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Features of Structural, Energetic and Electrokinetic Properties of Semiconductor Thermoelectric Material $TiNi_{1-x}Ag_xSn$

The structural, electrokinetic, and energetic properties of the semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$*, obtained by doping the TiNiSn compound with Ag atoms, were investigated. The nature of the generated energy states and mechanisms of electrical conductivity were established. It was shown that at various concentrations, Ag atoms* ($3d^{10}5s^1$) *can occupy different crystallographic positions, generating structural defects of both acceptor and donor nature. At concentrations of* $TiNi_{1-x}Ag_xSn$*,* $x = 0–0.02$*, Ag atoms predominantly replace Sn atoms* ($4d^{10}5s^25p^2$) *in the 4c position, generating acceptor states* $\varepsilon_A^{Ag(Sn)}$ *in the band gap* ε_g*. At higher concentrations,* $x > 0.02$*, Ag atoms replace Ni atoms* ($3d^84s^2$) *in the 4d position, generating structural defects of donor nature and the corresponding energy states* $\varepsilon_D^{Ag(Ni)}$*. The ratio of the concentrations of the generated donors and acceptors determines the position of the Fermi level* ε_F*. The performed studies allowed us to identify the mechanisms of electrical conductivity to determine the synthesis parameters of the thermoelectric material* $TiNi_{1-x}Ag_xSn$ *with the maximum efficiency of converting thermal energy into electrical energy. It is shown that the semiconductor solid solution* $TiNi_{1-x}Ag_xSn$ *is a promising thermoelectric material.*

Keywords: thermoelectric material, thermoelectric figure of merit, electronic structure, electrical resistivity, thermopower coefficient.

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Introduction

Research [1, 2] demonstrates that the optimal values for the thermoelectric figure of merit, denoted as Z (where $Z = \alpha^2 \cdot \sigma/\kappa$), in semiconductor thermoelectric materials can be achieved through doping. This is particularly effective when the type of doping impurity matches the conductivity type of the base semiconductor. Under such doping conditions, the Fermi level ε_F is located near the mobility threshold of the corresponding continuous energy band, which will lead to a rapid growth of the electrical conductivity $\sigma(T)$ and the preservation of high values of the thermopower coefficient $\alpha(T)$ and the invariance of the thermal conductivity coefficient $\kappa(T)$. In turn, by adjusting the type, concentration, and method of introducing the doping impurity into the semiconductor, one can purposefully create energy states within the band gap ε_g that define its properties. This is the essence of the process of optimizing the electrokinetic properties of a thermoelectric material to obtain the maximum values of the thermoelectric figure of merit Z [1, 2].

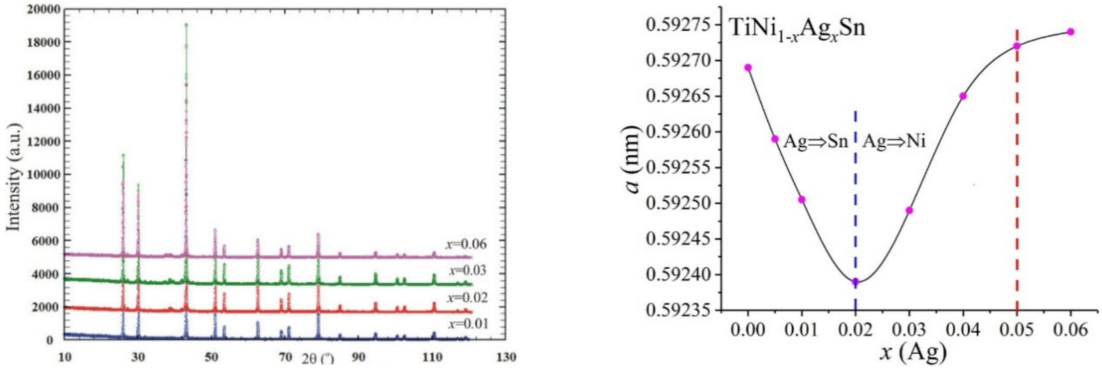
To search for a new thermoelectric material, the semiconductor solid solution $TiNi_{1-x}Ag_xSn$, $x = 0.01$–0.06, obtained by doping the basic semiconductor of the electronic conductivity type n-TiNiSn (structure type MgAgAs) with a donor impurity Ag ($3d^{10}5s^1$) by replacing Ni atoms ($3d^84s^2$) in the crystallographic position 4d (Ag atoms contain more 3d electrons than Ni atoms). Such doping meets the conditions to obtain maximum values of the thermoelectric figure of merit Z [1, 2]. To identify the optimal conditions for synthesizing the thermoelectric material $TiNi_{1-x}Ag_xSn$ with the maximum efficiency of converting thermal energy into electrical energy, a comprehensive study of its properties was carried out, which will allow us to clarify the features of the mechanisms of electrical conductivity.

Research methods

Modeling and experimental studies of the structural, energy, and electrokinetic properties of the new semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$, obtained by replacing Ni atoms in the TiNiSn compound with Ag atoms in the crystallographic position 4*d*, were carried out. Samples of $TiNi_{1-x}Ag_xSn$, $x = 0.01$–0.06, were produced by arc-melting of the charge of the initial components in an atmosphere of purified argon. To achieve equilibrium in the alloys, homogenizing annealing was performed at a temperature of 1073 K for 700 h, followed by quenching in cold water without breaking the ampoules beforehand. *X*-ray phase and structural analyses were performed using powder diffraction data obtained on DRON-2.0m (Fe $K\alpha$−radiation) and STOE STADI P (Cu $K\alpha_1$ − radiation) diffractometers. The chemical composition of the samples was controlled by energy-dispersive *X*-ray spectroscopy (electron microscope Tescan Vega 3 LMU). The structural parameters of the $TiNi_{1-x}Ag_xSn$ samples were calculated using the Fullprof Suite program [3]. For the ordered version of the $TiNi_{1-x}Ag_xSn$ crystal structure, the KKR method was was utilized in the coherent potential CPA approximation and local density LDA [4] to calculate the density of electronic states DOS. The calculations used experimental values of a constant unit cell on a *k*-grid with a size of $10 \times 10 \times 10$ and the Moruzzi-Janak-Williams exchange-correlation potential parameterization type [5]. The width of the energy window enclosed by the contour is 16 eV. The number of energy values for the DOS calculation was 1000. The accuracy of the calculation of the Fermi level position ε_F was ± 6 meV. To study the electrokinetic properties, samples of regular geometric shapes, measuring approximately $1.0 \times 1.0 \times 4$ mm^3, were utilized. The temperature and concentration dependences of the electrical resistivity $\rho(T)$ and the thermopower coefficient $\alpha(T)$ for the $TiNi_{1-x}Ag_xSn$ samples were measured in the ranges of $T = 80$–400 K and $x = 0.01$–0.06. The thermopower coefficient $\alpha(T)$ was measured by the potentiometric method relative to copper. The voltage drop on the samples was determined for different directions of the electric current to avoid the influence of a possible *p-n* junction at the contact points.

Study of structural properties of thermoelectric material $TiNi_{1-x}Ag_xSn$

Experimental studies of the phase composition of the $TiNi_{1-x}Ag_xSn$ samples, $x = 0$–0.06, established the correspondence of the composition of the charge of the initial components. Fig. 1 *a* shows the *X*-ray powder patterns of individual samples of the $TiNi_{1-x}Ag_xSn$ solid solution. According to *X*-ray phase analysis, the synthesized samples belong to the MgAgAs structure type [6]. At higher concentrations of Ag atoms, $x > 0.06$, the powder patterns contain insignificant reflections of impurity phases. Therefore, the study was performed for $TiNi_{1-x}Ag_xSn$ samples with an Ag content, $x = 0$–0.06. In the ordered version of the $TiNi_{1-x}Ag_xSn$ crystal structure, Ti atoms occupy the crystallographic position 4*a* (0, 0, 0), Ni(Ag) – 4*d* (¼, ¼, ¼) and Sn – 4*c* (½, ½, ½). Thus, the refinement of the crystal structure of the $TiNi_{0.98}Ag_{0.02}Sn$ sample by the Rietveld method confirmed its belonging to the MgAgAs structure type ($a = 0.59239$ nm, $R_I = 0.0424$, $R_p = 0.0792$, $R_{wp} = 0.104$, $\chi^2 = 1.39$). From the experimental results of *X*-ray structural studies of the $TiNi_{1-x}Ag_xSn$ samples, their crystallographic parameters were calculated, in particular, the unit cell parameter $a(x)$ (Fig. 1 *b*). As shown in [7], the structure of the TiNiSn compound is disordered, and the formation of substitutional solid solutions was usually accompanied by its ordering. We were unable to establish the fact of ordering the structure for the $TiNi_{1-x}Ag_xSn$ samples by *X*-ray structural analysis due to the insignificant concentrations of Ag atoms.



a) *b)*

Fig. 1. Diffraction patterns of samples (a) and change in the unit cell parameter a(x) (b) of the semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$

When synthesizing the thermoelectric material $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$, we expected a monotonic increase in the unit cell parameter $a(x)$ with increasing concentration of Ag atoms, since the atomic radius of Ag ($r_{\mathrm{Ag}} = 0.145$ nm) is much larger than the atomic radius of Ni ($r_{\mathrm{Ni}} = 0.125$ nm). In this case, structural defects of a donor nature should have formed in the structure of the semiconductor thermoelectric material $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$, since the Ag atom ($3d^{10}5s^1$) contains more $3d$-electrons than the Ni atom ($3d^8 4s^2$). At the same time, impurity donor states $\varepsilon_D^{\mathrm{Ag(Ni)}}$ should have been generated in the band gap of $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$. Since the TiNiSn compound is a semiconductor of the electronic conduction type [7], the generation of donor states in the $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$ solid solution corresponds to the condition for obtaining maximum values of the thermoelectric figure of merit Z [1, 2].

As seen from Fig. 1*b*, the nature of the change in the unit cell parameter $a(x)$ of $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$ does not meet our expectations. Thus, at $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$ concentrations, $x = 0$–0.02, the unit cell parameter $a(x)$ rapidly decreases, passes through a minimum at $x \approx 0.02$, and then, in the concentration range $0.02 < x \leq 0.05$, it also rapidly increases with quasi-saturation at $x > 0.05$. Based on the fact that the distribution of atoms in the crystal structure is the result of the interaction between the components, the smallest changes in the structure of the solid solution will be reflected in the behavior of the unit cell parameter $a(x)$. In this case, based on the behavior of the unit cell parameter $a(x)$ of $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$, it can be concluded that the introduction of Ag atoms into the structure of the TiNiSn compound is accompanied by complex structural transformations simultaneously in several crystallographic positions, and not only in the 4*d* position of Ni atoms, as predicted. Since the atomic radius of Ag ($r_{\mathrm{Ag}} = 0.145$ nm) is practically the same as the atomic radius of Ti ($r_{\mathrm{Ti}} = 0.146$ nm) and significantly larger than the atomic radius of Ni ($r_{\mathrm{Ni}} = 0.125$ nm), a decrease in the unit cell parameter $a(x)$ of $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$ at concentrations $x = 0$–0.02 is possible only if the largest Sn atoms ($r_{\mathrm{Sn}} = 0.162$ nm) are substituted in the crystallographic position 4*c*. In this case, structural defects of an acceptor nature will be generated in the structure of the compound, since Sn atoms ($4d^{10}5s^2 5p^2$) have a larger number of valence electrons than Ag atoms ($3d^{10}5s^1$). Such substitution will be attended by the generation of impurity acceptor states $\varepsilon_A^{\mathrm{Ag(Sn)}}$ within the band gap of $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$.

At the same time, we associate the increase in the cell parameter $a(x)$ of $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$ in the concentration range $0.02 < x \leq 0.05$ with the preferential substitution of Ni atoms ($r_{\mathrm{Ni}} = 0.125$ nm) by larger Ag atoms in the 4*d* position (Fig. 1 *b*). Such substitution, as shown above, is attended by the generation of structural defects of donor nature and the corresponding electronic states. Under such conditions, the thermoelectric material $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$ becomes a heavily doped and compensated semiconductor [8].

We associate the decrease in the rate of change of the lattice parameter of the $\mathrm{TiNi}_{1-x}\mathrm{Ag}_x\mathrm{Sn}$ with the transition to quasi-saturation at $x > 0.05$ (Fig. 1 *b*) with the solubility limit of Ag atoms in the TiNiSn compound matrix and the appearance of extraneous phases detected during *X*-ray structural studies. The insignificant solubility range of Ag atoms in the structure of the compound is the result of the destruction of the MgAgAs type structure [6] due to significant deformations of the unit cell, when atoms with significantly different atomic radii and charge states appear simultaneously in two crystallographic positions.

Thus, the analysis of the results of structural studies of the semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$ showed that at various concentrations, Ag atoms can replace Sn and Ni atoms in positions 4 *c* and 4 *d*, respectively, generating structural defects of acceptor and donor nature, as well as the corresponding energy states in the band gap ε_g. In this case, the type of main current carriers in $TiNi_{1-x}Ag_xSn$ will be determined by the ratio of the generated acceptor and donor states.

Modeling the electronic structure of thermoelectric material $TiNi_{1-x}Ag_xSn$

The density of states (DOS) distribution was calculated for the ordered version of the crystal structure of the semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$ (Fig. 2). In this case, Ag atoms replace only Ni atoms in the 4*d* position. Such modeling allows us to track the position of the Fermi level ε_F relative to the continuous energy bands, the dynamics of the band gap width ε_g, and to predict the behavior of the electrokinetic and energy properties of $TiNi_{1-x}Ag_xSn$.

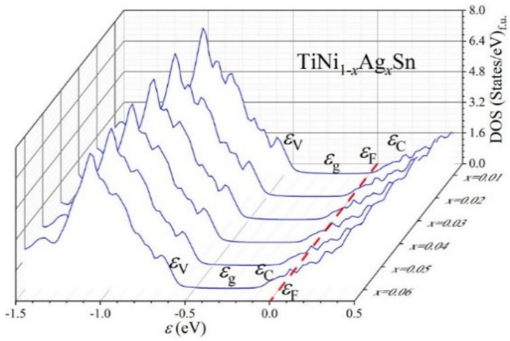


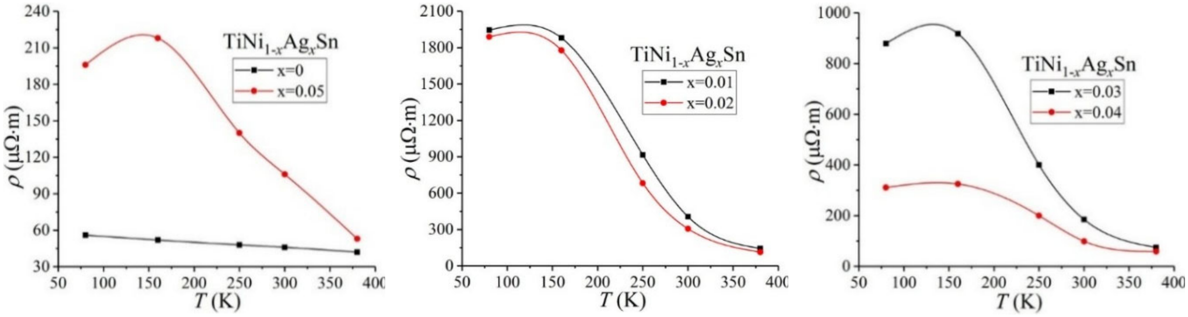
Fig. 2. Calculation of the distribution of the density of electronic states DOS for an ordered version of the structure of the semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$

We noted above that the TiNiSn compound is a semiconductor of the electronic conduction type, and the Fermi level ε_F is located at a distance of 16.9 meV from the percolation level of the conduction band ε_C [7]. The substitution of Ni atoms by Ag atoms generates structural defects of a donor nature, and donor states $\varepsilon_D^{Ag(Ni)}$ appear in the band gap ε_g of the thermoelectric material $TiNi_{1-x}Ag_xSn$. Thus, even at the lowest concentration of Ag atoms in the experiment ($x = 0.01$), the Fermi level ε_F will cross the percolation level of the conduction band ε_C. It will change the type of electrical conductivity of $TiNi_{1-x}Ag_xSn$ from an activated state to a metallic state, that is, an insulator-metal conductivity transition will occur, known as the Anderson transition [9]. The study of the electrokinetic properties of the thermoelectric material $TiNi_{1-x}Ag_xSn$ will show the degree of adequacy of the conclusions drawn above from structural and energy studies.

Electrokinetic and energetic properties of $TiNi_{1-x}Ag_xSn$

Fig. 3 illustrates the temperature dependences of the resistivity $\rho(T, x)$ of the semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$, $x = 0$–0.05. As seen from Fig. 3 *a*, the resistivity of the TiNiSn compound in the temperature range 80–400 K decreases, which is the result of an increase in the concentration of current carriers with temperature. This $\rho(T, x)$

behavior of the TiNiSn compound is consistent with previously obtained results, which indicate that it is a semiconductor with electronic-type conductivity [7]. In contrast, in samples doped with Ag atoms, an extremum appears in the temperature dependences ρ(*T, x*) of $TiNi_{1-x}Ag_xSn$ at a temperature of ~ 140 K. We can see that the resistivity ρ(*T, x*) increases with temperature in the range 80–140 K (Fig. 3), which is characteristic of the metallic type of conductivity. This means that at such temperatures the Fermi level ε_F of $TiNi_{1-x}Ag_xSn$ is in the continuous energy band, and the action of current carrier scattering mechanisms is one of the main reasons for the increase in the resistivity ρ(*T, x*).



a) b) c)

Fig. 3. Change in the resistivity ρ(T, x) with temperature for $TiNi_{1-x}Ag_xSn$

At higher temperatures, *T* > 140 K, there is a decrease in the resistivity ρ(*T, x*) of $TiNi_{1-x}Ag_xSn$, which is typical for semiconductors, when the Fermi level ε_F is located at the impurity level (band) in the band gap ε_g, from which thermal ejection of current carriers into the continuous energy band occurs. This leads to an increase in the concentration of current carriers, which is the reason for the decrease in the resistivity ρ(*T, x*) of $TiNi_{1-x}Ag_xSn$.

To calculate the energy parameters of the $TiNi_{1-x}Ag_xSn$ solid solution, *x* = 0–0.05, in particular, the position of the Fermi level ε_F in the band gap εg, the modulation amplitude of the continuous energy bands, we will use the traditional representation of the change in resistivity ln(ρ(1/*T, x*)) and the thermopower coefficient α(1/*T, x*) with temperature (Fig. 4).

The presence of activation parts in the temperature dependences ln(ρ(1/*T, x*)) of $TiNi_{1-x}Ag_xSn$ at high temperatures indicates that the samples studied are doped and compensated semiconductors. In these materials, the Fermi level ε_F is located within the band gap ε_g, near the percolation level of the conduction band ε_C. This is confirmed by the negative values of the thermopower coefficient α(1/*T, x*) at all concentrations and temperatures (Fig. 4), and the main current carriers in the $TiNi_{1-x}Ag_xSn$ semiconductor, as in TiNiSn, are electrons.

The temperature dependences ln(ρ(1/*T, x*)) of $TiNi_{1-x}Ag_xSn$ are described by formula (1) [8]:

$$\rho^{-1}(T) = \rho_1{}^{-1} exp\left(-\frac{\varepsilon_1{}^{\rho}}{k_B T}\right) + \rho_3{}^{-1} exp\left(-\frac{\varepsilon_3{}^{\rho}}{k_B T}\right), \quad (1)$$

where the first high-temperature term describes the activation of current carriers $\varepsilon_1{}^{\rho}(x)$ from the Fermi level ε_F to the percolation level of the conduction band ε_C and the second, low-temperature, term describes the jump conductivity $\varepsilon_3{}^{\rho}(x)$ with energies close to the Fermi level ε_F. Fig. 5 shows the change in activation energies $\varepsilon_1{}^{\rho}(x)$ of $TiNi_{1-x}Ag_xSn$ from the Fermi level ε_F to the percolation level of the conduction band ε_C.

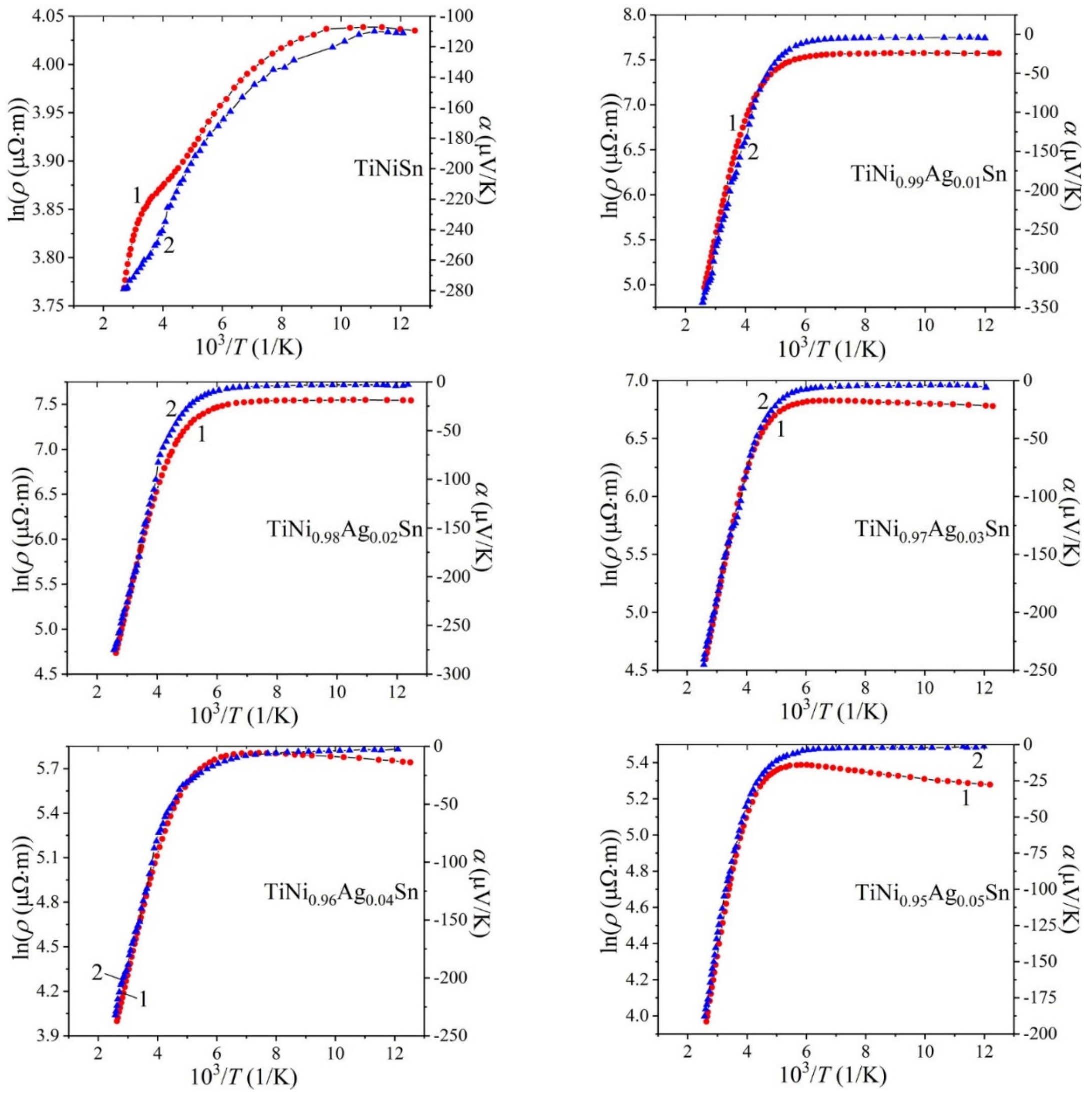


*Fig. 4. Temperature dependences of the resistivity ln(ρ(1/T, x)) (1)
and the thermopower coefficient α(1/T, x) (2) of TiNi$_{1-x}$Ag$_x$Sn*

In turn, the temperature dependences of the thermopower coefficient α(1/*T*, *x*) of TiNi$_{1-x}$Ag$_x$Sn can be described by the well-known formula (2) [9]:

$$\alpha = \frac{k_B}{e}\left(\frac{\varepsilon_i^{\alpha}}{k_B T} - \gamma + 1\right), \tag{2}$$

where γ is a parameter that depends on the nature of the scattering mechanisms. Using formula (2) from the high- and low-temperature activation parts of the α(1/*T*, *x*) dependence of TiNi$_{1-x}$Ag$_x$Sn, the activation energies $\varepsilon_1^{\alpha}(x)$ and $\varepsilon_3^{\alpha}(x)$ were calculated, which are proportional, respectively, to the amplitudes of the large-scale fluctuation of the continuous energy bands and the small-scale fluctuation of the doped and compensated semiconductor [8, 10].

Fig. 5 shows the change in the activation energy $\varepsilon_1^{\alpha}(x)$ of the semiconductor thermoelectric material TiNi$_{1-x}$Ag$_x$Sn. In this context, it is important to note that the amplitude of the large-scale fluctuation of the continuous energy bands depends on the compensation degree of the semiconductor: at a higher compensation degree, the amplitude of the band modulation is greater [8]. As can be seen from Fig. 5, the introduction of the smallest concentration of Ag atoms in the experiment into the TiNiSn compound ($x = 0.005$) is accompanied by a drift of the Fermi level ε_F from the percolation level of the conduction band ε_C into the depth of the band gap ε_g of $TiNi_{1-x}Ag_xSn$. Thus, if in the TiNiSn compound the Fermi level ε_F was at a distance of 16.9 meV from the percolation level of the conduction band ε_C, then in samples with the composition $TiNi_{0.995}Ag_{0.005}Sn$ it is already at a distance of 120.1 meV, and in $TiNi_{0.99}Ag_{0.01}Sn$ – 195.2 meV. Such a dip of the Fermi level ε_F into the depth of the band gap ε_g in a semiconductor of the electronic conduction type can be realized only under the condition of generating acceptor states that capture free electrons, reducing their concentration, which will lead to a rapid increase in the resistivity $\rho(x, T)$ (Fig. 6).

In addition, an increase in the concentration of acceptor states in semiconductor with *n*-type of conductivity will lead to an enlarge in the compensation degree (ratio of donors and acceptors), which is confirmed by the rapid growth of the activation energy ε_1^{α} of $TiNi_{1-x}Ag_xSn$ in the concentration range $x \approx 0–0.015$ (Fig. 5, curve 2).

Above, when analyzing the crystal structure, we assumed that the decrease in the unit cell parameter a(x) of $TiNi_{1-x}Ag_xSn$ at concentrations $x = 0–0.02$ is possible only under the condition of substitution in the 4*c* position of Sn atoms, which is accompanied by the generation of impurity acceptor states $\varepsilon_A^{Ag(Sn)}$ in the band gap. Thus, the results of electrokinetic and energy studies confirmed the correctness of the assumption made, supplementing structural studies.

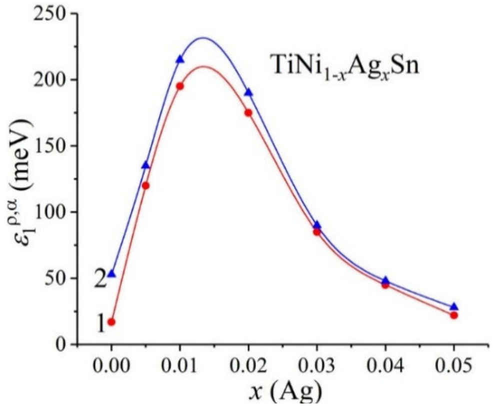


Fig. 5. Change in activation energies ε_1^{ρ} (1) and ε_1^{α} (2) of $TiNi_{1-x}Ag_xSn$

With an increase in the content of Ag atoms, $x > 0.015$, the Fermi level ε_F for $TiNi_{1-x}Ag_xSn$ begins to move back from the middle of the band gap ε_g in the direction of the conduction band ε_C. The fact that the movement occurs precisely towards the conduction band ε_C is indicated by the negative values of the thermopower coefficient $\alpha(x, T)$ (Fig. 4, 6). Thus, if in the $TiNi_{0.98}Ag_{0.02}Sn$ sample the Fermi level ε_F is at a distance of 175.2 meV from the percolation level of conduction band ε_C, then in the $TiNi_{0.97}Ag_{0.03}Sn$ sample it is at a distance of 85.2 meV, and in $TiNi_{0.95}Ag_{0.05}Sn$ – 22.4 meV. The observed behavior of the Fermi level ε_F in the thermoelectric material $TiNi_{1-x}Ag_xSn$ at Ag concentrations, $x > 0.02$, is due to the generation of donor states in the semiconductor. The appearance of additional donor states in the heavily doped and compensated semiconductor $TiNi_{1-x}Ag_xSn$ with electronic conduction will change the ratio of acceptors and donors. As a result, the compensation degree will decrease, as evidenced by the rapid decrease in the activation energy ε_1^{α} (Fig. 5, curve 2) in the concentration range $x \geq 0.015$.

From the results of structural studies above, it has been concluded that the increase in the unit cell parameter $a(x)$ of $TiNi_{1-x}Ag_xSn$ at concentrations $0.02 < x \leq 0.05$ is linked to the preferential substitution of Ni atoms in the 4*d* position, which is accompanied by the generation of donor states $\varepsilon_D^{Ag(Ni)}$ within the band gap. In this case, the results of electrokinetic and energy studies confirmed the correctness of the conclusions of structural studies, clarifying them.

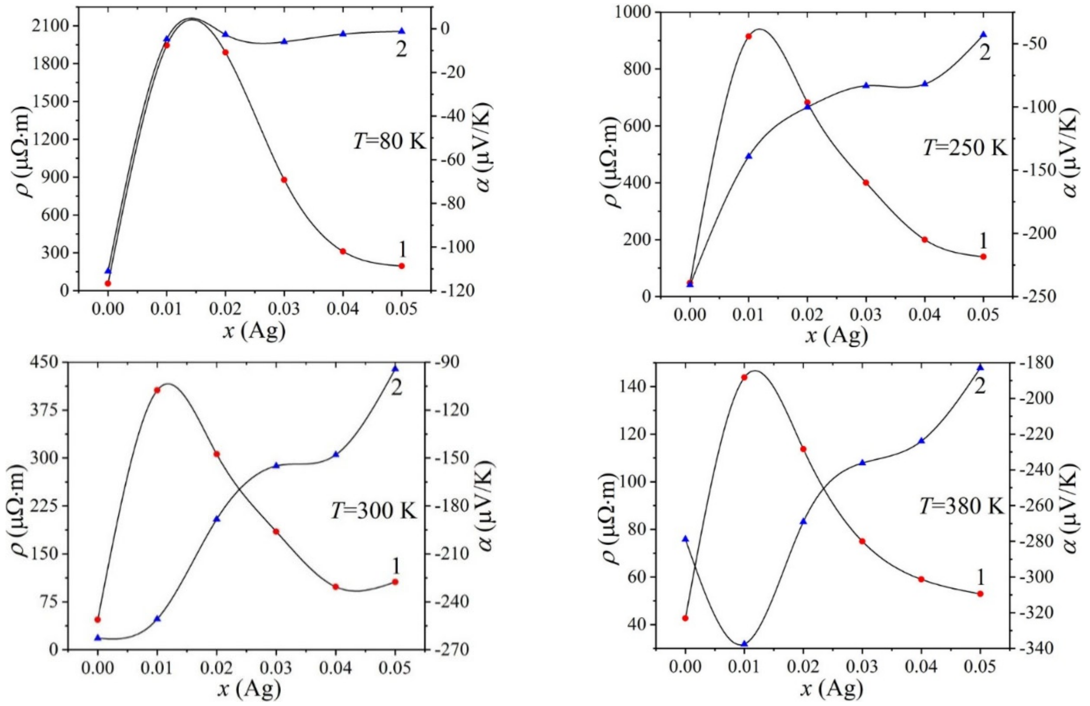


Fig. 6. Change in the resistivity ρ(x,T) (1) and the thermopower coefficient α(x, T) (2) of the thermoelectric material $TiNi_{1-x}Ag_xSn$ *at different temperatures*

Thus, studies on the electrokinetic and energetic properties of $TiNi_{1-x}Ag_xSn$ have confirmed the conclusions from structural studies regarding the substitution by Ag atoms, depending on their concentration, of Sn and Ni atoms in positions 4c and 4*d*, respectively. In this case, structural defects of both acceptor and donor nature are generated in the semiconductor, along with their corresponding energy states. The conducted studies helped us to identify the mechanisms of electrical conductivity to establish optimal conditions for synthesizing the thermoelectric material $TiNi_{1-x}Ag_xSn$ with the maximum efficiency in converting thermal energy into electrical energy.

Conclusions

Based on the results of the study of the crystal and electronic structure, electrokinetic properties and energy characteristics of the semiconductor thermoelectric material $TiNi_{1-x}Ag_xSn$, obtained by doping the TiNiSn compound with Ag atoms, the nature of the generated energy states and mechanisms of electrical conductivity have been established. It is shown that at various concentrations, Ag atoms ($3d^{10}5s^1$) can occupy different crystallographic positions, generating structural defects of acceptor and donor nature. At concentrations of $TiNi_{1-x}Ag_xSn$, $x = 0–0.02$, Ag atoms predominantly replace Sn atoms ($4d^{10}5s^25p^2$) in the 4*c* position, generating acceptor states $\varepsilon_A^{Ag(Sn)}$ in the band gap ε_g. At higher concentrations, $x > 0.02$, Ag atoms replace Ni atoms ($3d^84s^2$) in the 4*d* position, generating structural defects of donor nature and the corresponding energy states $\varepsilon_D^{Ag(Ni)}$. The ratio of the concentrations of the generated donors and acceptors determines the position of the Fermi level ε_F. The performed studies allowed us to identify the mechanisms of electrical conductivity to establish the synthesis parameters of the thermoelectric material $TiNi_{1-x}Ag_xSn$, optimizing its efficiency in converting thermal energy into electrical energy. It is shown that the semiconductor solid solution $TiNi_{1-x}Ag_xSn$ is a promising thermoelectric material.

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Особливості структурних, енергетичних та електрокінетичних властивостей напівпровідникового термоелектричного матеріалу $TiNi_{1-x}Ag_xSn$

Досліджено структурні, електрокінетичні та енергетичні властивості напівпровідникового термоелектричного матеріалу $TiNi_{1-x}Ag_xSn$*, отриманого легуванням сполуки TiNiSn атомами Ag. Встановлено природу генерованих енергетичних станів та механізмів електропровідності. Показано, що за різних концентрацій атоми Ag* ($3d^{10}5s^1$) *можуть займати різні кристалографічні позиції, генеруючи структурні дефекти акцепторної та донорної природи. За концентрацій* $TiNi_{1-x}Ag_xSn$, $x = 0–0.02$, *атоми Ag переважно заміщають у позиції 4c атоми Sn* ($4d^{10}5s^25p^2$)*, генеруючи в забороненій зоні* ε_g *акцепторні стани* $\varepsilon_A^{Ag(Sn)}$*. За більших концентрацій,* $x > 0.02$*, атоми Ag заміщають у позиції 4d атоми Ni* ($3d^84s^2$)*, генеруючи структурні дефекти донорної природи та відповідні енергетичні стани* $\varepsilon_D^{Ag(Ni)}$*. Співвідношення концентрацій генерованих донорів та акцепторів визначає положення рівня Фермі* ε_F*. Проведені дослідження дозволили ідентифікувати механізми електропровідності для визначення параметрів синтезу термоелектричного матеріалу* $TiNi_{1-x}Ag_xSn$ *з максимальною ефективністю перетворення теплової енергії в електричну. Показано, що напівпровідниковий твердий розчин* $TiNi_{1-x}Ag_xSn$ *є перспективним термоелектричним матеріалом.*

Ключові слова: термоелектричний матеріал, термоелектрична добротність, електронна структура, електроопір, коефіцієнт термо-ерс.

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