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The Variation of the Equilibrium of Chemical Reactions in the Process of $(Bi_2Te_3)(Sb_2Te_3)(Sb_2Se_3)$ Crystal Growing

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Abstract

Methods of computation for thermodynamic and differential thermal analysis were used to study the effect of the variation of the chemical equilibrium in the synthesis of $(Bi_2Te_3)_x(Sb_2Te_3)_y(Sb_2Se_3)_z$ (x+y+z=100%) in an ampoule on the characteristics of crystals grown by vertical zone-melting technique. Measurements of thermoelectric characteristics of reference samples were made. The case study of pseudo-binary systems (antimony telluride – antimony selenide, x=0; bismuth telluride – antimony selenide, y=0; bismuth telluride – antimony telluride, z=0) proves the following. As a result of some components turning to a gas-vapor phase, some unreacted original components may be found in a condensed phase. With a single-stage synthesis the products of side reactions of chemical interactions may be formed in the condensed phase. The case study of $(Bi_2Te_3)_{25}(Sb_2Te_3)_{72}(Sb_2Se_3)_3$; $(Bi_2Te_3)_{70}(Sb_2Te_3)_{25}(Sb_2Se_3)_5$; $(Bi_2Te_3)_{90}(Sb_2Te_3)_5(Sb_2Se_3)_5$ shows that both the synthesis temperature and the dopants greatly affect the thermodynamic equilibrium between the condensed and gas-vapour phases through the variation of the content of basic components in a condensed phase. On the basis of the performed research the recommendations on the synthesis conditions and crystal growing by zone melting technique are given.

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Introduction

In the production of the zone-melted $(Bi_2Te_3)_x(Sb_2Te_3)_y(Sb_2Se_3)_z$ material its synthesis conditions (free volume, pressure, zoning run rate, temperature gradient) can influence the variation of the equilibrium of chemical reactions and reciprocal solubility of complexes resulting from chemical reactions. In the development of the technology for the synthesis and zone melting for the commercial production it is rather important to have quantitative estimates of the variation of the equilibrium of chemical reactions depending on the synthesis conditions. Since the authors were quite aware of the task complexity at first they made such estimates for the following pseudobinary systems: Sb_2Te_3-Bi_2Te_3; Sb_2Te_3-Sb_2Se_3; Bi_2Te_3-Sb_2Se_3. For the sake of generalization the estimates were made for the pseudoternary systems, which are most often used in practice, such as

$(Bi_2Te_3)_{25}(Sb_2Te_3)_{72}(Sb_2Se_3)_3$;
$(Bi_2Te_3)_{70}(Sb_2Te_3)_{25}(Sb_2Se_3)_5$;
$(Bi_2Te_3)_{90}(Sb_2Te_3)_5(Sb_2Se_3)_5$.

Experimental Technique

The material was synthesized at a 1073K temperature in quartz ampoules evacuated to 0.1Pa. Elements such as Bi,Sb,Se,Te with a 99.99% of a primary element were used as a feedstock. The specific free volume of the material during the synthesis amounted to $0.000314 m^3/kg$. In the same ampoule the synthesized material underwent vertical zone melting at a 1113K temperature in two runs. Differential thermal analysis (DTA) was performed with a NTR-72 pyrometer, Pt-Pt/Rh thermocouple ignited and alumina (Al_2O_3) was used as a reference. The Stepanov's bulbs with a total sample weight of 1g filled with the material were evacuated to 0.1Pa. Both heating and cooling curves were recorded for samples. The maximum temperature ranged from 900 to 1,000^{0}C and the accuracy was $\pm 10^0$C. Thermodynamic analysis was performed with a help of a personal computer as described in a previous paper [1]. The maximum measurement error for conductivity and the Seebeck coefficient was $\pm 2\%$.

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Results and Discussion

The variation of conductivity and the Seebeck coefficient depending on the composition, allows to indirectly judge upon the nature of solubility of the basic product resulting from chemical interactions in the synthesis and zone melting. For instance,the gradual variation of thermoelectric characteristics, with the modification of the composition of samples of the Sb_2Te_3-Bi_2Te_3 section (Fig.1a) indicates the formation of continuous solid solutions. The continuity of the solution under high temperatures can be explained by the fact that the Sb_2Te_3 and Bi_2Te_3 complexes are isostructural. Both of them have a rhombohedral lattice and a layer structure. For the Sb_2Te_3-Bi_2Te_3 section the differential thermal analysis was performed of one sample with the following composition: 75mole% of Sb_2Te_3, 25mole% Bi_2Te_3. Fig.2a shows reference literature and experimental data for the compositions of Sb_2Te_3-Bi_2Te_3 section. The liquidus temperature here correlates with the liquidus temperature of the same composition indicated in [2], however, the crystallization of the solid solution goes in a more extended area that probably depends upon the variation of the rate of crystallization. Under high temperature the solid solution (δ) is formed however with the temperature lowering the retrograde melting of tellurium and the separation of liquid tellurium is observed, as it is also the case described in a previous study [2]. The crystallization of the alloy results in the separation of eutectic δ+Te+L under ≅400^{0}C. The excess tellurium does not probably influence the discontinuity of conductivity and the Seebeck coefficient in these solid solutions. Table 1 reflects the composition of condensed and gas-vapour phases before and after doping of the $(Sb_2Te_3)_{75}(Bi_2Te_3)_{25}$ sample with various dopants.

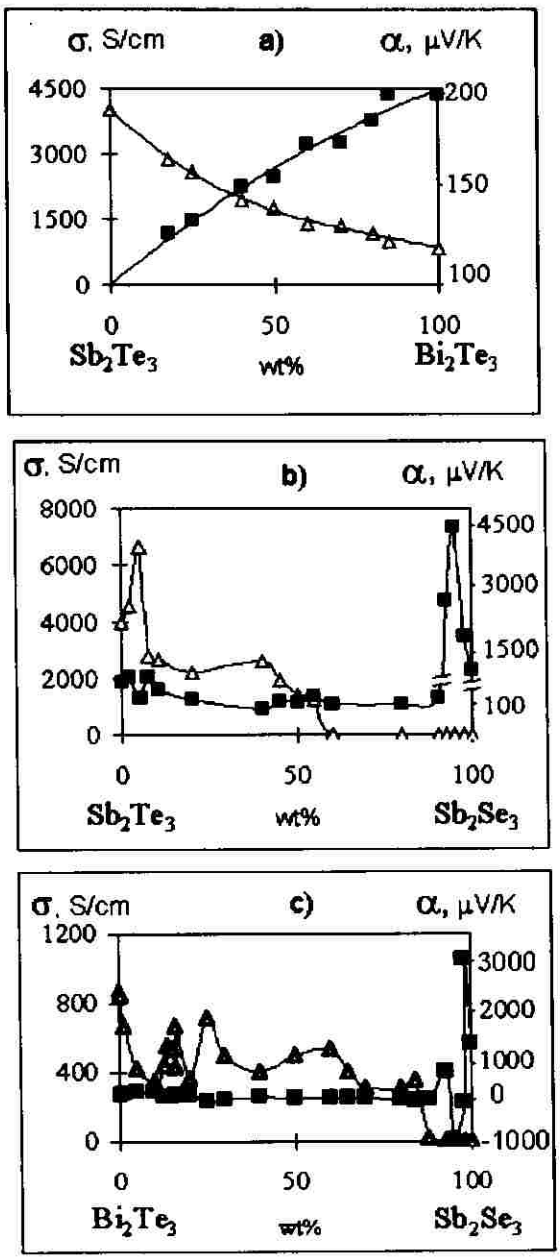

Fig.1. Composition dependence of conductivity (Δ –σ) and the Seebeck coefficient (■ - α) for:
a) Sb_2Te_3 and Bi_2Te_3;
b) Sb_2Te_3 and Sb_2Se_3;
c) Bi_2Te_3 and Sb_2Se_3.

Table 1. The composition of condensed and gas-vapour phases depending on the doping in the synthesis of $(Sb_2Te_3)_{75}(Bi_2Te_3)_{25}$.

Composition, wt%	No doping	2.5% Te	0.2% C_6Br_6	0.2% C_6Br_6	0.2%Te+ 0.2%C_6Br_6
T, K	1073	1073	1073	293	1073
Pressure, Pa	$1.47\cdot10^{2}$	$1.37\cdot10^{5}$	$2.97\cdot10^{4}$	0.33	$4.06\cdot10^{4}$
Condensed Phase					
Te	0	0	0	0.139	0
Sb	$1.66\cdot10^{-4}$	0	0	0	0
$SbBr_3$	0	0	0	0.262	0
Sb_2Te_3	70.114	68.404	69.751	69.751	69.613
Bi_2Te_3	29.883	29.154	29.811	29.824	29.754
C	0	0	$2.61\cdot10^{-2}$	$2.61\cdot10^{-2}$	$2.60\cdot10^{-2}$
Gas-Vapour Phase					
Br	0	0	$1.394\cdot10^{-6}$	0	$1.61\cdot10^{-6}$
Te	$1.12\cdot10^{-3}$	2.439	0.145	0	0.342
Sb	$4.65\cdot10^{-4}$	0	$3.77\cdot10^{-7}$	0	0
SbBr	0	0	$5.10\cdot10^{-3}$	0	$4.11\cdot10^{-3}$
$SbBr_3$	0	0	0.254	$2\cdot10^{-7}$	0.255
SbTe	$1.32\cdot10^{-4}$	$4.93\cdot10^{-5}$	$7.03\cdot10^{-5}$	0	$6.30\cdot10^{-5}$
Bi	$9.82\cdot10^{-6}$	0	$5.58\cdot10^{-7}$	0	$4.03\cdot10^{-7}$
BiBr	0	0	$6.59\cdot10^{-3}$	0	$5.31\cdot10^{-3}$
$BiBr_3$	0	0	$2.27\cdot10^{-3}$	0	$2.27\cdot10^{-3}$
BiTe	$3.31\cdot10^{-4}$	$1.23\cdot10^{-4}$	$1.76\cdot10^{-4}$	0	$1.58\cdot10^{-4}$

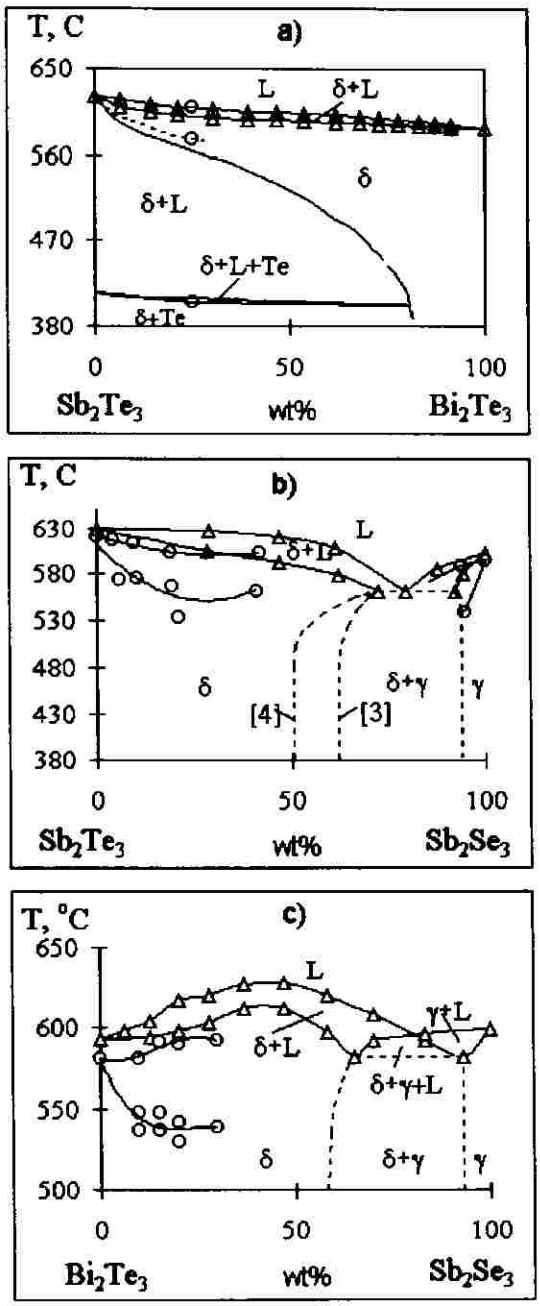

Fig.2. Shematic diagram of the section
a) Sb_2Te_3 - Bi_2Te_3 (Δ - reference data [2]; o – experimental data);
b) Sb_2Te_3 - Sb_2Se_3 (Δ - reference data [3,4]; o – experimental data).
c) Bi_2Te_3 - Sb_2Se_3 (Δ - reference data [5]; o – experimental data).

The performed thermodynamic analysis has shown, that in the non-doped composition the condensed phase contains a small quantity of free antimony, while according to the DTA results for the zone-melted sample the effect, which may result from antimony melting (≅630^{0}C),is not observed. It can be explained both by the insufficient sensitivity of the method and by the possible removal of antimony from the ingot in zone melting. At the same time the thermogram shows the effect corresponding to the eutectic (solid solution on the basis Sb_2Te_3(δ)+Te under 400^{0}C, which correlates with the data provided in [2]. As it follows from the results of the thermodynamic analysis (Table 1) the application of dopants (excess tellurium or haloid) excludes any presence of free antimony in the condensed phase. In case of haloid (Br) doping, free antimony occurs in a gas-vapour phase, and the content of tellurium in the latter is by an order of magnitude less than in the case of doping with the excess tellurium. With tellurium doping the proportion of basic components in the condensed phase does not change, while with bromine doping and combined bromine and tellurium doping it changes a higher relative concentration of bismuth telluride. Fig.1b shows the Sb_2Te_3-Sb_2Se_3 system composition dependence of conductivity and the Seebeck coefficient values one can come to a conclusion that the system forms limited solid solutions. For instance, the composition dependence of the Seebeck coefficient demonstrates two pronounced trends: the extensive growth of Seebeck coefficient and the area of gradual changing of the Seebeck coefficient value. With a 90% content of Sb_2Se_3 the value of the Seebeck coefficient does not exceed 65 μV/K, while with a 92.5% content of Sb_2Se_3 the value of the Seebeck coefficient amounts to 2,800 μV/K. With a 95% content of Sb_2Se_3 the value of the Seebeck coefficient grows to 4300 μV/K, with a 97.5% content of Sb_2Se_3 it falls to 2,040 μV/K, and with a 100% content of Sb_2Se_3 – to 1,350 μV/K. Such an extensive variation of the Seebeck coefficient value can be caused only by substantial deformation of the lattice resulting from the dissolution of the layer structure of Sb_2Te_3 in the Sb_2Se_3 chain structure. Large atoms of tellurium replace substantially smaller atoms of selenium in Sb_2Se_3 chains, thus making the chain structure unstable even with the dissolution of 7.5% of the layer of Sb_2Te_3. That is, the limitation of the homogeneous solubility occurs with 95% Sb_2Se_3 at the moment when the Seebeck coefficient reaches its maximum value. It is felt that with a 95% to 100% content of Sb_2Se_3 the solid solution is a monophase. With the decrease of

Sb_2Se_3 content from 90% the Seebeck coefficient value does not change radically, while the value of conductivity grows in a jumping manner with a 60% content of Sb_2Se_3 the chain structure of Sb_2Se_3 is completely dissolved in the layer structure of Sb_2Te_3, and the solid solution is a monophase. With a 60% to 95% content of Sb_2Se_3 the samples are doublephases, and in this case Sb_2Se_3 has a substantially influence on the value of conductivity. Thus the Sb_2Te_3-Sb_2Se_3 system forms limited solid solutions with the limits for zone-melted samples at 60% and 95% Sb_2Se_3.They do not actually differ from the limits of solubility given for synthesized samples in the paper [3] and do differ from the data in the paper [4]. This can be explained by the fact that the synthesis the conditions similar to equilibrium are provided, while zone-melting provides for non-equilibrium conditions for the formation of the material structure. And in this respect the samples described in the paper [4] can hardly be considered completely at equilibrium. For the Sb_2Te_3-Sb_2Se_3 section the differential thermal analysis of samples containing 95%,90%,80%,60% and 5% of Sb_2Te_3 was performed (Fig.2b). The portion of the diagram of the section meltability was constructed, which was contiguous mainly to Sb_2Te_3. It is shown, that in this zone solid solutions (δ) are formed, with the liquidus temperature being slightly (≈by 20°C) lower than the liquidus temperature given in the paper [3,4]. Crystallization of solid solutions goes in a more extended temperature zone it is also the case described in the papers [3,4]. It can be probably explained both by the difference in the rates of crystallization and by the difference in the purity of original components. For the compound with 80% of Sb_2Te_3 and 20% of Sb_2Se_3 at 530°C there was observed a complementary effect, to which the occurrence of very small quantities of SbTe can probably be contributed. The performed thermodynamic analysis of the Sb_2Te_3-Sb_2Se_3 system has shown (Table 2) that by basic components the composition of the condensed phase does not actually differ from the specified one, and it can be considered a solid solution of Sb_2Te_3 and Sb_2Se_3. Within the entire range of antimony selenide concentrations the condenced phase contains a small quantity of free antimony, which concentration changes insignificantly. However, the DTA, probably due to insufficient sensitivity to small concentrations of impurities, has not shown any effect of free antimony separation. The composition of the gas-vapour phase in the synthesis does not actually depend on the antimony telluride to antimony selenide ratio. Tellurium is the basic component of the gas-vapour phase. Fig.1c shows the Bi_2Te_3 and Sb_2Se_3 system dependence of conductivity and the Seebeck coefficient reasoning from the nature of the variation of these characteristics depending on the composition one can come to the conclusion that the system forms limited solid solutions. For instance, the composition dependence of the Seebeck coefficient demonstrates two pronounced effects: the area of gigantic jumps of the Seebeck coefficient value and the area of gradual changing of the Seebeck coefficient value. With an 88% content of Sb_2Se_3 the value of the Seebeck coefficient amounts to 65 μV/K, while with a 93% content of Sb_2Se_3 the value of the Seebeck coefficient dramatically grows to 685 μV/K, and with a 95% content of Sb_2Se_3 the Seebeck coefficient dramatically falls to a negative value of -870 μV/K. With a 98% content of Sb_2Se_3 the value of Seebeck coefficient again becomes positive and grows to 3,300 μV/K, and then it dramatically falls to 1,350 μV/K with a 100% of Sb_2Se_3. Such gigantic jumps of the Seebeck coefficient value can be caused only by substantial deformation of the lattice. It can be explained by the difference in the types of cells and in the types of the structure of complexes. For instance, Sb_2Se_3 has a rhomboid cell and a chain structure of Sb_2S_3 type. At same time, Bi_2Te_3 has a rhomboid cell and a layer structure of the Bi_2Te_2S type. With the dissolution

Table 2. The composition of condensed and gas-vapour phases in the Sb_2Te_3-Sb_2Se_3 synthesis (wt%).

Sb_2Te_3/ Sb_2Se_3	95/5	90/10	80/20	60/40	5/95
T, K	1073	1073	1073	1073	1073
Pressure, Pa	$1.81\cdot10^{2}$	$1.81\cdot10^{2}$	$1.81\cdot10^{2}$	$1.81\cdot10^{2}$	$1.81\cdot10^{2}$
Condensed Phase					
Sb	$5.13\cdot10^{-4}$	$4.71\cdot10^{-4}$	$4.82\cdot10^{-4}$	$5.13\cdot10^{-4}$	$5.03\cdot10^{-4}$
Sb_2Se_3	5.000	9.9996	19.9997	40.000	95.000
Sb_2Te_3	94.997	89.9993	79.9973	59.998	4.998
Gas-Vapour Phase					
Se	$1.14\cdot10^{-4}$	$7.08\cdot10^{-5}$	$7.08\cdot10^{-5}$	$7.08\cdot10^{-5}$	$1.14\cdot10^{-4}$
Te	$1.12\cdot10^{-3}$	$1.12\cdot10^{-3}$	$1.12\cdot10^{-3}$	$1.12\cdot10^{-3}$	$1.12\cdot10^{-3}$
TeSe	$2.86\cdot10^{-4}$	$2.86\cdot10^{-4}$	$2.86\cdot10^{-4}$	$2.86\cdot10^{-4}$	$2.86\cdot10^{-4}$
Sb	$4.66\cdot10^{-4}$	$4.66\cdot10^{-4}$	$4.66\cdot10^{-4}$	$4.66\cdot10^{-4}$	$4.66\cdot10^{-4}$
SbSe	$7.30\cdot10^{-5}$	$7.30\cdot10^{-5}$	$7.30\cdot10^{-5}$	$7.3\cdot10^{-5}$	$7.30\cdot10^{-5}$
SbTe	$7.93\cdot10^{-5}$	$1.32\cdot10^{-4}$	$1.32\cdot10^{-4}$	$1.32\cdot10^{-4}$	$7.93\cdot10^{-5}$

of the layer structure of Bi_2Te_3 large atoms of tellurium replace substantially smaller atoms of selenium in chains, thus making the chain structure unstable. Reasoning from the cessation of gigantic jumps of the Sebeck coefficient value, one can conclude that an 88% content of Sb_2Se_3 the process of the dissolution of the Bi_2Te_3 layer structure in Sb_2Se_3 chain structure discontinues. With further reduction of the Sb_2Se_3 content the dissolution process goes inversely, accompanied by the formation of a single phase zone: the Sb_2Se_3 chain structure is completely dissolved in the Bi_2Te_3 layer structure. In this case, small atoms of selenium relatively easily replace large atoms of tellurium and accordingly, Sb atoms replace Bi atoms. Reasoning from the composition dependence of conductivity one can conclude that with the content of Sb_2Se_3 exceeding 84% the value of conductivity begins to dramatically decrease. It indicates the predominant effect of Sb_2Se_3. It means that in the area ranging from 84% to 95% of Sb_2Se_3 content the double-phase ($\delta+\gamma$) zone is located. In the ranging from 95% to 100% there lies a single phase ($\delta+\gamma$) zone of gomogeneous dissolution of the Bi_2Te_3 layer structure in the Sb_2Se_3 chain structure. For the Bi_2Te_3-Sb_2Se_3 section the DTA was performed for four samples with 100 wt%, 95wt%, 85wt% and 80wt% of Bi_2Te_3, which were in the zone of solid solution with a rhomboid structure of tetradymite (δ). The effects correlating with the liberation of the eutectics of the Bi_2Te_{3-x} +Te solid solution, in contrast to the data given in the paper [5], do not appear in thermograms, however, some complementary effects in all three samples come into view and they appear both in heating curves and in cooling curves at 530-538°C. It can be probably attributed to the fact that in conditions of zone crystal growing a certain deviation from the Bi_2Te_3-Sb_2Se_3 section is observed. It is probable, that this temperature can be attributed to the occurrence of small quantities of the complementary phase, presumably BiTe (T_{melt}=540°C). Fig.2c shows our experimental curves within an interval of 80wt% - 100wt% of Bi_2Te_3. The course of experimental curves of the liquidus and solidus differs from the reference data given in [5], that can be presumably attributed both the occurrence of the complementary phase and to the changing of crystallization onditions. Thus, the Bi_2Te_3-Sb_2Se_3 system is characterized by limited solubility. The solubility limits of zone-melted samples lies within the range of 84% and 95% of Sb_2Se_3. They differ from the limits of solubility given in the reference data [5] for the samples syntheside in equilibrium conditions. To identify the influence of the synthesis flow sheet on the formation of end products in the condensed phase the thermodynamic calculations were made close to the boundaries between the first and the second zones of solubility for the composition containing 15wt% of Sb_2Se_3. The calculations were made for three options of the production of the Bi_2Te_3-Sb_2Se_3 solid solution at a 873K temperature and with the specific volume of the material in an ampoule amounting to 0.000314 m^3/kg. The first option implied the alloying of individual elements (Se,Te,Sb,Bi); the second option envisages the synthesis of Sb_2Se_3 and its eventual alloying with individual elements (Te,Bi); the third option implied separate processes for Bi_2Te_3 and Sb_2Se_3 production with the eventual alloying of both. As it can be seen from the Table 3, in case of a single-

Table 3. The influence of the synthesis flowsheet on the composition of the condensed and gas-vapour phases for 15 wt% Sb_2Se_3 – 85 wt% Bi_2Te_3.

Composition, wt%	Alloying Se+Te+Sb+Bi	Alloying Sb_2Se_3+Te+Bi	Alloying Sb_2Se_3+Bi_2Te_3
T, K	873	873	873
Pressure, Pa	597.2	89.9	2.38
Condensed Phase			
Sb_2Se_3	15.00889	14.99977	14.99978
Bi_2Se_3	0.01812	0.00001	0.00001
Bi_2Te_3	84.96973	84.99212	85.00018
Gas-Vapour Phase			
Se	$1.09\cdot10^{-5}$	$3.04\cdot10^{-7}$	$3.07\cdot10^{-7}$
Te	$3.11\cdot10^{-3}$	$6.62\cdot10^{-6}$	$6.71\cdot10^{-6}$
TeSe	$1.34\cdot10^{-4}$	$3.76\cdot10^{-6}$	$3.80\cdot10^{-6}$
Sb	0	$1.52\cdot10^{-6}$	$1.48\cdot10^{-6}$
SbSe	0	$4.62\cdot10^{-7}$	$4.61\cdot10^{-7}$
SbTe	$4.96\cdot10^{-7}$	$1.21\cdot10^{-6}$	$1.21\cdot10^{-6}$
Bi	0	$8.07\cdot10^{-3}$	$2.65\cdot10^{-6}$
BiSe	$1.26\cdot10^{-6}$	$3.06\cdot10^{-6}$	$3.05\cdot10^{-6}$
BiTe	$3.89\cdot10^{-6}$	$9.48\cdot10^{-6}$	$9.45\cdot10^{-6}$

stage synthesis the condensed phase contains a substantial quantity of the by-product of the chemical interaction, namely, bismuth selenide (Bi_2Se_3). Bismuth selenide is a n-type semiconductor (α= -300 μV/K). Its occurence may result in the formation of zones of the Seebeck coefficient sign reversal in microvolumes of the material. For instance, with the composition 85wt% Bi_2Te_3-15wt%Sb_2Se_3, which presents the material of a p-type, in case of a single-stage synthesis some small separate zones with n-type conductivity were discovered in zone-melted samples. In the two-stage or three-stage synthesis the quantity of by-products formed as a result of chemical interaction is less by three orders of magnitude. It can be explained by the fact that a two- or three-stage flow sheet the probability of antimony selenide participation in chemical reactions radically diminished, since this material is characterized by the highest enthalpy of the formation (ΔH^o_{293}):

$$2Sb+3Se \rightarrow Sb_2Se_3 - 127kJ/mole;$$
$$2Bi+3Se \rightarrow Bi_2Se_3 - 76.8kJ/mole;$$
$$2Sb+3Te \rightarrow Sb_2Te_3 - 57.72kJ/mole.$$

The samples of the Bi_2Te_3-Sb_2Te_3-Sb_2Se_3 system [6-8] present the material of the p-type. Donor doping, for instance haloid doping, allows to convert them into materials of n-type. Therefore, in thermodynamic calculations regarding the complexes (compositions) of the n-type due account was given to the presence of one of the most widely used dopants, namely, antimonous iodide (SbI_3). The best materials of the n-type are as follows $(Bi_2Te_3)_{90}(Sb_2Te_3)_5(Sb_2Se_3)_5$, $(Bi_2Te_3)_{70}(Sb_2Te_3)_{25}(Sb_2Se_3)_5$. The performed thermodynamic analysis of these compositions has shown (Tables 4 and 5) that the behavior of both n-type materials under consideration under different conditions of synthesis. So, the pressure rise in an ampoule by two orders of magnitude at a 1073K temperature does not influence the composition of the condensed phase. Therefore, it is technologically acceptable to perform the synthesis of a semi-conductive material both in evacuated ampoules and in the inert atmosphere (N_2). In the material synthesis it seems feasible to decrease temperature, since in this case the quantity of basic components (Te,Se,Sb,Bi) turning to the gas vapour phase is reduced. It makes smaller the difference between the composition of the synthesized material and the specified one. Besides, less intensive becomes the dissociation of molecules of the dopants, such as antimonous iodide SbI_3 and bismuth iodide BiI_3

Table 4. Composition of the condensed and gas-vapour phases depending on the synthesis temperature $(Bi_2Te_3)_{90}(Sb_2Te_3)_5(Sb_2Se_3)_5 + 0.09\%SbI_3$

Composition, wt%	Alloying Sb,Bi, Se,Te	Alloying Sb,Bi,Se,Te (in N_2)	Alloying Sb,Bi, Se,Te	Alloying Sb,Bi, Se,Te	Alloying Sb,Bi,Te, Sb_2Se_3
T, K	1073	1073	923	293	923
Pressure, Pa	$1.94\cdot10^{4}$	$2.49\cdot10^{6}$	$1.57\cdot10^{4}$	0.12	$1.57\cdot10^{4}$
Condensed Phase					
Te	0	0	0	$9.79\cdot10^{-5}$	0
BiI_3	0	0	0	0.106	0
Sb_2Se_3	3.235	3.235	3.237	3.238	3.237
Sb_2Te_3	21.169	21.169	21.163	21.164	21.162
Bi_2Te_3	75.349	75.349	75.362	75.492	75.362
Gas-Vapour Phase					
I	$1.02\cdot10^{-5}$	$1.00\cdot10^{-5}$	$1.43\cdot10^{-4}$	0	$1.43\cdot10^{-4}$
Se	$5.94\cdot10^{-4}$	$6.01\cdot10^{-4}$	$9.56\cdot10^{-5}$	0	$9.60\cdot10^{-5}$
Te	$6.41\cdot10^{-2}$	$6.41\cdot10^{-2}$	$6.24\cdot10^{-2}$	0	$6.29\cdot10^{-2}$
TeSe	$2.39\cdot10^{-3}$	$2.41\cdot10^{-3}$	$6.88\cdot10^{-4}$	0	$6.90\cdot10^{-4}$
Sb	$1.47\cdot10^{-6}$	$1.55\cdot10^{-6}$	0	0	0
SbI	$8.68\cdot10^{-6}$	$8.68\cdot10^{-6}$	$8.23\cdot10^{-6}$	0	$8.23\cdot10^{-6}$
SbI_3	0	0	$4.04\cdot10^{-3}$	0	$4.06\cdot10^{-3}$
SbSe	$4.29\cdot10^{-5}$	$4.42\cdot10^{-5}$	$8.71\cdot10^{-7}$	0	$8.70\cdot10^{-7}$
SbTe	$7.79\cdot10^{-5}$	$8.01\cdot10^{-5}$	$2.72\cdot10^{-6}$	0	$2.72\cdot10^{-6}$
Bi	7.60.10-7	7.86.10-7	0	0	0
BiI	$1.80\cdot10^{-1}$	$1.80\cdot10^{-1}$	$1.68\cdot10^{-1}$	0	$1.68\cdot10^{-1}$
BiI_3	0	0	$1.97\cdot10^{-3}$	10^{-7}	$1.98\cdot10^{-3}$
BiSe	$9.27\cdot10^{-5}$	$9.53\cdot10^{-5}$	$2.62\cdot10^{-6}$	0	$2.62\cdot10^{-6}$
BiTe	$1.95\cdot10^{-4}$	$2.00\cdot10^{-4}$	$9.59\cdot10^{-6}$	0	$9.58\cdot10^{-6}$

Table 5. Composition of the condensed and gas-vapour phases depending on the synthesis temperature $(Bi_2Te_3)_{70}(Sb_2Te_3)_{25}(Sb_2Se_3)_5 + 0.09\%SbI_3$

Composition, wt%	Alloying Sb,Bi, Se,Te	Alloying Sb,Bi,Se,Te (in N_2)	Alloying Sb,Bi, Se,Te	Alloying Sb,Bi, Se,Te	Alloying Sb,Bi,Te, Sb_2Se_3
T, K	1073	1073	923	293	923
Pressure, Pa	$1.94\cdot10^{4}$	$2.49\cdot10^{6}$	$1.57\cdot10^{4}$	0.12	$1.57\cdot10^{4}$
Condensed Phase					
Te	0	0	0	$1.87\cdot10^{-4}$	0
BiI_3	0	0	0	0.106	0
Sb_2Se_3	3.089	3.089	3.091	3.092	3.092
Sb_2Te_3	4.093	4.093	4.087	4.088	4.086
Bi_2Te_3	92.568	92.569	92.584	92.712	92.584
Gas-Vapour Phase					
I	$1.01\cdot10^{-5}$	$1.00\cdot10^{-5}$	$1.42\cdot10^{-4}$	0	$1.42\cdot10^{-4}$
Se	$5.91\cdot10^{-4}$	$5.98\cdot10^{-4}$	$9.51\cdot10^{-5}$	0	$9.55\cdot10^{-5}$
Te	$6.34\cdot10^{-2}$	$6.34\cdot10^{-2}$	$6.17\cdot10^{-2}$	0	$6.22\cdot10^{-2}$
TeSe	$2.37\cdot10^{-3}$	$2.40\cdot10^{-3}$	$6.84\cdot10^{-4}$	0	$6.87\cdot10^{-4}$
Sb	$1.49\cdot10^{-6}$	$1.57\cdot10^{-6}$	0	0	0
SbI	$8.68\cdot10^{-6}$	$8.68\cdot10^{-6}$	$8.24\cdot10^{-6}$	0	$8.23\cdot10^{-6}$
SbI_3	0	0	$4.01\cdot10^{-3}$	0	$4.03\cdot10^{-3}$
SbSe	$4.30\cdot10^{-5}$	$4.42\cdot10^{-5}$	$8.72\cdot10^{-7}$	0	$8.71\cdot10^{-7}$
SbTe	$7.80\cdot10^{-5}$	$8.02\cdot10^{-5}$	$2.72\cdot10^{-6}$	0	$2.72\cdot10^{-6}$
Bi	$7.63\cdot10^{-7}$	$7.89\cdot10^{-7}$	0	0	0
BiI	$1.80\cdot10^{-1}$	$1.80\cdot10^{-1}$	$1.69\cdot10^{-1}$	0	$1.68\cdot10^{-1}$
BiI_3	0	0	$1.96\cdot10^{-3}$	10^{-7}	$1.97\cdot10^{-3}$
BiSe	$9.28\cdot10^{-5}$	$9.54\cdot10^{-5}$	$2.62\cdot10^{-6}$	0	$2.62\cdot10^{-6}$
BiTe	$1.95\cdot10^{-4}$	$2.01\cdot10^{-4}$	$9.60\cdot10^{-6}$	0	$9.59\cdot10^{-6}$

resulting from the exchange reaction, thus allowing to exclude the presence of free antimony and bismuth in the gas-vapour phase. The use of preliminary synthesized antimony selenide (Sb_2Se_3) in the synthesis of the specified material does not cause any variation of the composition of the condensed and gas-vapour phase. The presence of substantial quantities of antimony telluride (Sb_2Te_3) in both specified compositions of the n-type material excludes any probability for the formation of bismuth selenide (Bi_2Se_3) resulting in the variation of the composition of the condensed and gas-vapour phases. The best material of the p-type is $(Bi_2Te_3)_{25}(Sb_2Te_3)_{72}(Sb_2Se_3)_3$ doped with excess Te. The performed thermodynamic analysis of this composition has shown (Table 6) that its behaviour in the synthesis is similar to that of a similarly

Table 6. Composition of the condensed and gas-vapour phases depending on the doping in the synthesis of $(Bi_2Te_3)_{25}(Sb_2Te_3)_{72}(Sb_2Se_3)_3$

Composition, wt%	No doping	2.5%Te	0.2%C_6Br_6	0.2%C_6Br_6	0.2%Te+ 0.2%C_6Br_6
T, K	1073	1073	1073	293	1073
Pressure, Pa	$2.25\cdot10^{2}$	$1.37\cdot10^{5}$	$2.97\cdot10^{4}$	0.33	$4.06\cdot10^{4}$
Condensed Phase					
Te	0	0	0	0.139	0
Sb	$4.18\cdot10^{-4}$	0	0	0	0
$SbBr_3$	0	0	0	0.262	0
Sb_2Se_3	2.165	2.093	2.157	2.161	2.150
Sb_2Te_3	67.753	66.125	67.396	67.396	67.264
Bi_2Te_3	30.079	29.345	30.007	30.020	29.950
C	0	0	$2.60\cdot10^{-2}$	0.026	$2.60\cdot10^{-2}$
Gas-Vapour Phase					
Br	0	0	$1.38\cdot10^{-06}$	0	$1.60\cdot10^{-06}$
Se	$7.08\cdot10^{-3}$	$3.78\cdot10^{-3}$	$8.81\cdot10^{-4}$	0	$1.37\cdot10^{-3}$
Te	$1.12\cdot10^{-3}$	2.414	0.139	0	0.334
Sb	$4.66\cdot10^{-4}$	0	$3.88\cdot10^{-7}$	0	0
TeSe	$2.86\cdot10^{-4}$	$1.48\cdot10^{-2}$	$3.53\cdot10^{-3}$	0	$5.49\cdot10^{-3}$
SbBr	0	0	$5.16\cdot10^{-3}$	0	$4.14\cdot10^{-3}$
$SbBr_3$	0	0	0.2540	$2\cdot10^{-7}$	0.2546
SbSe	$7.30\cdot10^{-5}$	$2.72\cdot10^{-5}$	$3.89\cdot10^{-5}$	0	$3.49\cdot10^{-5}$
SbTe	$1.32\cdot10^{-4}$	$4.93\cdot10^{-5}$	$7.06\cdot10^{-5}$	0	$6.32\cdot10^{-5}$
Bi	$9.83\cdot10^{-6}$	0	$5.66\cdot10^{-7}$	0	$4.07\cdot10^{-7}$
BiBr	0	0	$6.66\cdot10^{-3}$	0	$5.35\cdot10^{-3}$
$BiBr_3$	0	0	$2.27\cdot10^{-3}$	0	$2.27\cdot10^{-3}$
BiSe	$1.58\cdot10^{-4}$	$5.87\cdot10^{-5}$	$8.40\cdot10^{-5}$	0	$7.53\cdot10^{-5}$
BiTe	$3.31\cdot10^{-4}$	$1.23\cdot10^{-4}$	$1.77\cdot10^{-4}$	0	$1.58\cdot10^{-4}$

widely used in practice the $(Bi_2Te_3)_{25}(Sb_2Te_3)_{75}$ material doped with excess Te (Table 1) both in terms of pressure of the gas-vapour phase in an ampoule, and in terms of the variation of the content of its components depending on the type of dopants. The difference is in the presence of a relatively small quantity of free selenium and its complexes as compared with tellurium in the synthesis of pseudo-ternary composition. In the synthesis of non-doped material the condensed phase of both compositions contains small quantities of free antimony. Inclusion of dopants in both material compositions completely excludes any presence of free antimony in the condensed phase. With the excess-Te doping of both compositions tellurium most intensively turns to the gas-vapour phase thus providing for the maximum pressure in an ampoule. Bromine doping also results in the growth of free tellurium content in the gas-vapour phase due to the formation of antimony and bismuth bromides. Dissociation of antimony determines the presence of very small quantities of free antimony in gas-vapour phase. In case of combined excess tellurium and bromine doping this process is inhibited and the gas-vapour phase does not contain free antimony. Doping the pseudo-ternary composition both with tellurium and with bromine results in the variation of the relative concentrations of basic components in the condensed phase. The application of tellurium results in the increase of the relative concentration of antimony and bismuth tellurides. With bromine doping the relative concentration of antimony telluride slightly decreases and that of bismuth telluride slightly increases. Combined tellurium and bromine doping does not actually change the concentration of antimony telluride and slightly increases that of bismuth telluride.

Conclusions

Limited solid solutions (Bi_2Te_3-Sb_2Se_3, Sb_2Te_3-Sb_2Se_3) after zone-melting are characterized by gigantic jumps of the Seebeck coefficient value on the boundary of solid solutions. The continuous solid solutions (Bi_2Te_3-Sb_2Te_3) after zone-melting are characterized by the gradual variation of the Seebeck coefficient for the entire range of concentrations.

In the limited solid solutions (Bi_2Te_3-Sb_2Se_3, Sb_2Te_3-Sb_2Se_3) after zone-melting liquidus and solidus curves differ from those in synthesized equilibrium materials.

The synthesis flow sheet (single- or multi-stage) may influence the formation of end products after zone-melting.

The liquid condensed phase in evacuated ampoules at the synthesis temperature does not contain a

halogen dopant. With the temperature lowering the halogen dopant enters the solid condensed phase.

The variation of the equilibrium of chemical reactions must be taken into account in the process of zone-melted material production.

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