Matching of p-n extruded materials based on Bi-Sbchalcogenides for thermoelement

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Extruded thermoelectric materials of different conductivity types based on bismuth and antimony chalcogenides have quite various thermoelectric properties as shown by the experimental data given. The paper discusses how to match thermocouple pellets of such materials optimally. It is shown that the condition of equality of absolute values of the Seebeck coefficients at room temperature is a good criterion to match thermocouple materials for obtaining the maximum possible temperature difference.

*Keywords:*Extruded thermoelectric material;Thermocouple; Maximum temperature difference

1. Introduction

Crystalline bismuth-antimony chalcogenides are anisotropic in their physical properties. Their characteristics can differ by several times if compared along and perpendicular to the third order axis. There is no problem in matching n- and p-type pellets for zone melted materials because the thermoelectric parameters of pellets cut out of oriented crystals in the direction perpendicular to the trigonal axis are very close. Therefore, to match the pellets parameters, it is sufficient to take p- and n-types with similar values of electrical conductivity or the Seebeck coefficient.

When the materials are extruded, a deformation texture is formed. In this texture the axes of a great number of grains are directed perpendicular to the extrusion trigonal axis. In p-type materials the ratio of electrical conductivity in the direction perpendicular to the trigonal axis and the electrical conductivity along the trigonal axis (anisotropy of electrical conductivity) is 2-2.5 [1,2], the anisotropy of thermal conductivity is the same as that of electrical conductivity, there being no anisotropy of the Seebeck coefficient. Hence, there is no anisotropy of thermoelectric efficiency (figure-of-merit) in p-type material. Thus, in case of perfect contact between grains, the figure-of-merit of extruded p-type materials should be the same as in a single crystal. In n-type materials the anisotropy of electrical conductivity is about 4, while the anisotropy of the thermal conductivity is 2. The Seebeck coefficient anisotropy is absent. The difference in thermal conductivity and electrical conductivity anisotropies causes the fact that in extruded materials lines of the electric current and heat flux may not locally coincide, resulting in curl currents [3] and thermoelectric efficiency reduction. Therefore, the efficiency of n- type extruded thermoelectric materials is lower than that of p-type, and the optimal selection of pairs of materials becomes of vital concern.

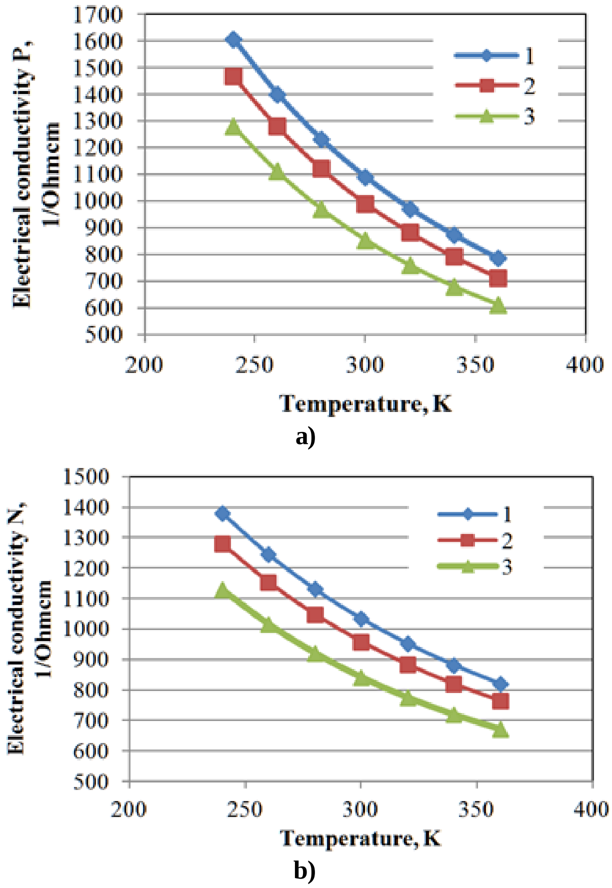

Figure 1. Temperature dependences of electrical conductivity: a) for p-type $Bi_{0,4}Sb_{1,6}Te_3$ (1: α_{300} = 200 µV/K, 2: α_{300} = 210 µV/K, 3: α_{300} = 216 µV/K), and b) for n-type $Bi_2Se_{0,15}Te_{2,85}$ (1: α_{300} = -208 µV/K, 2: α_{300} = -213 µV/K, 3: α_{300} = -219 µV/K).

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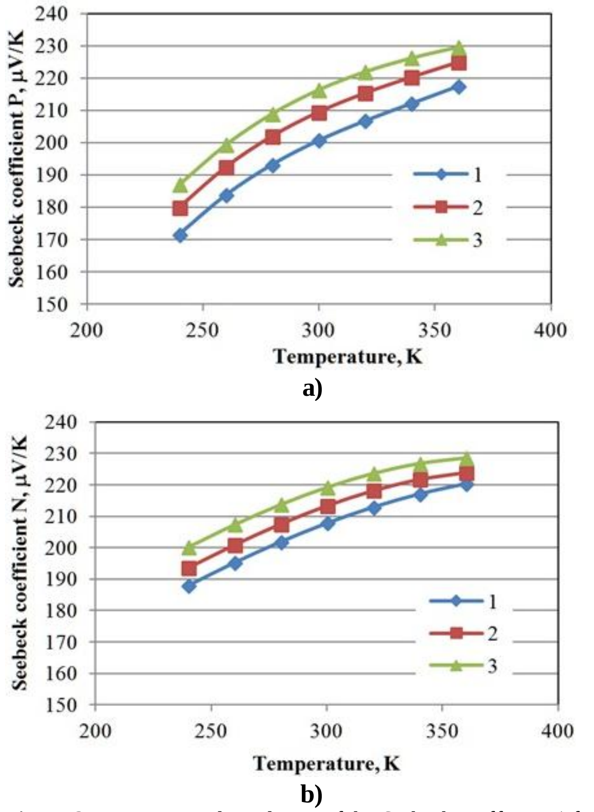


Figure 2. Temperature dependences of the Seebeck coefficent a) for p-type $Bi_{0,4}Sb_{1,6}Te_3$, and b) for n-type $Bi_2Se_{0,15}Te_{2,85}$. Designations are the same as in Figure 1.

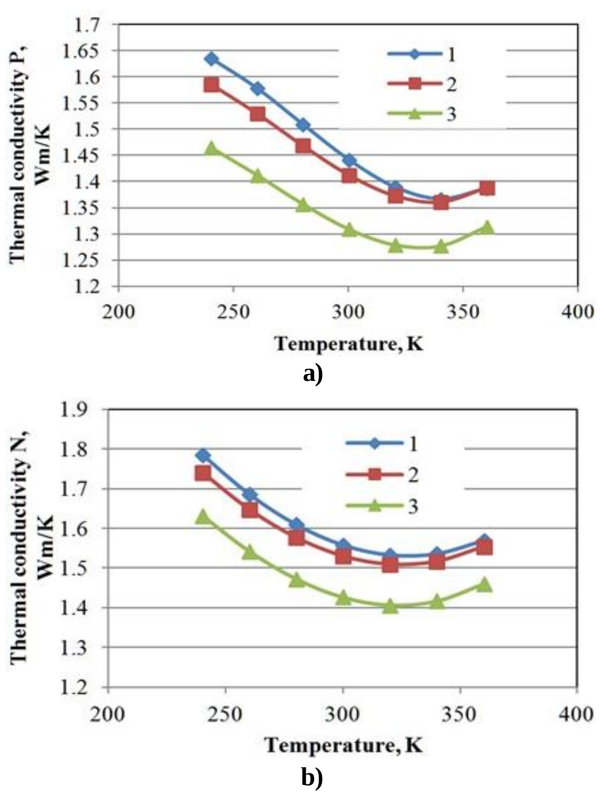


Figure 3. Temperature dependences of thermal conductivity a) for p-type $Bi_{0,4}Sb_{1,6}Te_3$ b) for n-type $Bi_2Se_{0,15}Te_{2,85}$ Designations are the same as in Figure 1.

2. Thermoelectric Parameters of Extruded Materials

Temperature dependences of thermoelectric properties of extruded thermoelectric materials produced in the company RMT were defined on the facilities DX8080 produced by RMT. The six-wire measurement by Harman's method [4,5] was used. The sample size was (length x width x height) 2x2x1.6 mm^3. The Ni antidiffusion layers were plated on the ends of the sample. The plating technology was the same as in mass production of thermoelectric modules. The results are shown in Figures 1-3.The temperature dependences of figure-of-merit are shown in Figure 4.For the samples studied the figure-of-merit Z at 300 K equals $(3{,}05\text{-}3{,}13)\cdot 10^{-3}$ K^{-1} for p-type and (2,83–2,87) 10^{-3} K^{-1} for n-type. These values are somewhat lower for p-type than those published in literature [6,7], which may be associated with a small elongation ratio (≈ 10) used in the extrusion tool. The figure shows that at 300 K the n-type figure-of-merit increases with the increase of the Seebeck coefficient, whereas in the p-type material it at first grows and then decreases. The average Z values of a thermocouple are within $(2{,}95\text{-}2{,}98)\cdot 10^{-3}$ K^{-1}.

It should be noted that at our disposal there were material samples obtained by other manufacturers. According to our measurements, their thermoelectric efficiency does not exceed the figure-of-merit of our samples.

In the Harman measurements the contact resistance is included in the measured pellet resistance. It would seem that thereby the problem of taking into account the contact resistance in thermoelectric processes is solved automatically. For temperature-independent thermoelectric parameters it does take place, but really the situation is more complicated. In fact, the temperature field in a pellet is determined, inter alia, by the Joule heat generated in it. And it is related to the temperature dependence of the electrical resistivity of the material, excluding the contact resistance. The contact resistance is only involved in heat generation on the ends of pellets. Therefore, when measured by Harman, to obtain the material electrical conductivity, it is necessary to estimate the contact resistance beforehand.

The most considerable manifestation of the contact resistance can be seen in ΔT_{max} as a function of pellet height. So, it is convenient to estimate the contact resistance ρ_c by the change of the maximum temperature difference for modules with pellets of varying heights. If while the height is varied from l to l', the maximum temperature difference changes from ΔT_{max} to $\Delta T'_{max}$, then within the approximation of temperature-independent thermoelectric parameters we obtain:

$$\rho_c = \frac{\rho}{2}\frac{A}{\left(\frac{1}{l}-\frac{1}{l'}\right)-\frac{1}{l'}A}, \qquad (1)$$

where ρ is material resistivity, and

Table 1. Values of ΔT_{max} calculated for different combinations of pairs of n- and p-type materials at the thermocouple hot end temperature T_h = 300 K

α_p at 300 K	200 μV/K	210 μV/K	210 μV/K
α_n at 300 K		ΔT_{max}, (K)	
-208 μV/K	73,6(72,39)	74,5	74,6
-213 μV/K	73,7	74,6(74,27)	74,9
-219 μV/K	73,5	74,6	75,2(74,35)

$$A = \frac{(\Delta T'_{max} - \Delta T_{max})(T + \Delta T_{max})}{(T - \Delta T_{max})\Delta T_{max}} . \qquad (2)$$

From the data of the RMT modules the contact resistance is 2-2,5·10-6Ohm·cm2. The electrical conductivity σ_m in this case is related to the electrical conductivity σ_H measured by the Harman method as:

$$\sigma_m = \frac{\sigma_H}{1 - \frac{2\rho_c}{l}\sigma_H} , \qquad (3)$$

where l is the height of the pellet measured by the Harman method. Because of the contact resistance, the electrical conductivity data given in Figure 1 are understated by 3-5%. Accordingly, the figure-of-merit results are also underestimated.

3. Characteristics of Thermoelectric Modules

The maximum temperature difference on the thermocouple corresponds to the maximum value of the thermocouple figure-of-merit Z_{th}. In the approximation of the temperature-independent thermoelectric parameters, for thermocouple pellets having the same cross-section, the condition for the maximum Z_{th} is given as [8]:

$$\sigma_n \kappa_n = \sigma_p \kappa_p . \qquad (4)$$

For the comparison of the dependences of electrical conductivities of the n-and p-type materials, Figure 5 shows the dependence of the electrical conductivity at 300 and 320 K on the absolute value of the Seebeck coefficient at 300 K.

From the above data we see that the curves for the n-type materials are slightly higher than the corresponding curves for the p-type materials. I.e. the n-type materials have a greater power density compared with the p-type materials. The thermal conductivity of n-type materials is also somewhat higher than that of the p-type materials for the same values of the Seebeck coefficient. However the n-type thermal conductivity relative excess is greater than that of the electrical conductivity, whereby the n-type material figure-of-merit is lower than that of the p-type material. But overall, to satisfy condition (4) it is necessary that the thermocouple materials have similar absolute values of the Seebeck coefficients.

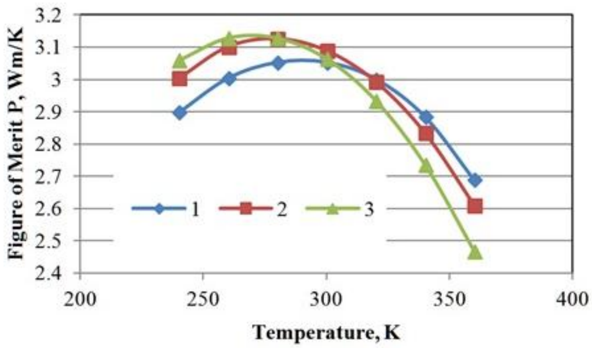
However, the temperature dependences of thermoelectric parameters can seriously impair the validity of (4). The temperature dependences can be most consistently taken into account by the optimal control methods [9].But, following this approach; it is difficult to trace the connection with the heat balance equations used in the temperature-independent approximation. Therefore, in this work we use the calculation of the effective values of thermoelectric parameters [10], which allows keeping the form of the heat balance equations. At the pellet cold end at zero heat flux the equation has the form:

$$\alpha_{ceff\,t} T_c I - \frac{1}{2} I^2 R_{ceff\,t} - K_{eff\,t} = 0 , \qquad (5)$$

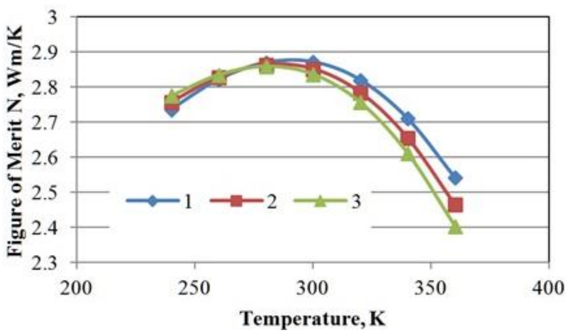
where T_c is the pellet cold end temperature, I is the pellet electrical current, and

Table 2. Mismatch parameter δ calculated for different pellets of n- and p-types.

α_p at 300 K	200 μV/K	210 μV/K	216 μV/K
α_n at 300 K		δ, (%)	
-208 μV/K	-6,3	7,0	37
-213 μV/K	-16,1	-4,1	22,7
-219 μV/K	-32,6	-23,4	-1,5



a)



b)

Figure 4. Figure-of-merit Z temperature dependences a) for p-type $Bi_{0,4}Sb_{1,6}Te_3$ and b) for n-type $Bi_2Se_{0,15}Te_{2,85}$. Designations are the same as in Figure 1.

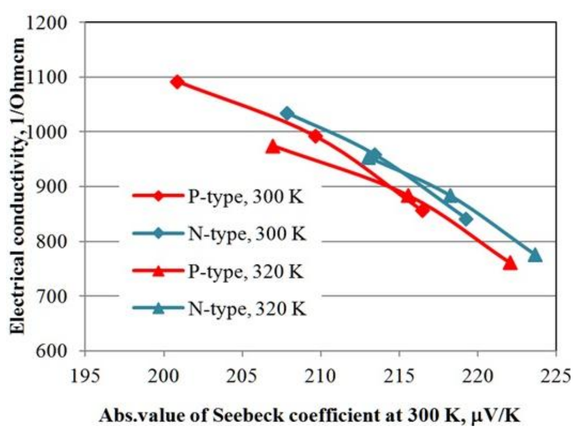


Figure 5. Dependence of electrical conductivity on the Seebeck coefficient at 300 K.

$$K_{eff\,t} = \overline{K} = \frac{s}{\int_0^L \frac{dx}{\kappa(T_x)}}, \qquad (6)$$

where L is the pellet length, and s is the cross-section of the pellet of the type t material.

$$R_{c.eff\,t} = \frac{2\overline{K}}{s^2}\int_0^L \rho(T_y)dy\int_y^L \frac{dx}{\kappa(T_x)}, \quad t = n, p. \qquad (7)$$

$$\alpha_{c.eff\,t} = \alpha(T_C) + \frac{\overline{K}}{sT_c}\int_0^L T_y \frac{d\alpha(T_y)}{dT}\frac{dT}{dy}dy\int_y^L \frac{dx}{\kappa(T_x)},$$
$$t = n, p, \qquad (8)$$

where T_x, T_y are the functions of the temperature distribution along the pellets. The comparison of the calculation methods [9] and [10] was done in paper [11], which showed that they yield the same results. To apply formulae (4) – (9) we need to know the temperature distribution along the pellets. To do this, we should first solve the heat equation, with some initial boundary conditions, and then by successive approximations we have to find the minimal cold end temperature T_c at a given hot end temperature T_h.

The calculation results are shown in Table 1.

We see that the difference in ΔT_{max} reaches two degrees, whereas, based on the average value of the figures-of-merit it should not exceed 0,3 K. Thus, the condition of matching pellets by the electrical properties (4), allowing for the temperature dependences, becomes:

$$\sigma_{ceff\,n}\kappa_{ceff\,n} = \sigma_{ceff\,p}\kappa_{ceff\,p}, \qquad (9)$$

where the appropriate values of electrical conductivities and thermal conductivities are obtained by (6) and (7). Table 2 shows the calculated values of the parameter of the pellets mismatch δ.

$$\delta = \frac{\sigma_{ceff\,n}\kappa_{ceff\,n}}{\sigma_{ceff\,p}\kappa_{ceff\,p}} - 1. \qquad (10)$$

The table 2 shows that a perfectly matched thermocouple are materials with α_n =-219 µV/K and α_p = 216 µV/K, for which the highest value ΔT_{max} is obtained, according to Table 1. The pellets for the diagonal elements of the table are best matched. The absolute value of the n-type Seebeck coefficient is by several units higher than that of p-type. The data of Table 1 are consistent with these results. Thus, the criterion of proximity of the absolute values of the Seebeck coefficients for a thermocouple of pellets is well justified and convenient in practical use.

The experimental verification of the compatibility of couples of pellets was performed by direct measurements of the value ΔT_{max} for modules specially manufactured of pellets with different properties. The measurement results are also shown in Table 1 in parentheses. The comparison of experimental and calculated data shows a fairly good agreement between the results. Moreover, the calculation correctly reflects the experimentally observed trend of ΔT_{max} increasing with the Seebeck coefficient growth.

4. Conclusions

The temperature dependence of thermoelectric parameters of extruded thermoelectric materials commercially manufactured by the company RMT Ltd. (Russia) were measured by the Harman method. The figure-of-merit at 300 K was obtained (3,05 – 3,13)·10-3 K-1 for the p-type material and (2,83 – 2,87) ·10-3 K-1 for the n-type material. Unlike the crystalline materials based on bismuth and antimony chalcogenides the thermoelectric properties of n- and p-type extruded materials differ markedly. The problem of matching such materials in a thermocouple was considered. The optimal match is given by the criterion of proximity of the absolute values of the Seebeck coefficients for a thermocouple of pellets.

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