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THERMOELECTRIC GENERATOR MODULES OF *n-InSe* AND *p-PbTe*-BASED MATERIALS FOR THE LEVEL OF OPERATING TEMPERATURES 30-500ºC

This paper gives the results of computer and experimental studies of thermocouple generator modules of InSe and PbTe-based materials to be used in thermoelectric power converters for the hot temperature level ~ 500°C. Computer methods based on optimal control theory are used to determine optimal conditions whereby maximum power and efficiency of InSe and PbTe is achieved. Design is performed with regard to temperature dependences of material parameters, thermal and electric losses on the contacts and module interconnects.

Key words: computer design, generator modules, efficiency, termoelement.

Introduction

To create one-segment generator modules for the hot temperature level 500 °C, *n-PbTe* and *p-GeTe-AgSbTe* (TAGS)-based materials are traditionally used [1, 2]. Maximum efficiency of such modules lies within 8-8.5 % [3]. However, the restricting factor for their mass use is high cost of TAGS source components [4]. In this connection, studies aimed at creating thermoelectric modules of other materials become of current concern [5-8].

Among the alternative thermoelectric materials for operation in medium-temperature range, *InSe*-based materials attract the attention of researchers owing to their low thermal conductivity, high Seebeck coefficient [9]. Besides the cost of indium and selenium about 3-4 times is lower than the cost TAGS components: germanium, tellurium, silver and antimony [10]. However, in the majority of cases, *InSe* is employed as thin films for the manufacture of photoelectric devices. The results of development and creation of thermoelements based on the bulk InSe materials have not been recorded.

The purpose of this work is computer design and creation of thermoelectric modules of *n-InSe–p-PbTe*-based materials and experimental study of their characteristics.

Physical model of thermoelectric generator module and its description

Thermoelectric generator module consists of a number of equal pairs of thermoelectric legs that are electrically connected in series and thermally in parallel. With regard to that, for the design of thermoelectric generator module this paper deals with one structural unit of module, namely thermoelement. The thermoelement model is given in Fig. 1. It comprises *n*- and *p*-type legs (1), connecting copper plates (2) and isolating ceramic plates (3). The model takes into account contact layer (4) between the legs and connecting plates. The hot and cold thermoelement surfaces are at constant temperatures T_{hot} and T_{cold}, respectively.

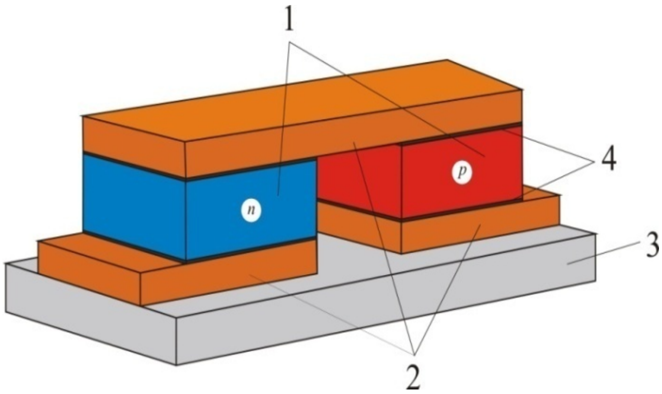

Fig. 1. Thermoelement model.
1 – thermoelement legs, 2 – connecting plates,
3 – ceramics, 4 –contact layers.

Parameters of thermoelectric materials, electric interconnects and connecting plates are a function of temperature. $\alpha_n(T)$, $\alpha_p(T)$ are the Seebeck coefficients of materials of *p*- and *n*-type legs. $\sigma_n(T)$, $\sigma_p(T)$ is the electric conductivity of leg materials; $\kappa_n(T)$, $\kappa_p(T)$ is the thermal conductivity of leg materials; $\sigma_{con}(T)$, $\kappa_{con}(T)$ is the electric conductivity and thermal conductivity of interconnect material; $\kappa_{ins}(T)$ is the thermal conductivity of ceramic plate.

The contacts of thermoelectric legs with connecting plates are characterized by the value of contact electric resistance $r_c(T)$ which is also a function of temperature. The space between the legs is filled with air of thermal conductivity κ_{air}. In this air space, heat exchange between the hot and cold ceramic plates takes place.

Maximum efficiency of thermoelectric module is described by the following expression:

$$\eta = \frac{Q_h - Q_c}{Q_h} = 1 - \varphi \,, \tag{1}$$

where Q_c, Q_h are external heat fluxes on the cold and hot surfaces of generator module, respectively. Function $\varphi = \frac{Q_c}{Q_h}$ can be regarded as a minimizing functional of the assigned task. Then it is necessary to pass to equivalent logarithmic functional $J = \ln \varphi$:

$$J = \ln q_c - \ln q_h \,, \tag{2}$$

where

$$q_c = \frac{Q_c}{nI} \,, \qquad q_h = \frac{Q_h}{nI} \,, \tag{3}$$

q_c, q_h are specific heat fluxes on the cold and hot thermoelement junctions, respectively.

To calculate the boundary heat fluxes q_c and q_h, use is made of a system of four differential equations of nonequilibrium thermodynamics

$$\left. \begin{aligned} \frac{dT(x)}{dx} &= -\frac{\alpha(T)\,j}{\kappa(T)}T(x) - \frac{j}{\kappa(T)}q(x) \\ \frac{dq(x)}{dx} &= \frac{\alpha(T)^2\,j}{\kappa(T)}T(x) + \frac{\alpha(T)\,j}{\kappa(T)}q(x) + \frac{j}{\sigma(T)} \end{aligned} \right\}_{n,p} , \tag{4}$$

where x is dimensionless coordinate, $0 \le x \le 1$, $j_{n,p} = \frac{Il}{s_{n,p}}$ is specific current density in thermoelement legs. The boundary conditions for system (4) are of the form:

$$T(0) = T_{cold} + \delta T_c, \quad T(1) = T_{hot} - \delta T_h, \tag{5}$$

where the losses in temperature difference on the ceramic and connecting plates δT_c and δT_h are defined in [11] with regard to the difference in parameters of ceramic and interconnect materials on the cold and hot sides:

$$\left.\begin{aligned} \delta T_c &= -\frac{q_c}{l\left(\frac{1}{j^n}+\frac{1}{j^p}\right)}\left(\frac{d_{ins}}{\kappa_{ins}(T_{cold})K_{ins}}+\frac{d_{con}}{\kappa_{con}(T_{cold})K_{con}}\right), \\ \delta T_h &= -\frac{q_h}{l\left(\frac{1}{j^n}+\frac{1}{j^p}\right)}\left(\frac{d_{ins}}{\kappa_{ins}(T_{hot})K_{ins}}+\frac{d_{con}}{\kappa_{con}(T_{hot})K_{con}}\right). \end{aligned}\right\}, \tag{6}$$

where K_{ins}, K_{con} are fill factors of ceramic and connecting plates.

The expressions for heat fluxes q_h and q_c with regard to temperature dependence of electric contact resistance will take on the form:

$$\left.\begin{aligned} q_h &= \sum_{n,p}\left[q^{n,p}(1) + \frac{j^{n,p}}{l} r_c(T_{hot})\right] + q^h_{con}, \\ q_c &= \sum_{n,p}\left[q^{n,p}(0) + \frac{j^{n,p}}{l} r_c(T_{cold})\right] - q^c_{con}. \end{aligned}\right\}, \tag{7}$$

where in order to find the specific Joule heat $q^{h,c}_{con}$ released in connecting plate, expression [12] is used:

$$q^h_{con} = \frac{2I^2 r_c(T_{hot})}{d_{con}}\left(K_{con} - \frac{2}{3}\right), \; q^c_{con} = \frac{2I^2 r_c(T_{cold})}{d_{con}}\left(K_{con} - \frac{2}{3}\right). \tag{8}$$

Heat fluxes q_h and q_c depend on specific current density $j_{n,p}$. The challenge is to determine the values of the current density $j_{n,p}$, which provide for a minimum of functional *J.* Herewith thermoelement efficiency reaches its highest value.

Optimal control theory [13, 14] gives a solution of the assigned task. It is realized by a numerical method of successive approximations and allows finding the optimal density of generated current to assure maximum efficiency of thermoelectric power converter. Through selection of the geometrical dimensions and the number of thermoelements one can achieve the assigned voltage and power of thermoelectric generator module. The complexity of the optimization problem enables its solving by computer methods.

Results of designing modules of *InSe – PbTe* based materials

In_4Se_3 based modules

Computer design and optimization of *InSe–PbTe* thermoelectric modules was performed with regard to the temperature dependences of thermoelectric materials obtained through synthesis of the source components and hot pressing of synthesized materials for the range of hot side temperatures 450-500°C, cold side temperatures 30-90 °C.

As a *p*-type thermoelement leg, sodium-dope *PbTe*-based material was selected, as long as in the temperature range 400-500ºC the figure of merit of *PbTe* is rather high (Fig.2). It should be noted that selection of *PbTe* is also motivated by the well-proven technique of samples production. However, this does not rule out the possibility of using in thermoelement of other *p*-type medium-temperature materials.

Experimental temperature dependences of thermoelectric parameters of *InSe* and *PbTe* based materials (Fig.2-5) were obtained on automated equipment Altec-10001 developed by the Institute of Thermoelectricity [15].

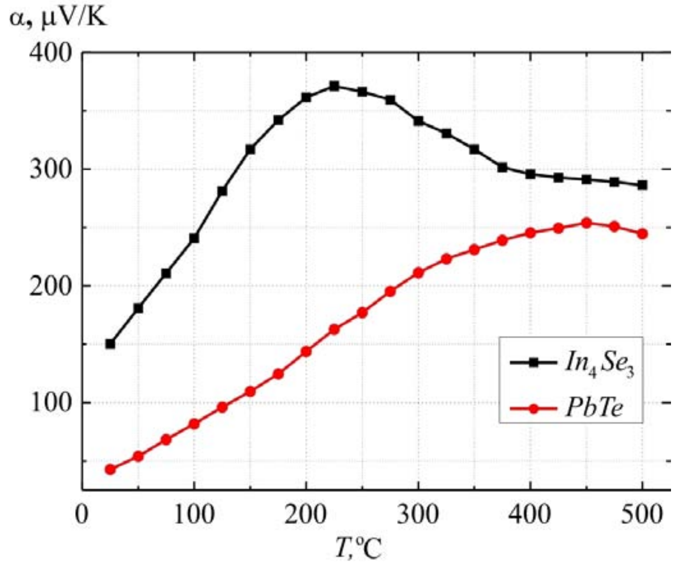

Fig.2.The figure of merit of n-In_4Se_3iand p-PbTe versus temperature.

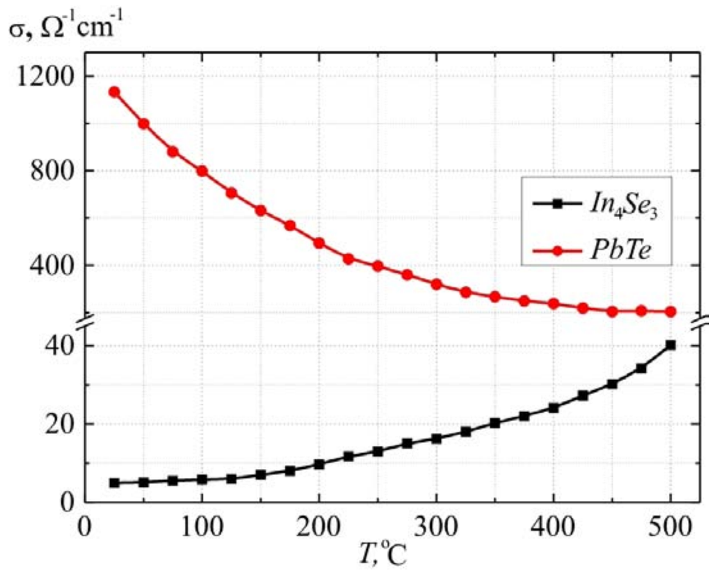

Fig. 3. The electric conductivity of n-In_4Se_3 and p-PbTe versus temperature.

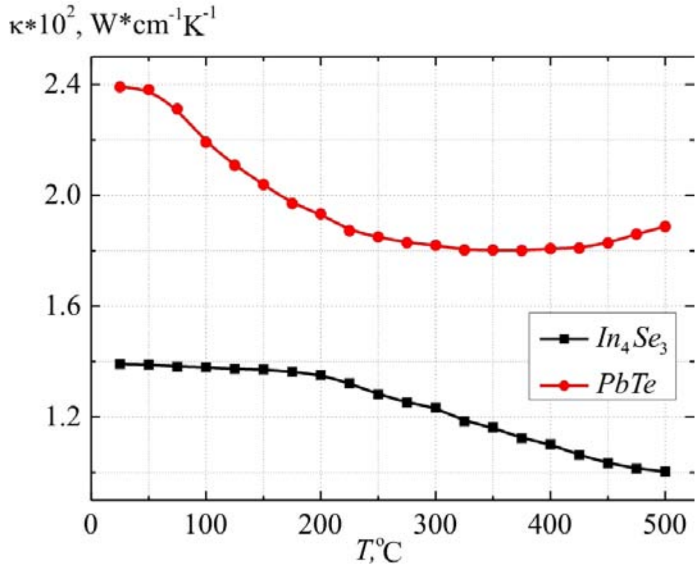

Fig. 4. The thermal conductivity of n-In_4Se_3 and p-PbTe versus temperature.

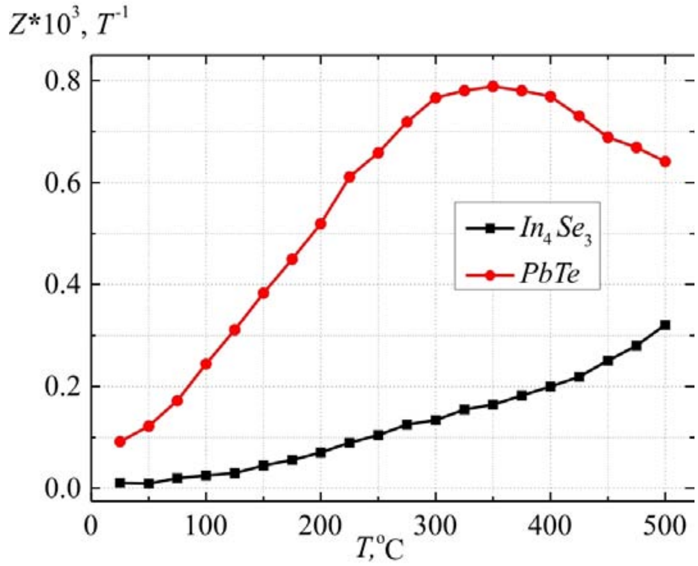

Fig.5. The Seebeck coefficient of n-In_4Se_3 and p-PbTe versus temperature.

As is evident from Fig.5, the value of α for *In_4Se_3* is rather high and, with a rise in temperature, it passes through the maximum (370 µV/K) at 225-250 ºC. At the operating temperatures of the module 400-500 ºC, the value of α for In_4Se_3 varies only slightly and is on the level of 300 µV/K. The electric conductivity of n-In_4Se_3 at 20 ºC is very low, increases with a rise in temperature and at 500ºC reaches 40 $\Omega^{-1}cm^{-1}$. The thermal conductivity of *n-In_4Se_3*, on the contrary, is reduced with a rise in temperature and at 500 ºC is 1.0 W/cm K. The calculated thermoelectric figure of merit of *n-In_4Se_3* at 500 ºC is $0.35\cdot10^{-3}$ K^{-1}.

The Seebeck coefficient for *p-PbTe* is also rather high and at 400-500ºC lies within 250-260 µV/K. The electric conductivity of *p-PbTe* at these temperatures is 200-220 $\Omega^{-1}cm^{-1}$. The thermal conductivity passes through the minimum and at 500 ºC reaches the value of 1.9 W/cm·K.

The electric power of modules made of the above described materials (*p-PbTe*, *n-*In_4Se_3) versus the cross-sectional area of legs for different values of output voltage is represented in Fig.6.

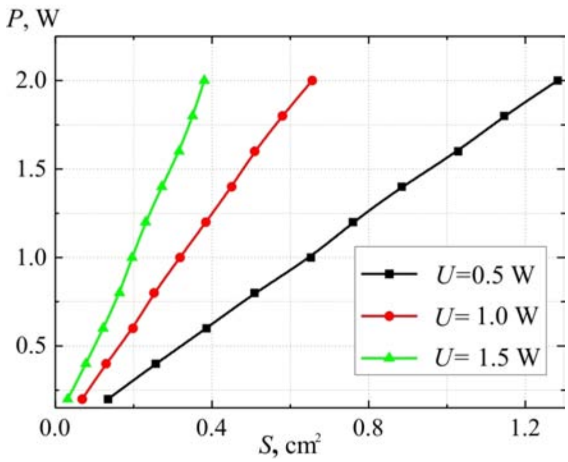

Fig.6. The electric power of In_4Se_3–PbTe module versus the cross-sectional area of legs for different values of output voltage, T_h=500°C, T_c=30 °C, h=5.5 mm.

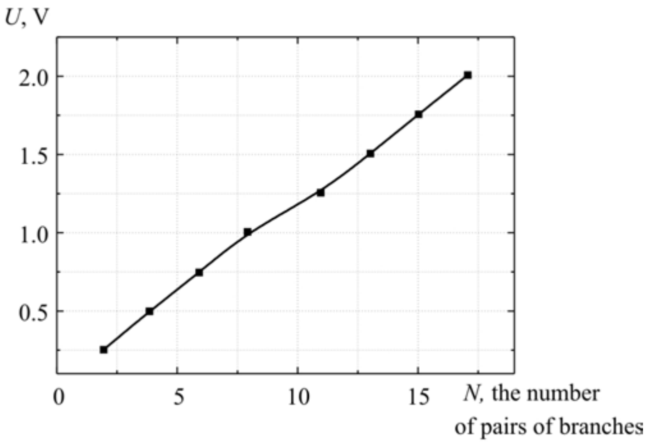

Fig.7. The output voltage of In_4Se_3–PbTe module versus the number of legs in a module, T_h=500 °C, T_c=30 °C, h=5.5 mm.

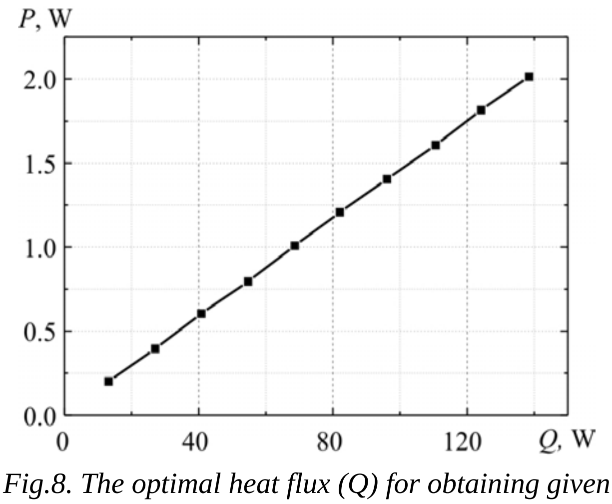

Fig.8. The optimal heat flux (Q) for obtaining given electric power (P) of In_4Se_3–PbTe module, T_h=500 °C, T_c=30 °C, h=5.5 mm

At module power 1 W and module voltages 0.5 V; 1.0 V; 1.5 V the cross-sectional area of leg is 68, 30 and 18 mm^2, respectively (Fig. 6). In so doing, to the get the voltage of 1 V in the assigned range of cold and hot temperatures, it is necessary to have 8 thermoelements (Fig. 7). Accordingly, for 2 V it is necessary to have 16 thermoelements, etc. The values of heat fluxes needed to obtain the assigned electric powers are given in Fig. 8. It is seen that to generate 1 W of electric power, the heat flux on the hot side of a module must come up to 65-70 W.

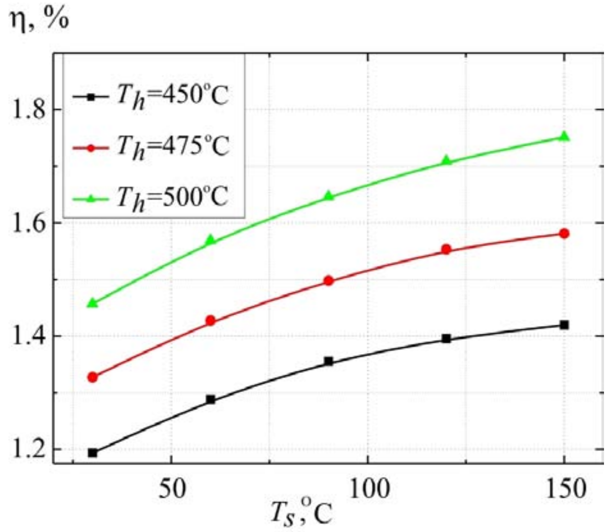

Fig.9. The efficiency of In_4Se_3–PbTe module versus the cold side temperature at different hot side temperatures of module.

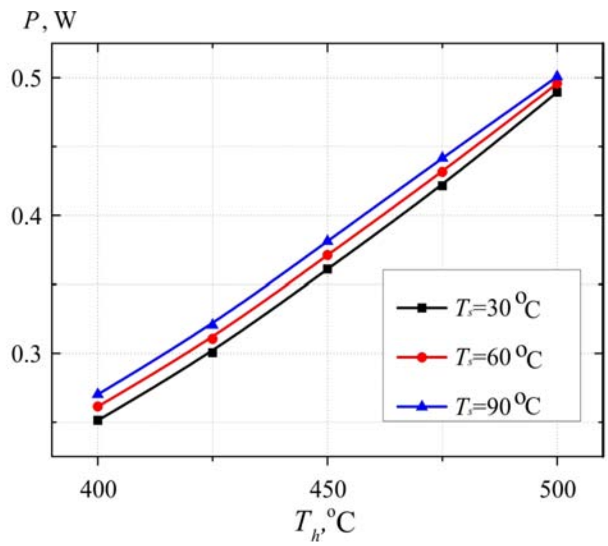

Fig.10. The electric power of In_4Se_3–PbTe module versus the hot side temperature.

A non-traditional dependence was obtained when studying the effect of cold side temperature on module efficiency. As is seen from Fig.9, with a rise in cold side temperature there is efficiency increase. In so doing, the electric power of a module, especially at high temperatures (~500 °C), is very weakly dependent on the cold side temperature (Fig. 10).

Such dependence is due to the fact that at low cold side temperatures of a module there is a mismatch between thermoelectric parameters α, σ, κ of In_4Se_3 and *PbTe* samples. Therefore, thermoelectric material on the cold side of a module works under conditions far from being optimal.

With a rise in temperature of In_4Se_3 samples, the thermal conductivity is essentially reduced and the electric conductivity is increased by about an order (Fig.3, 4), assuring higher *Z* value at elevated cold side temperatures of a module. The dependence passes through the maximum, and further increase of the cold side temperature (in this case over 160 °C) reduces the efficiency.

Modules designed using other compounds based on *InSe*

As is clear from the investigation results, the efficiency of a module of *InSe-PbTe*-based materials (Fig.2-5) is rather low as compared to other modules traditionally used in medium-temperature range [16]. One of the ways to enhance the efficiency of such module is to improve the thermoelectric figure of merit of In_4Se_3 via optimization of composition and the use of efficient doping impurities. In particular, in [17] it is shown that for $In_4Se_{2.35}$ single crystal grown by the Bridgman method maximum *ZT* value is 1.48 at 432 °C. In [18], through doping with *Cl* the figure of merit was increased to 1.53, in [19], by introducing *Pb* and *Sn* – to 1.4 at 427°C. Using the thermoelectric parameters of In_4Se_3 compounds given in [17 – 19] (Fig. 11) as the initial data, the authors of this paper used optimal control method to calculate the efficiency of modules (Fig. 12), where *PbTe* is *p*-leg, $In_4Se_{2.35}$, $In_4Se_{2.67}Cl_{0.03}$ and $In_4Pb_{0.01}Sn_{0.04}Se_3$ are *n*-leg.

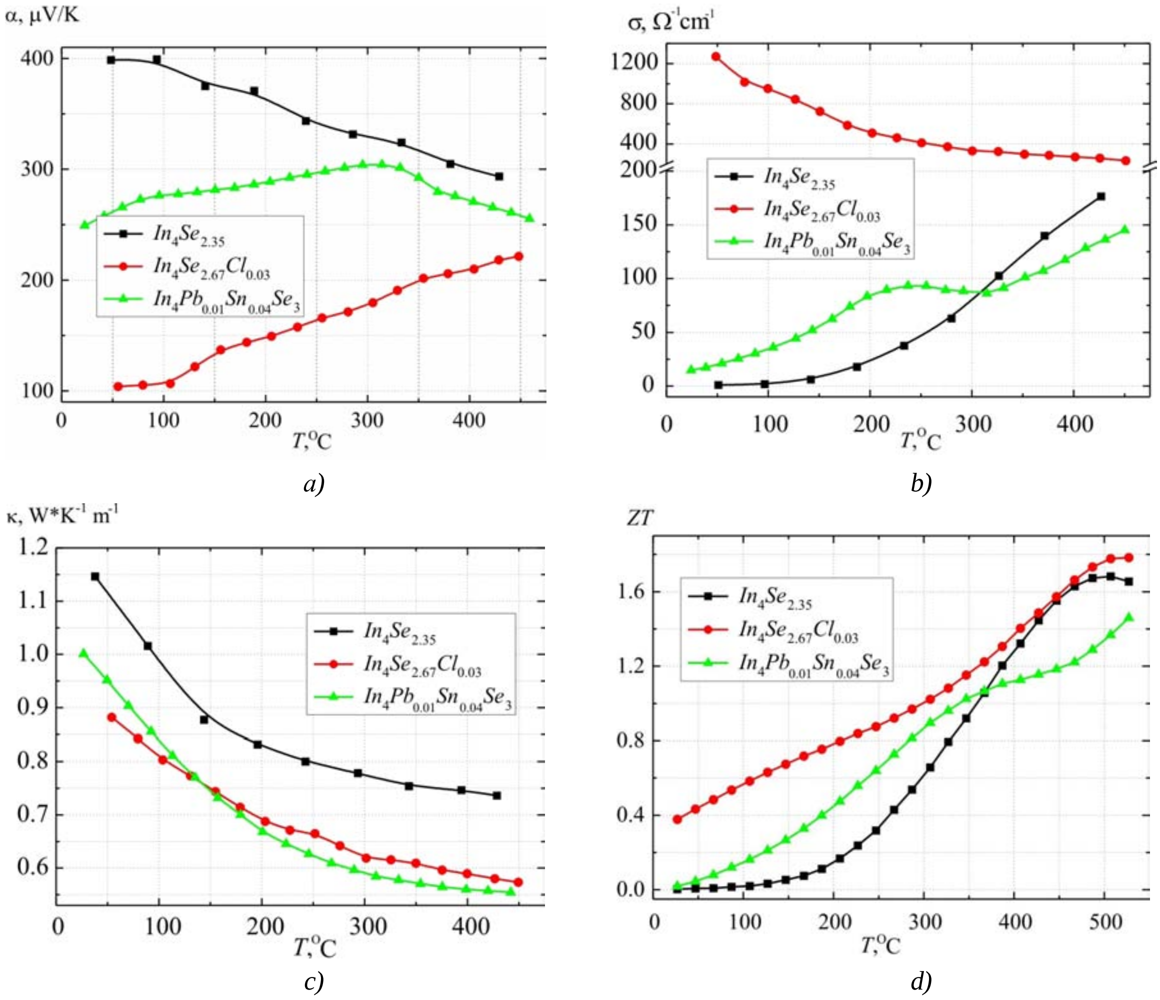

Fig. 11. Temperature dependences of the Seebeck coefficient (a), electric conductivity (b), thermal conductivity (c) and figure of merit (d) of In_4Se_3 materials [18 – 20].

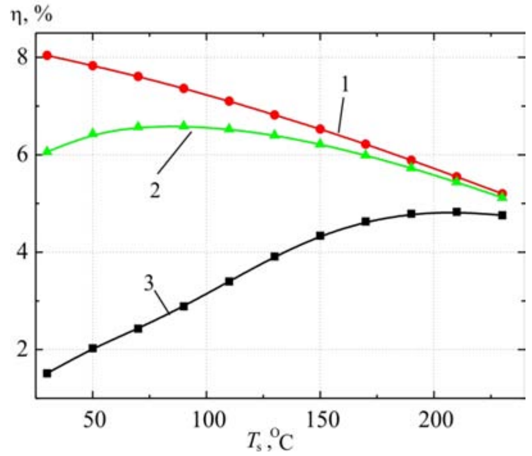

Fig. 12. The efficiency of thermoelectric modules of materials:
1 – p-PbTe – n-$In_4Se_{2.67}Cl_{0.03}$, 2 – p-PbTe – n-$In_4Se_{2.32}I_{0.03}$, 3 – p-PbTe – n-$In_4Se_{2.35}$
versus the cold side temperature. The hot side temperature is 500 °C.

Maximum efficiency η=8 % at constant hot side temperature and variable cold side temperatures was demonstrated by a module with *p-PbTe* and *n-*$In_4Se_{2.67}Cl_{0.03}$ (Fig. 12). For a module where *Pb* and *Sn*-doped In_4Se_3 is used as *n*-leg, efficiency maximum is shifted towards higher temperatures and makes ~6.6% at T_c= 90 °C. This is due to a mismatch in thermoelectric parameters (mostly σ) of *PbTe* and $In_4Pb_{0.01}Sn_{0.04}Se_3$ materials (Fig. 11 b). Further reduction of η to 5.1% is caused by the reduction of operating temperature difference, even though the figure of merit of $In_4Pb_{0.01}Sn_{0.04}Se_3$ is increasing (Fig. 11 d).

A non-traditional dependence was obtained when studying the efficiency of a module with *p-PbTe* and *n-*$In_4Se_{2.35}$ versus the cold side temperature (Fig. 12). A rise in T_c leads to efficiency increase that reaches its maximum 4.83% at 210 °C. Such dependence of η is due to non-optimal material operating conditions on the cold side and low figure of merit values of $In_4Se_{2.35}$ material in low temperature region (Fig.11 d).

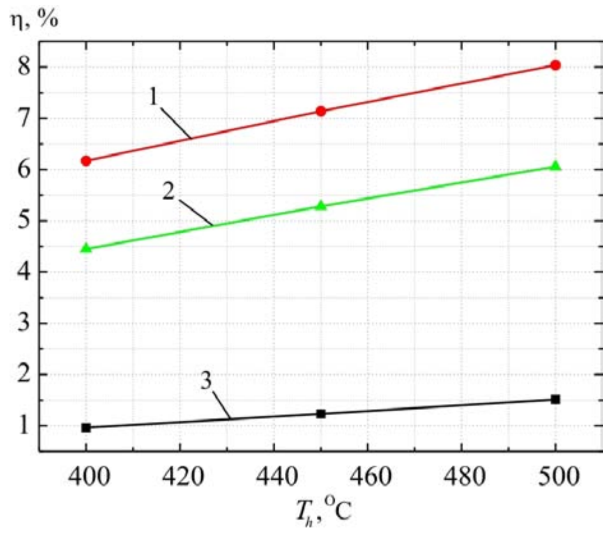

Fig. 13. The efficiency of thermoelectric modules of materials: 1 – p-PbTe – n-$In_4Se_{2.67}Cl_{0.03}$,
2 – p-PbTe – n-$In_4Se_{2.32}I_{0.03}$, 3 – p-PbTe – n-$In_4Se_{2.35}$
versus the hot side temperature. The cold side temperature is 30 °C

Fig. 13 shows the efficiency of thermoelectric modules based on *PbTe* and *InSe* compounds versus the hot side temperature.

It is clear that with a rise in the hot side temperature, the efficiency of a module is increased and reaches the level of 8% and 6% for $PbTe\text{-}In_4Se_{2.67}Cl_{0.03}$ and $PbTe\text{-} In_4Pb_{0.01}Sn_{0.04}Se_3$, respectively. At the cold side temperature 30 ^{o}C maximum efficiency for $p\text{-}PbTe$ – $n\text{-}In_4Se_{2,35}$ module is 1.5%, making inefficient the use of this material in pair with *p-PbTe* in traditional generator modules.

The results of experimental studies In_4Se_3 – *PbTe* based modules

On the basis of calculations performed, some alternate designs of thermoelectric modules of *p- PbTe* and *n-* In_4Se_3 materials of electric power 0.5-5 W were developed (Table 1).

Electric interconnect of *PbTe* and In_4Se_3 legs was made by silver plates via diffusion bonding technique. *Co* and *Fe* are used as anti-diffusion layers for *PbTe* and In_4Se_3. As transient layers, a mixture of *CoTe* and *PbTe* is used for *PbTe*, and a mixture of *CoTe* and In_4Se_3 - for In_4Se_3 [20].

Table 1

Geometric and electric parameters of PbTe - In_4Se_3*-based modules with a series connection of legs* (T_h = 500 ^{o}C, T_c = 30 ^{o}C)

Electric power, W	Electric voltage, V	Heat flux, W	Leg cross-section, mm^2	Number of leg pairs	Overall dimensions, mm
0.5	0.5	34.2	5.6×5.6	4	11.7×19.7×7.8
	1.0		4×4	8	17.5×25.5×7.8
	5.6		1.5×1.5	50	19.5×27.5×7.8
	3.2		1.6×1.6	28	14.2×23.3×6.3
3	0.5	205.4	13.8×13.8	4	28.1×36.1×7.8
	1		9.8×9.8	8	40.7×48.7×7.8
	8.8		3.1×3.1	78	46.3×50.7×7.8
	1		7.2×7.2	8	30.3×38.3×6.3
	5.6		2.9×2.9	50	33.5×41.5×6.3
5	3.2	342.4	6.7×6.7	28	49.9×65.1×7.8
	5.6		3.7×3.7	50	41.5×49.5×6.3

For 0.5 W modules the number of legs was increased from 4 to 50, and the cross-section of leg in this case was reduced from 5.6×5.6 mm to 1.5×1.5 mm, respectively. The overall dimensions of a module were in the range from 11.7×19.7 to 14.2×23.3 mm. For 5 W modules the cross-section of legs

should be increased with their invariable height. Maximum dimensions of a 5 W module of voltage 5.6 V were 50×65×7.8 mm.

Using of cheap thermoelectric materials and simple technology makes the prospect of wide use of *InSe-PbTe* based modules for thermoelectric energy converters on the level of operating temperatures 30-500°C.

Conclusions

1. Using the methods of optimal control theory, computer design has been performed and the efficiency of generator modules of *n-InSe–p-PbTe*-based materials in the temperature range of 30–500 °C has been determined. It has been shown that maximum efficiency of thermoelectric modules is 8% for $p\text{-}PbTe\text{–}n\text{-}In_4Se_{2.67}Cl_{0.03}$ and 6.6% for $p\text{-}PbTe\text{–}n\text{-}In_4Pb_{0.01}Sn_{0.04}Se_3$.
2. For the first time thermoelectric generator module based on $n\text{-}In_4Se_3\text{–}p\text{-}PbTe$ has been created for the operating temperature range 30-500 °C, and the results of theoretical calculations have been experimentally confirmed.
3. Thermoelectric modules of materials based on *n-InSe–p-PbTe* and *n-PbTe* and *p-GeTe-AgSbTe* are characterized by close efficiency values. However, *n-InSe–p-PbTe* modules have lower manufacturing cost which gives them the advantage for use in medium-temperature range.

References

1. Z.H. Dughaish. Lead telluride as a thermoelectric material for thermoelectric power generation // Physica B, 322, pp. 205-223 (2002).
2. E.A. Skrabek, D.S. Trimmer. Properties of the general TAGS system. // in CRC Handbook of Thermoelectrics, Eds. D.M. Rowe, pp.267-275, CRC Press, Boca Raton, FL (1995).
3. L.T.Strutynska, V.R.Bilinsky-Slotylo, and V.Ya.Mikhalovsky, Design of Segmented Modules Based on PbTe/TAGS for Thermoelectric Generators, *Physics and Chemistry of the Solid State.* – 2012.- № 4.- T13.-C. 1032-1036..
4. Mineral commodity summaries 2012 / U.S. Geological Survey. Reston: Virginia, 2012. 198 p.
5. Singh D.J. Electronic Transport in Old and New Thermoelectric Materials / D.J. Singh // Science of Advanced Materials. Vol.3. 2011. P.561-570.
6. High-performance nanostructured thermoelectric materials / J.-F. Li, W.-Sh. Liu [etc] // NPG Asia Mater. Vol.2, No.4. 2010. P.152-158.
7. Tritt T.M. Thermoelectric Phenomena, Materials, and Applications / T.M. Tritt // Annual Review of Materials Research. Vol.41. 2011. P.433-448.
8. Snyder G.J. Complex thermoelectric materials / G.J. Snyder, E.s. Toberer // Nature Materials. Vol.7. 2008. P.105-114.
9. Ju-Hyuk Yim et al. / Thermoelectric properties of indium-selenium nanocomposites prepared by mechanical alloying and spark plasma sintering // Journal of Electronic Materials.-2012.-Vol. 41.-№ 6.- P.1354-1359.
10. http://www.infogeo.ru/metalls/worldprice/.
11. L.I.Anatychuk, L.N.Vikhor, Computer Design of Staged Generator Modules, *J.Thermoelectricity*. – 2002. – №4. – C. 19 – 27.
12. L.I.Anatychuk, V.A.Semenyuk, *Optimal Control Over the Properties of Thermoelectric Materials and Devices* (Chernivtsi:Prut, 1992), 264 p.
13. L.N.Vikhor, Computer Design of Thermoelectric Generator Modules, *J.Thermoelectricity*. – 2005.

– №2. – P. 60-67.

14. L.I.Anatychuk, *Thermoelements and Thermoelectric Devices. Handbook* (Kyiv: Naukova Dumka, 1979), 766 p.
15. L.I.Anatychuk, M.V.Havrylyuk, and V.V.Lysko, Installation for Measuring the Properties of Semiconductor Thermoelectric Material, *J.Thermoelectricity*. – 2010, №3. P. 41-49.
16. L.M.Vikhor, V.Ya.Mikhailovsky, and R.M.Mochernyuk, Materials Optimization and Performance Evaluation of Generator Modules for Heat Recuperators, *Physics and Chemistry of the Solid State* 1(15), 206-213 (2014).
17. J.-S.Rhyee, K.H.Lee, S.M.Lee, E.Cho, S.I.Kim, E.Lee, Y.S. Kwon, J.H.Shim, G.Kotliar. Peierls distortion as a route to high thermoelectric performance in $In_4Se_{3-\delta}$ crystals.– Nature2009, 459, 965.
18. J.-S.Rhyee, K.Ahn, K.H.Lee, H.S.Ji, J.-H.Shim. Enhancement of the thermoelectric figure-of-merit in a wide temperature range in $In_4Se_{3-x}Cl_{0.03}$ bulkcrystals. –Adv. Mater. 2011, 23, 2191.
19. Z.-S.Lin, L.Chen, L.-M.Wang, J.-T.Zhao, L.-M.Wu. A promising mid-temperature thermoelectric material candidate: *Pb/Sn*-codoped $In_4Pb_xSn_ySe_3$. – Adv. Mater. 2013, 25, 4800.
20. Patent (UA) № 79960 InCl H01L 35/00 Method for Manufacture of Thermoelement Comprising n-In_4Se_3 / V.Ya.Mikhailovsky, R.M.Mochernyuk, Kim Sang Il, Lee Kyuhyoung – Publ. 13.05.2013, Bul.№9 Appl.u2012 12353 of 29.10.12.

Submitted 19.12.2014.