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EXTRUDED THERMOELECTRIC MATERIAL BASED ON SOLID SOLUTION $Bi_2Te_{2.7}Se_{0.3}$

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Abstract- The electrical conductivity (σ), Zeebeck (α), Hall (R_h) and thermal conductivity (χ) coefficients of the extruded sample of $Bi_2Te_{2.7}Se_{0.3}$ with different grain sizes are investigated in the temperature range of ~77-300 K after extrusion and the same samples passed annealing. It is established that when extruding samples of $Bi_2Te_{2.7}Se_{0.3}$ solid solution axial texture in the direction of the extrusion axis arises in them due to plastic deformation. There is a correlation between the degree of texture and the thermoelectric properties.

Keywords: Zeebeck, Extruded, Hall Coefficient, Size, Deformation.

1. INTRODUCTION

The main problem in solving thermoelectricity problems is the search for new thermoelectric materials, which should have a high thermoelectric efficiency $Z = \alpha^2\sigma / \chi$, where σ , α and χ are the coefficients of electrical conductivity, thermo-e.m.f. and thermal conductivity, respectively [1]. To obtain a material with the required parameters, it is necessary to establish the regularities of the influence of the composition, production mode, grain size, doping on the concentration of charge carriers and the conditions of scattering of electrons and phonons, leading to a sufficiently high ratio of the mobility of current carriers to the lattice thermal conductivity μ / χ_l , which directly affects thermoelectric efficiency of the material. It is also important to improve thermoelectric cooling by creating highly efficient materials for various cascades of low-temperature energy converters [2-4].

Single crystals of solid solutions based on the Bi-Sb-Te , Bi-Te-Se systems are model materials for studying a number of unique physical phenomena occurring in narrow-gap and layered semiconductors, as well as in semimetals. These systems also have high thermoelectric efficiencies, which makes them, at present, indispensable materials for creating various electronic converters. In modern thermoelectric energy converters, bulk materials based on these systems are mainly used [5-9].

Materials based on solid solutions of the system are used for the manufacture of branches of n-type conductivity of thermoelectric energy converters [10]. The Bi_2Te_3-Bi_2Se_3 system is a continuous series of solid solutions. In the subsolidus part of the phase diagram of this system, the solid solution in the composition range of 20-55 mol.% Bi_2Se_3 decomposes into two solid solutions from which the perfect phase Bi_2Te_2Se is formed at ~793K [11]. In the samples obtained by zone melting, the existence of the ordered phase Bi_2Te_2Se and the boundary at 300K between the solid solution based on Bi_2Te_3 and Bi_2Te_3-Bi_2Se_3 was determined [12].

In [13], materials of n-type conductivity were obtained by extrusion on the basis of a Bi_2Te_3-Bi_2Se_3 solid solution containing from 6 to 40 mol.% Bi_2Se_3 , which is not inferior to single-crystal samples grown by the Czochralski method. The figure of merit at temperatures below ~200K is characteristic of samples of the Bi_2Se_3 solid solution containing 6 mol% Bi_2Se_3 , doped with a halide. It is shown that the theory explaining the scattering mechanisms for single-crystal samples of a given composition can be extended to samples obtained by the extrusion method.

Therefore, solid solutions based on bismuth telluride constantly attract the attention of many researchers, since these materials, with various substitutions of atoms in the sublattices of the main compound by elements of the V-VI groups, have high thermoelectric figure of merit in the temperature range both below and above room temperature with optimal compositions and concentrations of charge carriers [14, 15].

The main disadvantage of single crystals of these systems when creating electronic converters based on them is their low mechanical strength, due to the layering of their structure [1].

The relevance of this work is that, studies of the phenomena of electron and phonon transfer in extruded samples with varying degrees of texture and grain size provide information on the relationship between the real structure and physical properties, on the mechanism of scattering of electrons and phonons by structural defects, as well as on the role of the degree grain orientation in the electrophysical and thermal properties of semiconductor materials.

In order to create a sufficiently strong material based on $Bi_2Te_{2.7}Se_{0.3}$ solid solutions with thermoelectric efficiencies close to their single-crystal samples, extruded materials based on $Bi_2Te_{2.7}Se_{0.3}$ compositions with different grain sizes were obtained in this work and their thermoelectric properties in the range ~77-300 K were studied.

One of the ways of obtaining fine-grained materials is the extrusion method. The materials obtained by extrusion possess a finely dispersed structure, texture, reduced thermal conductivity, higher mechanical strength, as well as resistance to thermal impacts. It has been experimentally established that the thermoelectric characteristics of the extruded materials are significantly influenced by factors such as extrusion pressure and temperature, particle size of the initial powder, temperature and annealing time of the obtained thermoelectric material [16, 17]. The production of polycrystals by extrusion is one of the promising ways to improve the thermoelectric and mechanical properties of semiconductor materials. It is established that these materials are characterized by some ordering of grains orientation: their cleavage planes are located mainly perpendicular to the direction of pressing [18-21].

2. EXPERIMENTAL

The synthesis was carried out by direct fusion of the components in the corresponding stoichiometry in a quartz ampoule previously etched in a solution of "aqua regia" and washed with distilled water. The ampoule was pumped out to a residual pressure of $\sim 10^{-3}$ Pa and was sealed off. As the initial components were used Bi, Te and Se contained 99.99% of the main substance. The synthesis was carried out at a temperature of ~1053 K for 2 hours. For good homogenization of the alloy, the furnace with ampoule was vibrated. Then the substance was cooled (by lowering the ampoule into water) to room temperature. The synthesized material was crushed in an AGO-2 mechanical planetary mill (activator mill).

Fractions with particle sizes of 50 were separated on a sieve; 100; 160; 200; 315; 630 and 1000 μm. Briquettes with a diameter of ~30 mm suitable for extrusion were pressed from $Bi_2Te_{2.7}Se_{0.3}$ solid solution powders. Pressing was carried out at room temperature and a pressure of ~8.0 T/cm^2. Extrusion was carried out on a hydraulic press MS-1000 with a diameter of 30 mm to a diameter of 6 mm using special equipment. The technological parameters of the extrusion process (temperature, pressure, drawing speed, etc.) were chosen so that the formation of structured rods would take place under conditions of superplasticity without macro- and micro-disturbances.

Using an XR DD8 ADVANCE X-ray setup, Bruker, Germany, the texture of extruded samples was investigated depending on the grain size and annealing by the method described in [22]. Based on the obtained diffraction patterns using the TOPAS-4.2 program, it was confirmed that the samples are powders of the $Bi_2Te_{2.7}Se_{0.3}$ solid solution.

From various structured extruded rods with the method of electric spark cutting (installation of electric spark cutting, grade A.207.40M), samples for research in the form of rectangular parallelepipeds 3-5-12 mm in size were cut out. The damaged layer formed on the surface of the samples during cutting was removed by electrochemical etching in a solution of $KOH+C_4H_4O_6+H_2O$. The samples were annealed in quartz ampoules pumped out to a pressure of $\sim 10^{-2}$ Pa at a temperature of ~690 K for 2 hours.

We studied samples that did not pass heat treatment after extrusion and the same samples that annealed at ~690 K for 2 hours in vacuum.

The electrical conductivity (σ), the coefficients of Zeebeck (α), Holl (R_h) and thermal conductivity (χ) of samples have been investigated in the temperature range of 77-300 K after extrusion and the same samples that passed annealing at ~ 690 K. The electrical parameters and thermal conductivity were measured by the method described in [23] along the length of the sample, i.e. in the direction of extrusion. The error in measurement of electrical parameters and thermal conductivity was ~3-5%.

Tests of specimens for ultimate strength in bending were carried out in a laboratory device according to the three-point scheme described in [24].

The ultimate bending strength of this composition was ~45 MPa, which is ~3 times higher than the ultimate strength for single-crystal samples.

3. RESULTS AND DISCUSSION

The results of measurements of the electrical and thermal parameters for $Bi_2Te_{2.7}Se_{0.3}$ samples are shown in Figures 1-4. It follows from the figures that the dependences of σ and α of the samples on the dispersity of the initial powders are non-monotonic, and the non-monotonicity manifests itself especially at small grain sizes (d). The annealing of the samples somewhat changes the character of the dependence of σ and α on d.

During extrusion due to plastic deformation in samples of the $Bi_2Te_{2.7}Se_{0.3}$ solid solution, the formation of texture and structural defects occurs simultaneously.

The mechanism for the formation of an oriented structure is usually associated with the formation of a stacking texture, when nonequilibrium grains, faceted along the wide side by a cleavage plane, when filling into a mold, predominantly assume a position corresponding to the stable position of the plate. Apparently, the nature of the dependence of σ, α and χ on d, as well as the effect of the post-extrusion annealing on these dependences are due to the contributions made by the texture and defects. In this case, the degree of texture of the samples will depend both on the technological parameters of the extrusion process and on the post-extrusion heat treatment.

These structural defects, in turn can create electroactive centers in the sample. With increasing particle sizes, the energy required for grain orientation, i.e. to form a texture, increases. Due to the fact that extrusion of the material is carried out at ~655K, during extrusion simultaneous thermal disorientation of grains, i.e. partial destruction of the texture takes place, which occurs due to deformation.

With increasing *d*, the process of easing the thermal destruction of the texture prevails and the orderliness in the structure is growing. During annealing, structural defects are healed and at the same time, a partial destruction of the texture occurs. This leads to an increase in the mobility of the charge carriers. Therefore, after annealing σ increases strongly, α decreases slightly and the dependence of α on *d* is opposite to the dependence of σ on d .

We note that the data obtained by us on the Hall coefficients and thermoelectric power also attests to an increase in the carrier density with decreasing grain sizes in the samples at ~77K (Table 1). In Table 1, R_h is the Hall coefficient of this sample, and R_{h0} is the Hall coefficient of the sample with grain sizes of 50 μm .

From the values of the Hall coefficient, it would be possible to calculate the concentration of structural defects in the samples studied. However, such calculations are not highly reliable, since it is difficult to unambiguously predict the fraction of electroactive structural defects in the samples [25, 26].

The above considerations also satisfactorily explain the dependence of the thermal conductivity of the samples on the dispersion of the initial powder and on the annealing.

Taking into account that at 77 K the thermal energy in the $Bi_2Te_{2.7}Se_{0.3}$ solid solution is mainly transferred by lattice vibrations and conduction electrons according to the expressions $\chi_l = \chi - \chi_e$ and $\chi_e = L\sigma T$.

the lattice (χ_l) and electronic (χ_e) components of thermal conductivity are calculated, respectively. Here χ is the total measured coefficient of thermal conductivity, σ is the coefficient of electrical conductivity at a given temperature *T*, $L = A(k/e)^2$ Lorentz number, *k* is the Boltzmann constant, *e* is the electron charge.

The values of A were estimated from the dependence of A on the thermo-emf coefficient [27]. It follows from the table that changes in the thermal conductivity of the samples upon annealing and depending on the grain size are due to a change in both the electronic part (χ_e) and the phonon part (χ_l) of the thermal conductivity.

In this case, the dependences of χ_e and χ_l on d and on annealing correspond to the dependences σ on the degree of texture (on *d*) and on annealing.

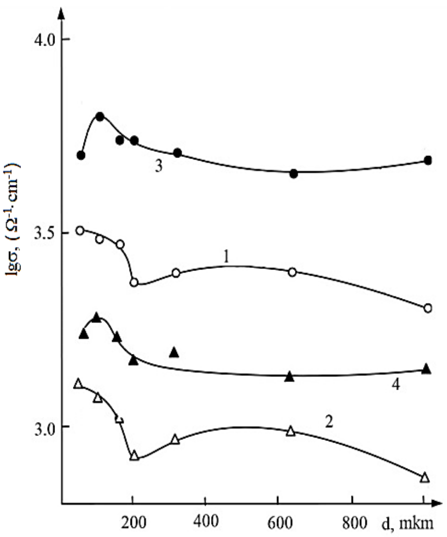

Figure 1. The dependence of the electrical conductivity of extruded samples of a solid solution of $Bi_2Te_{2.7}Se_{0.3}$ at 77 K (1, 3) and 300 K (2, 4) before (1, 2) and after (3, 4) annealing on the grain size of the initial powder

Table 1. The dependence of the lattice (χ_l) and electron (χ_e) components of the thermal conductivity, the coefficient of Zeebeck (α) , and the ratio R_h / R_{h0} for extruded samples of $Bi_2Te_{2.7}Se_{0.3}$ at 77 K on grain sizes

No	Grain sizes, μm	χ_l, Vt/m·K		χ_e, Vt/m·K		α, μ V/K		R_h / R_{h0}
		Before annealing	After annealing	Before annealing	After annealing	Before annealing	After annealing	
1	50	1.88	1.53	0.65	1.03	-77	-67	1.0
2	100	1.51	1.24	0.61	1.31	-85	-62	2.3
3	160	1.77	1.35	0.57	1.18	-94	-64	2.7
4	200	1.46	1.39	0.45	1.13	-112	-67	3.1
5	315	1.38	1.36	0.45	1.04	-100	-70	3.7
6	630	1.23	1.31	0.46	0.85	-100	-83	3.9
7	1000	1.23	0.86	0.39	0.96	-125	-90	4.3

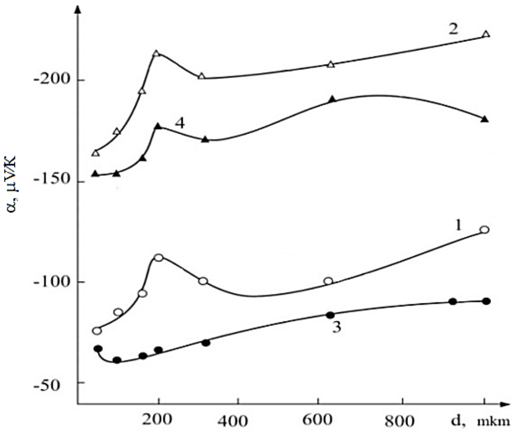

Figure 2. Dependence of the coefficient of thermo-e.m.f. (α) of the extruded samples of $Bi_2Te_{2.7}Se_{0.3}$ solid solutions at 77 K (1.3) and 300 K (2, 4) before (1, 2) and after (3, 4) annealing from grain sizes

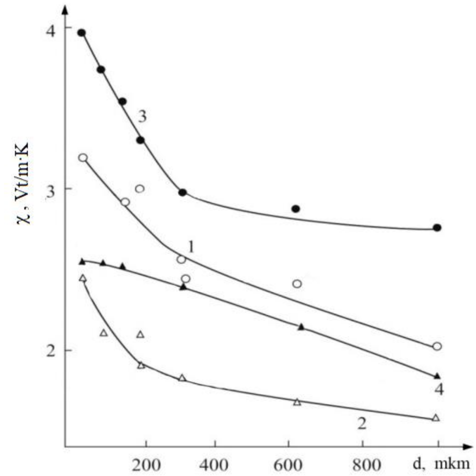

Figure 3. Dependence of the coefficient of thermal conductivity of extruded samples of $Bi_2Te_{2.7}Se_{0.3}$ solid solutions at 77 K (1.3) and 300 K (2, 4) before (1, 2) and after (3, 4) annealing on the grain size of the initial powder

Temperature dependences of σ, α and χ for samples of $Bi_2Te_{2.7}Se_{0.3}$ solid solutions were also studied. Such a dependence on the example of samples with grain sizes of ~ 315 μm is shown in Figure 4. It was found out that the character of the temperature dependence of the indicated parameters for powders with different grain sizes is the same. However, in all cases after heat treatment the slope of the temperature dependence of σ significantly increases (up to 1.3 times) and the degree in the dependence of $\sigma \sim T^{-n}$ and $\mu \sim T^{-n}$ approaches to -1.5. This again confirms that electrons at low temperatures are scattered on structural defects. After heat treatment, structural point defects are healed and in the scattering of electrons acoustic lattice vibrations play the main role [28].

The results of X-ray studies of the dependence of the degree of texture in unannealed and annealed extruded samples of $Bi_2Te_{2.7}Se_{0.3}$ and $Bi_{0.5}Sb_{1.5}Te_3$ on grain sizes are presented in Table 2. In this case, the degree of texture based on a powder with a grain size of ~50 μm was taken as a unit.

It can be seen from the table that the degree of texture of the samples, depending on the particle size, passes through a minimum at a particle size of ~200 μm. In addition, annealing leads to a decrease in the degree of texture of the samples.

The strongest decrease in the degree of texture upon annealing occurs in samples with a particle size of ~50 μm. With an increase in the particle size, the effect of annealing on the degree of texture is weakened and in the case of samples with a particle size of ~1000 μm, annealing does not affect the degree of texture.

Apparently, with the minimum grain size (equal to ~50 μm), the energy required for their orientation is also minimal. Therefore, extruded samples with grain sizes of ~50 μm have the highest texture degree among the samples studied. At the same time, the concentration of structural imperfections of grains decreases. However, in this range of grain sizes, the degree of texture of the samples plays a predominant role in the change in electrical conductivity and thermal conductivity at 77 K. Due to this, up to $d \approx 100 \div 160$ μm, the growth of grain sizes leads to a decrease in electrical conductivity and thermal conductivity.

Table 2. Dependence of the degree of texture of extruded $Bi_2Te_{2.7}Se_{0.3}$ samples on the particle size of the initial powder

No	Particle size, μm	The degree of texture of the sample in rel. units	
		$Bi_2Te_{2.7}Se_{0.3}$	
		Before annealing	After annealing
1	50	1.0	0.35
2	100	0.60	0.40
3	160	0.52	0.30
4	200	0.45	0.25
5	315	0.65	0.50
6	630	0.65	0.50
7	1000	0.55	0.55

Some decrease in the coefficient of thermo-e.m.f. in this region is apparently due to the weakening of the role of the scattering of current carriers on charged structural imperfections and to the amplification of the scattering of current carriers by acoustic vibrations [29, 30].

Plastic deformation during the extrusion of the $Bi_2Te_{2.7}Se_{0.3}$ solid solution is accompanied by an increase in its internal energy, the main carriers of which are crystal lattice defects. During extrusion, the texture of the deformation of the sample also occurs.

Structural changes caused by deformation during extrusion lead to a sharp change in the structure-sensitive properties of the material [31].

During extrusion, the following processes occur in parallel in the material: increased scattering of conduction electrons and phonons (due to scattering on the resulting lattice defects), leading to a decrease in the mobility of current carriers and lattice thermal conductivity; an increase in the concentration of charge carriers caused by electroactive centers on structural defects, leading to an increase in electrical conductivity and the electronic part of thermal conductivity; ordering of the structure of the samples due to the texture, which is accompanied by a decrease in the scattering of electrons and phonons.

The combination of these factors determines the dependences dependencies, σ, α, χ of $Bi_{0.5}Sb_{1.5}Te_3$ samples on the grain size of the initial powder and heat treatment.

With the growth of grain sizes, the disorientation of grains is weakened due to thermal energy during hot extrusion (at 665 K). Therefore, starting with the grain sizes $d \approx 100 \div 160$ μm, the degree of texture of the samples increases with increasing *d*.

At the same time, the perfection of grains is growing. This leads to an increase in the mobility of the current carriers and to a certain decrease in their concentration. Therefore, with increasing grain sizes after $d \approx 160$ μm, σ, α and χ in non-annealed samples grows. During the heat treatment of the extruded samples in them the concentration of structural defects decreases, grain disorientation (a decrease in the degree of texture of the samples) and recrystallization occurs.

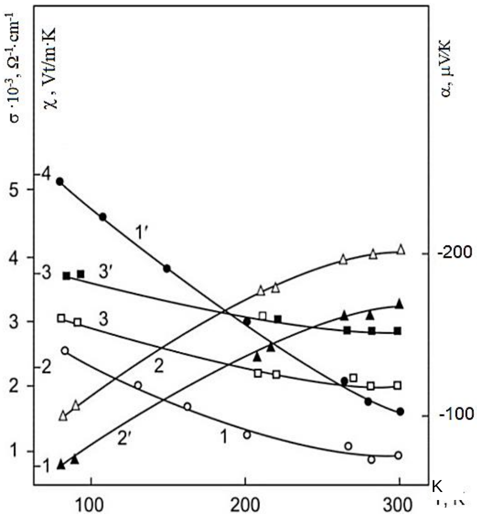

Figure 4. Temperature dependence of electrical conductivity (1, 1′), thermo-e.m.f. coefficient (2, 2′) and thermal conductivity (3, 3′) of the extruded samples of $Bi_2Te_{2.7}Se_{0.3}$ with grain sizes ~315 μm before (1, 2, 3) and after (1′, 2′, 3′) heat treatment

Each of these factors leads to a change in the concentration and mobility of charge carriers, as well as the mechanism of scattering of electrons and phonons. At 77 K heat treatment significantly increasing σ and χ, has little effect on α. This indicates that at 77 K in the scattering of electrons and phonons the main role plays the structural imperfections of the grains.

The results of measuring the dependences of the Hall coefficients R_h and the Hall mobility of the current carriers μ on grain sizes and heat treatment are in good agreement with the above arguments. These data are also presented in the table. Here $R_h\mu$ and R_{h0}, μ_0 are the Hall coefficients and the mobility of the current carriers of the given sample and a sample with dimensions of 50 μm, respectively, μ_1 and μ_2 are the mobilities of the current carriers in the samples before and after heat treatment, respectively.

Figure 4 shows the temperature dependences of σ, α, χ of samples of $Bi_2Te_{2.7}Se_{0.3}$ solid solution with grain sizes of 315 μm. It can be seen, that after the heat treatment the steepness of $\sigma(T)$ increases significantly. In the case of a sample with a grain size of 1000 μm, annealing almost does not affect the coefficient of temperature dependence of the electrical conductivity. Comparison of these data with the temperature dependence of the mobility of the current carriers with a change in the Hall coefficient during heat treatment also indicates that the concentration of structural defects decreases with heat treatment and some off-orientation of the grains occurs (i.e., the degree of texture of the samples is reduced).

4. CONCLUSION

It is established that when extruding samples of $Bi_2Te_{2.7}Se_{0.3}$ solid solution with different grain sizes, axial texture in the direction of the extrusion axis arises in them due to plastic deformation. The degree of the texture of the samples does not depend monotonically on the grain size, which is due to the difference in the ordering energy of crystallites with different sizes, the simultaneous ordering of the plastic deformation and the destructive effect of temperature during extrusion. There is a correlation between the degree of texture and the thermoelectric properties. The highest thermo- and magnetothermoelectric efficiencies that are close to single-crystal samples have extruded materials based on n-$Bi_2Te_{2.7}Se_{0.3}$ solid solutions with grain sizes of 315 μm, passed post-extrusion heat treatment in a certain mode.

Thus, on the basis of a comprehensive study of the influence of extrusion process technology, grain sizes, texture degree, heat treatment we managed to get mechanically strong extruded materials with a thermoelectric efficiency of $\sim 3.0 \cdot 10^{-3}$ K⁻¹ at ~300 K, which can be successfully applied in production of various electronic converters.

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