Guram Bokuchava[1], Karlo Barbakadze[1], Giorgiy Darsavelidzee[1],
Boris Shirokov[2]

[1]Sukhumi Ilia Vekua Institute of Physics and Technologya
7, Mindeli Str., 0186, Tbilisi, Georgia
[2]The National Scientific Centre "Kharkiv Institute of Physics and Technology"
1, Akademicheskaya Str., 61108, Kharkiv, Ukraine

ACHIEVEMENTS OF SUKHUMI ILIA VEKUA INSTITUTE OF PHYSICS AND TECHNOLOGY IN THE FIELD OF THERMOELECTRIC MATERIALS SCIENCE AND INSTRUMENT MAKING

The paper presents the stages of the development and manufacture of various-purpose thermoelectric generators at Sukhumi Ilia Vekua Institute of Physics and Technology (SIPT). Analytical and experimental studies conducted at SIPT in the late 1950s revealed great prospects for the creation of high-efficiency thermoelectric generators for nuclear power plants of terrestrial and space application. In 1964, a thermoelectric converter for the world's first nuclear power plant, "Romashka," was built at SIPT. In 1966, a single-stage thermoelectric converter "Buk" was created, followed in 1969 by a two-stage TEG "Buk" with an electric power of 2.8 kW. C Since the beginning of 2000, the institute has resumed work on the development of high-temperature thermoelectric materials and devices based on SiGe. The effect of reactor radiation on the thermoelectric characteristics of SiGe and other materials was analyzed. To develop radiation – resistant materials for high-temperature thermoelements, p-type B_4C and n-type $Si_{0.7}Ge_{0.3}$ were chosen. New thermoelectric converters are being developed on the basis of relatively inexpensive SiGe alloys containing 5 – 10 at. % Ge.

Key words: thermoelectric generator, SiGe alloys, "Romashka", "Buk", radioisotope fuel, boron carbide

Introduction

In chronological order, the main achievements of SIPT in thermoelectric materials science and instrument making are set forth, namely preparation of bulk *Ge*, *Si* and *SiGe* crystals (1955 – 1958), synthesis of thermoelectric alloys, development of technology of high-temperature interconnects, creation of high-temperature thermopiles together with I.Kurchatov Nuclear Energy Institute, Podolsk Research Institute and Kharkiv Institute of Physics and Technology, development and creation of nuclear power plant "Romashka" (1964), creation of an experimental prototype of a single-stage thermoelectric generator "Buk" (1966). The problem of developing low-resistance and stable interconnects to *Pb* and *Ge* tellurides, obtaining heat-resistant thermoelement legs and creating high-efficiency thermopile with anti-sublimation coating has been successfully solved. The results of the works were used to create a two-stage thermoelectric generator for the nuclear power plant of space application "Buk".

In the 1970s, a number of TEGs were created at SIPT, operating on radioisotope fuel in different temperature ranges.

In the 1980s, low-power TEGs were developed for use in microelectronics, medicine, and military field. TEGs "Gamma" for working in deep water conditions, environmentally friendly refrigerators, microcoolers that stabilize the temperature of high-sensitive photodetectors were also developed.

In 2003 – 2013, a number of international projects were carried out concerning the problems of thermoelectric instrumentation and optoelectronic devices based on *SiGe*.

At the present time, thermopiles and generators are being developed on the basis of *SiGe* alloys with a relatively low content of *Ge* (5 – 10 at. %) in TEGs intended for use in the furnaces of central gas heating systems, as well as for cathode protection of main pipelines of energy carriers. A joint project is being developed for creation of a three-stage thermoelectric generator with participation of Sukhumi Ilia Vekua Institute of Physics and Technology, Institute of Thermoelectricity of the NAS Ukraine and the National Scientific Center "Kharkiv Institute of Physics and Technology" of the NAS Ukraine.

In the early 1950s, Sukhumi Institute of Physics and Technology (SIPT) began to pursue research in the field of physics and technology of semiconductor materials. This was due to the need for creation of new high-purity materials – germanium and silicon – for the rapidly developing semiconductor electronics.

SiGe alloys, as a thermoelectric material, were first proposed by A. F. Ioffe in 1954 [1]. In 1956, for the first time at SIPT, studies began on technology for production of *Ge*-*Si* alloys. The work was continued by several researchers in the USSR and the USA.

In 1958, in connection with the need for outer space exploration, the institute was commissioned to develop a nuclear-fueled thermoelectric power converter. The choice of SIPT for this task was due to its successes and achievements in obtaining semiconductor-grade germanium and silicon and germanium-silicon alloys, obtaining for the first time in the USSR a germanium single crystal in 1954 and a silicon single crystal in 1956. In the years 1958 – 1960, devices and equipment for the synthesis and study of *SiGe* alloys were developed and manufactured; efficient thermoelectric alloys $Si_{0.93}$ $Ge_{00.7}$ of *n*- and *p*-type conductivity were obtained; technology for manufacturing high-temperature interconnects was developed (~1000 °C) and high-temperature thermopiles were made. In 1964, for the first time in the world under the direction of I. Gverdtsiteli, a thermoelectric generator for the nuclear power plant "Romashka" was developed and created (Fig. 1).

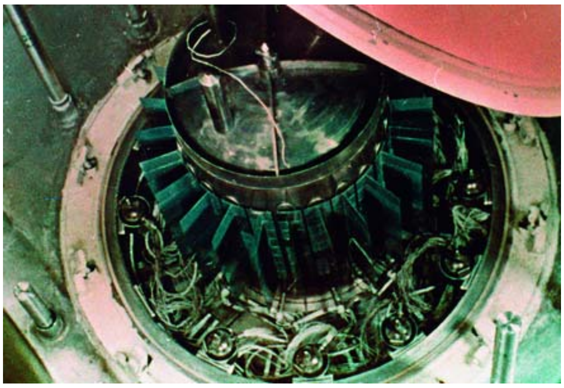


Fig. 1. "Romashka"

In creation of "Romashka" together with SIPT participated: I. Kurchatov Nuclear Energy Institute, Podolsk Research Institute and Kharkiv Institute of Physics and Technology.

The source of thermal energy for the "Romashka" plant was a nuclear reactor operating on fast neutrons. The released thermal energy was converted into electrical energy by means of thermoelements. The tests of the "Romashka" plant confirmed the high reliability of the entire system and the stability of the main operating parameters. In 1964, the results of these works were presented in Geneva at the III International Symposium on the Peaceful Uses of Atomic Energy (Report № 873) and aroused the great interest of world-famous specialists. These materials were published in a well-known scientific journal [2].

Thermoelectric materials science and instrument making at SIPT developed along two lines. The first one is creation of high-power TEGs of space application for nuclear power plants and their full-scale production. The second is production of medium and low power TEGs operating on isotope fuel for the needs of different sectors of economy. In 1962, studies began on the development of a thermoelectric generator for space power unit "Buk". High-performance $Si_{0.68}Ge_{0.32}$ alloys of *n*- and *p*-type conductivity, low-resistance interconnects and thermopiles with high mechanical strength were developed. On their basis, in 1966, a single-stage experimental thermoelectric generator “Buk” was created and successfully tested (Fig. 2).

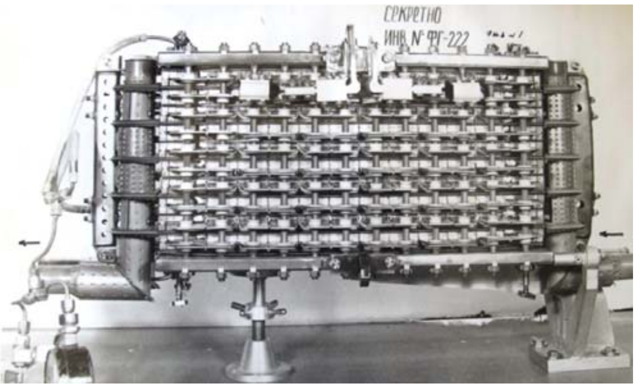


Fig. 2. “Buk”

After its testing, it was decided to create a more efficient two-stage TEG for the "Buk". Its first stage was to be made of $Si_{0.7}\ Ge_{0.3}$ alloys of *n*- and *p*-type conductivity and the second stage was to be based on thermoelectric alloys *PbTe* (*n*) and *GeTe* (*p*). The problem lied in the development of low-resistance and stable interconnects to *PbTe* and *GeTe* alloys, obtaining thermally stable thermoelement legs and creating on their basis the high-performance thermopile with anti-sublimation coating. These problems were successfully solved, and in 1968 a highly efficient two-stage TEG for the "Buk" plant with a capacity of 2.8 kW was created. Its first stage operated in the temperature range 715 – 530 °C, and the second – 530 – 350 °C. Unlike the "Romashka", in the "Buk" plant the reactor was separated from the TEG and connected to it by a two-circuit coolant (heat-supplying and heat-releasing) based on *Li*-*K*. This made it possible to practically exclude the effect of radiation on the structural units of the TEG.

In 1975, after many years of integrated research, "Buk" was put into serial production and more than 30 samples successfully worked in space vehicles of the "Cosmos" series.

In 1972, the technology of production of low-temperature thermoelectric materials ($Bi_2\ Te_3$-$Bi_2\ Se_3$ *n*-type and Bi_22Te_3-Sb_2Te_3 *p*-type) was developed at SIPT for manufacturing thermopiles on their basis, which significantly expanded the operating temperature range of TEGs developed at the institute. In 1975, a number of TEGs were created (Limon, Beta, Reut, Gong, Gorn, etc.), operating on radioisotope fuel in different temperature ranges, with power output of 8 – 70 Watt.

In the 1980s, SIPT was engaged in works on low-power TEG Hermes, Signal, etc., for use in microelectronics, medicine, and the military field.

In 1989, the modernized TEG "Buk" was completed and put into serial production at the institute with a doubled service life, due to the improvement of interconnects.

In thermoelectric instrument making, a significant step was the development of the TEG "Gamma" based on low-temperature thermoelectric materials for operation in deep-water conditions. In it, a thermoelectric annular module developed at the institute was used.

In the late 1980s, SIPT, in cooperation with other institutes, began developing a program similar to the American SP-100. The program included creation of a ~ 100 kW TEG, with a 7-year service life. In this direction, a modular TEG "Gloria" was created, capable of generating various capacities for replication. The work was suspended due to conversion. In the late 1980s, SIPT began to develop environmentally friendly cold devices based on the Peltier effect, using high-performance low-temperature thermopiles. Micro-refrigerating devices containing up to 100 thermocouples were developed and manufactured, which ensure temperature stabilization of highly sensitive photodetectors.

The main results of reactor tests of $Si_{0.7}Ge_{0.3}$ alloys at temperatures in the range of 773 – 973 K with a fast neutron fluence set to ~4.0 × 1020 sm^{-2} are presented in [3]. The studies were carried out on the water-to-water power reactor of the Institute for Nuclear Research of the Academy of Sciences of Ukraine under conditions that are as close as possible to the real operating conditions of nuclear power plants. As a donor impurity, samples of heavily doped $Si_{0.7}$ $Ge_{0.3}$ alloy with electron conductivity (*n*-type) used phosphorus (*P*), and a *p*-type alloy was doped with boron (*B*).

Summarizing the experimental results obtained, we can make the following practically important conclusions. The threshold values of fast neutron fluences on achieving which in silicon-germanium alloys there begins a sharp increase in the electric resistance and thermoelectromotive force, make $\Phi \approx 6{\cdot}1018$ sm^{-2} for the electron and $\Phi \approx 1{\cdot}1018$ sm^{-2} – for the hole material. For the first time for $Si_{0.7}Ge_{0.3}$ alloys, the dose dependences $\alpha = f(\Phi)$ and $\rho = f(\Phi)$ were observed to saturate at fluences $\Phi \approx 1{\cdot}1020$ sm^{-2} in the electron material and $\Phi \approx 2{\cdot}1019$ sm^{-2} in the hole one. By the end of the reactor irradiation, the coefficients of the thermoelectromotive force increased by a factor of ~1.8 – 2 in the electron material and by a factor of 1.4 – 1.7 in the hole one, compared with the initial value; the electrical resistivity in the electron material increased by a factor of 20 – 23, and in the hole one by a factor of 6 – 8. The radiation resistance of a boron-doped $Si_{0.7}Ge_{0.3}$ hole alloy can be considerably increased by substitution of isotope 11B for isotope 10B. It can be assumed that thermoelectric modules made of $Si_{0.7}Ge_{0.3}$ alloy in the radiation field of the reactor will be notable for the service life which can be further increased by programmed intra-zone regeneration annealings.

It is known [4] that boron carbide (B_4C) is a promising high-temperature thermoelectric material with good transfer properties. Bipolarons are charge carriers in B_4C and their concentration is ~ 10^{21} sm^{-3}. Electrical conductivity is activated with temperature. The transfer of heat is accomplished by phonons and strongly depends on the localization of boron and carbon atoms (stoichiometry). To reduce χ, the boron concentration was increased to $B_{6.5}C$. The Seebeck coefficient for boron carbide already reaches ~ 180 μV /°C at a temperature of 300K, and σ increases with a rise in temperature.

It can be concluded that the thermoelement created on the basis of $^{11}B_4C$ will not only be more efficient, but it will probably be resistant to radiation. In addition, B_4C has an electronic defect structure and is characterized as an acceptor-type semiconductor with a band gap ΔE = 1.2 eV without degradation of the thermoelectric parameters.

Taking into account all the above, it becomes possible to create high-efficiency high-temperature (≥1000 °C) radiation-resistant TEGs based on $^{11}B_4C$ *p*-type and *SiGe* *n*-type by changing the parameters of operating conditions. It is clear that the problem of connection between thermoelements must be solved. In order to implement the proposals, studies of thermal efficiency (*ZT*) were performed on the basis of isotope ^{11}B at high temperatures of B_4C. All thermoelectric parameters (ρ, S, χ) were investigated. The possibility of creating a high-temperature thermoelectric generator based on B_4C and *SiGe* materials was demonstrated [5]. The main problem encountered by researchers during their research and development on thermoelectric converters with a nuclear heat source is to improve or create high-quality materials both with high efficiency of *Z* conversion at high temperatures and with high radiation resistance. Production of materials was carried out using two methods: hot pressing in vacuum and crystallization caused by CVD. Boron carbide was used for *p*-leg of the thermoelectric converter, and the radiation-resistant *Si-Ge* alloy doped with phosphorus was used for *n*-leg of the thermoelectric converter.

This idea was implemented by two institutes: the National Scientific Center "Kharkiv Institute of Physics and Technology" (NSC-KIPT) and Sukhumi Institute of Physics and Technology (SIPT) within the framework of the STCU project Gr-20j "Development of radiation-resistant thermoelectric elements based on boron carbide (B_4C) and silicon-germanium (*SiGe*) alloys" (2003 – 2005, collaborator – Prof. Fernand D.S.Marquis, USA).

NSC – KIPT was engaged in the works on development of processes for production of boron carbide and silicon-germanium alloys by the gas-phase and plasma-chemical methods, SIPT – on production of boron carbide and silicon-germanium alloys by hot pressing in vacuum, and also on the study of the thermal and electrophysical properties of the materials obtained.

The effect of boron content on the thermoelectric properties of boron carbide samples obtained by hot pressing and gas-phase (including plasma-chemical) methods was studied.

From the results of measuring thermoelectric characteristics, the figure of merit *Z* of materials of samples obtained by hot pressing methods, as well as by gas-phase and plasma-chemical deposition methods was calculated. Over the entire temperature range (300 – 1300 K) the figure of merit of boron carbide samples obtained by the CVD-methods exceeds the figure of merit of the hot-pressed samples, and with a rise in temperature this difference is somewhat increased. The samples obtained by the CVD-methods have nearly equal values of *Z*, but the figure of merit of plasma-chemical samples is 10 –15 % higher than that of the samples obtained by the gas-phase method.

It is established that for the composition $B_{6.5}C$ the figure of merit of *p*-leg reaches $1\cdot10^{-4}$ 1/degree for the gas-phase manufacturing method and $1.3\cdot10^{-4}$ 1/degree – for plasma-chemical. The figure of merit of the pair ($Si_{0.7}Ge_{0.3}$ + 0.3 %P) gas – ($B_{6.5}C$) gas is $2.2\cdot10^{-4}$ 1/degree, and the efficiency – 4.4 %. When *p*-type leg is made of plasma-chemical $B_{6.5}C$, the figure of merit of this pair is $2.5\cdot10^{-4}$ 1/degree, and the efficiency – 5.0 % [6].

In order to determine the thermoelectric compatibility, the calculation of the thermoelectric efficiency of the $Si_{0.7}\ Ge_{0.3}$ alloy of *n*-type and boron carbide B_4C and $B_{6.5}C$ of *p*-type of different densities was carried out.The most optimal in compatibility with $Si_{0.7}\ Ge_{0.3}$ *n*-type in *Z* is a sample of boron carbide (*p*-type), made on the basis of 11B with a high boron content, i.e. BxC, where x ≥ 6.3. The 11B isotope in boron carbide samples also provides high radiation resistance, which is of considerable importance in the case of their use as a heat source of a nuclear reactor.

In 2008 – 2010, international STCU/GNSF project №4655 “Development of technology and creation of a prototype of high-temperature heliothermoelectric generator” was carried out. An experimental heliothermoelectric generator (HTEG) was developed. HTEG (up to 1000 °C) was created on the basis of a highly concentrated Cassegrain optical system and a thermoelectric generator based on $Si_{1-x}Ge_x$ alloys (x = 0.05 – 0.10) for electrical energy production.

The thermopiles with 32 legs were manufactured by collective interconnection method. Their energy and thermomechanical properties were studied.

Two-stage optical furnaces of the Cassegrain type were manufactured and their energy and thermomechanical characteristics were studied.

In 2009 – 2010, STCU / GNSF project №4996 "Development of *Si-Ge* nanostructured alloys by explosive compaction method and creation of energy-efficient thermopiles on their basis" was carried out. The raw materials used were powders of standard nanostructured *Si* and *Ge* obtained by grinding.

Experimental thermoelements and thermopiles have been created. Their structural and thermoelectric parameters have been investigated.

At present, the institute is developing thermoelectric alloys of *SiGe n-* and *p*-type with a low content of *Ge* (5 – 10 at. %). It is known [7] that the thermal resistance of *Si-Ge* alloys containing up to 10 at. % *Ge* increases sharply with increasing *Ge* content. This material is promising for creating thermoelectric generators, where waste heat is used for direct use, in heating furnaces and in central gas heating systems. Such a thermoelectric generator can operate in the open air and generate an electric power of ~ 1 W from the working area of 1 sm^2. The generated electrical energy can be used to operate these systems, as well as for the individual needs of consumers.

These alloys were obtained by co-grinding the original components into ultrafine powder and hot pressing in a vacuum of 10 *Pa* at 1250 – 1370 °C under a pressure of 480 $kg \cdot sm^{-2}$ for 20 – 40 minutes. As the main components of the alloys, polycrystalline *Si* and *Ge* were used, and the alloying components for the *p*-type alloy were amorphous *B*, and for the *n*-type alloy, amorphous phosphorus and polycrystalline *GaP*. Homogenizing isothermal annealing of the samples was carried out at 1200 – 1360 °C for 20 – 100 hours in vacuum and in the open air.

Fig. 3 shows *X*-ray profiles of the diffraction maximum (444) of samples of the $Si_{0.95}Ge_{0.05}$ alloy prior to and after annealing at 1360 °C for 34 hours. The alloy was pressed at 1355 °C for 40 min. The porosity of the material is 2%. Prior to annealing, the diffraction maximum of the sample corresponds to *Si-Ge* alloy with *Ge* content of 6 at.% and pure *Si*. After annealing, the sample is a homogeneous *Si-Ge* alloy with *Ge* content of 4.6 at.%. As a result of high-temperature pressing, fine powder particles collect together and form larger grains of alloys with sizes up to 10 μm.

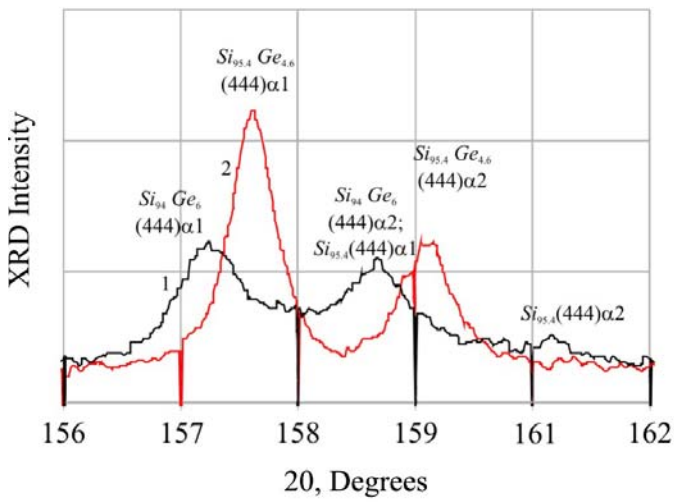
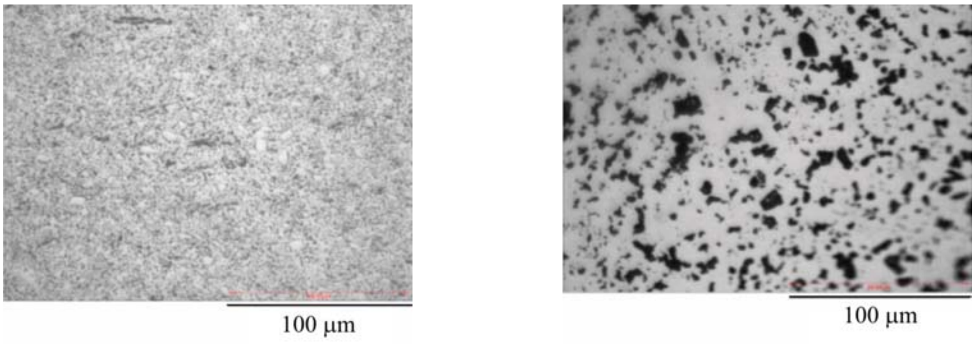


Fig. 3. X-ray profiles of the diffraction maximum (444) of the sample:
1 – prior to annealing; 2 – after annealing

The microhardness of this sample varies within 10.64 – 11.86 GPa (the average value is 11.29 GPa), and the microhardness of the molten $Si_{0.95}Ge_{0.05}$ alloy is 11.30 GPa [8]. In accordance with microhardness, this material is a fairly homogeneous alloy.

Fig.4 shows the microstructure of $Si_{0.95}Ge_{0.05}$ + *GaP* 3 w. % alloy pressed at 1290 °C for 30 min prior to and after annealing at 1350 °C for 25 hours.The porosity of the material is 17 %. Prior to annealing, the sample contains fine particles and pores. Around large pores there are large homogeneous regions enriched with germanium. After annealing, the material structure is uniform and contains pores up to 20 μm.



a) *b)*

Fig. 4. Microstructure of samples: a) prior to annealing; b) after annealing

Table shows the results of studying the concentration n and the mobility μ of the current carriers and the electrical conductivity σ of $Si_{0.95}Ge_{0.05}$ alloys doped with *B*, *P* or *GaP*. The alloys were pressed at 1335 °C for 30 min. The porosity of the material is 3 %. From the results obtained, when compressing powders, a deep dissolution of impurities takes place. The values of the measured parameters correspond to the results of known studies, but the mobility of holes of the p-type sample is 3 times higher [9]. As a result of isothermal annealing at 1300 ° C for 30 hours, the values of n, μ and σ of the samples studied did not change significantly.

Table

Electrophysical characteristics of Si-Ge alloys

Alloys	Type	n, 10^{20}. cm^{-3}	μ, cm^2. v^{-1}. sc^{-1}	σ, Ω^{-1}. cm^{-1}
$Si_{0.95}Ge_{0.05}$ + *B* 0.2 w. %	*p*	0.6	250	1725
$Si_{0.95}Ge_{0.05}$ + *P* 0.5 w. %	*n*	2.0	74	2000
$Si_{0.95}Ge_{0.05}$ + *GaP* 2 w. %	*n*	1.6	67	1400

The temperature dependences of α, σ, λ and *Z* were measured for three samples of each of the obtained alloys $Si_{0.95}Ge_{0.05}$ + *GaP*3 w.% and $Si_{0.95}Ge_{0.05}$ + *B* 0.2 w. %, pressed at 1325 °C for 30 min. Material porosity is 7 %. The data obtained from one sample of n-type alloy and one sample of *p*-type alloy is shown in Figs. 5 and 6.

The efficiency Z is calculated by the formula $Z = \alpha^2\sigma / \lambda$.

The nature of the changes in the measured parameters, depending on the temperature of the materials being studied, is similar to the character of such changes in the same parameters of all other thermoelectric *Si*-*Ge* alloys.The efficiency of investigated alloys is 20 % lower compared to *n*- and *p*-type $Si_{0.68}Ge_{0.32}$ alloys comprising 6.4 times more germanium. The values of α and λ of the *n*-type alloy in question are close to the nanostructured $Si_{0.95}Ge_{0.05}$ *n*-type alloy [10], but its electrical conductivity is 1.8 times lower. The reason for this is the oxidation of the resulting ultra-fine powder, as the operations for its manufacture and use were carried out in the air.

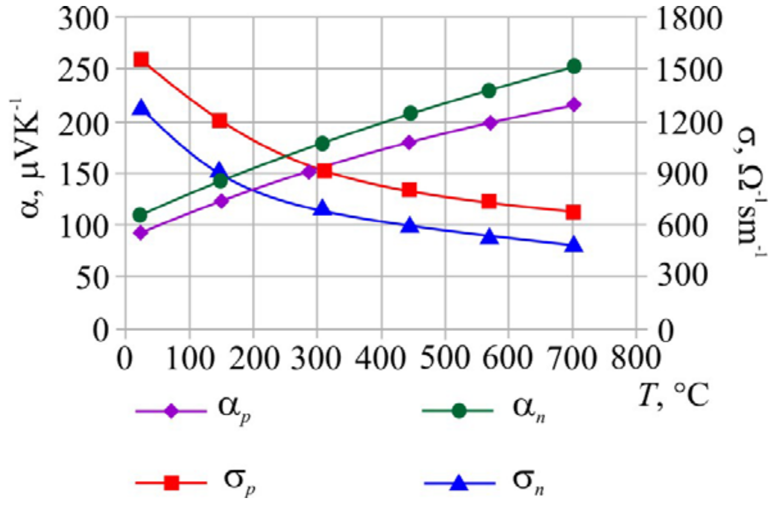


Fig. 5. Temperature dependence of σ and α of n- and p-type samples

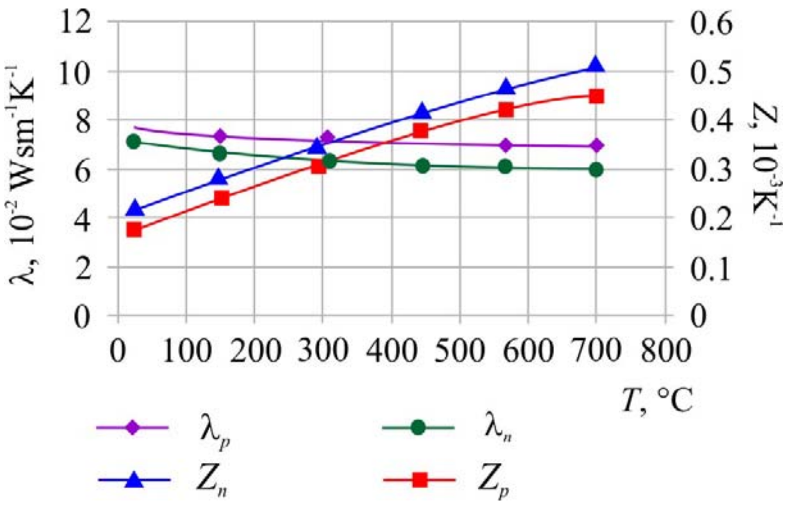


Fig. 6. Temperature dependence of λ and Z of n- and p-type samples

Further optimization of carrier concentration and technological regimes of the investigated alloys will increase their efficiency. The described method of obtaining alloys does not require expensive equipment and is easily realized. The use of the thermoelectric alloy *SiGe* synthesized by this method is suitable both for direct use (creation of thermoelectric converters) and for production of nanostructured materials.

The institute conducts research on the production of polycrystalline and single-crystal *SiGe* alloys with a content of up to 10 at.% *Ge* by the Czochralski method, intended for thermoelectric converters and optoelectronic devices.

With regard to new theoretical developments [11] and accumulated rich experience in creating two-stage thermoelectric generators, a joint project of a three-stage thermoelectric generator on the basis of high-performance thermoelectric materials is under development nowadays with participation of Sukhumi Ilia Vekua Institute of Physics and Technology, Institute of Thermoelectricity NAS of Ukraine and the National Scientific Centre "Kharkiv Institute of Physics and Technology" NAS of Ukraine.

Conclusions

This paper gives an overview of the results of research in the field of materials science and thermoelectric instrument making, conducted at Sukhumi Ilia Vekua Institute of Physics and Technology from the 50s of the last century to the present time.

Since the early 50s of the 20th century, technological devices have been designed and *Ge*, *Si* and *SiGe* semiconductor bulk crystals have been synthesized, methods for synthesis and subsequent hot pressing of thermoelectric *SiGe* alloys used in the future when creating high-temperature thermoelectric generators for the "Romashka" nuclear power plant (1964), and also for the construction of single-stage (1966) and two-stage (1972) thermoelectric generators for the "Buk" nuclear power unit have been developed.

For a long time (1970 – 1990), various thermoelectric converters operating in low, medium and high temperature regions with different applications have been developed and developed.

In the first years of this century, in cooperation with the Kharkiv Institute of Physics and Technology, the possibility in principle of creating high-temperature thermoelectric converters with *p*- and *n*-legs made of boron carbide and *SiGe* alloys obtained by various methods was shown.

Together with the Institute of Nuclear Research of the NAS of Ukraine, reactor tests of $Si_{0.7}Ge_{0.3}$ alloys were carried out in the temperature range from 773 to 973 K with a fast neutron fluence set up to 4·1020 cm^{-2} and threshold values of fluences for *p*- and *n*-legs of thermoelectric converters were determined. The possibilities of increasing their radiation resistance and resource capacity were estimated.

In recent years, a technology has been developed to create a high-temperature heliothermoelectric generator based on the highly concentrated Cassegrain optical system and thermoelectric $Si_{1-x}Ge_x$ alloys (x = 0.05-0.10).

The nanostructured *SiGe* alloys have been developed by explosive compaction method and energy-efficient thermopiles have been developed on their basis. Their structural and thermoelectric parameters have been investigated.

References

1. A. V. Ioffe and A. F. Ioffe, *Dokl. Akad Nauk SSSR* 98(5), 757 (1954).
2. M. L. Milionshikov, A. S. Abramov, I. G. Gverdtsiteli, L. V. Gorlov, et al., High-Temperature Reactor-Converter "Romashka", *J. Nuclear Energy* 17(35), 329 – 335 (1964).
3. G. Bokuchava, G. Murgulia, and V. Kashia, Study of Reactor Irradiation on Thermoelectric Properties of Highly Doped *n*- and *p*-$Si_{0.7}Ge_{0.3}$, *Atomic Science and Engineering Issues*, Series "Radiation defects physics and radiational material science" 86, Ukraine, NSC "Kharkiv Institute of Physics and Technology" 3, 68 – 72 (2005).
4. Ch. Wood, *Proceedings of the 9th International Symposium on Boron, Borides and Related Compounds* (Duisburg, 3, 236 – 248, 1987).
5. G. Bokuchava, G. Karumidze, B. Shirokov, To the Problem of Creation of High Temperature Thermoelectric Generator, *Georgian International Journal of Science and Technology* **1**(3), 19 – 24 (2008).

6. A. Zhuravlev, B. Shirokov, A. Shiyan, G. Bokuchava, and G. Darsavelidze, Vapour Phase Methods in the Developments of Thermoelectric Converters and Heteroepitaxial Structures. *Proc. of International Conference "Modern Materials and Technologies"* (Tbilisi, Georgia, October, 21 – 23, 2015), p. 115 – 119.
7. J. P. Dismukes, L. Ekstrom, E. F. Steigmeier, I. Kudman, and D. S. Beers, *J. Appl. Phys*. 35, 2899 (1964).
8. M. Kekua, E. Khutsishvili, Semiconducting Solute Solutions of *Ge*-*S*i System, Tbilisi, "Metsniereba" 1985, 156.
9. O. Golikova, E. Iordanishvili, and A. Petrov, *Fiz.Tverd.Tela* 8, 500 (1956) [Sov. Phys. Solid State] 8, 397 (1966)].
10. G. Zhu, H. Lee, Y. Lan, X. Wang, G. Joshi, D. Wang, J. Yang, D. Vashace, H. Guilbert, Pillitteri, M. Dresselhaus, G. Chen, and Z. Ren. *PRL*, 102, 196803 (2009).
11. L. I. Anatychuk, L. N. Vikhor, *Functionally Graded Thermoelectric Materials* (Chernivtsi: Bukrek Publ., 2012), 180 p.

Submitted 29.11.2016