Physical-Chemical Characterization of the Processes Occurring in Extrusion and Their Effect on Phase Diagram and Thermoelectric Properties of the Materials in Bi_2Te_3–Bi_2Se_3 and Sb_2Te_3–Bi_2Te_3 Systems

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Abstract

By methods of differential thermal and X-ray-phase analysis it has been proved that after the implementation of the process of hot extrusion of Bi_2Te_3-Bi_2Se_3 solid solutions, in the fusibility diagram for 33.3 %mole Bi_2Se_3 compound, below the solidus line, Bi_2Te_2Se compound is not formed. In the samples of the material containing up to 25 mole% of Bi_2Se_3 the presence of excess tellurium is observed. The effect is described of the gaseous medium (hydrogen, inert gas, air) on thermoelectric properties of extruded rods. Thermoelectric properties of non-doped extruded compositions of Sb_2Te_3-Bi_2Te_3 system have been investigated and the recommendations have been produced on their application in cooling modules in the temperature range from 100 K to 340 K.

1. Introduction

RoHS and WEE EC Directives of 27 January 2003 [1] restricted the use of certain hazardous substances in production processes. The need became pressing to give up using such conventional dopants as lead (Pb), cadmium compounds (e.g., $CdCl_2$) mercury compounds (e.g., Hg_2Cl_2). This resulted in the necessity of more detailed research into the effect of different actions (hot extrusion, zone melting, etc.) on physical-chemical processes and thermoelectric properties of the most efficient non-doped materials for cooling devices.

2. Test methods and procedures

Bi, Sb, Te and Se of ~99.99% purity served original materials for the production of thermoelectric (TE) material samples. The synthesized material ingots were crushed to a grain size less than 0.5 mm. The resulting powder was pressed to form billets of 35 mm diameter. After annealing the material underwent the process of hot extrusion with the resulting 10 mm diameter rods.

The maximum error of Seebeck coefficient (α) measurements was ±2%. The maximum error of the figure of merit (Z) measurements was ±3%. Differential-thermal analysis (DTA) was performed with an HTP-72 pyrometer. X-ray phase analysis (RFA) was performed by taking diffractograms with DRON-1. The parameters of lattice were specified by least-squares method with the accuracy of ±0.004-0.007 Å. Thermodynamic calculations were performed with the use of methods and procedures described in [2].

3. Results and discussion

3.1. Investigation of the characteristics of Bi_2Te_3-Bi_2Se_3 system materials

The parameters of the lattice of samples of (0-60) % mole Bi_2Se_3 composition show, that they (Table 1) decrease over this region, proving the presence of solid solutions.

Table 1. Variation of the lattice (a, c) parameters depending on the composition of solid solutions in Bi_2Te_3-Bi_2Se_3. system for extruded and zone-melted samples.

Bi_2Se_3, % mole	a, Å	c, Å	Phase composition
Hot extrusion			
0	4.393	30.573	Bi_2Te_3 (β)
6	4.372	30.418	β
10	4.359	30.384	β
15	4.343	30.291	β
20	4.344	30.282	β
25	4.329	30.219	β
33.3	4.311	29.970	β
40	4.289	29.890	β
60	4.244	29.607	β
Zone melting [3]			
0	4.459	30.393	Bi_2Te_3 (β_1)
6	4.451	30.317	β_1
10	4.445	30.275	β_1
15	4.423	30.089	$\beta_1+\gamma$
20	4.403	29.992	$\beta_1+\gamma$
33.3	4.361	29.719	Bi_2Te_2Se (γ)

In addition to that the parameters of the composition (33.3 mole% Bi_2Se_3) lattice differ from those of the compound. For the sake of comparison the data are given for zone-melted samples [3]. The difference in parameters of the lattice is explained by the use of different methods of material synthesizing. Zone-melted samples were actually in the state of equilibrium. The variation of the composition is typical of extruded samples due to the fact that in addition to the presence of solid solutions (β) small amounts of tellurium and probably of bismuth oxide are observed.

It must be noted that conditions for the production of our samples significantly differ from those for the production of samples in the state of equilibrium. For instance, most published works describe the cases, when Bi_2Te_2Se compound was produced either by way of very slow cooling from fusing temperature, or by way of annealing at nearly demising point of 500°C. The presence of the compound, by data from [3], was characterized by the presence of peaks on electrical properties of samples (Fig. 4, curve 1), while the absence of these on our samples (as it is shown below) coincides with RFA data, thus proving the absence of the compound.

Fig. 1 shows a part of the fusibility diagram of Bi_2Te_3-Bi_2Se_3 section in a range to 60 mole% Bi_2Se_3.

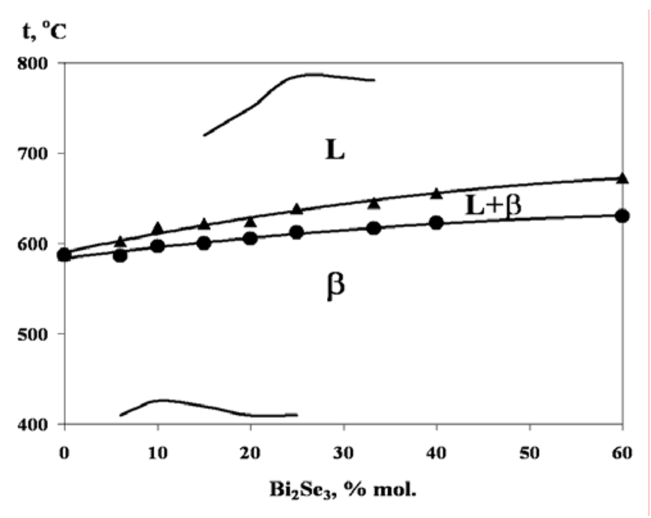

Fig.1. A fragment of the phase diagram of Bi_2Te_3-Bi_2Se_3 section for extruded samples

According to the test results, the section contains a number of continuous solid solutions. The temperatures of solidus and liquidus for extruded samples within the error of ±5°C correlates with the data for zone-melted samples [3]. However, in contrast to zone-melted samples, on the fusibility diagram, below the solidus line for 33.3 mole% Bi_2Se_3 compound there are actually only the lines of Bi_2Te_3 (β)-based solid solution. Low-intensity lines of Bi_2Te_2Se compound with hkl 0.0.9, 0.0.12, 0.1.11, 0.0.18, etc. making it different from β are not observed. Presumably, below the solidus line in conditions of our experiment no ordering and formation of Bi_2Te_2Se compound occur, rather, a continuous range of solid solution is observed there.

Changing of the Bi_2Te_3-Bi_2Se_3 section fusibility diagram is explained by the effect of pressure and high temperature in an open (non-evacuated) system. According to the literature data [4] at high pressure Bi_2Te_3 and Bi_2Se_3 compounds undergo polymorphous transition. In our conditions this transition is reversible and the structure of solid solutions after cooling does not change.

In the samples of the materials containing up to 25% of Bi_2Se_3 the presence of excess tellurium is observed. This is proved by significant thermal effects occurring at 410-426°C and being responsible for the eutectics of Bi_2Te_3 + Te (Fig. 2). According to the literature data [5], its fusion point is in the region of 412°C.

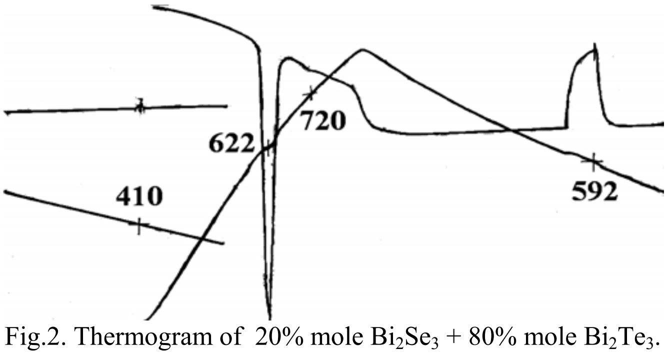

Fig.2. Thermogram of 20% mole Bi_2Se_3 + 80% mole Bi_2Te_3.

It is known [6] that Bi_2Te_3 evaporation in a temperature range of 700-1000°K is accompanied by the dissociation of $Bi_2Te_3 \rightarrow 2BiTe + \frac{1}{2} Te_2$ pattern. Evaporation of solid Sb_2Te_3 and Bi_2Se_3 goes according to a similar reaction pattern. Presumably, this dissociation may occur also due to crushing of the synthesized material as a result of local heating-ups. Furthermore, as is proved by thermodynamic calculations, the dissociation of bismuth telluride will be first and foremost (Fig. 3).

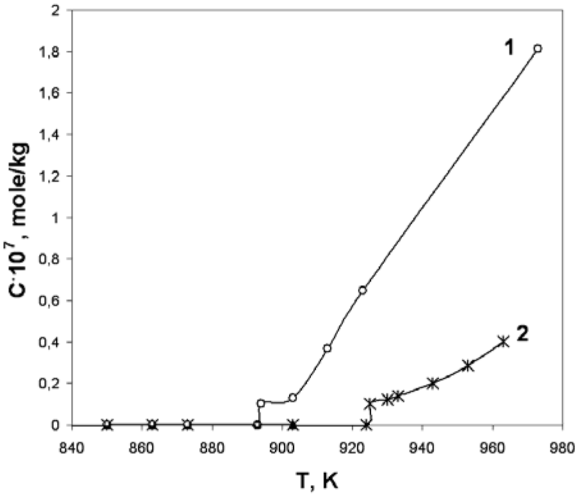

Fig.3. Temperature dependencies of the variation of concentrations of Bi_2Te_3 and Bi_2Se_3 compound dissociation products: 1 – BiTe; 2 – BiSe

The temperature at the start of dissociation at normal pressure for Bi_2Te_3 is 894 K, and for Bi_2Se_3 it is 925 K.

Furthermore, with samples within a range of Bi_2Se_3 15-33.3 mole% in the process of both heating and cooling some low heat effects are observed in a temperature range of 720-785° C that can be explained by the formation of additional compounds, such as, bismuth oxides, oxytellurides or oxyselenides. Their identification has proved to be problematic. One can only presume that in the process of crushing in the presence of air and in the course of the subsequent crushed material briquetting (pressing of billets) a certain amount of air is retained in the material. In the course of the subsequent annealing of billets (520° C) oxygen contained in the air interacts with $2Bi_2Te_3 + 3O_2 \rightarrow 2Bi_2O_3 + 6Te$; $2Bi_2Se_3 + 3O_2 \rightarrow 2Bi_2O_3 + 6Se$ material.

The liberated free tellurium in extrusion of Bi_2Te_3-Bi_2Se_3 compounds with 0-14 mole% Bi_2Se_3 serves a donor-type dopant ("donor effect"). The material acquires n-type conductivity (Fig. 4).

It must be noted that the zone-melted material of the same compositions has a p-type conductivity [3].

The figure of merit of the extruded non-doped material is the highest in the region of 6%mole and 20 % mole Bi_2Se_3 (Fig.5).

The effect was investigated of the gaseous medium on thermoelectric properties of the material. For instance, in the course of annealing of $(Bi_2Te_3)_{94}(Bi_2Se_3)_6$ material for extrusion in atmospheric oxygen, in addition to reducing reaction ($Bi_2O_3 + 3H_2 \rightarrow 2Bi + 3H_2O$) the formation of hydrogen telluride ($Te + H_2 \rightarrow H_2Te$ takes place. This causes the decrease of free tellurium concentration as a donor, that is accompanied by significant reduction of electrical conductivity and accordingly, by the increase of Seebeck coefficient of the extruded rods (Table 2).

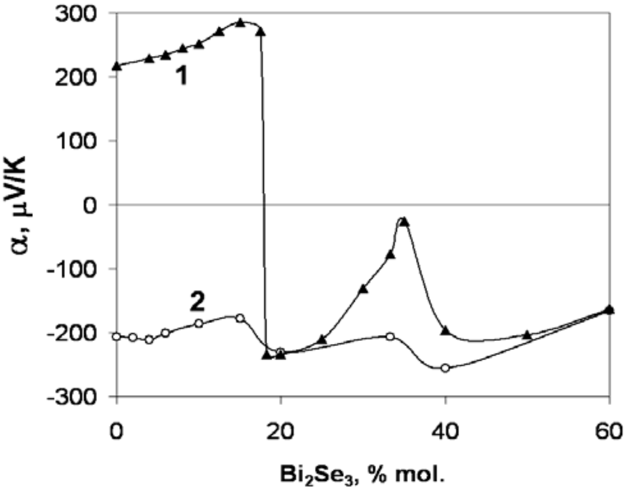

Fig.4. Seebeck coefficient dependence on the composition in Bi_2Te_3-Bi_2Se_3 section of extruded (2) and zone-melted [3] (1) samples.

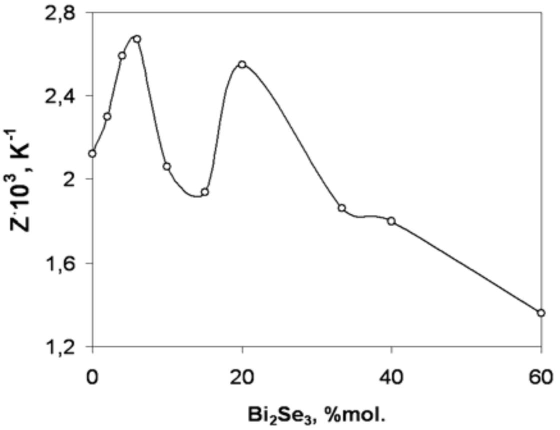

Fig. 5. Dependence of the extruded material thermoelectric figure of merit on the composition in Bi_2Te_3-Bi_2Se_3 section

Table 2. Gaseous medium effect on thermoelectric properties

Gaseous medium for crushing and pressing of billets	Gaseous medium for annealing of billets (520°C, 10 hours)	σ, S/cm	α, μV/K
Air	Argon	1,006	-201.7
Nitrogen	Argon	526	-237.7
Air	Hydrogen	471	-253.6

In the course of annealing of extruded rods (385° C, 10 h) the intensive liberation is observed of hydrogen telluride dissolved in the rods, and this causes the swelling of rods.

3.2. Investigation of characteristics of Sb_2Te_3-Bi_2Te_3 system materials

For $(Bi_2Te_3)_x(Sb_2Te_3)_{1-x}$ compositions within the interval x= 0-1.0 the value of Seebeck coefficient gradually increases with the growth of Bi_2Te_3 concentration to 30% mole. Then, a radical inversion of the sign from positive (+296 μV/K) to negative (-206 μV/K) values is observed (Fig. 6).

Such behaviour of the Seebeck coefficient is explained by the temperature dependences of dissociation product concentrations (Fig. 7).

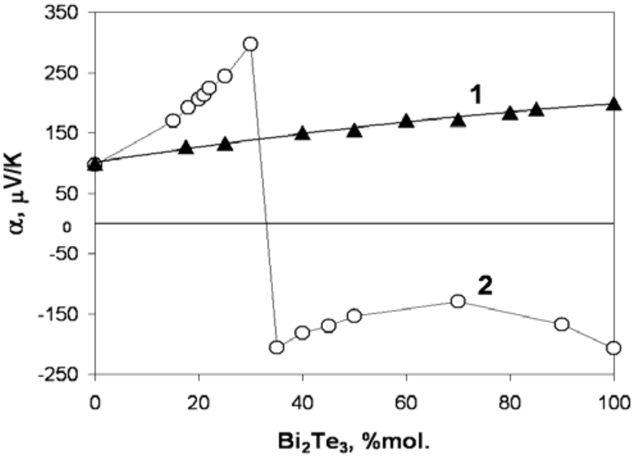

Fig.6. Dependence of Seebeck coefficient on the composition in Sb_2Te_3-Bi_2Te_3 section for extruded (2) and zone-melted [7] (1) samples

With the growth of Bi_2Te_3 concentration the share of free tellurium increases, and the concentration of donors grows respectively. In Bi_2Te_3 30% mole point the concentration of donors becomes equal to the concentration of acceptors, and with further growth of Bi_2Te_3 concentration the material acquires n-type conductivity.

It must be noted that the zone-melted material has a p-type conductivity within a Bi_2Te_3 range of 0-100 mole % [7] (Fig.6).

The temperature at the start of dissociation at normal pressure for Bi_2Te_3 is 894 K, and for Bi_2Se_3 its is 918 K.

For application in cascade cooling modules in a 15-50 mole% Bi_2Te_3 range three regions must be identified (Fig. 8).

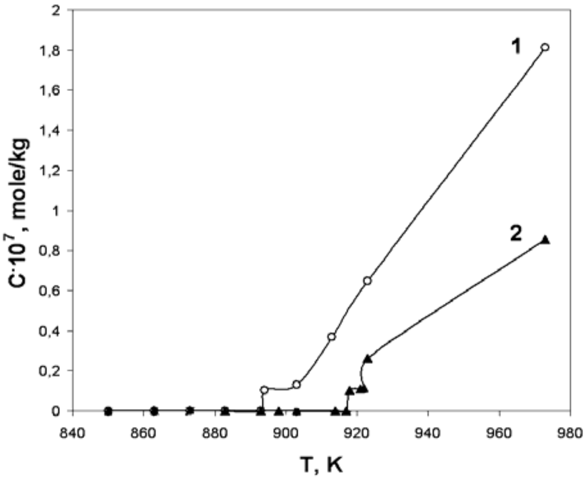

Fig.7. Temperature dependences of the variation of concentrations of Bi_2Te_3 and Sb_2Te_3 compound dissociation products: 1 – BiTe; 2 – SbTe.

For modules operating in a 200-340 K range, the highest figure of merit is typical of non-doped compositions within a range of x=0.19-0.23 (Fig.9).

For modules operating in a 150-200 K range, the highest figure of merit is typical of compositions within a range of x=0.23-0.27. For modules operating in a 100-150 K range, of the highest figure of merit are compositions within a range of x=0.27-0.30 (Fig.10).

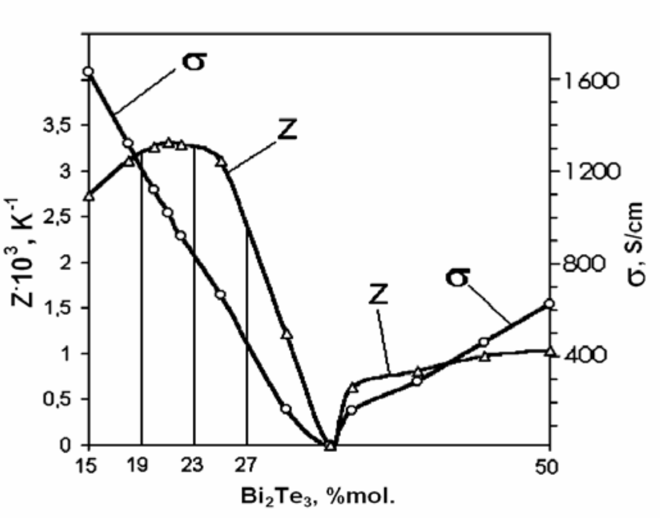

Fig. 8. Dependence of thermoelectric figure of merit (Z) and electrical conductivity (σ) at 25°C on the composition of Sb_2Te_3-Bi_2Te_3.system.

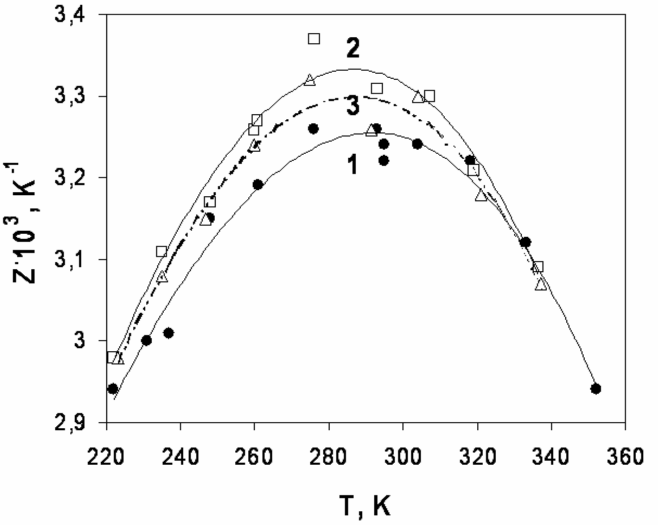

Fig.9. Temperature dependence of $(Bi_2Te_3)_x(Sb_2Te_3)_{1-x}$ figure of merit
1 - x=0.20; 2 – x=0.21; 3 – x=0.22.

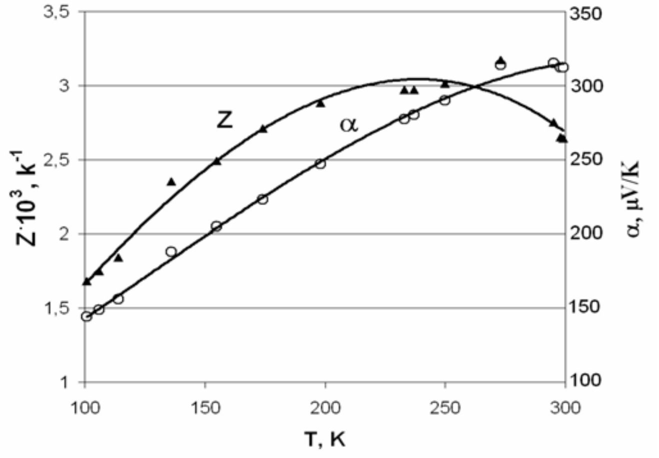

Fig.10. Temperature dependences of Seebeck coefficient (α) and thermoelectric figure of merit (Z) for 66.5% Sb_2Te_3 + 28.5% Bi_2Te_3 + 5% Sb_2Se_3 composition.

Acknowledgments

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Conclusions

After implementation of the process of hot extrusion of Bi_2Te_3-Bi_2Se_3 solid solutions the compound Bi_2Te_2Se is not observed in the fusibility diagram.

In the extruded samples containing up to 24 mole% Bi_2Se_3 the presence is observed of excess tellurium having a doping effect on the material.

Thermodynamic calculations show temperature dependences of the products resulting from the dissociation of Bi_2Te_3, Bi_2Se_3, Sb_2Te_3 compounds.

The figure of merit of the n-type extruded material is the highest in the region of 6% mole Bi_2Se_3.

For cooling modules it is recommended to use extruded material $(Bi_2Te_3)_x(Sb_2Te_3)_{1-x}$, as p-legs, where x=0.27-0.30 for a temperature range of 100-150 K; x=0.23-0.27 for a temperature range of 150-200 K; x=0.19-0.23 for a temperature range of 200-340 K.

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