

# Ohmic and Dielectric Relaxation in Copper-Containing Hafnium Diselenide

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**Abstract:** In hafnium diselenide intercalated with copper atoms, the components of the complex impedance are measured and the real and imaginary components of the relative permittivity are determined. A strong frequency dispersion of the imaginary part of the permeability is found. The use of the formalism of the electrical module made it possible for the first time for a given material to determine the characteristic times of dielectric relaxation at different temperatures and to estimate the values of the high-frequency dielectric constant.

**Key Word:** hafnium diselenide, intercalation, dielectric constant, electrical module.

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## I. Introduction

Dichalcogenides of transition elements of groups IV and V of the periodic table constitute an extensive class of materials with a natural layered structure. A feature of their crystal structure is the presence of MX<sub>2</sub> structural blocks (M-transition metal, X-chalcogen), between which there is a weak van der Waals (V-d-V) interaction. The introduction of various atoms and ions into the interblock gaps (intercalation) leads to significant changes in the state and physical properties of intercalated compounds in comparison with the initial matrices. Among these compounds, the most studied are titanium dichalcogenides and materials based on them, created by intercalation of 3d and 4f-elements [1-3]. Hafnium diselenide is a chemical and structural analogue of titanium diselenide and also belongs to the class of materials with a quasi-two-dimensional structure described within the framework of the structural type CdI<sub>2</sub>. Compared to TiSe<sub>2</sub>, due to an increase in the unit cell parameters, hafnium diselenide has a wider V-d-V gap, and from this point of view, the interaction between the HfSe<sub>2</sub> layers should be even weaker, and the two-dimensional nature of its structure should be manifested to a greater extent. Intercalation of 1 A group atoms is of interest due to the possibility of significant mobility of the ions of these elements, which provide ionic conductivity in superionic conductors [4]. So, for example, atoms of group 1A of the Periodic table, such as copper and silver, being introduced into this space, are transformed into charged monovalent ions and they have a close to spherical distribution of electron density. Therefore, are weakly bound to the dichalcogenide layers [5], which allows these ions to migrate within the layer upon application of an electric field. For example, in the compound Ag<sub>0.1</sub>HfSe<sub>2</sub>, when studying the electrical conductivity in constant fields, data on polarization phenomena in these materials were obtained for the first time [5]. In an earlier study of the resistive state of intercalated Cu<sub>x</sub>HfSe<sub>2</sub> compounds (x = 0.1; 0.18), the semiconductor nature of the conductivity in these compounds was established, and the changes in the electrical resistance value with time were determined at a constant potential difference [6].

Such processes are characteristic of materials exhibiting dielectric properties, including ionic conductors, and, as indicated in the literature, can be associated with polarization and the formation of a space charge near the electrodes. However, the dielectric properties of intercalated materials containing copper or silver are practically have not been studied. Such studies are often carried out using alternating current, which provides data on relaxation characteristics during charge transfer and polarization processes. In this work, this technique was applied to study the kinetic and dielectric properties of hafnium diselenide intercalated with copper atoms.

## II. Material and Methods

The compound Cu<sub>0.1</sub>HfSe<sub>2</sub> was synthesized by solid-phase reactions in evacuated quartz ampoules. For this, a two-stage technique was used. At the first stage, hafnium diselenide was synthesized and certified, which serves as a matrix for subsequent intercalation; at the second stage, this hafnium diselenide was mixed with the required amount of metallic copper. purity. This technique excluded the direct interaction of free selenium and

copper and the formation of copper selenides. The low copper content in the sample was due to the desire to prevent interaction between intercalated atoms in the space between the HfSe<sub>2</sub> layers. After the synthesis of several samples of a given composition and their subsequent homogenization, a sample was selected, the X-ray certification of which showed that the sample was free of copper selenide impurities, and its structure corresponded to the 1T modification of HfSe<sub>2</sub>. The real and imaginary components of the impedance were measured at temperatures from 250 K to 296 K in the range of line frequencies (f) from 10 Hz to 10 MHz on a Solartron 1260A universal impedance analyzer. The magnitude of the exciting signal was 0.2 V. The analysis of the results was carried out within the framework of an equivalent circuit with a parallel connected resistor and capacitor, which is often used as a first approximation for dielectric materials with noticeable conductivity [9]. The values of the real and imaginary parts of the permittivity were calculated from the impedance data [10].

### III. Results

Figure 1 shows the frequency dependences of the imaginary impedance component at different temperatures. These dependences have a maximum at frequencies  $f_{max}$ , according to which the relaxation times for charge transfer processes were determined for a given electric circuit (ohmic relaxation time  $\tau_j$ , which can be defined as  $\tau_j = 1 / (2\pi f_{max})$ ). The values of relaxation times determined from impedance data at different

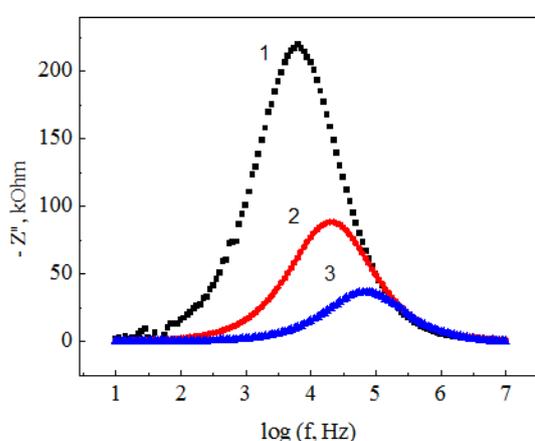


Figure 1. Frequency dependences of the imaginary component of the complex impedance of Cu<sub>0.1</sub>HfSe<sub>2</sub> at 250 K (1), 275 K (2), 296 K (3) 296K(3)

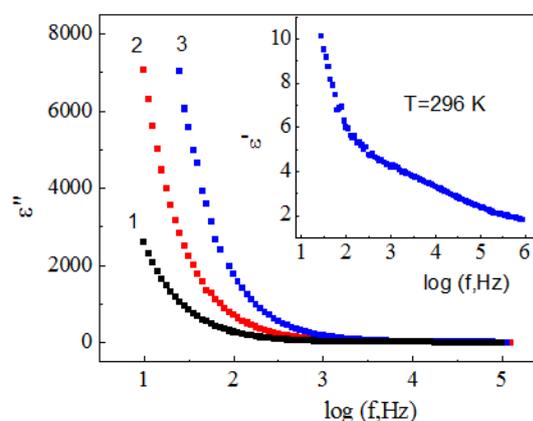


Figure 2. Frequency dependences of the real (in the inset) and imaginary parts of the complex permittivity of Cu<sub>0.1</sub>HfSe<sub>2</sub> at 250 K (1), 275 K (2), 296 K (3)

temperatures are given in Table 1. The imaginary part of the impedance is determined by the capacitive component of the used equivalent circuit, and therefore is related to the dielectric characteristics of the material under study.  $\epsilon^* = \epsilon' + i\epsilon''$ . The frequency dependences of  $\epsilon''$ , indicating the nature of losses in an alternating electric field, are shown in Fig. 2. This indicates the existence of significant dielectric relaxation in these samples, however, in the considered frequency and temperature range these dependencies do not show characteristic maxima, but are monotonic in nature, which is observed in the case of predominant conductivity losses. An increase in  $\epsilon''$  at low frequencies may be due to polarization effects, as is typical, in particular, for ion-conducting materials [11]. In this case, as can be seen from the data presented in Fig. 2, the  $\epsilon''$  values increase with increasing temperature, which corresponds to an increase in the conductivity of a semiconductor material and an increase in losses. The real part of the permittivity weakly depends on temperature and the dependence of  $\epsilon'$  on frequency is shown for example at T = 296 K. in the inset in Fig. 2. With a similar nature of the frequency dependences of the components of the dielectric constant, it is impossible to determine the relaxation characteristics of polarization processes.

To analyze the dielectric data in the case of a significant contribution of conductivity, the presentation of the obtained data in the formalism of the electric module was used, the complex value of which is the reciprocal of the complex dielectric constant  $M^* = 1 / \epsilon^* = M' + iM''$ . For this purpose, the experimental data were transformed in the values of real ( $M'$ ) and imaginary ( $M''$ ) parts of the electrical module [12-13] and are shown in Fig. 3. In this case, as noted in the literature [11], the contribution from electrode effects can be minimized, and the imaginary part of the dielectric modulus converts the low-frequency increase in the dielectric constant into a relaxation peak, from the position of which the relaxation time can also be determined.

The result of such transformations is shown in Fig. 3 in the form of the dependence of the imaginary part of the electrical modulus ( $M''$ ) on its real part ( $M'$ ). As can be seen, the spectra of the dielectric modulus on the

complex plane for  $\text{Cu}_{0.1}\text{HfSe}_2$  at each temperature are an arc of a circle, which corresponds to the Cole-Cole diagrams. values of  $M'$  and  $M''$  to zero values at  $\omega \rightarrow 0$  means the absence of additional spectra at lower frequencies. Extrapolation of the spectra to the region of high frequencies before crossing the real axis allows one to estimate the value of the high-frequency dielectric constant as  $\epsilon_\infty = 1 / M'_{\text{max}}$ . These values for different temperatures are also shown in the table. Since in the Cole-Cole diagrams (Fig. 3) there are no explicit frequency dependences of the real and imaginary parts of the electrical module, Fig. 4 shows such dependences for  $M''$ .

Frequency values corresponding to the maximum  $M''$  ( $f_{\text{max}}$ ) were used to determine the characteristic times of dielectric relaxation  $\tau_M$  (see table).

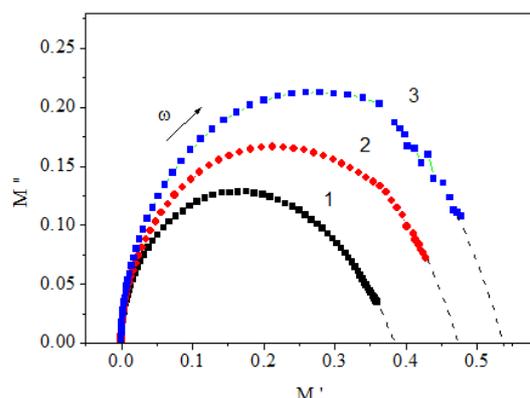


Figure 3. Cole-Cole diagrams on complex plane of the electric modul of  $\text{Cu}_{0.1}\text{HfSe}_2$  at 250 K(1), 275 K(2), 296K(3)

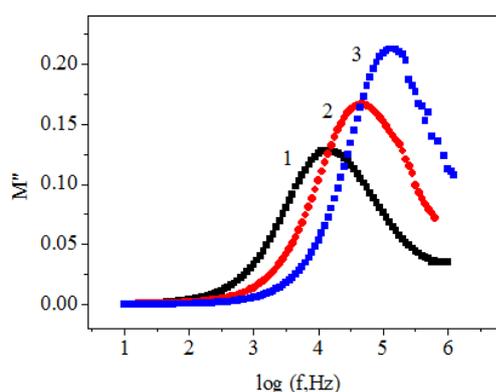


Figure 4. Frequency dependences of the imaginary component of the complex electric modul of  $\text{Cu}_{0.1}\text{HfSe}_2$  at 250 K (1), 275 K (2), 296 K (3), 296K(3)

Comparing the data in Fig. 1 and Fig. 4, we can note a general tendency that the positions of the maxima  $Z''$  and  $M''$  shift towards higher frequencies with increasing temperature, which is due to an increase in the mobility of charge carriers during conduction in the first case and reducing the time for changing the polarization sign when changing the polarity of the applied voltage in the second. On the other hand, it can be seen that the values of  $Z''_{\text{max}}$  decrease with increasing temperature, while the values of  $M''_{\text{max}}$  increase in this case. The latter is associated with a temperature change in both static and high-frequency dielectric permittivities, which, in particular, is reflected in the table 1 based on the results of data analysis in Fig. 3 .

**Table 1.** The times of ohmic  $\tau_j$  and dielectric  $\tau_M$  relaxation, the maximum values of the imaginary parts of the impedance  $-Z''_{\text{max}}$  and the electrical modulus  $M''_{\text{max}}$ , the values of the high-frequency dielectric constant  $\epsilon_\infty$  of the  $\text{Cu}_{0.1}\text{HfSe}_2$  compound at different temperatures

T, K	$-Z''_{\text{max}}$ , kOhm	$M''_{\text{max}}$	$\epsilon_\infty$	$\tau_j$ , $\mu\text{s}$ ,	$\tau_M$ , $\mu\text{s}$ ,
250	22.5	0.14	2.59	25	11
275	10	0.17	2.14	8	3.5
296	4.8	0.22	1.86	2.2	1.0

When analyzing the data given in the table, one should pay attention to the fact that the numerical values of the relaxation times determined from the modular representation of  $\tau_M$  turn out to be smaller than the relaxation times  $\tau_{RC}$  obtained from the impedance measurements.

#### IV. Conclusion

For the intercalated compound  $\text{Cu}_{0.1}\text{HfSe}_2$  in a wide frequency range and at several temperatures, the components of the complex impedance and the relative complex permittivity were determined. The characteristic relaxation times during charge transfer are determined from the impedance data. A significant frequency dispersion of the imaginary component of the dielectric constant is found, which changes in the investigated frequency range in inverse proportion to the frequency of the alternating field. The transformation of the obtained data in the form of an electrical module made it possible to reveal and determine the characteristics of dielectric relaxation, and also for the first time for intercalated compounds to estimate the values of the high-frequency dielectric constant of the  $\text{Cu}_{0.1}\text{HfSe}_2$  compound. It is also shown that the dielectric relaxation times determined from the modular representation are shorter than the ohmic (transport) relaxation times.

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