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Influence of heat treatment of the thermoelectrical and mechanical properties of *p*-type $Bi_{0.5}Sb_{1.5}Te_3$ solid solution obtained by extrusion method

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The work carried out a study of the effect of heat treatment on the mechanical strength and thermoelectric figure of merit of the $Bi_{0.5}Sb_{1.5}Te_3$ solid solution. A decrease in the ultimate strength and the appearance of yield after annealing associated with antistructural defects were revealed. It has been established that heat treatment reduces the conductivity and thermal conductivity of the thermoelectric material, and also increases the Seebeck coefficient, which leads to an increase in thermoelectric efficiency from $Bi_{0.5}Sb_{1.5}Te_3$ to $3.5 \cdot 10^{-3}K^{-1}$.

Keywords: Thermoelectricity, extrusion, solid solutions, density, quality factor, annealing.

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1. Introduction

Currently produced thermoelectric materials on which thermoelectric modules are based, are solid solutions with an inhomogeneous disordered distribution of components containing intrinsic and impurity defects, which is attributable to the degree of purity of the original materials, the doping level, the type of state diagram, the synthesis, crystallization and heat treatment conditions [1]. In particular, a material produced using ceramic technology can contain atmospheric corrosion products, pores and microcracks in large quantities. The use of extrusion technology with correctly selected original compositions and proven synthesis conditions makes it possible to obtain well-textured thermoelectric materials with low electrical resistivity and high mechanical strength [2]. It is the mechanical strength that is one of the important advantages of extruded thermoelectric materials based on solid solutions of $Bi_{0.5}Sb_{1.5}Te_3$, which is usually 4−5 times higher than the strength of samples produced by zonal melting [3]. Mechanical properties are of particular importance in case of usage of the material in thermoelectric generator and cooling modules and micromodules [4,5].

The materials produced by extrusion have a structural grain disordering that reduces the thermoelectric efficiency Z, which is determined using the following formula [6]

$$Z = \frac{\sigma S^2}{\chi}, \tag{1}$$

where σ — conductivity, S — thermo-emf, χ — thermal conductivity. A partial reduction of the thermoelectric Q-factor Z is compensated by a reduction of thermal conductivity χ because of the phonon scattering on defects [7]. Heat treatment [8] that can negatively affect the mechanical strength is an effective method of increasing the thermoelectric Q-factor. The effect of heat treatment on the mechanical strength and thermoelectric Q-factor of a solid solution of $Bi_{0.5}Sb_{1.5}Te_3$ was studied taking into account the above.

2. Experimental part

A thermoelectric material with the *p*-type conductivity of the $Bi_{0.5}Sb_{1.5}Te_3$ composition produced by extrusion was studied in the paper. Bismuth Vi-00, antimony Su-000, tellurium of special purity of the brand T-Y were used as initial components. The crushed materials were placed in a quartz flask, vacuumed and sealed at a residual pressure of $1 \cdot 10^{-3}$ mm Hg A muffle furnace with a mixing mechanism was used for synthesis at a temperature of 1020 K. The synthesized ingot of thermoelectric material was crushed in a vortex mill, and the obtained fine powder was sieved through sieves with 0.5 and 0.064 mm mesh size. Then the sieved material was briquetted into cylindrical blanks with a diameter of 40 mm at a pressure of 2 t/cm^2. Extrusion was performed at a temperature of 650−660 K and a plunger velocity of 0.05 mm/s on a test press IP-2500M with a maximum load of 500 MPa.

The extruded ingots were cut on an erosive cutting machine perpendicular to the extrusion axis into experimental samples for mechanical testing, and the thermoelectric parameters were measured along the extrusion axis. The heat treatment was performed in a vacuum thermostat at a temperature of 573 K for 24 hours.

The synthesized samples were certified using X-ray diffraction on the „Bruker D2 Phaser“ diffractometer. The density of the samples was measured by hydrostatic weighing. The electrical conductivity and the Seebeck coefficient were measured using Netzsch SBA458 analyzer by the four-probe method and the hot probe method, respectively, and the thermal conductivity was measured using Netzsch LFA467 analyzer by the flash method. Compression tests were carried out at the CCU named after prof. Yu.M. Borisov of the Voronezh State Technical University.

3. Experimental results and discussion

The diffractogram of the experimental samples confirms the presence of the phase $Bi_{0.5}Sb_{1.5}Te_3$, which corresponds to the specified stoichiometry of the initially synthesized composition (Figure 1). The sample is textured, which is associated with the production technology. The main phase of the solid composition $Bi_{0.5}Sb_{1.5}Te_3$ is $> 90\%$. The phase Bi_2Te_3 is present in a small quantity, but with a distorted cell.

The density measured by hydrostatic weighing was 6.5 g/cm^3, which is in good agreement with the literature data [9].

The compression tests of the obtained samples of thermoelectric solid solution of $Bi_{0.5}Sb_{1.5}Te_3$ were performed to study the effect of heat treatment on mechanical parameters. Figure 2 shows a compression diagram in stress (σ) — strain coordinates (ε). The compressive stress was calculated using the following formula

$$\sigma = P/F, \qquad (2)$$

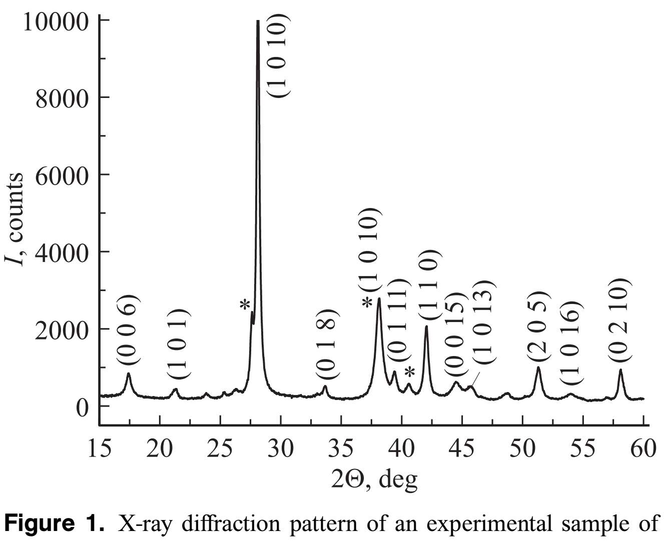

Figure 1. X-ray diffraction pattern of an experimental sample of a solid solution $Bi_{0.5}Sb_{1.5}Te_3$. The symbol $*$ marks the positions of reflexes from the phase Bi_2Te_3.

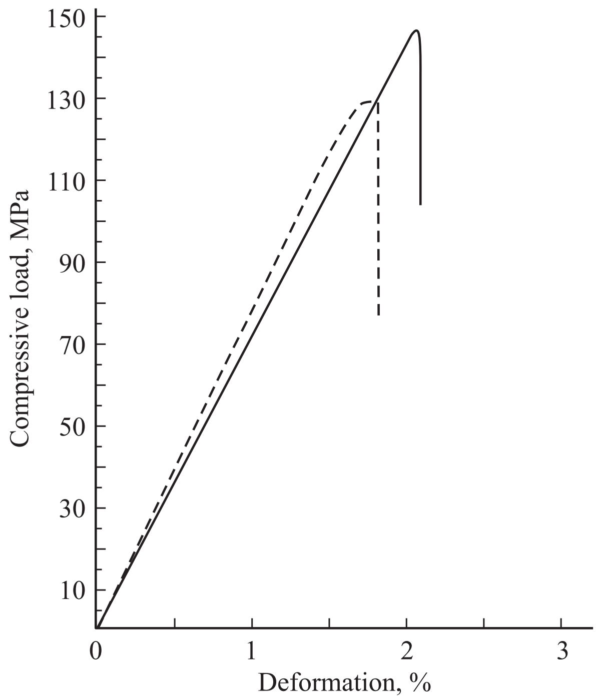

Figure 2. Curves $\sigma-\varepsilon$ of extruded samples of $Bi_{0.5}Sb_{1.5}Te_3$ before (solid) and after heat treatment at a temperature of 573 K for 24 hours (dashed).

where σ — compressive stress, MPa; P — applied load, N; F — average cross-sectional area, mm^2.

The relative compression strain was determined using the following formula

$$\varepsilon = [(h_0 - h)/h_0] \cdot 100\%, \qquad (3)$$

where h — the current height of the sample during deformation, mm; h_0 — the initial height of the sample before the test, mm.

The solid curve in Figure 2 corresponds to the initial sample after extrusion, and the dashed one — corresponds to the sample heat-treated at a temperature of 573 K for 24 hours.

The analysis of the experimental results presented in Figure 2 indicates a decrease of the tensile strength of the extruded sample after heat treatment (dashed curve) compared with the original sample (solid curve) by $\sim 13\%$. However, it should be noted that after heat treatment, a small yield point appeared on the stress-strain curve, which helps to reduce the fragility of the material and increase the reliability of the thermoelectric module made of this material. This pattern is probably related to the relaxation of internal stresses caused by the redistribution of point defects, which are stops for sliding dislocations, and the removal of nonequilibrium antistructural defects. The modulus of elasticity of the obtained samples was $E \sim 70$ GPa for the sample obtained by extrusion, and it increases after heat treatment, which is consistent with the results of paper [10].

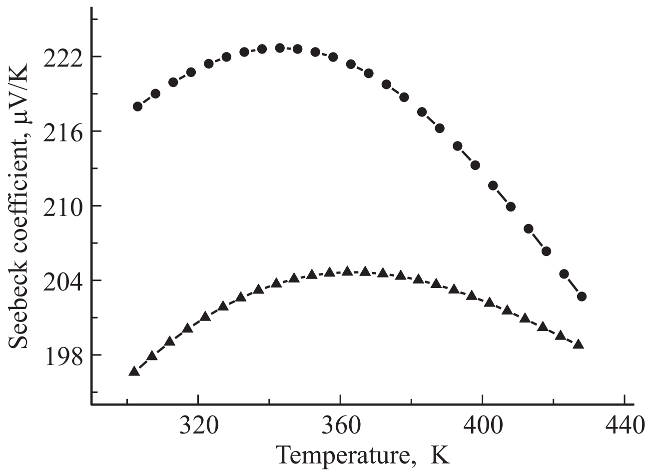

Figure 3. The temperature dependences of the Seebeck coefficient of extruded samples of $Bi_{0.5}Sb_{1.5}Te_3$ before (solid curve) and after heat treatment at a temperature of 573 K for 24 hours (dashed curve).

The temperature dependences of the thermoelectric parameters of the extruded samples before and after annealing are shown in Figures 3–6.

The temperature dependence of the Seebeck coefficient for the thermoelectric sample of $Bi_{0.5}Sb_{1.5}Te_3$ obtained by extrusion is represented by a solid curve in Figure 3. A peak is observed on the temperature dependence of the thermo-emf at $T \sim 363$ K, the height of which increases significantly and shifts to lower temperatures ($T \sim 343$ K) after heat treatment at $T = 573$ K for 24 h (dashed curve). Such a pattern of thermo-emf growth is probably associated with the removal of nonequilibrium antistructural defects, resulting in a decrease of the concentration of carriers of the charge.

The temperature dependence of the electrical conductivity for the thermoelectric sample of $Bi_{0.5}Sb_{1.5}Te_3$ obtained by extrusion decreases with the increase of the temperature (dashed curve in Figure 4), which is typical for degenerate semiconductors. Heat treatment at $T = 573$ K for 24 h results in a decrease of electrical conductivity throughout the studied temperature range (solid curve). A decrease of the electrical conductivity of the heat-treated sample in the studied temperature range confirms the above hypothesis of a decrease of the concentration of charge carriers. The Hall effect were measured to experimentally confirm the decrease of the concentration of charge carriers and it was found that the heat treatment of an extruded sample of $Bi_{0.5}Sb_{1.5}Te_3$ at a temperature of 573 K for 24 hours results in a decrease of the concentration of charge carriers from $3.0 \cdot 10^{19}\,cm^{-3}$ in the initial state to $1.8 \cdot 10^{19}\,cm^{-3}$ in the sample after heat treatment.

Figure 5 shows the temperature dependences of the thermal conductivity coefficient of thermoelectric material samples of $Bi_{0.5}Sb_{1.5}Te_3$ composition of *p*-type of conductivity obtained by extrusion, before (solid curve) and after heat treatment at $T = 573$ K for 24 h (dashed curve). A minimum is observed on the temperature dependence of the thermal conductivity coefficient at $T \sim 363$ K, the value of which decreases significantly, and the position shifts to lower temperatures ($T \sim 343$ K) after heat treatment at $T = 573$ K for 24 h (dashed curve). The obtained result indicates the redistribution of point defects, contributing to additional scattering of phonons.

The temperature dependences of the thermoelectric Q-factor Z of the studied thermoelectric material of $Bi_{0.5}Sb_{1.5}Te_3$ of *p*-type of conductivity according to (1) are shown in Figure 6. The thermoelectric Q-factor of the thermoelectric material obtained after heat treatment (dashed curve) increases in the range of room tempera-

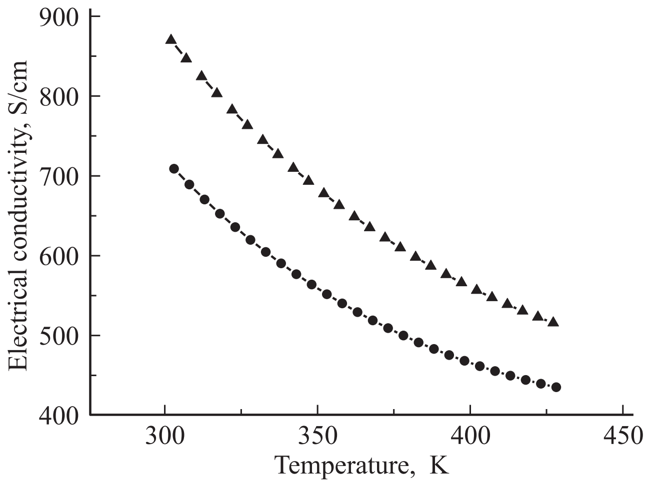

Figure 4. Temperature dependences of the electrical conductivity of extruded samples of $Bi_{0.5}Sb_{1.5}Te_3$ before (dashed curve) and after heat treatment at a temperature of 573 K for 24 hours (solid curve).

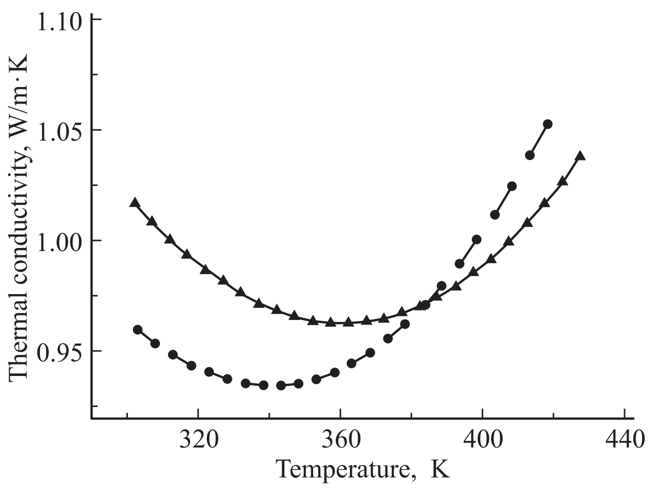

Figure 5. The temperature dependences of the thermal conductivity coefficient of extruded samples of $Bi_{0.5}Sb_{1.5}Te_3$ before (solid curve) and after heat treatment at a temperature of 573 K for 24 hours (dashed curve).

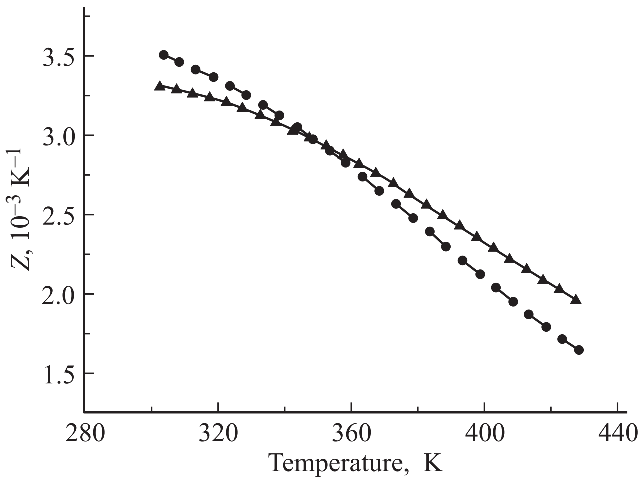

Figure 6. The temperature dependences of the thermoelectric Q-factor of samples $Bi_{0.5}Sb_{1.5}Te_3$ obtained by extrusion, before (solid curve) and after heat treatment at $T = 573$ K for 24 h (dashed curve).

tures and decreases with the increase of the temperature > 343 K compared with the initial sample after extrusion (solid curve). The obtained values of the thermoelectric Q-factor of extruded samples of $Bi_{0.5}Sb_{1.5}Te_3$ with *p*-type of conductivity after heat treatment exceed similar parameters provided in Ref. [11].

Therefore, the heat treatment at $T = 573$ K for 24 h of an extruded thermoelectrical sample of $Bi_{0.5}Sb_{1.5}Te_3$ with *p*-type of conductivity has a beneficial effect on thermoelectric properties.

4. Conclusion

Solid solution samples of $Bi_{0.5}Sb_{1.5}Te_3$ were synthesized by extrusion and the impact of heat treatment on mechanical strength and thermoelectric parameters was studied. It was found that heat treatment at $T = 573$ K for 24 h results in a decrease of the tensile strength from 150 to 130 MPa and the formation of a yield point. It is shown that heat treatment reduces the electrical conductivity and thermal conductivity of a thermoelectric material, but increases the Seebeck coefficient. As a result, an increase of thermoelectric efficiency from $3.3 \cdot 10^{-3}K^{-1}$ to $3.5 \cdot 10^{-3}K^{-1}$ is observed at room temperature.

Conflict of interest

The authors declare that they have no conflict of interest.

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