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MELT SPINNING AS A PROMISING METHOD FOR PREPARATION OF BISMUTH AND ANTIMONY TELLURIDE SOLID SOLUTION MATERIALS

This work is concerned with fabrication and study of pressed fine-crystalline materials based on p-type $Bi_{0.5}Sb_{1.5}Te_3$ solid solution of melt spun powder. The effect of melt spinning conditions (temperature and disc rotation rate, purity of inert gas used in the chamber) on the dimensions and morphology of powders, the structure of hot-pressed samples and their thermoelectric properties has been studied. Mechanical properties of samples obtained by different methods were studied during compression and bending tests. Thermoelectric properties of materials, namely thermoelectric coefficient, electrical conductivity and thermal conductivity were measured at room temperature and in the range of 100 to 700 K. For samples pressed of melt spun powder the maximum value of thermoelectric figure of merit ZT was ~ 1.3 , whereas for materials prepared by other methods ZT does not exceed 1.1. It became possible due to considerable reduction of lattice component of thermal conductivity and increase of thermoelectric coefficient of samples obtained by melt spinning method.

Key words: bismuth and antimony telluride solid solutions, melt spinning, scanning electron microscopy, mechanical properties, thermoelectric properties.

Introduction

Thermoelectric power converters are widely used in a variety of science and technology fields. Particularly topical is the problem of thermoelectric device efficiency improvement. Apart from traditional methods for improving thermoelectric material efficiency, such as doping and a search for novel materials, of large interest is a research on the effect of structure of known thermoelectric materials on their thermoelectric properties, where considerable increase of thermoelectric figure of merit ZT is possible due to their nanotexturing. The physics behind such ZT increase are changes in the energy spectrum of charge carriers and phonons in nanostructured materials. A number of researchers [1-5] think that ZT increase of nanostructured materials can be achieved due to the following mechanisms: additional phonon scattering at the grain boundaries, tunnelling of carriers between nanostructured elements and energy filtration of carriers on potential barriers between nanograins. Additional phonon scattering at the grain boundaries with a slight reduction of charge carrier mobility occurs in the case when grain size is less than the mean free path of electrons, which means less than 10 to 20 nm. According to theoretical estimates, the probability of tunneling thermoelectric material electrons becomes rather large with the gaps between grains of the order of several nanometers. In so doing, phonons cannot tunnel through vacuum gap and no longer participate in thermal conductivity processes.

In the nanostructured materials the structure of electron bands can change and energy filtration of carriers may occur, when high-energy charge carriers will overcome the boundary between nanograins, practically without being scattered. Reduced probability of scattering at the nanograin boundaries with increasing energy of carriers leads to thermoEMF increase. Theory predicts the increase in ZT of nanosized thermoelectric material up to 3.5, provided all three mechanisms of figure of merit increase are realized [1-5]. To this date, the bulk thermoelectric materials with grain size 10 to 20 nm and vacuum gaps between grains 1 to 2 nm have not been obtained yet. There are experimental works reporting on fine-dispersed materials with $ZT = 1.2 - 1.4$ [6-9].

Materials based on solid solution of Bi_2Te_3 - Sb_2Te_3 system are used to manufacture p -type legs for various purpose thermoelectric coolers and generators. This work employs a method of manufacturing fine-crystalline pressed samples from the above solid solution of powder prepared by melt spinning. This method has been elaborated and used to obtain quickly quenched powders and thin stripes of amorphous, composite and magnetic metal alloys [10]. Thermoelectric materials based on solid solutions of antimony and bismuth chalcogenides were first obtained by spinning method in Sukhumi Physics and Technical Institute, which was reported in 1988 in Uzhgorod at VII All-Union Conference "Chemistry and Technical Application of Chalcogenides" [11-13]. Papers have appeared recently which show the promising character of using this method to obtain nano-sized powders [14-17] of the above indicated materials. A combination of melt spinning and arc plasma powder sintering methods was used to obtain materials of bismuth and antimony chalcogenide solid solutions of the n -type with thermoelectric figure of merit $ZT \sim 1.0$ [14] and p -type with $ZT \sim 1.5$ [16, 17].

Experimental procedure

Samples of bismuth and antimony telluride solid solution were obtained by hot pressing from powder prepared by melt spinning technique. This technique lies in obtaining fine particles of alloys by superfast cooling the melt on the surface of rotating cold disc. A pre-alloyed ingot was heated to temperature 30 – 50 K exceeding material melting point. A flush of melt of diameter 1 – 1.5 mm was poured on the surface of water-cooled disc rotating at the rate of 900 to 1500 rpm, which assured cooling rate $\sim 10^6$ K/s. The process took place in argon atmosphere at excess pressure 0.2 MPa. From the obtained powders briquettes were prepared by cold pressing which were subsequently subject to hot pressing in the air or in vacuum at temperature 350 °C and pressure 5 MPa. The samples were annealed in different media: inert gas atmosphere, hydrogen current and air from 4 to 24 hours at 280, 300 and 350 °C.

The morphology and size of particles of powder obtained by melt spinning and the structure of cleavages of hot-pressed samples was studied on scanning electron microscope (SEM) (LEO 1420). The X -ray diffraction study of powders was conducted on DRON-UM diffractometer ($Cu K_\alpha$ -radiation) with a graphite monochromator. Qualitative and quantitative X -ray phase analysis of powders obtained by melt spinning was conducted with the use of XRAYAN program and the PDF (The Power Diffraction File) international database. Mechanical properties (strength limits, deformation ratio, elongation) of samples having identical dimensions and shape, obtained by different methods, were studied under compressive and bending strains at room temperature on INSTRON-5800 setup at strain rate $v_{strain} \sim 1$ mm/min. Thermoelectric properties of samples: thermoelectric coefficient α , electric conductivity σ and thermal conductivity κ were measured at room temperature and in the range of 100 to 700 K. The lattice component of thermal conductivity was determined as $\kappa_p = \kappa - \kappa_{el}$, where $\kappa_{el} = A\sigma T$ (A is the Lorentz number, T is the ambient temperature). The thermoelectric figure of merit of materials was calculated from the formula $Z = \alpha^2 \sigma / \kappa$.

Discussion of results

The powders of bismuth and antimony telluride solid solution were obtained under different conditions of melt spinning. While the powders prepared according to traditional technology of ingot grinding in the ball mill are characterized by considerable oxidability in the air, no oxides were observed on the surface of particles obtained by melt spinning method. Powder compositions were analyzed using X-ray phase analysis. It was established that powders retain their crystalline structure, and their compositions in the main components meet the compositions of the initial charge. The X-ray diffraction pattern of one of the powders and its indexing results are given in Fig. 1.

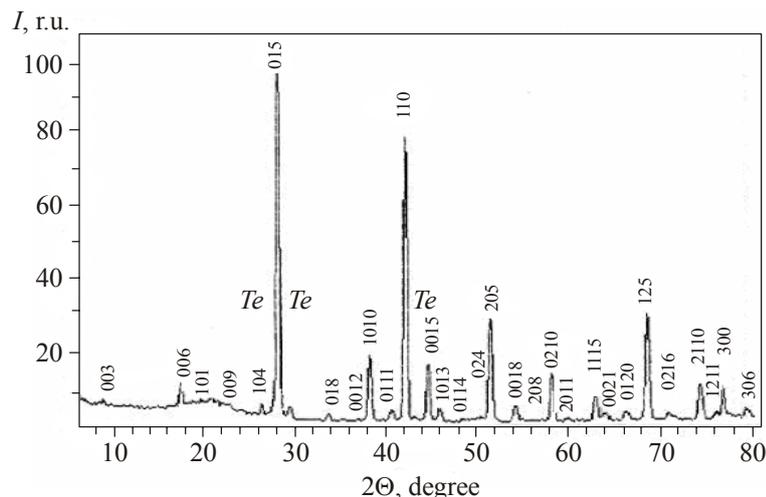


Fig. 1. X-ray diffraction pattern of powder obtained by melt spinning of $Bi_{0.5}Sb_{1.5}Te_3$ solid solution.

Analysis of this X-ray pattern and comparison of the results obtained to the PDF international database have shown that the main portion of peaks in the intensity, reflection angles and interplanar spaces coincides with the respective characteristics of $Bi_{0.5}Sb_{1.5}Te_3$ solid solution having the following parameters of hexagonal lattice: $a = 0.42852_{(1)}$ nm and $c = 3.04916_{(13)}$ nm. Moreover, there were lines on the X-ray pattern that can be referred to tellurium spectrum, the amount of which is estimated as $\sim 3\%$ of the total volume. Thus, it was established that powder under study has $Bi_{0.5}Sb_{1.5}Te_3$ composition and comprises Te excess that was introduced into the initial ingot.

SEM-images of powders obtained by melt spinning and grinding in the ball mill, as well as of cleavages of hot-pressed samples are represented in Fig. 2.

Powder obtained by melt spinning had rather coarse particles shaped as plates of size from units to hundreds of microns (Fig. 2 a, b, c). However, on the cleavage of sample after hot pressing of this powder the size of grains is considerably smaller than the size of particles of the initial powder, their maximum dimensions did not exceed tens of microns (Fig. 2 d, e), though it is known that at hot pressing the grains in the samples are enlarged due to recrystallization. Investigation of powder particles with a large magnification (Fig. 2 b, c) has shown that powder plates consist of thin flakes located with their flat side perpendicular to cooled disc surface. The thickness of scales is from units to hundreds of nanometers, their length is several microns. The size of flakes depends on the value of crystallization gradient (the temperature of disc where the melt finds itself). On hot pressing, powder particles disintegrate into small flakes of which sample grains are formed. In so doing, grains in the structure of samples retain their plate-like shape (Fig. 2 d, e). Powder obtained by grinding in the ball mill comprises both large particles to several hundreds of microns, and small particles, of less than micron in size, having round edges (Fig. 2 f, g). The samples pressed of such powders (Fig. 2 h, i)

retain a layered structure typical of these materials, but in the bulk the distribution of grains according to size is more heterogeneous as compared to samples pressed of powder obtained by melt spinning.

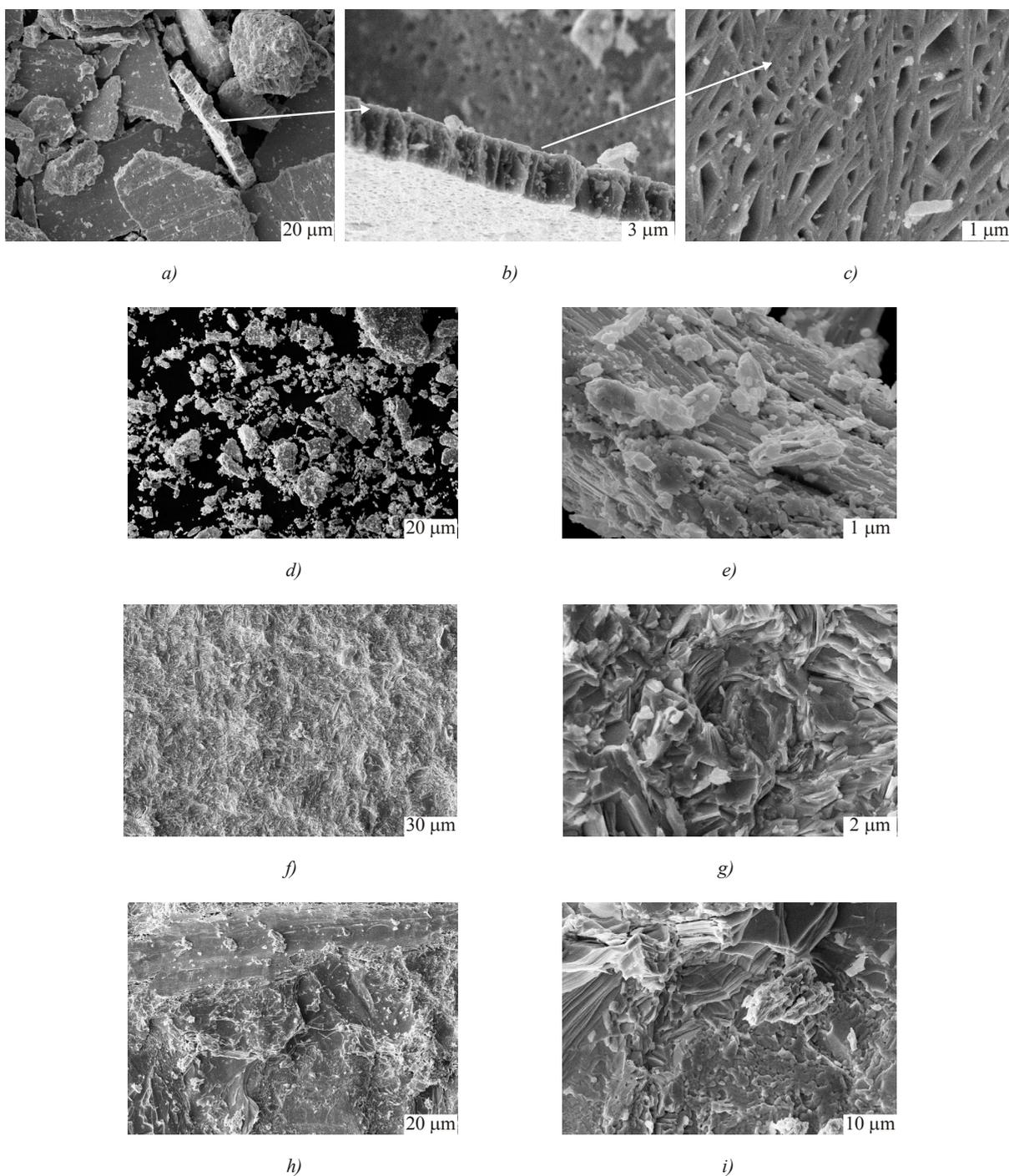


Fig. 2. SEM-images of powders obtained by $Bi_{0.5}Sb_{1.5}Te_3$ melt spinning (a, b, c) and ingot grinding in the ball mill (f, g), as well as of cleavages of hot-pressed samples from powders obtained by melt spinning (d, e) and grinding in the mill (h, i).

Fig. 3 shows the diagrams of strain due to compressive (Fig. 3 a) and bending loads (Fig. 3 b) of materials of bismuth and antimony telluride solid solutions prepared by different methods.

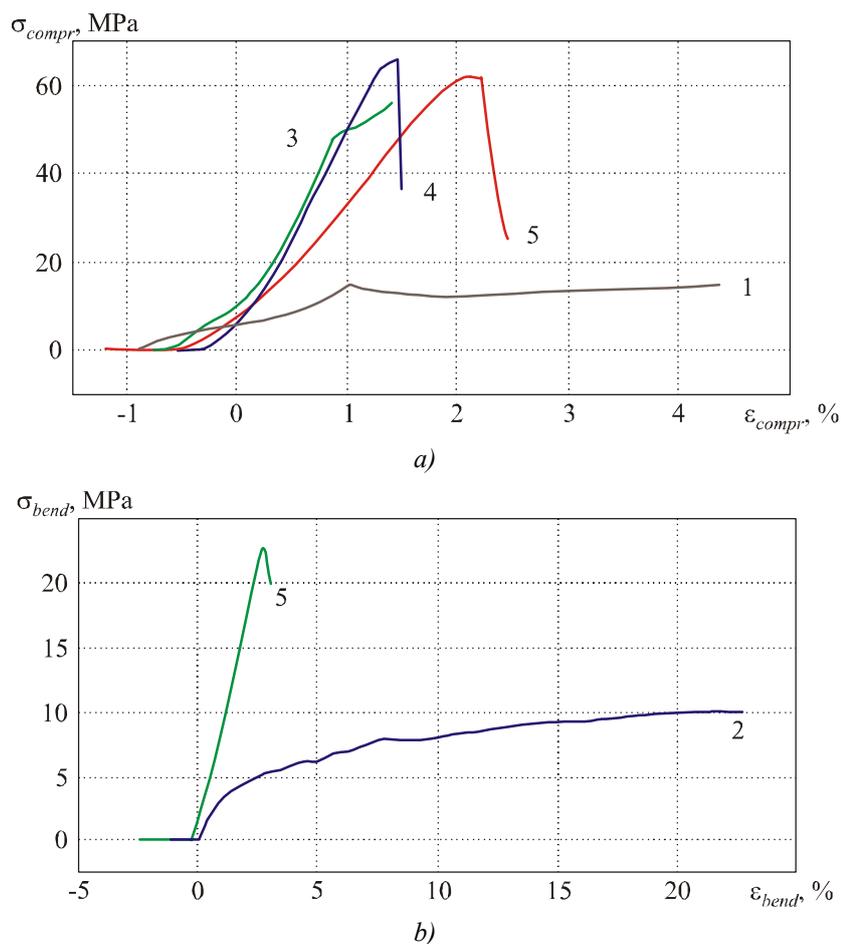


Fig. 3. Dependences of strain on compressive (a) and bending load (b) of samples obtained by different methods (curve numbers correspond to the numbers of samples in Table 2), deformed at strain rate $v_{strain} = 1 \text{ mm/min}$.

Table 1 gives strength limits (σ_B^{compr} , σ_B^{bend}) and strains (ϵ_B^{compr} , ϵ_B^{bend}) of samples obtained from the strain diagrams.

Table 1

Maximum permissible strains (ϵ_B^{compr} , ϵ_B^{bend}) and strength limits (σ_B^{compr} , σ_B^{bend}) during compression and bending tests of samples obtained by different methods

№	Fabrication method	Compression		Bending	
		ϵ_B^{compr} , %	σ_B^{compr} , MPa	ϵ_B^{bend} , %	σ_B^{bend} , MPa
1	Czochralski method, Se doping	4.7	15		
2	Zone melting			22.7	10
3	Extrusion	1.4	48		
4	Hot pressing (ingot ground in the mill)	1.5	67		
5	Hot pressing (powder after melt spinning)	2.5	62	2.7	23

It has been established that hot-pressed samples of powder obtained by melt spinning of these solid solutions have rather high strength limits at compressive and bending strains. Brittle failure of such

samples takes place at strain 2.5 – 2.7 %. The strength limits made 62 MPa on compression and 23 MPa on bending. Samples obtained by Czochralski method and zone melting had the lowest compression strength (sample № 1) and bending strength (sample № 2), however, they are more ductile, and failure occurs due to shift of layers along cleavage planes. In such samples cracks appeared rather early which grew in number with further load increase, but, unlike pressed samples, these samples did not fail.

Research on thermoelectric properties (thermoelectric coefficient, electrical conductivity and thermal conductivity) of hot pressed samples of powder obtained by $Bi_{0.5}Sb_{1.5}Te_3$ melt spinning yielded the optimal conditions and modes for production of powders and bulk samples with high thermoelectric figure of merit. The results of research at room temperature on thermoelectric properties of samples depending on thermal treatment modes, powder particle dimensions and the rotation rate of disc where the melt comes are given in Tables 2, 3 and in Fig. 4.

The necessity of thermal treatment of samples was established. Annealing of samples can be conducted in the inert atmosphere, in hydrogen atmosphere (at 350 °C) or in the air (at 280 °C). It increases their thermoelectric figure of merit. The unannealed samples had different concentration of charge carriers: the values of thermoelectric coefficient of samples were ~ 230 $\mu V/K$ (№ 1 and № 2), ~ 220 $\mu V/K$ (№ 3) and 200 $\mu V/K$ (№ 4 and № 5) (Table 2).

Table 2

Thermoelectric properties: α , σ , κ and Z at room temperature of materials depending on conditions of melt spinning and thermal treatment of pressed samples

№	Particle size, mm	Disc rotation rate, rpm	Annealing			α , $\mu V/K$	σ , S/cm	$\kappa \times 10^3$, W/cm·K	$Z \times 10^3$, K^{-1}
			T , °C	atm	time, h				
1	0.5 – 0.064	900	–	–	–	234	509	10.9	2.6
			350	H_2	4	220	764	10.8	3.4
2	0.5 – 0.064	900	–	–	–	232	523	10.2	2.5
			350	Ar	4	218	762	11.0	3.3
3	< 0.064	900	–	–	–	222	556	11.0	2.5
			350	H_2	4	221	600	9.6	3.0
4	without size grading	1500	–	–	–	204	657	11.0	2.5
			350	H_2	4	219	768	11.2	3.3
5	without size grading	1500	–	–	–	203	681	11.0	2.5
			280	Air	14	216	654	9.8	3.1

On annealing, the value of α of all these samples made ~ 220 $\mu V/K$. In so doing, σ increased and thermal conductivity was almost unchanged. Possibly, due to thermal treatment, charge carrier concentration became equalized and the nonequilibrium structure became ordered. As a result of annealing for 4 hours at 350 °C or 14 hours at 280 °C in the air (Fig. 4) an increase in Z by 10 – 20 % was obtained. A change in disc rotation rate (from 900 to 1500 rpm) hardly increased Z of these samples at room temperature.

To determine the effect of particle size of melt-spun powder on Z of materials made of this powder (Table 3, № 6 and № 7) as compared to materials made of powder ground in the mill (Table 3, № 8 and № 9), these samples were studied on annealing for 24 hours at 600 K in argon atmosphere. At room temperature the thermoelectric figure of merit of samples № 6 and 7 made $(3.5 \pm 0.2) \times 10^{-3} K^{-1}$ which is considerably higher compared to samples № 8 and № 9, for which $Z = (2.8 \pm 0.2) \times 10^{-3} K^{-1}$.

Table 3

Thermoelectric properties: α , σ , κ , κ_p and Z at room temperature of materials annealed for 24 hours at 300 °C in argon atmosphere, depending on the particle size of powder obtained by melt spinning (№ 6, № 7) and ingot grinding in the ball mill (№ 8, № 9)

№	Disc rotation rate, rpm	Particle size, mm	A , $\mu\text{V/K}$	σ , S/cm	$\kappa \times 10^3$, W/cm·K	$\kappa_p \times 10^3$, W/cm·K	$Z \times 10^3$, K ⁻¹
6	1500	0.5 – 0.064	226	626	9.1	6.2	3.5
7	1500	< 0.064	240	580	9.0	6.3	3.5
8	–	0.5 – 0.064	203	800	11.2	7.4	2.9
9	–	0.5 – 0.064	194	1030	14.6	9.6	2.6

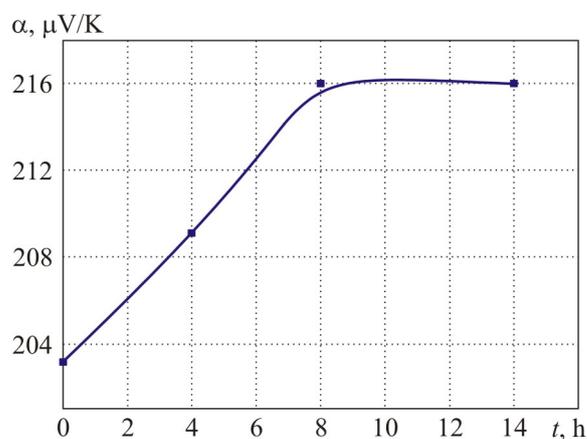


Fig. 4. Dependence of thermoelectric coefficient on annealing time at 280 °C in the air of samples made of melt spun powder.

Thermoelectric characteristics α , σ , κ , κ_p and Z at room temperature of bismuth and antimony telluride solid solution samples with close values of charge carrier concentration (α value), obtained by different methods, are given in Table 4.

Table 4

Thermoelectric properties: α , σ , κ , κ_p and Z at room temperature of materials depending on fabrication methods

№	Method of samples fabrication	α , $\mu\text{V/K}$	σ , S/cm	$\kappa \times 10^3$, W/cm·K	$\kappa_p \times 10^3$, W/cm·K	$Z \times 10^3$, K ⁻¹
1	Czochralski method, Se doping	200	1060	13.5	8.5	3.1
2	Zone melting	200	1200	16.0	10.2	3.0
3	Extrusion	208	960	12.9	8.2	3.2
4	Hot pressing, ingot ground in the mill	200	700	10.2	6.8	2.75
5	Hot pressing, powder after melt spinning	212	780	10.0	6.3	3.5
6	Hot pressing, powder after melt spinning	230	587	9.4	6.7	3.3

In the hot-pressed samples of powders obtained by ingot grinding in the ball mill and melt spinning there was a reduction of both total and lattice component of thermal conductivity as compared to other samples. Besides, samples made of melt-spun powder had higher thermoelectric coefficient owing to which their Z is higher compared to samples obtained by other methods. A hot-pressed sample with $\alpha = 212 \mu\text{V/K}$ made of melt-spun powder has $Z \sim 30\%$ higher than Z of a sample having the same composition and obtained by ingot grinding in the ball mill and 15% higher than Z of a sample having the same charge carrier concentration and obtained by extrusion.

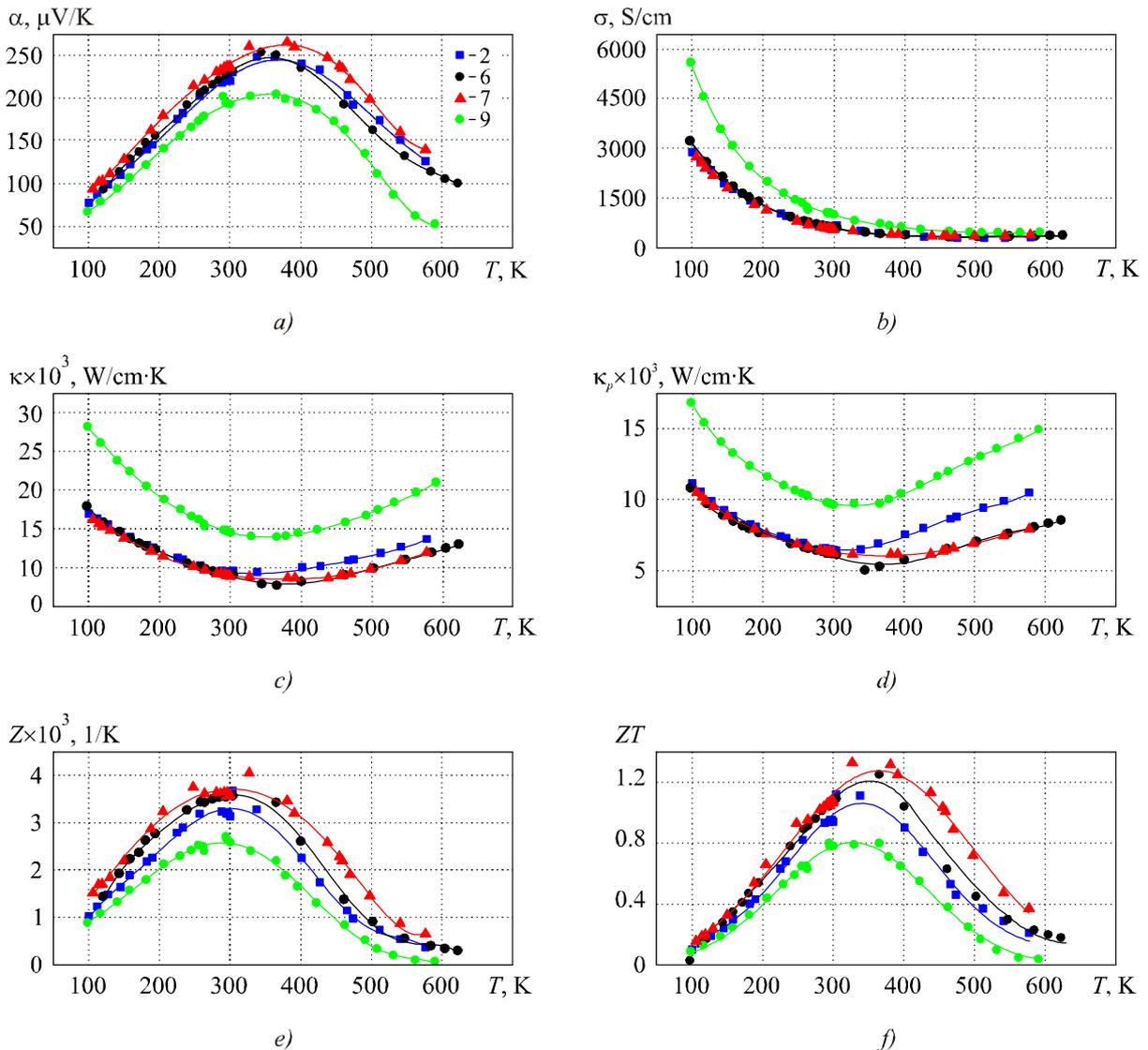


Fig. 5. Temperature dependences of thermoelectric coefficient (a), electric conductivity (b), total (c) and lattice thermal conductivity (d), thermoelectric figure of merit (e) and ZT (f) of samples made of melt-spun powders (№ 2, № 6, № 7) and ground in the ball mill (№ 9) (curve numbers correspond to numbers of samples in Tables 2 and 3).

Temperature dependences of thermoelectric properties (α , σ , κ , Z and ZT) in the range of 100 to 700 K of hot-pressed samples made of powders obtained by bismuth and antimony telluride melt spinning under different spinning conditions (№ 2, № 6, № 7), and of powders ground in the ball mill (№ 9) are represented in Fig. 5. The powders were prepared using ingot of the same solid solution

composition. The samples were annealed for 24 hours at 300 °C in argon atmosphere. Materials of various-size powders obtained by melt spinning (№ 6 and № 7, Table 2), had maximum $ZT = 1.32$ and 1.2. For the hot-pressed sample (№ 9, Table 3), obtained of powder ground in the ball mill, maximum ZT value did not exceed 0.8. The thermoelectric figure of merit of samples made of melt-spun powder increased mainly due to low lattice thermal conductivity and higher thermoelectric coefficient value, which resulted in ZT increase by $\sim 30\%$.

Conclusions

The effect of melt spinning modes on the size and morphology of particles of p -type $Bi_{0.5}Sb_{1.5}Te_3$ solid solution powders was studied. Thermoelectric and mechanical properties of the above solid solution materials prepared by different methods were investigated. Optimal conditions were found to obtain samples with the use of melt spinning method with thermoelectric figure of merit $Z = (3.5 \pm 0.2) \times 10^{-3} \text{ K}^{-1}$ at room temperature and $ZT \sim 1.3$. As compared to conventionally used materials prepared by directional crystallization or extrusion methods, in the hot-pressed samples based on bismuth and antimony telluride solid solution made of melt-spun powder the lattice component of thermal conductivity is essentially reduced and thermoelectric coefficient is increased, which results in material thermoelectric figure of merit increase by $\sim 15\%$.

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References

1. P.J. Lin-Chung and T.I. Reinecke, Thermoelectric Figure of Merit of Composite Superlattice Systems, *Physical Review B* **51**(19), 13244-13247 (1995).
2. L.D. Hicks, T.C. Harman and M.S. Dresselhaus, Use of Quantum-Well Superlattices to Obtain a High Figure of Merit from Nonconventional Thermoelectric Materials, *Appl. Phys. Lett.* **63**(23), 3230-3232 (1993).
3. L.D. Hicks, M.S. Dresselhaus, Effect of Quantum-well Structure on Thermoelectric Figure of Merit, *Physical Review B* **47**(19), 2727-2731 (1993).
4. R.G. Yang and G. Chen, Thermal Conductivity Modeling of Periodic Two-Dimensional Nanocomposites, *Phys. Rev. B* **69**, 195316/1-10 (2004).
5. L.P. Bulat, D.A. Pshenai-Severin, V.V. Karatayev, V.B. Osvensky, Yu.N. Parkhomenko, I.A. Drabkin, G.I. Pivovarov, V.T. Bublik and N.Yu. Tabachkova, On the Limit of Thermoelectric Figure of Merit in the Bulk Nanocrystalline Structures Based on Bismuth Telluride, *Thermoelectrics and Their Application: Reports to XII Interstate Workshop* (Saint-Petersburg: A.F.Ioffe Physics and Technical Institute of RAS, 2010, p.41).
6. Yi Ma, Q. Hao, B. Poudel, Y. Lan, B. Yu, D. Wang, G. Chen, Z. Ren, Enhanced Thermoelectric Figure-of-Merit in p -Type Nanostructured Bismuth Antimony Tellurium Alloys Made from Elemental Chunks, *Nano Letters* **8**, 2580/1-4 (2008).
7. B. Poudel, Q. Hao, Yi Ma, Y.C. Lan, A. Minnich, Yu Bo, X. Yan, D. Wang, A. Muto, D. Vashaee, X.Y. Chen, Y.M. Lui, M.S. Dresselhaus, G.G. Chen, Z. Ren, High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys, *Science* **320**(5876), 634-638 (2008).
8. L.P. Bulat, V.T. Bublik, I.A. Drabkin, V.V. Karatayev, V.B. Osvensky, G.I. Pivovarov, D.A. Pshenai-Severin, E.V. Tatyani, N.Yu. Tabachkova, Bulk Nanostructured Thermoelectrics

- Based on Bismuth Telluride, *J. Thermoelectricity* **3**, 70-75 (2009).
9. M.S. Dresselhaus, G. Chen, M.Y. Tang, R.G. Yang, H. Lee, D.Z. Wang, Z.F. Ren, J.P. Fleurial, P. Gogna, New Directions For Low-Dimensional Thermoelectric Materials, *Adv.Mater.* **19**, 1043-1053 (2007).
 10. A.I. Gusev, *Nanomaterials, Nanostructures, Nanotechnologies*. 2-nd edition (Moscow: Nauka, 2007), p. 416.
 11. O.Sh. Gogishvili, G.G. Kononov, S.P. Krivoruchko, I.P. Lavrinenko and I.I. Ovsyanko, Structure of $(Bi, Sb)_2Te_3$ Alloy Obtained by Liquid State Quenching, *VII All-Union Conference "Chemistry and Technical Application of Chalcogenides"* (Uzhgorod, 1988), p.367.
 12. O.Sh. Gogishvili, S.P. Lalykin, S.P. Krivoruchko, E.V. Krasnenkov, K.I. Puruchidi, E.S. Tsanova, Production of Alloys Based on Bismuth and Antimony Chalcogenides by Superfast Cooling of Melts, *VII All-Union Conference "Chemistry and Technical Application of Chalcogenides"* (Uzhgorod, 1988), p. 368.
 13. O.Sh. Gogishvili, S.P. Krivoruchko, I.I. Ovsyanko, G.N. Samoilenko, K.I. Puruchidi and E.S. Tsanova, Properties of Hot-Pressed Samples of $Bi_{0.52}Sb_{1.48}Te_3$ Alloy Obtained by High-Speed Quenching, *VII All-Union Conference "Chemistry and Technical Application of Chalcogenides"* (Uzhgorod, 1988), p. 372.
 14. S. Wang, W. Xie, H. Lie, X. Tang, Enhanced Performances of Melt Spun $Bi_2(Te, Se)_3$ for *n*-type Thermoelectric Legs, *Intermetallics* **19**, 1024-1031 (2011).
 15. W. Xie, X. Tang, Y. Yan, Q. Zhang, T. Tritt, Unique Nanostructures and Enhanced Thermoelectric Performance of Melt-Spun $BiSbTe$ Alloys, *J. Appl. Phys.* **94**, 102111/1-3 (2009).
 16. W. Xie, X. Tang, Y. Yan, Q. Zhang and T. Tritt, High Thermoelectric Performance $BiSbTe$ Alloy with Unique Low-Dimensional Structure, *J. Appl. Phys.* **105**, 113713/1-8 (2009).
 17. W. Xie, J. He, H. Kang, X. Tang., S. Zhu, M. Laver, S. Wang, J. Copley, C. Brown, Q. Zhang and T. Tritt, Identifying the Specific Nanostructures Responsible for the High Thermoelectric Performance of $(Bi, Sb)_2Te_3$ Nanocomposites, *Nano Lett.* **10**, 3283-3289 (2010).

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