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Nature of electrotransport and mechanisms of relaxation in an alternating field in silver intercalated hafnium diselenide

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Received May 17, 2022

Revised May 27, 2022

Accepted May 30, 2022

The features of charge transfer in electrochemical cells with electrodes of various types and with an intercalated compound Ag_xHfSe_2 ($x = 0.1, 0.2$) as an electrolyte were studied by the method of impedance spectroscopy. Based on the analysis of the obtained data, the presence of mixed electron-ionic conductivity in this compound was shown, and the numbers of ionic and electron transfer in these compounds were determined for the first time. The different nature of relaxation processes in mixed and ionic charge transfer is shown.

Keywords: hafnium diselenide, silver, intercalation, impedance, ionic and electronic conductivity.

DOI: 10.21883/PSS.2022.10.54230.317

1. Introduction

High ionic mobility in binary halides and chalcogenides of copper and silver is well known [1,2]. In addition, many ternary compounds, such as Ag_3SI , RbAg_4I_5 , also belong to materials with high ionic conductivity [2–4]. The main factor leading to the high mobility of ions is the disorder in the atomic structure of such compounds, when there are enough of positions equivalent in energy for the mobile ion. A similar feature is also characteristic of atoms embedded (intercalated) in matrices that have layered atomic structures. A number of works were devoted to the study of the structural features and properties of intercalated compounds based on dichalcogenides of transition elements of 4 and 5 groups of the Periodic Table with the general formula TX_2 . A characteristic feature of their crystal structure is the presence of a weak Van der Waals (V-d-W) bond between $X-T-X$ layers, which makes it possible to introduce atoms of other elements into the interlayer space [5,6], including copper and silver atoms. In this case, the ions of the elements of the 1 group, having a closed electron shell, do not tend to establish covalent linkages with molecular orbitals TX_2 and, as a result, are weakly linked in the interlayer space [7]. Studies of the kinetic properties of such materials were previously carried out on titanium and zirconium dichalcogenides intercalated with silver, where, along with the characteristics of electron transfer, data were obtained on the presence of a sufficiently high mobility of silver ions in these compounds [8,9].

The physical properties of intercalated compounds based on hafnium dichalcogenides, which are chemical and structural analogues of titanium dichalcogenides, have been studied much less. There are well-known works dedicated to the synthesis and study of silver-containing phases, such as Ag_2HfS_3 and Ag_4HfS_8 , also having a layered structure

and possessing sufficiently high ionic conductivity [10]. In previously performed work on the study of Ag_xHfSe_2 compounds, the phenomena of the formation and decay of polarization upon passing a direct current were found [11]. The observed patterns of polarization processes when using various combinations of current and measuring electrodes corresponded to the theoretical analysis performed for mixed electron-ionic conductors [12].

Data obtained under AC in electrochemical cells using electrodes of various types make it possible to obtain new data on the processes of charge and mass transfer, as well as to determine the relative contributions of various charge carriers to the total conductivity. Such studies were performed in this work using Ag_xHfSe_2 ($x = 0.1, 0.2$) compounds as a solid electrolyte.

Experimental part

Compounds Ag_xHfSe_2 were obtained by mixing in the required proportions of metallic silver and pre-synthesized hafnium diselenide. The preparations were synthesized in evacuated quartz ampoules at a temperature of 800°C and was accompanied by a series of homogenization anneals. To increase the density of the tablets after pressing, they were sintered at temperature of 800°C for 100 hours. X-ray diffraction certification of the obtained compound and determination of its structural characteristics were performed at Bruker D8 Advance diffractometer in CuK_α -radiation. Processing of X-ray data [13] showed that the crystal structure of the Ag_xHfSe_2 samples corresponds to the CdI_2 structure type, as shown in Fig. 1.

The obtained samples were used as a solid electrolyte in electrochemical cells with different types of electrodes. In one case, the cell was an $\text{Ag}/\text{Ag}_x\text{HfSe}_2/\text{Ag}$ system with reversible electrodes (cell 1), where both electron

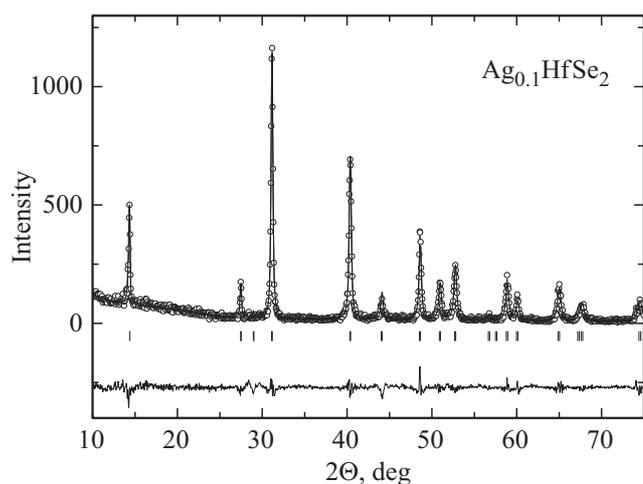


Figure 1. X-ray diffraction pattern of the $\text{Ag}_{0.1}\text{HfSe}_2$ sample. Points are experimental intensity values, solid line is calculated profile. The difference curve between them is shown below. The vertical dashes indicate the positions of the Bragg reflections corresponding to the CdI_2 structure type.

charge carriers and silver ions could contribute to charge transfer. In another cell $\text{Ag}/\text{RbAg}_4\text{I}_5/\text{Ag}_x\text{HfSe}_2/\text{RbAg}_4\text{I}_5/\text{Ag}$ composite electrodes blocking electron transfer (cell 2) were used. The RbAg_4I_5 compound used for this purpose is one of the best ionic conductors, the conductivity of which, even at room temperature, is carried out exclusively by silver ions [2–4]. The test specimens were made as discs of the diameter of 10 mm and the thickness of 2 mm. RbAg_4I_5 filters were prepared in the form of tablets of the same geometric dimensions. The impedance spectra were measured at room temperature using a Solartron 1260A impedance meter in the linear frequency range (f) from 10 Hz to 5 MHz. The amplitude of the variable signal was 0.2 V.

2. Results and discussion

Figure 2 shows the impedance spectra obtained using the $\text{Ag}/\text{Ag}_x\text{HfSe}_2/\text{Ag}$ cell. Similar type of dependence of the imaginary component of the complex impedance on its real part in the form of arcs of circles, according to the literature [14,15], can be considered in the approximation of an equivalent circuit consisting of active resistance R_a and a capacity C connected in parallel with each other. Within the framework of this representation, the tendency of the left part of the arc to zero mark on the real axis indicates the insignificance of the contact resistance connected in series with the parallel circuit. The intersection of the right part of the arc with the real axis at $f \rightarrow 0$ indicates the value of the active resistance of the sample R_a . It can be seen that the value of R_a decreases significantly with increase in the silver content in the samples, which in this case is associated with increase in the concentration of both ionic and electronic charge carriers. Since the centers of each

arc lie below the real axis, this means that the relaxation processes that occur in the samples under study when an alternating current flows do not correspond to the Debye model with a certain relaxation time. At the same time, it can be seen that the spectra are fairly smooth lines, which does not allow us to explicitly and with sufficient confidence select the spectra that reflect processes with different relaxation times. Since different contributions to charge transfer have their own characteristics, this should lead to some distribution of relaxation times around the most probable (effective) value. In this approximation, the width of the distribution region can be estimated from the angle $\pi \cdot \alpha/2$ between the real axis and the radius of the circle, drawn from the left point of the spectrum to the center of these circles (Fig. 2), and is expressed by the value a , which quantitatively characterizes the degree of deviation of relaxation processes from the Debye model [14,15]. The magnitudes of effective relaxation times were determined from the value f_{\max} corresponding to the maximum of the spectrum, and the values of the impedance components at this point as $\tau = R_a \cdot C = -Z''/(Z' \cdot 2\pi f_{\max})$. These values were $1.12 \mu\text{s}$ and $0.15 \mu\text{s}$ for samples with $x = 0.1$ and $x = 0.2$, respectively.

Figures 3 and 4 show the impedance spectra of electrochemical cells with Ag_xHfSe_2 samples and ionic electrodes. At high frequencies, the spectra can be represented by arcs of circles, and in this frequency range they show a change in the impedance associated with charge transfer through the volume of the samples under study. As in the previous case, when estimating the effective relaxation times, the values $\tau = 4.4 \mu\text{s}$ for $\text{Ag}_{0.1}\text{HfSe}_2$ and $\tau = 2.1 \mu\text{s}$ for $\text{Ag}_{0.2}\text{HfSe}_2$ were obtained. These values turned out to be several times larger than for Ag_xHfSe_2 samples in cells 1 (Fig. 2). The reason for this may be that the charge transfer in this case

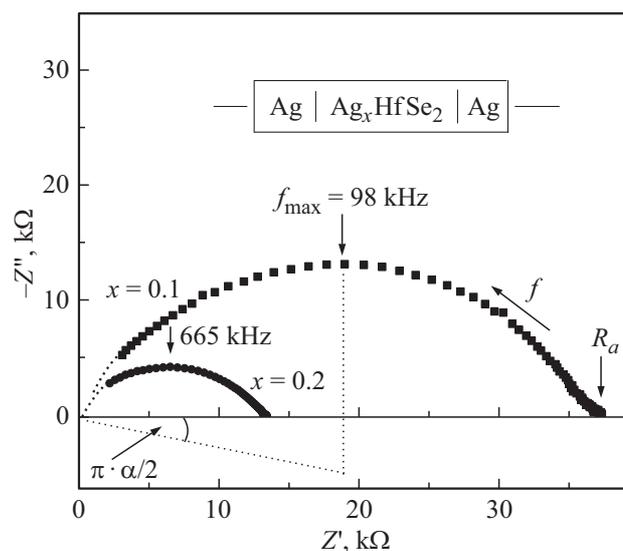


Figure 2. Complex impedance spectra of Ag_xHfSe_2 samples in cells 1 with reversible electrodes. The Figure shows the values of the linear frequencies corresponding to the maxima of the curves.

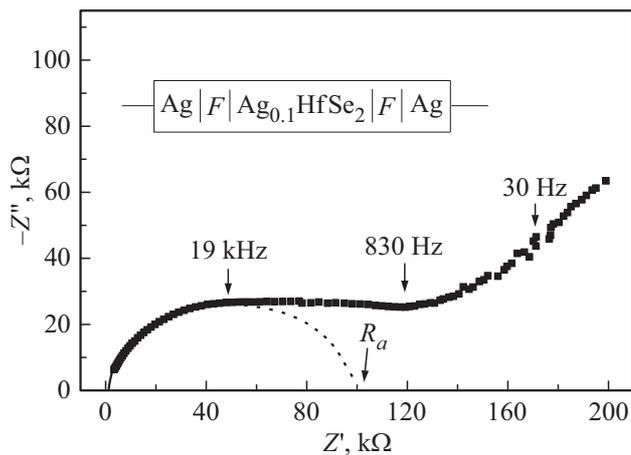


Figure 3. Complex impedance spectrum of electrochemical cell $\text{Ag}/F/\text{Ag}_{0.1}\text{HfSe}_2/F/\text{Ag}$, where $F = \text{RbAg}_4\text{I}_5$. The Figure shows the values of the linear frequencies in different parts of the spectrum.

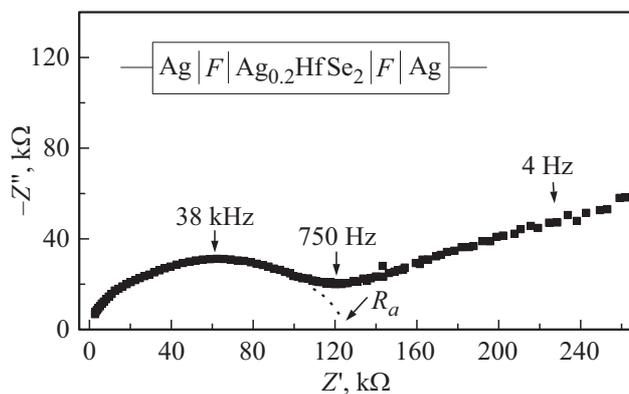


Figure 4. Complex impedance spectrum of electrochemical cell $\text{Ag}/F/\text{Ag}_{0.2}\text{HfSe}_2/F/\text{Ag}$, where $F = \text{RbAg}_4\text{I}_5$. The Figure shows the values of the linear frequencies in different parts of the spectrum.

is carried out only by silver ions, which have a much lower mobility compared to electronic charge carriers.

With decrease in the frequency of the alternating current, the form of the spectrum changes dramatically and is represented a straight ray. This type of low-frequency component of the impedance spectrum is usually associated with the presence of diffusion processes through interphase boundaries. Polarization regions can form at these boundaries, which represent potential barriers to the transport of diffusing particles. Since, when using cells with blocking electrodes, one can only talk about the diffusion of silver ions, this simultaneously indicates ionic charge transfer [16,17], which is determined, in particular, by the well-known Nernst–Einstein relation. The frequencies of polarization change in the alternating electric field will depend on the nature of the conjugated phases in the electrochemical cells used.

The total impedance of cells 2 with ionic electrodes (Figs. 3,4) is the sum of the impedances of the electrodes and the Ag_xHfSe_2 samples themselves. In order to determine the contribution of the electrodes, an experiment was performed using an $\text{Ag}/\text{RbAg}_4\text{I}_5/\text{Ag}$ auxiliary cell, the impedance spectrum of which is shown in Fig. 5. As can be seen, this spectrum is similar in its form to the spectrum of cells 2 with Ag_xHfSe_2 samples (Figs. 3,4) and also represents a combination of two different regions. The first of them has the form of a circular arc, which describes the transport of Ag^+ ions in the volume of the RbAg_4I_5 electrolyte.

The low-frequency section of the spectrum has the form of a straight ray, which describes the diffusion of silver ions through the phase boundaries. Such a qualitative agreement gives reason to believe that the kinetic processes in these cells also occur in a similar way and are due to the transfer of silver ions. Additional evidence of the identity of the charge transfer processes are the frequency dependences of the dielectric loss tangent, which are usually used to characterize the processes of energy dissipation in the alternating field. These dependences, shown in Fig. 6 and related to different cells with ionic charge transfer, are characterized by the maximum values of $\text{tg } \delta$ at certain frequencies. The process that occurs in this case can be associated with losses due to ion-relaxation polarization in materials with ionic or mixed conductivity. As can be seen, this frequency in Ag_4RbI_5 is approximately by two orders of magnitude higher than such frequencies for cells with Ag_xHfSe_2 . Since the maximum loss means that the period of the field change is comparable with the polarization establishment time, it can be concluded that the limiting process in cells with Ag_xHfSe_2 and ionic electrodes is the polarization loss precisely in the samples under study. From the value of this frequency, it was possible to determine the characteristic time of polarization establishment in these compounds,

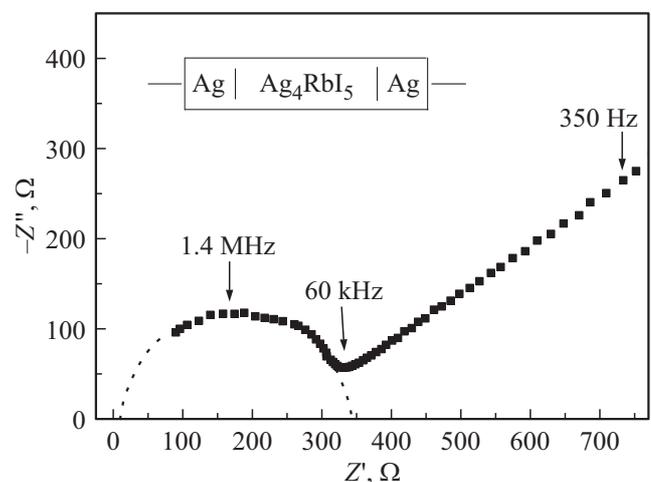


Figure 5. Complex impedance spectrum of a cell with RbAg_4I_5 compound.

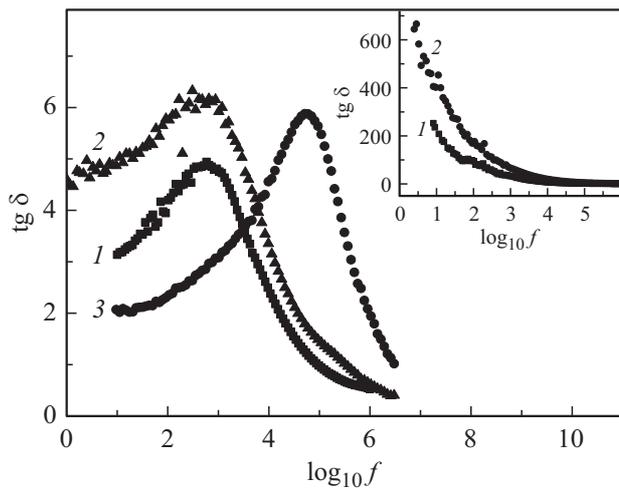


Figure 6. Frequency dependences of the dielectric loss tangent in Ag/RbAg₄I₅/Ag_xHfSe₂/RbAg₄I₅/Ag cells at $x = 0.1$ (curve 1) and $x = 0.2$ (curve 2) and in Ag/RbAg₄I₅/Ag cell (curve 3). Inset: frequency dependences of $\text{tg } \delta$ in Ag/Ag_xHfSe₂/Ag cells at $x = 0.1$ (curve 1) and $x = 0.2$ (curve 2).

which was approximately equal to 0.3 ms. By contrast to this, in cells with reversible electrodes, $\text{tg } \delta$ decreases monotonically with increasing frequency for both samples, indicating the predominant contribution of conduction losses (Fig. 6, inset).

When comparing the given data for cells with Ag_xHfSe₂ (Figs. 3 and 4) and with RbAg₄I₅ (Fig. 5), it can be seen that the values of the real and imaginary components of the cell impedance Ag/RbAg₄I₅/Ag turn out to be several orders of magnitude smaller compared to such values for cells Ag/RbAg₄I₅/Ag_xHfSe₂/RbAg₄I₅/Ag. This also confirms that the contribution of ionic electrodes to the total cell impedance 2 can be considered insignificant, and therefore, the spectra presented in Figs. 3 and 4 mainly reflect the impedance properties of the electrolyte itself (Ag_xHfSe₂) during ionic charge transfer.

The values of active resistances to charge transfer R_a corresponding to the right boundaries for the circles in one case (Fig. 2) and in the other case (Figs. 3, 4) differ significantly from each other. This difference is probably related to the different contributions of ions and electrons to the charge transfer process in these cells. Thus, in cells 1 with reversible electrodes, the resulting conductivity $\sigma_r = 1/R_a$ will be determined by the sum of the contributions of electrons σ_{el} and silver ions σ_{ion} . In cells 2 with electrodes that block electron transfer, the charge is transferred only by silver ions, and the active resistance R_a in Fig. 3 and Fig. 4 reflects only their contribution to the conductivity σ_{ion} . Based on these data, the transfer numbers in the studied samples were estimated. So, for Ag_{0.1}HfSe₂, this estimate showed that the electron transfer number is $n_{el} = \sigma_{el}/\sigma_r \approx 0.7$, and the ion transfer number is $n_{ion} = \sigma_{ion}/\sigma_r \approx 0.3$. For the Ag_{0.2}HfSe₂ sample, similar estimates gave the values $n_{el} \approx 0.9$ and $n_{ion} \approx 0.1$. The

decrease in the fraction of ion transfer in a sample with a higher content of silver ions, on the one hand, can be associated with an increase in the electron concentration during ionization of silver atoms, and on the other hand, a decrease in the fraction of free positions for silver ions in the VdW gaps, which leads to a decrease in their mobility. This fact correlates with estimates of the conjugate diffusion coefficient in these materials [11], made from the results of studying polarization processes in a constant electric field.

3. Conclusion

The paper presents the results of impedance studies of electrotransport in hafnium diselenide intercalated with silver atoms by impedance spectroscopy. Electrochemical cells containing Ag_xHfSe₂ compounds as a solid electrolyte were used for the experiment for the first time. The use of electrodes of various types made it possible to obtain data on the possibility for realization of mixed electron-ionic conductivity in Ag_xHfSe₂. Based on the obtained data, the transport numbers of electrons and silver ions in the studied compounds were estimated. These values for silver ions were 0.3 and 0.1 for compounds with $x = 0.1$ and $x = 0.2$, respectively. A similar relationship between the results obtained correlates with the previously obtained data for the conjugate diffusion coefficients obtained for these compounds in the study of polarization phenomena in a constant electric field.

In the work, it is shown that the nature of charge carriers, which determine the conductivity in cells with different types of electrodes, affects the nature of energy losses in an alternating electric field. For example, in cells with mixed electron-ion charge transfer, the main factor is conduction losses. In cells where silver ions are charge carriers, the nature of the frequency dependence of the dielectric loss tangent points to the process of ion-relaxation polarization.

Acknowledgments

We would like to express our gratitude to N.V. Selezneva for her help in performing radiographic certification of the objects of study.

Funding

This study was funded by the Ministry of Science and Higher Education of the Russian Federation (project No. FEUZ-2020-0054).

Conflict of interest

The author declares that he has no conflict of interest.

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