V.Ya. Mykhailovsky

THERMOELECTRIC STAGED MODULES OF MATERIALS BASED ON Bi_2Te_3-$PbTe$-TAGS

V.Ya. Mykhailovsky, V.R. Bilinsky-Slotylo
(Institute of Thermoelectricity, 1, Nauky Str., Chernivtsi, 58029, Ukraine)

V.R. Bilinsky-Slotylo

• *Results of computer design of two-stage thermoelectric modules made of materials based on Bi_2Te_3-PbTe-TAGS for waste heat recovery are presented. Design was made with regard to temperature dependences of material parameters, thermal and electric losses on the contacts and stage interconnects. The module construction is described. The results of experimental research on parameters of staged module with the cold side temperature 30 °C and hot side temperature 200 to 550 °C are presented.*

Introduction

Thermoelectric generators are of considerable interest for conversion into electricity of waste heat from industry, internal combustion engines and the heat from organic fuel combustion [1, 2]. The temperature range of these heat sources (500 to 600 °C) is regarded as promising due to their large quantity and high thermal power that can be converted into electricity.

For creation of modules working in the above temperature range it is customary to use *PbTe* of *p*- and *n*-type [3]. However, unlike *n-PbTe*, *p*-type has a low mechanical strength and unstable parameters, particularly at elevated temperatures [4]. Hence the relevance of studies aimed at using material with improved parameters as a *p*-type leg.

The purpose of this work is to design and study parameters of two-stage modules made of materials based on Bi_2Te_3-*PbTe-TAGS* to expand the opportunities of practical use of thermogenerators.

Calculation procedure

Design of a two-stage module schematically shown in Fig. 1 was made on condition of a series connection of thermoelements of the cold and hot stages for given values of electric power P and voltage U on the load. Each stage consists of thermocouples connected electrically in series and thermally in parallel.

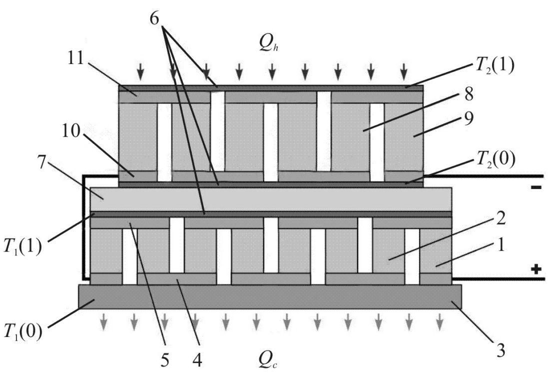


Fig. 1. Schematic of a two-stage module: 1, 2 – n- and p-type legs of the cold stage; 3 – ceramic plate; 4, 5 – interconnects of the cold and hot sides of the cold stage; 6 – electric insulation; 7 – heat-conducting plate; 8, 9 – n- and p-type legs of the hot stage; 10, 11 – interconnects of the cold and hot sides of the hot stage.

Apart from the technological problems related to chemical stability and thermal compatibility of materials, the development of staged structures is involved with a problem of electric matching of stages.

Maximum module efficiency is described by expression

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

where Q_c, Q_h are external heat fluxes on the cold and hot module surfaces, respectively. Function ϕ can be conveniently represented as [5]

$$\phi = \prod_{k=1}^{m} \phi_k, \quad \phi_k = \frac{Q_0^k}{Q_1^k}, \tag{2}$$

where Q_0^k, Q_1^k is thermal flux on the cold and hot surfaces of k-th stage; m is the number of module stages. In so doing, the equalities of thermal matching of stages were used

$$Q_0^{k+1} = Q_1^k, \; Q_0^1 = -Q_c, \; Q_1^k = -Q_h. \tag{3}$$

Now we pass on to equivalent logarithmic functional $J = \ln\phi$ which with regard to (2) and (3) will assume the form

$$J = \sum_{k=1}^{m} \left(\ln q_0^k - \ln q_1^k \right), \tag{4}$$

where $q_1^k = Q_1^k / n_k I$, $q_0^k = Q_0^k / n_k I$ are specific (related to current strength) heat fluxes on thermocouple junctions.

For calculation of the boundary heat fluxes q_1^k, q_0^k appearing in (4) it is necessary to use a system of $4N$ differential equations of nonequilibrium thermodynamics [5]

$$\left. \begin{aligned} \frac{dT}{dx} &= -\frac{\alpha_k j_k}{\kappa_k} T - \frac{j_k}{\kappa_k} q \\ \frac{dq}{dx} &= \frac{\alpha_k^2 j_k}{\kappa_k} T + \frac{\alpha_k j_k}{\kappa_k} q + \frac{j_k}{\sigma_k} \end{aligned} \right|_{n,p}, \quad k = 1,...,m \tag{5}$$

where $x = \bar{x} / l_k$ $(0 \le x \le 1)$ is dimensionless coordinate along the length of leg l_k of k-th stage, $j_k^{n,p}$ is specific current density in thermoelement legs of k-th stage.

Using the boundary conditions for system (5) in the form:

$$\begin{aligned} &T_n^k(0) = T_p^k(0) = T_k(0), \quad T_n^k(1) = T_p^k(1) = T_k(1), \\ &T_1(0) = T_c, \quad T_k(0) = T_{k-1}(1), \quad T_m(1) = T_h, \quad k = 1,...,m \\ &T_1(1) = T_c + \delta T_1, \quad T_{k-1}(1) = T_h - \delta T_k, \end{aligned} \tag{6}$$

where T_c, T_h are the cold and hot module temperatures, we obtain expressions for heat fluxes q_1^k, q_0^k

$$\begin{aligned} q_1^k &= \sum_{n,p} \left[q_k^{n,p}(1) + \frac{j_k^{n,p}}{l} r_0^{n,p} \right], \\ q_0^k &= \sum_{n,p} \left[q_k^{n,p}(0) - \frac{j_k^{n,p}}{l} r_0^{n,p} \right]. \end{aligned} \quad k = 1,\ldots,m \tag{7}$$

Heat fluxes q_1^k, q_0^k depend on parameters of specific current density in stages $j_k^{n,p}$. It is necessary to find such their values which create minimum of functional J. In this connection, the following conditions should be met:

1. Current densities in the stages should satisfy the equalities

$$-\frac{\partial J}{\partial j_{n,p}^k}+\int_{x_{k-1}^+}^{x_k^-}\frac{\partial H^k(\psi,T,q,j_n^k,j_p^k)}{\partial j_{n,p}^k}dx=0,\quad k=1,\ 2 \tag{8}$$

where the Hamiltonian function H^k is of the form [5]

$$H^k=\sum_{n,p}(\psi_1^k f_1^k+\psi_2^k f_2^k), \tag{9}$$

$(f_1^k, f_2^k)_{n,p}$ are right-hand sides of equations (5), $\psi = (\psi_1, \psi_2)_{n,p}$ is pulse vector conjugate with phase variables vector $y = (T, q)_{n,p}$ [6].

2. Temperatures at the stage boundaries must satisfy the system

$$\sum_{n,p}\psi_1^{k+1}(0)=\sum_{n,p}\psi_1^k(1),\qquad k=1,...,m-1. \tag{10}$$

This problem is solved using a numerical method of successive approximations by development of a computer program which allows calculating the optimal distribution of generated current densities in the stages with the optimal sequence of interstage temperatures to assure maximum efficiency of thermoelectric generator.

Through the choice of the geometric dimensions of thermoelements in the stages and the number of thermoelements one can achieve an optimal current of uniform value in each stage. It allows a series electric connection of stages. In this case the optimal conditions of heat flux matching between stages are retained.

The above algorithm is used to calculate the optimal parameters of design and the energy parameters of module, namely:

– module efficiency η_{total};
– amount of heat that must be supplied to the hot junctions of module Q_h;
– cross-section area of leg S;
– number of thermoelements (leg couples) N.

The total efficiency of two-stage module is described by the expression

$$\eta_{total}=\eta_1+\eta_2-\eta_1\cdot\eta_2\,. \tag{11}$$

The distribution of electric powers over the stages is determined by the formulae:

$$P_1=\eta_1\cdot Q_h(1-\eta_2),\quad P_2=\eta_2\cdot Q_h \tag{12}$$

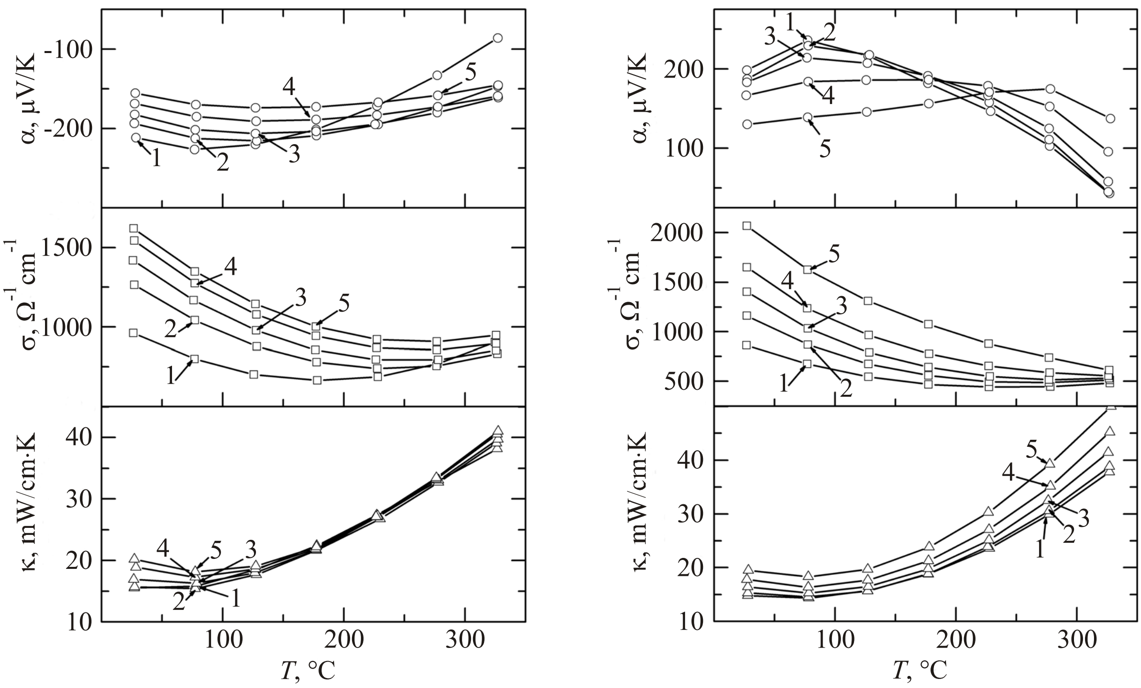
On condition of retaining the necessary heat flux supply and assuring the optimal current, the cross-section area of stage legs and the number of thermoelements (leg couples) of each stage are determined as follows:

$$S_k=\frac{l_k\cdot I}{j_k},\ N_k=\frac{U_k}{q_1^k-q_0^k}, \tag{13}$$

where U_k is the necessary voltage of k-th stage.

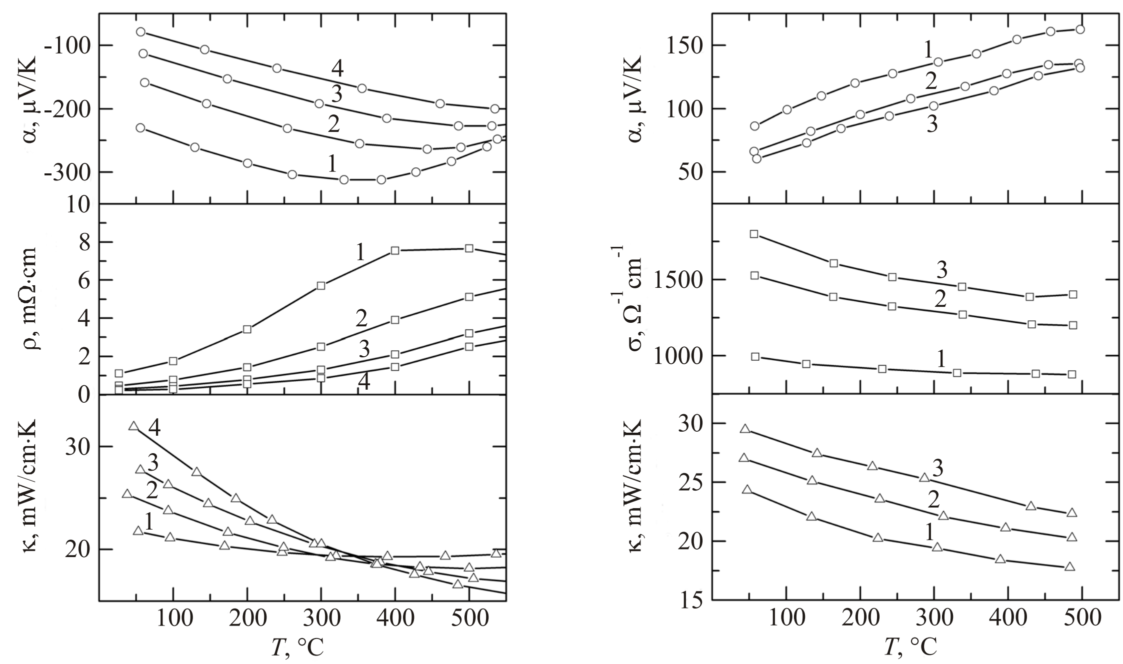
Research results

Using the method set forth above, calculations of two-stage modules were carried out which employed experimentally measured by the authors of [7-9] temperature dependences of thermoelectric parameters α, σ, κ of *n*- and *p*-Bi_2Te_3 materials for the cold stage, as well as *n-PbTe* and *p*-TAGS – for the hot stage. Their temperature dependences for samples with different doping degree are given in Fig. 2, 3.



a) *b)*

Fig. 2. Temperature dependences of thermoelectric parameters of the cold stage materials with different electric conductivity values σ_0^n, σ_0^p at T = 300 K [7]: a) n-$(Bi_2Te_3)_{0.90}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$, doped with iodine ($1 - \sigma_0^n = 970\ \Omega^{-1}cm^{-1}$; $2 - \sigma_0^n = 1250\ \Omega^{-1}cm^{-1}$; $3 - \sigma_0^n = 1400\ \Omega^{-1}cm^{-1}$; $4 - \sigma_0^n = 1550\ \Omega^{-1}cm^{-1}$; $5 - \sigma_0^n = 1650\ \Omega^{-1}cm^{-1}$); b) p-$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$, doped with lead ($1 - \sigma_0^p = 880\ \Omega^{-1}cm^{-1}$; $2 - \sigma_0^p = 1100\ \Omega^{-1}cm^{-1}$; $3 - \sigma_0^p = 1380\ \Omega^{-1}cm^{-1}$; $4 - \sigma_0^p = 1660\ \Omega^{-1}cm^{-1}$; $5 - \sigma_0^p = 2000\ \Omega^{-1}cm^{-1}$).



a) *b)*

Fig. 3. Temperature dependences of thermoelectric parameters of the hot stage materials: a) n-PbTe < x mol.% PbI_2 > (1 – x = 0.01; 2 – x = 0.03; 3 – x = 0.055; 4 – x = 0.1) [8]; b) p-$(Ag_{0.5}Sb_{0.5}Te)_{100-x}(Pb_{0.16}Ge_{0.84}Te)_x$ (1 – x = 80; 2 – x = 85; 3 – x = 90) [9].

The choice of materials for the legs of each stage was based on the methods of optimal control theory [10] in such a way that the cold and hot stages were characterized by maximum efficiency in the temperature range of 50 to 250 °C and 250 to 500 °C, respectively. The results of calculations are presented in Table 1.

Table 1

Optimal materials for a two-stage module

Designation of stages and legs		Leg material	Concentration
Cold	*n*-type	$(Bi_2Te_3)_{0.90}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$, doped with iodine	σ_0^n = 1365 $\Omega^{-1}cm^{-1}$
	p-type	$(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$, doped with lead	σ_0^p =1570 $\Omega^{-1}cm^{-1}$
Hot	*n*-type	*PbTe*+*x* mol.% PbI_2	*x* = 0.042
	p-type	$(Ag_{0.5}Sb_{0.5}Te)_{100-x}(Pb_{0.16}Ge_{0.84}Te)_x$	*x* = 87.5

The efficiency of a two-stage module made of optimal materials based on Bi_2Te_3, *n-PbTe* – *p*-TAGS of electric power 10 W and voltage 3 V (the height of module leg is 5 mm) as a function of interstage temperature is given in Fig. 4 *a, b*.

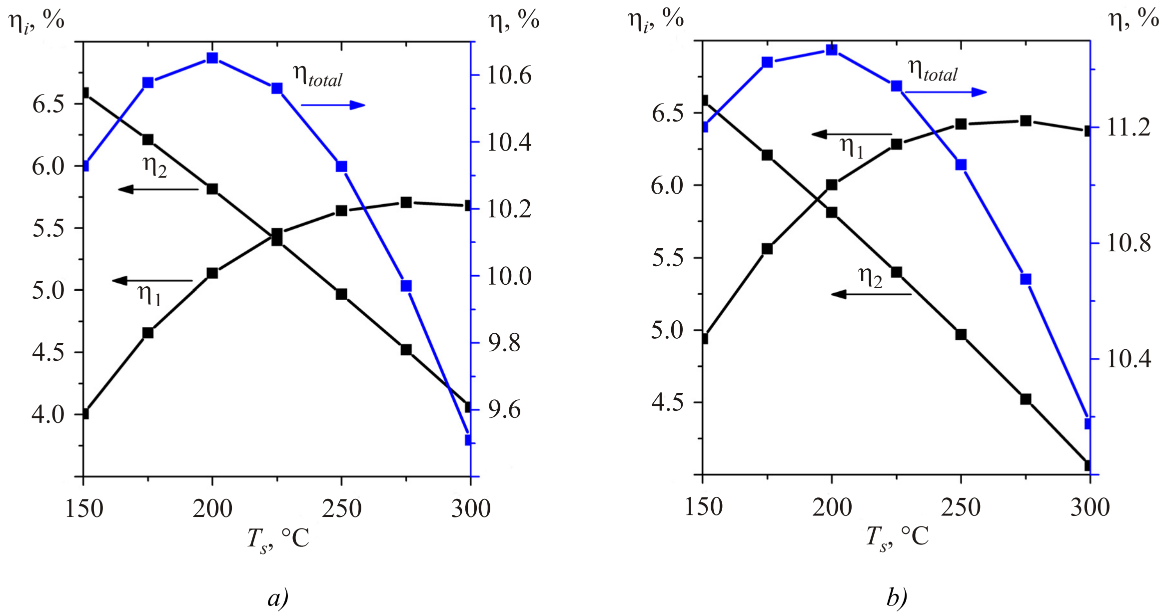
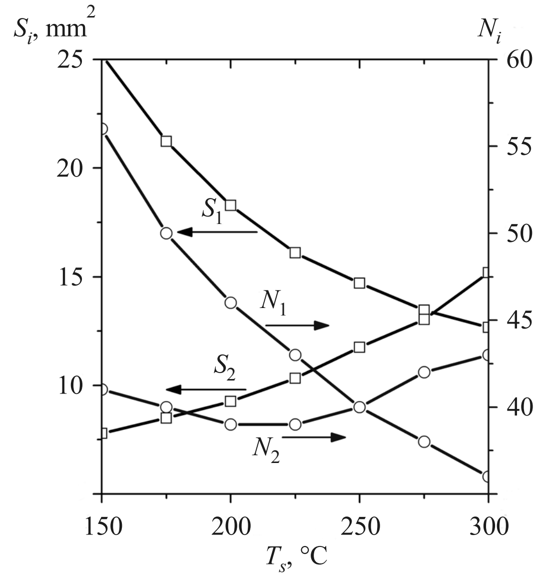


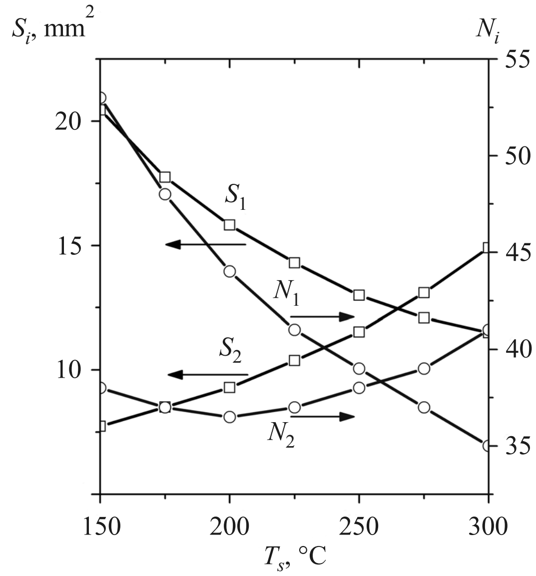
Fig. 4. The cold stage η_1 and the hot stage η_2 efficiency of a two-stage module, as well as total efficiency η_{total} as a function of interstage temperature T_s (T_h = 500 °C, P = 10 W, U = 3 V, L_{leg} = 5 mm): a) T_c = 50 °C; b) T_c = 30°C.

As can be seen from the data presented above, the efficiency of a staged module in the cold temperature range of 30 to 50 ºC varies as a function of interstage temperature from 9.5 to 11.45%. The optimal interstage temperature whereby maximum efficiency value is achieved (11.45% at the cold temperature 30 ºC) is on the level of 200 °C. At this interstage temperature, the hot temperature 500 ºC and the cold temperature 50 ºC the efficiency distribution in the stages is as follows: the cold stage – 5.14%, the hot stage – 5.8% (Fig. 4 *a*).

Dependence of the cross-section area of leg in the stages and the number of leg couples on the interstage temperature of a two-stage module (the legs in both stages are connected in series) of power 10 W and voltage 3 V and the leg height 5 mm is given in Fig. 5 *a*, *b*.



a)



b)

Fig. 5. Dependences of cross-section area and the number of leg couples in module stages (N_i) on the interstage temperature T_s to obtain the electric power 10 W at U = 3 V (T_h = 500 °C, L_{leg} = 5 mm): a) T_c = 50 °C; b) T_c = 30 °C.

From the data given in Fig.5 it follows that at the interstage temperature 250 °C the number of leg couples of the cold and hot stages is practically identical, and cross-section of both stages is equal at the interstage temperature 270 °C.

Maximum efficiency of a two-stage module made of optimal materials with the cold temperature 50 °C, power 10 W at the voltage of 3 V and leg height 5 mm is achieved on condition: S_1 = 18.3mm^2, S_2 = 9.3mm^2, N_1 = 46 couples, N_2 = 40 couples.

Technologically, it is convenient to use standard geometrical dimensions of legs for stages. Taking into account this feature, a similar calculation of a two-stage module made of materials given in Table 1 was performed. The stage parameters were selected as follows:

– cold stage: the area of legs S_1 = 1.8·4.3 mm^2; the height L_1 = 3 mm; the number of couples N_1 = 16; stage dimensions 17.9 × 17.9 mm^2;

– hot stage: the area of legs S_2 = 4·4 mm^2; the height L_2 = 5.6 mm; the number of couples N_2 = 8; stage dimensions 17.5 × 17.5 mm^2.

At the hot temperature 500 °C, cold temperature 50 °C and interstage temperature T_s = 270 °C the general efficiency made ~ 10%, the efficiency distribution in the stages was as follows: the cold stage - 5.6%, the hot stage – 4.6%, which is comparable to the data presented in Fig. 4 *a*. Thus, with regard to thermal and electric matching of stages, the power of such a module is 3.1 W at the voltage of 1 V.

Based on the results of design, a construction was developed and two-stage modules were created of *n-, p-*Bi_2Te_3 – *n-PbTe* – *p-*TAGS materials with the rated electric power ~ 3 W. The results of experimental research on the module parameters with the cold temperature 30°C and the hot temperature 200 to 550 °C are given in Table 2.

The maximum electric power of module at T_c = 30 °C and T_h = 500 °C is 2.6 W, the efficiency is 9.2 %. With the hot side temperature increase to 550 °C, the efficiency of module increases to 10.4%. The obtained experimental results correlate well with the above theoretical calculations of module parameters.

Table 2

Dependence of parameters of a two-stage thermoelectric module based on n-, p- Bi_2Te_3 and PbTe-TAGS on the hot temperature at T_c = 30 °C

№	T_h, °C	U, V	I, A	P, W	Q_h, W	η, %
1	200	0.195	1.45	0.28	10.73	2.57
2	250	0.260	1.80	0.47	13.90	3.26
3	300	0.328	2.35	0.77	17.77	4.16
4	400	0.480	2.72	1.31	22.90	5.70
5	450	0.605	3.10	1.88	25.72	7.31
6	500	0.720	3.55	2.60	28.40	9.20
7	550	0.820	3.87	3.17	30.40	10.40

Conclusions

Using the methods of optimal control theory, design of two-stage modules made of materials based on Bi_2Te_3 and *PbTe*-TAGS was made. Optimal concentrations of dopants for leg materials of both stages, optimal geometrical parameters of legs and the distribution of densities of generated current whereby maximum efficiency of two-stage thermoelectric modules is achieved were determined. It was shown that maximum efficiency of modules of such materials is achieved at the interstage temperature 200 to 220 °C.

At the hot side temperature 500 to 550 °C and the cold side temperature 30 °C, maximum efficiency of modules is 10 to 11%, which creates good prospects for using such thermoelectric converters for the recovery of heat wastes on the temperature level of 500 to 600 °C. The results of theoretical investigations and calculations were confirmed by experimental studies of two-stage module parameters.

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