Improving the characteristics of thermoelectric generator batteries based on bismuth telluride by optimizing the parameters of hot pressing n-Bi$_2$Te$_{2.4}$Se$_{0.6}$

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Abstract. The effect of hot pressing modes (pressing pressure and holding time under pressure) on the thermoelectric properties of n-type bismuth telluride Bi$_2$Te$_{2.4}$Se$_{0.6}$ doped with Hg$_2$Cl$_2$ was investigated. Samples were obtained by powder metallurgy technology - the synthesis of a chemical compound followed by hot pressing. A change in the hot pressing modes does not significantly influence the value of the thermo-EMF and conductivity of the samples. A change in the hot pressing mode significantly influences on the value of thermal conductivity. Both the increase of pressing pressure and the increase of the holding time under pressure leads to a decrease in the thermal conductivity of the material. Thus, the thermoelectric figure of merit of bismuth telluride can be increased by increasing the pressing pressure, holding time under pressure, or both parameters simultaneously. The increase of the thermoelectric figure of merit was 15% in the investigated samples. As a result of the tests of thermoelectric generator batteries, it was found that the output power of the battery made from a material with a high figure of merit was 27 W at temperatures 70 °C on the cold side, 300 °C on the hot side. The output power of the battery which was made from the material with a lower figure of merit was 25 W at a similar temperature regime.

1. Introduction

The use of generating equipment that is safe, environmentally friendly, use alternative energy sources is an actual task for the energy sector. Thermoelectric power generators have a number of advantages over traditional electric generators. The simplicity of design and the absence of moving parts provides high reliability - the most important criterion for the autonomous energy supply of remote and inaccessible objects such as technological communications and telemetry facilities, field systems for collecting and preparing gas for transport and cathodic protection systems for gas and oil pipelines [1-3].

The characteristics of thermoelectric generators substantially depend on the parameters of thermoelectric materials from which thermoelectric batteries and modules are made. Currently, bismuth telluride and solid solutions based on it are widely used for the manufacture of branches of thermoelectric generator batteries. This is due to the high values of the thermoelectric figure of merit.
in the temperature range of ~ 200 - 350 °C and high values of thermoelectromotive force [4-6]. Bismuth telluride and solid solutions based on it currently have no alternative [7] for the production of thermoelectric generators despite the active search of cheaper and environmentally friendly thermoelectric materials. Therefore, the search for technologies to improve the thermoelectric properties of bismuth telluride is an extremely urgent and practically significant task.

The possibilities of increasing the thermoelectric figure of merit by obtaining low-dimensional structures [8,9] are being actively studied in recent years. The use of low-dimensional structures such as thin films [10, 11], superlattices [10, 12], whiskers [13], nanoscale structures [14, 15], quantum wells [16, 17], quantum wires [18, 19, 20], etc. leads to a decrease in the thermal conductivity of the lattice or to an increase in the density of electronic states [21]. However, there are significant technological difficulties in obtaining such materials. What is more, their mechanical properties are practically unstudied. In this regard, low-dimensional structures are interesting only for scientific research. It is premature to consider the possibility of their introduction to industrial production.

The idea of increasing the thermoelectric figure of merit by using graphite-based nanomaterials proved unjustified. Thus, it was shown in [22, 23] that the introduction of carbon nanotubes, as well as amorphous carbon into the bismuth telluride matrix, leads to a significant decrease in the electrical conductivity, thermoEMF, and thermoelectric figure of merit. The introduction of fullerene C60 into bismuth telluride leads to an increase in thermoEMF and a decrease in the thermal conductivity, the electrical conductivity and thermoelectric figure of merit [24].

Powder metallurgy methods are most popular for obtaining thermoelectric materials based on bismuth telluride and its solid solutions. The most promising among them are melt spinning (MS) methods for producing powders of synthesized materials and spark plasma sintering (SPS) for consolidating the obtained powders. The figure of merit (ZT) of bismuth telluride samples obtained using these methods exceeds 1.0 [25-28]. At the same time, their introduction into production is associated with difficulties, the most significant of which are changes in the existing technology process and the re-equipping of rather expensive technological equipment. The problem of structural stability at elevated temperatures of materials obtained by this technology is also unresolved.

Hot pressing of pre-synthesized powder of thermoelectric material is simpler in comparison with MS and SPS methods. This implementation of powder metallurgy technology is used in production as a rule. However, the results obtained by different authors depend on the synthesis conditions of the initial powders of the thermoelectric material and its sintering and can significantly differ (see [29-33] for example). Therefore, the determination of the optimal parameters of the technological cycle that can allow us to obtain thermoelectric materials with the highest figure of merit by powder metallurgy technology is an actual problem.

The effect of hot pressing on the thermoelectric properties of bismuth telluride is investigated. It is shown that a change in pressing pressure or holding time under pressure affects the electrical conductivity and thermal conductivity of the material, which leads to a change in the thermoelectric figure of merit.

2. Methods

Samples of Bi2Te2.4Se0.6 doped with calomel were used as objects of study. The samples were obtained using a two-stage technology of powder metallurgy, including the synthesis of a chemical compound followed by hot pressing. The modes of hot pressing are shown in table 1, where T is the pressing temperature, p is the pressing pressure, t is the holding time under pressure.
Table 1. Hot pressing Formatting modes of Bi₂Te₂.₄Se₀.₆.

| Sample No. | T, °C | p, t/sm² | t, min |
|------------|-------|----------|--------|
| 1          | 400   | 5        | 5      |
| 2          | 400   | 5        | 20     |
| 3          | 400   | 5.5      | 10     |

The thermal conductivity of the samples was investigated using Netzsch LFA 467, the conductivity and the thermo-EMF coefficient was investigated using Netzsch SBA 458 in the temperature range of 30 - 300 °C.

3. Results and discussion
The temperature dependences of the thermo-EMF of Bi₂Te₂.₄Se₀.₆ samples are shown in figure 1. The resulting dependencies are similar. Curves are typical for degenerate semiconductors [34].

![Figure 1. Temperature dependences of thermo-EMF of Bi₂Te₂.₄Se₀.₆.](image)

Negative values of thermo-EMF mean that the main charge carriers are electrons, therefore, the samples are n-type thermoelectric material. The increase of absolute values thermo-EMF with increasing temperature is associated with an increase in the energy of the main charge carriers [34]. At temperatures above 200 °C, intrinsic conductivity appears, which leads to a decrease in the absolute value of thermo-EMF.

The values of thermo-EMF (α) of samples No. 1 and 3 are close over the entire temperature range. The α values of sample No. 2 are on average 3.5% less (in absolute value) than values of No. 1 and 3, which may be due to a higher concentration of free charge carriers.

The temperature dependences of the conductivity of samples No. 1, 3 practically coincide (figure 2). The conductivity of sample No. 2 is greater than that one of No. 1 and 3, which is consistent with the results of measuring thermo-EMF. As is known [34], large values of conductivity at lower values of thermo-EMF are associated with a higher concentration of charge carriers in doped semiconductors.

The conductivity of all samples decreases with increasing temperature. Such a dependence is observed in heavily doped semiconductors [35]. In this case, the semiconductor degenerates at cryogenic temperatures and the material begins to exhibit properties close to the ones of metal. The
concentration of impurities is so high in a degenerated semiconductor that the intrinsic properties are practically not manifested, but mainly the properties of the impurity.

An analysis of the temperature dependence of conductivity allows us to determine the temperature ranges in which impurity or intrinsic conduction mechanisms predominate, as well as determine the mechanisms of charge carrier scattering. In doped semiconductors in a degenerated state, a change in the conductivity with a change in temperature occurs in the same way as in metal, inversely proportional to the temperature, so the dependence \( \sigma(1/T) \) is linear.

The dependence \( \sigma(1/T) \) for sample No. 1 is shown in figure 3. Up to the temperature of 145 °C (indicated by a dotted line in figure 3), the dependence \( \sigma(1/T) \) is linear. Impurity conductivity is realized in this interval. A deviation of the dependence on the line is observed at temperatures above 145 °C, which corresponds to the appearance of intrinsic conductivity in the sample. The temperature of occurrence of intrinsic conductivity for samples No. 2 and 3 was determined similarly. Its values were 155 and 100 °C respectively.

The temperature dependences of the thermal conductivity of samples No. 1 and 2 almost coincide (figure 4). Thermal conductivity values of sample No. 3 in the entire temperature range are lower than for No. 1 and 2.

As it is known, thermal conductivity \( (\lambda) \) consists of the electronic \( (\lambda_e) \) and phonon \( (\lambda_p) \) components [35,36]. The value of the electronic component of thermal conductivity \( \lambda_e \) can be determined according to the Wiedemann-Franz law, which for degenerated semiconductors has the form:

\[
\lambda_e = 2.44 \cdot 10^{-8} T \sigma
\]  \( \text{(1)} \)

Then the value of the phonon component of thermal conductivity is:

\[
\lambda_p = \lambda - \lambda_e
\]  \( \text{(2)} \)

The results of calculating the \( \lambda_e \) and \( \lambda_p \) are shown in figures 5 and 6.
Figure 4. Temperature dependences of thermal conductivity of Bi$_2$Te$_{2.4}$Se$_{0.6}$.

Figure 5. Temperature dependences of the electronic component of thermal conductivity of Bi$_2$Te$_{2.4}$Se$_{0.6}$.

Figure 6. Temperature dependences of the phonon component of the thermal conductivity of Bi$_2$Te$_{2.4}$Se$_{0.6}$.

As it is shown in figures 5 and 6, a change in the hot pressing mode leads to an increase (in comparison with sample No. 1) of the electronic and a decrease in the phonon component. The increase of the electronic component is due to an increase in the mobility and concentration of charge carriers. The $\lambda_e(T)$ dependences of samples No. 2 and 3 differ insignificantly, whereas in comparison with sample No. 1 their average integral values $\lambda_{\mu}$ are less by 12 and 16% respectively. The pressing technology of samples No. 1 and 2 differs only in the exposure time under pressure, for samples No. 1 and 3 differs by the exposure time and pressing pressure (table 1). It follows that the reduction of the phonon component is achieved, first of all, by increasing the exposure time of the material under pressure, the influence of the pressing pressure is not high.
The difference in the electrical and thermal properties of the studied samples caused a difference in the thermoelectric figure of merit (figure 7). A simultaneous increase in pressing pressure and holding time under pressure (samples No. 1 and 3) has the greatest effect on the value of ZT. As a result, ZT increases by an average of 10.0%.

Materials for the branches of thermoelectric generator batteries were obtained by the proposed technology to verify the influence of the properties of materials on the operational characteristics of the products. Two thermoelectric generator batteries based on a material with high ZT (sample No. 3) and standard material (sample No. 1) were made for testing. As a result of tests of thermoelectric generator batteries, it was found that the output power of the battery made from a material with high ZT was 27 W at temperatures 70 °C on the cold side, 300 °C on the hot side. The output power of a battery which was made from a material with a lower ZT was 25 W at a similar temperature regime.

4. Conclusion
An increase in the holding time under pressure during hot pressing of n-type bismuth telluride leads to a decrease in thermo-EMF and an increase in electrical conductivity. An increase in holding time with a simultaneous increase in pressing pressure does not lead to a significant change in thermo-EMF and electrical conductivity.

The increase in exposure time under pressure during hot pressing does not influence on the thermal conductivity of n-type bismuth telluride. An increase in holding time with a simultaneous increase in pressing pressure leads to a decrease in thermal conductivity.

The selection of optimal pressing modes allows us to increase the value of ZT without changing the composition of materials or the main stages of the technological cycle of obtaining materials. As a result, an increase in the output power of thermoelectric generator batteries is achieved without any significant change in the technological cycle of their production.

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