

# Specific Features of the Charge and Mass Transfer in a Silver-Intercalated Hafnium Diselenide

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**Abstract**—The specific features of the charge transfer in intercalated samples of  $\text{Ag}_x\text{HfSe}_2$  have been studied for the first time by alternating current (ac) impedance spectroscopy. It has been found that relaxation processes in an ac field are accelerated with increasing silver content in the samples. The complex conductivity ( $Y$ ) shows a frequency dispersion described by power law  $Y \sim \omega^s$ , which is characteristic of the hopping conductivity mechanism. The  $\text{Ag}_x\text{HfSe}_2$  compounds demonstrate shorter relaxation times as compared to those observed in hafnium diselenide intercalated with copper atoms, and this fact indicates that the charge carrier mobility in the silver-intercalated compounds is higher. The possibility of silver ion transfer in  $\text{Ag}_x\text{HfSe}_2$  is confirmed by the measurements performed by the method of electrochemical cell emf.

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## 1. INTRODUCTION

Dichalcogenides of transition metals of Groups IV and V elements having the general formula  $\text{TX}_2$  exhibit a natural layered structure in which hexagonally packed layers of a transition metal ( $T$ ) are located between two chalcogen layers ( $X$ ). A weak coupling between the neighboring chalcogen layers provides a way of inserting (intercalating) atoms of other elements into the interlayer space and, thus, causing significant changes in the physical properties of the compounds [1–3]. Among compounds of this class, in last decades much attention has been paid to the study of intercalated titanium dichalcogenides  $M_x\text{TiX}_2$ , which exhibit a wide variety of behavior of the physical properties depending on the kind and concentration of introduced atoms ( $M$ ) and on the type of the matrix compound. In particular, the intercalated titanium dichalcogenides demonstrate the formation of superstructures, phase transitions to the charge-density wave state, the occurrence of the superconducting state or various magnetic states [4–6]. Of a specific interest are the studies of the electronic and ionic charge transfer in similar compounds which can open new possibilities of their application in practice. For example, some lithium-intercalated dichalcogenides of transition metals are already used as electrodes of chemical current sources [7, 8]. According to available data, significant ionic conductivity can also take place in  $M_x\text{TX}_2$  compounds, in which intercalated atoms  $M$  are copper and silver atoms. The study of the electron density distribution of copper ions in the  $\text{Cu}_x\text{TiS}_2$

compounds shows that the copper ions are weakly coupled with sulfur ions in adjacent layers. As a result, they can exhibit significant mobility, which makes these and similar compounds promising as electrodes for chemical current sources [9]. In addition, there are experimental data on the ionic conductivity in titanium and zirconium chalcogenides due to the transfer of silver ions [10–12]. In particular, the  $\text{Ag}_x\text{TiS}_2$  compound is found to have quite high coefficients of conjugated chemical diffusion  $D \sim 10^{-5} \text{ cm}^2/\text{s}$  and the ionic conductivity  $\sigma_i \sim 10^{-1} \text{ S/cm}$  at temperatures of 450–550 K [12].

Despite fact that the hafnium dichalcogenide-based intercalated compounds are scantily known, nevertheless, several Ag–Hf–S compounds with a layered structure were found, which exhibit a quite high ( $\sim 10^{-3} \text{ S/cm}$ ) ionic conductivity at room temperature [13]. Our studies of the  $\text{Ag}_x\text{HfSe}_2$  samples [14] showed the existence in them of polarization phenomena, which, according to [15, 16], are characteristic of materials with a mixed electronic–ionic conductivity. In this work, the  $\text{Ag}_x\text{HfSe}_2$  compounds are studied by impedance spectroscopy and the method of electrochemical cell emf to obtain additional data on the charge- and mass-transfer in intercalated dichalcogenides of transition metals.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The  $\text{Ag}_x\text{HfSe}_2$  ( $x = 0.1, 0.2$ ) samples were prepared from materials synthesized and attested for previous

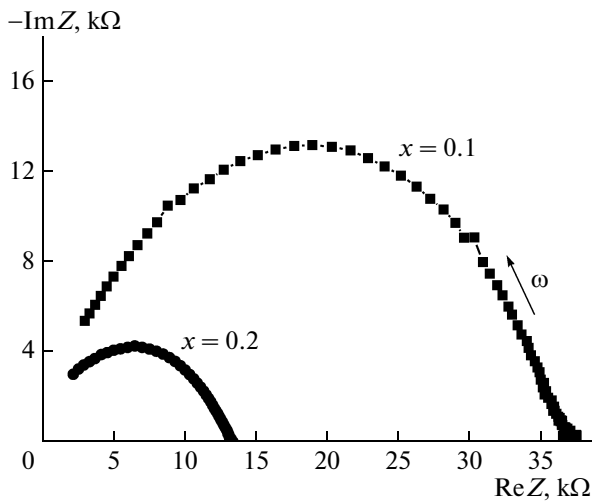


Fig. 1. Impedance spectra of  $\text{Ag}_x\text{HfSe}_2$ .

studies of the system [14]. The samples under study were 2-mm-thick pellets 10 mm in diameter. The impedance spectra of the samples were measured by a Z-3000 impedance meter in the range of linear frequencies ( $\nu$ ) from 10 Hz to 3 MHz. The chemical potential difference of silver in the samples was determined with respect to metallic silver using the electrochemical cell  $\text{Ag1/RbAg}_4\text{I}_5/\text{Ag}_x\text{HfSe}_2/\text{RbAg}_4\text{I}_5/\text{Ag2}$ . Such a cell design allows one to transmit an ionic current through it owing to the use of  $\text{RbAg}_4\text{I}_5$  having a high ionic conductivity [17] and also to measure electromotive forces appeared between electrodes Ag1 and Ag2 and corresponding cross-sections of the samples as the external circuit is disconnected. All the measurements were carried out at room temperature.

### 3. RESULTS

The impedance spectra measured on the  $\text{Ag}_x\text{HfSe}_2$  ( $x = 0.1, 0.2$ ) samples are shown in Fig. 1 as the dependences of the imaginary part of the impedance ( $-\text{Im}Z$ ) on the real part ( $\text{Re}Z$ ). At the complex plane, these dependences are circle arcs whose radii decrease with increasing silver concentration in the samples. According to [18, 19], such a shape of the dependences can be described in an approximation of the equivalent circuit consisting of an active resistor and capacitor connected in parallel. However, as one can see, the curves obtained are not ideal semicircles. In particular, we can note some asymmetry of these curves and also the shift of the center of the semicircles below the abscissa axis. These distortions demonstrate an inconsistency of the impedance behaviors in the samples to the Debye relaxation model and can be related to either the existence of several discrete parameters of the equivalent circuit or a continuous distribution of these parameters around an average value. In particular, the deviations from the Debye

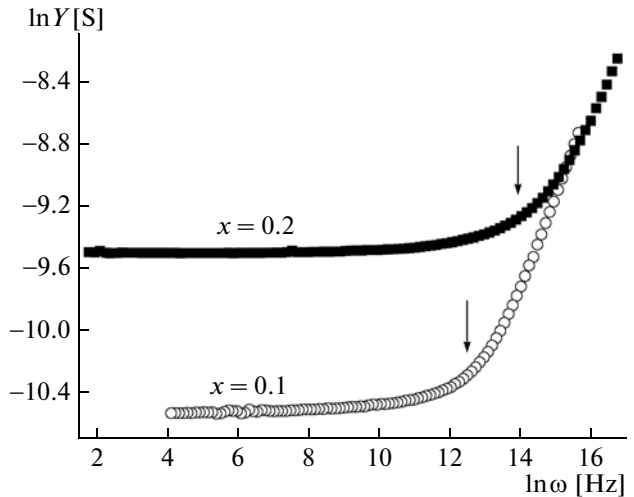
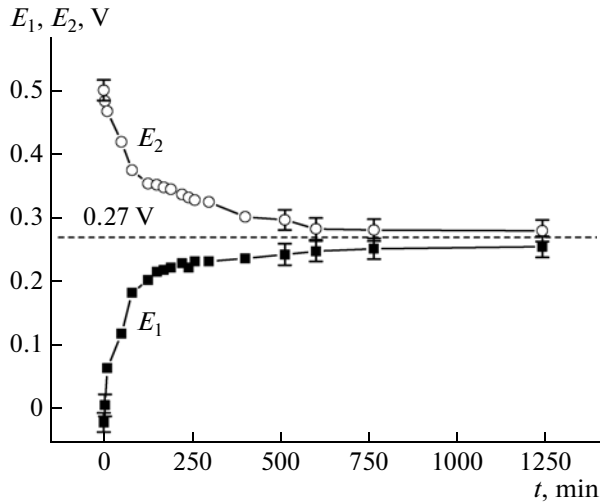


Fig. 2. Frequency dependences of the complex conductivity of  $\text{Ag}_x\text{HfSe}_2$ . The arrows indicate the region of the transition to the frequency dispersion.

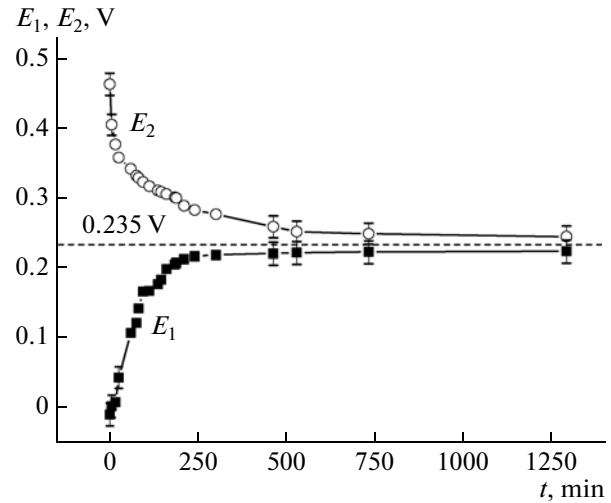
relaxation model can be related to the charge transfer processes over both the grain bulk and the grain boundaries, and each process is characterized by various values of the parameters.

The frequencies at which the impedance imaginary part shown in Fig. 1 takes the maximum value ( $\omega_m = 2\pi\nu_m$ ) are 615 kHz and 4.1 MHz for the samples with  $x = 0.1$  and  $0.2$ , respectively. These data allow us to find the characteristic relaxation times  $\tau = 1/\omega_m$  which are  $1.6 \times 10^{-6}$  s and  $2.4 \times 10^{-7}$  s and can be interpreted as the lifetimes of the charge carriers. The values obtained are substantially lower than those found in our similar studies performed on copper-containing samples of comparable compositions [20]. This difference testifies that, when the same matrices ( $\text{HfSe}_2$ ) are used for intercalation, the charge transfer in the silver-containing samples is faster than that in the copper-containing samples; this fact seems to be related to higher mobility of the silver ions. In turn, the latter can be result of a lower binding energy of the intercalated silver ions with the matrix lattice as compared to the copper ions.

The data of impedance spectroscopy can give useful information on the microscopic mechanism of the charge carrier motion. Figure 2 shows the frequency dependences of the complex conductivity ( $Y$ ) in the logarithmic scale. Two regions can be separated in these dependences for both samples. The first region is a frequency-independent plateau, and the second region is the region of frequency dispersion that can be described by expression  $Y \sim A\omega^s$ . The power dependence of the complex conductivity on frequency is characteristic of many materials, in which the charge carriers behave by the hopping mechanism, and is known as “universal dynamic response” (UDR) [21–23]. According to the theoretical concepts [24], in the



**Fig. 3.** Time dependences of the emf of electrochemical cells ( $E_1$ )  $\text{Ag}_1/\text{F}/\text{Ag}_{0.1}\text{HfSe}_2$  and ( $E_2$ )  $\text{Ag}_2/\text{F}/\text{Ag}_{0.1}\text{HfSe}_2$  ( $F = \text{RbAg}_4\text{I}_5$ ).



**Fig. 4.** Time dependences of the emf of electrochemical cells ( $E_1$ )  $\text{Ag}_1/\text{F}/\text{Ag}_{0.2}\text{HfSe}_2$  and ( $E_2$ )  $\text{Ag}_2/\text{F}/\text{Ag}_{0.2}\text{HfSe}_2$  ( $F = \text{RbAg}_4\text{I}_5$ ).

case of hopping conductivity, exponent  $s$  in the expression of the frequency dispersion must be smaller than unity. The values of  $s$  determined by approximation of the dependences in the high-frequency region are 0.58 and 0.44 for the samples with  $x = 0.1$  and 0.2, respectively. These values are close to the frequency dispersion exponents for the  $\text{Cu}_x\text{HfSe}_2$  samples (0.55 and 0.41) [20], which indicate the identity of the conductivity mechanisms in these compounds. However, the frequencies ( $\omega$ ), at which the frequency dispersion begins to be pronounced in the  $\text{Ag}_x\text{HfSe}_2$  samples and which are called hopping frequencies [25], are 270 and 1190 kHz for  $x = 0.1$  and 0.2, respectively. These hopping frequencies are almost twice as high as those obtained earlier for the  $\text{Cu}_x\text{HfSe}_2$  samples identical in composition; this result adequately correlates with the above noted decrease in the relaxation times obtained from the comparison of the impedance spectra of these two systems.

We studied the mass-transfer in the samples using the electrochemical cell  $\text{Ag}_1/\text{RbAg}_4\text{I}_5/\text{Ag}_x\text{HfSe}_2/\text{RbAg}_4\text{I}_5/\text{Ag}_2$  that allows the transmission of an ionic current through the sample. When a current passes through the cell, a silver ion chemical potential gradient is formed in the sample due to the formation of the concentration gradient opposite to the direction of the transmitted current; the gradient provides the diffusion transfer of a charge from the positive pole of the current source to its negative pole. The steady-state concentration gradient is also retained at the moment of switching off the current. The difference of silver atom concentrations at opposite sample boundaries can be controlled by measuring the electromotive forces (emf) induced in the electrochemical cell between the silver electrodes and corresponding boundaries of the  $\text{Ag}_x\text{HfSe}_2$  samples.

As known, the cell emf ( $E$ ) is determined by the difference of the chemical potentials of silver in the sample and silver in the metallic silver (electrode) according to the relationship [26, 27]  $eE = (\mu_{\text{Ag}}^{\text{Ag}} - \mu_{\text{Ag}}^{\text{smpl}})$ , where  $\mu_{\text{Ag}}^{\text{Ag}}$  is the chemical potential of silver in metallic silver, and  $\mu_{\text{Ag}}^{\text{smpl}}$  is the chemical potential of silver in the sample. In the case of ideal solutions, the chemical potential of particles is dependent on their concentration ( $C$ ) and is determined by the relationship  $\mu = \mu^* + RT \ln C$ . In nonideal systems, concentration  $C$  must be replaced by the component activity  $a = \gamma C$ , where  $\gamma$  is the activity coefficient.

Figures 3 and 4 show the time dependences of the electrochemical cell emf for the samples with  $x = 0.1$  and  $x = 0.2$  after transmitting the ionic current in the direction from  $\text{Ag}_1$  to  $\text{Ag}_2$ . In the plots, the emf sign corresponds to the sign of the metallic electrode potential. The lower  $E_1(t)$  curves correspond to the left cell, i.e., to its edge which was connected with the positive pole of the current source during transmitting current, and it reflects the difference of the chemical potentials between electrode  $\text{Ag}_1$  and the left sample edge. At the initial instant of time after switching off the current, the values of emf in the lower curves are close to a zero within the experimental error, and this fact corresponds to equilibrium with pure silver. At the opposite cell edge, emf is markedly higher (upper  $E_2(t)$  curves in Figs. 3 and 4), and this result corresponds to higher difference of the chemical potentials between electrode  $\text{Ag}_2$  and the right sample edge and, thus, to lower silver concentration (activity) in this cross-section of the samples. As is seen,  $E_1$  and  $E_2$  are equalized in time tending to the same values for each of the samples, which corresponds to the equalization of the sil-

ver concentration along the sample length. These steady-state values are  $(235 \pm 10)$  mV for  $\text{Ag}_{0.1}\text{HfSe}_2$  and  $(270 \pm 10)$  mV for  $\text{Ag}_{0.2}\text{HfSe}_2$ . After transmitting the current in the opposite direction (from Ag2 to Ag1), the initial value of  $E_2$  is close to a zero. The curves of the time dependences of the emf for the corresponding cells are changed by their places, but they have similar shapes, and this fact demonstrates the reversibility of the kinetic processes occurring in the materials under study. This work is an important addition to the previous data of studies of the polarization phenomena in these materials [14] and confirms the possibility of coexistence of the ionic charge- and mass-transfer in the  $\text{Ag}_x\text{HfSe}_2$  compounds.

#### 4. CONCLUSIONS

The ac complex impedance of polycrystalline samples of silver-intercalated hafnium diselenide has been measured for the first time. The impedance spectra have the shape of semicircles, which corresponds to the equivalent circuit with parallel connection of an active resistor and capacitor. It is found that the increase in the silver content in the  $\text{Ag}_x\text{HfSe}_2$  compounds decreases the relaxation times from  $1.6 \times 10^{-6}$  s at  $x = 0.1$  to  $2.4 \times 10^{-7}$  s at  $x = 0.2$ . These values are substantially lower as compared to the relaxation times in  $\text{Cu}_x\text{HfSe}_2$  [20]; this fact demonstrates higher charge carrier mobility in the silver-intercalated compounds. This is also confirmed by the increase in the hopping frequency, at which the frequency dispersion of the complex conductivity begins to be observed.

The method of electrochemical cell emf used for the first time for studying  $\text{Ag}_x\text{HfSe}_2$  confirms the conclusion on the silver ion mobility in these compounds, which was previously made based on the observation of the polarization phenomena [14].

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