharp peaks which are accompanied with a broad hump at around $2\theta \approx 25^\circ$. Also it is noticed that compound 3 has no sharp peaks and has only a hump at $2\theta \approx 25^\circ$ Fig 3. This confirms that this compound has a completely amorphous phase. To determine the crystal structure of compounds 1 and 2, Fullproof software [9] is used to find suitable solutions for the XRD peaks and Checkcell software [10] is also used for indexing the peaks. According to the results obtained from the theoretical analysis by FullProf and Checkcell software, the best solutions for the two compounds showed that they both have monoclinic system but with different space groups. The best space group for 1 and 2 are P2₁/a and P2₁, respectively. The lattice parameters for 1 and 2 are presented in Table 1. Also the calculated miller indices for 1 and 2 are tabulated in Tables 2(a,b), respectively. The average crystallite size, L, can be calculated by using the following Scherrer's

equation [11]:

$$L = \frac{0.98\lambda}{\gamma \cos \theta}, \quad (1)$$

where γ is the width at the half-maximum peak

intensity, measured in radians, λ is the X-ray wavelength and θ is the Bragg's angle.). the values of the average crystallite size for 1 and 2 are calculated and found to be 35.5 nm and 25.6 nm, respectively.

Table 1: Lattice parameters of Chloroquinoxaline derivatives.

Compound	a (Å)	b (Å)	c (Å)	α°	β°	γ°	Crystal system/ Space group
1	21.4108 ± 0.0152	12.6393 ± 0.0058	7.4320 ± 0.0058	90	97.67 ± 0.142	90	Monoclinic/ P2 ₁
2	20.8532 ± 0.0282	6.7970 ± 0.0043	16.7048 ± 0.0243	90	124.26 ± 0.076	90	Monoclinic/ P2 ₁ /a

Table 2 (a): Miller indices of derivative 1.

Peak No.	$2\theta_{\text{obs}}$	$2\theta_{\text{cal.}}$	$\Delta(2\theta)$	h k l
1	8.1304	8.1304	-0.0052	<u>1</u> 10
2	10.8807	10.8807	0.002	2 <u>1</u> 0
3	11.9993	11.9993	-0.0068	0 0 <u>1</u>
4	13.9986	13.9986	-0.0037	0 2 0
5	14.6174	14.6174	0.004	<u>1</u> 20
6	16.3356	16.3356	0.023	<u>2</u> 20
7	18.8485	18.8485	0.0336	<u>3</u> 20
8	19.6064	19.6064	-0.0169	<u>2</u> 21
9	21.4712	21.4712	-0.0147	<u>1</u> 30
10	22.7085	22.7085	0.0178	<u>2</u> 30
11	24.3293	24.3293	0.0106	0 3 <u>1</u>
12	25.1532	25.1532	-0.0077	6 0 0
13	26.0931	26.0931	0.0074	4 2 <u>1</u>
14	26.6536	26.6536	-0.0289	<u>3</u> 12
15	27.9977	27.9977	-0.0218	0 2 <u>2</u>
16	28.8849	28.8849	-0.0224	<u>6</u> 20
17	30.9672	30.9672	-0.0043	<u>3</u> 40
18	32.21	32.21	-0.0489	0 3 <u>2</u>
19	36.6062	36.6062	0.0361	0 0 <u>3</u>
20	42.5577	42.5577	-0.0136	1 0 0

Table 2 (b): Miller indices of derivative 2.

Peak No.	$2\theta_{\text{obs}}$	$2\theta_{\text{cal.}}$	$\Delta(2\theta)$	h k l
1	6.3844	6.3967	-0.0123	0 0 <u>1</u>
2	10.7821	10.7862	-0.0041	<u>1</u> 02
3	12.9161	12.925	-0.0089	<u>3</u> 01
4	14.1336	14.1388	-0.0052	<u>1</u> 11
5	17.0603	17.0408	0.0195	<u>4</u> 02
6	20.1449	20.2226	-0.0777	<u>3</u> 10
7	22.8218	22.8181	0.0037	<u>4</u> 13
8	24.3711	24.3604	0.0107	2 <u>1</u> 2
9	25.3653	25.3591	0.0062	<u>2</u> 14
10	26.0066	26.0181	-0.0115	<u>6</u> 02
11	27.0103	26.9977	0.0126	0 2 <u>1</u>
12	28.38	28.3861	-0.0061	3 <u>1</u> 2
13	39.5161	39.5234	-0.0073	3 <u>1</u> 4
14	44.4739	44.4786	-0.0047	6 2 <u>1</u>

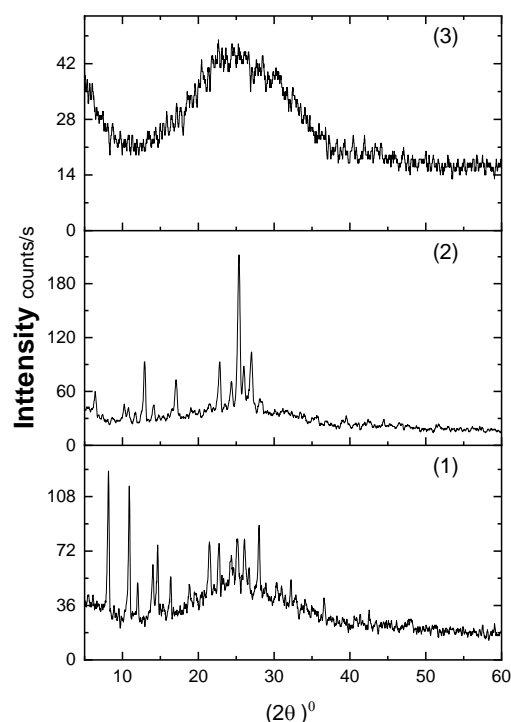


Fig. 2: X-ray diffraction pattern (XRD) for the compound 1,2 and 3 in powder form.

Differential scanning calorimetric (DSC) analysis

The DSC charts for compound 1,2 and 3 are presented in Figs.3 (a,b and c) respectively. Fig. 3a demonstrates a single exothermic peak at 496 K. This result confirms that compound 1 is thermally and chemically stable up to ≈ 473 K and starts to decompose at higher temperature. In compound 2 (Fig.3b), the DSC chart demonstrates one endothermic peak at ≈ 525 K which may correspond to melting process and exothermic peaks at 538, 556, and 583 K which may be appeared due to multi stages decomposition process. Also, compound 3 (Fig.3c), shows the same thermal and chemical stability as compound 1 but to higher

temperature (≈ 488 K) while an endothermic peak appeared at ≈ 517 K corresponding to decomposition.

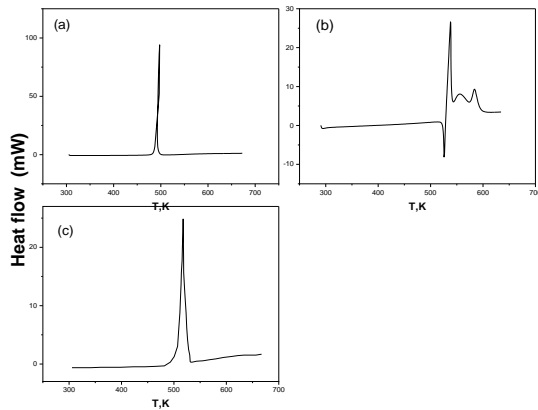


Fig. 3: DSC thermo graphs for compound 1 (a), compound 2 (b) and compound 3 (c).

AC electrical properties

Dielectric functions relate the electron transitions between energy bands of a solid to its structure; hence we may obtain useful information from the dielectric spectrum on the band structure of a solid. The dielectric constant is an important element in the design of capacitors, and knowing the properties of materials that can create capacitance. Smaller capacitors can also be manufactured using materials with a large dielectric constant, as is the case in electronics and printed circuit boards. The complex dielectric constant (ϵ^*) can be determined from the measured values of the capacitance measured in parallel mode (C_p), and loss tangent ($\tan\delta$). The measured values of C_p and $\tan\delta$ for three materials under investigation are presented in Figs.4 and 5, respectively. The complex dielectric constant can be expressed as [12]:

$$\epsilon^* = \epsilon_r + i \epsilon_i, \quad (2)$$

in which its real part, ϵ_r , and imaginary part, ϵ_i , can be calculated by using the following relations [13,14]:

$$\epsilon_r = \frac{C_p d}{\epsilon_o A}, \quad (3)$$

$$\epsilon_i = \epsilon_r \tan \delta, \quad (4)$$

where ϵ_o is the permittivity of free space, d and A are the thickness and the area of the samples, respectively. The calculated values of ϵ_r and ϵ_i in the temperature range 320–460 K and frequency range 100Hz – 5 MHz are shown in Fig.6(a,b,c) and Fig.7(a,b,c), respectively. The

real and imaginary parts of the dielectric constant for a fixed temperature are found to decrease with increasing frequency. Such behavior reflects dielectric relaxation process occur in the material.

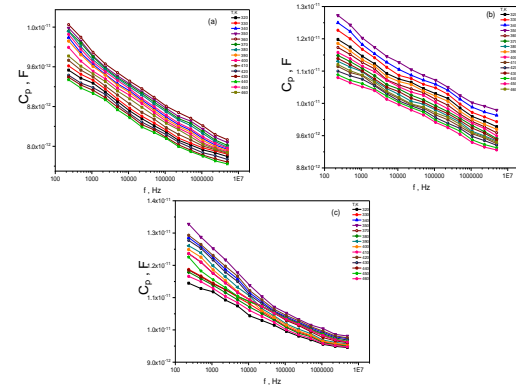


Fig. 4 (a,b,c) :the relation between the capacitance(C_p) and frequency (f) for compounds 1,2, and 3 respectively .

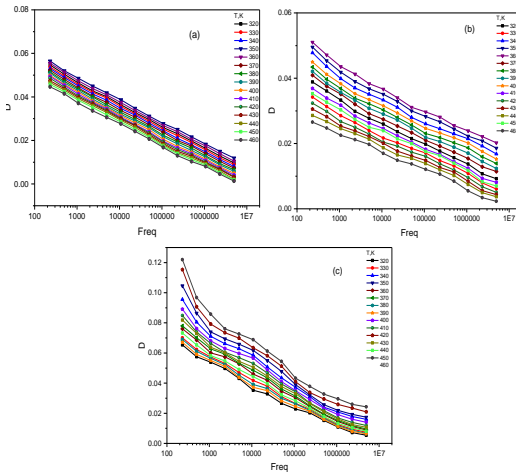


Fig. 5 (a,b,c) :the relation between loss tangent ($\tan \delta$) and frequency (f) for compounds 1,2, and 3 respectively .

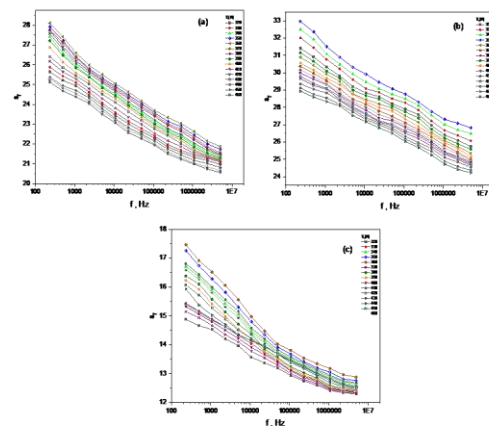


Fig. 6 (a,b,c) : Temperature and frequency dependence of the real part of the dielectric constant for compounds 1,2, and 3 respectively .

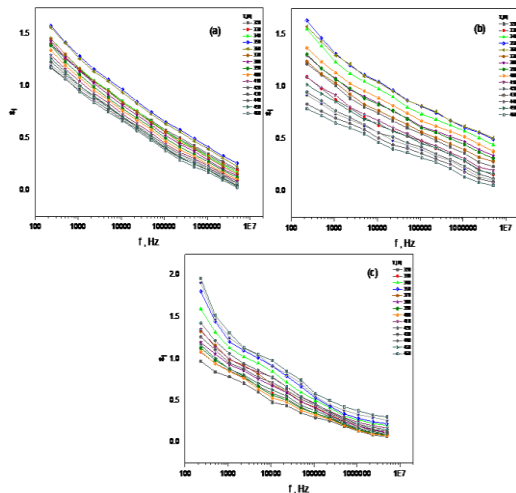


Fig. 7 (a,b,c) : Temperature and frequency dependence of the imaginary part of the dielectric constant for compounds 1,2,and 3 respectively .

The AC conductivity σ_{ac} for the compounds at a fixed temperature can be calculated by using the following relation [14]:

$$\sigma_{ac} = \omega \epsilon_i \epsilon_o, \quad (5)$$

where ω is the angular frequency. The AC conductivity σ_{ac} can be also expressed as [15]:

$$\sigma_{ac} = A^* \omega^S, \quad (6)$$

where A^* is a constant, and S is the power exponent that its behavior with temperature determines the type of charge carrier's conduction mechanism. The dependence of $\log \sigma_{ac}$ on $\log \omega$ at different temperatures for compounds 1, 2 and 3 is shown in Fig.8 (a,b,c). It can be understood that conduction occurs in the samples due to hopping of charge carriers as σ_{ac} is proportional to ω . It is found that all three derivatives have the same behavior. We can notice that the values of σ_{ac} increase with increasing the frequency. This increase of σ_{ac} can be attributed to the increase of the oscillation of electric field accompanied with increasing frequency which will lead to an increase in the polarization in compounds 1,2 and 3 in the form of conductivity increase.

The value of S is directly the slope of the $\log \sigma_{ac}$ versus $\log \omega$ curves at higher frequency region for each fixed temperature. The temperature dependence the exponent S for compound 1,2 and 3 is shown in Fig.9. The value of S is almost constant with increasing the temperature. This behavior recommends the Quantum Mechanical Tunneling (QMT) mechanism to be the dominant mechanism for AC conduction. This

model assumes that the carrier motion occurs through quantum mechanical tunneling between localized (defect) states near the Fermi level. For the QMT mechanism, the real part of the ac conductivity and the exponent S are given by:

$$\sigma_{ac}(\omega) = C'e^2k_B T(\alpha')^{-1}[N(E_F)]^2 \omega R^4 \omega, \quad (7)$$

$$S = 1 - [4 / \ln (1/\omega\tau_0)], \quad (8)$$

where $N(E_F)$ is the density of states at the Fermi level ($\text{cm}^{-3} \text{ eV}^{-1}$), $(\alpha')^{-1}$ is the spatial decay parameter of the localized wave function, τ_0 is the characteristic relaxation time, k_B is Boltzmann's constant, T , is the absolute temperature and C' is a numerical constant for which different values have been obtained by various authors, but can be taken as $\pi/24$ [15]. The above results are obtained in a wide band limit, i.e for $\Delta_0 \gg k_B T$, where Δ_0 is the bandwidth. Thus for QMT model the frequency exponent, S , is temperature independent but frequency dependent.

Bulk Modulus

The complex Bulk modulus M^* is defined as the reciprocal of the complex dielectric permittivity according to the following relation [16]:

$$M^* = \frac{1}{\epsilon^*} = M_r + i M_i, \quad (9)$$

where M_r and M_i are the real and imaginary parts of the electrical modulus, respectively. Both of M_r and M_i can be calculated by use of expressions below [18]:

$$M_r = \frac{\epsilon_r}{(\epsilon_r)^2 + (\epsilon_i)^2}, \quad (10)$$

$$M_i = \frac{\epsilon_i}{(\epsilon_r)^2 + (\epsilon_i)^2}. \quad (11)$$

The behaviors of both M_r and M_i as a function of angular frequency, at different selected temperatures, are depicted in Fig.10(a,b,c) and Fig.11(a,b,c), respectively. M_r is found to increase with increasing frequency, which become more effective in depletion and accumulation regions . On the other hand, M_i decreases with increasing angular frequency.

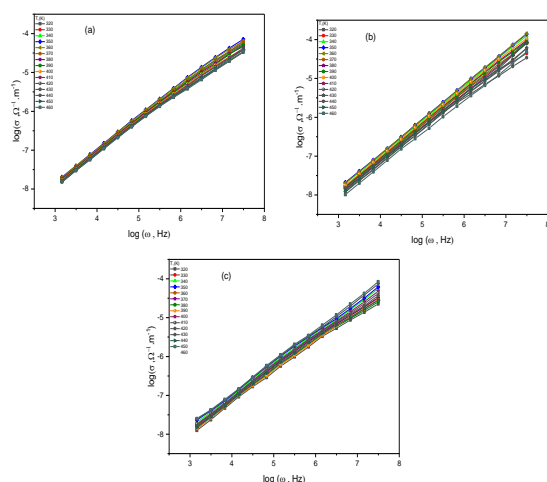


Fig. 8 (a,b,c) :the relation between $\log \sigma_{ac}$ and $\log \omega$ for compounds 1, 2 and 3, respectively .

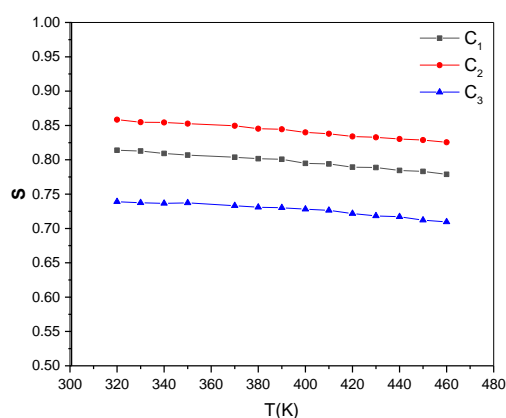


Fig. 9: The dependence of S on temperature for compounds 1, 2 and 3.

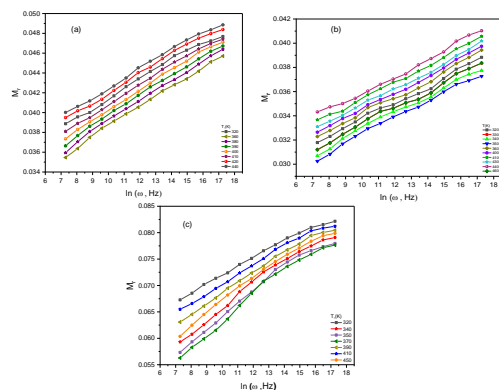


Fig.10 (a,b,c): Real part of the electric modulus, M_r , as a function of frequency for various temperatures for compounds 1, 2 and 3, respectively.

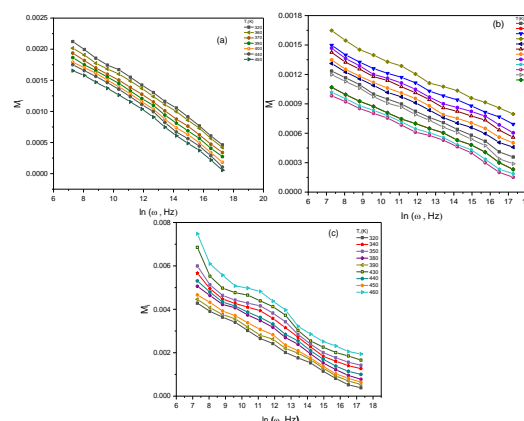


Fig.11 (a,b,c): Imaginary part of the electric modulus, M_i as a function of frequency for various temperatures for compounds 1, 2 and 3, respectively.

Conclusion

Structural, thermal and electrical investigations were performed on three new Chloroquinoxaline derivatives. XRD results of powder form of compounds 1 and 2 demonstrated polycrystalline and amorphous phases. Also, compound 3 had a completely amorphous phase. According to the results the best solutions for the two compounds showed that they both have monoclinic system but with different space groups and lattice parameters. DSC analyses showed that the chemical stability range differs from one derivative to another. Compound **1** is stable up to 473K, compound **2** up to 500 K, and compound **3** up to 488 K. Real and imaginary parts of the dielectric constant for a fixed temperature are found to decrease with increasing frequency. Such behavior reflected dielectric relaxation process occur in the material. AC conductivity σ_{ac} for all three derivatives increase with increasing the frequency. The effect of temperature on the ac conductivity or dielectric properties doesn't follow certain behavior and the change in the values is not much considerable. The value of S for three compounds was almost constant with temperature which recommended that Quantum Mechanical Tunneling (QMT) mechanism was the dominant mechanism for AC conduction. The values of the real and imaginary parts of bulk modulus was estimated and it was found that M_r increased with increasing frequency while M_i decreases with increasing angular frequency.

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الملخص العربي

عنوان البحث : دراسة عن الخواص التكوينية و العزل الكهربائي لبعض مشتقات الكلوروكينوكساليين

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تم التحقق من الخواص التكوينية، الحرارية والكهربائية لثلاثة من مشتقات الكلوروكينوكساليين عن طريق حيود أشعة اكس

والماسح التفاضلي الحراري. وجد أن اختلاف التركيب الكيميائي قد أثر على الخواص التكوينية و الثبات الحراري لكل مركب من المشتقات. تم التحقق من خواص العزل الكهربائي للمشتقات الثلاثة في مدى الترددات من ١٠٠ هرتز إلى ٥ ميغا هرتز و مدى درجات الحرارة من ٣٠٠ إلى ٤٧٠ كلفن. تم التحقق من سلوك المركبتين الحقيقية و التخيلية من ثابت العزل الكهربائي. أيضا، تم دراسة التوصيلية الكهربائية في حالة التيار المتردد كدالة في كلا من درجة الحرارة و التردد. وجد أن آلية التوصيل لحاملات الشحنات تتبع نظام الحفر النفقي ميكانيكي الكم. تم أيضا دراسة معامل الحجم المركب.