Transport Properties and Polarization Phenomena in Intercalated Ag_xHfSe_2 Compounds

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Abstract—The electrical properties of intercalated Ag_xHfSe_2 compounds ($x = 0.1, 0.2$) have been investigated for the first time. Investigations have been performed using various current electrodes, which make it possible to pass either the electron current or the ion current across the sample. Polarization effects, which indicate the self-consistent migration of charge carriers in the samples, have been found for the samples at room temperature. Based on the characteristic features of polarization decay, coefficients of conjugated chemical diffusion have been evaluated.

1. INTRODUCTION

It is known that a large series of compounds containing copper or silver ions, which possess high mobility, form a whole class of superionic conductors [1–3]. The nature of this phenomenon is associated with the existence of the intrinsic structural disorder in them, at which the copper and silver ions are weakly bonded with a crystalline skeleton, and a large number of equivalent sites separated by insignificant potential barriers exist in them. A similar situation can be implemented for intercalated dichalcogenides of transition metals TX_2 (T is the transition metal of Group IV or V, and X is the chalcogen). The main feature of their crystalline structure is the presence of a weak van der Waals bond between $X–T–X$ three-layer blocks, which allows us to intercalate atoms of other elements into the interlayer spacing [4–7]. Some dichalcogenides of transition metals, which are intercalated by lithium ions, are already used as electrodes for chemical current sources [8]. Intercalated atoms can occupy only some equivalent sites in the van der Waals gap depending on their concentration in the TX_2 structure. In contrast to silver and copper chalcogenides, where structural disorder, which leads to a high ion mobility, occurs at elevated temperatures as a result of phase transformations [1, 2], such state in intercalated compounds can be formed by the change of the concentration of the intercalated element at lower temperatures.

The structure and physical properties of intercalated M_xTX_2 compounds after the intercalation of M atoms can differ considerably from those characteristic of the initial compounds [7, 9, 10]. During the intercalation of $3d$ atoms of transition metals into the TX_2 structure, intercalated atoms form the bonds with the atoms of adjoining layers of the parent matrix. The nature of such bonds depends on the sort of $3d$ atoms and the chalcogen type in the TX_2 matrix. Particularly, as it was established for intercalated titanium dichalcogenides, the degree of covalence of the bonds increases as the atomic number of chalcogen increases in a series $TiS_2–TiSe_2–TiTe_2$ [9, 11]. The preferentially covalent character of bonds in M_xTiX_2 systems manifests itself in a decrease in unit cell parameter c during intercalation as compared with the initial compounds [9–11]. As opposed to this fact, copper and silver atoms, due to a spherical symmetry of $4s$ and $5s$ states, correspondingly, do not possess the tendency to establishment of such bonds, and their intercalation leads to an increase in parameter c as a rule. This was particularly shown in calculations of the distribution of the electron density in the Cu_xTiS_2 compounds [12]; it also follows from the data on the determination of concentration dependences of unit cell parameters in the Cu_xTiS_2, Cu_xTiSe_2, and Cu_xHfSe_2 compounds [13–15].

There are several articles devoted to the investigation of kinetic properties of compounds intercalated with silver (Ag_xTX_2), where the data on high mobility of silver ions in these compounds were obtained along with the characteristics of the electron transfer [16–19]. Physical properties of intercalated compounds based on hafnium dichalcogenides are much less studied; however, there are the articles devoted to the synthesis and investigation of silver-containing phases such as the Ag_2HfS_3 and Ag_4HfS_8 compounds, which also have the layered structure and possess rather high ion conductiv-
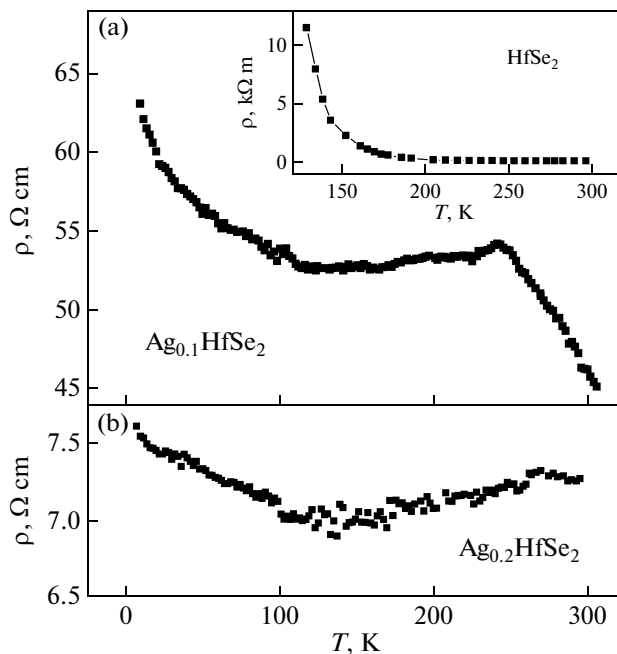
Fig. 1. Temperature dependences of the resistivity of the Ag_xHfSe_2 samples: (a) $x = 0.1$ and (b) 0.2. The same dependence for the Ag_xHfSe_2 sample at $x = 0$ is shown in the inset.

ity. For example, it is noted that the ion conductivity in the Ag_2HfS_3 compound is ~10^{-3} $(\Omega\,cm)^{-1}$ at room temperature, while the transfer number of silver ions is close to unity [20, 21].

The data available in publications show that the further studies of silver-containing transition metal chalcogenide compounds are of doubtless interest. In this connection, our study is devoted to the investigation of charge-transfer phenomena in hafnium diselenide intercalated by silver ions.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Parent hafnium diselenide was synthesized by the method of solid-phase reactions from initial elements in evacuated quartz ampules as it was performed previously for the synthesis of titanium dichalcogenides and intercalated materials on their base [9–11]. Thus prepared $HfSe_2$ was used for the subsequent synthesis of intercalated Ag_xHfSe_2 samples ($x = 0.1, 0.2$) by the same procedure. The X-ray diffraction attestation of these samples and the subsequent determination of structural characteristics was performed using a Bruker D8 Advance diffractometer in CuK_α radiation.

To investigate the charge transfer in materials with the electron–ionic conductivity, several methods differing by various combinations of current electrodes and measuring probes is used. We used two circuits in this work. The first one is a standard four-probe circuit with electron current leads blocking the transfer of silver ions and electron measuring probes. It allowed us to determine the characteristics of the electron charge transfer. Measurements using this circuit were performed for compacted and annealed cylindrical samples 4.2 mm in diameter and 8 mm in length. The second circuit was the $Ag/Ag_4RbI_5/Ag_xHfSe_2/Ag_4RbI_5/Ag$ electrochemical cell, which makes it possible to pass the ion current across the sample and to block the electron transfer. The Ag_4RbI_5 compound is one of better ion conductors, which can be used at room temperature, when its ion conductivity is ~0.3 $(\Omega\,cm)^{-1}$ [2]. The sample was a pellet 10 mm in diameter and 2 mm thick in this case. The Ag_4RbI_5 pellets had the same diameter and a thickness of 1.8 mm. To measure the potential difference, we used electronic measuring probes connected to sample ends and neutral with respect to silver. Electric resistance was measured in a temperature range of 10–300 K, and polarization phenomena were investigated at room temperature.

3. RESULTS

The results of X-ray diffraction attestation of the samples showed that the structure of all obtained materials corresponded to the CdI_2 structural type. It was established by the phase analysis that the samples were almost single-phased. Only a small (no larger than 5%) amount of the HfO_2 phase was found as a foreign impurity apparently introduced with metal hafnium when it was milled during the sample preparation. The data obtained by the X-ray diffraction analysis for the parent hafnium diselenide and Ag_xHfSe_2 samples are tabulated. Unit cell parameters of parent hafnium diselenide correspond to these found previously in [4, 5], while the data for intercalated samples (similarly to the Cu_xHfSe_2 system [15]) indicate an increase in parameters during intercalating the samples.

The results of studying the temperature dependences of electrical resistance $\rho(T)$ of the Ag_xHfSe_2 samples performed using the first circuit give the information on the features of the electron transfer (Fig. 1). An increase in the silver content in the samples leads to a decrease in electrical resistance, which, as it was mentioned for $Ag_{0.33}TiS_2$ [16], can be associated with the transfer of $5s$ electrons of silver into $5d$ band of hafnium. Measurements of thermopower for both samples indicate the electron type of charge carriers. It is seen from Fig. 1 that the character of dependence $\rho(T)$ for the $Ag_{0.1}HfSe_2$ sample changes from the activation at low temperatures to metallic in the intermediate region (120–250 K). Above 250 K, its electrical resistance starts to decrease again. The activation energy of conductivity for the $Ag_{0.1}HfSe_2$ sample in a low-temperature region is very low (~10^{-4} eV). Despite the fact that electrical conductivity of the

$Ag_{0.2}HfSe_2$ samples varies rather weakly as the temperature increases, we can see that it also exhibits the tendency to the change of the character of the temperature dependence from activation (with a very low activation energy) to metallic. Taking into account that the temperature regions of the transition from the activation dependence to the metallic one almost coincide for both samples, we can assume the general nature of such a transition. Since the activation energy of conduction in a low-temperature region is very low, this region is associated probably with the electron excitation from impurity centers into the conduction band, and scattering of charge carriers in this band at thermal oscillations prevails starting from a certain temperature. In view of low excitation energy of charge carriers, the change of the character of the $\rho(T)$ dependence in a region of 120−250 K can correspond to the depletion of impurities known for semiconductors. To clarify if the transition from the metallic-type dependence to the activation dependence at temperatures above 250 K is the consequence of the change in the atomic structure, we performed X-ray diffraction investigations of the sample with $x = 0.1$ at 290 and 113 K. These investigations had not revealed the qualitative structural changes excluding an increase in unit cell parameters with an increase in temperature (see table). It follows from here that this transition is not associated with structural transformations. When measuring electrical resistance of intercalated samples, we noted that the room-temperature magnitude of the electric current passing across the samples was unstable and varied as the polarity of the supplied voltage changed. It is possible that the interaction of the electron and ion charge carriers starts to manifest itself in this temperature region.

In order to investigate the charge-transfer phenomena in more detail, we measured the current−voltage characteristics of the samples. It was found that they are nonlinear at room temperature and exhibit the hysteresis as the direction of the applied field changes. Figure 2 shows the current−voltage characteristic for the $Ag_{0.1}HfSe_2$ sample during the cyclic ($0 \longrightarrow U_{max} \longrightarrow 0 \longrightarrow -U_{max} \longrightarrow 0$) variation of the applied potential difference. As the temperature decreases, the shape of the current−voltage characteristic approaches the linear one, while the hysteresis almost disappears. Based on this fact, we can assume the occurrence of certain relaxation processes, which are associated with migration of silver ions under the applied electric field. Since this migration should have the activation character, it is suppressed at low temperatures, and the current−voltage characteristic becomes ohmic.

When passing the electric current across the samples, its decrease with time was found, which corresponds to an increase in effective resistance of the samples at a constant applied potential difference and indicates the appearance of barriers preventing the electron transfer. Such processes are characteristic of
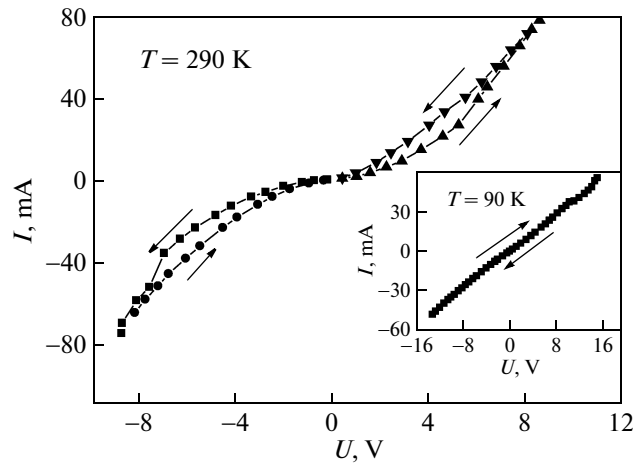

Fig. 2. Current−voltage characteristics of the $Ag_{0.1}HfSe_2$ sample at temperatures of 290 and 90 K (in inset).

the materials which manifest dielectric properties, including ionic conductors, and, as was mentioned in [22, 23], they can be associated with the polarization and the formation of a bulk charge near blocking electrodes.

With switching off the current after the establishment of the steady polarization, the measured potential difference abruptly decreased to a certain residual value $U_{res}(0)$ and then tended to zero with time. Figure 3 shows the dependences $U_{res}(t)$ for the $Ag_{0.1}HfSe_2$ sample after passing the current in two opposite directions. The difference of electric potentials measured experimentally reflects the difference of electrochemical potentials of electrons, which is in turn governed by the difference in the concentration of silver ions over the sample length, which appears during the polarization. The observed dependences $U_{res}(t)$ can be considered as a consequence of the polarization decay, when the charge-carrier concentration over the sample length is leveled as a result of diffusion processes. The difference of electrochemical potentials of electrons also disappears in this case. It should be specially noted that the sign of the residual potential difference coincides with the sign of the potential difference during passing the current. Such characteristic signs of the polarization decay for this measuring circuit (electron electrodes and electron probes) were established by the theoretical analysis of the potential distribution in

Unit cell parameters a and c of the Ag_xHfSe_2 samples found at room temperature (the values found at $T = 113$ K are shown in parentheses)

x	a, Å	c, Å
0	3.7428	6.1553
0.1	3.7444 (3.7442)	6.1563 (6.1548)
0.2	3.7449	6.1567

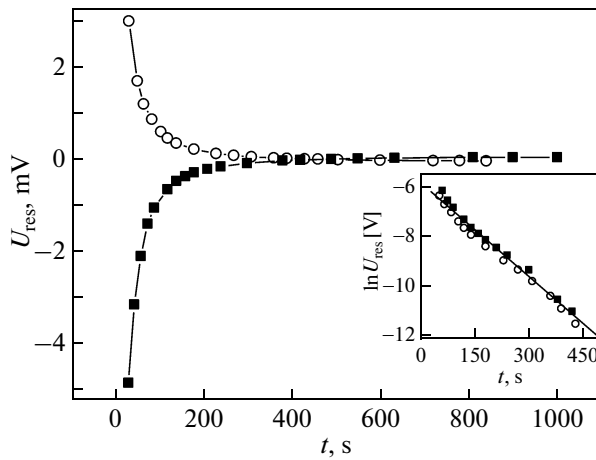**Fig. 3.** Polarization decay curves for the $Ag_{0.1}HfSe_2$ sample after passing the electron current in two opposite directions.

Fig. 4. Curves of (*1*) establishing polarization under passing the ion current and (*2*) its decay after switching off the current for the $Ag_{0.2}HfSe_2$ sample. The measuring circuit is shown in the inset, $F = Ag_4RbI_5$.

mixed electron−ion conductors [24] and verified experimentally for silver chalcogenides [24, 25]. When analyzing the presented dependences, it was shown that they follow the exponential dependence of the $U_{res}(t) \sim \exp(-t/\tau)$ type, which corresponds to the solution of the second Fick law (inset in Fig. 3), where τ is the relaxation time, which is 80 s for the made evaluation.

Polarization phenomena were also investigated using the second circuit, in which the charge transfer could be performed only by silver ions. The phenomena indicating the appearing polarization in the samples were also observed during passing the ion current across the cell. Time dependences of the potential difference during passing the current for the $Ag_{0.2}HfSe_2$ sample, which correspond to the process of establishment of polarization (curve *1*) and describing the polarization decay after switching off the current (curve *2*) are also shown in Fig. 4. It is seen that after switching off the current, the potential difference between the measuring probes changed the sign (in contrast to similar measurements performed using the first circuit upon passing the electron current) and tended to zero with time. These data also qualitatively correspond to the results obtained for the case of ion current electrodes and electron measuring probes [24]. The curves of polarization establishment and decay, which are presented in Fig. 4, were described satisfactorily by the exponential function. In this case, characteristic relaxation times τ for both processes were approximately the same and equal to 180−200 s.

When analyzing these results, we should take into account the fact that two types of charged particles, namely, electrons and silver ions, the migration of which is self-consistent, are present in the samples under study. In this case, only the conjugated chemical diffusion coefficients (CCDC) can be found from the presented experimental data. We determined the
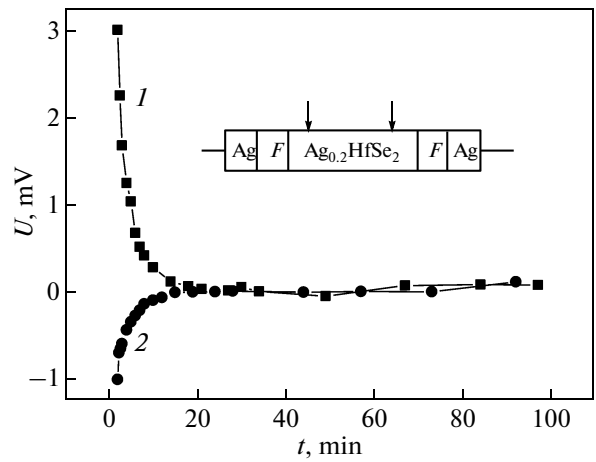
CCDC values using the expression following from the solution of the second Fick equation: $D^* = L^2/\pi^2 t$, where L is the diffusion length and t is the time of reaching the steady state. This time was determined from the polarization decay curves (Figs. 3, 4) and constitutes approximately 500 s for the $Ag_{0.1}HfSe_2$ sample and 1300 s for the $Ag_{0.2}HfSe_2$ sample. When calculating diffusion coefficients, we found the values of 1.2×10^{-5} cm²/s for $Ag_{0.1}HfSe_2$ and 3.0×10^{-6} cm²/s for $Ag_{0.2}HfSe_2$. According to the conceptions developed for materials with mixed conductivity [26, 27], the values of CCDC reflect the migration of both sorts of diffusing particles and can be represented in a form $D^* = z_e D_i + z_i D_e$, where z_e and z_i are the transfer numbers for electrons and ions, respectively; and D_i and D_e are the partial diffusion coefficients for ions and electrons, respectively. We can isolate the ion diffusion coefficient from the presented expression only if $z_e \sim 1$. Since we had not found the data on the investigation of transfer phenomena in compounds under consideration, it seems impossible to do this based on the results found in our study only.

The fact seems to be unusual that a smaller diffusion coefficient is found for the sample with a higher silver concentration. However, allowing for the expression describing the CCDC, this situation can be realistic with a certain variation in the ratio of transfer numbers from one hand and partial diffusion coefficients from the other hand. One possible cause is that as the silver concentration increases, the fraction of free sites in the van der Waals gap per one silver ion decreases, which can lead to a decrease in their mobility.

4. CONCLUSIONS

In this study, the possibility to implement rather high mobility of silver ions in intercalated compounds

based on hafnium diselenide is investigated for the first time. Polarization phenomena associated with the self-consistent migration character of silver ions and electrons under applying the external electric field and after its switching off are found for the studied samples. The established character of time dependences of the potential difference between various sections of the samples corresponds qualitatively to the analysis of the potential distribution in mixed electron–ion conductors for combinations of current electrodes and measuring probes used by us [24].

Thus, the obtained data indicate that intercalated Ag_xHfSe_2 compounds posses rather high mobility of silver ions and can be considered as materials with mixed electron–ion conductivity, which is essential, for example, for the development of electrode materials. To determine diffusion coefficients of silver ions and the magnitude of ion conductivity directly, additional experiments should be performed.

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