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SEMICONDUCTORS AND DIELECTRICS

Investigation into the Structural and Electrical Properties of Silver-Intercalated Zirconium Diselenide

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Abstract—Silver-intercalated zirconium diselenides of the general formula Ag_xZrSe_2 are synthesized for the first time. The phase diagram of the Ag_xZrSe_2 compound is determined in the temperature range 423–523 K and at room temperature. An analysis has revealed the coexistence of two compounds, namely, $Ag_{0.125}ZrSe_2$ and $Ag_{0.25}ZrSe_2$, of which only the latter compound is stable at room temperature. The structural and electrical properties of Ag_xZrSe_2 diselenides are investigated. The results obtained indicate a polaron nature of charge-carrier localization. A comparison with isostructural intercalation compounds shows that free charge carriers play a dominant role in screening of the impurity potential. © *2003 MAIK "Nauka/Interperiodica"*.

1. INTRODUCTION

Intercalation of transition metals and silver into titanium diselenide and titanium ditelluride leads to a lattice distortion (layers of the host lattice approach each other) and localization of charge carriers in the form of polarons of small radius [1]. It should be noted that the degree of localization of charge carriers for a heavier chalcogen atom proves to be considerably greater than that for other atoms. For example, no localization of charge carriers occurs upon intercalation of silver into titanium disulfide [2], whereas intercalation of iron into titanium disulfide leads to a very weak localization of charge carriers [3] (the polaron shift, which is defined as the energy of lattice deformation, becomes close to zero [4]). However, intercalation of these metals into titanium ditelluride brings about strong localization of charge carriers [1] even in the case where silver serves as an intercalant [5]. The difference in the degrees of localization of charge carriers in these lattices can be explained in terms of polarizability: the higher the polarizability of the lattice, the greater the degree of localization of charge carriers. In this case, proper allowance must be made for two main contributions to the lattice polarizability, namely, the polarizability of charge carriers, which is governed by the density of states at the Fermi level [2], and the polarizability of ion cores, which depends on the number of electron shells of the ions. A more complex situation arises with intercalation compounds of titanium dichalcogenides. This is associated with the fact that, in the sequence TiS_2–$TiSe_2$–$TiTe_2$, an increase in the density of states at the Fermi level due to an increase in the degree of overlap of the valence band and the conduction band [6] is accompanied by an increase in the polarizability of ion cores upon changing over to a heavier chalcogen atom. We believe that, in order to separate these contributions, it is necessary to investigate the structural and electrical properties of intercalation compounds of zirconium dichalcogenides and, in particular, zirconium diselenide $ZrSe_2$. This compound is isostructural to titanium dichalcogenides, exhibits semiconductor properties with a gap at the Fermi level (as is the case in TiS_2), and possesses an increased polarizability of ion cores (as compared to $TiSe_2$) due to the larger atomic weight of zirconium as compared to titanium. Therefore, by comparing the degrees of localization of charge carriers of $ZrSe_2$, TiS_2, and $TiSe_2$ upon their intercalation with the same metal, for example, silver, it is possible to determine the dominant contribution to the polarizability in the course of the formation of polarons. The purpose of the present work was to solve this problem.

2. SAMPLES AND EXPERIMENTAL TECHNIQUE

Samples used in our experiments were synthesized from the following elements: zirconium subjected to iodine cleaning (purity, 99.95), selenium of the OSCh 19-5 grade (purity, 99.999), and silver subjected to electrolytic cleaning (purity, 99.995). At the first stage of the synthesis, weighed portions of granular zirconium and selenium were placed in hermetically sealed and evacuated (to 10^{-5} Torr) silica glass ampules and were then sintered at temperatures in the range from 1100 to 1200 K for 7–10 days. Thereafter, the resultant compound $ZrSe_2$ and silver were mixed in the stoichiometric ratio. The mixture was placed in hermetically sealed and evacuated (to 10^{-5} Torr) Pyrex glass ampules and was then heated at temperatures in the range from 650 to 720 K for 100 h. The Ag_xZrSe_2 compounds thus

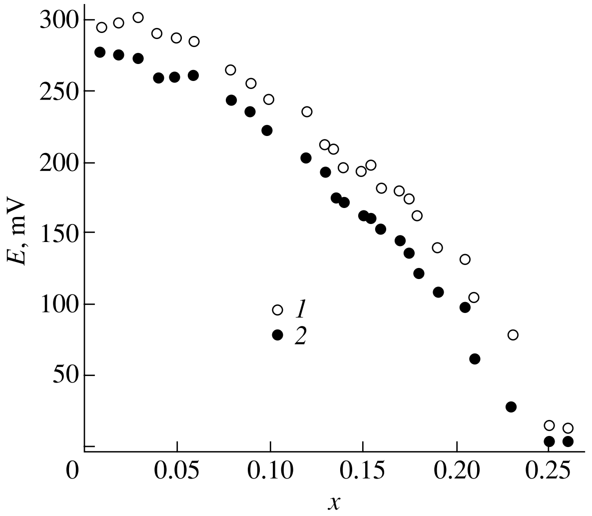

Fig. 1. Dependences of the partial free energy of formation of the Ag_xZrSe_2 compound on the silver content x at temperatures of (*1*) 573 and (*2*) 423 K.

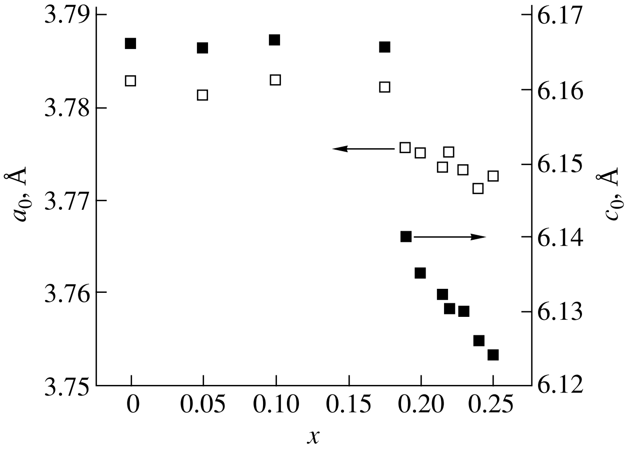

Fig. 2. Dependences of the lattice constants a_0 (open squares) and c_0 (closed squares) of the $ZrSe_2$ compound with a hexagonal structure on the intercalated silver content x at room temperature.

prepared, as a rule, were homogeneous to within the accuracy of the x-ray diffraction analysis (DRON-4-13 x-ray diffractometer, CuK_α radiation, room temperature). The electrical conductivity and the Seebeck coefficient were measured according to the standard four-point probe method with the use of polycrystalline cold-pressed samples. The nitrogen atmosphere used in the electrical measurements was preliminarily dried and purified from oxygen. The residual pressure of impurities was no higher than 10^{-15} Torr. Owing to the high mobility of silver ions in Ag_xZrSe_2 compounds, the technique of measuring the voltage difference (electromotive force) across the electrochemical cell was used to determine the concentration dependences of the thermodynamic functions and to construct isothermal sections of the phase diagram in the "silver content x–temperature T" coordinates. In these experiments, the silver content was varied using coulometric titration, i.e., by passing a current pulse of specified amplitude and width through the following electrochemical cell:

$$\mathrm{Ag/AgI/Ag_xZrSe_2/graphite}. \qquad (1)$$

For an electrochemical cell of this type, the operating temperature range is governed by the conditions under which the ionic conductivity of AgI (an electron filter suppressing electron conduction) is rather high and far exceeds the n-type conductivity. These conditions are satisfied in the temperature range 450–600 K, in which the ionic conductivity exceeds the n-type conductivity by a factor of 10^4. According to [7], the electromotive force E of electrochemical cell (1) is related to the chemical potential μ_{Ag} of a silver atom dissolved in Ag_xZrSe_2 through the expression

$$eE = -(\mu_0 - \mu_{Ag}), \qquad (2)$$

where e is the elementary charge and μ_0 is the chemical potential of a silver atom in a standard state (in bulk silver). Therefore, knowing the dependences of the emf E of electrochemical cell (1) on the temperature and silver content, we can determine the boundaries of the single-phase regions in the phase diagram.

3. RESULTS AND DISCUSSION

Figure 1 shows the dependences of the partial free energy of formation of the Ag_xZrSe_2 compound on the silver content x at two temperatures. As can be seen, these dependences are characteristic of materials in which the Fermi level is located between the bottom of the conduction band and the center of an impurity band of polaron nature [8]. This can also be judged from the formation of a two-phase region, which manifests itself in the form of a plateau in the dependence $E(x)$ and can be observed upon intercalation of even the first silver atoms. According to the Gibbs phase rule, the fact that the free energy of formation is independent of the concentration of one of the components under isothermal conditions at equal pressures can be explained only in terms of an inhomogeneous (non-single-phase) state of the sample. It should be noted that the Ag–$ZrSe_2$ system is characterized by two single-phase regions. Their boundaries are determined by the portions in the dependence $E(x)$ at $T = 473$ K in the concentration ranges $0.06 < x < 0.14$ and $0.175 < x < 0.23$.

Upon cooling of the sample to room temperature, the phase with a lower silver content most likely undergoes a decomposition of peritectic nature. This is indicated by the fact that the lattice parameters at room temperature do not depend on the content of intercalated silver in the range $x = 0$–0.175 (Fig. 2). In this region of compositions, the x-ray diffraction patterns of

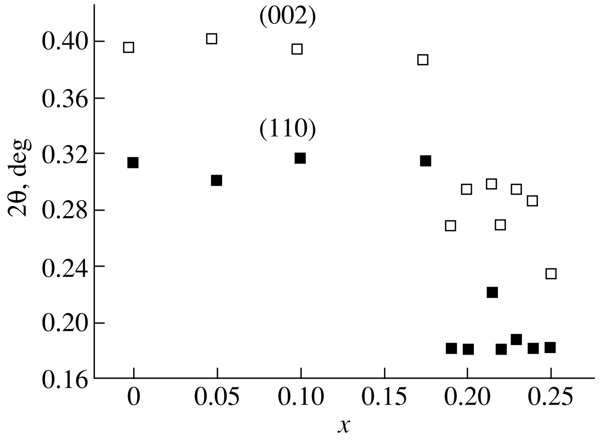

Fig. 3. Concentration dependences of the half-width of the diffraction lines (002) (open squares) and (110) (closed squares) on the silver content x in Ag_xZrSe_2 compounds (half-widths are expressed in terms of the diffraction angle 2θ).

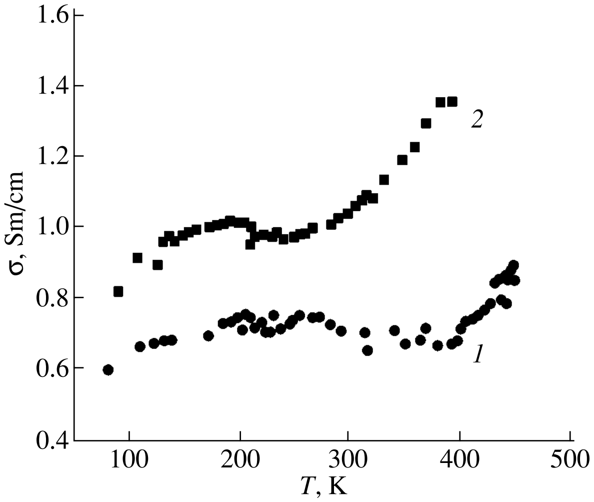

Fig. 4. Temperature dependences of the electrical conductivity for two single-phase Ag_xZrSe_2 compositions with silver contents x = (*1*) 0.20 and (*2*) 0.25 over the entire temperature range covered.

Ag_xZrSe_2 intercalation compounds are identical to the diffraction pattern obtained for the initial $ZrSe_2$ compound. The same situation was observed in the Ag–$TiSe_2$ system, for which the lattice parameters of the $TiSe_2$ and $Ag_{0.25}TiSe_2$ phases proved to be close to each other to such an extent that the diffraction lines of these phases could not be resolved [9]. These inference is in agreement with the concentration dependences of the half-width of the diffraction lines for the (110) and (002) reflections which correspond to the parameters a_0 and c_0 of the hexagonal lattice, respectively (Fig. 3). It can be seen from Fig. 3 that, in the system under investigation, there exist two composition regions for which the diffraction lines differ in width. Apparently, this circumstance is associated with the fact that the lattice parameters of the $ZrSe_2$ and $Ag_{0.175}ZrSe_2$ phases are also close to each other to such an extent that the diffraction lines of these phases cannot be resolved.

In the homogeneity region of the sole room-temperature stable phase, which can be designated as $Ag_{0.25}ZrSe_2$ or, what amounts to the same, $AgZr_4Se_8$, both lattice parameters, a_0 and c_0, decrease in the concentration range $x > 0.175$. This indicates that the volume of the unit cell of $ZrSe_2$ decreases upon incorporation of silver. The above behavior differs from that observed for intercalation compounds based on titanium dichalcogenides in which the contraction of the unit cell along the c axis is attended by an increase in the lattice parameter a_0, so that the total volume of the unit cell slightly increases with an increase in the intercalant content. It is generally believed that the observed decrease in the lattice parameter c_0 for intercalation compounds based on titanium dichalcogenides with charge-carrier localization of the polaron type is associated with a decrease in the distance between layers of the host lattice due to the formation of Ti–*Me*–Ti centers with covalent bonds (*Me* is an intercalated metal) [1, 4]. Most probably, the same is also true for Ag_xZrSe_2 intercalation compounds. The formation of these centers is usually explained by the hybridization of d_{z^2} orbitals of the host transition metal (Ti or Zr) and valence states of the intercalated metal (in our case, the 5*s* states of silver). The origin of the lattice contraction in the basal plane is not yet entirely understood. This behavior can also be explained by the formation of covalent bonds. However, the question regarding the sublattice and states associated with the formation of these bonds remains open.

The x-ray powder diffraction pattern of the $AgZr_4Se_8$ compound was indexed in a trigonal crystal system with space group $P\bar{3}m1$, which coincides with the space group of the initial $ZrSe_2$ compound. It is worth noting that no indication of silver ordering throughout the sample is revealed at room temperature. This is another argument in support of the polaron nature of the stability of the $AgZr_4Se_8$ phase, because the ordered state of intercalated silver becomes unstable at temperatures well below the point of polaron band collapse [10].

Figure 4 depicts the temperature dependences of the electrical conductivity for two Ag_xZrSe_2 compositions with silver contents x = 0.20 and 0.25. It can be seen from Fig. 4 that, although the concentration of electrons introduced with intercalated silver is relatively high (~10^{20} cm^{-3}), the temperature dependence of the electrical conductivity exhibits activation behavior. This suggests that, in contrast to the predictions made in the framework of the rigid-band model, the electrons introduced are not involved in the conduction band of $ZrSe_2$.

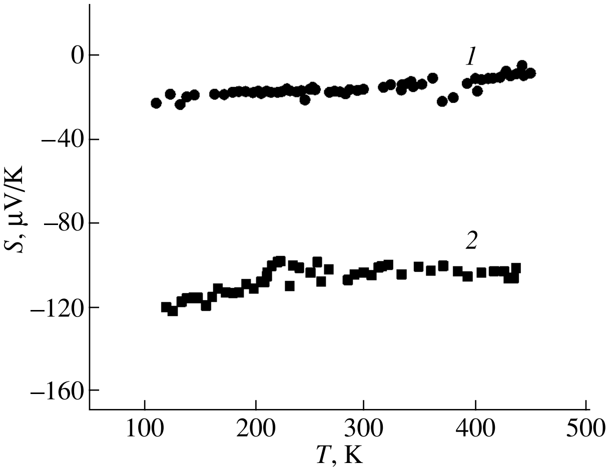

Fig. 5. Temperature dependences of the Seebeck coefficient for two single-phase Ag_xZrSe_2 compositions with silver contents x = (*1*) 0.25 and (*2*) 0.20 over the entire temperature range covered.

It seems likely that electron transfer upon intercalation occurs toward the band of hybrid Ag 5*s*–Zr 4*d* states localized in the vicinity of the Fermi level. The temperature dependence of the electrical conductivity at temperatures $T > 300$ K can be described by the expression $\sigma = \sigma_0 \exp(U/kT)$, where U is the activation energy. An increase in the magnitude of the electrical conductivity and, correspondingly, in the activation energy with an increase in the silver content x can be interpreted as resulting from the increase in the contribution made to the electrical conductivity by the localized electrons introduced with intercalated silver. This interpretation is in good agreement with the decrease in the Seebeck coefficient with increasing x. An analysis of the temperature dependence of the Seebeck coefficient revealed the presence of several types of charge carriers in Ag_xZrSe_2 (Fig. 5). It can be assumed that these carriers are silver impurity electrons and intrinsic electrons and holes of $ZrSe_2$. The Zr–Ag–Zr covalently bound centers serve as centers of localization of conduction electrons and strain centers of the lattice simultaneously. These objects can be treated as covalent polarons.

Thus, the experimental results lend support to the predicted polaron type of localization of charge carriers in the Ag–$ZrSe_2$ system. As was shown earlier in [8], the boundary of the single-phase state with a minimum intercalant content corresponds to the coincidence of the energies at the Fermi level and at the center of the polaron band (in our case, the band of hybrid Ag 5*s*–Zr 4*d* states). The concentration of electrons that need to be introduced into the material in order to ensure half filling of the polaron band depends on its position with respect to the Fermi level in the initial material, which, in turn, is determined by the effective ionization potential I_{eff} of the intercalated atom [4]. The effective ionization potential I_{eff} differs from the tabulated value by the screening constant γ; i.e., $I_{\text{eff}} = \gamma I_i$, where I_i is the ionization potential of a free atom or ion. For $TiSe_2$-based intercalation compounds, the screening constant is determined to be $\gamma = 1/33$ [4]. The ionization potential of the silver intercalated into $TiSe_2$ is estimated as $I_{\text{Ag}}^{\text{TiSe}_2} = \gamma 7.5763 \approx 0.23$ eV [11], which corresponds to the energy at the Fermi level located near the center of the polaron band. Therefore, intercalation of atoms whose ionization potential is less than $I_{\text{eff}} = 0.23$ eV should not lead to the formation of covalently bound centers. For $TiSe_2$-based intercalation compounds, the ionization potential of intercalated lithium $I_{\text{Li}}^{\text{TiSe}_2} = \gamma 5.3918 \approx 0.16$ eV is the closest in magnitude to the ionization potential of intercalated silver $I_{\text{Ag}}^{\text{TiSe}_2}$. It was proved that intercalation of lithium results in charge transfer from the intercalant to the lattice of $TiSe_2$; in this case, the introduced electrons remain completely free without any indication of electron localization [12]. This can be explained by the fact that the hybrid band formed upon incorporation of lithium is located very far above the Fermi level and, therefore, turns out to be empty. It is evident that, in the situation where silver atoms are intercalated into the $TiSe_2$ and $ZrSe_2$ compounds, the positions of the hybrid bands with respect to the Fermi level of the initial material should differ from each other because of the difference in the screening constants γ. Hence, if the dispersion of the polaron band is ignored, the width ratio of the two-phase regions for these materials should be equal to the ratio of their screening constants $\gamma(TiSe_2)/\gamma(ZrSe_2) = 1.31$. As a result, we obtain the quantity $\gamma(ZrSe_2) \approx 1/25$. Therefore, upon incorporation of lithium into $ZrSe_2$, the effective ionization potential of intercalated lithium $I_{\text{Li}}^{\text{ZrSe}_2}$ is approximately equal to 0.22 eV. This ionization potential is close to the critical value to such an extent that the formation of Ti–Li–Ti covalent centers (polarons) becomes quite possible.

According to experimental data available in the literature on the structural and electrical properties of $ZrSe_2$ diselenides containing lithium, the lattice parameters of intercalation compounds in the Li–$ZrSe_2$ system do not depend on the content of intercalated lithium up to $x = 0.4$. This composition corresponds to the crossover from semiconductor conductivity to metallic conductivity. An extended discussion of the nature of this crossover and the relevant experimental results is given in the review by Friend and Yoffe [13]. In our opinion, Berthier *et al.* [14] most clearly demonstrated that the two-phase region exists in the concentration range $0 < x < 0.4$. This suggests that intercalation of lithium into $ZrSe_2$ also leads to the formation of polarons. The shift observed in the concentration boundary of the phase instability upon replacement of silver by lithium is in good agreement with the fact that the ionization potential of intercalated lithium is less than the ionization potential of intercalated silver. Moreover, the fact that the lattice parameters of the intercalation compounds do not depend on the intercalant content in the concentration range below the critical value confirms the validity of the proposed model.

4. CONCLUSIONS

Thus, the results obtained have demonstrated that the screening constant of the potential of the intercalated metal in $ZrSe_2$ is less than that in $TiSe_2$. The fundamental difference between these materials lies in the fact that, unlike the latter compound, the former compound is characterized by a gap at the Fermi level. Therefore, we can conclude that the presence of charge carriers capable of screening the potential of the intercalated ion and, thus, preventing the formation of covalent bonds between the intercalant and the host lattice is of crucial importance.

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