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Research on a New Semiconductor Thermoelectric Material n-$Zr_{1-x}Nb_xNiSn$. II. Property Modeling

The electronic structure, thermodynamic, structural, energy, and electrokinetic properties of the semiconductor thermoelectric material $Zr_{1-x}Nb_xNiSn$ *were modeled using density functional theory. The nature of the generated energy states and mechanisms of electrical conductivity were analyzed. It is shown that when Nb atoms are introduced into the structure of the ZrNiSn compound in varying ratios, two processes occur simultaneously: Zr atoms are substituted by Nb atoms, resulting in a substitutional solid solution, and Nb atoms also occupy the tetrahedral voids within the structure, leading to the formation of an inclusion solid solution. Structural changes create two types of donor defects in* $Zr_{1-x}Nb_xNiSn$*, along with their corresponding energy states, which are essential for achieving maximum efficiency in converting thermal energy to electrical energy. Modeling of thermoelectric properties showed that the semiconductor solid solution of* $Zr_{1-x}Nb_xNiSn$ *is a promising thermoelectric material.*

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Introduction

In [1], a study of a new thermoelectric material $Zr_{1-x}Nb_xNiSn$, obtained by doping the n-ZrNiSn semiconductor with Nb atoms ($4d^45s^1$) by replacing Zr atoms ($4d^25s^2$), was initiated. Doping generates defects of donor nature in the crystal structure of n-ZrNiSn, and in the electronic structure, the corresponding electronic states (Nb has more *d*-electrons than Zr). Such doping of $Zr_{1-x}Nb_xNiSn$ meets the condition of achieving maximum efficiency of converting thermal energy into electrical energy [2]. As a result, at the concentration of Nb atoms, $x \approx 0.04$, the thermoelectric power factor of $Zr_{1-x}Nb_xNiSn$ reached maximum values [1]. When studying similar semiconductor thermoelectric materials $Ti_{1-x}Nb_xNiSn$ [3] and $Hf_{1-x}Nb_xNiSn$ [4], at certain concentrations of the Nb donor impurity, it was also possible to achieve the maximum thermoelectric power factor.

However, the mechanism of generating donor states during doping of the semiconductor, which led to an increase in electrical conductivity and a slight decrease in thermopower coefficient, is unclear from the point of view of structural transformations, both in the cases of $Zr_{1-x}Nb_xNiSn$, as well as $Ti_{1-x}Nb_xNiSn$ and $Hf_{1-x}Nb_xNiSn$. On the one hand, the substitution of Zr, Ti, and Hf atoms in the crystal structure of semiconductors n-ZrNiSn, n-TiNiSn, and n-HfNiSn, respectively, by Nb atoms generates defects and electronic states of a donor nature. In turn, modeling of the thermodynamic properties of $Ti_{1-x}Nb_xNiSn$ and $Hf_{1-x}Nb_xNiSn$ showed that the solubility region of Nb atoms is insignificant. On the other hand, *X*-ray structural studies of $Zr_{1-x}Nb_xNiSn$, $Ti_{1-x}Nb_xNiSn$, and $Hf_{1-x}Nb_xNiSn$ samples have established a larger extent of the region of existence of these solid solutions. Based on experimental studies of the properties of $Zr_{1-x}Nb_xNiSn$, it has been *assumed* that the crystal structure undergoes simultaneous structural transformations in varying ratios, associated with the partial substitution of Zr atoms by Nb atoms, as well as the occupation of tetrahedral voids of the structure by Nb atoms [1].

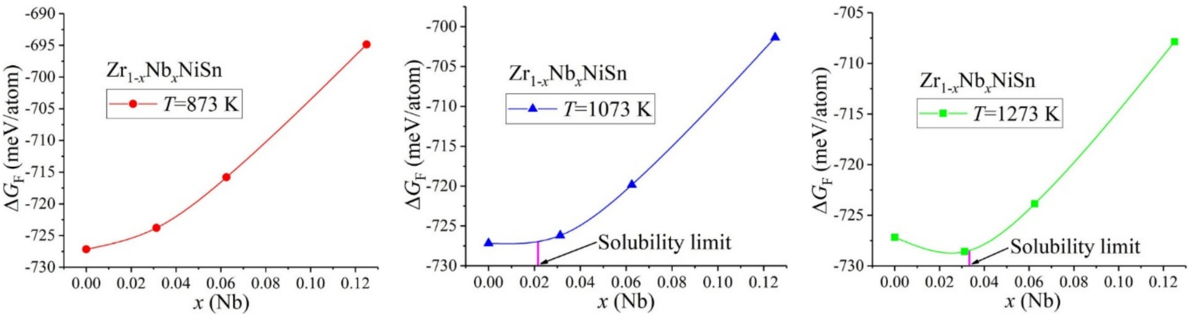
In this case, it is essential to understand the reason behind the discrepancy between the modeling results and structural studies. After all, understanding the features of structural transformations, for example, in $Zr_{1-x}Nb_xNiSn$, which are accompanied by the generation of defects of donor nature and the corresponding electronic states, will allow achieving the maximum figure of merit *Z* in the thermoelectric material. The results of modeling the properties of the semiconductor thermoelectric material $Zr_{1-x}Nb_xNiSn$, presented below, will help clarify the methods for generating donor states. This clarification could lead to improved efficiency in converting thermal energy into electrical energy at specific concentrations.

Research methods

The calculation of the density of states (DOS), thermodynamic, structural and electrokinetic properties of the thermoelectric material $Zr_{1-x}Nb_xNiSn$, $x = 0$–0.125, was carried out for an ordered version of its crystal structure. The calculations were performed by the KKR method [5] in the approximation of the coherent potential CPA and the local density LDA for the exchange-correlation potential with the Moruzzi-Janak-Williams parameterization [6], as well as by the method of adjoint plane waves FLAPW within the framework of the density functional theory DFT. The Vienna Ab initio Simulation Package VASP v. 5.4.4 program package was used with PAW-type potentials and the Perdew-Burke-Enzerhoff exchange-correlation functional in the generalized gradient in the Monkhorst-Pack approximation for the 11×11×11 k-grid [7–11]. The simulation of the specific electrical conductivity, thermopower coefficients, and thermal conductivity was carried out using the Exciting code (FLAPW method) by solving the linear Boltzmann equation with both the relaxation time determined during the simulation (SERTA) and the constant relaxation time (CRTA). The accuracy of the calculation of the Fermi level position was ε_F ±4 meV.

Modeling of thermodynamic and structural properties of $Zr_{1-x}Nb_xNiSn$

Figure 1 shows the results of modeling the thermodynamic Gibbs potential $\Delta G_F(x)$ in the approximation of harmonic vibrations of atoms for $Zr_{1-x}Nb_xNiSn$ samples, $x = 0–0.125$, at various temperatures of the homogenizing annealing process to achieve thermodynamic equilibrium.



a *b* *c*

Fig. 1. Calculations of the thermodynamic Gibbs potential $\Delta G_F(x)$ $Zr_{1-x}Nb_xNiSn$ at various temperatures of homogenizing annealing process of samples

The $\Delta G_F(x)$ simulation was performed for an ordered variant of the $Zr_{1-x}Nb_xNiSn$ crystal structure space group $F\bar{4}3m$), when Zr(Nb) atoms occupy the crystallographic position 4a (0, 0, 0), Ni – 4d (¼, ¼, ¼) and Sn – 4c (½, ½, ½). Such a simulation allows us to assess the energetic feasibility of substituting Zr atoms for Nb atoms in the crystal structure and to estimate the limits of the existence of a $Zr_{1-x}Nb_xNiSn$ substitutional solid solution.

As shown in Fig. 1, the extent of the substitutional solid solution depends on the temperature of homogenizing annealing. Thus, at temperatures $T \leq 873$ K, the calculations show only a monotonic increase in the $\Delta G_F(x)$ dependence (Fig. 1 *a*). It means that the substitution of Zr atoms by Nb atoms in the structure of the ZrNiSn compound is energetically disadvantageous; therefore, the $Zr_{1-x}Nb_xNiSn$ substitution solid solution does not exist under such conditions. In contrast, calculations of the Gibbs potential $\Delta G_F(x)$ at a higher temperature, $T = 1073$K, which corresponds to the annealing temperature of the samples studied in the experiment [1], show the energetic feasibility of substituting Zr atoms by Nb atoms up to a concentration of $x \approx 0.28$. It is indicated by the appearance of a minimum and a plateau in the $\Delta G_F(x)$ dependence up to $x \approx 0.28$ (Fig. 1*b*). At higher concentrations of Nb atoms, $x > 0.28$, the monotonic growth of the $\Delta G_F(x)$ dependence of $Zr_{1-x}Nb_xNiSn$ indicates the absence of solubility due to delamination (spinoidal phase decomposition). Calculations have shown that increasing the annealing temperature leads to a larger range of existence for the $Zr_{1-x}Nb_xNiSn$ substitutional solid solution. Thus, at a temperature of $T = 1273$ K, the boundary of the solubility region of Nb atoms in the structure of the thermoelectric material is $x \approx 0.36$ (Fig. 1*c*).

The results obtained from the density functional theory (DFT) calculations of the change in unit cell parameter $a(x)$ for $Zr_{1-x}Nb_xNiSn$, specifically for the ordered structure variant, indicate a linear decrease in the parameter a (see Fig. 2). This behavior in the dependence $a(x)$ is predictable because the atomic radius of Nb ($r_{Nb} = 0.1468$ nm) is smaller than that of Zr (r_{Zr}=0.1602 nm). Consequently, a linear increase in the concentration of Nb atoms leads to a corresponding linear decrease in the unit cell parameter $a(x)$.

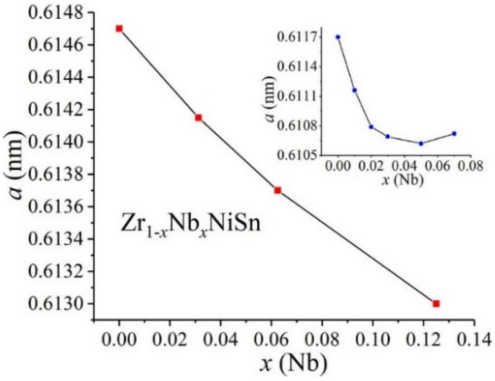


Fig. 2. Calculation of the change in the unit cell parameter a(x) for $Zr_{1-x}Nb_xNiSn$.
Inset: change in the unit cell parameter a(x) for $Zr_{1-x}Nb_xNiSn$ in the experiment [1]

This behavior of the parameter $a(x)$ corresponds with the results of *X*-ray diffraction studies [1] only for concentrations in the range of $0 < x \leq 0.02$ (see Fig. 2, inset). However, for $Zr_{1-x}Nb_xNiSn$ concentrations in the range of $0.02 < x \leq 0.05$, the rate of change of $a(x)$ begins to decrease, and beyond this point, when $x > 0.05$, the cell parameter even shows a slight increase (see Fig. 2, inset). Notably, *X*-ray diffraction studies of $Zr_{1-x}Nb_xNiSn$ samples with x ranging from 0 to 0.05, along with microprobe analysis of their surface's chemical and phase composition, indicated no presence of other phases' traces [1].

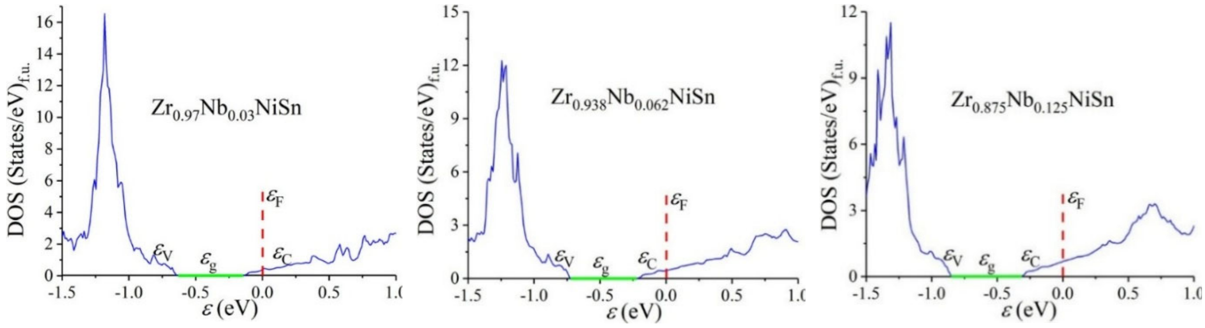
The difference between the modeling results for the thermodynamic and structural properties of $Zr_{1-x}Nb_xNiSn$ and the experimental data is clearly due to structural transformations beyond the mere substitution of Zr atoms by Nb atoms. In fact, the unit cell parameter of the solid solution within its range of existence is highly sensitive to even the smallest changes in the spatial arrangement of atoms.

In this context, it is important to note that the calculations of the thermodynamic Gibbs potential, $\Delta G_F(x)$, for $Zr_{1-x}Nb_xNiSn$, as well as $Ti_{1-x}Nb_xNiSn$ and $Hf_{1-x}Nb_xNiSn$ [3–4], were performed specifically for the ordered variant of the crystal structure. That is, only the case was analyzed when Nb atoms replace Zr atoms. With this approach, other possible structural transformations were not taken into account, when Nb atoms can occupy both other crystallographic positions and the existing tetrahedral voids of the crystal structure ("traps" [1]). Let us recall that a feature of the crystal structure of the ZrNiSn compound is the presence of tetrahedral voids ("traps") in the unit cell, which occupy ~ 24 % of its volume. Therefore, we can assume that the introduction of Nb atoms into the structure of the ZrNiSn compound involves two simultaneous processes in varying ratios: the substitution of Zr atoms by Nb atoms, resulting in a substitutional solid solution, and the occupancy of tetrahedral voids in the structure by Nb atoms, leading to the formation of an inclusion solid solution.

However, when modeling the structural and thermodynamic properties of $Zr_{1-x}Nb_xNiSn$, only the mechanism of substitution of Zr atoms for Nb atoms was considered; the inclusion of Nb atoms in the crystal structure of $Zr_{1-x}Nb_xNiSn$ was not taken into account in the modeling. Therefore, the results of calculations of the thermodynamic Gibbs potential $\Delta G_F(x)$ for $Zr_{1-x}Nb_xNiSn$ are only estimated, not absolute. The results of modeling the energetic and electrokinetic properties presented below will allow us to clarify the assumption made.

Modeling the electronic structure of $Zr_{1-x}Nb_xNiSn$

Fig. 3 shows a fragment of the results of modeling the density of states distribution DOS $Zr_{1-x}Nb_xNiSn$, $x = 0–0.125$. Calculation of the DOS of the solid solution allows us to estimate the band gap width ε_g, the position of the Fermi level ε_F, as well as the electrokinetic properties. Comparison of the results of modeling and experimental studies [1] of the $Zr_{1-x}Nb_xNiSn$ solid solution will allow us to assess the degree of their adequacy.



a *b* *c*

Fig. 3. Calculation of the distribution of the density of electronic states DOS $Zr_{1-x}Nb_xNiSn$

From the results shown in Fig. 3, we can see that at the lowest calculated concentration of Nb atoms, the Fermi level ε_F is located deep in the conduction band ε_C, while in *n*-ZrNiSn it lies in the forbidden band ε_g near the edge of the conduction band ε_C. In addition, with an increase in the concentration of Nb atoms in the $Zr_{1-x}Nb_xNiSn$ structure, the Fermi level ε_F goes deeper into the conduction band ε_C. Such behavior of the Fermi level ε_F can only be caused by the generation of donor states in the semiconductor thermoelectric material $Zr_{1-x}Nb_xNiSn$.

This is also evidenced by the results of the calculation of the density of electronic states at the Fermi level DOS(ε_F) $Zr_{1-x}Nb_xNiSn$ (Fig. 4), the values of which increase with increasing concentration of Nb atoms that generate donor states. The results of the simulation of the change in DOS(ε_F) are fully correlated with the results of experimental measurements of the specific magnetic susceptibility $\chi(x)$ [1] (Fig. 4, inset). Considering that the thermoelectric material $Zr_{1-x}Nb_xNiSn$ is a Pauli paramagnet, in which the magnetic susceptibility is determined by the electron gas, the change in the dependence $\chi(x)$ is proportional to the change in the density at the Fermi level DOS(ε_F).

Thus, in $Zr_{1-x}Nb_xNiSn$, the concentration of donor states increases with increasing concentration of Nb atoms. Already at this stage of modeling, we can predict with high probability that when modeling the electrokinetic properties of the $Zr_{1-x}Nb_xNiSn$ solid solution, we will obtain a metallic type of electrical conductivity, and the sign of the thermopower coefficient $\alpha(T)$ will be negative. This is indicated by the location of the Fermi level ε_F deep in the conduction band ε_C (Fig. 3).

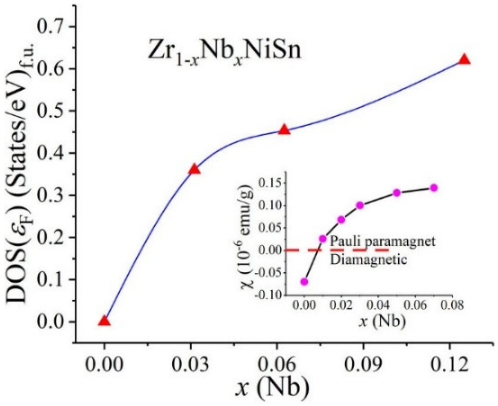


Fig. 4. Calculation of the density of electronic states distribution DOS for the ordered variant of the $Zr_{1-x}Nb_xNiSn$ structure. Inset: change in magnetic susceptibility $\chi(x)$ $Zr_{1-x}Nb_xNiSn$ [1]

Modeling the electrokinetic properties of $Zr_{1-x}Nb_xNiSn$

The results of modeling the behavior of the temperature dependences of the resistivity $\rho(T, x)$ and the thermopower coefficient $\alpha(T, x)$ of the semiconductor thermoelectric material $Zr_{1-x}Nb_xNiSn$ are shown in Fig. 5.

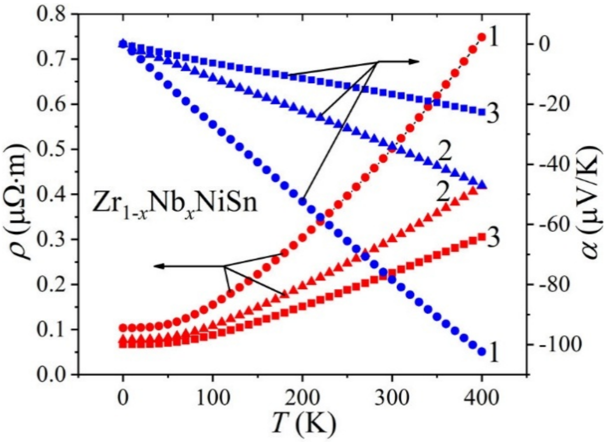


Fig. 5. Modeling the behavior of temperature dependences of resistivity $\rho(T, x)$ and thermopower coefficient $\alpha(T, x)$ $Zr_{1-x}Nb_xNiSn$: 1 – x = 0.01; 2 – x = 0.03; 3 – x = 0.07

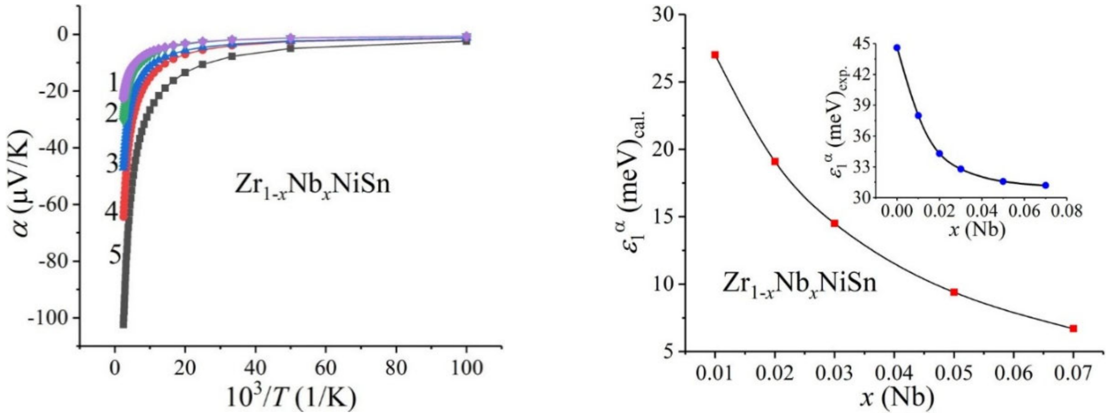
As we predicted based on DOS calculations, the resistivity ρ(T, x) for all $Zr_{1-x}Nb_xNiSn$ concentrations increases with increasing temperature. This behavior of ρ(T, x) indicates a metallic type of conductivity, when the Fermi level ε_F has moved from the forbidden band ε_g to the conduction band ε_C: a dielectric-metal conductivity transition has occurred, which is an Anderson transition [12]. The negative values of the thermopower coefficient α(T, x) of $Zr_{1-x}Nb_xNiSn$ are evidence that donor states are generated in the semiconductor thermoelectric material, which made it heavily doped and heavily compensated (HDCS) [13].

Thus, the results of modeling the temperature dependences of the resistivity ρ(T, x) and the thermopower coefficient α(T, x) show that in the thermoelectric material $Zr_{1-x}Nb_xNiSn$ only donor states appear as a result of the generation of structural defects of donor nature. The fact that the nature of the change with temperature of the dependences ρ(T, x) and α(T, x) is similar both according to the results of calculations (Fig. 5) and experimental studies [1] deserves special attention. Such consistency, in particular, indicates a successful choice of tools for modeling the electrokinetic properties of the thermoelectric material $Zr_{1-x}Nb_xNiSn$.

Another proof that in the thermoelectric material $Zr_{1-x}Nb_xNiSn$ exclusively donor states are generated is the nature of the change in the degree of compensation of the semiconductor. The authors [13, 14] showed that in HDCS the numerical values of the activation energy $\varepsilon_1^{\alpha}(x)$, determined from the activation sections of the temperature dependences of the thermopower coefficient α(1/T), are proportional to the degree of compensation of the semiconductor. Fig. 6 *a* shows the results of modeling the temperature dependences of the thermopower coefficient α(1/T, x) $Zr_{1-x}Nb_xNiSn$, which are described by the formula [12]:

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

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



a *b*

Fig. 6. Modeling of temperature dependences of thermopower coefficient α(1/T) (a) and change in activation energy $\varepsilon_1^{\alpha}(x)$ (b) $Zr_{1-x}Nb_xNiSn$. a: 1 – x = 0.07; 2 – x = 0.05; 3 – x = 0.03; 4 – x = 0.02; 5 – x = 0.01. Inset b: experimental data of change in $\varepsilon_1^{\alpha}(x)$ [1]

From the high-temperature activation sections of the α(1/T, x) dependences of $Zr_{1-x}Nb_xNiSn$ (Fig. 6*a*), the activation energies $\varepsilon_1^{\alpha}(x)$ (Fig. 6*b*) were calculated, which are proportional to the degree of compensation of the HDCS. From Fig. 6 *b*, we can see that with an increase in the concentration of Nb atoms in the structure of the thermoelectric material $Zr_{1-x}Nb_xNiSn$, the activation energy $\varepsilon_1^{\alpha}(x)$ decreases. This behavior of $\varepsilon_1^{\alpha}(x)$ is the result of a decrease in the degree of compensation of the semiconductor thermoelectric material of the electronic conductivity type $Zr_{1-x}Nb_xNiSn$ due to the additional generation of donor states. As emphasized above, this can only occur under the condition of simultaneous partial substitution of Zr atoms by Nb atoms (substitution solid solution) and occupation of tetrahedral voids by Nb atoms (inclusion solid solution). As noted above, this can occur only under the condition of simultaneous partial substitution of Zr atoms by Nb atoms and occupation of tetrahedral voids by Nb atoms. We also draw attention to the similar course of the activation energy dependences $\varepsilon_1^{\alpha}(x)$ of $Zr_{1-x}Nb_xNiSn$ both according to the simulation results and the experiment (Fig. 6). This is a sign of the correct choice of tools for modeling the electrokinetic and energetic properties of $Zr_{1-x}Nb_xNiSn$.

The calculation of the electronic structure of the thermoelectric material $Zr_{1-x}Nb_xNiSn$ also allowed us to simulate, in addition to the aforementioned specific electrical conductivity $\sigma(T, x)$ and thermopower coefficient $\alpha(T, x)$, the temperature dependences of the thermal conductivity coefficient $\kappa(T, x)$. This, in turn, based on the known ratio Z ($Z = \alpha^2 \cdot \sigma/\kappa$)) [2] made it possible to calculate both the value of the thermoelectric figure of merit Z and the product $Z \cdot T$ for $Zr_{1-x}Nb_xNiSn$ in a wide temperature and concentration ranges. Fig. 7 presents the results of such modeling, from which it can be seen that the dependence $Z \cdot T(T, x)$ of $Zr_{1-x}Nb_xNiSn$ at a concentration of $x = 0.01$ and a temperature of $T \approx 600$ K reaches maximum values, which corresponds under these conditions to the maximum efficiency of converting thermal energy into electrical energy. At higher concentrations of Nb atoms in the structure of the thermoelectric material, the maximum values of $Z \cdot T(T, x)$ lie outside the simulation temperature. By the way, experimental studies of $Zr_{1-x}Nb_xNiSn$ [1] also recorded the presence of a maximum in the dependence of the thermoelectric power coefficient $Z^*(x)$ at $T = 300$ K (Fig. 7, inset). The obtained results show that the semiconductor solid solution of $Zr_{1-x}Nb_xNiSn$ is a promising thermoelectric material.

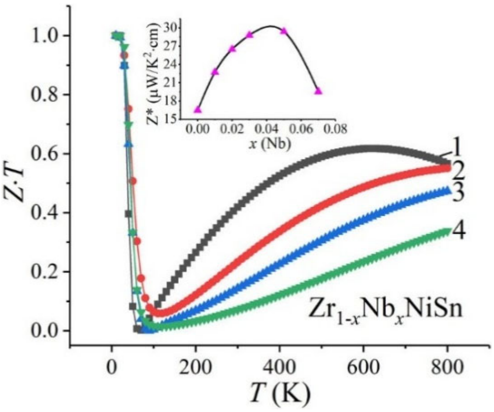


Fig. 7. Modeling of Z·T behavior of thermoelectric material $Zr_{1-x}Nb_xNiSn$: 1 – x = 0.01; 2 – x = 0.02; 3 – x = 0.03; 4 – x = 0.05. Inset: change in thermoelectric power $Z^*(x)$ at 380 K [1]

Thus, the results of the calculation of the electronic structure, thermodynamic, structural, electrokinetic and energy properties of the semiconductor thermoelectric material $Zr_{1-x}Nb_xNiSn$ confirmed the conclusions of experimental studies [1] that the crystal simultaneously undergoes structural transformations in different ratios associated with the partial substitution of Zr atoms by Nb atoms, as well as the occupation of tetrahedral voids of the structure by Nb atoms [1]. In this case, only structural defects of donor nature and the corresponding energy states are generated in $Zr_{1-x}Nb_xNiSn$.

Conclusions

Based on the results of modeling the thermodynamic, structural, energy and electrokinetic properties of the semiconductor thermoelectric material $Zr_{1-x}Nb_xNiSn$, the nature of the generated energy states and mechanisms of electrical conductivity have been established. The limits of the existence of the $Zr_{1-x}Nb_xNiSn$ substitution solid solution have been determined, the length of which depends on the temperature of homogenizing annealing. It is shown that when Nb atoms are simultaneously introduced into the structure of the ZrNiSn compound in different ratios, both the substitution of Zr atoms by Nb atoms and the formation of a substitution solid solution occur, and the occupation of tetrahedral voids of the structure by Nb atoms with the formation of an inclusion solid solution occur. Such structural changes in $Zr_{1-x}Nb_xNiSn$ generate two types of defects of a donor nature and the corresponding energy states, which meets the condition for obtaining the maximum efficiency of converting thermal energy into electrical energy. According to the calculated thermoelectric parameters, the $Zr_{1-x}Nb_xNiSn$ substitution solid solution is a promising thermoelectric material.

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Дослідження нового напівпровідникового термоелектричного матеріалу n-$Zr_{1-x}Nb_xNiSn$. II. Моделювання властивостей

Проведено моделювання електронної структури, термодинамічних, структурних, енергетичних та електрокінетичних властивостей напівпровідникового термоелектричного матеріалу $Zr_{1-x}Nb_xNiSn$ в рамках теорії функціоналу густини. Визначено природу генерованих енергетичних станів та механізмів електропровідності. Показано, що при уведенні до структури сполуки ZrNiSn атомів Nb одночасно у різних співвідношеннях відбувається як заміщення атомів Zr на атоми Nb та утворення твердого розчину заміщення, так і зайняття атомами Nb тетраедричних пустот структури з утворенням твердого розчину включення. Такі структурні зміни генерують в $Zr_{1-x}Nb_xNiSn$ два сорти дефектів донорної природи та відповідні енергетичні стани, що відповідає умові отримання максимальної ефективності перетворення теплової енергії в електричну. Моделювання термоелектричних властивостей показало, що напівпровідниковий твердий розчин заміщення $Zr_{1-x}Nb_xNiSn$ є перспективним термоелектричним матеріалом.

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