PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 18, № 3 (2017) P. 328-333
DOI: 10.15330/pcss.18.3.328-333

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 18, № 3 (2017) С. 328-333

UDK 537.311.322

ISSN 1729-4428

L.P. Romaka[1], Yu.V. Stadnyk[1], V.A. Romaka[2,3], A.M. Horyn[1]

Features of Structural, Electrokinetic and Energy State Characteristics of $V_{x+y}Co_{1-y}Sb_3$ Skutterudite

[1]Ivan Franko National University of Lviv, Kyryla and Mefodiya Str., 6, 79005, Lviv,Ukraine, e-mail: romakal@franko.lviv.ua;
[2]Ya. Pidstryhach Institute for Applied Problems of Mechanics and Mathematics, NAS of Ukraine,
Naukova Str., 3-b, 79060, Lviv, Ukraine;
[3]National University "LvivskaPolitechnika", St. Bandera Str., 12, 79013, Lviv,Ukraine

The structure characteristics, temperature and concentration dependences of the electrical resistivity and the thermopower coefficient for the $V_{x+y}Co_{1-y}Sb_3$ skutterudite were investigated in the ranges: T = 80 - 400 K, x = 0.02 - 0.20. It was shown that the introduction of V atoms into the structure of $CoSb^3$ thermoelectric material was accompanied by an increase in the efficiency of conversion of thermal energy into electrical energy. It was established that the inversion in the sign of the thermopower coefficient for $V_{x+y}Co_{1-y}Sb_3$ not observed for these concentrations of V impurity atoms. Based on the analysis of electrokinetic and energy state characteristics of $V_{x+y}Co_{1-y}Sb_3$, it was assumed that the V ($3d^34s^2$)impurity atoms simultaneously replaced Co ($3d^74s^2$)atoms, generating structural defects of acceptor nature, and were located in the icosahedral voids of the crystal structure and generated donors.

Keywords: crystal structure, electrical resistivity, thermopower coefficient.

Article acted received 11.07.2017; accepted for publication 05.09.2017.

Introduction

Thermoelectric materials obtained by the way of heavy doping of the *n*-$CoSb_3$ skutterudite by acceptor and/or donor impurities, exhibit high values of figure of merit, possess high efficiency of conversion of thermal energy into electric one, and at present are the most investigated. In the crystal structure of $CoSb_3$ skutterudite the Co atoms form a primitive cubic lattice, the anion groups of Sb atoms $[Sb]_4$ occupy the six of eight smaller cubes in the unit cell [1]. Two empty cubes contain the voids of icosahedral type, formed by octahedra of Sb atoms around Co atoms (Fig. 1) which can be filled by electropositive metal cations (*M*) corresponding formula M_xCoSb_3. This feature of the crystal structure of $CoSb_3$ is mostly used for optimization of the thermoelectric characteristics by introduction of the doping atom into icosahedral cavities (the interstitial solid solution) influencing on the electronic structure of material, at which the efficiency of conversion of thermal energy into electric energy will be maximal.

Introduction of rare-earths atoms with considerable sizes La [2], Sm [3], Gd [4], and also commensurable in size Ca atoms [5] into the structure of $CoSb_3$ skutterudite under high pressure resulted in increase of figure of thermoelectric merit values. In particular, for $La_{0.29}Co_4Sb_{12}$ sample the maximum value $ZT = 1.06$ was obtained at 863 K, for $Sm_{0.6}Co_4Sb_{12}$ sample $ZT = 0.8$ at the temperature 716 K, and $Ca_{0.31}Co_4Sb_{12}$ skutterudite was characterized by $ZT = 0.8$ at 840 K. Inclusion of Pd and Te atoms into the structure of *n*-$CoSb_3$ semiconductor under high pressure [6] led to an increase of the efficiency of conversion of thermal energy into electric energy, and the maximum value $ZT = 1$ was obtained at 873 K. At the same time for *n*-$Co_4Sb_{11.5}Te_{0.5}$ sample [7] a maximum value $ZT = 0.92$ was reached at 710 K. By powder pressing of the components with the following sintering under vacuum the skutterudite $Y_{0.18}Co_4Sb_{12}$ was synthesized, for which values of figures of thermoelectric merit increase due to the enlargement of electric conductivity values and decrease of the coefficient of thermal conductivity. In all analyzed cases impurity atoms of big size were located in icosahedral voids of $CoSb_3$ structure.

In addition, optimization of thermoelectric characteristics is possible by a substitution of one of the components in *n*-$CoSb_3$ by an impurity atom (substitutional solid solution). By changing the type of impurity atoms, their concentration, one can affect the electronic structure of thermoelectric material and its properties. In particular, study of structural and electrokinetic characteristics of *n*-$CoSb_3$, doped by the Fe

($3d^64s^2$) atoms by induction melting [9] showed that the impurity Fe atoms replace Co ($3d^74s^2$) atoms in their crystallographic positions generating the structural defects of acceptor nature in crystal because 3***d***-electrons number of Fe atom is smaller than for Co one. Acceptor nature of the structural defects in p-$Co_{1-x}Fe_xSb_3$ is confirmed by the positive values of the thermopower coefficient at all temperatures of investigation. During this there occurs the change of the type of conductivity of semiconductor, and holes become the basic charge carriers. Taking into account the near atomic radii of Co (r_{Co} = 0.1252 nm) and Fe (r_{Fe} = 0.127nm) the substitution of Co atoms for Fe does not cause the substantial changes in the crystal structure of semiconductor, however the electronic structure changes fundamentally. Such doping leads to reduction of thermal conductivity coefficient and increase of the figure of thermoelectric merit coefficient values.

The aim of the present investigation is to receive the thermoelectric material with high efficiency of conversion of thermal energy into electric energy by realization of “hybrid” variant of introduction of impurity V atoms into the structure of $CoSb_3$ compound: both substitution of the Co atoms that generates the defects of acceptor nature in crystal and appearance of the donor defects during the location of V atoms in the icosahedral voids. At choosing the impurity atoms the size factor (correlation between atomic radii of impurity atom and substituted atom) and the charge state of these atoms were taken into account.

I. Experimental details

The crystal structure, electrokinetic and energy state characteristics of $V_{x+y}Co_{1-y}Sb_3$ were investigated. The samples were synthesized by a direct arc melting of the constituent elements (overall purity up to 99.9 wt. %) followed by homogenizing annealing at a temperature of 870 K for 1440 hours. The phase analysis was performed using X-ray powder patterns obtained on the DRON–2.0M powder diffractometer (Fe K_a radiation). Calculations of the crystallographic parameters were carried out using the WinPLOTR program packages [10]. Chemical and phase compositions of the samples were examined by Scanning Electron Microscopy (EPMA, energy-dispersive *X*-ray analyzer). The temperature and concentration dependencies of electric resistivity (ρ) and thermopower coefficient (α) (pure copper as a reference material) for $V_{x+y}Co_{1-y}Sb_3$ samples were measured in the temperature range 80-400 K and concentration range $N_V \approx 3.8 \cdot 10^{20}$ cm^{-3} (x = 0.02) – $3.8 \cdot 10^{21}$ cm^{-3} (x = 0.20).

II. Experimental results

According to EPM analysis, the atomic concentration on the surface of $V_{x+y}Co_{1-y}Sb_3$ samples corresponded to the initial compositions of alloys, and X-ray phase and structural analyses indicated that prepared samples up to x = 0 - 0.20 composition can be indexed in the $LaFe_4P_{12}$-structure type [11] (space group *Im*-3) and do not contain the traces of other phases. Taking into account the larger atomic radius of V (r_V = 0.135 nm) in comparison with Co, the increase of the lattice parameter ***a***(x) of $V_{x+y}Co_{1-y}Sb_3$ from ***a***(x = 0) = 0.9016(1) nm to ***a***(x = 0.20) = 0.9028(1) nm is clear.

At this stage of structural research we could not definitely establish one or another number of V atoms in the crystallographic position of Co or in the icosahedral voids of the skutterudite, since such information is beyond the accuracy of the X-ray diffraction method. In this work the results of the qualitative estimation of occupancy of crystallographic positions by certain type of atoms are given. Thus, the crystal structure modeling of $V_{x+y}Co_{1-y}Sb_3$ for the case of occupation by V impurity atoms the crystallographic position of Co shows the larger change of lattice parameter values $a(x)$, than experimentally obtained. In the case of filling of icosahedral voids of $CoSb_3$ by V atoms (Fig. 1) the crystal structure modeling gives insignificant increase of $a(x)$ values. Exactly based on these results the assumption about simultaneous substitution of Co atoms by V impurity and filling of icosahedral voids by V atoms in the $CoSb_3$ structure was made.

At the same time, the combination of the results of structural and electrophysical studies allows to reduce the variability of occupation of definite crystallographic position by certain type of atoms or statistical atomic mixture. Exactly this problem is solved in the present work. The result of atomic distribution in $V_{x+y}Co_{1-y}Sb_3$, as close as possible to the real distribution of atoms in the structure can be obtained only after comparison of the results of electronic structure calculation with the results

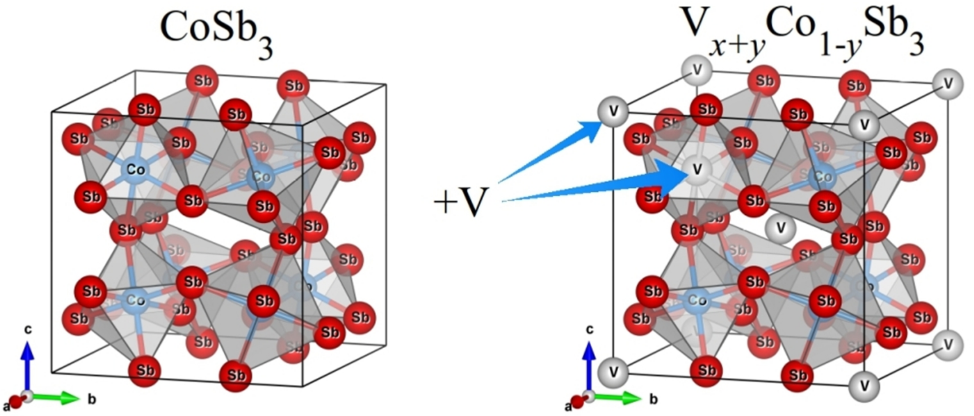


Fig. 1. Model of crystal structure transformation of $CoSb_3$ in $V_{x+y}Co_{1-y}Sb_3$ ($LaFe_4P_{12}$-type, space group *Im*-3).

of electrophysical studies [12], which our next research will be devoted to.

The temperature and concentration dependences of electric resistivity ρ and thermopower coefficient α for $V_{x+y}Co_{1-y}Sb_3$ are shown in Fig. 2, 3. The $\ln\rho(1/T)$ and $\alpha(1/T)$ dependences for $V_{x+y}Co_{1-y}Sb_3$ samples (Fig. 2) are typical for heavily doped and highly compensated semiconductors (HDHCS) [13], and existing activation regions indicate several mechanisms of charge transport [12]. The dependences of $\ln\rho(1/T)$ are approximated by the relation [13]:

$$r^{-1}(T) = r_1^{-1}\exp\left(-\frac{e_1^{\,r}}{k_B T}\right) + r_3^{-1}\left(-\frac{e_3^{\,r}}{k_B T}\right), \qquad (1)$$

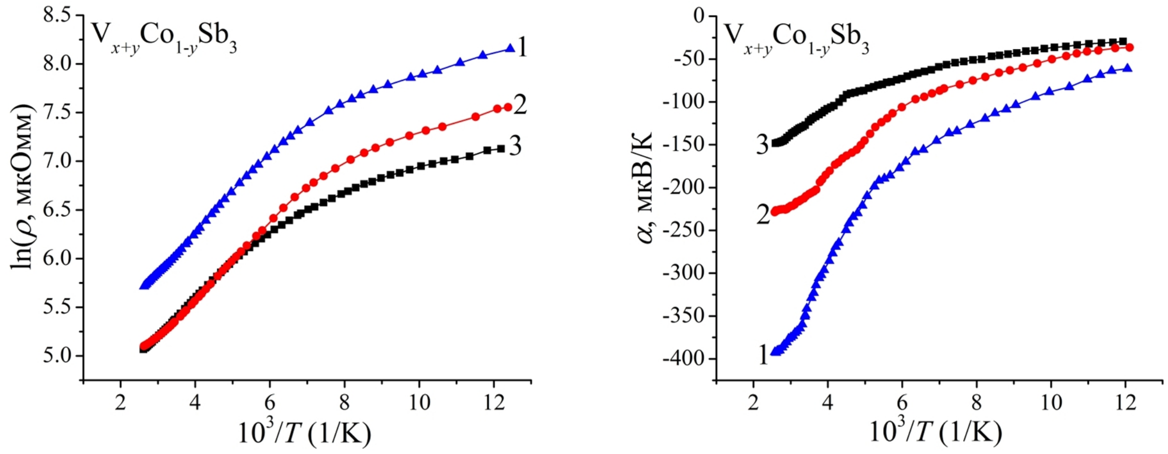
where the first high-temperature constituent describes an activation of current carriers ε_1^{ρ} from the Fermi level ε_F to the percolation level of continuous energy band, and second, low-temperature, – hopping conductivity ε_3^{ρ}. In turn, the temperature dependences of thermopower coefficient $\alpha(1/T)$ for $V_{x+y}Co_{1-y}Sb_3$ can be approximated by the following dependence [14]:

$$a = \frac{k_B}{e}\left(\frac{e_i^{\,a}}{k_B T} - g + 1\right), \qquad (2)$$

where γ is a parameter that depends on the nature of scattering. From the high temperature part of $\alpha(1/T)$ dependence the values of activation energy ε_1^{α} were calculated, which, as shown in [12], are proportional to the amplitude of large-scale fluctuation of continuous energies band, and from the low-temperature part – the values of activation energy ε_3^{α}, which are proportional to amplitude of modulation of small-scale fluctuation of HDHCS [12, 13].

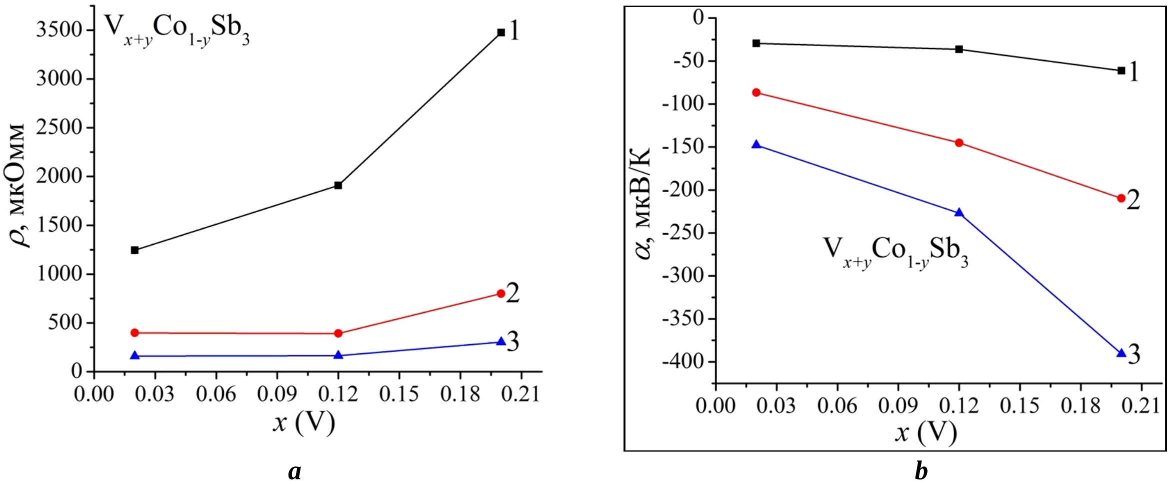
The presence of high-temperature activation parts in the $\ln\rho(1/T)$ dependences (Fig. 2, *a*) for all $V_{x+y}Co_{1-y}Sb_3$ samples indicates that the Fermi level ε_F is located in the band gap, from which the thermal activation of current carriers to the percolation levels of continuous energies band occurs. At the same time, negative values of thermopower coefficient (Fig. 2, *b*) for all $V_{x+y}Co_{1-y}Sb_3$ compositions and temperatures indicate that electrons are the main current carriers, and the Fermi level ε_F is located closer to the percolation level of conduction band than to the valence band.

Increase of electric resistivity $\rho(x,T)$ and thermopower coefficient $\alpha(x,T)$ values of $V_{x+y}Co_{1-y}Sb_3$ (Fig. 3) for all temperatures indicates that V impurity atoms generate the structural defects of acceptor nature in the crystal. Thus, the introduction of V impurity atoms



a ***b***

Fig. 2. Temperature dependences of electric resistivity $\ln\rho(1/T)$ (***a***) and differential thermopower $\alpha(1/T)$ (***b***) for $V_{x+y}Co_{1-y}Sb_3$: 1 – $x = 0.02$; 2 – $x = 0.12$; 3 – $x = 0.20$.



a ***b***

Fig. 3. Variation of electric resistivity $\rho(x)$ (***a***) and thermopower coefficient $\alpha(x)$ (***b***) for $V_{x+y}Co_{1-y}Sb_3$ at different temperatures: 1 – $T = 80$ K; 2 – $T = 200$ K; 3 – $T = 380$ K.

rapidly increases the value of the resistivity $\rho(x)$ at $T = 80$ K from $\rho(x = 0.02) = 1245.2$ μΩ·m to $\rho(x = 0.12) = 1908.5$ μΩ·m and $\rho(x = 0.20) = 3475.3$ μΩ·m. Such a rapid growth of $\rho(x)$ dependence is possible only if the concentration of the main current carriers decreases with their "freezing" into the band gap to the generated acceptor levels due to the substitution of Co atoms to V.

On the other hand, the negative values of the thermopower coefficient for $V_{x+y}Co_{1-y}Sb_3$ during the generation of structural defects of acceptor nature in the crystal indicates that more complicated structural changes occur in the crystal. We can assume that structural defects of acceptor and donor nature (donor-acceptor pairs) are simultaneously generated in $V_{x+y}Co_{1-y}Sb_3$ crystal to ensure the stability of the structure and the principle of electroneutrality. Such defects can be the V atoms, which are located in the icosahedral voids of $V_{x+y}Co_{1-y}Sb_3$. Thus, the analysis of the behavior of the energy state characteristics for $V_{x+y}Co_{1-y}Sb_3$, in particular the changes in the values of the activation energy $\varepsilon_1^{\rho}(x)$ and amplitude of modulation of continuous energies band ε_1^{α} also shows that acceptors and donors are simultaneously generated in a semiconductor (Fig. 4).

At first let us perform an analysis of change of the position of the Fermi level ε_F for $V_{x+y}Co_{1-y}Sb_3$ during the concentration increase of V impurity atoms. Taking into account that at high temperatures the sign of thermopower coefficient remains negative we can conclude that in $V_{x+y}Co_{1-y}Sb_3$, $x = 0.02$, the value of activation energy $\varepsilon_1^{\rho}(x = 0.02) = 29.8$ meV represents the energy gap between the position of the Fermi level ε_F and the percolation level of conduction band. It's worth to remind that the value of activation energy $\varepsilon_1^{\rho}(x)$ is calculated exactly from the high-temperature activation part of $\ln\rho(1/T)$ dependence (Fig. 2*a*).

Further increase of V impurity concentration in the *n*-type semiconductor up to the values $x = 0.12$ results in deepening of the Fermi level ε_F into the band gap to the distance $\varepsilon_1^{\rho}(x = 0.12) = 34.2$ meV. Such behavior of the Fermi level ε_F can only be caused by the generation of structural defects of acceptor nature in the $V_{x+y}Co_{1-y}Sb_3$ crystal. Acceptor defects may appear in $V_{x+y}Co_{1-y}Sb_3$ only in the case of occupation of the crystallographic position of Co ($3d^74s^2$) atoms by V atoms ($3d^34s^2$), because the number of 3*d*-electrons of V is smaller than that of Co. Generated structural defects cause the appearance of impurity acceptor levels in the *n*-$V_{x+y}Co_{1-y}Sb_3$ semiconductor which are situated near the top of the valence band and take the part of free electrons, lowering the position of the Fermi level ε_F, that we observed during the experiment with the increase of ε_1^{ρ} values in the concentration range $x = 0.02 - 0.12$. In addition, decrease of the free electron concentration in the semiconductor with electron type of conductivity at their "freezing" to the acceptor levels certainly will result in the increase of electric resistivity values that also takes place in an experiment (Fig. 3, *a*).

However, at the higher concentration of V impurity in the concentration range $x = 0.12 - 0.20$ the motion rate of Fermi level ε_F for *n*-$V_{x+y}Co_{1-y}Sb_3$ semiconductor into the depth of energy band gap halves, and the Fermi level in *n*-$V_{x+y}Co_{1-y}Sb_3$ is located at the distance of 35.1 meV from the percolation level of the conduction band.

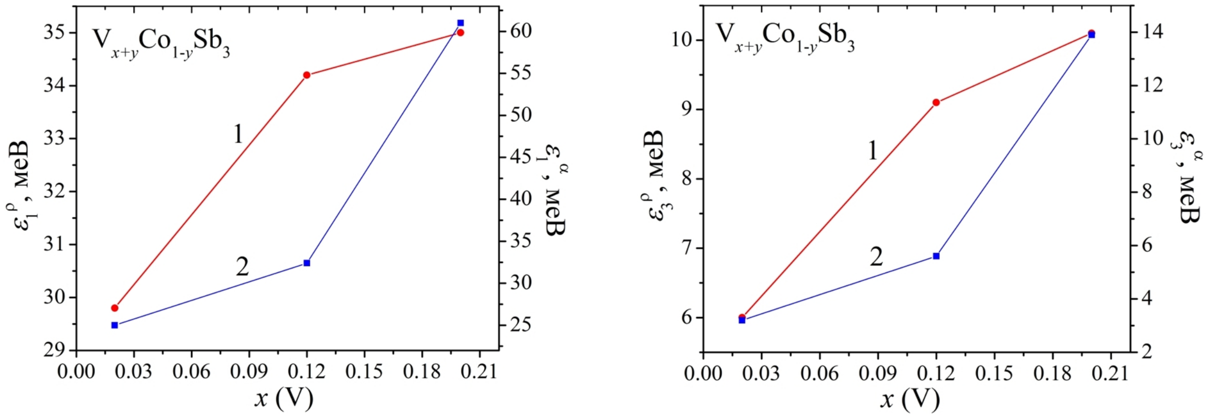
There appears a question, what caused the "braking" of motion of the Fermi level ε_F at the constant rate of introduction of impurity V atoms into the $V_{x+y}Co_{1-y}Sb_3$ crystal?

Decrease of the motion rate of the Fermi level ε_F in the direction from the percolation level of conduction band at the $x > 0.12$ concentrations allows to assume that occupation of crystallographic position of Co atoms by V atoms at such concentrations becomes less energy advantageous, and impurity concentration $x = 0.20$ is close to the V solubility limit during the realization of substitutional solid solution $V_{x+y}Co_{1-y}Sb_3$.

Thus, the following question arises, where are the impurity V atoms introduced into the skutterudite?

The answer to this question can be the assumption about simultaneous occupation of icosahedral voids of $V_{x+y}Co_{1-y}Sb_3$ structure by the part of V atoms (Fig. 1), which generates the structural defects of donor nature in the crystal. In this case impurity donor levels generated in the band gap are the source of electrons, which are locked by the part of acceptors, and the semiconductor becomes more compensated (ratio of the ionized acceptors and donors). This leads to the nonlinear change of the Fermi level values ε_F at the different concentrations of impurity V atoms.

Thus, analysis of change of activation energy values of current carriers $\varepsilon_1^{\rho}(x)$ from the Fermi level ε_F to the percolation level of conduction band of *n*-$V_{x+y}Co_{1-y}Sb_3$ indicates the simultaneous generation of the structural defects of acceptor and donor nature in a crystal in



a ***b***

Fig. 4. Variation of activation energy $\varepsilon_1^{\rho}(x)$ (1), $\varepsilon_1^{\alpha}(x)$ (2) (***a***) and $\varepsilon_3^{\rho}(x)$ (1), $\varepsilon_3^{\alpha}(x)$ (2) (***b***) of $V_{x+y}Co_{1-y}Sb_3$.

different ratios that changes the compensation degree of semiconductor.

On the other hand, if in the band gap of *n*-$V_{x+y}Co_{1-y}Sb_3$ semiconductor the impurity acceptor and donor levels are generated simultaneously in different relations, changing the compensation degree, it must be accompanied by the increase of modulation amplitude value of bands of continuous energies of HDHCS [12, 13]. Indeed, we can see from Fig. 4*a* the increase of activation energy values $\varepsilon_1^{\alpha}(x)$ of $V_{x+y}Co_{1-y}Sb_3$, which are proportional to the modulation amplitude of bands of continuous energies of $V_{x+y}Co_{1-y}Sb_3$. In case of $V_{x+y}Co_{1-y}Sb_3$, $x = 0.02$, the value of modulation amplitude is $\varepsilon_1^{\alpha}(x = 0) = 25.1$ meV. The growth of concentration of impurity V atoms increases the compensation degree, which is indicated by the growth of modulation amplitude values from $\varepsilon_1^{\alpha}(x = 0.12) = 32.4$ meV to $\varepsilon_1^{\alpha}(x = 0.20) = 61.2$ meV. Such behavior of activation energy values $\varepsilon_1^{\alpha}(x)$ is possible under the condition of the simultaneous generation of the acceptors and donors in the $V_{x+y}Co_{1-y}Sb_3$ structure by the mechanism described above.

Behavior of activation energy values of hopping conductivity ε_3^{ρ} and modulation amplitude of small-scale fluctuation ε_3^{α} of HDHCS $V_{x+y}Co_{1-y}Sb_3$ (Fig. 4*b*) supports the proposed above model of simultaneous occupation by the impurity V atoms the crystallographic positions of Co atoms and icosahedral voids of $V_{x+y}Co_{1-y}Sb_3$ structure in different ratios (Fig. 1). Increase of the length of electron jump (ε_3^{ρ} value) within the impurity states of donor band of *n*-V_xCoSb_3 in the concentration range $x = 0.02$ - 0.12 can take place only at the condition that part of donors is compensated by the acceptors generated in the semiconductor that is possible at the occupation of crystallographic positions of Co atoms by V atoms. In opposite, twofold reduction of the length of electron jump in the concentration range $x = 0.12$ - 0.20 indicates that simultaneously with the acceptors the donors appear in a crystal. The behavior of modulation amplitude of small-scale fluctuation ε_3^{α} is also clear.

As it is known, one of the important characteristics of thermoelectric materials is the thermoelectric power factor ($Z^* = S^2/\rho$). Comparing Z^* values (Fig. 5) for initial $CoSb_3$ compound and doped alloys we can see that at higher temperatures the thermoelectric power factor for alloys at $x \geq 0.12$ compositions is much higher than for the initial compound, which makes these alloys more perspective for further optimization of their thermoelectric characteristics.

Conclusions

Thus, results of the structural, electrokinetic and energy state studies of $V_{x+y}Co_{1-y}Sb_3$ allow to talk about the complicated mechanism of generation of structural defects in the crystal and to make assumptions about the mechanisms of generation of donor-acceptor pairs that finally increases the efficiency of conversion of thermal energy into electric. More precise result of atomic distribution in $V_{x+y}Co_{1-y}Sb_3$, maximally close to the real state of crystal that will allow to predict its thermoelectric properties, will be obtained after the electronic structure calculation for skutterudite, which will be the aim of our further investigations.

Romaka L.P. **-** Ph.D., Leading Researcher;
Stadnyk Yu.V. **-** Ph.D., Leading Researcher;
Romaka V.A. **-** Professor, PH.D., Ph.D.
Horyn A.M. **-** Ph.D., Senior Researche.

[1] E. Bauer, A. Grytsiv, X. Chen, N. Melnychenko-Koblyuk, G. Hilscher, H. Kaldarar, H. Michor, E. Royanian, G. Giester, M. Rotter, R. Podloucky, P. Rogl, Rev. Letter 99, 217001 (2007).
[2] C. Chen, L. Zhang, J. Li, F. Yu, D. Yu, Y. Tian, B. Xu, J. Alloys Compd. 699, 751 (2017).
[3] Q. Zhang, C. Chen, Y. Kang, X. Li, L. Zhang, D. Yu, Y. Tian, B. Xu, Materials Letters 143, 41 (2015).
[4] J. Yang, B. Xu, L. Zhang, Y. Liu, D. Yu, Z. Liu, J. He, Y. Tian, Materials Letters 98, 171 (2013).
[5] X. Li, Q. Zhang, Y. Kang, C. Chen, L. Zhang, D. Yu, Y. Tian, B. Xu, J. Alloys Compd. 677, 61 (2016).
[6] M. Chitroub, F. Besse, H. Scherrer, J. Alloys Compd. 467(1–2), 31 (2009).
[7] L. Deng, L.B. Wang, X.P. Jia, H.A. Ma, J.M. Qin, Y.C. Wan, J. Alloys Compd. 602, 117 (2014).
[8] H. Liu, H. Gao, Y. Gu, X. Zhao, Journal of Rare Earths 29(6), 596 (2011).
[9] I.-H. Kim, S.-C.Ur. Materials Letters 61(11–12), 2446 (2007).
[10] T. Roisnel, J. Rodriguez-Carvajal, Mater. Sci. Forum, Proc. EPDIC7, 378-381, 118 (2001).
[11] W. Jeitschko, D. Braun, Acta Crystall ogr. B. 33(11), 3401 (1977).
[12] V.A. Romaka, V.V. Romaka, Ju.V. Stadnik, Intermetalichni napivprovidniki: vlastivosti ta zastosuvannja (L'vivs'ka politehnika, L'viv, 2011).
[13] B.I. Shklovskij, A.L. Jefros, Jelektronnye svojstva legirovannyh poluprovodnikov (Nauka, Moskva, 1979).
[14] N. Mott, Je. Djevis, Jelektronnye processy v nekristallicheskih veshhestvah (Mir, Moskva, 1982).

Л.П. Ромака[1], Ю.В. Стадник[1], В.А. Ромака[2,3], А.М. Горинь[1]

Особливості структурних, кінетичних та енергетичних характеристик скутерудиту $V_{x+y}Co_{1-y}Sb_3$

[1]Львівський національний університет ім. І.Франка, вул. Кирила і Мефодія, 6, Львів, 79005, Україна,
e-mail: romakal@franko.lviv.ua;
[2]Інститут прикладних проблем механіки і математики ім. Я.С. Підстригача НАН України, вул. Наукова, 3-б, Львів, 79060, Україна;
[3]Національний університет "Львівська політехніка", вул. С. Бандери, 12, Львів, 79013, Україна

Досліджено структурні характеристики, температурні і концентраційні залежності питомого електроопору та коефіцієнта термо-ерс скутерудиту $V_{x+y}Co_{1-y}Sb_3$ у діапазонах: T = 80 - 400 К, x = 0,02 - 0,20. Показано, що уведення у структуру термоелектричного матеріалу $CoSb_3$ атомів V супроводжується збільшенням ефективності перетворення теплової енергії в електричну. Встановлено, що за даних концентрацій домішкових атомів V не відбувається зміна знаку коефіцієнта термо-ерс $V_{x+y}Co_{1-y}Sb_3$. На основі аналізу електрокінетичних та енергетичних характеристик $V_{x+y}Co_{1-y}Sb_3$ зроблено припущення, що домішкові атоми V ($3d^34s^2$) одночасно витісняють атоми Co ($3d^74s^2$), генеруючи структурні дефекти акцепторної акцептори, та розташовуються в октаедричних порожнинах кристалічної структури, генеруючи донори.

Ключові слова: кристалічна структура, електроопір, коефіцієнттермо-ерс.