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Review Article

Quantum Emphasis on Electro-Chemical Behaviour of an Organometallic Compound: Guanidinium Chromate

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Abstract

The operative electronic, ionic, orientational, or dipolar and interfacial polarizations are made active by imposing an oscillatory electric field to a dielectric material. It is noted that, dielectric material precedes a huge impact on the AC-DC electric conductivity and its dielectric effects. In our current study, guanidinium chromate (GC) compound was successfully synthesized via solvent evaporation method. The sharp peaks of PXRD pattern exhibits atomic arrangements at definite lattices. Moreover, we come up with a mainstream focus on electric and dielectric behaviours of GC compound as a function of temperature with the corresponding frequencies respectively. The impedance data were fitted in the equivalent operating circuit system with the predominant combinations of resistors and constant phase elements (CPE). Complex impedance measurement of GC compound is focused at all the temperature occurrences resulting an improved conductivity with more resistant to frequency at higher temperatures. Imaginary dielectric constant (☐”) and dielectric loss were also predominantly noted and observed to be declining at higher frequencies, suggesting that GC is an appropriate material for high frequency device applications. Further at maximum temperatures and frequencies, the complex imaginary part M" of electric modulus shows a shift in the relaxer peak. On evaluating the results obtained, it is well apprehend that the GC compound could be a propitious candidate for high-frequency device application.

INTRODUCTION

A broad understanding of investigating the dielectric analysis is intensively characterised to scientific techniques that measure changes in various physical properties of a dipolar material with changing temperatures or frequencies, such as polarisation, permittivity, and conductivity. Amine groups like guanidine crystals are serving as useful material for applications in nonlinear optic, electro-optic device [1-3]. Currently, many researches are been carried out to suit guanidine single crystals for the frequency doubling diode. In order to emphasise the frequency influence on both constant and changing temperatures, the basis of dipoles reorientation with applied oscillating electric field on alternating-current measures complex permittivity. During phase transitions (melting or crystallisation) and secondary transitions, a compound's dielectric constant and related polarizability alter quite a bit in comparison to tiny changes in enthalpy, volume, or heat capacity (localized relaxation mechanisms). In an effort to create materials for cutting-edge engineering devices, conducting dielectric materials using macromolecular systems and their molecular structures have been proposed. Dielectric examinations, in particular, also offer the characteristics of discrete constituents and methods for describing the bulk properties, particularly the rheological behaviour of the material under study. The current work makes appropriate physical and chemical alterations to the conjugated structures of cationic guanidine and anionic chromium trioxide in order to explore the protonation between them along the process of polarisation. The ionic conduction behavior inferred from the measurements of the frequency dependent conductivity and dielectric constant. The electrical relaxation in ionically conduction of GC crystal analysed in terms of complex modulus formalism [4,5]. Since knowledge of the sample's composition, structure, and morphology is typically required to comprehend the relationship of a particular molecular or ionic pattern. Due to their intramolecular charge transfer interaction (ICT) processes, organic derivatives' electron transfer mechanisms exhibit notable nonlinear optical (NLO) activity. Large hyperpolarizabilities caused by the intermediate push-pull substituent pairs in molecular systems boost the NLO behaviour of solid materials like crystals [6]. With the help of the associated hydrogen bonding and the well-known extended molecular arrangement, which consists of strong electron donor and acceptor groups, structural asymmetry appears when crystal material is used in NLO applications. Ionic salt crystallisation is designed to produce cohesive crystal structures with sufficient ionic conductivity for their important potential applications in solid state batteries and high density power sources. In many opto-electronic applications, the ability to materialise strong electrical and optical conducting qualities is highly advantageous. To produce bulk single crystals, physical property tailoring is essential. Hence earlier studies on guanidinium chromate's synthesis and some of its physio-chemical properties were published [7]. The current in-depth

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analysis measured the frequency dependence of the dielectric constant and the ac conductivity as a function of temperature. Using electric modulus presentation, the conduction behavior of GC crystal was characterized over wide ranges of frequency and temperature is expanded to reveal the electrical impedence and electric modulus of the GC compound using calculated values for both the intended quantitative and qualitative outcomes.

EXPERIMENTAL PROCEDURE

Synthesis

To make a homogeneous solution using the solvent evaporation approach, the stoichiometric ratio of guanidine carbonate and chromium trioxide with 98.9% purity was dissolved in 250 ml of deionized water and agitated constantly for 6 hours. To make the final product free of impurities, the resulting saturated solution was repeatedly recrystallized at 40 ˚C in accordance with the solubility data provided in the literature [7]. The temperature bath in which the filtered solution was kept was accurate to within 0.01°C. The solution's temperature was lowered by 0.05 ˚C per day until it reached room temperature. Optically clear single crystals of the GC compound of a yellow colour were collected. Finally, to achieve a homogeneous surface, the crystallised GC was pulverised and converted into disc pellets by uniaxial pressing at a pressure of 10tons/cm^2. The prepared pellets were utilized further for structural, optical and electrical characterization studies.

CHARACTERIZATION

Guanidinium Chromate particle is allowed to perform under X-ray diffraction analysis of wavelength 1.5406 Å using Bruker AX500 X-ray with CuKα radiation. The electrical property was examined using a N4L Impedence Analyzer PSM 1735 LCR meter for a frequency 1 Hz–1 MHz at various temperatures ranging from 313K – 373K with a regular interval of 20K for a constant bias voltage.

Impedance measurement

An impedance analyzer was used to obtain complex impedance data over a frequency range of 1 Hz to 1 MHz at four different temperatures (313K, 333K, 353K, and 373) for the pelleted sample, which was then placed between two platinum electrodes (Agilent 4294A).

RESULTS AND DISCUSSION

Structure analysis

The powdered GC sample was subjected to x-ray diffraction analysis using a Reich-Seifert diffractometer with CuK (1.5418) radiation over the range of 10-50, with a scan rate of 2°/min. We confirmed the crystal system and space group as triclinic with P1 space group, respectively, in our earlier publication on the GC crystal [7]. In the current publication, we assessed lattice characteristics from powder XRD spectral patterns and we performed Powder X software to refer the peak indexing. The peak-indexed powder XRD pattern of the GC compound is depicted in Figure 1. The reported single crystal X-ray diffraction data are highly relevant to the estimated lattice parameter values. The spectrum's discrete, sharp diffraction peaks indicate that the produced crystal has a good crystalline nature. Additionally, an increase in the surface-to-volume ratio may be the cause of the broad peak decline with density. Additionally, a significant portion of the evolution of crystal formation is governed by the protonation of ions.

Impedance measurements

Impedance spectroscopy was used to analyse the electrical behaviour of GC compounds by passing an AC electric field through the pelletized sample [8]. The produced electrical response and its corresponding impedance as a function of the frequency of the respective perturbation are examined for a sinusoidal perturbation that the sample experiences. The Nyquist plot from the circuit model could be plotted with the representation of three separate zones [9]. The parallel combination of resistance over the pellet surface and their constant phase is often justified by the intercepts of the semicircle on the real axis. Figure 2 displayed the GC compound's as-obtained Nyquist plot. Different temperatures and different frequencies were used to measure the experimental results. The results of the impedance measurements for the sample's temperature-dependent conductivity are in comparison with the literature [10] and are presented in

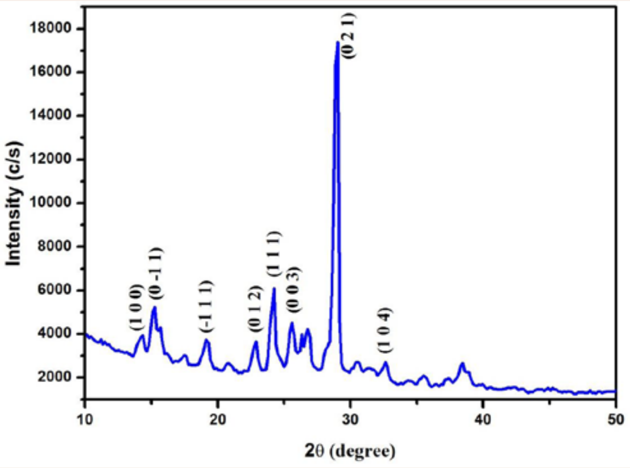


Figure 1 XRD pattern of GC sample.

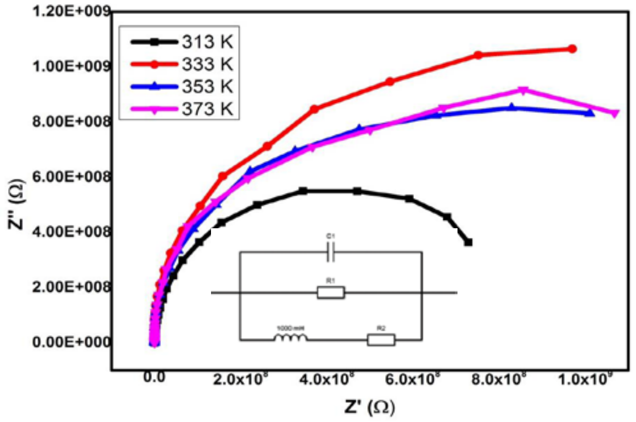


Figure 2 Nyquist plot of GC compound. (Insert. Equivalent circuit for GC compound)

Figure 2. The homogenous and pure phases of the GC sample compound are shown in the as-obtained resulting plot's semi-circular pattern. As the temperature rise, the GC compound's conductivity exponents increased and the radius of the semicircle shrank [11]. As a result, a parallel RC equivalent circuit could be used to build an equivalent circuit to identify the conductivity process, from which the semi-circle plot in the frequency range was developed [12]. Where R and C in the circuit represents sample's geometric resistance and capacitance. The equivalent circuits for the GC sample are described in the inset of Figure 3, and the origin-8.0 programme was used to fit the semi-circles of the Nyquist plot.

Dielectric permittivity

Electrical properties of crystal compounds are largely determined for the energy stored and dissipated by distribution and type of lattice configurations to utilize the material in high frequency device applications [13]. According to their investigations, the higher frequency electrical activity of GC is what makes it a good dielectric compound. At ambient temperature and other higher temperatures, such as 313K, 333K, 353K, and 373K, there have been reports of the frequency range 1 Hz-1 MHz. For the manufactured powder samples of the GC compound, the dielectric parameters (i.e., real and imaginary parts of the relative permittivity, dielectric tangent loss) have been investigated. Figures 3,4 depict the frequency with a real and imaginary part of relative permittivity. The relative permittivity decreases with increasing frequency and eventually becomes strident at high frequency. When the smear frequency increases dramatically, the permittivity declines more quickly in the frequency functions and goes into active [14]. As seen in Figure 3, decreases as the frequency is increased, mimicking the reduction in the number of dipoles, and helps to polarise the system, rendering the dipoles incapable of responding to the applied electric field. The temperature dependence of' GC compounds at a few chosen frequency is shown in Figure 3. To put it another way, the behaviour of' at lower temperatures results from the thermal energy that is absorbed by the dipolar material, and a few dipoles will subsequently rotate in the direction of the applied electric field [15]. As the temperature rises, the viscosity also decreases, giving the dipoles more energy to quickly reorient themselves in the direction of the applied electric field. As a result, ε' rises at higher temperatures. The fluctuation of the dielectric constant with real permittivity (ε') and imaginary permittivity (ε'') with frequency at four different temperatures is depicted in Figures 3,4 respectively. The charts show how frequency is affected in the opposite direction by. The presence of all four polarisation types—interfacial, atomic, dipolar, orientational, or space charge that are necessary to study the electrical behaviour of the dielectric material is suggested by the greater values of ε'' at low frequency.

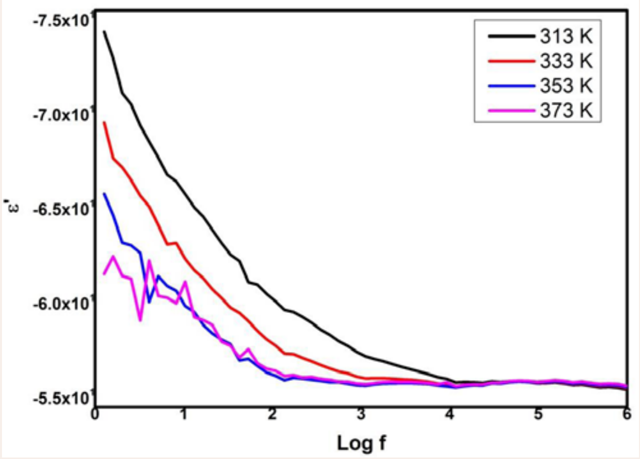


Figure 3 Real permittivity of GC with frequency.

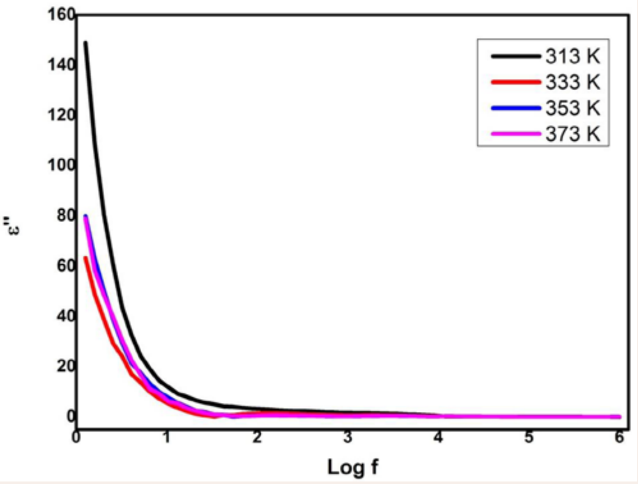


Figure 4 Imaginary permittivity of GC with frequency.

Conductivity studies

The behaviour of a dielectric material with conductive ac conductivity, σ_{ac} which exhibits frequency dependency, is a common electrical feature. The measurement of ac conductivity is regarded as a crucial tool for understanding the ionic transport characteristics of such dielectric materials. In particular, it is understood that charge transfer occurs within the molecule in response to the applied ac electric field in various frequency ranges when an ac electric current flows through a solid dielectric material. It was discovered that the typical universal dynamic response can adequately explain the ac of GC compounds [16, 17]. Figure 5 illustrates the linear behaviour between log (σ_{ac}) and log (f) that was found. This conduction process results from the absorbed energy's increased intensity, which causes an increase in the number of charge carriers. In general, band conduction is what causes the increase in conductivity with regard to frequency. In this discussion, the conduction mechanism attributes to localized or reorientional processes taking place within the material interaction [18]. Figure 5 also shows the temperature dependence of the ac conductivity, σ_{ac}.

Electric modulus

The increase in conductivity with respect to frequency is typically brought on by band conduction. The conduction mechanism is attributed in this discussion to confined or reorientional processes occurring within the material interaction [19]. The temperature dependency of the ac conductivity, σ_{ac}

is likewise depicted in Figure 5. The clearly resolved spectrum at particular frequencies with increasing temperatures at a constant bias voltage characterises the dielectric response of GC compound generated by ion relaxation utilising frequency over a range of temperatures. Because it does not apply to the material in bulk, the reported value of dielectric permittivity at low frequencies and high temperatures is connected to the predominant "interfacial polarizations" [20]. In order to understand the dielectric behaviour of GC compounds and prevent the contribution of electrode polarisation, modulus formalism is first analysed. The real portions of complex electric modulus (M'), which are defined as the inverse of the imaginary parts of complex permittivity, are used in this article to describe the recorded dielectric data in Figure 6 (M"). M' and M' chose traditional methods "utilising common formulae, the electric modulus was determined from the impedance data [21]. Figure 6 depicts the dielectric modulus M' Vs frequency at four different temperatures. It is evident that M' increases with rising frequency and reaches a peak at about 1 MHz. Additionally, the absence of electrode polarisation is shown by the extremely low value of M' (zero) at low frequency. The thermally activated region of the dielectric permittivity is the reason why the values of M' decrease as temperature rises [22]. M's dependence on frequency Figure 7,8 depicts for GC molecule at various temperatures. A maximal asymptotic value of M is where the dispersion of M' is said to saturate with increasing frequency for all temperatures in all higher frequency areas. Such observations might be explained by the absence of a restoring force that prevents charge carriers from being immobilised when subjected to an induced electric field. This results in long-range mobility of charge carriers. Further, the conduction phenomenon of charge carriers at short-range mobility is linked to a sigmoidal increase in the value of M" with the frequency ultimately approaching M".

Dc conductivity

As illustrated in the inset of Figure 9, the complex impedance plane analysis using packed Boukamp equivalent circuit [23] was used to further investigate the direct electrical conductivity, dc, of GC. The sample dimensions and Rb values were directly used to determine the dc conductivity, dc magnitude. According to the hopping conduction process, the thermally induced drift mobility of ions is what causes the dc conductivity to soar with

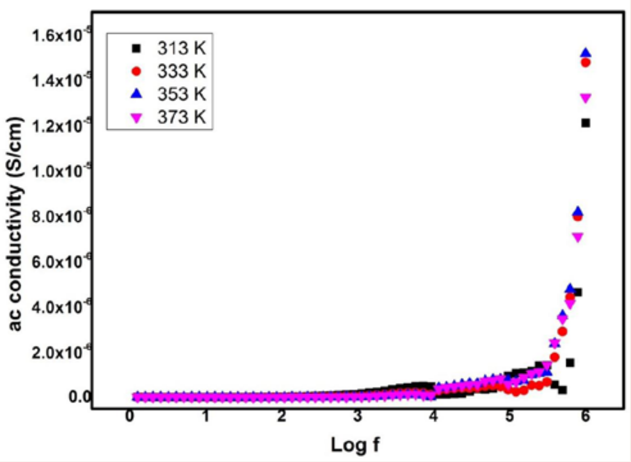


Figure 5 Conductivity analysis of GC material.

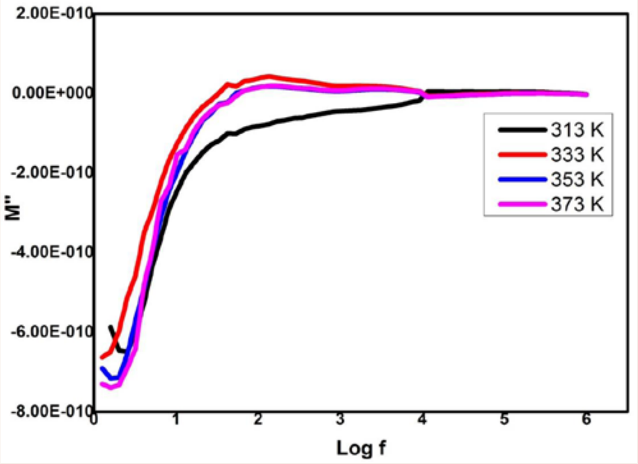


Figure 7 Imaginary parts of electric modulus on GC compound.

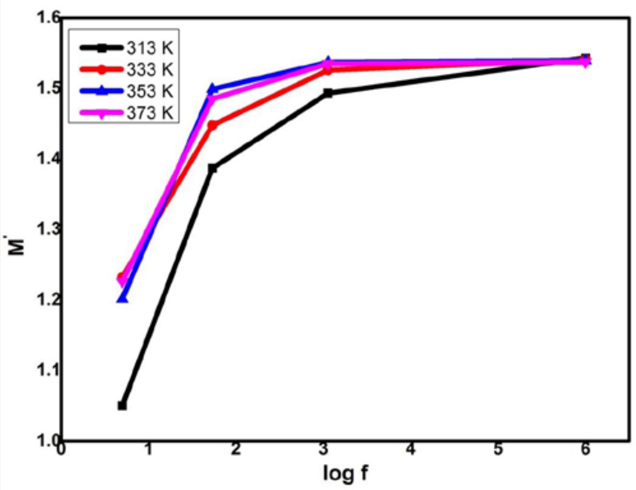


Figure 6 Real parts of electric modulus on GC compound.

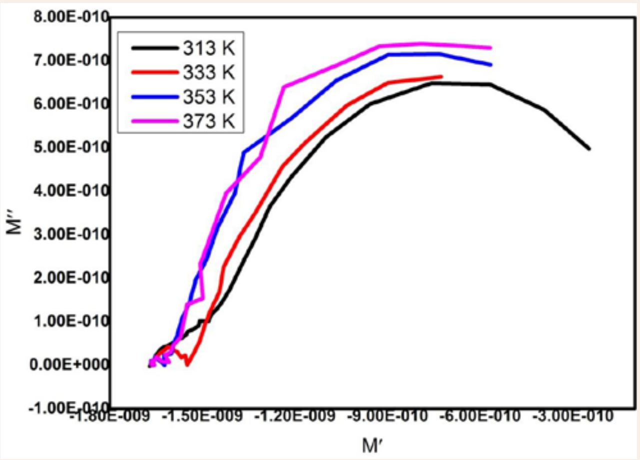


Figure 8 Complex parts of electric modulus on GC compound.

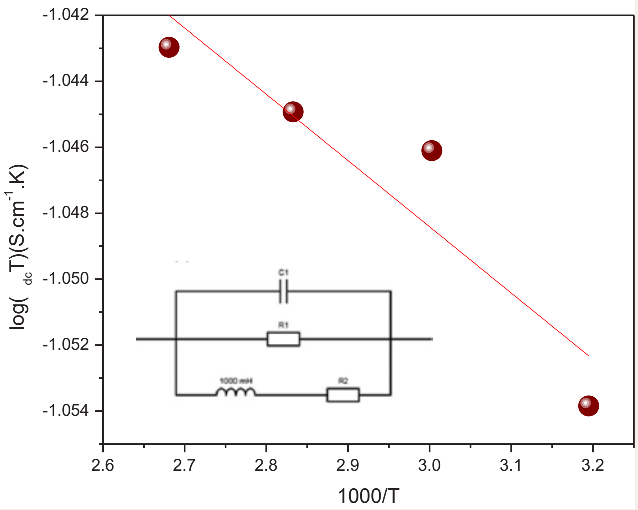
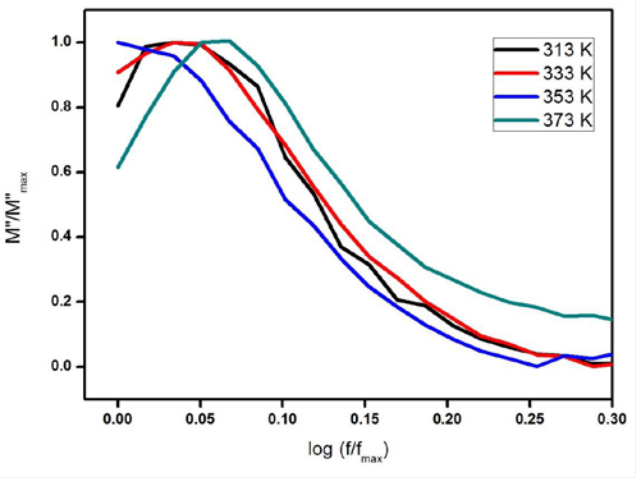


Figure 9 Arrhenius plot of dc conductivity from complex impedance plot.



d Modulus spectroscopy plot for GC compound.

temperature. The Arrhenius relation is used to extract the direct conductivity data:

$$\sigma_{dc.}T = \sigma_0 \exp\left(-\frac{E_a}{TK_b}\right)$$

where, σ_{dc} is the dc conductivity, σ_0 is the pre-exponential factor, T is the temperature in K, *Ea* is the activation energy of dc conductivity and K_b is the Boltzmann's constant. Arrhenius plot of the pelleted GC sample is shown in Figure 9. The slope of the ensuing straight line plot of log (σ_{dc}T) vs reciprocal of temperature 1000/T in Kelvin revealed the conduction mechanism for the organometallic sample with activation energy *Ea*. Within the domain of thermally activated conductivity, the activation energy's quantum magnitude was quantized to be 0.210. The outcome showed that the material's dc conductivity increased as a result of the GC organometallic compound's restriction of electronic mobility.

The frequency temperature superposition (FTS) principle is essential to designate the microscopic mechanisms of organomettalic molecular systems. According to the FTS spectral shapes displayed in Figure 10, it is likely that all of the frequencies relevant to the GC temperature dependency requirements will line up on a single master curve. This evidence supports some similarities in the physical microscopic mechanisms behind different materials processing that are not temperature-dependent [24]. Examples of materials that have been found to adhere to the FTS principle include organometallic solids, semiorganic compounds, semiconductors, and polymeric structures [25]. Figure 10 in the present form, explains the dielectric spectra of the normalized imaginary electric modulus (M"/M"max) parts as a function of the normalized frequency f/fmax parts at four variant temperatures. In addition, it is predominantly considered that both low-frequency (f/fm<1) and high-frequency (f/fm>1) on the relaxation peak is in absolute agreement with FTS functional principle [26].

CONCLUSION

This work presents the findings of the complicated impedance spectroscopy examination into the electrically dependent features of an organometallic combination of guanidine carbonate and chromium trioxide. It has been reported that structural confirmation utilising the PXRD spectrum. The compound demonstrates a dielectric nature, according to the experimental results of the dielectric measurements. The dispersion mechanism in conductivity was primarily seen in the lower frequency area for all specified temperature sources, and the AC conductivity follows the power law. Additionally, the frequency dependence of the AC conductivity of the organomettalic compound GC at various temperatures indicated that the conduction mechanism was a healthy thermally activated process, and the activation energy was calculated from the DC conductivity. The molecular sample system further supports the relationship between the basic dielectric research and the hitherto unrecognised electric modulus. The possibility of a hopping mechanism for electrical transport processes in organometallic compounds with non-exponential type conductivity has been highlighted by modulus analysis.

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