RESEARCH OF N-TYPE Bi_2Te_3-Bi_2Se_3 And P-Type Bi_2Te_3-Sb_2Te_3 MATERIALS FOR LOW TEMPERATURE OPERATION

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https://doi.org/10.5281/zenodo.8360455

Abstract. *The technology has been developed for manufacturing polycrystalline thermoelectric materials of p - branches based on bismuth - antimony telluride, obtained by fusing components under inert gas pressure, and the results of their research are presented in this article.*
Keywords: *semiconductor, converter, branch, thermoelectric generator, technology, efficiency.*

It is known[1] that thermoelectric generators, made of semiconductor materials and work on the basis of their p and n-type elements, which are made in the form of briquettes. The branches are connected coherently and for their operation in the generator regime, one end is heated to temperature of $300 \div 500$ K. Depending on their field of application, various sources of energy, including concentrated solar radiation, can be the source of heat.

Traditionally, solid solutions of bismuth and tellurium (Bi_2Te_3) are used as the material for manufacturing the basis of the elements of a thermoelectric generator. To obtain high thermoelectric indices, various impurities are set into them. Such attempts were crowned with success, thus these indicated compounds have high thermoelectric characteristics [1]. In the work [2], the technological foundations of the synthesis of polycrystalline thermoelectric elements based on n-type Bi_2Te_3 solid solutions were described. It is shown, that for the manufacture elements of thermoelectric generator used materials grown by the zone melting method or Bridgman method. These substances are crushed into a fine fraction in technological process of manufacturing, and then coherently briquetted with cold, then hot pressing and thermal annealing. The formed material has an anisotropic polycrystalline structure. Due to deviations from structural stoichiometry and the introduction of impurities they have optimized thermoelectric properties. The results of the research of the effect of excess Te atoms (up to 0.1 at.%) and thermal treatment of samples are presented in the work [3]. Heat treatment was carried out in a spectrally pure argon, at temperature 473 and 573 K, for 120 hours. It has been established that small excess tellurium strongly influence on the values $\sigma, \alpha, and\ R$ at 77 K. Reliable measurements were made on direct current by the probe method, along the length of the sample (ingot), at the temperature $77 \div 300$K. The purpose of this work is to develop a technology for producing a p-type material, based on Bi_2Te_3, for using in thermoelectric converters, designed to work at hot junction operating temperatures of $300 \div 500$ K. In contrast to the technology for producing n-type elements, the production of a p-type half cell has some difficulties. This is due to the fact that with the introduction of impurities into the main material, which form holes, the thermoelectric parameters of the element are deteriorated. For this reason, the attention of many researchers is focused on obtaining effective p-elements based on bismuth and tellurium solutions with practical parameters.

This interest has so far not weakened, on the contrary, intensive research is being conducted in this direction [5].

Usually, to obtain the initial material of the p-type element, intended for the temperature range indicated above, solutions with a composition close to $Bi_{2-x}Sb_xTe_3$ (where $x \approx 1{,}5$) are used. In this case, the charge is enriched with an excess of tellurium (up to 4%), and various impurities are added to the base material, which create acceptor levels (Se, Pb, Zn, C). It is known that increasing in thermoelectric materials in the concentration of holes leads to decreasing of the value of the main parameter - the thermoelectric figure of merit of the thermoelement - Z. The quality factor, which is characterized by the relations

$Z=\alpha^2\sigma/\chi$

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is a function of α - the thermopower coefficient, σ- electrical conductivity and χ-thermal conductivity of the material. Recently, in order to optimize and improve the parameter values of semiconductor polycrystalline materials, the method of alloying materials under inert gas pressure has been used in the work[3]. Depending on the gas pressure, the stoichiometry of the material, i.e. the structural periodicity of atoms acquire different meanings. This contributes to the change of parameters of the resulting material.

To obtain the positive branches of the element, according to the above indicated technology, we selected the composition of the solid solution in the amount of 74 mol. This was used as a raw material for fusing the base. 74% Sb_2Te_3 + 26 mol.% Bi_2Te_3. The thermoelectric properties of unalloyed alloys depend on the purity of the starting components. In practice, it is not always possible to reproduce the necessary properties. In the transition from one batch of raw materials to another, the properties of the alloys obtained from them also are changed. Typically, the properties of alloys obtained under inert gas pressure have the following parameter scatter values $\sigma=(800\cdot1000)$ $Ом^{-1}\cdot см^{-1}$, $\alpha=(220\text{-}200)$ $мкВ/К$. In our case, the unalloyed base was $\sigma\approx1000$ $Ом^{-1}\cdot см^{-1}$, $\alpha\approx200$ $мкВ/К$. Precisely these values σ and α that served as the criterion for the selecting of the base material. In this case, the maximum value of ZT occurred in the temperature range $T\approx 320\div340К$.

Super stoichiometric over measures of *Te, Sb* and *Bi* lead to the following consequences: the over measure of *Te* has a donor effect and, as a result, increases α and lowers σ. The introduction of overcharges bismuth and antimony into the mixture, due to the acceptor action, increases the electrical conductivity, but reduces the thermopower coefficient. The technology should allow to keep high Z values in the material at alloying, which can be achieved by simultaneously deviating the composition from stoichiometry in the direction of enrichment with chalcogen and doping with lead.

Effective thermoelements from alloyed bismuth-antimony telluride can only be obtained by appropriately enriching the composition of the base material with tellurium. The results of the technological experiment are given in table 1. For comparison, the results of the study of the effect of overmeasure selenium, as an analogue of Te, on the thermoelectric properties of the base are also given.

As can be seen from the table 1. *Te* and *Se* have an affect on the thermoelectric properties of the material. Despite the fact that identical results can be achieved by setting into the mixture a smaller amount of selenium than tellurium, preference is given to the latter.

The composition of the initial components, weight. %	Fusing temperature *T*, ℃	The overmeasure of the component, weight.%	σ,$Ом^{-1}\cdot sm^{-1}$	α, *mkV/K*	$\alpha^2\sigma$, *mkV/sm*C²*
Bi – 16,179 *Sb – 26,826* *Te – 56,993*	850	-	2590	104	28,0
		1,75 Te	1130	185	38,7
		1,85 Te	1045	191	38,1
		2,0 Te	760	217	35,8
		0,75Se	1490	164	40,1
		0,85 Se	1235	169	35,3
		0,95 Se	950	206	40,3
		1,10 Se	807	216	37,3
	750	0,25 Te	1200	185	41,0
		0,35 Te	1080	205	45,4
		0,50 Te	667	220	32,3
		0,10 Se	1350	184	45,7
		0,20 Se	1030	196	39,6
		0,25 Se	770	210	34,0

Analysis of these technological experiments showed that the basis of $p\text{-}Bi_{0,5}\,Sb_{1,5}\,Te_3$ for the preparation of half elements, depending on the fusion temperature and the diameter of the quartz crucible, should contain from 0.25 to 1.0 weight. % excess tellurium.

Figure 1 shows the temperature characteristics of the thermoelectric figure of the merit solid solution $p\text{-}Bi_{0,5}Sb_{1,5}Te_3$ with different hole concentrations (curves 1-4). As can be seen from the figure, an increasing in the concentration of positive charge carriers due to the increasing in the percentage ratio of bismuth and tellurium leads to a decrease in the amplitude of *ZT*. This is due to the fact that the increasing in the concentration of holes leads to the increasing σ, but at the same time, the value σ falls significantly, and Z eventually is decreased.

For comparison, Figure 1 also shows the dependence of the quality factor from the temperature [1] in the samples alloyed by the lead (curves 5-6). During the alloyage of the main material by the lead, there is a satisfactory effect on the thermoelectric properties of the material in the range of T> 300 K.

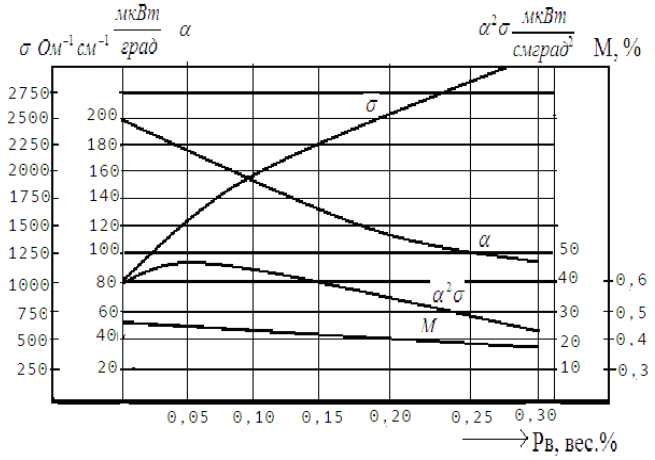

Fig.1. Thermoelectric figure of the merit solid solution $p\text{-}Bi_{0,5}Sb_{1,5}Te_3$ with different concentration of holes. For curves 1-4, p1> p2> p3> p4 [1]. 5,6 - curves obtained by the experiment, for the material alloyed by the lead, : 0,05 and 0.25 weight. %.

This is due to the fact that the lead in the base, obtained with the overcharge of tellurium, forms lead telluride, the vapor pressure of which is much lower than that of $Bi_xSb_{2-x}Te_3$ This led to the reduction technological losses.

Lead as an alloying additive was chosen for the following reason. Other impurities (Zn, Sb, Co), despite the fact that the compounds also manifest themselves as acceptors and give increasing in the concentration of current carriers (holes). They lead to the dropping in their mobility significantly more than Pb additives [5]. The weak dependence of the hole mobility on the amount of doping lead can be explained by the proximity of the atomic radiuses of Pb, Bi and Te. Besides, the main mechanism of scattering is scattering by acoustic phonons [1] and, further, the correction of such materials about the dominant mechanisms was said in the source [4].

To determine the optimal concentration of the alloy addition, the lead was set into the charge in the amount from 0.05 to 0.25 wt.%. The effect of the amount of the lead i shown in Fig. 2. From Fig. 2, we can see that with the increasing in the amount of the alloy addition, the electrical conductivity and the thermopower coefficient are changed almost linearly. The concentration of holes also varies linearly.

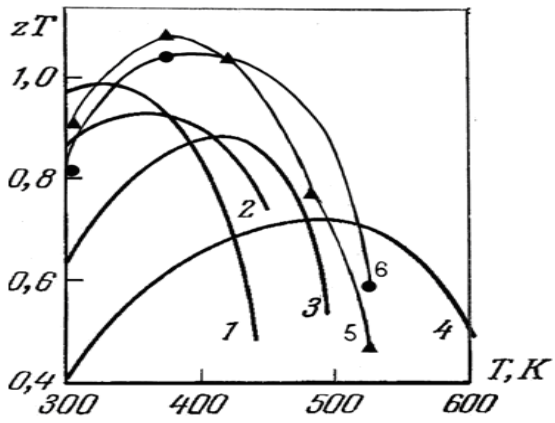

Fig.2 Study of the effect of concentration alloy addition on the changing thermoelectric material properties Bi2Te3-Sb2Te3, Pb and the number of losses.

The highest thermoelectric power has an alloy with the addition of Pb 0.05 wt%. In this case $\sigma \approx 1500\ Om^{-1}sm^{-1}$, $\alpha \approx 175$ мкВ/К, $p \approx 1{,}5 \cdot 10^{19}\ sm^{-3}$.

The amount of losses with increasing concentration of the alloy addition is decreasing, which can be explained with the formation of a very thin layer of the lead telluride on the surface of the melt, the vapor pressure of which, as noted above, is less than the vapor pressure of the synthesized compound.

Table 2

alloy addition *Pb*, weight. %	Properties before annealing				Properties after annealing			
	σ, $Om^{-1}\cdot sm^{-1}$	α, *mkV/K*	$p\cdot10^{19}$, *sм*$^{-3}$	$\alpha^2\sigma$, *mkVt/sm·K*^{2}	σ, $Om^{-1}\cdot sm^{-1}$	α, *MkV/K*	$p\cdot10^{19}$, sm^{-3}	$\alpha^2\sigma$, *mkVt/sm·K*^{2}
0,10	1800	160	2,0	44	1100	190	1,2	40
0,20	2250	150	2,4	52	1250	185	1,3	43
0.25	2600	130	3,5	45	1600	160	2,0	41
0,30	2820	125	3,8	46	1700	155	2,2	41
0,40	3000	105	4,8	33	2000	135	3,6	36

To optimize the properties of the synthesized material is usually exposed to their homogenizing annealing. The results of changes in the parameters of the base are given in table 2, before and after annealing at temperature of 370 ° C for 17 hours. As can be seen from this table, after annealing in samples, alloyed with *Pb*, in the range of additions of 0.1-0.3 weight. %, the alignment of the values $\alpha^2\sigma$ is occured. Although the value of $\alpha^2\sigma$ is somewhat lower during

annealing, it is more important that the annealing ensures uniformity of the polycrystalline material by volume.

One of the main criteria for choosing the base as half- elements in thermal converters is a shift in the working temperatures of a substance towards higher temperatures. For this purpose, we investigated the temperature dependences of the thermoelectric parameters of the substrate with different lead contents.

In fig. 3 and 4 such dependencies are shown. Analyzing these dependences, we can conclude that the most optimal for obtaining the material are lead additives in quantities from 0.25 to 0.4 wt.%.

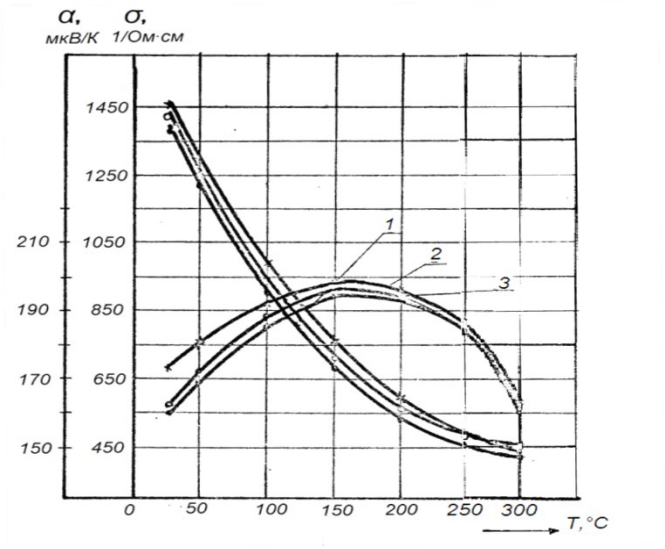

Fig.3. Influence of hot pressing temperature on temperature dependences of electrical conductivity and thermopower:

If, when analyzing the data of Fig. 4, from the thermoelectric power factor $\alpha^2\sigma$ cross to the quality factor Z, then we can be sure that the last parameter in the temperature range 300 500K remains almost unchanged. Taking into account this experimental fact, for the synthesis of p-type half-elements, a base alloyed with 0.25 wt.% lead was selected.

To obtain the working substance, fused according to the technology described above, was crushed to a fine fraction, as described in [2]. The grinding after mixing was successively exposed to cold and hot pressing and thermo annealing. The temperature of hot pressing varied from 300 to 400 ° C. With a shutter speed of 5 min. thermal annealing was carried out with a duration of 17 hours. The measurement results (at T = 300K) are given in table 3.

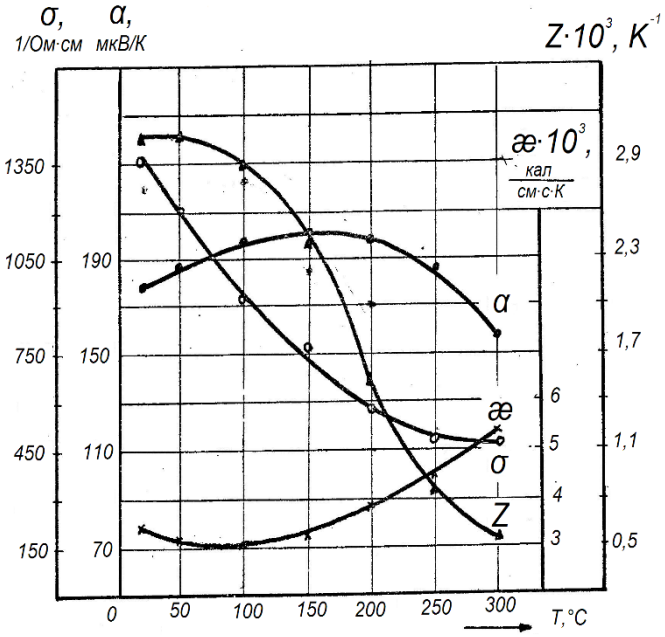

Fig.4. Change of thermoelectric properties of lead-alloyed material:

Table 3

Technological operation	σ, $Om^{-1} \cdot sm^{-1}$	α, mkV/K	$\alpha^2\sigma$, $mkVt/sm \cdot K^2$
Cool pressing Hot pressing under 300 With annealing under 390°C, 17 hours	1300 2600 1450	120 110 160	19 32 37
Cool pressing Hot pressing under 360 With annealing under 390°C, 17 hours	1300 2700 1550	120 120 160	19 39 40
Cool pressing Hot pressing under 400 With annealing under 390°C, 17 hours	1300 2650 1550	120 120 160	19 38 40

The data given in Table 3 shows that the parameters of the samples are rather weakly depend on the temperature of hot pressing.

The developed p-type material [3-4] as well as n-type half cells, the production technology of which is described in [1], can make an effective pair when creating thermal converters for the operating temperature range of $300 \div 500K$.

The work was partially financed by the grant ITD-12-56 (Fergana State University).

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