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Optimization of Properties of a New Thermoelectric Material Obtained by Doping of n-Ti_{1-x}Nb_xNiSn Semiconductor with Sb Atoms

The structural, electrokinetic, and energetic properties of the new thermoelectric material n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y, x = 0.01–0.02, y = 0–0.03, obtained by doping the semiconductor n-Ti_{1-x}Nb_xNiSn with Sb atoms (4d¹⁰5s²5p³) by replacing Sn atoms (4d¹⁰5s²5p²) were investigated. The nature of the generated energy states and mechanisms of electrical conductivity were established. It was shown that at varying concentrations of Sb atoms in the crystallographic position 4c, structural defects of a donor nature are generated, and the corresponding energy states $\varepsilon_D^{Sb(Sn)}$ are generated in the band gap ε_g of the semiconductor. Optimization of the properties of the n-Ti_{1-x}Nb_xNiSn solid solution by doping the n-type semiconductor with a donor impurity leads to a decrease in the compensation degree and meets the conditions for achieving maximum efficiency of thermal energy conversion into electrical energy. A new semiconductor thermoelectric material, Ti_{1-x}Nb_xNiSn_{1-y}Sb_y, with high thermoelectric power values, was obtained.

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

Introduction

The experimental study of the semiconductor solid solution n-Ti_{1-x}Nb_xNiSn showed that it is a promising thermoelectric material (Fig. 1 a). The simulated thermoelectric figure of merit values are maximum ($ZT = 0.76$) at the concentration n-Ti_{0.99}Nb_{0.01}NiSn and the temperature

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$T \approx 650$ K [1]. Doping the semiconductor $n\text{-TiNiSn}$ [2] with Nb atoms ($4d^45s^1$) by replacing Ti atoms ($3d^24s^2$) in the crystallographic position $4a$ met the condition of achieving maximum values of the thermoelectric figure of merit Z ($Z = \alpha^2 \cdot \sigma / \kappa$), when the type of doping impurity and the type of conductivity of the base semiconductor are the same [3, 4]. In this case, only structural defects of donor nature and their corresponding energy states in the band gap ε_g should be generated in the crystal, as Nb has more d -electrons than Ti. Modeling of the distribution of the density states DOS in $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ confirmed that under such doping conditions the Fermi level ε_F should approach the percolation level of the conduction band ε_C (Fig. 1 b). This would lead to a rapid increase in the electrical conductivity $\sigma(T)$ while maintaining high values of the thermopower coefficient $\alpha(T)$ and the invariance of the thermal conductivity coefficient $\kappa(T)$.

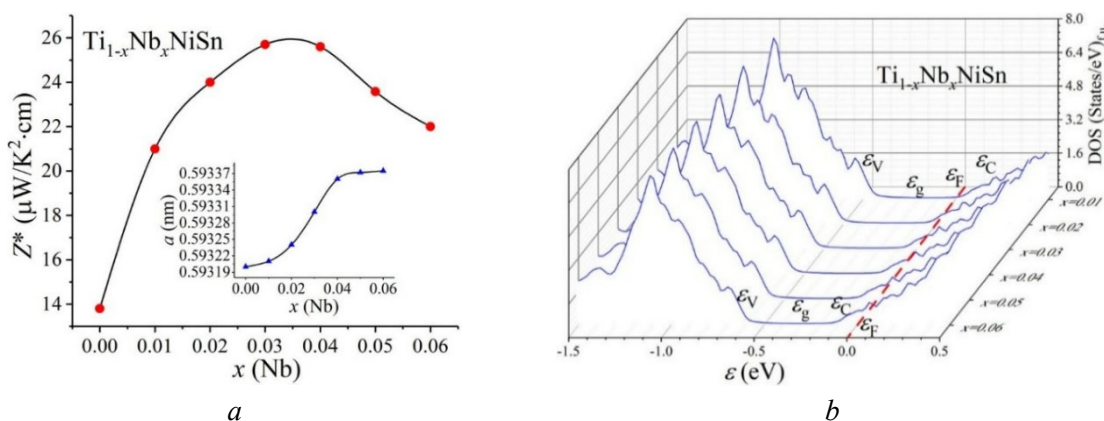


Fig. 1. Change in the thermoelectric power factor $Z^*(x)$ (a) and the distribution of density states DOS (b) of the semiconductor solid solution $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$.

Inset 1a: change in the unit cell parameter $a(x)$ of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$

However, the study of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ solid solution established [1] that Nb atoms can occupy different crystallographic positions, generating structural defects of both acceptor and donor nature simultaneously in various ratios. It is indicated, in particular, by the behavior of the unit cell parameter of $\text{Ti}_{1-x}\text{Nb}_x\text{NiSn}$ (Fig. 1 a, inset). At concentrations of $\text{Ti}_{1-x}\text{Nb}_x\text{NiSn}$, $x = 0\text{--}0.03$, Nb atoms simultaneously in different ratios replace Ti and Ni atoms ($3d^84s^2$), generating donor and acceptor states in the band gap ε_g , respectively. The appearance of acceptor states significantly compensates for the generated donors, which slows down the movement of the Fermi level ε_F to the percolation level of the conduction band ε_C . In this case, the values of the electrical conductivity $\sigma(T)$ increased more slowly than predicted and reached maximum values at concentrations $x > 0.04$. But at such concentrations of Nb impurity atoms, the value of the thermopower coefficient $\alpha(T)$ rapidly decreased, which ultimately limited the growth of the thermoelectric figure of merit of $\text{Ti}_{1-x}\text{Nb}_x\text{NiSn}$.

To obtain maximum thermoelectric figure of merit values in the $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ semiconductor, it is necessary to optimize its electrokinetic properties. For this purpose, $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ was doped with a donor impurity Sb ($4d^{10}5s^25p^3$), replacing Sn atoms ($4d^{10}5s^25p^2$) (Sb has more valence electrons than Sn), which should bring the Fermi level ε_F

closer to the percolation level of the conduction band ε_c . Such doping meets the conditions for obtaining maximum Z values [3, 4]. To determine the conditions for the synthesis of a new semiconductor thermoelectric material $\text{Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ with maximum efficiency of converting thermal energy into electrical energy, it is necessary to establish the nature of the generated energy states and mechanisms of electrical conductivity, which is the subject of the study presented below.

Research methods

Modeling and experimental studies of the structural, energy, and electrokinetic properties of a new semiconductor thermoelectric material $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, obtained by replacing Sn atoms in $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ with Sb atoms in the crystallographic position 4c, were carried out. Samples of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, $x = 0.01\text{--}0.05$, $y = 0.01\text{--}0.03$, were produced by arc-melting of a charge of starting components in a purified argon atmosphere. To achieve an equilibrium state for 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 analysis of the synthesized samples was performed using X-ray diffraction (DRON-2.0m diffractometer with Fe K_α -radiation). The chemical composition of the samples was controlled by energy-dispersive X-ray spectroscopy (Tescan Vega 3 LMU electron microscope). The structural parameters of the $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ samples were calculated using the WinCSD program [5]. For the ordered version of the $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ crystal structure, the distribution of the density of electronic states DOS was calculated using the KKR method in the CPA coherent potential approximation and the LDA local density [6]. The experimental values of the constant unit cell on a k -grid with a size of $10 \times 10 \times 10$ and the Moruzzi-Janak-Williams type of exchange-correlation potential parameterization [7] were used for the calculations. The width of the energy window enclosed by the contour is equal to 16 eV. The number of energy values for the DOS calculation was 1000. The accuracy of the Fermi level position calculation ε_F was ± 6 meV. To study the electrokinetic properties, samples in a regular geometric shape measuring $\sim 1.0 \times 1.0 \times 4$ mm³ were used. The temperature and concentration dependences of the resistivity $\rho(T)$ and the thermopower coefficient $\alpha(T)$ for the $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ samples were measured in the temperature range from 80 to 400 K. The thermopower coefficient $\alpha(T)$ was measured by the potentiometric method relative to copper. The voltage drop on the samples was determined for different current directions to avoid the influence of a possible p-n junction at the contact points.

Study of structural properties of thermoelectric material $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$

The study of the phase composition of the surface of the $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ samples, $x = 0.01\text{--}0.05$, $y = 0.01\text{--}0.03$, established the correspondence of the composition of the charge of the initial components. X-ray structural studies of all synthesized $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ samples showed that they belong to the MgAgAs structure type [8]. In this case, the Ti(Nb)

atoms occupy the crystallographic position $4a$ (0, 0, 0), Ni – $4d$ ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and Sn(Sb) – $4c$ ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

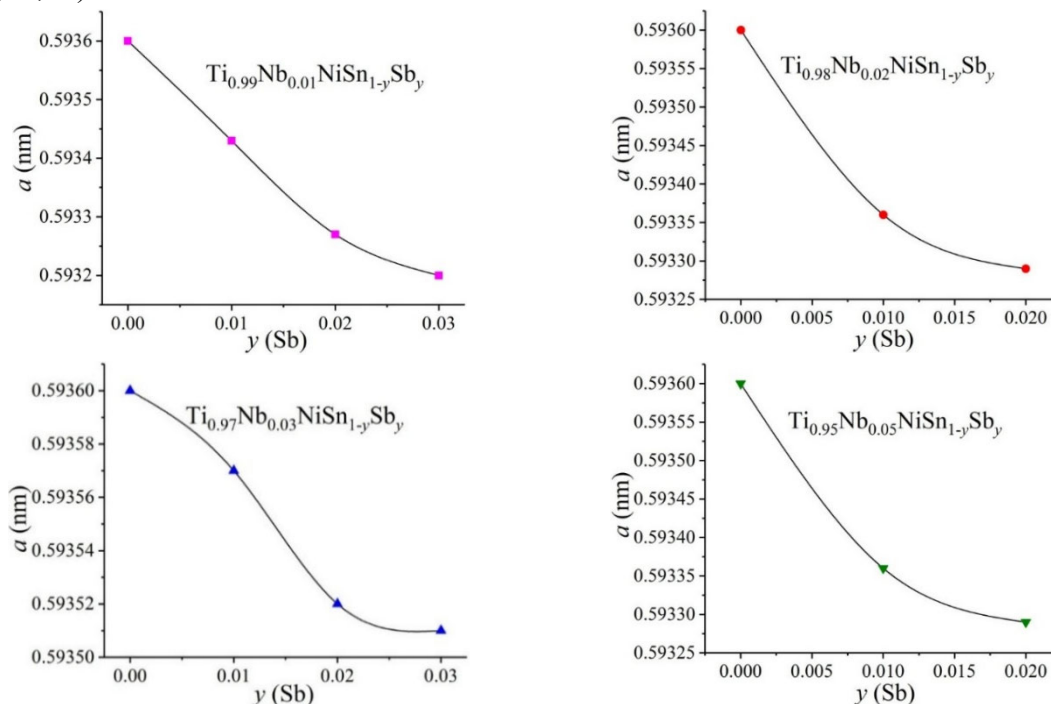


Fig. 2. Change in the the unit cell parameter $a(x,y)$ of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$

From the powder diffraction data of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ samples, $x = 0.01\text{--}0.05$, $y = 0.01\text{--}0.03$, the unit cell parameter $a(x,y)$ was calculated (Fig. 2). As seen from Fig. 2, the unit cell parameter $a(y)$, as we predicted, monotonically decreases in all $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ samples. This means that in the crystal structure of the semiconductor, larger Sn atoms ($r_{\text{Sn}} = 0.162$ nm) are replaced by smaller Sb atoms ($r_{\text{Sb}} = 0.159$ nm). Taking into account that Sb atoms ($4d^{10}5s^25p^3$) have a higher number of valence electrons than Sn atoms ($4d^{10}5s^25p^2$), structural defects of donor nature and corresponding energy states $\varepsilon_D^{\text{Sb}}$ in the semiconductor band gap ε_g are generated in the crystal. Such doping of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ should bring the Fermi level ε_F closer to the percolation level of the conduction band ε_c and ensure high Z values.

Thus, the analysis of the results of X-ray structural studies of the thermoelectric material $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, $x = 0.01\text{--}0.05$, $y = 0.01\text{--}0.03$, showed that at all concentrations of Sb atoms in the semiconductor, impurity donor states are generated, which corresponds to the conditions for obtaining maximum values of the thermoelectric figure of merit [3, 4]. Therefore, at some concentrations of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, we can expect an increase in the efficiency of converting thermal energy into electrical energy, which corresponds to the stated goal (aim) of this work.

Modeling the electronic structure of thermoelectric material $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$

The KKR method was used to calculate the density of electronic states (DOS) distribution for all samples $\text{Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, where $x = 0.01\text{--}0.05$ and $y = 0.01\text{--}0.03$, under the condition

of an ordered variant of their crystal structure. This assumes that Nb atoms replace only Ti atoms in position 4a, and Sb atoms replace Sn atoms in position 4c. Figure 3, as an example, illustrates the results of the DOS calculation for two solid solution compositions, highlighting the dynamics of the Fermi level (ϵ_F) movement.

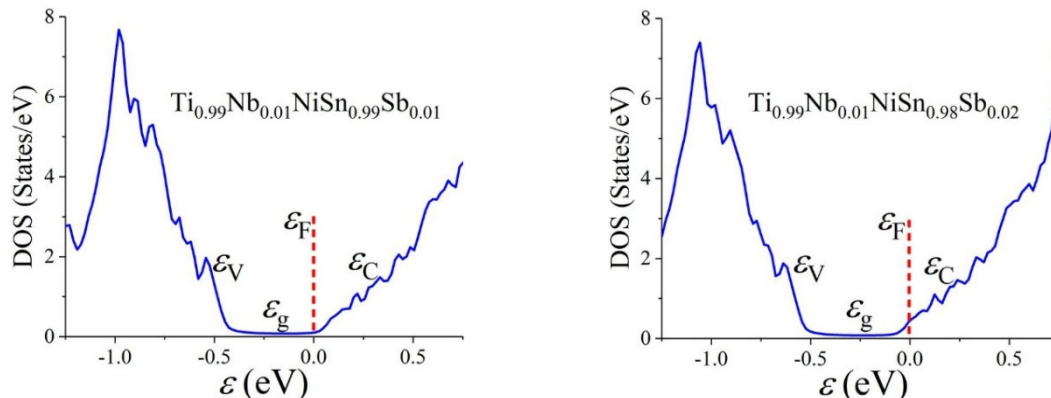


Fig. 3. Calculation of the density of electronic states (DOS) distribution for $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}_{1-y}\text{Sb}_y$

Since the substitution of Sn atoms for Sb atoms generates donor states ϵ_D^{Sb} in the band gap ϵ_g of the semiconductor, then at a concentration of $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}_{0.99}\text{Sb}_{0.01}$, the Fermi level ϵ_F will be located near the percolation level of the conduction band ϵ_C . At higher concentrations of Sb atoms, in particular, $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}_{0.8}\text{Sb}_{0.02}$, the Fermi level ϵ_F will cross the edge of the conduction band ϵ_C : a dielectric-metal conduction transition (Anderson transition) will occur [9].

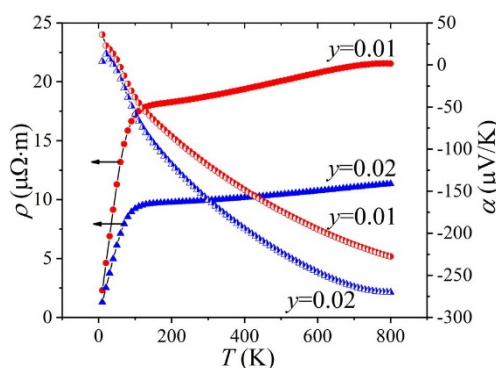


Fig. 4. Modeling of the behavior of the temperature dependences of electrical resistivity $\rho(T,y)$ and thermopower coefficient $\alpha(T,y)$ for $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}_{1-y}\text{Sb}_y$:

Modeling the behavior of the temperature dependences of the resistivity $\rho(T)$ and the thermopower coefficient $\alpha(T)$ for the $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ samples, $x = 0.01\text{--}0.05$, $y = 0.01\text{--}0.03$, showed a metallic type of electrical conductivity at all concentrations and temperatures. Figure 4, as an example, shows the modeling results for the $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}_{1-y}\text{Sb}_y$ semiconductor at two concentrations of Sb atoms: $y = 0.01$ and $y = 0.02$. As the concentration of the donor impurity Sb increases, the resistivity $\rho(T)$ significantly decreases, while the thermopower coefficient $\alpha(T)$ shows a slight increase. Based on the obtained modeling results, we can predict an increase in the thermoelectric figure of merit at certain concentrations of the

n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y semiconductor solid solution. The results of electrokinetic and energy studies of n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y will show the degree of adequacy of the conclusions drawn above regarding the increase in the efficiency of converting thermal energy into electrical energy.

Electrokinetic and energetic properties of n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y

In Fig. 5, as an example, the temperature dependences of the resistivity $\rho(T, y)$ and the thermo-power coefficient $\alpha(T, y)$ of the semiconductor solid solution n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y, $x = 0.01-0.02$, $y = 0-0.03$, are presented. It can be seen that the resistivity $\rho(T, y)$ of n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y at temperatures of 80–400 K only increases, indicating a metallic type of electrical conductivity, when the Fermi level ε_F crosses the percolation level of the conduction band ε_C : the dielectric-metal conductivity transition predicted by calculations occurs.

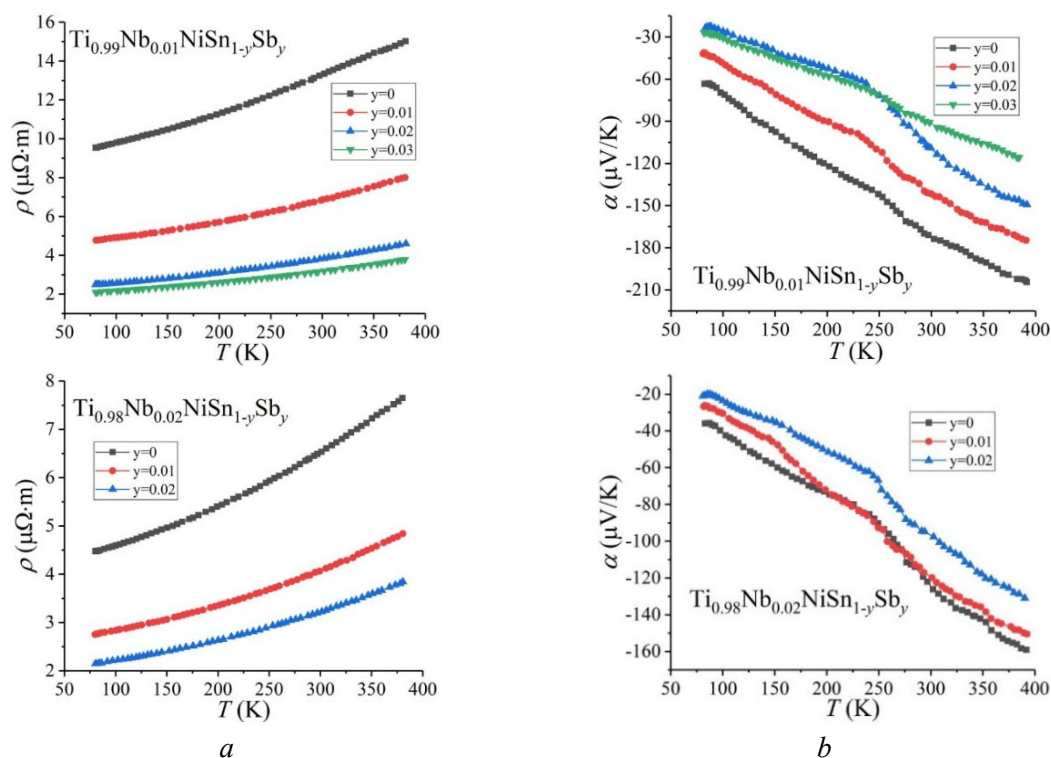


Fig. 5. Temperature dependences of the resistivity $\rho(T, y)$ (a) and the thermopower coefficient $\alpha(T, y)$ (b) of n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y

The fact that the Fermi level ε_F crossed the percolation level of the conduction band ε_C is evidenced by the negative values of the thermopower coefficient $\alpha(T, y)$ at all studied concentrations and temperatures (Fig. 5 b). Instead, the action of current carrier scattering mechanisms is one of the main reasons for the increase in resistivity $\rho(T, y)$ with temperature. This behavior of the temperature dependences of the electrical resistivity $\rho(T, y)$ and the thermopower coefficient $\alpha(T, y)$ of n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y is consistent with the simulation results (Fig. 4). Therefore, n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y, $x = 0.01-0.02$, $y = 0-0.03$, is a heavily doped semiconductor of the electronic conduction type, when the Fermi level ε_F approached the edge of the conduction band ε_C , crossing its percolation level [10]. After all, a priori we planned

exactly such dynamics of the Fermi level ε_F , which corresponds to the condition for achieving maximum values of the thermoelectric figure of merit [3, 4]. The negative values of the thermopower coefficient $\alpha(T, y)$ at all studied concentrations and temperatures (Fig. 5 b) indicate that the Fermi level ε_F crosses the percolation level of the conduction band ε_C .

It is informative to present the change in the resistivity $\rho(y, T)$ and thermopower coefficient $\alpha(y, T)$ of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ with a change in the concentration of Sb atoms at different temperatures. Fig. 6, for example, illustrates the changes in $\rho(y, T)$ and $\alpha(y, T)$ for semiconductor solid solutions $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, with $x = 0.01\text{--}0.02$ and $y = 0\text{--}0.03$. We can see that with an increase in the concentration of the donor impurity Sb, the resistivity $\rho(y, T)$ decreases at all studied temperatures, since the concentration of free electrons, which are the main current carriers, increases.

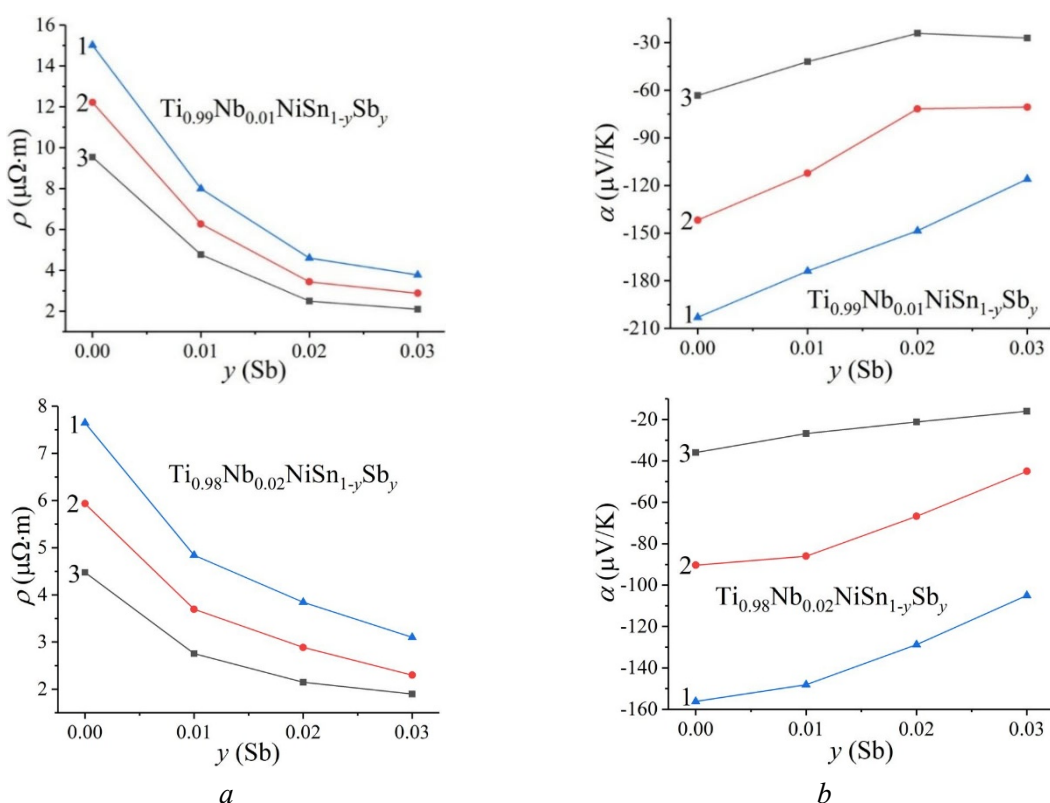


Fig. 6. Change in resistivity $\rho(y, T)$ (a) and thermopower coefficient $\alpha(y, T)$ (b) of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ at different temperatures: 1 – $T=80\text{ K}$; 2 – $T=250\text{ K}$; 3 – $T=380\text{ K}$

Recall that in [1], it was shown that in $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$, Nb atoms can occupy different crystallographic positions, generating structural defects of both acceptor and donor nature simultaneously in various ratios. The solid solution obtained in this way contains significant local structural disorders and is a heavily doped and highly compensated semiconductor (HDHCS) [10]. On the other hand, the presence of a significant number of different charged defects in a semiconductor, the location of which is of a fluctuating nature, radically changes its electronic structure, which leads to fluctuations in the potential relief and modulation of continuous energy bands [10]. The authors of [11] showed that the numerical values of the

activation energies ε_1^α and ε_3^α , determined from the activation parts of the temperature dependences of the thermopower coefficient $\alpha(1/T)$, are proportional, respectively, to the modulation amplitude of the continuous energy bands and to the small-scale fluctuation of the HDHCS.

Fig. 7, as an example, presents the temperature dependences of the thermopower coefficient $\alpha(1/T, y)$ of the semiconductor solid solution $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, $x = 0.01\text{--}0.02$, $y = 0\text{--}0.03$, which can be described by the well-known formula [9]:

$$\alpha = \frac{k_B}{e} \left(\frac{\varepsilon_1^\alpha}{k_B T} - \gamma + 1 \right),$$

where γ is a parameter that depends on the nature of the scattering mechanisms.

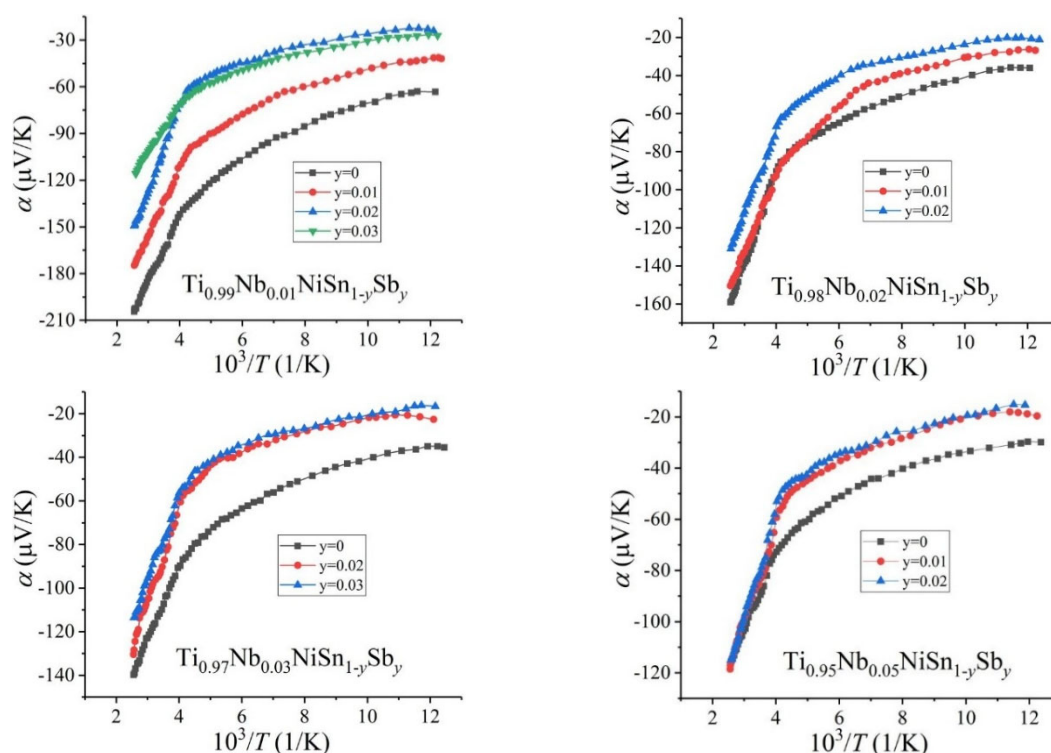


Fig. 7. Temperature dependences of the thermopower coefficient $\alpha(1/T, x)$ of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$

Using this formula from the high-temperature activation parts of the $\alpha(1/T, y)$ dependence of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ (Fig. 7), the activation energies $\varepsilon_1^\alpha(y)$ (Fig. 8 a) were calculated, which are proportional to the amplitude of the large-scale fluctuation of the continuous energy bands of the HDHCS [10, 11]. Fig. 8 a shows the change in the activation energy $\varepsilon_1^\alpha(y)$ of the semiconductor thermoelectric material $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, $x = 0.01\text{--}0.02$, $y = 0\text{--}0.03$. 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: a higher compensation degree leads to a greater amplitude of band modulation [10].

As seen from Fig. 8 *a*, doping the $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ semiconductor with the donor impurity Sb at all concentrations of impurity atoms Nb and Sb leads to a decrease in the activation energy $\varepsilon_1^a(y)$ (read – the amplitude of the band modulation). Thus, if the activation energy in the $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}$ semiconductor was $\varepsilon_1^a(y=0) = 42.7$ meV, then at the concentration of $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}_{0.98}\text{Sb}_{0.02}$, it decreased to $\varepsilon_1^a(y=0.02) = 37.3$ meV, and to the values $\varepsilon_1^a(y=0.03) = 35.4$ meV for the $n\text{-Ti}_{0.99}\text{Nb}_{0.01}\text{NiSn}_{0.97}\text{Sb}_{0.03}$ semiconductor. Such a decrease in the activation energy values $\varepsilon_1^a(y)$ for $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ means that the amplitude of the modulation of the continuous energy bands in the semiconductor decreases. It occurs in an electron-conducting semiconductor only when it is doped with a donor impurity. The obtained results provide independent confirmation that Sb atoms introduced into the crystal structure of the $\text{Ti}_{1-x}\text{Nb}_x\text{NiSn}$ solid solution generate donor-type structural defects and the corresponding energy states within the semiconductor's band gap.

Experimental measurements of the electrical conductivity $\sigma(y, T)$ and the thermopower coefficient $\alpha(y, T)$ allowed us to construct, for example, for 300 K, the dependence of the thermoelectric power factor Z^* of the semiconductor solid solution $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, $x = 0.01\text{--}0.02$, $y = 0\text{--}0.03$, (Fig. 8 *b*). The results shown in Fig. 8 *b* indicate that at specific concentrations of the impurity atoms Nb and Sb, the dependence of $Z^*(y)$ reaches a maximum, which suggests the highest efficiency of converting thermal energy into electrical energy for this composition $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$. By the way, if in the semiconductor thermoelectric material $\text{Ti}_{1-x}\text{Nb}_x\text{NiSn}$ at a concentration of $x = 0.03$ the maximum values of $Z^* = 25.7$ $\mu\text{W/K}^2\text{ cm}$ were reached (see Fig. 1), then its doping with a donor impurity Sb at a concentration of $n\text{-Ti}_{0.98}\text{Nb}_{0.02}\text{NiSn}_{0.99}\text{Sb}_{0.01}$ allowed us to obtain $Z^* = 35.1$ $\mu\text{W/K}^2\text{ cm}$ (Fig. 8 *b*).

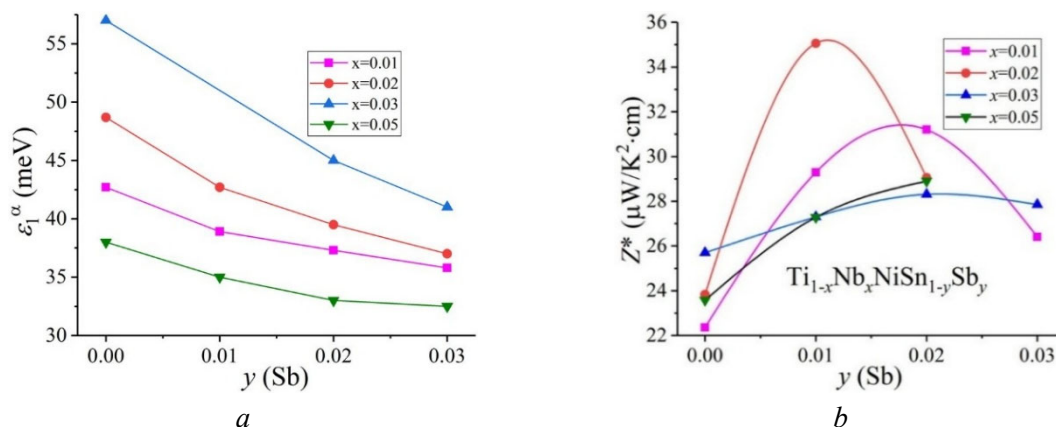


Fig. 8. Change in activation energy ε_1^a (*a*) and thermoelectric power factor $Z^*(y)$ (*b*) of $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ at $T=300$ K

Thus, the study of the structural, electrokinetic and energy properties of the semiconductor solid solution $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, $x = 0.01\text{--}0.02$, $y = 0\text{--}0.03$, established that at all concentrations of impurity Sb atoms in the semiconductor, structural defects of donor nature are generated, as well as the corresponding energy states which corresponds to the conditions to obtain maximum values of the thermoelectric figure of merit [3, 4]. Therefore, at

certain (or specific) concentrations of n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y, we can expect an increase in the efficiency of converting thermal energy into electrical energy, which corresponds to the stated aim of this work. The performed studies enabled us to identify the mechanisms of electrical conductivity to determine the conditions for synthesizing the thermoelectric material n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y with maximum efficiency of converting thermal energy into electrical energy.

Conclusions

The structural, electrokinetic and energetic properties of the new semiconductor thermoelectric material n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y, $x = 0.01-0.02$, $y = 0-0.03$, obtained by doping n-Ti_{1-x}Nb_xNiSn with Sb atoms ($4d^{10}5s^25p^3$) by replacing Sn atoms ($4d^{10}5s^25p^2$) were investigated. The nature of the generated energy states and mechanisms of electrical conductivity were established. It was shown that at different concentrations of Sb atoms in the crystallographic position 4c, structural defects of donor nature and the corresponding energy states $\varepsilon_D^{Sb(Sn)}$ within the semiconductor band gap ε_g are generated. Optimization of the properties of the n-Ti_{1-x}Nb_xNiSn solid solution by doping the n-type semiconductor with a donor impurity leads to a decrease in the compensation degree and meets the conditions for achieving maximum efficiency of thermal energy conversion into electrical energy. A new semiconductor thermoelectric material, n-Ti_{1-x}Nb_xNiSn_{1-y}Sb_y, was obtained, exhibiting high values for the thermoelectric power factor.

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**Оптимізація властивостей нового термоелектричного
матеріалу, отриманого легуванням
напівпровідника $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ атомами Sb**

Досліджено структурні, електрокінетичні та енергетичні властивості нового термоелектричного матеріалу $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$, $x=0.01\text{--}0.02$, $y=0\text{--}0.03$, отриманого легуванням напівпровідника $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ атомами Sb ($4d^{10}5s^25p^3$) шляхом заміщення атомів Sn ($4d^{10}5s^25p^2$). Встановлено природу генерованих енергетичних станів та механізмів електропровідності. Показано, що за різних концентрацій атомів Sb у кристалографічній позиції 4c генеруються структурні дефекти донорної природи, а в забороненій зоні ε_g напівпровідника – відповідні їм енергетичні стани $\varepsilon_D^{\text{Sb(Sn)}}$. Оптимізація властивостей твердого розчину $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}$ шляхом легування напівпровідника n -типу провідності донорною домішкою приводить до зменшення ступеню компенсації та відповідає умовам досягнення максимальної ефективності перетворення теплової енергії в електричну. Отримано новий напівпровідниковий термоелектричний матеріал $n\text{-Ti}_{1-x}\text{Nb}_x\text{NiSn}_{1-y}\text{Sb}_y$ з високими значеннями термоелектричної потужності.

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

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