

Microstructure and Thermoelectric Properties of Medium-Entropy $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe Compounds Prepared by Reactive Spark Plasma Sintering

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Abstract—Reactive spark plasma sintering (RSPS) is used to obtain single-phase samples of medium-entropy $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ compounds (low-temperature thermoelectric electronic type of conductivity) and PbSnTeSe (medium temperature hole-type thermoelectric conductor) from a mixture of powders of the corresponding elemental metals. The obtained samples are polycrystalline with lamellar grains with the average size of $\sim 3.3 \mu\text{m}$ in $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and with irregularly shaped grains with the average size of $\sim 18.9 \mu\text{m}$ in PbSnTeSe . The maximum thermoelectric figure-of-merit of the samples is ~ 0.43 (at 500 K for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$) and ~ 0.35 (at 725 K for PbSnTeSe).

Keywords: thermoelectric materials, medium entropy alloys, reactive spark plasma sintering, microstructure

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1. INTRODUCTION

The development of high- and medium-entropy alloys is one of the effective approaches of modern physical materials science, which is used to improve the properties of materials [1–3]. Such alloys are characterized by increased mixing of the entropy values compared to traditional multicomponent alloys. High entropy alloys contain at least 5 elements, the amount of each of which should not be less than 5 at % and should not exceed 35 at %. In turn, medium-entropy alloys consist of 3 or 4 main elements. Due to the efficient scattering of phonons on the structural inhomogeneities characteristic of high- and medium-entropy alloys, these alloys have low thermal conductivity, which is important for increasing the thermoelectric figure-of-merit of ZT materials. The thermoelectric figure-of-merit is expressed as $ZT = [S^2/(\rho k)]T$, where S is the Seebeck coefficient, ρ is electrical resistivity, k is the total thermal conductivity, and T is the absolute temperature. High-entropy and medium-entropy alloys are a new class of promising thermoelectric materials with low thermal conductivity [4–6]. At present, the main way to create such materials is based on the use of a known thermoelectric material, taken as a parent compound, which can be converted into an appropriate high-entropy or medium-entropy alloy. For the medium-entropy alloys $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSbTeSe developed in this study, such parent compounds are bismuth telluride Bi_2Te_3 (low-tem-

perature thermoelectric of electronic type of conductivity) and lead telluride PbTe (medium-temperature thermoelectric of the hole type of conductivity). The main aim of this study is to obtain polycrystalline samples of medium-entropy $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe compounds and determine the features of the microstructure and thermoelectric properties of the samples using reactive spark plasma sintering (RSPS). Usually, when obtaining thermoelectric materials, the stage of synthesis of the initial powder of the required chemical composition and the stage of sintering of the initial powder are carried out separately. In the RSPS method, these stages are combined; i.e., both the formation of the required compound and the preparation of a bulk sample of the required shape and size from this compound occur in one process [7–9]. The obvious advantage of RSPS is the reduction in the number of stages of the technological process, which, in principle, makes it possible to obtain purer materials. To obtain materials using RSPS of a mixture of elemental metal powders, the desired compound can be synthesized as a self-propagating high-temperature synthesis (SHS), when an exothermic chemical process such as combustion is initiated in the mixture of powders, leading to the formation of a compound. The SHS method alone (not as the RSPS stage) is used for the synthesis of initial powders of some thermoelectric materials intended for further sintering [10–12].

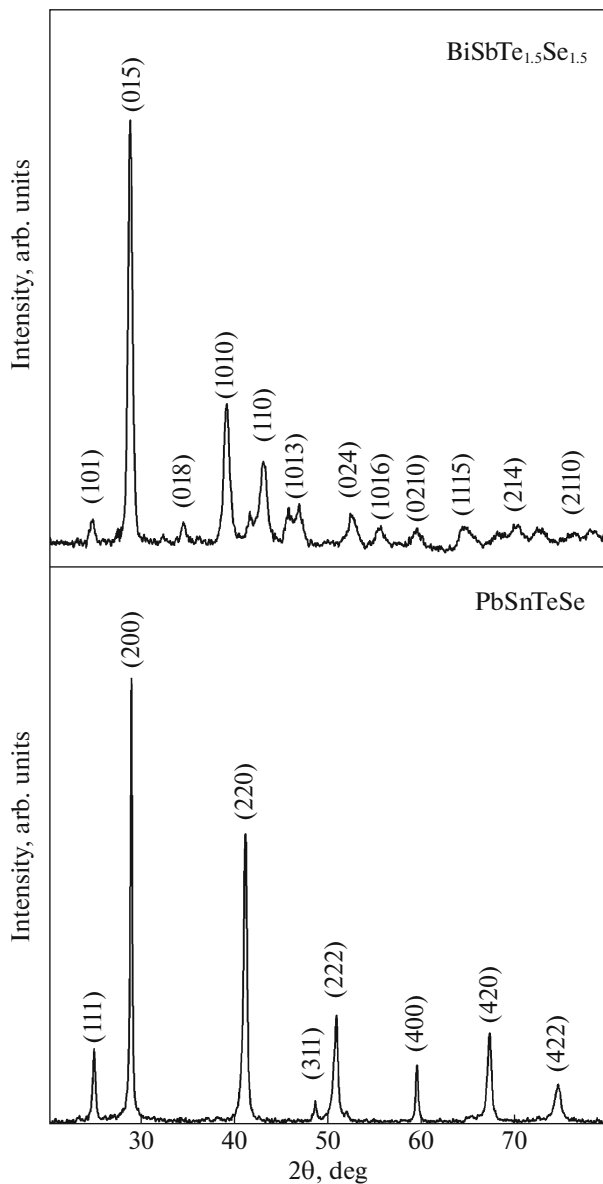


Fig. 1. X-ray diffraction patterns of bulk $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe samples.

2. EXPERIMENTAL

To obtain samples of the materials developed in this study, the initial Bi, Sb, Pb, Sn, Se, and Te powders taken in the stoichiometric ratio for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe , were thoroughly mixed with a ball mill. To implement the RSPS, a mixture of powders was poured into a graphite mold, which was placed in the setup chamber. SPS 25/10 and subjected to uniaxial compression at a pressure of 20 MPa in a vacuum. A current of 1500 A was passed through the mold in the pulsed mode for 2–3 s. The beginning of the SHS process (the first stage of RSPS) is recorded by a jump in the temperature of the mixture of powders in the mold and the simultaneous shrinkage of the synthe-

sized material. Then, the synthesized material was subjected to direct spark plasma sintering (the second stage of RSPS) without increasing the pressure for 15 min at temperatures of 723 and 823 K for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe compositions, respectively.

3. DISCUSSION

According to the results of the X-ray phase analysis completed using the Rigaku SmartLab X-ray diffractometer, the samples obtained by the RSPS method are indeed single-phase $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe compounds, respectively (Fig. 1). Thus, the selected RSPS method for obtaining materials allows initiating the SHS process for the synthesis of the necessary chemical compounds. The $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ samples have a hexagonal crystal structure (symmetry space group $R\bar{3}m$) with lattice parameters $a = b = 4.182 \text{ \AA}$ and $c = 29.752 \text{ \AA}$. Such a hexagonal structure is characteristic of alloys based on Bi_2Te_3 . The PbSnTeSe samples have a cubic structure ($Fm\bar{3}m$) with a period of 6.216 \AA . A similar cubic structure is characteristic of PbTe-based alloys. The sample density determined using the Archimedes method was $\sim 6.87 \text{ g cm}^{-3}$ ($\text{BiSbTe}_{1.5}\text{Se}_{1.5}$) and $\sim 7.07 \text{ g cm}^{-3}$ (PbSnTeSe). According to the scanning electron microscopy data (microscope Nova NanoSEM 450), the obtained samples are polycrystalline (Fig. 2). In $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ the grains have a lamellar shape with the average size of $\sim 3.3 \text{ \mu m}$. The grains in PbSnTeSe have an irregular shape with the average size of $\sim 18.9 \text{ \mu m}$.

The electrical resistivity and the Seebeck coefficient were measured using a ZEM-3 setup. For samples of both types, ρ increases with temperature (from ~ 23 at 300 K to $\sim 30 \text{ \mu}\Omega \text{ m}$ at 550 K for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$, and from ~ 7 at 300 K to $\sim 38 \text{ \mu}\Omega \text{ m}$ at 760 K for PbSnTeSe), demonstrating the behavior characteristic of metals and degenerate semiconductors. This behavior is due to the scattering of the majority current carriers on phonons. The Seebeck coefficient for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ has a negative sign (the majority current carriers are electrons), and for PbSnTeSe , it is positive (holes). For samples of both types S changes monotonically as the temperature increases (from ~ -108 at 300 K to $\sim -130 \text{ \mu V K}^{-1}$ at 550 K for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$, and from ~ 20 at 300 K to $\sim 130 \text{ \mu V K}^{-1}$ at 760 K for PbSnTeSe). To measure the total thermal conductivity of the samples by the laser flash method, a TC-1200 setup was used. The temperature dependences k of samples of both types are shown in Fig. 3. For the purpose of comparison, the same figure shows the same dependences for samples of the same compositions, but obtained according to the classical scheme of the preliminary synthesis of the initial powders and their subsequent sintering (the data for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ are taken from [5]; and for PbSnTeSe , from [13]). For

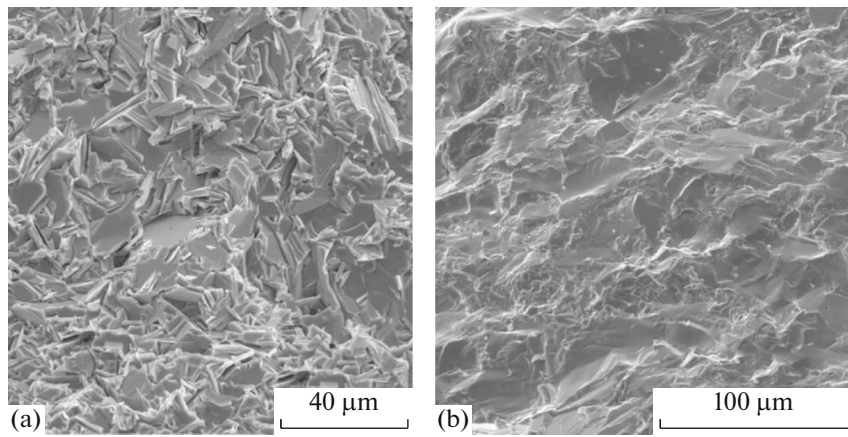


Fig. 2. Surface images of bulk $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ (a) and PbSnTeSe (b) samples.

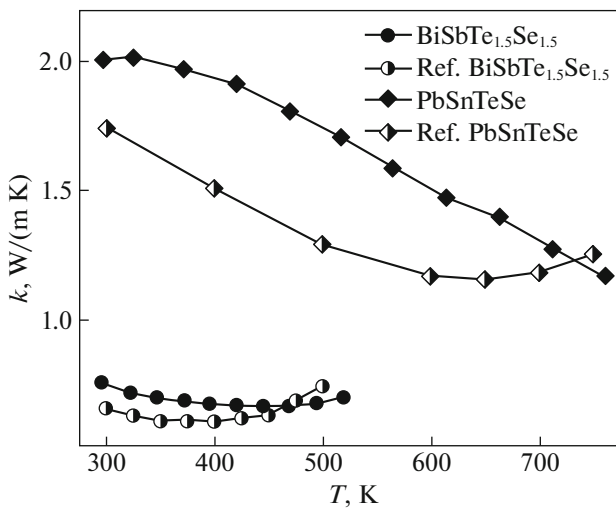


Fig. 3. Temperature dependences of the total thermal conductivity of bulk $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe samples.

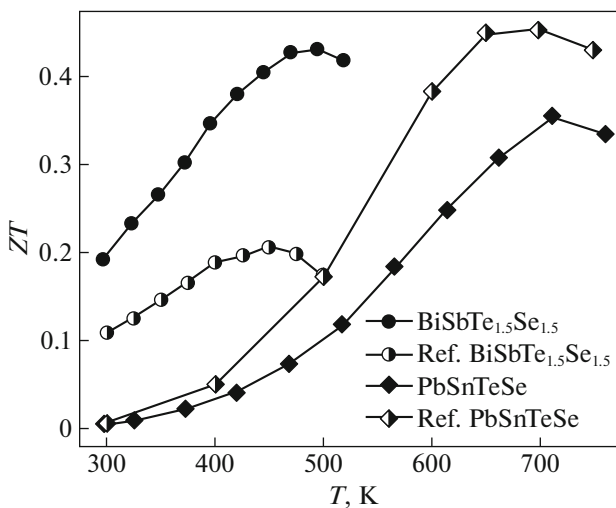


Fig. 4. Temperature dependences of the thermoelectric figure-of-merit of bulk $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe samples.

samples of $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ compounds, obtained in various ways, dependences $k(T)$ practically coincide, while the thermal conductivity of the PbSnTeSe sample obtained using RSPS at low temperatures is approximately 20% higher than that of the reference sample, but at high temperatures (at which this medium-temperature thermoelectric can be used), the thermal conductivity of both PbSnTeSe samples is just slightly different. The temperature dependences of the thermoelectric figure-of-merit of $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe samples, both obtained in this study and reference samples, are shown in Fig. 4. Throughout the temperature range, the ZT values of the $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ sample obtained using RSPS is much higher than the thermoelectric figure-of-merit of the reference sample. For PbSnTeSe samples, even the RSPS sample has lower figure-of-merit factors. The maximum ZT value of the samples obtained in this study is ~ 0.43 (at 500 K for $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$) and ~ 0.35 (at 725 K for PbSnTeSe).

4. CONCLUSIONS

The use of the RSPS method makes it possible to obtain single-phase samples of medium-entropy $\text{BiSbTe}_{1.5}\text{Se}_{1.5}$ and PbSnTeSe thermoelectrics with acceptable thermoelectric properties.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. E. P. George, D. Raabe, and R. O. Ritchie, *Nat. Rev. Mater.* **4**, 515 (2019).
2. Y. F. Ye, Q. Wang, J. Lu, C. T. Liu, and Y. Yang, *Mater. Today* **19**, 349 (2016).
3. Y. Zhou, D. Zhou, X. Jin, X. Du, and B. Li, *Sci. Rep.* **8**, 1236 (2018).
4. A. Raphel, P. Vivekanandhan, and S. Kumaran, *Mater. Lett.* **269**, 127672 (2020).
5. Z. Fan, H. Wang, Y. Wu, X. J. Liu, and Z. P. Lu, *RSC Adv.* **6**, 52164 (2016).
6. O. Ivanov, M. Yaprntsev, A. Vasil'ev, and E. Yaprntseva, *J. Alloys Compd.* **872**, 159743 (2021).
7. R. Orru and G. Cao, *Materials* **6**, 1566 (2013).
8. D. V. Dudina and A. K. Mukherjee, *J. Nanomater.* **2013**, 1 (2013).
9. H. T. Liu and G. J. Zhang, *J. Korean Ceram. Soc.* **49**, 308 (2012).
10. R. Liu, X. Tan, G. Ren, Y. Liu, Z. Zhou, C. Liu, Y. Lin, and C. Nan, *Crystals* **7**, 257 (2017).
11. G. K. Ren, J. L. Lan, S. Butt, K. J. Ventura, Y. H. Lin, and C. W. Nan, *RSC Adv.* **5**, 69878 (2015).
12. D. W. Yang, X. L. Su, Y. G. Yan, T. Z. Hu, H. Y. Xie, J. He, C. Uher, M. G. Kanatzidis, and X. F. Tang, *Chem. Mater.* **28**, 4628 (2016).
13. Z. Fan, H. Wang, Y. Wu, X. Liu, and Z. Lu, *Mater. Res. Lett.* **1** (2016).