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Research of Thermoelectric Material $Ti_{1-x}Nb_xNiSn$

The structural, kinetic, energetic, and magnetic properties of the semiconductor thermoelectric material $Ti_{1-x}Nb_xNiSn$, obtained by doping n-TiNiSn with Nb atoms, have been studied. It has been shown that Nb atoms ($4d^45s^1$) simultaneously occupy different crystallographic positions, generating structural defects of donor and acceptor nature. At $Ti_{1-x}Nb_xNiSn$ concentrations, $x=0$–0.04, Nb atoms predominantly replace Ti ($3d^24s^2$) and Ni ($3d^84s^2$) atoms present there in position 4a, generating donor and acceptor states in the band gap ε_g, respectively. At higher concentrations, $x>0.04$, Nb atoms replace only Ti atoms, generating structural defects and energetic states of donor nature. It is shown that the semiconducting solid solution $Ti_{1-x}Nb_xNiSn$ is a promising thermoelectric material, and at $T\approx650$ K and $Ti_{0.99}Nb_{0.01}NiSn$ concentration ZT is equal to 0.76. The studies allowed us to identify the mechanisms of electrical conductivity to determine the conditions for the synthesis of thermoelectric materials $Ti_{1-x}Nb_xNiSn$ with maximum efficiency of converting thermal energy into electrical energy.

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

Introduction

It is known that in semiconductor thermoelectric materials, the condition for achieving maximum values of the thermoelectric figure of merit Z is their doping with acceptor and/or donor impurities to concentrations at which the Fermi level ε_F is fixed by the mobility of the corresponding continuous energy band. Moreover, the maximum values of Z are achieved with

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the same nature of the impurity and the type of conductivity of the semiconductor [1, 2]. The choice of semiconductor doping conditions, in particular, the type and concentration of the impurity, the method of introduction, and the modes of homogenizing annealing allows the formation of energy states in the band gap ε_g that determine its properties. This allows to optimizing the values of the electrical conductivity $\sigma(T)$, thermopower coefficient $\alpha(T)$, and thermal conductivity $\kappa(T)$ to values that meet the condition for obtaining maximum Z values ($Z = \alpha^2 \cdot \sigma/\kappa$) [1, 2].

Semiconductor substitutional solid solutions based on half-Heusler phases, in particular, MNiSn (M – Ti, Zr, Hf) (structure type MgAgAs, space group $F\bar{4}3m$ [3]) are among the most studied thermoelectric materials, which have a high efficiency of converting thermal energy into electrical energy [4 – 6]. In this context, it is interesting to study the solid solution $Ti_{1-x}Nb_xNiSn$, obtained by doping the semiconductor *n*-TiNiSn with a donor impurity Nb ($4d^45s^1$) by substituting Ti ($3d^24s^2$) atoms in the crystallographic position 4*a* (*Nb* has more *d*-electrons than Ti). Such doping meets the conditions for obtaining maximum values of the thermoelectric figure of merit Z [1, 2].

Previous studies of the crystal and electronic structures of the TiNiSn compound have established a number of features of its structure [7]. It has been shown that the structure of the TiNiSn compound is disordered due to partial, up to 0.5 %, substitution of Ti atoms in position 4*a* by Ni atoms ($3d^84s^2$). In this case, the formula of the compound is transformed into $(Ti_{1-x}Ni_x)NiSn$ and structural defects of a donor nature are formed in position 4*a* (*Ni* atom has more *d*-electrons than Ti atom). At the same time, corresponding donor states are formed in the band gap ε_g of the semiconductor, which determine the electronic type of its conductivity ("*a priori* doping" by donors [7]). Another feature of the structure of the TiNiSn compound is the presence of tetrahedral voids, which constitute ~ 24 % of the total volume of the unit cell and are "traps" for both impurity atoms and compound atoms, generating structural defects and corresponding energy states in the band gap ε_g [7].

Knowledge of the features of the crystal structure of the TiNiSn compound is an important basis for understanding structural, energetic, and kinetic transformations in $Ti_{1-x}Nb_xNiSn$. A comprehensive study of the properties of the semiconductor thermoelectric material $Ti_{1-x}Nb_xNiSn$ will establish the mechanisms of electrical conductivity, which will help determine the conditions for the synthesis of materials with the maximum efficiency of converting thermal energy into electrical energy and the prospects for their practical application.

Research methods

Modeling and experimental studies of the structural, thermodynamic, magnetic, energy, and kinetic properties of a semiconductor solid solution $Ti_{1-x}Nb_xNiSn$, obtained by doping the *n*-TiNiSn semiconductor by replacing Ti atoms with Nb atoms in position 4*a*, were carried out. Samples of the solid solution $Ti_{1-x}Nb_xNiSn$, $x = 0 – 0.10$, were prepared by arc-melting the constituent components in an electric arc furnace with a tungsten electrode (cathode) in protected argon atmosphere on a copper water-cooled bottom (anode). For homogenization, the obtained alloys were sealed in evacuated (up to 1.0 Pa) quartz ampoules and annealed in muffle electric furnaces with temperature control with an accuracy of ± 10 K at a temperature of 1073 K for 720 h with subsequent quenching in water. Phase analysis of the alloys was performed using *X*-ray diffraction data obtained on a DRON-2.0M powder diffractometer (FeKα-radiation). The structural characteristics of the $Ti_{1-x}Nb_xNiSn$ samples were calculated using the FullProf Suite program [8].

The electronic structure of $Ti_{1-x}Nb_xNiSn$ was calculated by the Koringa-Kohn-Rostoker (KKR) method in the coherent potential (CPA) and local density approximation (LDA) [9]. The experimental values of the constant unit cell on a *k*-grid of size 10 × 10 × 10 and the Moruzzi-Janak-Williams type of exchange-correlation potential parameterization [10] were used for the calculations. 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 calculating the Fermi level position ε_F was ± 6 meV.

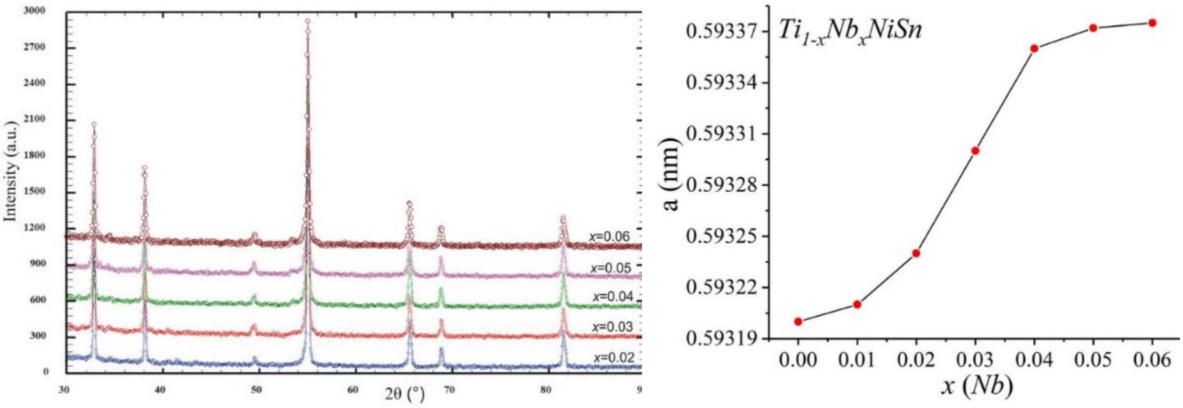
Measurements of the temperature dependences of the resistivity $\rho\,(T, x)$ and the thermopower coefficient $\alpha\,(T, x)$ of $Ti_{1-x}Nb_xNiSn$ were carried out in the temperature range of $80 \div 400$ K on samples in the form of rectangular parallelepipeds with a size of $\sim 1.0 \times 1.0 \times 5$ mm^3. Measurements of the thermopower coefficient $\alpha\,(T, x)$ were carried out by the potentiometric method relative to copper. Measurements of the voltage drop on the samples were carried out at different directions of the electric current to reduce the influence of a possible *p*-*n* junction at the contact points. The specific magnetic susceptibility $\chi\,(x)$ of $Ti_{1-x}Nb_xNiSn$ was measured by the relative Faraday method at a temperature of 300 K in a magnetic field of 10 kOe.

Study of structural properties of thermoelectric material $Ti_{1-x}Nb_xNiSn$

Experimental studies of the phase composition of the samples $Ti_{1-x}Nb_xNiSn$, $x = 0 - 0.06$, established the correspondence of the composition of the charge of the initial components. Fig. 1 *a* shows the powder patterns of samples of the solid solution $Ti_{1-x}Nb_xNiSn$. According to *X*-ray phase analysis, the synthesized samples belong to the MgAgAs structure type [3]. At higher concentrations of Nb atoms in samples $Ti_{1-x}Nb_xNiSn$, $x > 0.06$, insignificant reflections of the impurity phases were observed on powder patterns. For this reason, the properties of $Ti_{1-x}Nb_xNiSn$ were studied for samples with Nb content of $x = 0 - 0.06$.

Based on results of *X*-ray structural studies of $Ti_{1-x}Nb_xNiSn$, the crystallographic parameters of the samples were calculated, in particular, the unit cell parameter $a(x)$ (Fig. 1 *b*). It can be seen from Fig. 1 *b* that in the concentration range of $Ti_{1-x}Nb_xNiSn$, $x = 0 - 0.04$, there is a rapid increase in the values of the unit cell parameter $a\,(x)$. However, at higher concentrations, $x > 0.04$, the values of the unit cell parameter $a\,(x)$ of $Ti_{1-x}Nb_xNiSn$ grow much more slowly.

Since the change in the unit cell parameter of the solid solution is sensitive to the smallest changes in the atom distribution, the behavior of $a\,(x)$ $Ti_{1-x}Nb_xNiSn$ indicates more complex structural changes than the simple substitution of Ti atoms by Nb atoms. Above, attention was drawn to the features of the TiNiSn crystal structure, which is disordered as a result of the presence of *Ni* atoms in position 4*a* with partial substitution of Ti atoms [7]. Since the atomic radius of Ni ($r_{Ni} = 0.125$ nm) is smaller than the atomic radius of Nb ($r_{Nb} = 0.1468$ nm), the increase in the unit cell parameter *a* (*x*) $Ti_{1-x}Nb_xNiSn$ at concentrations $0 < x \leq 0.04$ (Fig. 1 *b*) is the result of the preferential substitution of Ni atoms presented in the crystallographic position 4 *a* by Nb atoms. The substitution of Ni atoms ($4d^4 5s^1$) in the 4*a* position by Nb atoms ($4d^4 5s^1$) is accompanied by the generation of defects of acceptor nature and corresponding acceptor states in the band gap ε_g (Nb has fewer *d*-electrons than Ni). The substituted Ni atoms can localize in the tetrahedral voids of the structure, generating donor states [7].



a *b*

Fig. 1. Diffraction patterns of samples (a) and change in the unit cell parameter a(x) (b) of the semiconductor solid solution $Ti_{1-x}Nb_xNiSn$

We attribute a slight increase in the unit cell parameter *a* (*x*) of $Ti_{1-x}Nb_xNiSn$ at higher concentrations, $x > 0.04$, to the preferential substitution of Ti atoms ($r_{Ti} = 0.1462$ nm) by slightly larger Nb atoms ($r_{Nb} = 0.1468$ nm) in position 4*a* (Fig. 1 *b*). The substitution of Ti atoms ($3d^2 4s^2$) by Nb atoms in position 4*a* is accompanied by the generation of structural defects of donor nature and the corresponding electronic states (Nb has more *d*-electrons than Ti). As a result, the $Ti_{1-x}Nb_xNiSn$ semiconductor becomes heavily doped and compensated [11].

Thus, structural studies of $Ti_{1-x}Nb_xNiSn$ have established that at different concentrations, the Nb atoms can displace Ni and Ti atoms from position 4*a*, generating structural defects of acceptor and donor nature, as well as the corresponding energy states in the band gap ε_g. The ratio of donor and acceptor states will determine the type of electrical conductivity, as well as the type of main current carriers.

Modeling the electronic structure of the thermoelectric material $Ti_{1-x}Nb_xNiSn$

To predict the behavior of the Fermi level ε_F, the band gap ε_g, and the kinetic properties of $Ti_{1-x}Nb_xNiSn$, the distribution of the density of electronic states (DOS) was calculated for the ordered version of the structure (Fig. 2). In this case, Nb atoms replace only Ti atoms in position 4 *a*.

Since the substitution of Ti atoms by Nb atoms generates structural defects of a donor nature, donor states ε_D^{Nb} appear in the band gap ε_g of the $Ti_{1-x}Nb_xNiSn$ semiconductor near the conduction band ε_C. As seen from Fig. 2, at a concentration of $Ti_{0.99}Nb_{0.01}NiSn$, the Fermi level

ε_F will approach the conduction band ε_C. At higher concentrations of Nb atoms, the concentration of donor states ε_D^{Nb} will increase, and the Fermi level ε_F will cross the conduction band ε_C: a dielectric-metal transition of conductivity will occur [12]. In addition, the crossing of the conduction band ε_C by the Fermi level ε_F will fundamentally change the type of semiconductor conductivity from activation (in *n*-TiNiSn) to metallic (in $Ti_{1-x}Nb_xNiSn$) [11]. In the experiment on the temperature dependences of the resistivity $\rho\ (T, x)$ of $Ti_{1-x}Nb_xNiSn$, activation parts will disappear, and the value of $\rho\ (T, x)$ will increase with temperature. In this case, electrons are the main current carriers since the thermopower coefficient $\alpha\ (T, x)$ has negative values at all concentrations and temperatures.

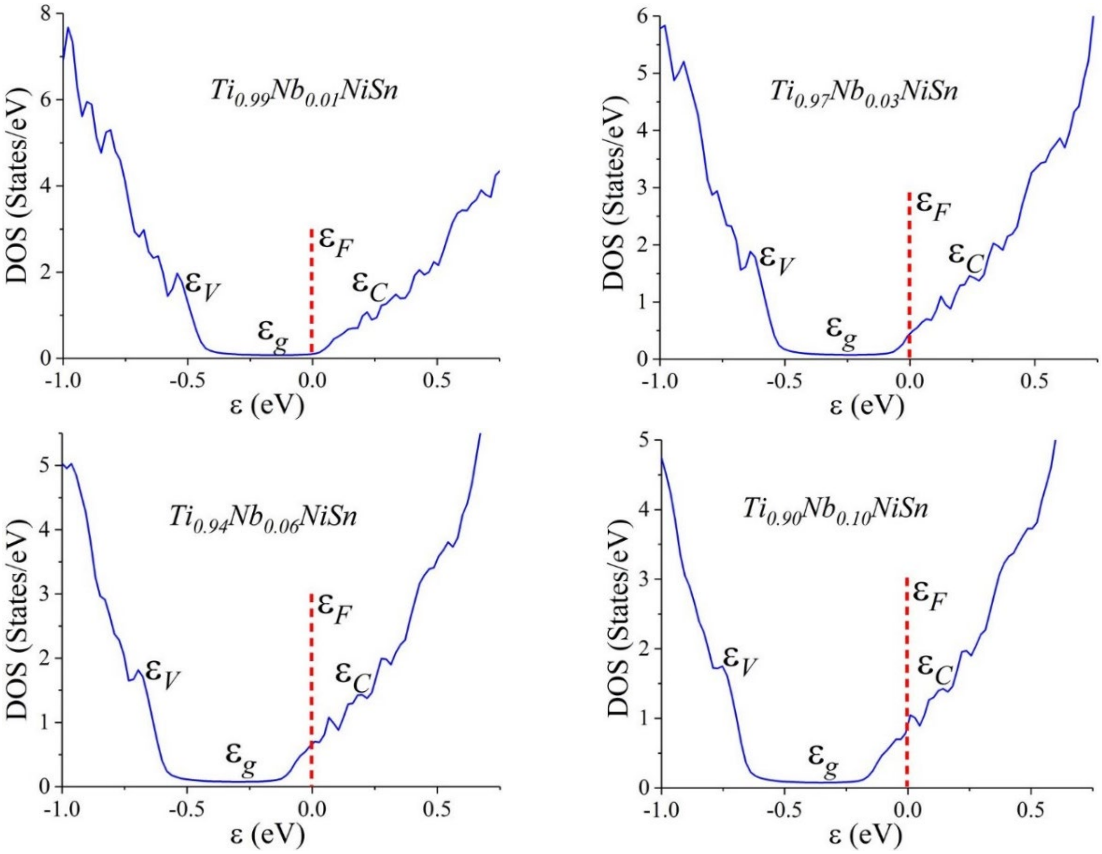
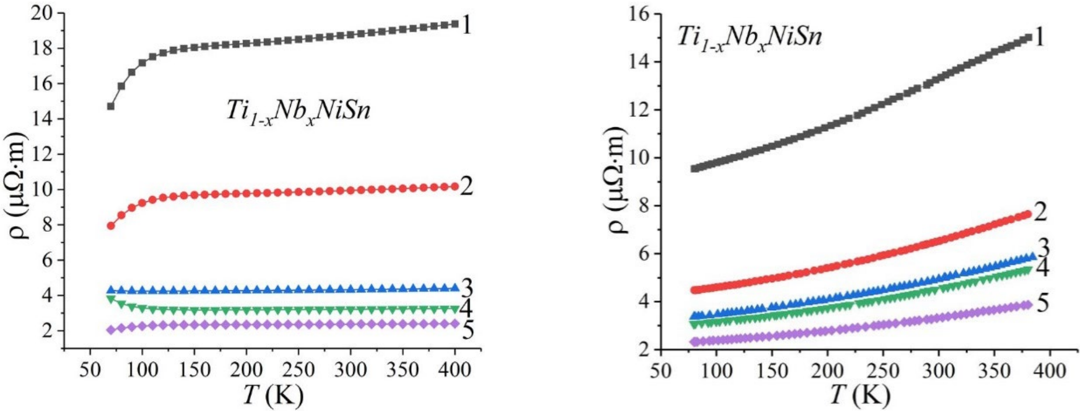


Fig. 2. Calculation of the distribution of the density of electronic states DOS for $Ti_{1-x}Nb_xNiSn$

Investigation of the electrokinetic properties of $Ti_{1-x}Nb_xNiSn$

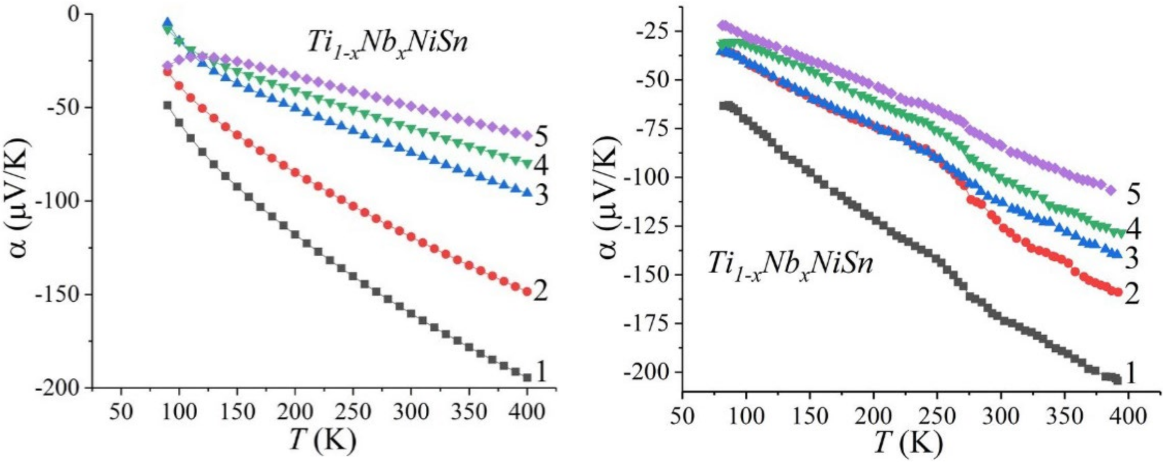
Fig. 3 and 4 show the results of modeling and experimental studies of the temperature dependencies of the resistivity $\rho\ (T, x)$ and the thermopower coefficient $\alpha\ (T, x)$ of $Ti_{1-x}Nb_xNiSn$. From the given dependences it can be seen that the results of experimental measurements of the resistivity $\rho\ (T, x)$ and the thermopower coefficient $\alpha\ (T, x)$ of $Ti_{1-x}Nb_xNiSn$ are as close as possible to the modeling results.

As shown above, doping of *n*-TiNiSn with Nb atoms by substituting Ti atoms at position 4*a* generates structural defects of donor nature in the $Ti_{1-x}Nb_xNiSn$ semiconductor, and corresponding donor states ε_D^{Nb} appear in the band gap ε_g. Modeling the behavior of the resistivity ρ (*T*, *x*) in the temperature range *T* = 80 – 400 K shows that at the lowest concentration of Nb impurity (*x* = 0.01), the conductivity of the $Ti_{0.99}Nb_{0.01}NiSn$ semiconductor has a metallic character: the values of ρ (*T*, *x*) increase with increasing temperature (Fig. 3 *a*). This behavior of ρ (*T*, *x*) is a consequence of the entry of the Fermi level ε_F into the conduction band ε_C, and the increase in the resistivity values with increasing temperature is caused exclusively by the action of the current carrier scattering mechanisms. In this case, the main current carriers are free electrons, as indicated by the negative values of the thermopower coefficient α (*T*, *x*) of $Ti_{1-x}Nb_xNiSn$ at all concentrations and temperatures (Fig. 4 *a*).



a *b*

Fig. 3. Modeling (a) and experimental studies (b) of temperature dependences of resistivity ρ (T, x) $Ti_{1-x}Nb_xNiSn$: 1 – x = 0.01; 2 – x = 0.02; 3 – x = 0.03; 4 – x = 0.04; 5 – x = 0.06

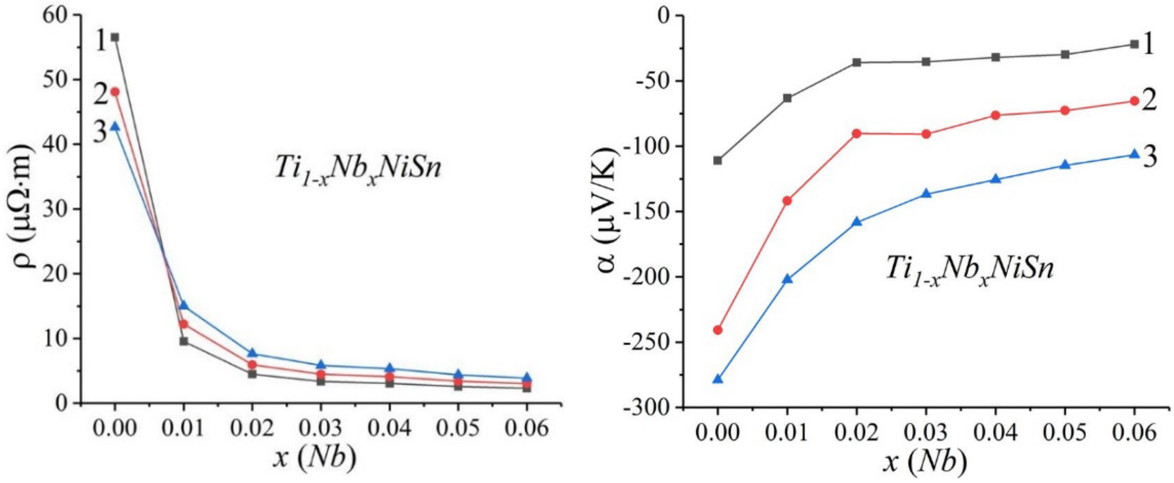


a *b*

Fig. 4. Modeling (a) and experimental studies (b) of the temperature dependences of the thermopower coefficient α (T, x) of $Ti_{1-x}Nb_xNiSn$: 1 – x = 0.01; 2 – x = 0.02; 3 – x = 0.03; 4 – x = 0.04; 5 – x = 0.06

From the experimental results (Fig. 3 *b*) it appears that in $Ti_{1-x}Nb_xNiSn$, the concentration of Nb atoms, *x* = 0.01, is sufficient for the Fermi level ε_F to move from the band gap ε_g to the conduction band ε_C, and there are no activation parts on the temperature dependences ρ (*T*, *x*). In addition, the substitution of Ti atoms by Nb atoms in the crystallographic position 4*a* is accompanied by a decrease in the width of the band gap ε_g of the semiconductor since Ti atoms participate in the formation of its continuous energy bands [7]. This also facilitates the thermal emission of electrons from the donor states of the band gap ε_g into the conduction band ε_C of $Ti_{1-x}Nb_xNiSn$. At the same time, the values of the resistivity ρ (*T, x*) only increase with increasing temperature (Fig. 3 *b*), which indicates the metallization of electrical conductivity. Under such conditions, the determinant of the electrical conductivity of $Ti_{1-x}Nb_xNiSn$ is not the change in the concentration of free electrons but their scattering by thermal lattice vibrations (phonons), structural defects, etc. [11].

An increase in the concentration of Nb atoms in $Ti_{1-x}Nb_xNiSn$ leads to a simultaneous rapid decrease in the resistivity ρ (*x, T*) and an increase in the thermopower coefficient α (*x, T*) (Fig. 5).



a *b*

Fig. 5. Change in resistivity ρ (x, T) (a) and thermopower coefficient α (x, T) (b) of $Ti_{1-x}Nb_xNiSn$ at different temperatures: 1 – T = 80 K; 2 – T = 250 K; 3 – T = 380 K

This behavior of the dependences ρ (*x, T*) and α (*x, T*) is understandable since an increase in the concentration of donor states leads to an increase in the concentration of free electrons, which increases the electrical conductivity σ of the semiconductor. The highest change in the electrical resistivity ρ (*x, T*) is at the lowest concentration of the Nb impurity ($x = 0.01$) when the Fermi level ε_F passes from the band gap ε_g to the conduction band ε_C (Fig. 5 *a*).

Magnetic properties of $Ti_{1-x}Nb_xNiSn$

Fig. 6 presents the results of experimental measurements of the specific magnetic susceptibility χ(*x*) of $Ti_{1-x}Nb_xNiSn$, $x = 0 – 0.06$, at room temperature. Studies have shown that the semiconductor $Ti_{1-x}Nb_xNiSn$ is a Pauli paramagnet, in which the magnetic susceptibility χ (*x*) is determined exclusively by the electron gas and is proportional to the density of states at the Fermi level *g* (ε_F). As seen from Fig. 6, the nature of the change in the specific magnetic susceptibility χ(*x*) of $Ti_{1-x}Nb_xNiSn$ is close to the behavior of the unit cell parameter *a* (*x*) (Fig. 6, inset). Both dependences undergo significant changes at concentrations $x = 0 – 0.02$.

The increase in the values of the magnetic susceptibility $\chi(x)$ $Ti_{1-x}Nb_xNiSn$ (read – the density of states at the Fermi level $g(\varepsilon_F)$) is caused by a rapid increase in the concentration of free electrons during the ionization of donor states formed when Ti atoms are replaced by Nb atoms. At higher Nb concentrations, the rate of change of the magnetic susceptibility $\chi(x)$ of $Ti_{1-x}Nb_xNiSn$ as well as $a(x)$, decreases, indicating a decrease in the rate of generation of free electrons when the activation of electrons from donor states to the conduction band ε_C is insignificant, since the Fermi level ε_F is located in the conduction band ε_C.

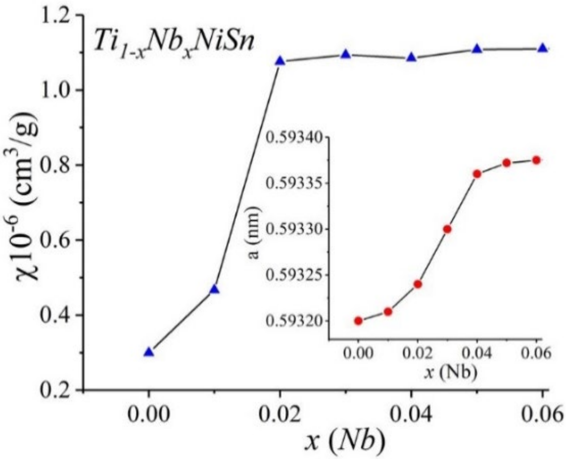


Fig. 6. Change in the specific magnetic susceptibility $\chi(x)$ of $Ti_{1-x}Nb_xNiSn$ at $T = 300$ K. Inset: change in the unit cell parameter $a(x)$ of $Ti_{1-x}Nb_xNiSn$

Thermoelectric characteristics of $Ti_{1-x}Nb_xNiSn$

A comprehensive characteristic of thermoelectric material in terms of its efficiency in converting thermal energy into electrical energy is the value of the thermoelectric figure of merit (*ZT*) at different temperatures. Fig. 7 shows the results of *ZT* simulation in the temperature range $T = 80 – 800$ K for the solid solution $Ti_{1-x}Nb_xNiSn$, $x \leq 0.10$.

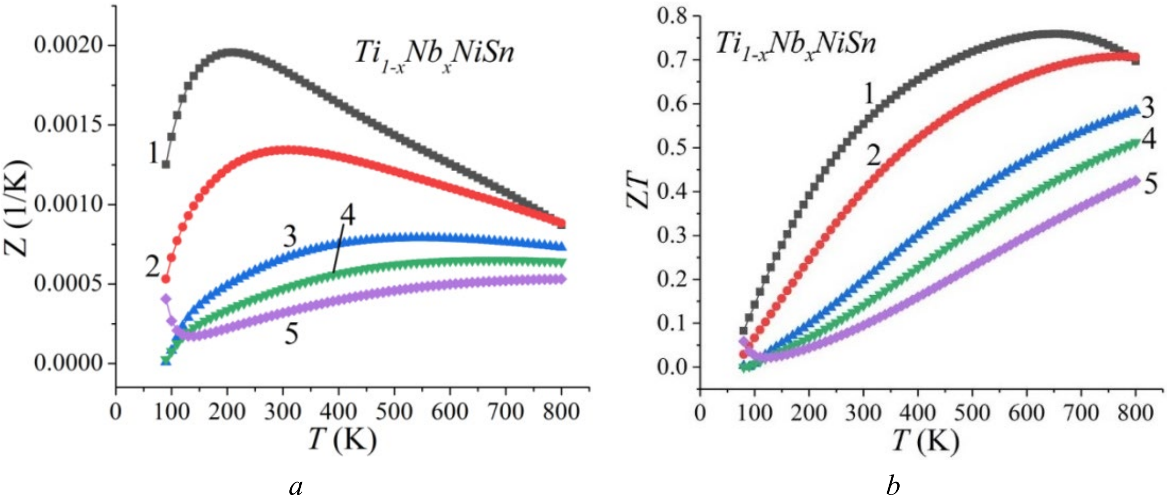


Fig. 7. Simulation of the change in the thermoelectric figure of merit Z (a) and ZT (b) of $Ti_{1-x}Nb_xNiSn$: $1 – x = 0.01$; $2 – x = 0.02$; $3 – x = 0.05$; $4 – x = 0.07$; $5 – x = 0.10$

It is important to note, that when modeling the thermoelectric figure of merit *Z*, the electronic component of the thermal conductivity coefficient κ_e was considered. Fig. 7 shows that for the $Ti_{0.99}Nb_{0.01}NiSn$ semiconductor at a temperature of $T \approx 650$ K, the figure of merit values are maximum and reach the value $ZT = 0.76$. The thermoelectric figure of merit values for $Ti_{1-x}Nb_xNiSn$, $x \leq 0.10$, obtained by mathematical modeling, indicate the prospects of the obtained solid solution as a thermoelectric material.

Experimental measurements of the electrical conductivity σ (*x, T*) and the thermopower coefficient α (*x, T*) allowed us to construct the dependence of the thermoelectric power factor *Z** of the semiconductor solid solution $Ti_{1-x}Nb_xNiSn$ (Fig. 8). The results presented in Fig. 8 indicate the prospects for using the $Ti_{1-x}Nb_xNiSn$ substitution solid solution as an effective thermoelectric material.

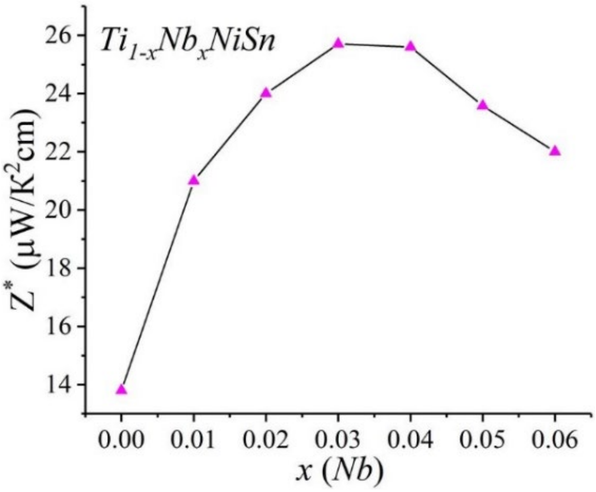


Fig. 8. Change in the thermoelectric power factor Z $Ti_{1-x}Nb_xNiSn$ at T=300 K*

Conclusions

The result of modeling and experimental studies of the crystal and electronic structures, electrokinetic, energetic, and magnetic properties of the $Ti_{1-x}Nb_xNiSn$ substitutional semiconductor solid solution obtained by doping of *n*-TiNiSn with Nb atoms is the establishment of the nature of the generated energy states and mechanisms of electrical conductivity. It is shown that Nb atoms ($4d^45s^1$) can occupy different crystallographic positions, generating structural defects of acceptor and donor nature. At $Ti_{1-x}Nb_xNiSn$ concentrations, $x = 0 – 0.04$, Nb atoms predominantly substitute Ti ($3d^24s^2$) and *Ni* ($3d^84s^2$) atoms in position 4*a*, generating donor and acceptor states in the band gap ε_g, respectively. At higher concentrations, $x > 0.04$, Nb atoms substitute only Ti atoms in position 4*a*, generating structural defects of donor nature and the corresponding energetic states. The ratio of the concentrations of the generated energy states determines the position of the Fermi level ε_F. It is shown that the semiconductor solid solution $Ti_{1-x}Nb_xNiSn$ is a promising thermoelectric material, at a concentration of $Ti_{0.99}Nb_{0.01}NiSn$ and $T \approx 650$ K *ZT* is 0.76. The performed studies allowed us to identify the mechanisms of electrical conductivity to determine the synthesis parameters of the thermoelectric material $Ti_{1-x}Nb_xNiSn$ with the maximum efficiency of converting thermal energy into electrical energy.

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Дослідження термоелектричного матеріалу $Ti_{1-x}Nb_xNiSn$

Досліджено структурні, кінетичні, енергетичні та магнітні властивості напівпровідникового термоелектричного матеріалу $Ti_{1-x}Nb_xNiSn$*, отриманого легуванням n-TiNiSn атомами Nb. Показано, що атоми Nb* ($4d^45s^1$) *одночасно займають різні кристалографічні позиції, генеруючи структурні дефекти донорної та акцепторної природи. За концентрацій* $Ti_{1-x}Nb_xNiSn$, $x = 0 – 0.04$, *атоми Nb переважно заміщають у позиції 4a присутні там атоми Ti* ($3d^24s^2$) *та Ni* ($3d^84s^2$)*, генеруючи в забороненій зоні* ε_g *відповідно донорні та акцепторні стани. За більших концентрацій,* $x > 0.04$*, атоми Nb заміщають лише атоми Ti, генеруючи структурні дефекти та енергетичні стани донорної природи. Показано, що напівпровідниковий твердий розчин* $Ti_{1-x}Nb_xNiSn$ *є перспективним термоелектричним матеріалом, а за* $T \approx 650$ *K та концентрації* $Ti_{0.99}Nb_{0.01}NiSn$ $ZT = 0.76$*. Проведені дослідження дозволили ідентифікувати механізми електропровідності для визначення умов синтезу термоелектричних матеріалів* $Ti_{1-x}Nb_xNiSn$ *з максимальною ефективністю перетворення теплової енергії в електричну.*

Ключові слова: термоелектричний матеріал, термоелектрична добротність, електронна структура, електроопір, коефіцієнт термоЕРС.

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