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EFFICIENCY IMPROVEMENT OF GENERATOR MODULES BASED ON *CoSb* THROUGH USE OF SEGMENTED AND MULTI-STAGE STRUCTURES

Results of computer simulation of thermoelectric generator modules of homogeneous, segmented and functionally graded materials (FGM) based on CoSb are presented. It is shown that the efficiency of modules made of homogeneous materials reaches ~ 8 %, two-segmented materials – ~ 10 %, FGM – ~ 11 %. Studies on characteristics of two-stage modules have shown that bismuth telluride materials as the cold stage, and skutterudites as the hot stage improve the efficiency of thermoelectric converters to 12 %.
Key words: generator modules, heat recovery, thermoelectric energy converters, FGM.

Introduction

Waste heat from industrial production and internal combustion engines is one of the factors of environmental pollution. This heat recovery by direct thermal into electric energy conversion and its return to working cycles will improve the ecological situation considerably. Therefore, creation of efficient waste heat recuperators is a relevant economical and ecological task.

Thermoelectric method of direct thermal into electric energy conversion is rather attractive for recovery of waste heat from various industrial heating plants and engines. Absence of movable parts and possibility of operation under extreme conditions make thermoelectric generators highly reliable. The main factor restricting wide use of thermal generators in recuperators is low efficiency of thermal into electric energy conversion due to low dimensionless figure of merit of thermoelectric materials $ZT = \alpha^2 \cdot \sigma \cdot T/\kappa$ (where α – the Seebeck coefficient, T – temperature, σ – electric conductivity, κ – thermal conductivity).

This generates a need for new efficient, cheap and ecologically clean materials. During recent decade the researchers' attention has been attracted by skutterudites [1]. These are promising materials based on *CoSb* for a wide use in thermal generators operated at the hot side temperature to 773 K. They are characterized by rather high values of the Seebeck coefficient and electric conductivity. Two main techniques are employed for their figure of merit improvement [1]: the first technique is based on filling crystal lattice voids of *CoSb* materials with atoms of rare-earth elements by doping; the second technique is the use of doping to increase scattering on point defects, as to well as to control of charge carrier concentration.

Analysis of the results of experimental studies on thermoelectric characteristics of skutterudites [1-9] shows that to obtain *n*-type materials the most efficient doping impurities for $CoSb_3$ are *In, Ga, Ni, Eu, Te, Se, S* [2-6], and for *p*-type materials with improved parameters it is reasonable to perform doping with several elements at once, namely *Fe* and *Yb*; *Fe*, *Yb* and *La*; *Ca* and *Fe*; *Ca* and *Mn* [7-9].

The purpose of this study is to evaluate the possibility of efficiency improvement of generator modules made of homogeneous, segmented, functionally graded and multi-stage structures through determination of the optimal doping level of skutterudite-based materials.

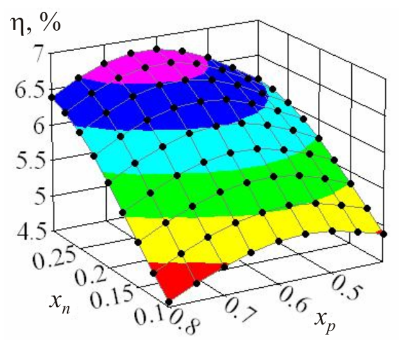
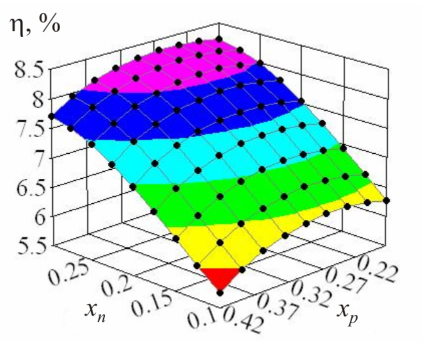
Design of thermoelectric modules from segmented and FGM legs

A search for optimal composition of *CoSb* based materials for homogeneous and segmented legs of thermoelectric modules was performed with the use of optimal control theory methods [10, 11]. In the calculations, the experimental dependences of thermoelectric parameters thermoEMF, electric conductivity and thermal conductivity on the temperature and concentration of doping impurities in *n*- and *p*-*CoSb* samples were employed. Calculations were performed for modules with the following parameters: number of thermoelements – 32 couples, height of legs – 5.6 mm, cross section areas of legs – 4×4 mm^2. The values of contact resistances were assumed equal to $5\cdot10^{-5}$ $\Omega\cdot$cm^2.

The results of calculation of characteristics of thermoelectric modules of homogeneous materials based on *CoSb* in the operating temperature range 323 – 773 K are represented in Table 1. Optimal concentrations of doping impurities x_n and x_p in leg materials are given whereby maximum efficiency η and the corresponding power P of modules are achieved, and dependences of efficiency on impurity concentration in the legs are given.

Table 1

Parameters of generator modules of homogeneous materials based on $CoSb_3$ at T_h = 773 K, T_c = 323 K

<table>
<tr><td>p-type leg / n-type leg</td><td colspan="2">$Yb_xFe_2Co_2Sb_{12}$ (x = 0.4 – 0.8) [7]</td><td colspan="2">$Yb_xLa_{0.85-x}Fe_{2.7}Co_{1.3}Sb_{12}$ (x = 0.17 – 0.42) [9]</td></tr>
<tr><td rowspan="2">$Tl_{0.1}In_xCo_4Sb_{12}$ (x = 0.1 – 0.3) [12]</td><td>x_n = 0.3
x_p = 0.65</td><td>P = 19 W
η = 6.8 %</td><td>x_n = 0.3
x_p = 0.25</td><td>P = 22 W
η = 8.3 %</td></tr>
<tr><td colspan="2">
</td><td colspan="2">
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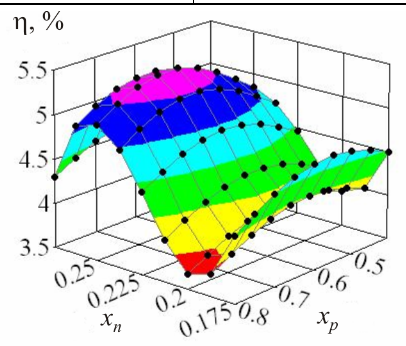
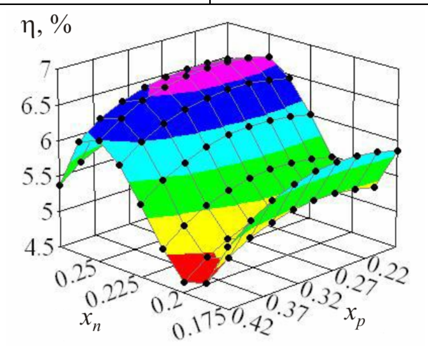
<tr><td rowspan="2">$CoSb_{2.875-x}Ge_{0.125}Te_x$ (x = 0.175 – 0.275) [13]</td><td>x_n = 0.25
x_p = 0.62</td><td>P = 15 W
η = 5.35 %</td><td>x_n = 0.25
x_p = 0.25</td><td>P = 18.4 W
η = 6.75 %</td></tr>
<tr><td colspan="2">
</td><td colspan="2">
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Analysis of data presented in Table 1 shows that dependences of module efficiency on the distribution of ytterbium impurity in materials for *p*-type legs, namely $La_{0.85}Fe_{2.7}Co_{1.3}Sb_{12}$ and $Fe_2Co_2Sb_{12}$, are characterized by a smooth change indicating to marginal impact of *p*-type leg doping component on module characteristics. As regards *n*-leg, dependences of module efficiency on indium concentration in $Tl_{0.1}Co_4Sb_{12}$ are characterized by essential growth with increase in the concentration of doping component, whereas *Te* doping of n-$CoSb_{2.875}Ge_{0.125}$ leads to the appearance of two extremums.

Maximum efficiency η = 8.3 % is exhibited by module of n-$Tl_{0.1}In_{0.3}Co_4Sb_{12}$/$p$-$Yb_{0.25}La_{0.6}Fe_{2.7}Co_{1.3}Sb_{12}$ materials. So, exactly these compounds are reasonable to be used for creation of functionally graded thermoelectric materials by formation of nonuniform impurity distribution.

Fig. 1 shows optimal distributions of indium concentration x_n along the leg of *n*-type $Tl_{0.1}In_xCo_4Sb_{12}$ and ytterbium concentration x_p along the leg of *p*-type $Yb_xLa_{0.85-x}Fe_{2.7}Co_{1.3}Sb_{12}$ determined by computer methods.

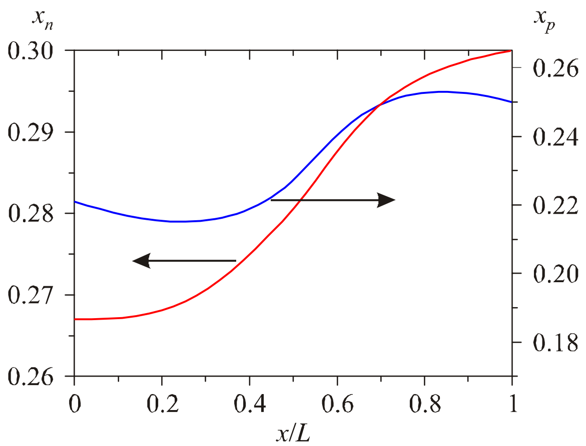

Fig. 1. Distributions of optimal impurity concentration along the height of legs for generator modules of FGM based on n-$Tl_{0.1}In_xCo_4Sb_{12}$/p-$Yb_xLa_{0.85-x}Fe_{2.7}Co_{1.3}Sb_{12}$. x/L = 0 corresponds to the cold side of leg.

Maximum efficiency of module with an optimal distribution of doping impurities in the legs (Fig. 1) with temperature difference 323 – 773 K reaches 10.6 %, and the generated electric power – 29.7 W.

The results of calculation of modules with two-segmented legs are presented in Table 2. Optimal materials for each segment of *n*- and *p*-legs are determined, as well as the heights of segments whereby maximum efficiency η of modules is achieved.

Table 2

Parameters of generator modules of two-segmented legs based on $CoSb_3$ at T_h = 773 K, T_c = 323 K

p-type leg / *n*-type leg	$Yb_xFe_2Co_2Sb_{12}$ (x = 0.4 – 0.8) [7]		$Yb_xLa_{0.85-x}Fe_{2.7}Co_{1.3}Sb_{12}$ (x = 0.17 – 0.42) [9]	
$Tl_{0.1}In_xCo_4Sb_{12}$ (x = 0.1 – 0.3) [12]	x_n^h = 0.3 x_n^c = 0.27 x_p^h = 0.68 x_p^c = 0.62	ℓ_n^h = 2.8 mm ℓ_n^c = 2.8 mm ℓ_p^h = 2.8 mm ℓ_p^c = 2.8 mm	x_n^h = 0.295 $x_n^{c.л}$ = 0.27 x_p^h = 0.25 x_p^c = 0.218	ℓ_n^h = 2.9 mm ℓ_n^c = 2.7 mm ℓ_p^h = 2.7 mm ℓ_p^c = 2.9 mm
	P = 27 W η = 9.1 %		*P* =28.8 W η = 10.3 %	
$CoSb_{2.875-x}Ge_{0.125}Te_x$ (x = 0.175 – 0.275) [13]	x_n^h = 0.25 x_n^c = 0.238 x_p^h = 0.7 x_p^c = 0.632	ℓ_n^h = 2.8 mm ℓ_n^c = 2.8 mm ℓ_p^h = 2.8 mm ℓ_p^c = 2.8 mm	x_n^h = 0.25 x_n^c = 0.24 x_p^h = 0.234 x_p^c = 0.202	ℓ_n^h = 2.9 mm ℓ_n^c = 2.7 mm ℓ_p^h = 2.7 mm ℓ_p^c = 2.9 mm
	P = 22.6 W η = 7.35 %		*P* = 24.6 W η = 8.5 %	

For modules of homogeneous materials and double-segmented legs the highest efficiency is achieved with the use of *n*-type $Tl_{0.1}In_xCo_4Sb_{12}$ and *p*-type $Yb_xLa_{0.85-x}Fe_{2.7}Co_{1.3}Sb_{12}$ (Table 2).

Research on multi-stage generator modules

Optimal materials were selected for each stage using optimal control theory methods such that the cold and hot stages were characterized by maximum efficiency in the temperature range 323 – 523 K and 523 – 773 K, respectively. Design calculation of two-stage modules 40 × 40 mm^2 (Table 3) was made for series connection of the cold and hot stages at thermal and electric compatibility of stages.

In the calculations, experimental concentration-temperature dependences of thermoelectric parameters of *BiTe* materials were employed [14]. In module № 1 skutterudite based materials were selected for both stages. In modules № 2 and № 3 for the low-temperature stage use was made of *Bi-Te*. In Table 3, the values of electric conductivity σ of *Bi-Te* based materials at 300 K and impurity concentrations in skutterudites, optimal for each stage, are presented, as well as power and efficiency values of modules are calculated.

Table 3

Parameters of two-stage generator modules of $CoSb_3$ based materials at T_h = 773 K, T_c = 323 K

№	Parameter		Parameter value		
			Module № 1	Module № 2	Module № 3
1.	Cold stage leg materials	*n*-type leg	$Tl_{0.1}In_{0.27}Co_4Sb_{12}$	$(Bi_2Te_3)_{0.90}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$, doped with I_2, σ_0^n = 1365 Ω^{-1}cm^{-1}	
		p-type leg	$Yb_{0.196}La_{0.654}Fe_{2.7}$-$Co_{1.3}Sb_{12}$	$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$, doped with *Pb*, σ_0^p = 1570 Ω^{-1}cm^{-1}	
2.	Hot stage leg materials	*n*-type leg	$Tl_{0.1}In_{0.295}Co_4Sb_{12}$		
		p-type leg	$Yb_{0.24}La_{0.61}Fe_{2.7}Co_{1.3}Sb_{12}$		
3.	Cross-sectional area of cold and hot stage legs, mm^2		1.8 × 4.3		
4.	The height of cold stage leg, mm		2.9	2.7	3
5.	The height of hot stage leg, mm		3	3.3	3
6.	The number of leg couples of cold and hot stages		48		
7.	Electric power *P*, W		14.1	13.8	16
8.	Voltage *U*, V		4.1	4.4	3.6
9.	Current *I*, A		3.5	3.2	4.4
10.	Efficiency η, %		10.2	11.2	11.9

From the data presented in Table 3 it is apparent that the efficiency of generator module where *CoSb* based materials are selected for both stages, reaches ~ 10.2 % (module № 1), which is inferior to *BiTe* based materials selected for the cold stage (η ≈ 11.2 %, module № 2). In this case, the electric compatibility of stages is assured by optimal height values of thermoelements in each stage. The use of parallel-in-series connection of cold stage thermoelements (module № 3) allows improving module efficiency nearly to 12 %. Dependences of efficiency and generated electric power of two-stage modules based on $Bi_2Te_3/CoSb_3$ on their hot side temperature are presented in Fig. 2.

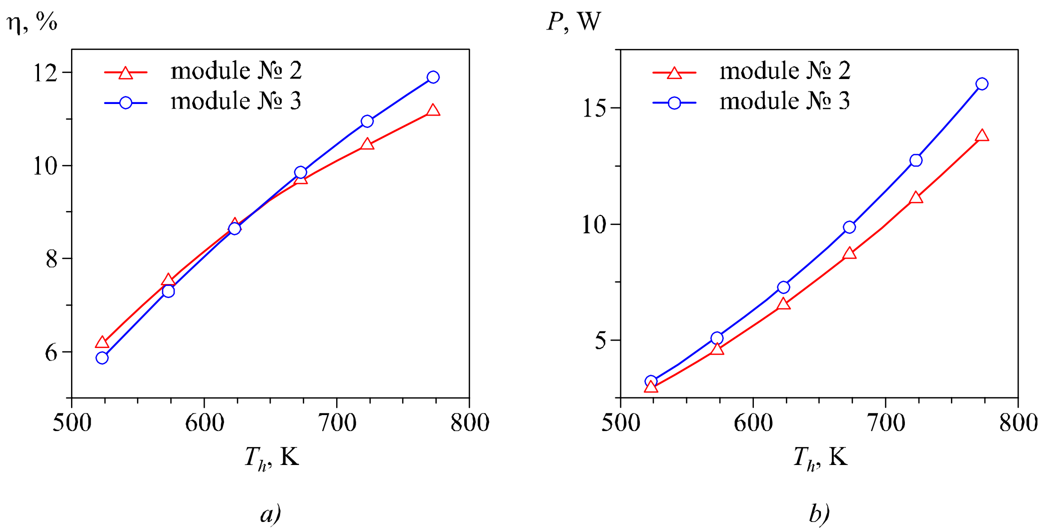

Fig. 2. Dependences of efficiency η (a) and electric power P (b) of two-stage modules based on $Bi_2Te_3/CoSb_3$ on their hot side temperature T_h at cold temperature T_c = 323 K.

At hot side temperature 773 K the efficiency of module № 3 (η = 11.9 %) is higher than that of module № 2 (η = 11.16 %). With a reduction in temperature T_h, the efficiency drops and at T_h = 623 K the efficiency of both modules is identical, and with further reduction of hot side temperature, the efficiency of module № 2 is somewhat higher.

From the data presented above it is evident that with the use of similar materials for stages and segments the efficiency of two-stage modules actually does not exceed the efficiency of modules with double-segmented legs.

Conclusions

Computer simulation methods were used to determine optimal parameters of materials for segments and optimal inhomogeneity functions of functionally graded materials whereby maximum efficiency of thermoelectric generator modules made of skutterudites is achieved.

The efficiency of modules in the operating temperature range 323 – 773 K lies within 5 – 8 % for modules of homogeneous materials, 7 – 10 % for modules of two-segmented legs and approaches 11 % for FGM modules. Using in *CoSb* based modules of two-segmented legs instead of homogeneous materials allows increasing their efficiency by a factor of 1.2 – 1.4.

Research on multi-stage structures has shown that using *BiTe* materials in the cold stage and skutterudites in the hot stage allows assuring the efficiency of thermoelectric conversion of thermal energy on the level of 11 – 12 %.

References

1. C. Uher, Skutterudite-Based Thermoelectrics. *Thermoelectrics Handbook. Macro to Nano*. Edited by D.M. Rowe (CRC Press, 2006), P.34-1–34-13.

2. A. Harnwunggmoung, K. Kurosaki, T. Plirdpring, T. Sugahara, Yu. Ohish, H. Muta, and Sh. Yamanaka, Thermoelectric properties of *Ga*-added $CoSb_3$ based Skutterudites, *J. Applied Physics* **110**, 013521 – 013521-5 (2011).
3. S.-Ch. Ur, Il-H. Kim, Electronic Transport Properties of *Ni*-doped $CoSb_3$ Prepared by Hot Pressing, *J. Korean Physical Society* **55** (3), 942-946 (2009).
4. Y.Z. Pei, S.Q. Bai, X.Y. Zhao, W. Zhang and L.D. Chen, Thermoelectric Properties of $Eu_yCo_4Sb_{12}$ Filled Skutterudites, *Solid State Sciences* **10** (10), 1422-1428 (2008).
5. B. Duan, P. Zhai, L. Liu, Q. Zhang, and X. Ruan, Beneficial Effect of *Se* Substitution on Thermoelectric Properties of $Co_4Sb_{11.9-x}Te_xSe_{0.1}$ Skutterudites, *J.Solid State Chemistry* **193**, 8-12 (2012).
6. B. Duan, P. Zhai, L. Liu, and Q. Zhang, Enhanced Thermoelectric Performance in Sulfur-Doped $Co_4Sb_{11.9-x}Te_xS_{0.1}$ Skutterudites, *Materials Letters* **79**, 69-71 (2012).
7. Ch. Zhou, D. Morelli, X. Zhou, G. Wang, and C. Uher, Thermoelectric Properties of *p*-type *Yb*-filled Skutterudite $Yb_xFe_yCo_{4-y}Sb_{12}$, *Intermetallics* **19** (10), 1390-1393 (2011).
8. K.-H. Park, Il-H. Kim, Thermoelectric Properties of *Ca*-filled $CoSb_3$-based Skutterudites Synthesized by Mechanical Alloying, *J. Electronic Materials* **40** (5), 493-498 (2011).
9. L. Zhou, P. Qiu, C. Uher, X. Shi, and L. Chen, Thermoelectric Properties of *p*-type $Yb_xLa_yFe_{2.7}Co_{1.3}Sb_{12}$ Double-Filled Skutterudites, *Intermetallics* **32,** 209-213 (2013).
10. L.M. Vikhor, Computer design of thermoelectric generator modules, *Journal of Thermoelectricity* **2**, 60-67 (2005).
11. L.I. Anatychuk, L.N. Vikhor, *Thermoelectricity. Vol. IV. Functionally Graded Thermoelectric Materials* (Chernivtsi: Bukrek, 2012), 180 p.
12. A. Harnwunggmoung, K. Kurosaki, A. Kosuga, M. Ishimaru, Th. Plirdpring, R. Yimnirun, J. Jutimoosi, S. Rujirawat, Yu. Ohishi, H. Muta, and Sh. Yamanaka, Enhancement of Thermoelectric Properties of $CoSb_3$-based Skutterudites by Double Filling of *Tl* and *In*, *J. Applied Physics* **112**, 043509 – 043509-6 (2012).
13. X. Su, H. Li, Q. Guo, X. Tang, Q. Zhang, and C. Uher, Structure and Thermoelectric Properties of *Te*- and *Ge*-doped Skutterudites $CoSb_{2.875-x}Ge_{0.125}Te_x$, *J. Electronic Materials* **40** (5), 1286-1291 (2011).
14. L.N. Vikhor, L.I. Anatychuk, Generator Modules of Segmented Thermoelements, *Energy Conversion and Management* **50**, 2366-2372 (2009).

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