Thermoelectric and mechanical properties of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution extruded from granules obtaining by melt crystallization

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Abstract. The microstructure, composition, mechanical and thermoelectric properties of samples cut from different sections of a rod with a diameter of 20 mm, a length of 300 mm, extruded from a briquette pressed from granules obtained by crystallization of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution in water were investigated. It was established that the composition of the samples does not change along the length of the rod, while there is a small amount of the second phase (tellurium-based eutectic) is observed both at the beginning and at the end of the rod. A compression test at room temperature showed that the ultimate strength of specimens cut from the end of a rod is ~10% higher than that of specimens cut from the middle. Thermoelectric parameters (electrical conductivity, thermal conductivity, Seebeck coefficient and thermoelectric figure of merit) at room temperature of samples cut from different areas of the rod were $\sigma = 814 \pm 55$ S/cm, $k = 13.2 \pm 0.3$ W/cm K, $\alpha = 234 \pm 5$ $\mu$V/K, $ZT = 0.93-1.12$. Measurements of the thermoelectric properties of these samples in the temperature range of 100-600 K showed that the intrinsic conductivity occurs at temperatures above 450 K. The maximum thermoelectric figure of merit $ZT_{\text{max}} = 1.2 \pm 0.1$ was obtained at a temperature of 340 K.

1. Introduction
This work is a continuation of the study of thermoelectric materials of solid solutions of bismuth and antimony chalcogenides obtained from granules prepared by rapid melt crystallization in various liquids [1-4]. With this method of producing granules, it is sufficient to load individual components into the installation container, without first synthesizing the mixture in quartz ampoules. It is established that samples obtained by extrusion of granules crushed in planetary mills have high thermoelectric figure of merit. Previously, the properties of the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution, which were obtained by extrusion of rectangular rods with a section of 5×5 mm from granules prepared by crystallization from melt containing 99.99% of the main substances were studied [3, 4]. In this work, the microstructure, thermoelectric and mechanical properties of p-type material of extruded extruded granules, obtained by crystallization of the melt into water using raw materials containing 99.9999% of the basic substances, are investigated. The diameter of the extruded rod was 20 mm, length 300 mm. The purpose of the study is to determine how homogeneous in length and cross section is the obtained rod by mechanical and thermoelectric parameters and compare the properties of the obtained samples with the properties of the samples previously studied in [3, 4].
2. Experimental technique
To prepare granules of the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution, Sb, Bi and Te containing 99.9999% of the basic substances were loaded into a graphite container of the inductive granulating machine in a stoichiometric composition, melted using high-frequency heating and crystallization in water. The loading weight was 1 kg. The granules were ground in a planetary ball mill and the powder particles were compacted in briquette, which was extruded and obtained a rod with a diameter of 20 mm and a length of ~400 mm. The samples 8×8×15 mm and 5×5×12 mm in size were cut from different parts of the rod (figure 1, 1-4) to measure thermoelectric and mechanical characteristics. The samples were heat treated.

![Figure 1. The scheme of cutting extruded rod.](image)

X-ray microscopic and fractographic analyzes of samples cut from different sections of the rod were performed on a scanning electron microscope. The microstructure of the samples was studied on an optical microscope on chips parallel and perpendicular to the extrusion after etching thin sections in an HNO$_3$:H$_2$O = 1:1 solution.

Strength characteristics: limiting strength, relative elongation, elasticity coefficient were determined from the deformation curves obtained by deforming the specimens by compression on a Model 5800 Instron universal testing machine at crosshead speed of ~1 mm/min at room temperature. The electrical conductivity $\sigma$, the Seebeck coefficient $\alpha$ and the specific thermal conductivity $k$ of the samples were measured in the temperature range 100-700 K. The thermoelectric figure of merit was calculated as $ZT = \alpha^2\sigma T/k$, where $T$ is the temperature in degrees Kelvin.

3. Results and discussions
The X-ray microscopic analysis of different parts of the samples showed that with respect to the composition of the charge the content of Bi is ~4 wt.% less, Te is ~2 wt.% more, and Sb ~2 wt.% is greater than the calculated one. The distribution of components along the rod is uniform since their number in the studied samples cut from 2 and 4 rod areas is the same within the accuracy of the method (with an accuracy of 1%). The data obtained are shown in Table 1.

A fractographic analysis of the cleavage surfaces parallel and perpendicular to the extrusion direction reveals the fine-grained layer structure of these samples (figure 2a, b) grain sizes do not exceed several tens of micrometers. The photographs of these the cleavage surfaces obtained with an optical microscope show light inclusions of the second phase (A) which is a tellurium-based eutectic (figure 2c). Thus, despite the fact that the charge was of stoichiometric composition, a small amount of tellurium-based eutectic is present in the crystallized granules, i.e. the crystallization proceeded with a
deviation from the stoichiometric composition and, in order to obtain a single-phase extruded ingot, one must take the initial composition with a slight lack of tellurium.

| Samples | Composition, wt. % | X-ray microscopic analysis of the samples |
|---------|--------------------|------------------------------------------|
|         | Bi  | Te  | Sb  | Bi  | Te  | Sb  |
| 2       | 16.12/22.1 | 57.01/59.07 | 26.87/28.73 | 11.95 | 59.03 | 29.02 |
|         | 12.46 | 59.10 | 28.44 |
|         | 12.28 | 58.61 | 29.10 |
| 4       | 16.12/22.7 | 57.01/58.72 | 26.87/29.0 | 11.83 | 59.03 | 29.14 |
|         | 11.92 | 59.21 | 28.83 |
|         | 13.04 | 58.04 | 28.92 |

Figure 2. SEM images of the cleavage surfaces (a, b) and microstructure images (c, d) on an optical microscope of the samples cut parallel (a, c) and perpendicular (b, d) to extrusion. A — eutectic based on tellurium.

Compression deformation at room temperature was carried out on 16 samples cut from the second and fourth areas of the rod (figure 1). The data are shown in the Table 2. It has been established that limiting strength of the samples cut from the fourth part of the rod reaches $\sigma_B = 201 \pm 7$ MPa while the destruction of the samples is fragile and occurs with a relative deformation of $\varepsilon_B$ about 1%, elasticity coefficient of the samples is $\frac{d\sigma}{d\varepsilon} = 17.5 \pm 0.5$ GPa. The samples cut from the middle of the rod (area 2) are slightly inferior in strength to the samples cut from the end of the rod by ~15 MPa. The obtained values of the limiting strength turned out to be higher than we obtained earlier for materials of $p$-type
conductivity extruded into rods with a cross section of 5×5 mm from pellets crushed in a planetary mill, crystallized in a liquid using less pure starting materials ($\sigma_B \approx 150$ MPa) [3].

**Table 2.** Strength characteristics (limiting strength $\sigma_B$, relative deformation $\varepsilon_B$, elasticity coefficient $d\sigma/d\varepsilon$ and average values) at room temperature obtained by deformation by compression of samples cut from 2 and 4 areas of the rod (figure 1)

| Sample | $\sigma_B$, MPa | $\sigma_B_{av}$, MPa | $\varepsilon_B$, % | $\varepsilon_B_{av}$, % | $d\sigma/d\varepsilon$, GPa | $(d\sigma/d\varepsilon)_{av}$, GPa |
|--------|----------------|----------------------|-------------------|------------------------|--------------------------|-----------------------------|
| 2-1    | 174            | 186±13               | 1.07              | 1.1±0.1                | 16.2                     | 16.7±0.8                    |
| 2-2    | 201            |                      | 1.13              |                        | 17.8                     |                             |
| 2-3    | 196            |                      | 1.33              |                        | 14.7                     |                             |
| 2-4    | 169            |                      | 1.01              | 1.1±0.1                | 16.8                     | 16.7±0.8                    |
| 2-5    | 194            |                      | 1.07              |                        | 18.2                     |                             |
| 2-6    | 204            |                      | 1.20              |                        | 17.0                     |                             |
| 2-7    | 178            |                      | 1.10              |                        | 16.2                     |                             |
| 2-8    | 172            |                      | 1.03              |                        | 16.7                     |                             |
| 4-1    | 203            |                      | 1.09              |                        | 18.6                     |                             |
| 4-2    | 212            |                      | 1.20              |                        | 17.7                     |                             |
| 4-3    | 208            |                      | 1.03              |                        | 20.1                     |                             |
| 4-4    | 208            | 201±7                | 1.07              | 1.1±0.03               | 19.4                     | 18.1±1.4                    |
| 4-5    | 195            |                      | 1.13              |                        | 17.3                     |                             |
| 4-6    | 185            |                      | 1.03              |                        | 17.9                     |                             |
| 4-7    | 194            |                      | 1.11              |                        | 17.4                     |                             |
| 4-8    | 199            |                      | 1.20              |                        | 16.6                     |                             |

The values of thermoelectric parameters (Seebeck coefficient $\alpha$, electrical conductivity $\sigma$, total $k$ and lattice $k_l$ thermal conductivity and thermoelectric figure of merit $ZT$) at room temperature of samples cut from different areas of extruded rod are given in the Table 3.

**Table 3.** Thermoelectric properties at a temperature of 300 K of $p$-type specimens cut from 2, 3 and 4 areas of the rod (figure 1)

| Sample | $\alpha$, $\mu$V/K | $\sigma$, S/cm | $k \times 10^3$, W/cm K | $k_l \times 10^3$, W/cm K | ZT |
|--------|---------------------|----------------|--------------------------|--------------------------|----|
| 2-1    | 235                 | 807            | 12.2                     | 8.4                      | 1.09 |
| 2-2    | 234                 | 758            | 13.1                     | 9.5                      | 0.95 |
| 2-3    | 233                 | 828            | 13.5                     | 9.6                      | 1.00 |
| 2-4    | 234                 | 827            | 14.6                     | 10.7                     | 0.93 |
| 3-1    | 239                 | 869            | 13.6                     | 9.5                      | 1.09 |
| 3-2    | 236                 | 828            | 13.3                     | 9.4                      | 1.04 |
| 3-3    | 235                 | 840            | 13.5                     | 9.5                      | 1.03 |
| 4-1    | 235                 | 800            | 12.1                     | 8.3                      | 1.12 |
| 4-2    | 238                 | 784            | 12.1                     | 8.4                      | 1.04 |
| 4-3    | 229                 | 818            | 12.4                     | 8.6                      | 1.04 |
| 4-4    | 233                 | 813            | 12.3                     | 8.4                      | 1.08 |

The samples studied have similar thermoelectric parameters which are: $\sigma = 814 \pm 55$ S/cm, $k = 13.2 \pm 0.3$ W/cm K, $\alpha = 234 \pm 5$ $\mu$V/K, $ZT = 0.93$-1.12.

The temperature dependences of these parameters in the temperature range of 100-600 K for some samples cut from different areas of the rod are shown in figures 3-5. Measurements of sample No.3 were carried out at the A.F. Joffe Institute of physics and technology RAS (St. Petersburg) by Ph.D. Konstantinov P.P. As shown by measurements of the temperature dependences of thermoelectric parameters, these materials are degenerate semiconductors. The dependences of the Seebeck
coefficient on temperature have the form of curves with a maximum at 340-370 K (figure 3a). In the range of 100-500 K, the electrical conductivity decreases with increasing temperature (figure 3b). The thermal conductivity of the samples begins to increase at temperatures above 350 K (figure 4). The intrinsic conductivity occurs at temperatures above 450 K. The exponents $r$ of logarithmic dependencies $\lg \sigma = f(\lg T)$ and the slope tangents $\Delta$ of dependences $\alpha = f(\ln T)$ in the temperature range from Debye temperature (155 K) to 300 K which amounted to $r = -1.5$, $\Delta \approx 130 \text{ mV/K}$ which indicates the parabolic band structure, the acoustic mechanism of scattering of charge carriers when the effective mass of charge carriers does not depend on temperature [5].

**Figure 3.** Temperature dependences of the Seebeck coefficient (a), electrical conductivity (b) extruded samples of the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution obtained from 2 (1), from 3 (2,3) and from 4 (4) areas of the rod. Sample 3 measured in St. Petersburg.
Figure 4. Temperature dependences of the total thermal conductivity (a), lattice thermal conductivity (b) extruded samples of the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution obtained from 2 (1), from 3 (2.3) and from 4 (4) areas of the rod. Sample 3 measured in St. Petersburg.

Figure 5. Temperature dependence of the thermoelectric figure of merit extruded samples of the Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution obtained from 2 (1), from 3 (2.3) and from 4 (4) areas of the rod. Sample 3 measured in St. Petersburg.
The calculated maximum thermoelectric figure of merit $ZT_{\text{max}}$ for these samples was $1.2 \pm 0.1$ at 340 K (figure 5). The same $ZT_{\text{max}}$ at 370 K was obtained for samples of $p$-type conductivity extruded from granules, ground in a planetary mill, into rods with a section of $5 \times 5$ mm [4].

4. Conclusions

The homogeneity of a rod with a diameter of 20 mm, a length of 350 mm extruded from granules obtained by quenching a melt of a Bi$_{0.4}$Sb$_{1.6}$Te$_3$ solid solution and ground in a planetary mill was investigated. It has been established that the composition along of the rod does not change on the main components. A small amount of the second phase (tellurium-based eutectics) was observed in all the studied samples. The tensile strength obtained by compressing samples at room temperature, cut from the end of the rod, is ~10% higher than that of samples cut from the middle. It was established that samples cut from an extruded rod with a diameter of 20 mm ($\sigma_B \approx 200$ MPa) are stronger than samples extruded into rods with a section of $5 \times 5$ mm ($\sigma_B \approx 150$ MPa). All measured samples have similar values of thermoelectric characteristics (electrical conductivity, thermal conductivity, Seebeck coefficient) at room temperature and in the temperature range of 100-600 K. The maximum thermoelectric figure of merit is $ZT_{\text{max}} = 1.2 \pm 0.1$ at a temperature of 350-370 K.

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