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Investigation of thermal linear expansion for nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ in wide temperature range

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Abstract. The results of investigation of thermal linear expansion for high temperature thermoelectric material nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type with maximum thermoelectric figure of merit Z = 0.98 10^{-3} K are presented. Investigations were carried out by dilatometric method in the temperature range from 300 to 1220 K in dynamic heating and cooling regimes with using of infrared radiation source. Temperature dependence of thermal linear expansion coefficient (TLEC) was analyzed. The average value of TLEC for $Si_{0.8}Ge_{0.2}P_{0.022}$ was determined, which is equal to ~$5.9\cdot10^{-6}$ K^{-1}.

1. Introduction

Development of alternative sources of energy is one of the most challenging directions in the modern science and technology. Thermoelectric generators (TEG), which directly convert heat into electric energy, are one of these alternative sources. Different sources can be used for their work. Thermoelectric generators are used when extremely reliable power sources are required, which need no service and have long exploitation time. Thereby thermoelectricity can and should become one of the alternative technologies for generation of electric power.

TEG undergo multiple thermal cycling in the temperature range of 300-1200 K, when exist extremely high temperature gradient of 45 K/mm. The work of TEG is based on the semiconductor thermoelements. Due to the thermal expansion of materials during the TEG operation thermoelements must withstand high mechanical stresses. Mechanical strength of semiconductors used for the fabrication of thermoelements is much less than that of the other TEG construction units. So, mechanical strength of the device is limited by the strength of the thermoelectric materials.

Strength of any construction, which is exploited at varying temperature conditions, cannot be calculated without thermal expansion data for construction materials. This is especially important for thermoelectric generators.

This work is devoted to the experimental investigation of the thermal linear expansion for effective nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type, which have high value of Z in the range from $0.85\cdot10^{-3}$ K^{-1} (900 K) to $0.89\cdot10^{-3}$ K^{-1} (1200 K) with maximum of $0.98\cdot10^{-3}$ K^{-1} at 1050 K.

Experimental investigation of thermal expansion for SiGe solid solution is very insufficient and is limited by dilatometric [1, 2] and X-ray [3] data. Thermal expansion coefficient like other thermo- and electrophysical properties of SiGe is dependent not only on the composition, but on the structure, and so on the method of the thermoelectric material preparation [4].

One of the perspective fabrication methods of the effective nanostructured thermoelectric materials is hot pressing at sufficiently high temperatures. The main problems, which faces technologists producing solid nanostructured materials are connected with the need to maintain nanostructure as during the fabrication, so during the exploitation of thermoelements.

2. Experiment

In this work thermal linear expansion of $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type fabricated by hot pressing of synthesized nanoparticles with given composition and nanoparticle size of 20 nm were investigated. Initial materials were monocrystalline Si p-type ingot with resistivity of 10 Ohm·cm, diameter of 63 mm and grown by zone melting in the direction of [100], and granulated Ge with 99.99 wt.% purity. Si and Ge were taken in the ratio of 4:1 with doping 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. The glove box with inert atmosphere (argon) was used for grinding to prevent oxidation. Hot pressing was carried out with using of hydraulic press IP-1000M at the pressure of 120 MPa, temperature of 1100 °C during 5 min.

Thermal linear expansion coefficient was studied by dilatometeric method with using of high-rate dilatometer DL-1500RH (ULVAC Sinku-Riko, Japan). Heating of sample was carried out in infrared oven RHL-E45P. Pt - (Pt10%Rh) thermocouples were used for the measuring of temperature.

Relative linear elongation of the sample of electrolytically pure copper was measure at different rates for the calibration of dilatometer. Results of our measurements of $\Delta L/L_0$ at different heating rates of 3, 5 and 50 K/min in comparison with the data for copper standard are presented in figure 1.

As can be seen from the figure 1, experimental results obtained at slow heating rate of 3 K/min are most close to the Cu standard in all temperature range.

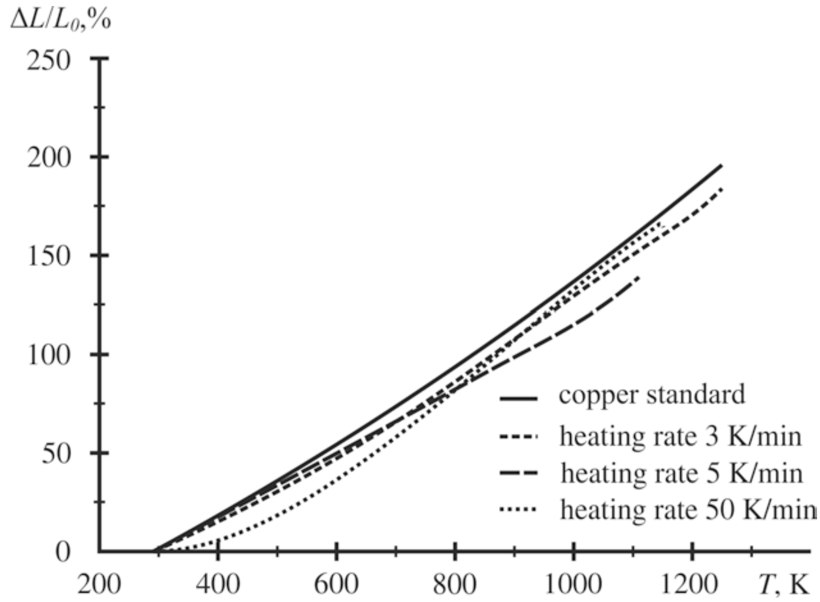

Figure 1. Comparison of the temperature dependences of relative linear expansion for electrolytically pure copper measured at heating rates of 3, 5 and 50 K/min with the data for copper standard.

3. Results

Dilatometric measurements of $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type were carried out in the temperature range from 300 to 1220 K in the dynamic heating and cooling conditions. Samples with rectangular parallelepiped sizes of 4×4×20 mm were tested. Temperature dependences of the samples elongations were measured during the experiments. The accuracy of the samples elongation measurements was ±0.1 mcm.

Thermal cycling is a type of thermal treatment of the material. Due to the possible deformations of the sample after the first heating, dilatometric data for the following cycles can differs from that of the first measurement. The reasons for the deformation can be not only high plasticity [5] of the material, but also different structural and phase transformations observed after the infrared heating of the sample during a long period of time [6-8].

Results of the thermal expansion measurements of nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ for two heating and cooling cycles at different rates (3 and 30 K/min) are presented in figure 2. Reliability of each cycle of measurement was controlled by the returning of the expansion curve to the initial point after cooling.

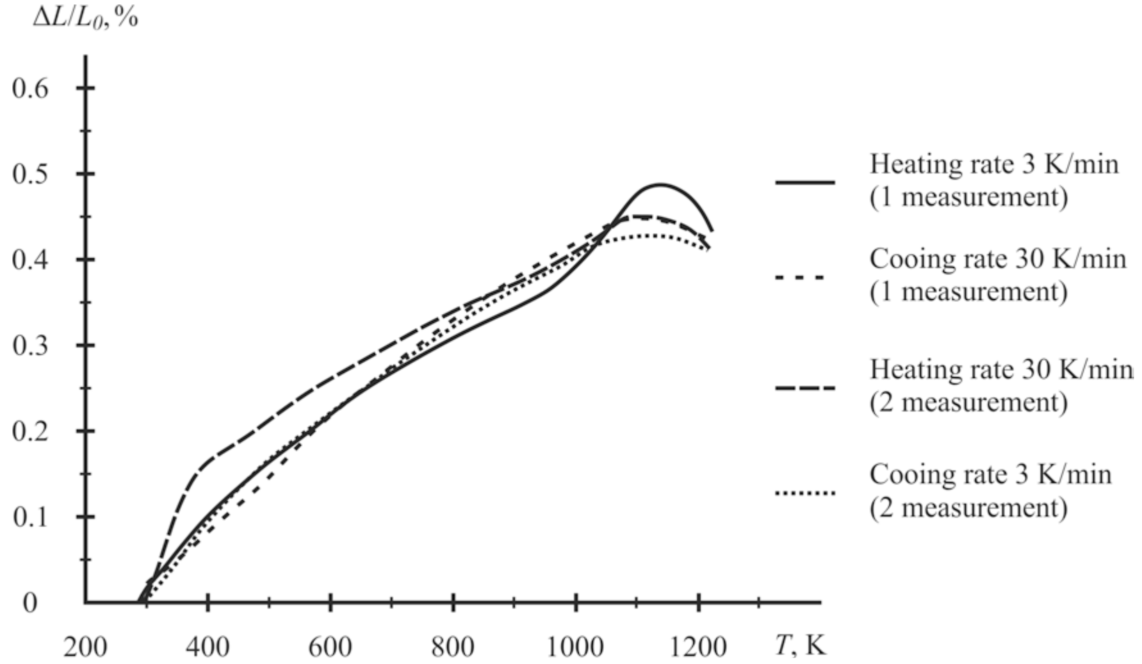

Figure 2. Temperature dependences of the relative linear elongation of $Si_{0.8}Ge_{0.2}P_{0.022}$ sample.

The data of first and second heating with the rates of 3 and 30 K/min are poorly reproduced, while cooling curves at different rates differs much less. This indirectly indicates on the structural transformations in the investigated alloy, which are possibly connected with the transformations in pure silicon [9] and agglomeration of nanoparticles during infrared heating.

It is seen from the figure 2 that all curves has maximums at the temperature of about 1050 K, especially pronounced for first heating. This is also indirect evidence of the structural transformations in the investigated material.

The data of relative linear elongation for $Si_{0.8}Ge_{0.2}P_{0.022}$ *n*-type obtained at different heating rates (3 and 30 K/min) on the dilatometer DL-1500 RH are compared with the data for nanostructured and mechanically alloyed SiGe *n*-type [2] obtained at the horizontal type dilatometer DIL-402C (NETZSCH) in figure 3. It should be noted that convective heating of samples is used in the dilatometer DIL-402C. Temperature dependence of relative linear elongation for pure silicon obtained with using of dilatometer AD-80 [9] is also shown in this figure.

Processing of the experimental data for $\Delta L/L_0$ was carried out with using of interpolation polynomial:

$$\frac{\Delta L}{L_0}(\%) = 0.86639 - 8.9197\cdot10^{-3}T + 3.2952\cdot10^{-5}T^2 - 5.26027\cdot10^{-8}T^3 + \\ +3.9062\cdot10^{-11}T^4 - 1.0952\cdot10^{-14}T^5 . \quad (1)$$

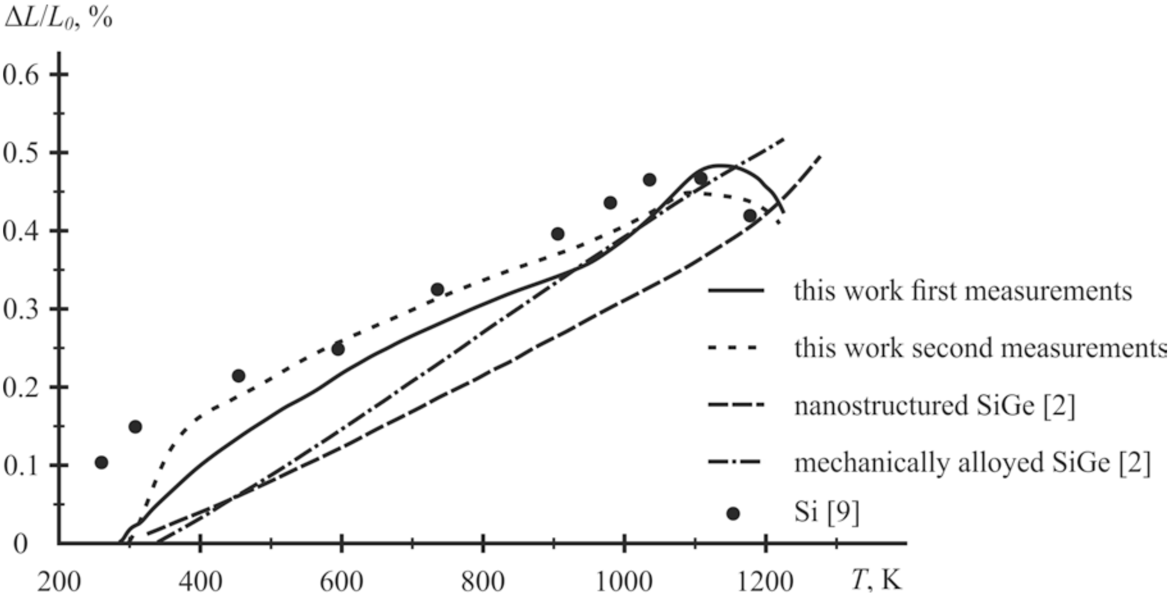

Figure 3. Temperature dependences of relative linear elongation for SiGe fabricated by different method, and Si.

It should be noted that data obtained for $Si_{0.8}Ge_{0.2}P_{0.022}$ at heating rate of 30 K/min are close to those for the silicon. At high temperatures for silicon can be also seen maximum for $\Delta L/L_0$ [9].

The values of relative linear elongation for $Si_{0.8}Ge_{0.2}P_{0.022}$ at heating rate of 3 K/min were used for the calculation of average value of thermal linear expansion coefficient (TLEC). Calculations were carried out with using of equation:

$$\alpha = \Delta L / L_0 \cdot (T - T_0)\,, \quad (2)$$

where α is average value of thermal linear expansion coefficient in the temperature range of T-T_0; T is the temperature of TLEC estimation; L_0 is the length of the sample at the initial temperature T_0. The initial temperature of the measurements was 297.15 K.

The error of the determination of thermal linear expansion coefficient does not exceed 10 %.

Temperature dependence of the average TLEC for $Si_{0.8}Ge_{0.2}P_{0.022}$ is presented in figure 4. Experimental temperature dependences of the average TLEC for $Si_{0.8}Ge_{0.2}$ n-type [1-3] are also shown for comparison. Curve 1 correspond to the data of this work obtained with using of the equation (1); curves 2-4 correspond to the dilatometric data for $Si_{0.8}Ge_{0.2}$ obtained by the zone melting, and nunostructuring and mechanical alloying, respectively [1, 2]; dots correspond to the X-ray data [3].

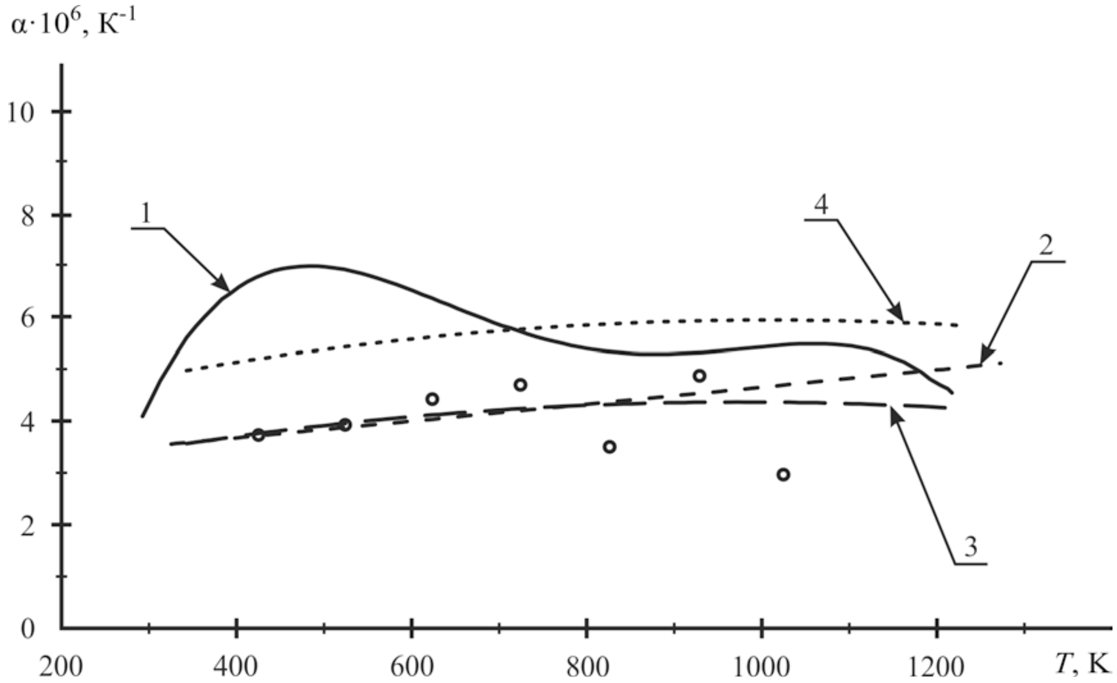

Figure 4. Temperature dependences of the average TLEC for $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type in comparison with the data of works [1-3].

Obtained in this work average value of TLEC for investigated material in the temperature range of 300-1200 K was estimated as ~$5.9 \cdot 10^{-6}$ K^{-1} and correlates with that for the mechanically alloyed SiGe [2].

4. Conclusion

Analysis of the information showed that investigation of the thermal expansion of effective high temperature thermoelectric material $Si_{0.8}Ge_{0.2}$ is quite limited.

Investigation of thermal expansion of nanostructured $Si_{0.8}Ge_{0.2}P_{0.022}$ n-type was carried out by the dilatometric method in the temperature range of 300-1200 K in the dynamic heating and cooling conditions with using of infrared source of heating.

Non-monotonous character of TLEC temperature dependence for investigated material was established which can be due to the different processes in the material such as phase transformations.

The average value of thermal linear expansion coefficient for investigated material in the temperature range of 300-1200 K was estimated as ~$5.9 \cdot 10^{-6}$ K^{-1} and correlates with that for the mechanically alloyed SiGe.

Acknowledgments

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