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Resistive and dielectric response in hafnium diselenide intercalated with copper atoms, under excitation by an alternating electric field

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A joint study of relaxation processes during charge transfer and polarisation change under dynamic excitation has been carried out by impedance spectroscopy in intercalated Cu_xHfSe_2 samples. The maximum values of the imaginary component of the impedance allowed us to determine the relaxation times in the system of mobile charge carriers. A significant frequency dispersion of the real and imaginary components of the dielectric permittivity was found in the used samples. Using the dielectric modulus formalism, dielectric relaxation times decreasing in magnitude with increasing copper content in the samples and with increasing temperature have been determined. It is shown that the dielectric relaxation times appear to be smaller than the relaxation times for charge transfer determined from the frequency dependences of the imaginary part of the complex impedance.

Keywords: hafnium diselenide, copper, impedance, dielectric permittivity, dielectric modulus, relaxation times.

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1. Introduction

Studies of materials with special and practically important electrophysical properties based on phases with low-dimensional structures have been of interest in the scientific and applied aspects in the recent years [1–3]. Among the compounds of this class, much attention has been paid in recent decades to the study of intercalated transition element dichalcogenides with the general formula $MyTX_2$. The presence of a weak Van der Waals (V-d-W) bond between the layers $X-T-X$ is a characteristic feature of their crystal structure, which allows the introduction of the interlayer space contains atoms of other elements. A wide variety of physical properties has been revealed in these compounds, depending on the nature and concentration of interstitial (M) atoms and the type of matrix compound (TX_2). In particular, the formation of superstructures, phase transitions to a state with a charge-density wave, the appearance of a superconducting state, as well as various magnetic states, were observed in titanium dichalcogenides intercalated with $3d$-elements [4–6].

Copper and silver atoms unlike intercalated $3d$-elements, when embedded in the space between $X-T-X$ layers, are transformed into charged monovalent ions. At the same time, they have a spherical electron density distribution and are therefore weakly bound to the dichalcogenide layers. This was evidenced by the nature of the electron density distribution in Cu_xTiS_2 [7], and was also confirmed by data on the determination of concentration dependences of lattice cell parameters in Cu_xTiS_2 and Cu_xTiSe_2, showing an increase of lattice cell parameters a and c, which is typical for interstitial solid solutions [8,9].

A variety of kinetic and magnetic properties were also found in compounds based on hafnium diselenide, which is a chemical and structural equivalent of titanium diselenide [10–12]. Hafnium dichalcogenides, as well as titanium dichalcogenides, crystallize in a structure corresponding to the structural type CdI_2 [13,14].

Their lattice cell contains one layer of HfX_2 with an octahedral environment of metal atoms. Interstitial atoms can occupy only a part (depending on their concentration) of equivalent positions in the Van der Waals gap. Weak bond with the matrix layers and the presence of free equivalent positions makes it possible for ions of group I to migrate within the layer when an electric field is applied. For example, in the study of electrical conductivity in a constant field obtained the data for the first time on the presence of polarization phenomena in hafnium diselenides intercalated with copper and silver atoms [9,15], and the presence of mixed electron-ion conductivity was demonstrated in these compounds [16], which allows them to be considered in as a possible electrode material for electrochemical current sources. A significant frequency dispersion of the real and imaginary components of the permittivity was found in Ag_xHfS_2 system, indicating the existence of dielectric relaxation [17]. The study of materials using alternating current helps to study the properties of materials in the best possible way, since various quantities of a complex nature can be determined in such experiments, including electrical impedance, permittivity, dielectric modulus and electrical capacity. However, the relationship between charge transfer processes and charge accumulation dynamics under alternating excitation has not been studied in detail before. This work is devoted to a joint study of the resistive and dielectric characteristics of Cu_xHfSe_2 ($x = 0.1; 0.2$) compounds under conditions of excitation by an alternating electric field.

2. Experiment

Such materials were synthesized by method of solid-state reactions in vacuum in vacuum-sealed quartz tubes. The starting materials were hafnium iodide (HFI-1), ultra-high purity (UHP) granular selenium of high purity and ultra-high purity (UHP) electrolytic copper. Finished products were synthesized using a two-stage procedure when the initial hafnium diselenide was initially synthesized, and it was mixed with the required amount of copper at the second stage. In our opinion, this made it possible to exclude the direct interaction of free selenium with each of the metals, which is possible in the case of simultaneous synthesis of samples from the initial elements. This was especially true for metallic copper, which forms binary compounds with selenium, such as CuSe and Cu_2Se, which could significantly distort the transport characteristics of the materials under study. The primary and subsequent homogenization annealing after crushing and compaction of the products was conducted at $T = 750°C$ with the duration of each operation not less than 100 hours. X-ray certification of the initial $HfSe_2$ matrix and intercalated samples of Cu_xHfSe_2 was performed using Bruker D8 Advance diffractometer in CuK_α-radiation. It was confirmed that this procedure and the temperature-time regime used ensured the formation of the structure of the studied compounds corresponding to the $1T$-modification of both the initial $HfSe_2$ and copper-containing materials based on it. Figure 1 shows a diffraction pattern of the initial hafnium diselenide processed by full-profile analysis, showing the correspondence of the description of the structure of $HfSe_2$ to the spatial group $P\bar{3}m1$ with parameters $a = 3.742 \pm 0.004$ Å and $c = 6.154 \pm 0.007$ Å, the values of which correspond to the previously received data [13,14].

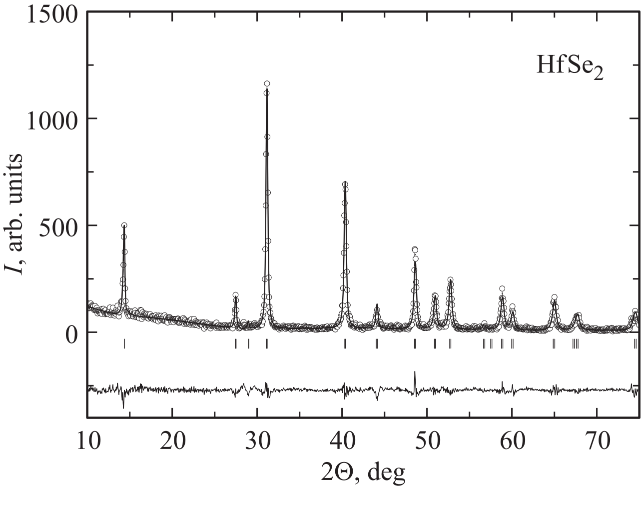

Figure 1. Diffraction pattern of the original compound $HfSe_2$. Points — experimental intensity values, line — calculation, bottom — difference curve between them. The vertical strokes under the diffraction pattern correspond to the angular position of the Bragg reflections for the structural type CdI_2 (SG: $P\bar{3}m1$).

The measurements were conducted using compacted and additionally sintered samples of the same geometric shape at several temperatures in the linear frequency range (ν) from 10 to 5 MHz using universal analyzer Solartron 1260A. The amplitude of the excitation signal for all measurements was 0.2 V. The contact resistance was reduced by applying a conductive paste to the end surfaces of the samples which ensured their equipotence and the same current values over the cross-section of the samples. The analysis of the results was conducted within the framework of an equivalent circuit with a resistor (R) and a capacitor (C) connected in parallel, which is often used as a first approximation for dielectric materials with noticeable conductivity [18,19]. The dielectric characteristics were calculated from the impedance data [20].

3. Results

As a result of the conducted study, data were obtained on the values of the real and imaginary components of the impedance at different AC frequencies and temperatures. Figure 2 demonstrates one of the options of representations of such data for $Cu_{0.1}HfSe_2$ and $Cu_{0.2}HfSe_2$ on the complex plane in the form of dependencies of the imaginary component of the impedance (Z'') of the actual component (Z'), which, in the case of the accepted substitution scheme, may be arcs of regular or distorted circles. As can be seen, the imaginary component of the impedance for the studied $CuHfSe_2$ compounds passes through a peak at certain AC frequencies. The right branches of the spectra (at $\nu \to 0$) indicate the values of the active resistance of the circuit, which, as can be seen, have lower values for a sample with a high copper content. An increase of temperature leads to a shift of the hodographs to the left along the real axis, which is attributable to a decrease of the active resistance characteristic of the activation character of charge transfer. The tendency of the left edge to the origin indicates the absence of any processes at high frequencies and the insignificance of contact resistance.

It can also be noted that the centers of each depicted arc are located below the actual axis. This means that the processes taking place are not fully described by the Debye model with one fixed relaxation time, and the values of the circuit parameters acquire averaged (effective) values. As is often the case when experimental hodographs feature a semicircle compressed along the axis Z'', a constant phase element is introduced into the equivalent circuit, which allows for the dependence of capacitance on frequency, and the capacitance value can be associated with the dielectric properties of the substance and, taking into account the geometric dimensions of the sample, converted into a dielectric permeability [19]. Since the frequency of alternating current

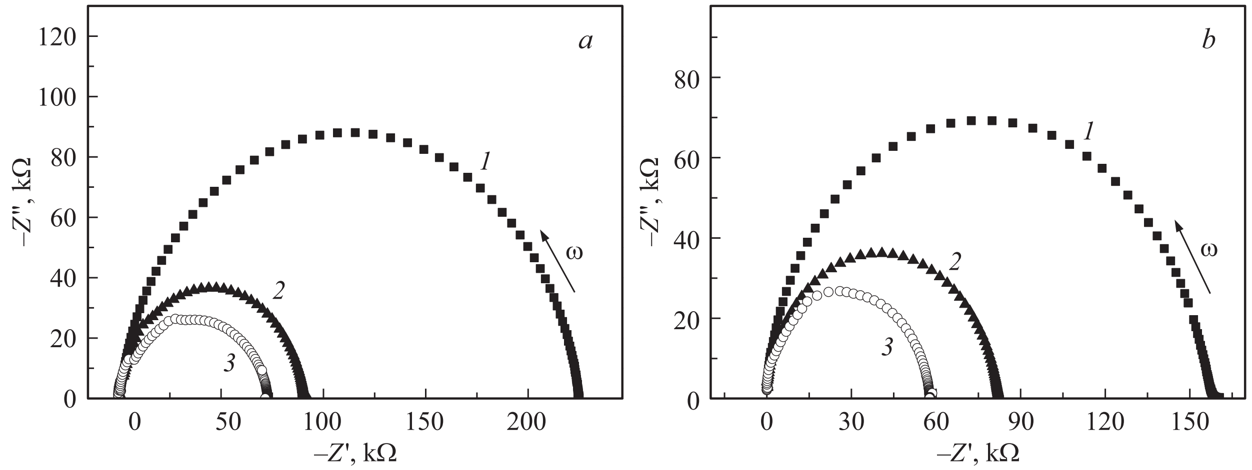

Figure 2. Complex impedance spectra $Cu_{0.1}HfSe_2$ (*a*) and $Cu_{0.2}HfSe_2$ (*b*) at different temperature T, K: *1* — 275, *2* — 296 and *3* — 305.

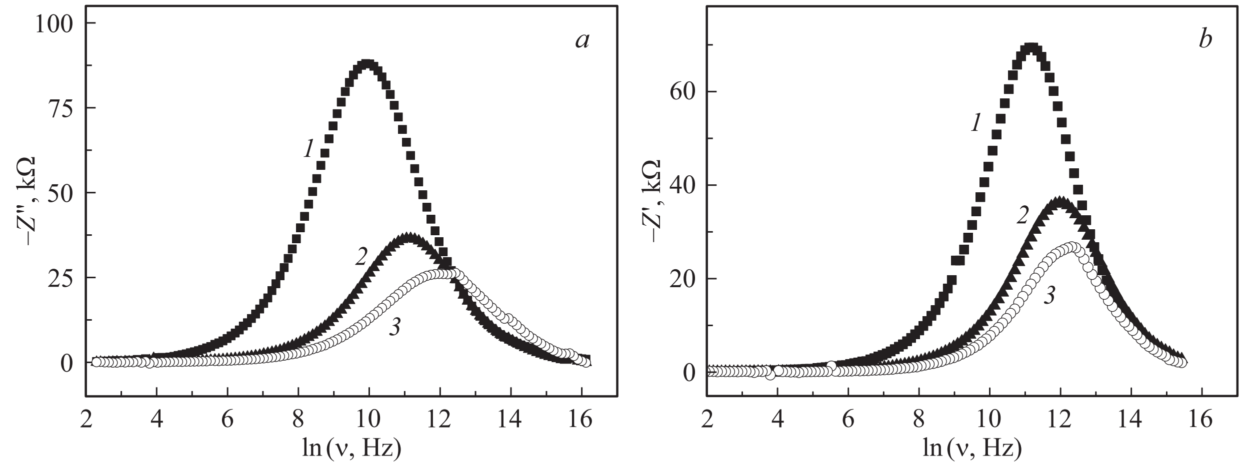

Figure 3. Frequency dependences of the imaginary component of the complex impedance of $Cu_{0.1}HfSe_2$ (*a*) and $Cu_{0.2}HfSe_2$ (*b*) at different temperatures T, K: *1* — 275, *2* — 296 and *3* — 305.

is not explicitly present in the graphs in this representation, Figure 3 shows the frequency dependences of the imaginary components of the complex impedance (Bode diagrams) for samples of different compositions. The values of the cyclic frequency $\omega = 2\pi\nu$, at which the imaginary part of the impedance has a maximum value ($\omega^{Z''}_{\max}$), for samples of different compositions increase with the increase of the temperature (see table). The value $\tau_Z = 1/\omega^{Z''}_{\max}$ is the time constant of *RC*-circuit, which characterizes the average relaxation times as an indicator of the dynamic response to alternating excitation in a system of mobile charge carriers. The data listed in the table indicate an acceleration of relaxation processes during charge transfer in an alternating field, both with an increase of the copper content in the samples and with an increase of the temperature of each of them.

Values of characteristic frequencies $\omega^{Z}_{\max}$ and $\omega^{M}_{\max}$, and relaxation times τ_Z and τ_M, at different temperatures for compounds Cu_xHfSe_2

Compound	T, K	$\omega^{Z}_{\max}$, kHz	τ_Z, μs	$\omega^{M}_{\max}$, kHz	τ_M, μs
$Cu_{0.1}HfSe_2$	275	125	8	280.7	3.56
	296	441	2.26	886.7	1.12
	305	1248	0.8	3843	0.26
$Cu_{0.2}HfSe_2$	275	473	2.11	497.4	2.01
	296	992	1.0	1248	0.8
	305	1407	0.7	1524	0.65

The features and characteristics of the dielectric response are usually determined by the frequency dependences of the dielectric constant, which exhibit a characteristic maximum. However, as shown in Figure 4, the frequency dependences of the real ε' and imaginary ε'' components of permeability for the studied compounds are characterized by a monotonic character, showing a dependence inversely proportional to frequency, which, in particular, may be due to the predominance of energy losses for transport

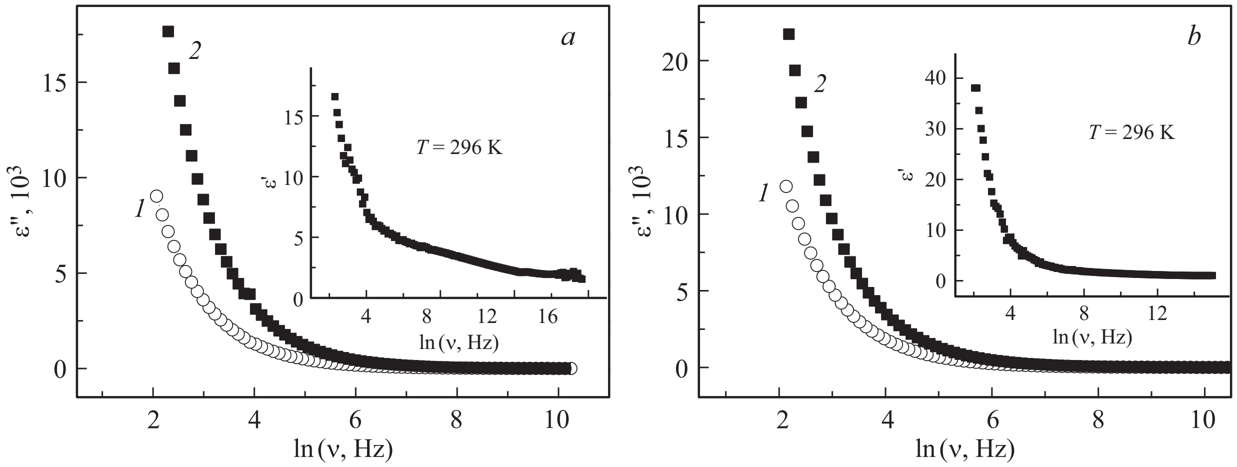

Figure 4. Frequency dependences of the real at $T = 296\,\text{K}$ (in the inserts) and the imaginary component of the dielectric constant of compounds $Cu_{0.1}HfSe_2$ (*a*) and $Cu_{0.2}HfSe_2$ (*b*) at $T = 275\,\text{K}$ (*1*) and $T = 296\,\text{K}$ (*2*).

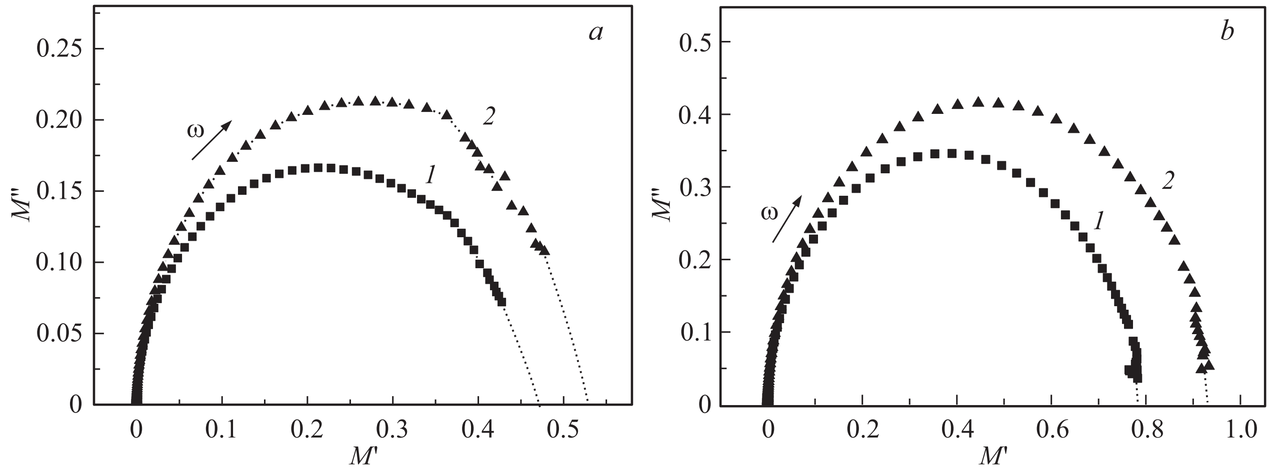

Figure 5. Spectra of the complex dielectric module $Cu_{0.1}HfSe_2$ (*a*) and $Cu_{0.2}HfSe_2$ (*b*) for $T = 275\,\text{K}$ (*1*) and $T = 296\,\text{K}$ (*2*).

charge (conductivity). This does not allow using these data to quantify the characteristics of dielectric relaxation. The method of a complex dielectric module can be used when relaxation peaks on the dependence $\varepsilon''(\nu)$ cannot be observed. This makes it possible to identify the intrinsic dielectric behavior of the materials under study, as well as to investigate the characteristics of relaxation processes hidden by the electrical conductivity of dielectrics, since the values of the real and imaginary components of the module are more influenced by the bulk properties of crystallites. In this case the imaginary part of electrical modulus transforms the low-frequency growth of permittivity into a relaxation peak whose position allows to determine the relaxation time [21–23]. The complex value of the dielectric modulus is the inverse of the complex permittivity and is the sum of the real and imaginary parts $M^* = 1/\varepsilon^* = M' + iM''$, while each of the components is defined as $M' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2)$, and $M'' = \varepsilon/(\varepsilon'^2 + \varepsilon''^2)$ [20,21]. The results of such a transformation are shown in Figure 5 in the form of spectra of a dielectric module on a complex plane, representing arcs of circles. The maximum values of the real part of the module in the limit $\nu \to \infty$ can be used to estimate the value of the high-frequency dielectric constant as $\varepsilon_\infty = 1/M'_{\text{max}}$.

The dependences of M'' on frequency at different temperatures are shown in Figure 6, where their values pass through the peak at certain frequencies — ω^M_{max}. As can be seen, the position of the peaks on these curves in both samples shifts to the region of higher frequencies with the increase of the temperature. The inverse values of frequency ω^M_{max} allow estimating the dielectric relaxation times $-\tau_M$. Calculations show that the relaxation times τ_M decrease with an increase of the copper content in the samples, as well as with an increase of temperature, as well as the values of τ_Z determined from the resistive characteristics, which is attributable to a reduction of the time for changing the sign of polarization in case of change of the polarity of the applied voltage in the first case and an increase of the

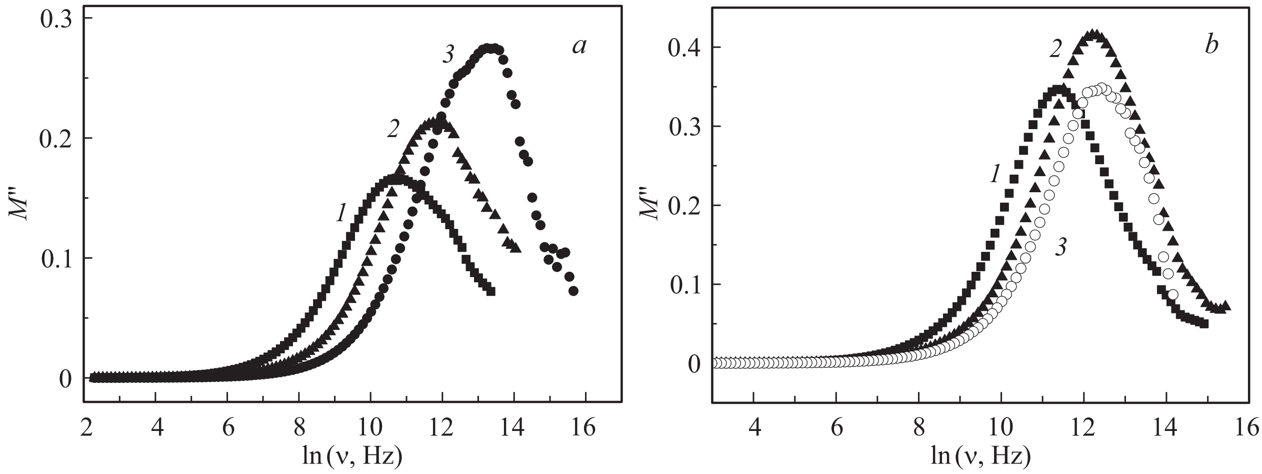

Figure 6. Frequency dependences of the imaginary component of the dielectric module $Cu_{0.1}HfSe_2$ (*a*) and $Cu_{0.2}HfSe_2$ (*b*) at different temperature T, K: *1* — 275, *2* — 296 and *3* — 305.

concentration and/or mobility of charge carriers in case of conductance in the second case. These frequencies and calculated relaxation times are shown in the table.

Analyzing the results obtained, attention should be paid to the fact that the relaxation times τ_M are shorter compared to τ_Z, which indicates that the change in the sign of polarization occurs faster than the response to alternating excitation in a system of mobile charge carriers. An increase of the concentration and/or mobility of such carriers should lead to an alignment of these values, as can be seen when comparing data for $Cu_{0.1}HfSe_2$ and $Cu_{0.2}HfSe_2$.

4. Conclusion

A comparative study of the effect of temperature on the resistive and dielectric characteristics of intercalated Cu_xHfSe samples with different copper contents was conducted for the first time in this paper using the impedance spectroscopy technique. The characteristic frequencies and relaxation times in the system of mobile charge carriers were determined depending on the composition and temperature.

An analysis of the values of the real and imaginary parts of the complex permittivity confirmed the presence of dielectric relaxation in the studied compounds. Relaxation processes in the system of mobile dipoles under alternating excitation turned out to be hidden by conduction losses, leading to a strong increase of the dielectric constant in the low frequency region. For this reason the dielectric data was analyzed in the representation of the dielectric module. It is shown that the modular formalism in this case is more informative for quantifying the characteristics of dielectric relaxation in these materials. This representation made it possible to determine the relaxation times, the values of which decrease with an increase in the copper content in the samples and with an increase in temperature, since the dissipated thermal energy promotes the movement of the formed dipoles in an alternating electric field. At the same time, it was shown that the relaxation times defined in the modular representation turn out to be shorter than those for charge transfer processes determined from the complex impedance data. A comparative analysis of these values shows that an increase of conductivity in a sample with a high copper content leads to a decrease of differences of relaxation times for different subsystems.

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Conflict of interest

The author declares that he has no conflict of interest.

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