V.R. Bilinsky-Slotylo, L.N. Vikhor, V.Ya. Mykhailovsky

Institute of Thermoelectricity of NAS and MESYS of Ukraine,
1, Nauky Str., Chernivtsi, 58029, Ukraine

DESIGN OF THERMOELECTRIC GENERATOR MODULES MADE OF *Mg* AND *Mn* SILICIDE BASED MATERIALS

The results of computer simulation of segmented thermoelectric modules, functionally graded materials based modules, as well as stage structures from Mg and Mn silicide-based materials are presented in this work. The optimal concentrations of doping impurities for the materials of segments and optimal inhomogeneity distributions in functionally graded materials (FGTM) based thermoelements have been defined. The optimal values of thermoelectric parameters have been estimated thus providing maximum efficiency for the two-stage generator modules within the temperature range of 323 – 773 K. It has also been demonstrated that in silicide-based modules manufactured from homogeneous silicide-based materials maximum efficiency equals $\eta \approx 6.5$ *%, whereas in modules made of two-segmented thermoelements it is* $\eta \approx 8.5$ *%, and* $\eta \approx 8.1$ *% for two-stage generator modules. The use of* Bi_2Te_3*-based materials for cold segments or for cold stage of the module, can improve their efficiency up to ~ 10 %.*

Key words: generator modules, heat recovery, energy converters, efficiency.

Introduction

A thermoelectric way of conversion of heat energy into electric one is widely used for waste heat of various industrial devices and combustion engines utilization [1, 2]. The temperature level of such sources can reach 800 – 900 K. Therefore the design and development of high-efficient, low-cost and environmentally friendly thermoelectric energy converters (generator modules) for heat recovery with the range of operating temperatures from 300 to 800 K is a topical task.

For generator modules such materials should be used whose figure of merit *Z* temperature dependence reaches its maximum in the interval of generator operating temperatures. Moreover, along with demands for high values of the figure of merit, important features for industrial applications are considered to be the low cost of the initial materials, mechanical strength and ecological safety. For generator modules with operational temperatures in the range from 300 to 800 K thermoelectric materials based on some metals (*Mg*, *Mn*, *Fe*) silicides [3-5], are the best option and among those the most promising seem doped solid solutions on the base of *MgSi* and *MnSi* of *n*-type and *p*-type, correspondingly. Such compositions are characterized by similar physicochemical, mechanical and cost criteria and can, therefore, be used as materials for fabrication of generator thermoelements of the medium temperature range.

The objective of the present research is the calculation of the optimal doping level for magnesium and manganese silicides and estimation of characteristics of generator modules fabricated from homogeneous, segmented, as well as functionally graded and stage structures on the base of the said materials.

Optimization of materials and modules made of homogeneous, segmented and functionally graded *MgSi* and *MnSi* based thermoelements

A number of scientific publications [6-17] give examples of technologies of fabrication of specimen and results of experimental research into thermoelectric properties of magnesium and manganese based silicides. The analysis of these results has shown that, considering high values of the figure of merit, the following materials can be effective for generator thermoelements:

for *n*-type conductivity legs:

– $Mg_2Si_{0.58}Sn_{0.42-x}Bi_x$ ($0.005 \leq x \leq 0.01$), obtained by melting of the initial components followed by hot pressing [6]. Maximum figure of merit ZT of such bismuth doped silicide reaches 0.62 at 675 K for the composition $x = 0.0075$.

– $Mg_2(Si_{0.3}Sn_{0.7})_{1-x}Sb_x$ ($0.02 \leq x \leq 0.03$), obtained by way of two-stage solid-state reaction in connection with spark plasma sintering [7]. Maximum figure of merit of this antimony doped silicide $ZT \approx 1.0$ at 640 K for the composition $x = 0.025$.

for *p*-type conductivity legs:

– $Mn(Al_xSi_{1-x})_{1.80}$ ($0 \leq x \leq 0.003$), obtained using induction melting of compressed powders of the initial components with further spark plasma sintering [8]. Maximum figure of merit of this aluminium doped manganese silicide $ZT \approx 0.65$ at 850 K for the composition $x = 0.0015$.

– $Mn(Si_{1-x}Ge_x)_{1.733}$ ($0.2 \leq x \leq 1.6$), obtained using induction melting with further hot compaction [9]. Maximum figure of merit of such germanium doped specimen $ZT \approx 0.6$ at 830 K for the composition $x = 0.8$.

Experimental dependences of thermoEMF α, electric conductivity σ and thermal conductivity κ of those materials on the temperature T and concentration x of corresponding impurities have been used to estimate optimal characteristics of generator modules in the maximum efficiency mode. The calculations have been carried out with computer methods designed on the base of the theory of optimal control [18-20]. Concentration-temperature dependences α, σ, κ have been approximated with the help of two-dimensional polynomial in the form of $\alpha^{n,p} = \alpha^{n,p}(x, T)$, $\sigma^{n,p} = \sigma^{n,p}(x, T)$, $\kappa^{n,p} = \kappa^{n,p}(x,T)$. Polynomial coefficients were entered into the computer programme as input data for thermoelectric modules design.

The results of calculations for optimal impurity concentrations in silicides for homogeneous two-segmented thermoelements and parameters of generator modules based on such materials in the maximum efficiency mode within the range of operating temperatures from 323 to 773 K are presented in Table 1. The estimation of parameters was performed for the modules with the dimensions 40×40 mm^2, containing 32 thermoelements, with the height of legs $L = 5.6$ mm and cross section area 4×4 mm^2. The values of contact resistances in calculations were accepted to be equal $5 \cdot 10^{-5}$ $\Omega \cdot$cm^2.

Analysis of the results obtained shows that the efficiency of modules with two-segmented thermoelements exceeds the efficiency of modules from homogeneous materials by 1.3 to 1.5 times. The highest efficiency of about 8.5 % can be reached on the modules from two-segmented thermoelements fabricated from *n*-type conductivity $Mg_2(Si_{0.3}Sn_{0.7})_{1-x}Sb_x$ materials and *p*-type $Mn(Al_xSi_{1-x})_{1.80}$ materials. That is why these very compositions are appropriate for creation of functionally graded thermoelectric materials, those being created by way of inhomogeneous impurity distribution.

Fig. 1 demonstrates optimal antimony concentrations distributions x_n along the *n*-type conductivity $Mg_2(Si_{0.3}Sn_{0.7})_{1-x}Sb_x$ leg and aluminium concentration x_p along *p*-type $Mn(Al_xSi_{1-x})_{1.80}$ leg calculated by computer methods. The calculated maximum efficiency of the module fabricated from the said FGTM is reached 8.5 % at the temperature difference from 323 to 773 K at the power of

19.9 W thus giving no significant advantages to a FGTM module over a similar on fabricated from two-segmented thermoelements.

Table 1

Optimal impurity concentrations in Mg and Mn silicides and parameters of generator modules on their base at the temperature differences 323 – 773 K

Parameters \ Materials of the legs		*n*-type $Mg_2Si_{0.58}Sn_{0.42-x}Bi_x$ *p*-type $Mn(Al_xSi_{1-x})_{1.80}$	*n*-type $Mg_2Si_{0.58}Sn_{0.42-x}Bi_x$ *p*-type $Mn(Si_{1-x}Ge_x)_{1.733}$	*n*-type $Mg_2(Si_{0.3}Sn_{0.7})_{1-x}Sb_x$ *p*-type $Mn(Al_xSi_{1-x})_{1.80}$	*n*-type $Mg_2(Si_{0.3}Sn_{0.7})_{1-x}Sb_x$ *p*-type $Mn(Si_{1-x}Ge_x)_{1.733}$
Modules with homogeneous legs					
Optimal impurity concentration	x_n	0.008	0.008	0.025	0.025
	x_p	0.0021	0.8	0.00203	1.04
Power, W		8	7.3	15.8	13.7
Efficiency %		4.2	4.2	6.5	6.2
Modules with two-sectional legs					
Optimal impurity concentration	x_n^h	0.00825	0.008	0.027	0.02675
	x_n^c	0.0074	0.00725	0.0255	0.02575
	x_p^h	0.00204	0.92	0.0021	0.98
	x_p^c	0.0018	0.8	0.00165	0.896
Height of legs, mm	ℓ_n^h	2.8	2.8	3.2	3.2
	ℓ_n^c			2.4	2.4
	ℓ_p^h			2.4	2.4
	ℓ_p^c			3.2	3.2
Intersectional temperature, K	T_n	547	550	505	507
	T_p	545	539	582	580
Power, W		12.7	11.4	20.4	17.6
Efficiency %		6.3	6.1	8.5	8.0

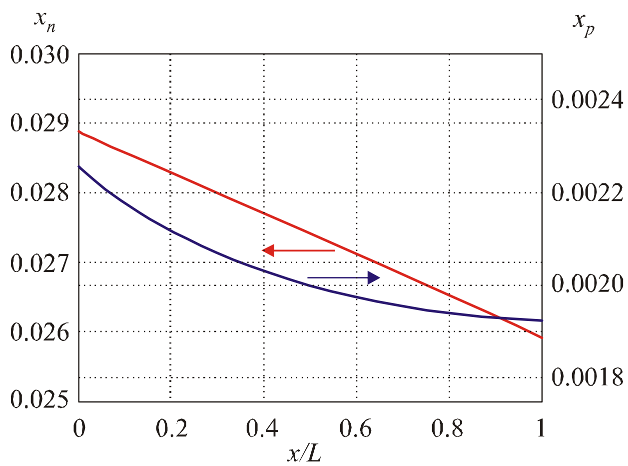


Fig. 1. Antimony concentration optimal distribution x_n along the n-type leg from $Mg_2(Si_{0.3}Sn_{0.7})_{1-x}Sb_x$ and aluminium concentration x_p along the p-type leg from $Mn(Al_xSi_{1-x})_{1.80}$ for generator modules. x/L = 0 corresponds to the cold side of the leg.

Results of optimization of modules from *Bi-Te* and *Mg* i *Mn* silicides based materials

It is a well-known fact that in the temperature range from 300 to 450 K *Bi-Te* based compositions is the most efficient materials for thermoelectric generators. Thus reasonable models of generator modules with the range of operating temperatures from 323 to 773 K the following ones can be considered:

– modules with two-segmented legs where low-temperature sections are fabricated from *Bi-Te* based materials, whereas high-temperature ones from *Mg* and *Mn* based silicides;

– two-stage modules with a low-temperature *Bi-Te* based stage and a high-temperature one based on *Mg* and *Mn* silicides.

The results of calculations for parameters of modules from two-segmented legs are given in Table 2. There optimal values of characteristics (electric conductivity σ and thermoEMF α) of materials based on *n*- and *p*-type conductivity *Bi-Te* for low-temperature sections and impurity concentrations x_n, x_p in *Mg* and *Mn* silicides for high-temperature sections. Electric power and efficiency were calculated for the modules of two different designs. It has been found out that if *Bi-Te* based materials are used for cold sections instead of silicides the efficiency can be increased from 8.5 % to 9.6 % (Module No. 1). Optimizing the module design by search of optimal segments heights ratio optimal cross section areas of legs allows reaching the efficiency as high as 10 % (Module No. 2). Here wastes of thermoelectric materials are 2.5 times reduced for such module design.

Table 2

Parameters of generator modules from two-segmented legs fabricated from Bi-Te-based materials and Mg and Mn silicides under operating temperatures within the temperature difference of 323 – 773 K

Parameter			Parameter value	
			Module No. 1	Module No. 2
Parameters of the materials of segments	cold	n-$(Bi_2Te_3)_{0.90}(Sb_2\text{-}Te_3)_{0.05}(Sb_2Se_3)_{0.05}$, I_2-doped [19]	$\sigma_n(300\ K) = 1340\ \Omega^{-1}\ cm^{-1}$ $\alpha_n(300\ K) = 187\ \mu V/K$	
		p-$(Bi_2Te_3)_{0.25}(Sb_2\text{-}Te_3)_{0.72}(Sb_2Se_3)_{0.03}$, *Pb*-doped [19]	$\sigma_p(300\ K) = 1680\ \Omega^{-1}cm^{-1}$ $\alpha_p(300\ K) = 164\ \mu V/K$	
	hot	n-$Mg_2(Si_{0.3}\text{-}Sn_{0.7})_{1-x}Sb_x$ [7]	$x_n = 0.027$	
		p-$Mn(Al_xSi_{1-x})_{1.80}$ [8]	$x_p = 0.00195$	
Segments height, mm	cold	n-$(Bi_2Te_3)_{0.90}(Sb_2\text{-}Te_3)_{0.05}(Sb_2Se_3)_{0.05}$, I_2-doped [19]	$\ell_n = 2.4$	$\ell_n = 0.9$
		p-$(Bi_2Te_3)_{0.25}(Sb_2\text{-}Te_3)_{0.72}(Sb_2Se_3)_{0.03}$, *Pb* doped [19]	$\ell_p = 3.2$	$\ell_p = 0.9$
	hot	n-$Mg_2(Si_{0.3}\text{-}Sn_{0.7})_{1-x}Sb_x$ [7]	$\ell_n = 3.2$	$\ell_n = 2.1$
		p-$Mn(Al_xSi_{1-x})_{1.80}$ [8]	$\ell_p = 2.4$	$\ell_p = 2.1$
Intersectional temperature, K		T_n	526	473
		T_p	582	480
Number of thermocouples			32	48
Cross-section area of legs, mm^2			4 × 4	1.8 × 4.3
Electric power *P*, W			22.9	30.8
Efficiency η, %			9.6	10

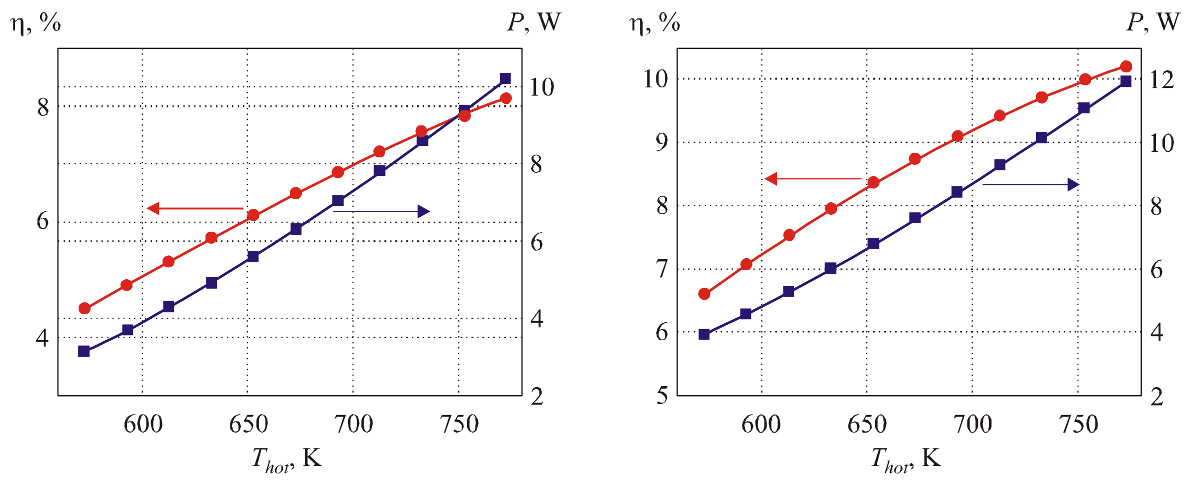
The results of calculation of two-stage modules of different designs provided the cold and the hot stages are connected in series under the electrical and thermal compatibility are given in Table 3. For both stages of the module No. 3 silicides based materials have been chosen. *Bi-Te* is suggested for the low-temperature stage in modules No. 4 and No. 5. Table 3 gives optimal values of parameters of *Bi-Te* based materials and optimal impurity concentrations in *Mg* and *Mn* silicides, as well as calculated values of modules power and efficiency for every stage. Efficiency and power dependences of modules No. 3 and No. 4 on the modules hot side temperature are shown in Fig. 2.

Table 3

Parameters of two-stage generator modules fabricated from Bi-Te-based materials and Mg and Mn silicides under operating temperatures within the temperature difference of 323 – 773 K

Parameter		Parameter value		
		Module No. 3	Module No. 4	Module No. 5
Parameters of materials	Cold stage	n-$Mg_2(Si_{0.3}$-$Sn_{0.7})_{1-x}Sb_x$ [7] $x = 0.0255$	n-$(Bi_2Te_3)_{0.90}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$, I_2-doped [19] $\sigma_n(300\text{ K}) = 1365\ \Omega^{-1}\cdot\text{cm}^{-1}$ $\alpha_n(300\text{ K}) = 189\ \mu\text{V/K}$	
		p-$Mn(Al_xSi_{1-x})_{1.80}$ [8] $x = 0.00165$	p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$, Pb-doped [19] $\sigma_p(300\text{ K}) = 1570\ \Omega^{-1}\cdot\text{cm}^{-1}$ $\alpha_p(300\text{ K}) = 175\ \mu\text{V/K}$	
	Hot stage	n-$Mg_2(Si_{0.3}$-$Sn_{0.7})_{1-x}Sb_x$ [7] $x = 0.027$	n-$Mg_2(Si_{0.3}Sn_{0.7})_{1-x}Sb_x$ [7] $x = 0.025$	
		p-$Mn(Al_xSi_{1-x})_{1.80}$ [8] $x = 0.0021$	p-$Mn(Al_xSi_{1-x})_{1.80}$ [8] $x = 0.00203$	
Height of legs, mm	Cold stage	3		
	Hot stage	3	3	5.6
Number of thermocouples	Cold stage	48		
	Hot stage	48	48	32
Cross-section area of legs, mm^2	Cold stage	1.8 × 4.3		
	Hot stage	1.8 × 4.3	1.8 × 4.3	4 × 4
Temperature between stages, K		518	501	489
Electric power P, W		10.2	11.9	8.9
Efficiency η, %		8.1	10.2	9.4

Application of *Bi-Te* based materials instead of silicides for the low-temperature stage and design optimization can ensure the efficiency of such modules as high as 10 %. It should be stated here that the waste of material for module No. 4 fabrication is 2.5 times less than that for module No. 5, whereas its efficiency and power are higher.



a) *b)*

Fig. 2. Efficiency η and electric power P of two-stage modules No. 3 (a) and No. 4 (b) as a function of module hot side surface temperature T_{hot}. Module cold side surface temperature T_c = 323 K.

The data presented make it evident that, when similar materials are used for stages and segments, the efficiency of two-stage modules does not, actually, exceed the efficiency of modules fabricated from two-segmented legs.

Conclusions

With computer simulation methods implemented, both optimal composition and impurity concentrations in *Mg* and *Mn* silicides have been found that ensure maximum efficiency of the generator modules fabricated from such materials provided the operational temperature difference is from 323 to 773 K.

When two-segmented or FGTM legs are used for *Mg* and *Mn* silicides based modules instead of homogeneous materials, their efficiency can be increased by 1.3 to 1.5 times. Furthermore, if silicides in low-temperature sections of the legs is substituted by bismuth telluride, the efficiency can even reach 10 %.

Research into two-stage structures has shown that the use of *Bi-Te* based materials for the cold stage and magnesium and manganese silicides for the hot stage enables the heat energy conversion within the temperature range from 323 – 773 K with the efficiency of ~ 10 %.

Such values of the generator modules efficiency together with the relatively low cost of silicides allows expanding of both possibilities and spheres of practical application of thermoelectric converters of heat power into electric one.

References

1. T. Kajikawa. Current State of Thermoelectric Power Generation Technology in Japan, *J. Thermoelectricity* **2,** 21-31 (2007).
2. Kh.M. Saqr, M.Kh. Mansour, M.N. Musa. Thermal Design of Automobile Exhaust-Based Thermoelectric Generators: Objectives and Challenges, *J. Thermoelectricity* **1**, 59-66 (2008).
3. C.B. Vining. Thermoelectric properties of Silicides. *CRC Handbook of Thermoelectrics*, edited by D.M. Rowe, 1995, p. 277-285.

4. U. Birkholz, E. Gross, U. Stoehrer. Polycrystalline iron disilicide as a thermoelectric generator material. *CRC Handbook of Thermoelectrics*, edited by D.M. Rowe, 1995, p. 287-298.
5. M.I. Fedorov, V.K. Zaitsev. Silicides. *CRC Thermoelectrics Handbook. Macro to Nano*. Edited by D.M. Rowe, (2006), p. 31-1 – 31-14.
6. Zh. Du, T. Zhu, X. Zhao. Enhanced thermoelectric properties of $Mg_2Si_{0.58}Sn_{0.42}$ compounds by *Bi* doping, *Materials Letters*, **66 (**1), (2012). p. 76-78.
7. W. Liu, Q. Zhang, X. Tang, H. Li, J. Sharpet. Thermoelectric Properties of *Sb*-doped $Mg_2Si_{0.3}Sn_{0.7}$, *Journal of Electronic Materials*, **40** (5), (2011), p. 1062-1066.
8. W. Luo, H. Li, F. Fu, W. Hao, X. Tang. Improved Thermoelectric Properties of *Al*-doped Higher Manganese Silicide Prepared by a Rapid Solidification Method, *Journal of Electronic Materials*, **40** (5), (2011), p. 1233-1237.
9. A.J. Zhou, T.J. Zhu, X.B. Zhao, S.H. Yang, T. Dasgupta, C. Stiewe, R. Hassdorf, E. Mueller. Improved Thermoelectric Performance of Higher Manganese Silicides with *Ge* Additions, *Journal of Electronic Materials,* **39** (9), (2010). p. 2002-2007.
10. M.J. Yang, L.M. Zhang, L.Q. Han, Q. Shen, C.B. Wang. Simple fabrication of Mg_2Si thermoelectric generator by spark plasma sintering, *Indian Journal of Engineering and Materials Sciences*. **16**,(2009), p. 277-280.
11. T. Sakamoto, T. Iida, A. Matsumoto, Ya. Honda, T. Nemoto, J. Sato, T. Nakajima, H. Taguchi, Y. Takanashi. Thermoelectric Characteristics of a Commercialized Mg_2Si Source Doped with *Al*, *Bi*, *Ag*, and *Cu*, *Journal of Electronic Materials*, **39** (9), (2010), p. 1708-1713.
12. T. Sakamoto, T. Iida, Sh. Kurosaki, K. Yano, H. Taguchi, K. Nishio, Y. Takanashi. Thermoelectric Behavior of *Sb*- and *Al*-doped *n*-Type Mg_2Si Device Under Large Temperature Differences, *Journal of Electronic Materials*, **40** (5), (2011), p. 629-634.
13. R. Song, Y. Liu, T. Aizawa. Solid State Synthesis and Thermoelectric Properties of *Mg-Si-Ge* System, *Journal of Materials Science & Technology*, **21** (5), (2005), p. 618-622.
14. Q. Zhang, J. He, T.J. Zhu et al. High Figures of Merit and Natural Nanostructures in $Mg_2Si_{0.4}Sn_{0.6}$ Based Thermoelectric Materials, *Applied Physics Letters*, **93**, (2008), 102109. 3 p.
15. J. Zhou, X. Li, G. Chen, R. Yang. Semiclassical Model for Thermoelectric Transport in Nanocomposites, *Physical Review B*, **82**, (2010), 115308. 16 p.
16. J. Tani, H. Kido. Thermoelectric Properties of *Al*-doped $Mg_2Si_{1-x}Sn_x$ ($x \leq 0.1$), *Journal of Alloys and Compounds*, **466**, (2008), p. 335-340.
17. Y.-J. Shi, Q.-M. Lu, X. Zhang, J.-X. Zhang. Microstructure and Thermoelectric Properties of Higher Manganese Silicides, *Journal of Inorganic Materials*. **26** (7), (2011), p. 691-695.
18. L.I. Anatychuk, L.N. Vikhor. *Thermoelectricity, Vol.IV, Functionally Graded Thermoelectric Materials* (Chernivtsi: Bukrek, 2012), 180 p.
19. L.N. Vikhor, L.I. Anatychuk. Generator modules of segmented thermoelements, *Energy Conversion and Management*, **50**, (2009), p. 2366-2372.
20. L.N. Vikhor. Computer-aided design of thermoelectric generator modules, *J. Thermoelectricity* **2,** (2005), p. 60-67.

Submitted 18.01.2013.