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Thermoelectric properties of Bi–Te–Se tapes obtained by rapid quenching

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The thermoelectric properties (electrical conductivity and thermopower) of thin tapes obtained by rapid quenching (melt spinning) of a solid solution of $Bi_2(Te_{0.85}Se_{0.15})_3$ in the range of 100–700 K are studied. The tapes were compacted into briquettes at room temperature at different pressures. The thermoelectric properties of the briquettes were studied in the range of 300–700 K. The results obtained for samples from spinning tapes are compared with the data for samples prepared from powder of the same composition.

Keywords: thermoelectrics, rapid hardening, melt-spun tapes, tellurides.

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1. Introduction

Thermoelectric conversion — one of fast-growing areas in the field of alternative energy sources. The main advantages of the method may be the ability to convert heat regardless of the source type into power under extreme conditions. The operation of such converters requires no continuous maintenance, they are resistant to vibration loads, high temperatures, and require no oxygen.

Efficiency coefficient of a thermoelectric converter depends on the quality of thermoelectric cells it is made of. Properties of thermoelectric cells, which are in fact batteries, are characterized by internal electric resistance, value of the generated EMF and thermal conductivity. The values of these parameters define the value of thermoelectric figure of merit

$$Z = \frac{\sigma S^2}{\kappa},$$

where σ — specific electric conductivity, S — thermopower coefficient, κ — specific thermal conductivity. You can see from the equation that the increase in the efficiency of thermoelectric conversion — is a complex physical task due to directly proportional relation κ and σ.

To increase the efficiency of thermoelectric materials, nanostructuring is applied, which allows substantial reduction of thermal conductivity and accordingly increase the thermopower coefficient value [1–5]. Due to the presence of nanoinclusions in the volume, additional phonon scattering takes place, and such small dimensions of inhomogeneities cause centers of selective scattering, capable of additional contribution to the thermopower coefficient value.

Nanostructured materials in the form of nanocrystalline specimens may be obtained by method of fast tempering (melt spinning), making it possible to achieve amorphous and/or nanocrystalline materials [6–8].

In the paper the specimens were obtained by the method of spinning of solid solution $Bi_2(Te_{0.85}Se_{0.15})_3$ melt in the form of thin nanocrystalline tapes and pellets pressed from these tapes at room temperature. The studied solid solutions of n-type have the structure of tetradymite, are van der Waals crystals and consist of anisotropic quintets (–Te(1)–Bi–Te(2)–Bi–Te(1)–), where Se atoms substitute Te atoms. Strong covalent chemical bonds are effective between the layers in the quintets, with a small addition of an ion bond, and between quintets — weak van der Waals forces that define light flaking of the material at quintet boundaries Te(1)–Te(1) along the cleavage planes (0001) [9,10].

The material synthesis process — is just the first step towards creation of a thermoelectric branch. The next most important step is material compaction into volume specimens of the required geometric size. As a rule, the produced spinning tapes are compacted into pellets to measure thermoelectric properties. However, in process of compaction the material properties are exposed to external conditions: oxidation, contamination, sintering of nanograins into a micropowder. Therefore, the end material properties do not fully reflect the properties of the source substance charged into a press die. The study of the thermoelectric properties of source thin spinning tapes provides an idea on the extent of the impact of melt spinning process and compaction process at the end parameters of thermoelectric branches. This paper pays attention to the properties of the source spinning substance.

2. Experiment procedure

A well known thermoelectric material $Bi_2(Te_{0.85}Se_{0.15})_3$ — semiconductor of *n*-conductivity type was chosen for the studies. The source ingot was

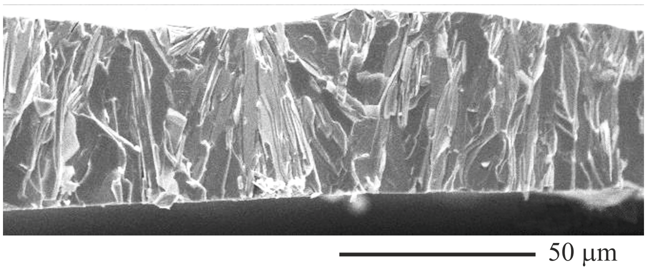

Figure 1. SEM-image of cross section of spinning tape $Bi_2(Te_{0.85}Se_{0.15})_3$.

obtained by zone melting method. For comparative analysis of the result, a powder was prepared from the source ingot used for specimen pelleting.

The obtained ingot was divided into parts, which then were placed in a special crucible for fast tempering of the melt. The setup used was the melt spinning setup, making it possible due to the incidence of a liquid melt jet onto a quick-rotating cooled drum to achieve the cooling speeds 10^5 K/s. Fast transition from the liquid phase to the solid one also made it possible to obtain thin tapes of the same composition as the source ingot.

In process of work several batches of tapes were made at different speed of drum rotation: 5, 10, 17, 26 m/s. Each batch was divided and pelletized with different pressure at room temperature and the same pressing time. The cooled drum speed determines both the melt cooling speed and the thickness and texture of the obtained tapes. Tape thicknesses decrease in the interval from 20 to 55 μm as the speed increases. The tape width in all cases was not constant, but at slower speeds the tapes were wider. The width changes from 2 to 4 mm. In process of melt spinning usually three fractions of the material are produced: regular tapes, needles with width of 0.5 mm in average and flakes.

For structural measurements and thermoelectric studies, the specimens in the form of tapes were selected. Using the setup described in paper [11], temperature dependences were measured for electric conductivity and thermopower coefficient in individual tapes and pellets in the interval of 100–700 K. The produced tapes and pelleted specimens were studied by the method of X-ray diffraction analysis before and after thermal treatment.

3. Measurement data

The study of the structure of the tapes produced under different spinning conditions shows that the structure has no signs of amorphization and does not depend on the drum rotation speed (cooling speed) and matches the structure of the source ingot and powder. No secondary phase was found. The results of energy-dispersive X-ray spectroscopy (EDS) indicate that the composition is homogeneous at a micrometer scale and coincides at both sides of the tapes.

Figure 1 presents an image of an electronic microscope (SEM) for the tape cross section. Tapes consist of flakes with the length of the order if its thickness and with the transverse dimensions of the order of hundreds of nanometers. Flakes are arranged perpendicularly to the tape surface and have chaotic orientation in two other directions. Similar structures were observed for other spinning materials *p*-BiTeSb [12,13].

Spinning tapes have two different surfaces Figure 2. The side that was in contact with the cooled drum is called contact and consists of crystallites in the form of thin needles. Needle growth of crystals is related to the presence of growth anisotropy in the preferable crystallographic directions. Free side — the side that did not interact with the cooled surface, has certain periodic structure in the surface that reminds of a wave. Similar lamellar (plate) periodical structures in spinning materials arise due to the release of one of melt components in the grain boundaries [14].

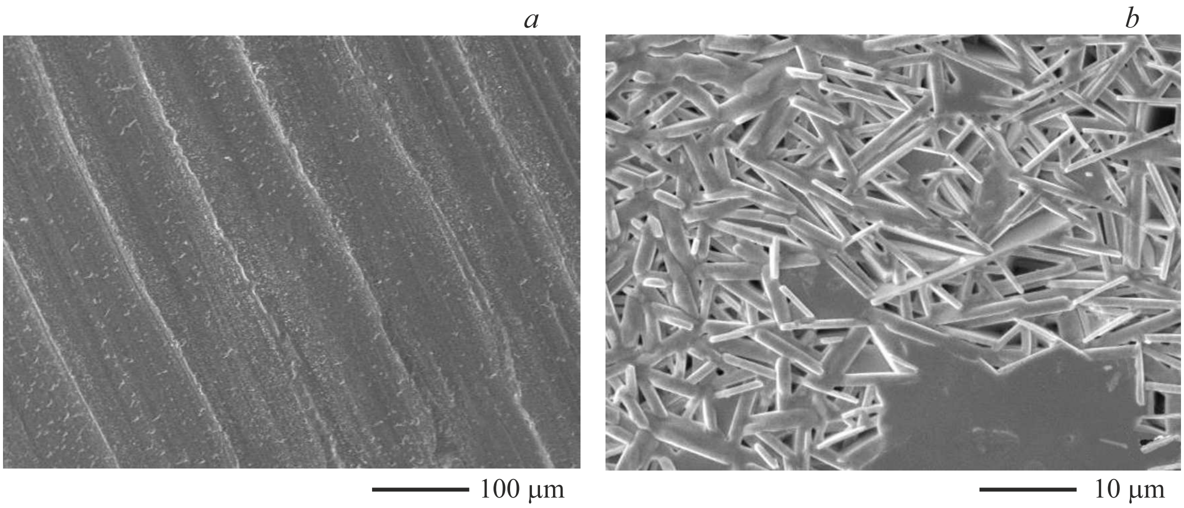

Figure 2. SEM-image of free (*a*) and contact (*b*) surface of the tape $Bi_2(Te_{0.85}Se_{0.15})_3$.

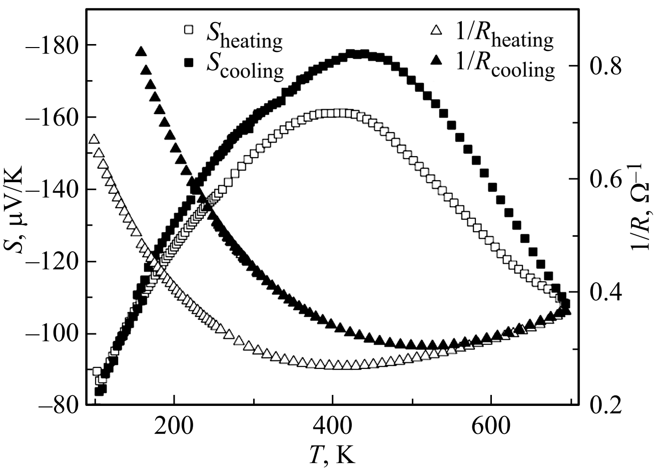

Figure 3. Temperature dependence of thermopower coefficient and electric conductivity of an individual spinning tape $Bi_2(Te_{0.85}Se_{0.15})_3$.

Specimens were selected among the tapes with the necessary length to measure thermoelectric properties. The complexity of measurements consisted in brittleness of tapes due to their stressed structure and curvature, which complicated the process of arrangement on the holder for the specimens.

Figure 3 presents temperature dependences of electric conductivity and thermopower coefficient in an individual tape produced by melt spinning at the speed of cooled drum 10 m/s. It is not possible to estimate the specific value of electric conductivity due to the inability to assess the cross section. You can see that curves of heating and cooling do not coincide: thermopower coefficient increases, and electric conductivity drops after heating (annealing). Changes in the electric properties of the tape are related to certain structural changes. These may be the processed related to sintering of flakes and to the change in the structure of five-layer bags (−Te(1)−Bi−Te(2)−Bi−Te(1)−). In process of spinning some Te(1) atoms may be torn off from the five-layer bags due to poor bonds between the bags. Such atoms Te(1) may form nanostructures. Besides, in process of spinning and/or pressing of solid solution tapes, distances between the layers both in five-layer bags and distances between the bags, i. e. van der Waals slot dimensions, may vary. All these deformation changes of the structure create a large number of point defects that cause appearance of additional charge carriers (donor effect) [15]. The observed growth of thermopower coefficient after annealing (Figure 3) is related to reduction in the number of point defects in the volume of the material causing concentration of carriers. Growth of conductivity (Figure 3) after annealing is related to the growth of mobility of carriers due to sintering of flakes and decrease in the number of grain boundaries and defects of the structure. Dependence on Figure 3 is typical for the tapes produced at various cooling speeds.

Pelletizing method was used to assess the specific values of conductivity of the obtained spinning material. Pelletizing was done by pressing method at room temperature. Low pressing temperature was selected to minimize the changes in the structure of spinning tapes, and at the same time to assess the quantitative changes of conductivity in process of thermal treatment.

Pellets were prepared to study the thermoelectric properties in three pressing modes: 0.8, 1.0 and 1.2 GPa. It should be noted that the typical pressure to press specimens for this material is 0.05−0.2 GPa. Figure 4 presents the results of thermopower coefficient and electric conductivity measurements for the pellets (drum rotation speed 26 m/s), cooling curves are provided. As expected, the thermopower coefficient does not depend on the geometric factor (density of material) and is only determined by the composition, therefore it does not depend on the pelletizing pressure. Specific electric conductivity increases with the growth of pressing pressure, which means a denser packing of spinning tapes in a pellet. At the same time you can see that pressure 1 GPa is the limit for pelletizing, and its increase does not result in the material density growth.

To study the effect of the spinning mode at the properties of the final thermoelectric material, pellets were prepared from spinning material, as well as specimens of the powder of the source ingot, which was used for spinning. Figure 5 presents the temperature dependences of the thermopower coefficient and specific electric conductivity of the specimen obtained by the pelletizing of the source powder (0 m/s) and specimens produced by pelletizing of spinning tapes. Dark symbols correspond to cooling curves, and light ones — to heating curves. Only cooling curves are provided for the specimens pressed from tapes.

Reduction in the thermopower coefficient of pelletized specimens with the growth of drum rotation speed may be related to the stronger deformation of the crystalline

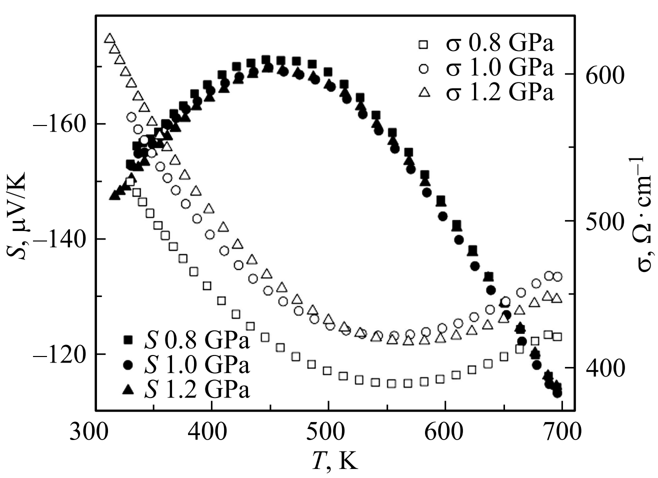

Figure 4. Temperature dependence of thermopower coeffcient and electric conductivity of pellets $Bi_2(Te_{0.85}Se_{0.15})_3$, produced at different pressure of pressing.

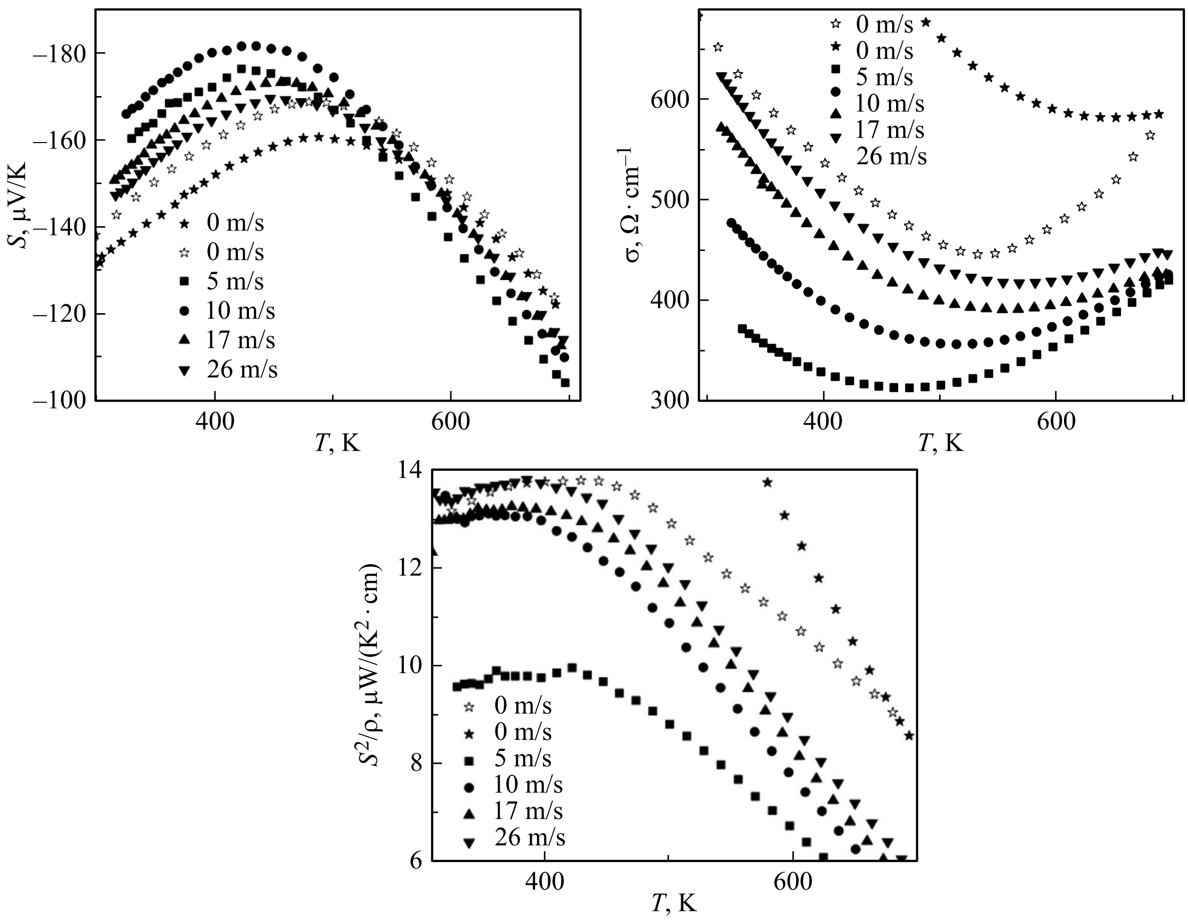

Figure 5. Temperature dependences of power factor of specimens $Bi_2(Te_{0.85}Se_{0.15})_3$ produced by cold pressing and cold-pressed specimen from the source ingot powder. Dark icons — cooling curves, light icons — heating curve.

lattice in process of fast tempering and formation of smaller crystallites due to shorter time of melt contact with the cooled surface of the drum. In this case the donor effect will be more pronounced for the tapes obtained at higher cooling speeds. Accordingly, the concentration of charge carriers in such tapes will also rise. You can see in Figure 5 that the increase of concentration not only causes reduction in the thermopower coefficient value, but the shift of the maximum to the area of higher temperatures. The lower values of thermopower coefficient in the specimen pressed from the powder are explained by more chaos in the crystal-lattice orientation of grains in the material. Increase in electric conductivity of the tapes with the growth of the cooling speed is related not only to the increased concentration of the charge carriers, but also to the fact that the tapes with smaller crystallites are sintered better, i.e., grains with smaller sizes merge into larger grains, containing fewer low-conducting boundaries. As you can see in Figure 5, powder sintering (heating and cooling curve 0 m/s) causes substantial growth of conductivity. Such drastic increase may only be related to the sintering of powder and reduction in the number of low-conducting boundaries.

4. Conclusion

The paper studied the thin tapes produced by melt spinning method. It was shown that thermopower of the tapes decreases, and conductivity increases with the increase of the cooling speed. The main cause for the differences is the increasing deformation of the crystalline lattice with increase of the cooling speed, causing charge carrier concentration growth.

Despite the fact that tapes at any cooling speeds have higher values of thermopower coefficient compared to the specimen from the powder of the source ingot, the conductivity of the specimens from the pelletized tapes has quite low values due to the presence of many intercrystalline boundaries.

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Conflict of interest

The authors declare that they have no conflict of interest.

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