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INVESTIGATION OF $TiNi_{1-x}Cu_xSn$ THERMOELECTRIC MATERIAL

The crystalline structure, the temperature and concentration dependences of electrical resistivity, the Seebeck coefficient and magnetic susceptibility of $TiNi_{1-x}Cu_xSn$ thermoelectric material were investigated in the ranges of $T = 80 – 400$ K, $x = 0.005 – 0.10$. The mechanism for generation of donor nature structural defects upon the substitution of Cu atoms for Ni which reduce the compensation degree and determine the electrical conduction mechanisms of $TiNi_{1-x}Cu_xSn$ was identified. It was shown that thermoelectric power factor Z reaches maximal values at concentration $x \approx 0.01$ at intersection of the percolation level of conduction band by the Fermi level ε_F. The investigated $TiNi_{1-x}Cu_xSn$ semiconductor is a promising thermoelectric material, and ordering of its crystal structure provides stability and reproducibility of its characteristics.*

Key words: resistivity, Seebeck coefficient, thermoelectric material.

Introduction

Thermoelectric materials obtained by heavy doping of *n-TiNiSn, n-ZrNiSn, n-HfNiSn* and *p-TiCoSb* intermetallic semiconductors with acceptor and/or donor impurities, possess high efficiency of thermal into electric energy conversion [1]. In [2] it is shown that maximum values of thermoelectric figure of merit [3] are achieved in *n*-type thermoelectric semiconductor materials under the condition of doping with donor impurities, and in *p*-type materials – with acceptor impurities. Due to such doping, at the lowest impurity concentrations, the Fermi level ε_F can get closer to the percolation levels of conduction band and valence band by the distance k_BT, which assures, on the one hand, high electric conductivity values, and, on the other hand, still high values of the Seebeck coefficient. At the same time, doping, for instance, of *p-TiCoSb* intermetallic semiconductor with donor impurity *Ni* ($3d^84s^2$) by substitution of *Co* ($3d^74s^2$) atoms (*Co* has a smaller number of 3*d*-electrons than *Ni*) was not attended by the increase in the efficiency of thermal into electric energy conversion [4]. Here, ensuring the condition of the Fermi level ε_F approaching the percolation level of conduction band required overcompensation from the hole to electron semiconductor and a drift of the Fermi level from the valence band to conduction band, which is possible under the condition of considerable impurity concentrations which significantly reduced the value of the Seebeck coefficient.

However, recent results of integrated studies of crystalline and electronic structures, kinetic and magnetic characteristics of $TiNiSn_{1-x}Ga_x$ [5] and $ZrNiSn_{1-x}Ga_x$ thermoelectric materials [6] allowed

specifying the conditions for obtaining materials with maximum efficiency of thermal into electric energy conversion [2]. Thus, on doping of *n-TiNiSn* and *n-ZrNiSn* with *Ga* ($4s^2 4p^1$) acceptor impurity by substitution of *Sn* ($5s^2 5p^2$), mechanisms were revealed for a *simultaneous* generation in crystal of structural defects of both acceptor (*Ga* has less *p*-electrons than *Sn*) and donor nature due to the appearance and increasing the number of vacancies in position 4*b* of *Sn* atoms. It appeared that simultaneous formation in thermoelectric material of donor-acceptor pairs contributes to improving the thermoelectric figure of merit.

This paper investigates thermoelectric material $TiNi_{1-x}Cu_xSn$ obtained by substitution of *Ni* ($3d^8 4s^2$) atoms by *Cu* ($3d^{10} 4s^1$), which generates in crystal structural defects of donor nature (*Cu* has more 3*d*-electrons than *Ni*). The synthesized thermoelectric material $TiNi_{1-x}Cu_xSn$ in conformity with conditions [2] must possess high efficiency of thermal into electric energy conversion. On the other hand, the results of investigation of similar thermoelectric material $ZrNi_{1-x}Cu_xSn$ [1] have confirmed the formulated conditions [2] for obtaining maximum values of thermoelectric figure of merit.

Investigation procedures

The object to be investigated included structural, energy, kinetic and magnetic characteristics of thermoelectric material $TiNi_{1-x}Cu_xSn$. The samples were synthesized by melting batch mixture of the source components in electric arc furnace in an inert atmosphere with subsequent homogenizing annealing for 720 hours at a temperature of 1073 K. The *X*-ray structural analysis method was used to obtain the data arrays (diffractometer Guinier-Huber image plate system, $CuK\alpha_1$), and FullProf program [7] was employed for the calculation of structural characteristics. The chemical and phase compositions of the samples were controlled by microprobe analyzer (EPMA, energy-dispersive X-ray analyzer). The temperature and concentration dependences of the electrical resistivity (ρ) and the Seebeck coefficient (α) were measured with respect to copper and magnetic susceptibility (χ) (Faraday's method) of $TiNi_{1-x}Cu_xSn$ samples in the ranges: $T = 80 – 400$ K, $N_D^{Cu} \approx 3.8 \cdot 10^{19}$ cm^{-3} ($x = 0.005$) – $1.9 \cdot 10^{21}$ cm^{-3} ($x = 0.10$) and magnetic field strength $H \leq 10$ кE.

Research on structural features of $TiNi_{1-x}Cu_xSn$

A microprobe analysis of the concentration of atoms on the surface of $TiNi_{1-x}Cu_xSn$ samples up to composition $x = 0 – 0.10$ has established their conformity to the initial batch compositions, and
X-ray phase and structural analyses have shown that *X*-ray diffraction patterns have no traces of other phases apart from the main phase which is indexed in structural type *MgAgAs* [8] (face-centered cubic lattice, spatial group $F43m$ (№ 216), Pearson symbol $cF12$).

Taking into account a larger atomic radius of *Cu* ($r_{Cu} = 0.128$ nm) as compared to *Ni* ($r_{Ni} = 0.124$ nm), it would be logical to expect a monotonous increase in the values of unit cell period $a(x)$ in $TiNi_{1-x}Cu_xSn$. Exactly this result of change in the values of $a(x)$ was obtained at computer simulation of $TiNi_{1-x}Cu_xSn$ crystalline structure (Fig. 1, dependence 2). However, *X*-ray diffraction studies of $TiNi_{1-x}Cu_xSn$ showed that the introduction of *Cu* atoms into the structure of *TiNiSn* by replacing *Ni* atoms in the concentration range $x = 0 – 0.01$ was not accompanied by a monotonous increase in the values of the period $a(x)$ (Fig. 1, dependence 1), indicating more complex structural changes in the crystal than simply substituting *Cu* atoms for *Ni*. From Fig. 1 it is seen that in the concentration range $x = 0 – 0.005$ the values of unit cell period $a(x)$ drastically increase, but in the range $x = 0.005 – 0.01$ they drastically decrease as well, and at concentrations

$x \geq 0.01$ there is practically monotonous reduction of $a(x)$ values which is close to the results of computer simulation of $TiNi_{1-x}Cu_xSn$ structure. It is clear that structural changes in $TiNi_{1-x}Cu_xSn$ in the concentration range $0 \leq x \leq 0.01$ will lead to unpredictable changes in the electronic structure of thermoelectric material and determine its properties. Let us try to identify structural changes in $TiNi_{1-x}Cu_xSn$ that caused this, at first sight, unpredictable behavior of unit cell period $a(x)$.

In our work [9] it is shown that crystalline structure of *n-TiNiSn* is disordered (local amorphization) due to partial, up to ~1% ($z \approx 0.01$), occupancy by *Ni* atoms of 4*a* position of *Ti* ($3d^2 5s^2$) atoms, which generates in crystal structural defects of donor nature ("a priori doping"), as long as *Ni* has more 3*d*-electrons, and the compound formula takes on the form $(Ti_{1-z}Ni_z)NiSn$. In the energy gap of *n-TiNiSn* at the distance of 16.9 meV from the percolation level of conduction band there appears impurity donor level ε_D^1 caused by structural defects generated in the crystal.

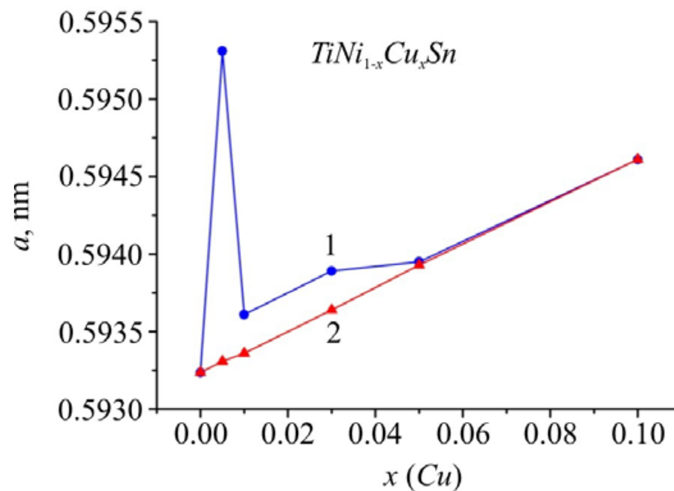

Fig. 1. Change in the values of unit cell period a(x) of $TiNi_{1-x}Cu_xSn$ semiconductor solid solution: 1 – experimental results; 2 – results of simulation of substitutional solid solution

At the same time, refinement of $TiNi_{1-x}Cu_xSn$ crystalline structure by powder method with a simultaneous refinement of the isotropic parameters of atomic displacement and occupancy of *Ti* crystallographic position (4*a*) has shown that the lowest value of coefficient of mismatch between crystalline structure model and the array of Bragg reflections within *MgAgAs* structural type was obtained for a model where occupancy of position of *Ti* atoms for $x \geq 0.01$ is 100%. In other words, in the concentration range of *Cu* $0 \leq x \leq 0.01$ impurity atoms there is a displacement from 4*a* position of small *Ni* atoms by greater *Ti* ($r_{Ti} = 0.146$ nm) atoms, which *puts in order* $TiNi_{1-x}Cu_xSn$ crystalline structure and "heals" structural defects of donor nature.

Alongside with displacement of *Ni* atoms from position 4*a* there is a process of simultaneous substitution in 4*c* position of *Ni* atoms by greater *Cu* atoms. Taking into account that the difference in atomic radii between *Ti* and *Ni* is $(r_{Ti} - r_{Ni}) = 0.022$ nm, and between *Ni* and *Cu* $(r_{Cu} - r_{Ni}) = 0.004$ nm, a change in $a(x)$ values at concentration range $x = 0 - 0.005$ will be determined by the process of displacement of *Ni* from 4*a* position by large *Ti* atoms, as long as the contribution of this substitution to total change of $a(x)$ value is 5 times that at substitution of *Cu* atoms for *Ni*. Exactly such structural changes in $TiNi_{1-x}Cu_xSn$ at concentration range $x = 0 - 0.005$ will cause rapid growth of the values of unit cell period $a(x)$ (Fig. 1, dependence 1). After the displacement of the main part of *Ni* atoms from *Ti* position *(4a)* (structure ordering) a change in $a(x)$ values will be determined by the occupancy by *Cu* atoms of *Ni* position (4*c*), which only now will lead to a monotonous growth of $a(x)$ values, as predicted in the simulation of $TiNi_{1-x}Cu_xSn$ structure. Note that *ordering* of $TiNi_{1-x}Cu_xSn$ crystalline

structure makes it stable to temperature and temporal changes, creating prerequisites for obtaining material with stable characteristics.

Changes in crystalline structure of $TiNi_{1-x}Cu_xSn$ during its ordering will necessarily lead to a respective transformation of electronic structure. It is clear that donor impurity level ε_D^1 present in *n-TiNiSn* as a result of displacement of ~ 1% of *Ti* atoms by *Ni* atoms [9], must disappear at concentrations $x > 0.01$. On the other hand, since *Cu* atom possesses a greater number of 3*d*-electrons than *Ni*, the substitution of *Cu* for *Ni* atom generates in 4*c* position a structural defect of donor nature, which will cause the emergence in the energy gap of another donor impurity level ε_D^2. The presence of a large number of donors ε_D^2 will determine the kinetic characteristics of $TiNi_{1-x}Cu_xSn$ which is bound to appear in the investigation of the dependences of resistivity and the Seebeck coefficient.

Research on the kinetic, energy and magnetic characteristics of $TiNi_{1-x}Cu_xSn$

The temperature and concentration dependences of the electric resistivity ρ and the Seebeck coefficient α of $TiNi_{1-x}Cu_xSn$ are presented in Figs. 2 – 4. The dependences lnρ(1/*T*) and α(1/*T*) for *n-TiNiSn* (Fig. 2) are typical for heavily doped and compensated semiconductors [10], and the high-temperature activation areas testify that the Fermi level ε_F is located in the energy gap from which thermal activation of electrons to percolation level of conduction band takes place. The result obtained for *n-TiNiSn* is fully consistent with the results of [10] where it is shown that in a semiconductor the Fermi level ε_F is located at the distance of 16.9 m·eV from the bottom of conduction band ε_C.

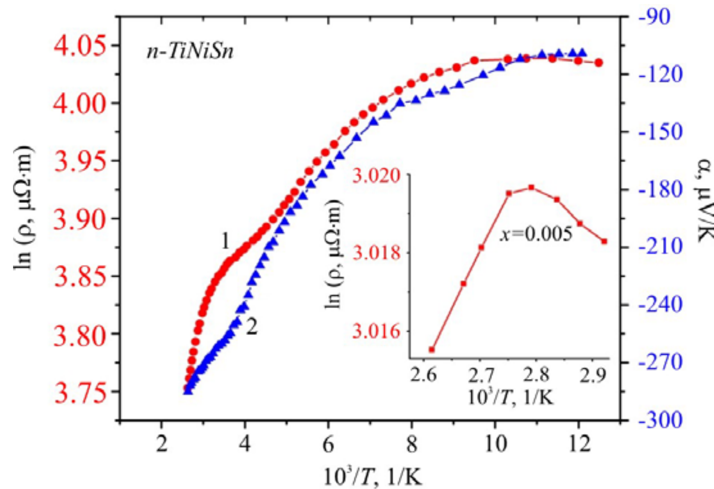

Fig. 2. Temperature dependences of electric resistivity lnρ(1/T) (1) and the Seebeck coefficient α(1/T) (2) of n-TiNiSn. Inset: dependence lnρ(1/T) of $TiN_{x0.995}Cu_{0.005}Sn$

Doping of *n-TiNiSn* semiconductor with the lowest concentration of *Cu*, $x = 0.005$ donor impurity leads, as is shown by the dependence lnρ(1/*T*) of $TiNi_{0.995}Cu_{0.005}Sn$ (Fig. 2, inset), to conduction metallization in the temperature range of $T = 80 – 360$ K (Fig. 3*a*, curve 1). It means that at the concentrations of $TiNi_{0.995}Cu_{0.005}Sn$ impurity and at temperatures $T = 80 – 360$ K the Fermi level ε_F intersected the percolation level of conduction band. From this we can conclude that drastic approach of the Fermi level ε_F to the percolation level of conduction band shows that the generated impurity donor level ε_D^2 is located at the distance of k_BT from the bottom of conduction band, and the temperatures $80 \leq T \leq 360$ K are sufficient for intersection by the Fermi level ε_F of the percolation level of conduction band.

However, further temperature increase at $T > 360$ K is suddenly accompanied by a reverse metal-dielectric conductivity transition [10], and the electric resistivity values of $TiNi_{0.995}Cu_{0.005}Sn$ decrease with a rise in temperature (Fig. 2, inset). Such behavior of lnρ(1/T) $TiNi_{0.995}Cu_{0.005}Sn$ dependence makes it clear that at temperatures $T > 360$ K the Fermi level ε_F goes beyond the band of continuous energies to the energy gap. Note that the sign of the Seebeck coefficient of $TiNi_{0.995}Cu_{0.005}Sn$ at all temperatures remained negative (Fig. 3*b*), which gives us the right to identify dielectric-metal and metal-dielectric conductivity transitions at intersection by the Fermi level ε_F of the percolation level of conduction band.

This, at first sight, unexpected behavior of the Fermi level of ε_F $TiNi_{0.995}Cu_{0.005}Sn$ in the temperature range of $80 \le T \le 360$ K actually has a very simple explanation. Indeed, donor concentration of the impurity donor level ε_D^1 ($z = 0.01$) [9] exceeds the concentration of donors ε_D^2 generated in a semiconductor at the lowest concentration of *Cu*, $x = 0.005$ donor impurity. At the same time, as shown by the results of the experiment, the depth of donor level ε_D^1 [9] is much larger than ε_D^2. The inverse metal-dielectric conductivity transition is caused by depletion of impurity donor level ε_D^2 at temperatures $T \ge 360$ K [10].

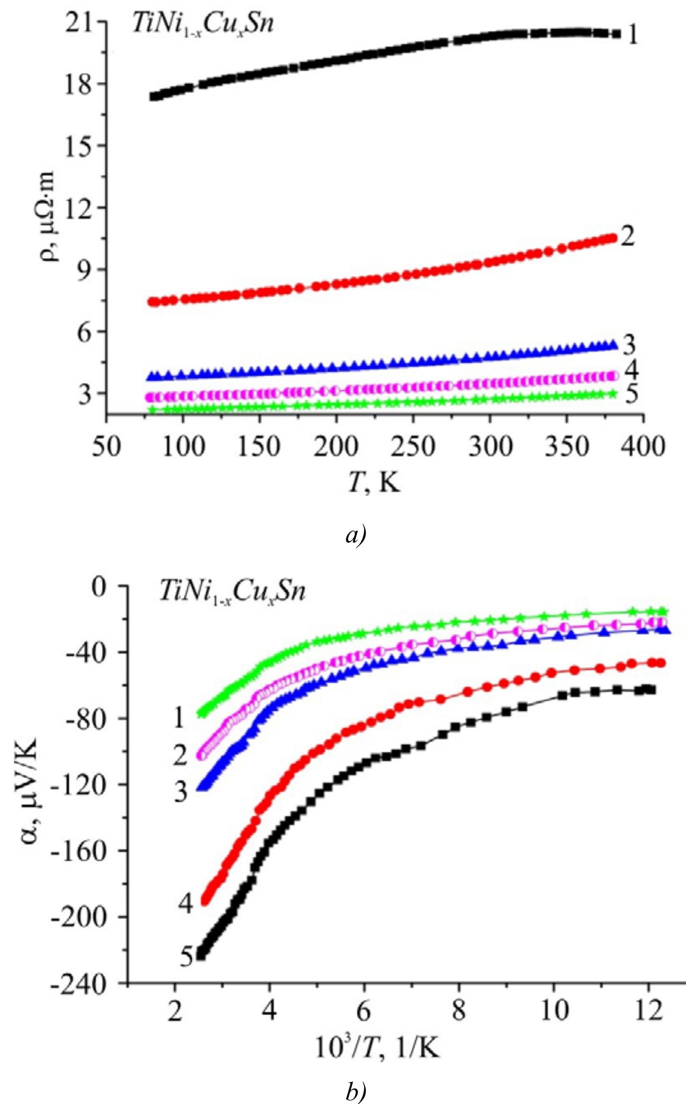

Fig. 3. Temperature dependences of electric resistivity ρ(T) (a) and the Seebeck coefficient α(1/T) (b) of $TiNi_{1-x}Cu_xSn$: 1 – x=0.005; 2 – x=0.01; 3 – x=0.03; 4 – x=0.05; 5 – x=0.10

As long as concentration of donors at donor level ε_D^1 is higher than ε_D^2, and after temperatures $T \geq 360$ K there is thermal activation of electrons from the deeper donor level ε_D^1, this is represented in the appearance of activation area on the dependence lnρ(1/*T*) of $TiNi_{0.995}Cu_{0.005}Sn$ (Fig. 2, inset).

The fact that *Cu* atoms introduced into *n-TiNiSn* generate structural defects of donor nature is also demonstrated by the dependences of change in the values of resistivity ρ(*x,T*) and the Seebeck coefficient α(*x,T*) over the entire concentration and temperature ranges (Fig. 4).

Thus, introduction of the lowest in the experiment concentrations of *Cu* drastically reduces the value of resistivity ρ(*x*) at *T* = 80 K from the values of ρ(*x* = 0) = 56.5 μΩ·m to ρ(*x* = 0.005) = 17.4 μΩ·m and ρ(*x* = 0.01) = 7.4 μΩ·m, which is due to increase in the number of free electrons at ionization of donors generated in the crystal. In so doing, the sign of the Seebeck coefficient of $TiNi_{1-x}Cu_xSn$ remains negative for all concentrations, and electrons are majority carriers.

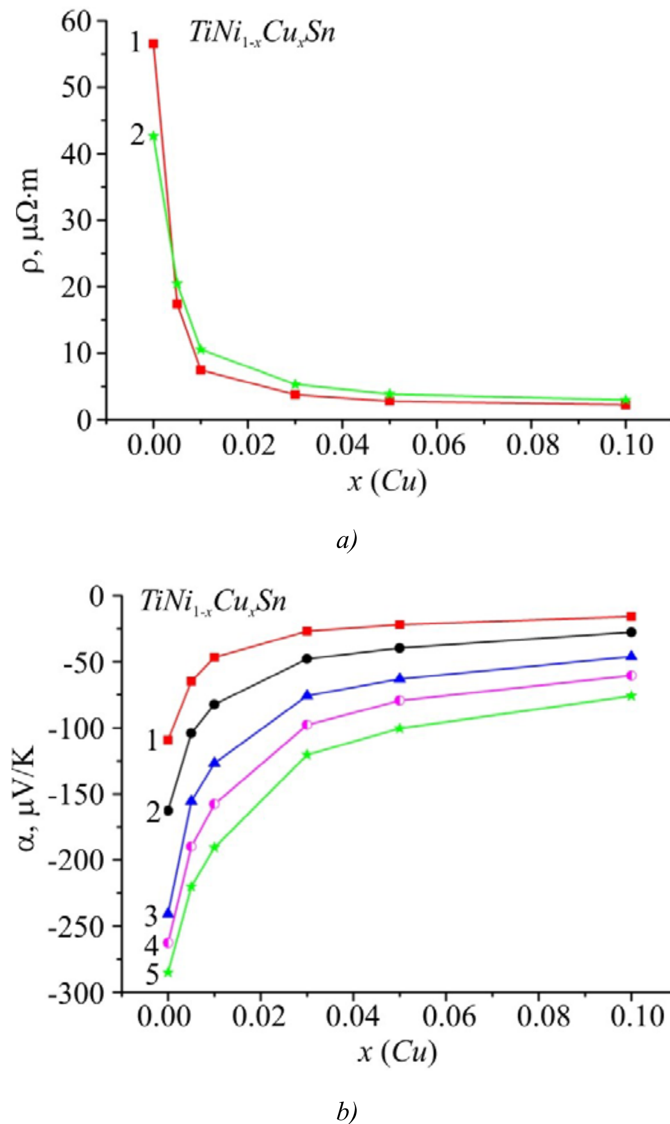

Fig. 4. Change in the values of electric resistivity ρ(x) (a) and the Seebeck coefficient α(x) (b) of $TiNi_{1-x}Cu_xSn$ at different temperatures; a: 1 – T=80 K, 2 – T=380 K; b: 1 – T=80, 2 – T=160, 3 – T=250, 4 – T=300, 5 – T=380 K

The results of kinetic investigations of $TiNi_{1-x}Cu_xSn$ are consistent with the results of experimental measurements of magnetic susceptibility χ at a temperature of *T* = 300 K (Fig. 5).

Investigations showed that all the samples of $TiNi_{1-x}Cu_xSn$ are Pauli paramagnetics wherein magnetic susceptibility is determined exceptionally by electronic gas and is proportional to density of states at the Fermi level $g(\varepsilon_F)$.

As can be seen from Fig. 5, dependence $\chi(x)$ of $TiNi_{1-x}Cu_xSn$ at $x > 0$ monotonously increases, hence increases the density of states at the Fermi level, which is possible only under the condition of generation of semiconductor thermoelectric material of structural defects of donor nature. Precisely this result was predicted by the studies of the structure and kinetic characteristics of $TiNi_{1-x}Cu_xSn$.

Maximum values of thermoelectric power factor Z^* ($Z^* = \alpha^2 \cdot \sigma$, where α is the Seebeck coefficient, σ is electric conductivity) are achieved under the condition when the Seebeck coefficient values are still high and the electric conductivity values of $TiNi_{1-x}Cu_xSn$ semiconductor solid solution have become even greater [2].

Under these conditions, on the dependences $Z^*(x)$ of $TiNi_{1-x}Cu_xSn$ at all investigated temperatures, an extremum appears at the concentrations of the impurity atoms Cu $x \approx 0.01$. Fig. 6 shows a dependence $Z^*(x)$ at a temperature of $T = 380$ K from which it follows that the values of $Z^*(x)$ are greater than in *n-TiNiSn* undoped semiconductor.

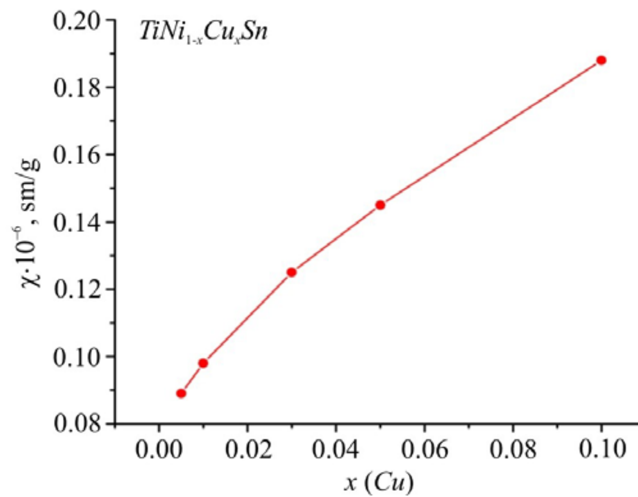

Fig. 5. Change in the values of magnetic susceptibility $\chi(x)$ of $TiNi_{1-x}Cu_xSn$ at a temperature of $T = 300$ K

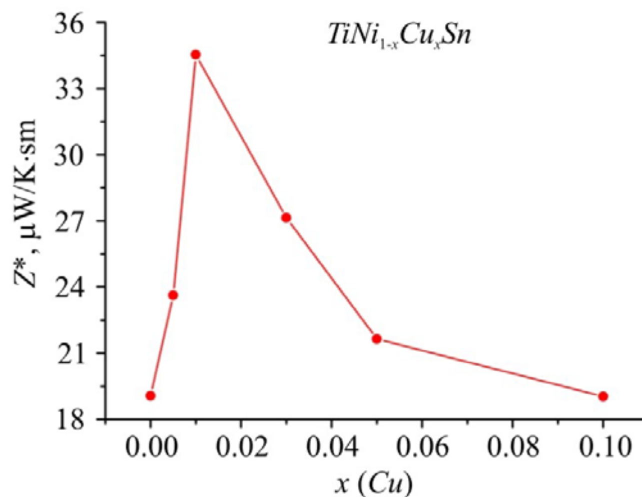

Fig. 6. Change in the values of thermoelectric power factor $Z^*(x)$ of $TiNi_{1-x}Cu_xSn$ at a temperature of $T = 380$ K

The appearance of maximum on the dependence $Z^*(x)$ at the concentration of impurity atoms $TiNi_{1-x}Cu_xSn$, $x \approx 0.01$, is expected, since, as has been shown by the research on the kinetic characteristics, exactly at these concentrations the Fermi level ε_F is at the distance k_BT from the percolation level of conduction band, which assures, on the one hand, high values of electric conductivity, and on the other hand – still high values of the Seebeck coefficient.

Taking into account that calculations show slight (by ~ 3 %) increase in thermal conductivity κ for $TiNi_{1-x}Cu_xSn$, $x = 0.01$, the values of thermoelectric figure of merit Z will be also higher than in *n-TiNiSn* undoped semiconductor, which makes the investigated semiconductor solid solution a promising thermoelectric material.

Conclusions

Thus, as a result of integrated research on the crystalline structure, the kinetic and magnetic characteristics of $TiNi_{1-x}Cu_xSn$ semiconductor thermoelectric material, we have identified the mechanism for generation of structural defects of donor nature at substitution of *Cu* atoms for *Ni* that reduce the compensation ratio and determine the electric conductivity mechanisms of material. The investigated $TiNi_{1-x}Cu_xSn$ semiconductor is a promising thermoelectric material, and crystalline structure orderliness is a guarantee of stability and reproducibility of characteristics.

The work was performed in the framework of grants of Ministry of Education and Science of Ukraine, № 0115U003257 and № 0114U005464.

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Submitted 12.11.2016