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Short Communication

Investigation of Nanostructured Thermoelectric Material $Si_{0.8}Ge_{0.2}P_{0.022}$ for Application in Multisectional Legs of Thermoelectric Elements

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Complex investigations of high-temperature thermoelectric material nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type were carried out. Temperature dependencies of conductivity, thermoelectric coefficient and thermal conductivity were studied. Obtained data were used for the calculation of temperature dependence of ZT. Maximum value of ZT = 1.04 is observed at 900 °C. Differential scanning calorimetry indicates on the high thermal stability of the nanostructured material. It was established that optimal temperature range for the application of the material in the multisectional legs of thermoelements is 600-900 °C.

Keywords: Thermoelectricity, High-temperature, $Si_{0.8}Ge_{0.2}P_{0.022}$, Nanostructured, Thermoelectric generators, Thermoelement, Multisectional leg.

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1. INTRODUCTION

Thermoelectric energy converters are actively applied now in different fields of science and technology for cooling, temperature controlling and electricity generation. The increased interest in recent years has thermoelectric generators (TEG) as alternative power sources. However, for widespread TEG application it is necessary sufficiently increase efficiency. The efficiency of thermoelectric generators is determined as [1]:

$$\eta = \frac{T_h - T_c}{T_h} \cdot \frac{(1+ZT_{av})^{1/2}}{(1+ZT_{av})^{1/2} + T_c / T_h}, \qquad (1)$$

where T_h and T_c are temperatures of hot and cold junctions; $T_{av} = (T_h + T_c)/2$.

Thermoelectric figure of merit Z determines quality of thermoelectric materials:

$$Z = \alpha^2 \sigma / \kappa, \qquad (2)$$

where α is the thermoelectric coefficient; σ is electrical conductivity; and κ is the thermal conductivity of the material.

It follows from this equations that for increasing of the thermoelectric generators efficiency it is necessary to increase ZT of thermoelectric materials and working temperature range (ΔT).

Currently thermoelectric materials, which allow to create TEG in wide working temperature range from 300 to 1300 K are developed [2]. However, for all these materials the dimensionless figure of merit ZT has sufficient temperature dependence with rather sharp maximum. This limits application of thermoelectric materials by sufficiently narrow temperature range, out of which efficiency of TEG significantly decreases.

Therefore to create effective TEG with wide working temperature range different materials with maximum values of ZT in neighbor temperature ranges must be used.

This approach can be implemented by two ways. The first way suggests production of thermoelectric modules for various operating temperatures, in which thermoelectric materials are used having a peak figure of merit for these temperatures. In this case, effective TEG is created as cascade thermoelectric device on the basis of these modules.

Second way is connected with the fabrication of thermoelectric generators with complex, multisectional legs of thermoelectric element [3-5]. In this case, each section of thermoelement leg is made from different thermoelectric materials having a maximum ZT value for the operating temperature range of each section. This allows increasing the average value of ZT of a whole leg. In this case more effective TEG can be fabricated. This is explained by the absence of commutation arrays of thermoelectric modules and additional transition layers, which increase thermal resistance of TEG. In addition thermal inertia, weight and size of TEG are decreased, which is important for space and transport application.

However, creation of thermoelectric elements with multisectional legs is very complicated technological challenge. TEG undergo multiple thermal cycling in the temperature range of 300-1300 K, and must withstand very high temperature gradient exceeding 45 K/mm. Therefore, electrical parameters and heat flows of each section of the legs must be carefully matched, and heat balance conditions on the interfaces must be provided. The problem is complicated by the difference of the thermal linear expansion coefficients of the materials used in different sections, which can lead to the sufficient mechanical stresses in legs and even to their destruction.

So, for the successful development of multisectional legs of thermoelectric element exact knowledge of a number of thermoelectric materials characteristics (such as electrical conductivity, thermopower, thermal conductivity, thermal linear expansion coefficients, and thermal properties) is necessary in working tempera-

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ture range of each section of legs and influence on them thermal cycling.

Thus, the aim of this work is investigation of thermoelectric and thermal properties in the wide temperature range for thermoelectric material nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type perspective for the application in high temperature range of multisectional legs of thermoelements.

2. EXPERIMENT

Nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type was fabricated by hot pressing of synthesized material nanopowder with the size of nanoparticles 20 nm.

Initial materials were monocrystalline Si p-type ingot with resistivity of 10 Ohm·cm grown by zone melting, and granulated Ge with 99.99 wt. % purity. Si and Ge were taken in the ratio of 4 : 1, and doped by 2.2 at. % of phosphorus. Preliminary initial materials were grinded in the knife mill XS-10, and the average particle size of 500 mcm was obtained. Then grinding was carried out in the planetary ball mill Activator 2S. The average particle size of 80-120 nm was obtained after the grinding during 30 min at the rate of 350 rev/min. After that mechano-chemical synthesis of $Si_{0.8}Ge_{0.2}P_{0.022}$ in the planetary high-energy mill Retsch PM400-MA was carried out. The average particle size of 20 nm was obtained after the grinding during 22 hours at the rate of 400 rev/min. At last, powder was hot pressed during 5 min at the pressure of 120 MPa, temperature of 1100 °C.

Improved procedure and measuring complex were used for measuring of thermophysical and electrophysical parameters of investigated materials [6]. Thermal conductivity was investigated by absolute stationary method. Conductivity, thermopower and thermal conductivity measuring errors were 3, 3 and 5 %, respectively.

Thermal properties were investigated by differential scanning calorimetry (DSC-50, Shimadzu). Measurements were carried out at the heating rate of 5 °C/min in a nitrogen flow (20 ml/min) with using of alundum pans. Temperature measuring range was from room temperature to 725 °C. Several successive measurements were carried out for estimation of the influence of thermal cycling on the thermal properties.

3. RESULTS AND DISCUSSION

Temperature dependences of thermo- and electrophysical parameters of investigated materials are presented in Fig. 1-3.

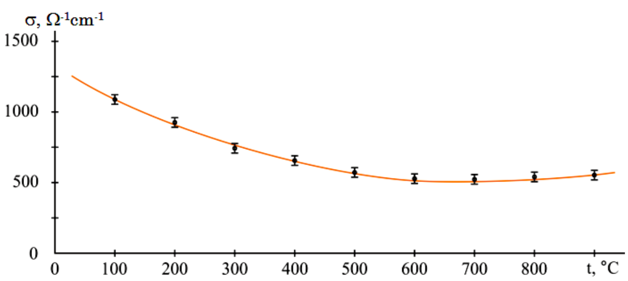

Fig. 1 – Temperature dependence of electrical conductivity for $Si_{0.8}Ge_{0.2}P_{0.022}$

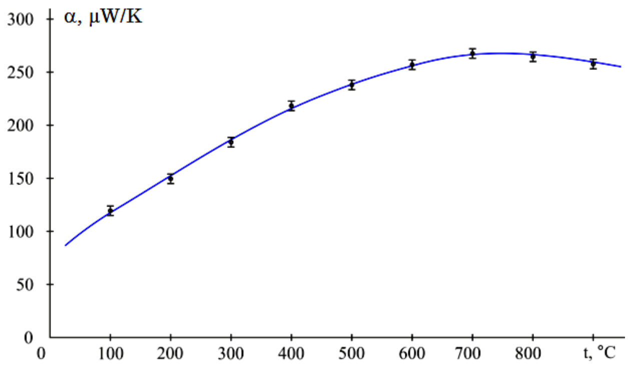

Fig. 2 – Temperature dependence of thermopower for $Si_{0.8}Ge_{0.2}P_{0.022}$

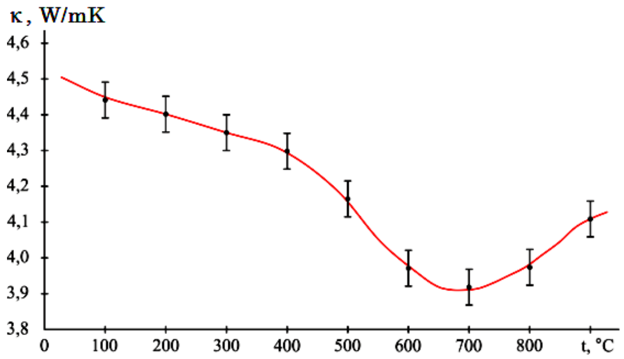

Fig. 3 – Temperature dependence of thermal conductivity for $Si_{0.8}Ge_{0.2}P_{0.022}$

As can be seen from the Fig. 1, electrical conductivity decreases with the temperature, which is due to the decrease of the charge carrier mobility. Stabilization of the electrical conductivity at temperatures higher than ~ 600 °C is due to the increase of the minor charge carrier contribution to the conductivity, which is supported by the stabilization of thermopower at these temperatures (see Fig. 2).

Fig. 3 shows that thermal conductivity of investigated material decreases up to the temperature of ~ 700 °C, which is due to the decrease of the electron component contribution, and correlates with the temperature dependence of the electrical conductivity. Following increase of the thermal conductivity is explained by the increase of the bipolar component contribution, and correlates with the temperature dependencies of electrical conductivity and thermopower (see Fig. 1 and 2).

Thus, temperature dependences for electrical conductivity, thermopower and thermal conductivity correlate with each other.

Obtained results were used for the calculation of temperature dependence of ZT with using of equation (2). Temperature dependence of ZT is presented in Fig. 4.

The values of ZT corresponds to the best high temperature thermoelectric materials used in practice. The optimal working temperature range for the nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ is from 600 to 900 °C with ZT in the range from 0.8 to 1.04, respectively.

Next, thermal properties of nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type were investigated by differential scanning calorimetry (Fig. 5).

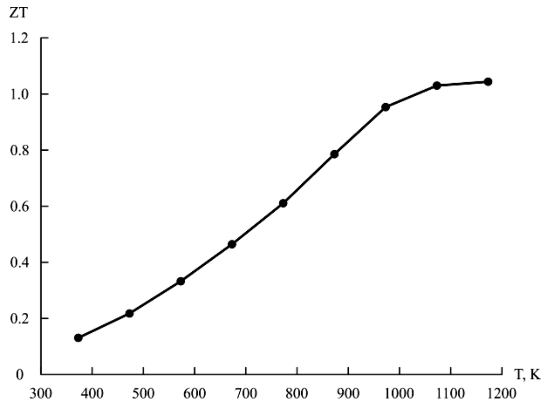

Fig. 4 – Temperature dependence of ZT for $Si_{0.8}Ge_{0.2}P_{0.022}$

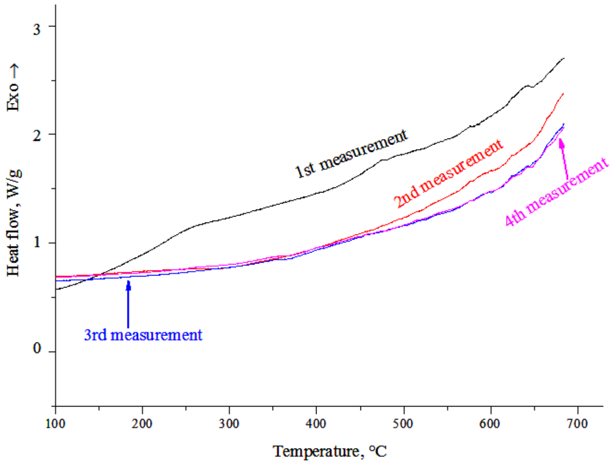

Fig. 5 – DSC curves for $Si_{0.8}Ge_{0.2}P_{0.022}$

Measurements were repeated four times, which allowed to estimate influence of thermal cycling on the thermal properties. No heat effects were observed in this temperature range, and DSC scans stabilized after the third measurement. These results indicate on the high thermal stability of the investigated material.

4. CONCLUSION

Thus, complex investigations of thermoelectric material nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ *n*-type were carried out in the wide temperature range.

Investigations showed that this material possess high thermal stability and dimensionless figure of merit ZT, and is perspective for the application in high temperature range of 600-900 °C in multisectional legs of thermoelectric elements. In this temperature range it has ZT from 0.8 to 1.04, respectively.

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REFERENCES

1. A. Gulyaev, et.al., *Electronics: STB* **2**, 64 (1999).
2. A.A. Sherchenkov, Yu.I. Shtern, R.E. Mironov, M.Yu. Shtern, M.S. Rogachev, *Nanotech. Russia* **10**, 827 (2015).
3. T. Caillat, A. Borshchevsky, J.-P. Fleurial, *15th Symposium on Space Nuclear Power and Propulsion*, 1647 (Albuquerque, New Mexico, USA: AIP proceedings No 420: 1998).
4. T. Caillat, J-P. Fleurial, G.J. Snyder, A. Zoltan, D. Zoltan, A. Borshchevsky, *34th Intersociety Energy Conversion Engineering Conference*, 2567 (Vancouver: British Columbia: Warrendale, PA: 1999).
5. M.L. Olsen, E.L. Warren, P.A. Parilla, E.S. Toberer, C.E. Kennedy, G.J. Snyder, S.A. Firdosy, B. Nesmith, A. Zakutayev, A. Goodrich, C.S. Turchi, J. Netter, M.H. Gray, P.F. Ndione, R. Tirawat, L.L. Baranowski, A. Gray, D.S. Ginley, *Energ. Procedia* **49**, 1460 (2014).
6. Yu.I. Shtern, *Inorg. Mater.* **45**, 1631 (2008).