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Development of a High Performance Gas Thermoelectric Generator (TEG) with Possible Use of Waste Heat

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Abstract: A huge concern regarding global warming, as well as the depletion of natural fuel resources, has led to a wide search for alternative energy sources. Due to their high reliability and long operation time, thermoelectric generators are of significant interest for waste heat recovery and power generation. The main disadvantage of TEGs is the low efficiency of thermoelectric commercial modules. In this work, a unique design for a multilayer TE unicouple is suggested for an operating temperature range of 50–600 °C. Two types of thermoelectric materials were selected: «low temperature» *n*- and *p*-type TE materials (for the operating temperature range of 50–300 °C) based on Bi₂Te₃ compounds and «middle temperature» (for the operating temperature range of 300–600 °C) *n*- and *p*-type TE materials based on the PbTe compound. The hot extrusion technology was applied to fabricate *n*- and *p*-type low-temperature TE materials. A unique design of multilayer TEG was experienced to achieve an efficiency of up to 15%. This allows for the possibility of extracting this amount of electrical power from the heat generated for domestic and water heating.

Keywords: TEG; dimensionless figure of merit; thermoelectric materials; waste heat



Citation: Dashevsky, Z.; Jarashneli, A.; Unigovski, Y.; Dzundza, B.; Gao, F.; Shneck, R.Z. Development of a High Performance Gas Thermoelectric Generator (TEG) with Possible Use of Waste Heat. *Energies* **2022**, *15*, 3960. <https://doi.org/10.3390/en15113960>

Academic Editor: Bertrand Lenoir

Received: 10 April 2022

Accepted: 24 May 2022

Published: 27 May 2022

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1. Introduction

One of the main challenges at present is to increase the fraction of available energy from the energy consumed by humanity worldwide. Gas boilers are widely utilized in cold countries to heat apartments and water [1]. Thermoelectric generators (TEGs) may be used to convert a fraction of the heat into electricity, without a significant effect on the heating power [2–8].

A thermoelectric effect is a physical phenomenon consisting of the direct conversion of heat into electrical energy (Seebeck effect). The low efficiency of thermoelectric devices has limited their applications to certain areas, such as power generation and renewable energy. However, the main advantage of the thermoelectric energy converters is their operating time of up to 20 years operating time up to 20 years. Therefore, for specific applications such as space probes, where efficiency is not as important as availability, reliability, and predictability, thermoelectricity has noteworthy potential [9,10]. The challenge is making thermoelectricity a future leader in waste heat recovery. Thermoelectricity applications can be grouped into two main domains. The first group deals with the use of heat emitted from a radioisotope to supply electricity to various devices. In this group, space exploration was the only application for which thermoelectricity was successful. In the second group, a natural heat source could prove useful in the production of electricity. In this group, gas thermoelectric generators (TEGs) are widely used for the cathodic defense of gas tube lines (north areas of Russia, Canada, USA) and play the role of autonomic energy stations [9].

The development of TEGs, including their novel materials (skutterudites) and different applications, are presented in Refs. [10–13].

The efficiency of a TEG is the product of two terms: Carnot efficacy and a thermoelectric efficiency depending on an average dimensionless thermoelectric figure of merit ZT_{av} , which is defined as:

$$(ZT)_{av} = \frac{1}{T_h - T_c} \int_{T_c}^{T_h} ZT \cdot dT \quad (1)$$

Here, T_h , T_c are the hot-side and cold-side temperatures:

$$ZT = \frac{S^2 \sigma}{\kappa} T \quad (2)$$

where S is the Seebeck coefficient, σ and κ are the electrical and the thermal conductivities, and T is the absolute temperature.

Since the first suggestion by A.F. Ioffe, the best-known TE materials are semi-conductors [5]. With an electron (hole) concentration $n(p) \sim 1 \times 10^{19} \text{ cm}^{-3}$, heat transport is mainly determined by phonons k_L . In this carrier concentration, the Fermi level E_F is close to the bottom of the conduction band E_C for the n -type semiconductor or the top of the valence band E_V for the p -type semiconductor. In this case, Z practically depends on three parameters [14]:

$$Z \sim m_n^{*3/2} (\mu/k_L) \quad (3)$$

where m_n^* —is effective mass for electrons at n -type of semiconductor and for holes at p -type, μ —their mobility, and k_L is the phonon thermal conductivity.

The dimensionless figure of merit ZT for different n - and p -type thermoelectric materials in the operated temperature range of 30–900 °C is illustrated in Figure 1 [15–26]. Today, there is no known thermoelectric material with the optimal ZT over the entire operated temperature range. However, as is evident from Figure 1, the maximum ZT for Bi_2Te_3 , $\text{A}^{\text{IV}}\text{B}^{\text{VI}}$ (PbTe , GeTe), and $\text{Si}_{1-x}\text{Ge}_x$ semiconductor compounds may create a constant envelope of high ZT over a range of temperatures.

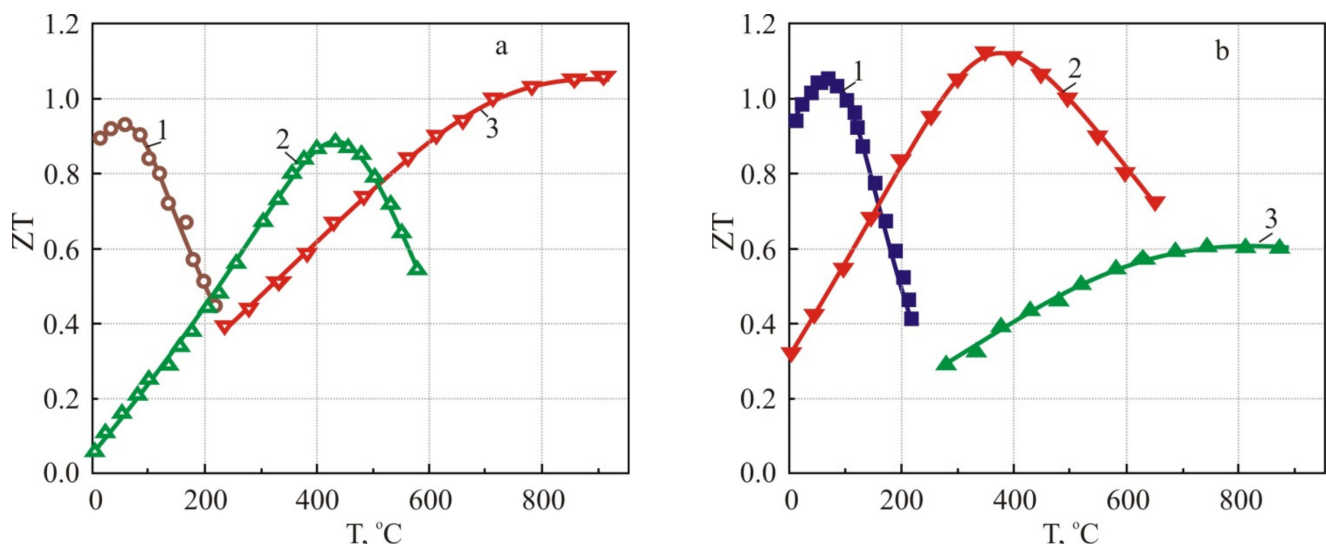


Figure 1. Temperature dependence of dimensionless figure of merit zt for various thermoelectric materials over 30–900 °C [15–26]. (a) n -type: 1— $\text{Bi}_2\text{Te}_{3-x}\text{Sb}_x$. 2— PbTe . 3— $\text{Si}_{1-x}\text{Ge}_x$. (b) p -type: 1— $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$. 2— GeTe . 3— $\text{Si}_{1-x}\text{Ge}_x$.

The legs of typical commercial thermoelectric generators are conventionally fabricated from one type of semiconductor material [9]. Therefore, one means of increasing the efficiency of thermoelectric conversion of TEGs is the creation of multilayer thermoelectric

unicouples, which can provide a high figure of merit ZT between 50 and 600 °C. To achieve this goal, several thermoelectric materials have been suggested in the design of multilayer thermoelectric unicouples with improved efficiency.

The main goal of the research is to enhance the efficiency of the energy conversion of gas TEG using the offered TE uncouple. We looked at the additional possibility of TEG application using heat accumulation following thermoelectric energy conversion. For the first time, we offered a unique hybrid system consisting of the TEG and a gas boiler, as the autonomic source of the electric energy and heat had a total efficiency of up to 80%.

2. Technology

2.1. Hot Extrusion

The n - and p -type Bi_2Te_3 based compounds were prepared using a hot extrusion method (Figure 2), which involves several consecutive steps [14,27–30]. The materials were synthesized in evacuated silica tubes. The compounds were crushed, compacted, and annealed. The annealed samples were extruded in a 150-ton hydraulic press to extrusion ratio $k = 16$ at 400 °C. The resultant rods were annealed in an inert atmosphere at $T_t = 400$ °C in an argon atmosphere for 100 h.

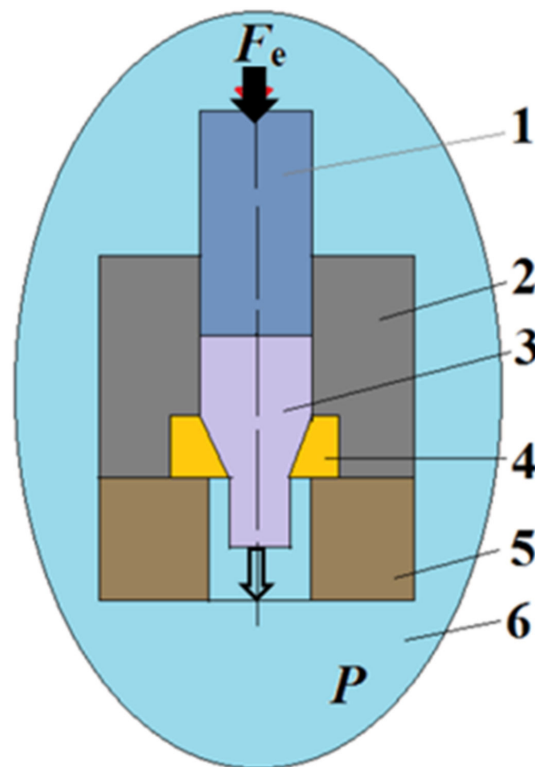


Figure 2. Schema of Hot Extrusion; 1—plunger. 2—container. 3—deformable thermoelectric material. 4—die. 5—support washer. 6—working fluid. P —working fluid pressure. F_e —extrusion force.

2.2. SPS Method

The n -type $\text{Pb}_{1-x}\text{In}_x\text{Te}_{1-y}\text{In}_y$ and p -type $\text{Ge}_{1-x}\text{Bi}_x\text{Te}$ were prepared using Spark Plasma Sintering (SPS) technique [31–34]. The powder was compacted in a protective atmosphere at room temperature to form 20-mm diameter and 5-mm thick tablets at 1 GPa. Then, the tablets were heated at a rate of 50 °C/min and sintered at 600 °C for 20 min under an axial compressive stress of 60 MPa in an argon by SPS. The schematic view of the SPS unit is presented in Figure 3.

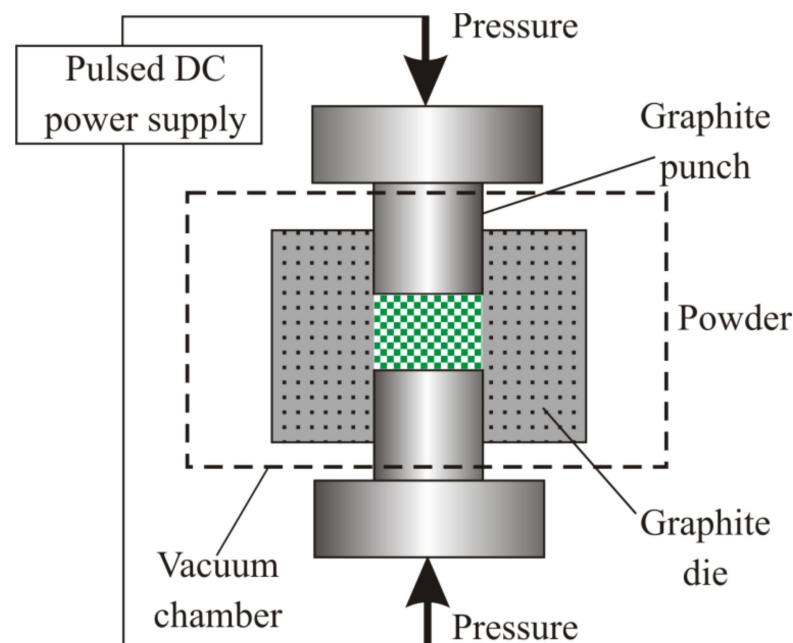


Figure 3. Schematic view of SPS technique.

3. Characterization

3.1. Structural Characterization

The structural analyses of the films were performed using X-ray diffractometer STOE STADI P (by STOE and Cie GmbH, Munich, Germany) in transmission mode using modified Guinier geometry ($\text{CuK}\alpha_1$ -radiation, concave Ge-monochromator (111) of the Johann type; $2\theta/\omega$ -scan, angle interval $20^\circ \leq 2\theta \leq 80^\circ$ with the scanning step of 0.02° . The scan time in a step was 100 s. SEM images were taken with Quanta 200 environmental scanning electron microscope (HRSEM).

3.2. Mechanical Testing

Three-point bending tests were performed on specimens with dimensions $20 \times 5 \times 5$ mm [35].

3.3. Thermoelectric Properties Measurement

Seebeck coefficient and electrical conductivity were measured using the standard methods, which can be found in Ref. [36]. The measurements were made in argon at a temperature range of 30–600 °C. Thermal diffusivity α was measured by the Netzsch LFA 457 equipment, and the specific heat capacity C_p was derived from a reference sample (Pyroceram 9606).

The Hall coefficient for the estimation of carrier concentration was measured at room temperature in the constant electric and magnetic fields with the magnetic field induction $B = 2$ T. The uncertainty of Hall measurements was ~10%.

The original setup was developed for the measurement of the outside characteristics of the multilayer TE uncouple or TE module, as well as the contact resistance between metallic contact and thermoelectric legs and thermal losses between these layers in a uncouple. A detailed description of the measuring system is presented in our previous publication in Ref. [17]. The schema of the measurement unit for output characteristics of TE uncouples and TE modules over a 100–600 °C temperature range is presented in Figure 4.

The block diagram of the measurement unit is demonstrated in Figure 5. Measurements were spent in argon at a temperature range of 100–600 °C. Two identical TE modules (TEuncouples) are placed in a vacuum chamber on both sides of an electric heater. Two water radiators (upper and lower) were pressed against the cold sides of TE uncouples

from the outside of the chamber. The heat screen was situated in a vacuum chamber to decrease the radiation heat.

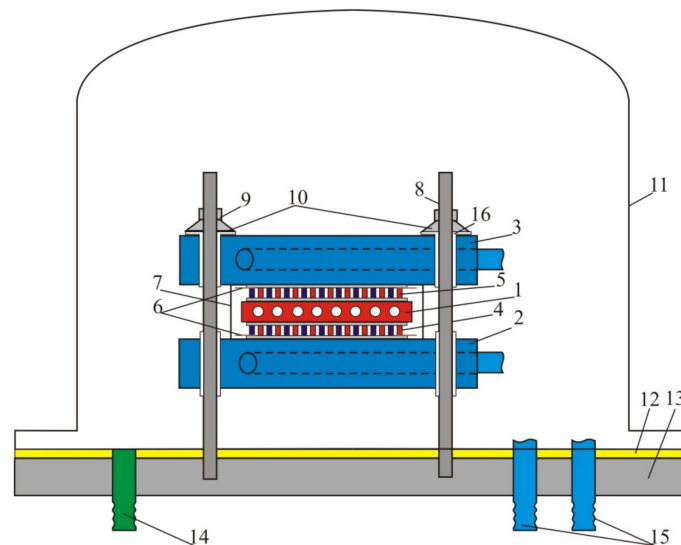


Figure 4. Schema of measurement unit of output characteristics of generator TE uncouples and TE modules over 100–600 °C temperature range; 1—copper electric heater with thermocouple. 2, 3—copper water radiator with thermocouple. 4, 5—upper and lower TE modules (TE uncouples). 6—electrical contacts. 7—heat shield. 8—clamping pins. 9—nuts. 10—springs. 11—vacuum chamber. 12—vacuum gasket. 13—base. 14, 15—fittings. 16—fluoroplastic insulation.

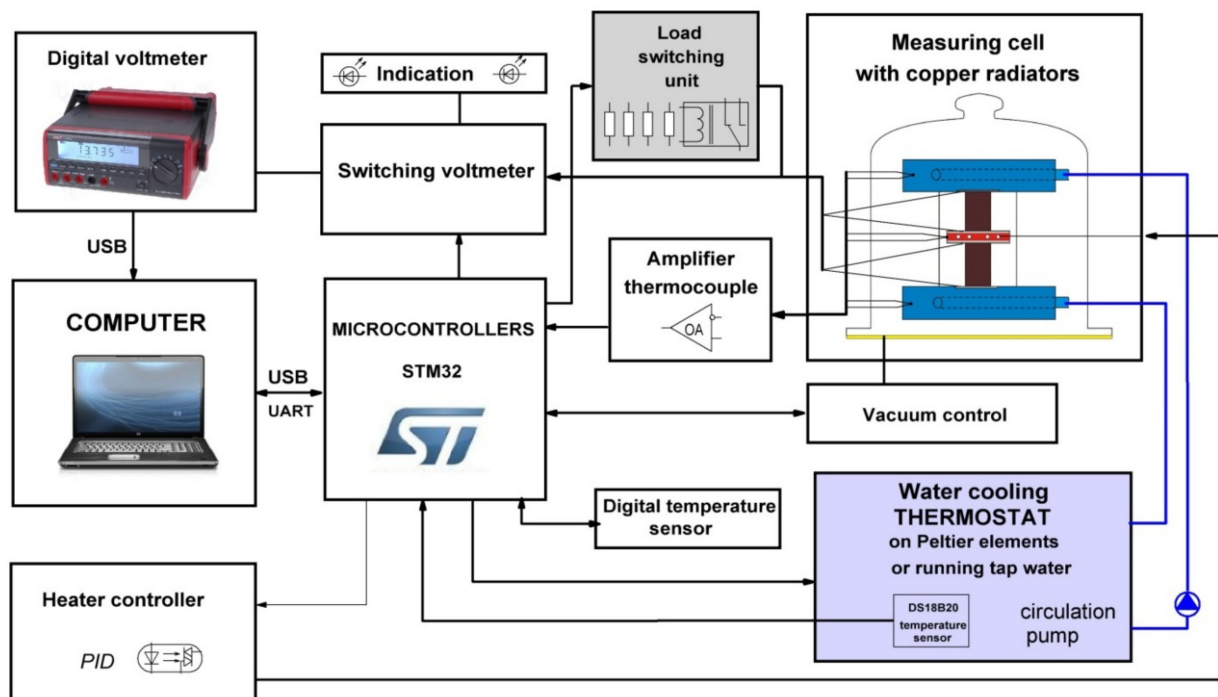


Figure 5. Block diagram of setup for measuring output characteristics.

The efficiency of TE uncouple (TE module) is defined as:

$$h = (P_1 + P_2)/Q, \quad (4)$$

where P_1 and P_2 are the electric power of the upper and lower TE uncouple (TE module), and Q is the heater power.

The temperature of the heater is changed in the 100–600 °C temperature range with an accuracy of 2%. The temperature of the radiators was determined to be 50 °C by a thermostat with an accuracy of 1%. The estimated accuracy of the efficiency measurement was ~3%.

4. Low-Temperature (50–300 °C) Thermoelectric Materials Based on *n*-Type and *p*-Type Bi_2Te_3 Compounds

Bismuth-telluride-based compounds: solid solutions $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ for *n*-type and $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ for *p*-type are the most effective thermoelectric materials, and operate at temperatures up to $T_h \sim 300$ °C [37–40]. In our last paper, we discussed that these materials, prepared using the SPS technique, were optimized to improve TEGs efficiency [17]. In this paper, we investigated these compositions, prepared by hot extrusion, with a view to improve their mechanical properties and thermoelectric efficiency, which are necessary for the long-term operation of TEGs [9,14].

4.1. Structure Properties

After fabrication, the specimens were examined by XRD from perpendicular plane to extrusion (pressing) direction. The results are demonstrated in Figure 6 and provide evidence of the high-quality texture of the samples prepared by Float zone [41] and hot extrusion techniques. The virtual (00*l*) peaks were dominant in these samples. TE materials based on Bi_2Te_3 compounds have the maximal figure of merit *Z* in this direction [14].

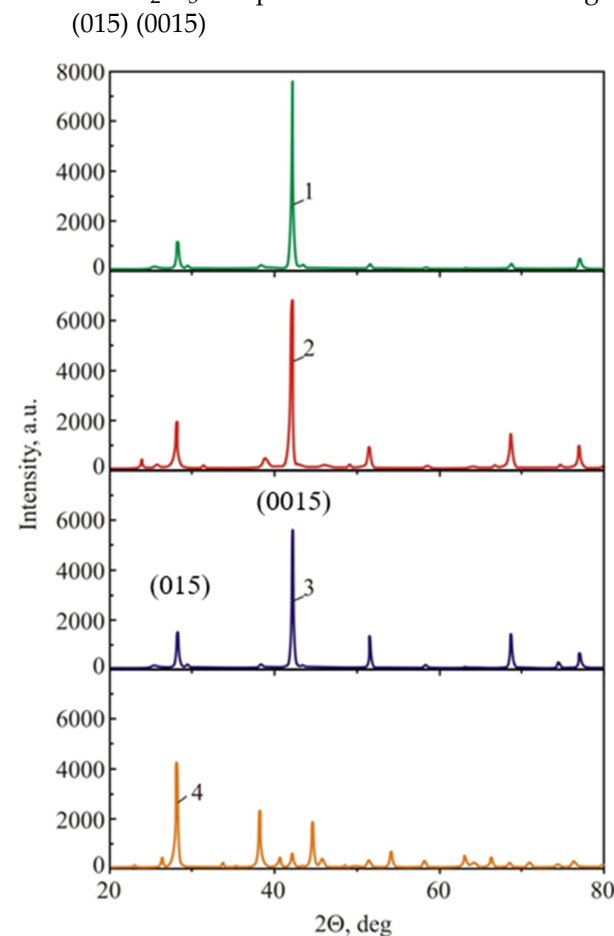


Figure 6. X-ray diffractograms of Bi_2Te_3 -based compounds prepared by different techniques; 1—*p*-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ prepared by Float zone technique [41]. 2—*n*-type $\text{Bi}_2\text{Te}_{2.7}\text{S}_{0.3}$ prepared by hot extrusion. 3—*p*-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ prepared by hot extrusion. 4—*p*-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ prepared by SPS technique [17].

4.2. Mechanical Properties

The mechanical properties of TE materials are of much concern for reliable operation, since all the high- ZT materials are brittle compounds. Bi_2Te_3 is a layered structure [14,41]. The processing of Bi_2Te_3 by plastic deformation could improve strength and ductility, probably by entangling the grains' retard microcrack propagation. However, plastic deformation generates preferred an orientation that can be utilized in the best crystallographic orientation of the thermoelectric properties.

The thermoelectric modules (TEMs) consist of several layers, which experience significant mechanical stresses during operation due to their different expansion coefficients [42–45]. Therefore, the bending and compression strengths of the candidate materials were studied, and the results are represented in Tables 1 and 2, respectively. All studied specimens had practically zero elongation. As expected, n -type specimens had a higher strength compared to p -type materials produced using both hot extrusion and Zone float. Hot extruded n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ had a compression strength that was almost an order of magnitude higher than that found with zone floated n -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ material.

Table 1. Bending strength σ_b and deflection y_b of Bi_2Te_3 -based compound specimens prepared with different technologies.

No.	Composition	Technology	F_b , N	y_b , mm	σ_b , MPa
1	n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	Hot extrusion	86.1	0	36.6
2	p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	Hot extrusion	81.8	0	28.2
3	p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	Zone float	>10	0	>3.5
4	n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	Zone float	-	-	-

Table 2. The compression strength σ_c of of Bi_2Te_3 -based compound specimens prepared with different technologies.

	Composition	Technology	Force, F , N	σ_c , MPa
1	p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	Hot extrusion	1782.0	71.3
2	p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	Hot extrusion	1940.0	77.9
3	p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	Hot extrusion	1998.0	80.7
4	n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	Hot extrusion	2980.0	119.4
5	n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	Hot extrusion	2749.4	107.8
6	n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	Hot extrusion	2877.4	122.9
7	p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	Zone float	200.0	7.9
8	p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	Zone float	285.0	11.9
9	n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	Zone float	431.7	17.6
10	n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	Zone float	352.3	14.2

Figure 7 presents the stress–strain behavior of compression tests for n -type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ specimens prepared with different technologies.

4.2.1. N-Type Thermoelectric Materials

The temperature dependences of Seebeck coefficient S , electrical conductivity σ , thermal conductivity κ and dimensionless figure of merit ZT over a 30–300 °C temperature range for n -type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ samples prepared by hot extrusion are presented in Figure 8. The temperature behavior of S , σ , and κ defines the maximum value of $ZT \sim 1.2$ for the optimal composition of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution with electron concentration $n \sim 5 \times 10^{19} \text{ cm}^{-3}$ and $S \approx -165 \mu\text{V/K}$ at $T \sim 30 \text{ °C}$. Consequently, the best TE material for n -type leg appli-

cation in the thermoelectric low-temperature converters is represented by the extruded, SbI_3 -doped $n\text{-Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ compound.

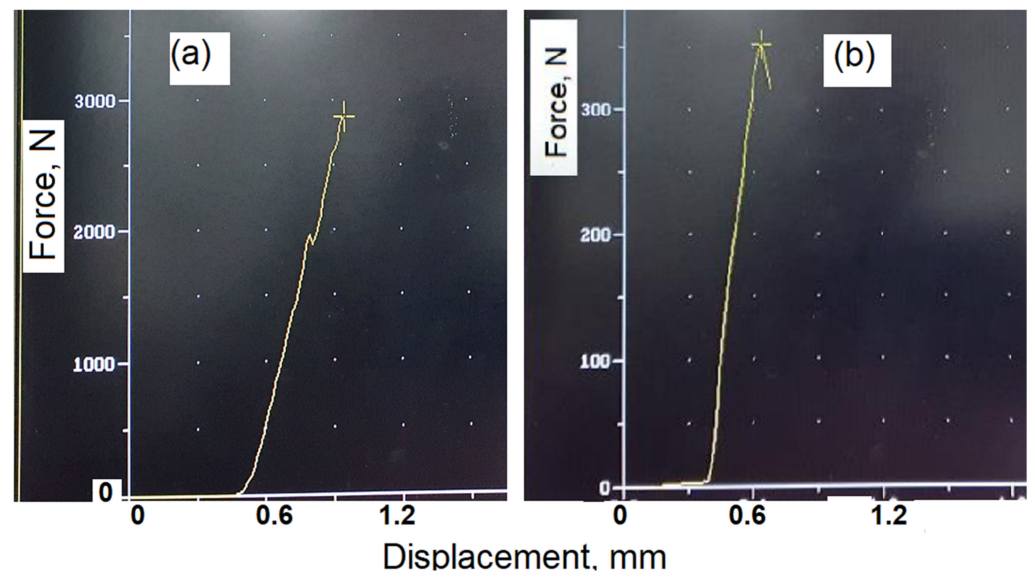


Figure 7. The force–displacement curves (stress–strain behavior) for the compression test; (a)—hot extruded $n\text{-Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ specimen. (b)—zone float $n\text{-Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ specimen.

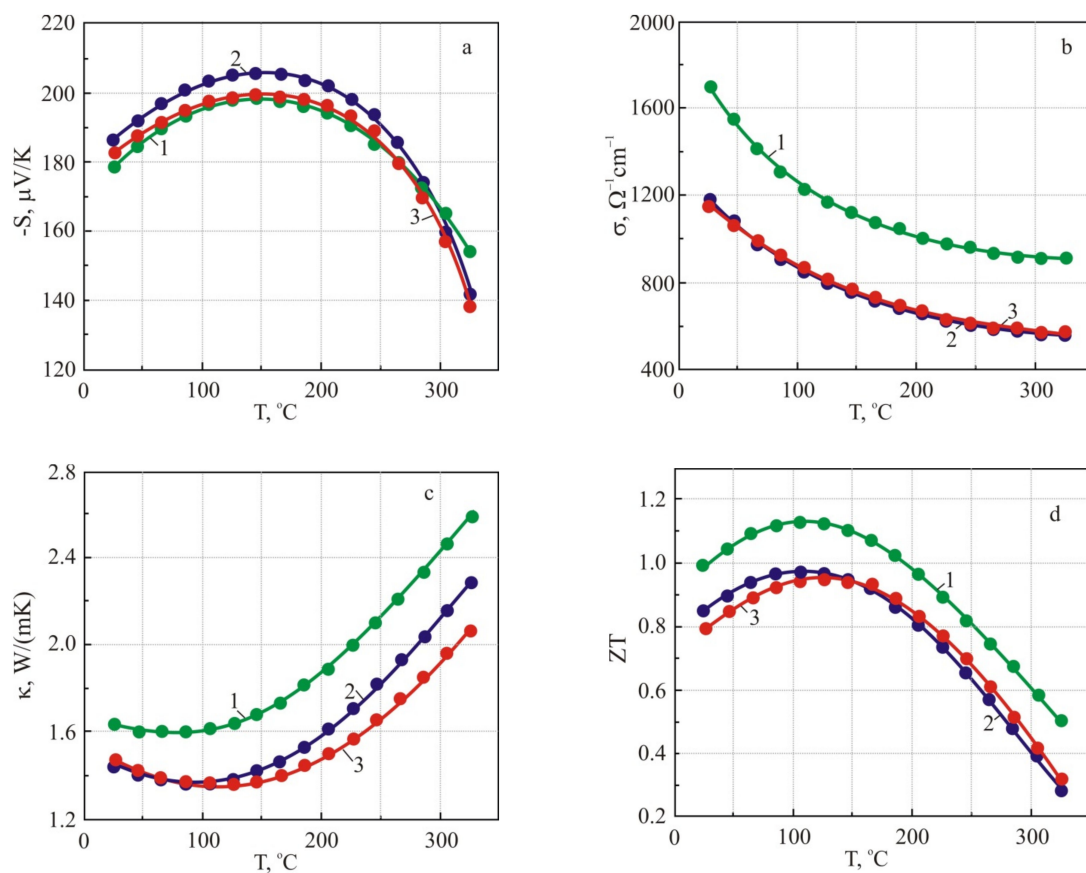


Figure 8. The temperature dependence of Seebeck coefficient (a), electrical conductivity (b), thermal conductivity (c), and the dimensionless figure of merit ZT (d) over 30–300 °C temperature range for $n\text{-Bi}_2\text{Te}_{3-x}\text{Se}_x$ samples, fabricated by hot extrusion. 1— $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. 2— $\text{Bi}_2\text{Te}_{2.55}\text{Se}_{0.45}$. 3— $\text{Bi}_2\text{Te}_{2.4}\text{Se}_{0.6}$.

4.2.2. P-Type Thermoelectric Materials

The temperature dependences of Seebeck coefficient S , electrical conductivity σ , thermal conductivity κ and dimensionless figure of merit ZT over 30–300 °C temperature range for p -type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ prepared by hot extrusion are presented in Figure 9.

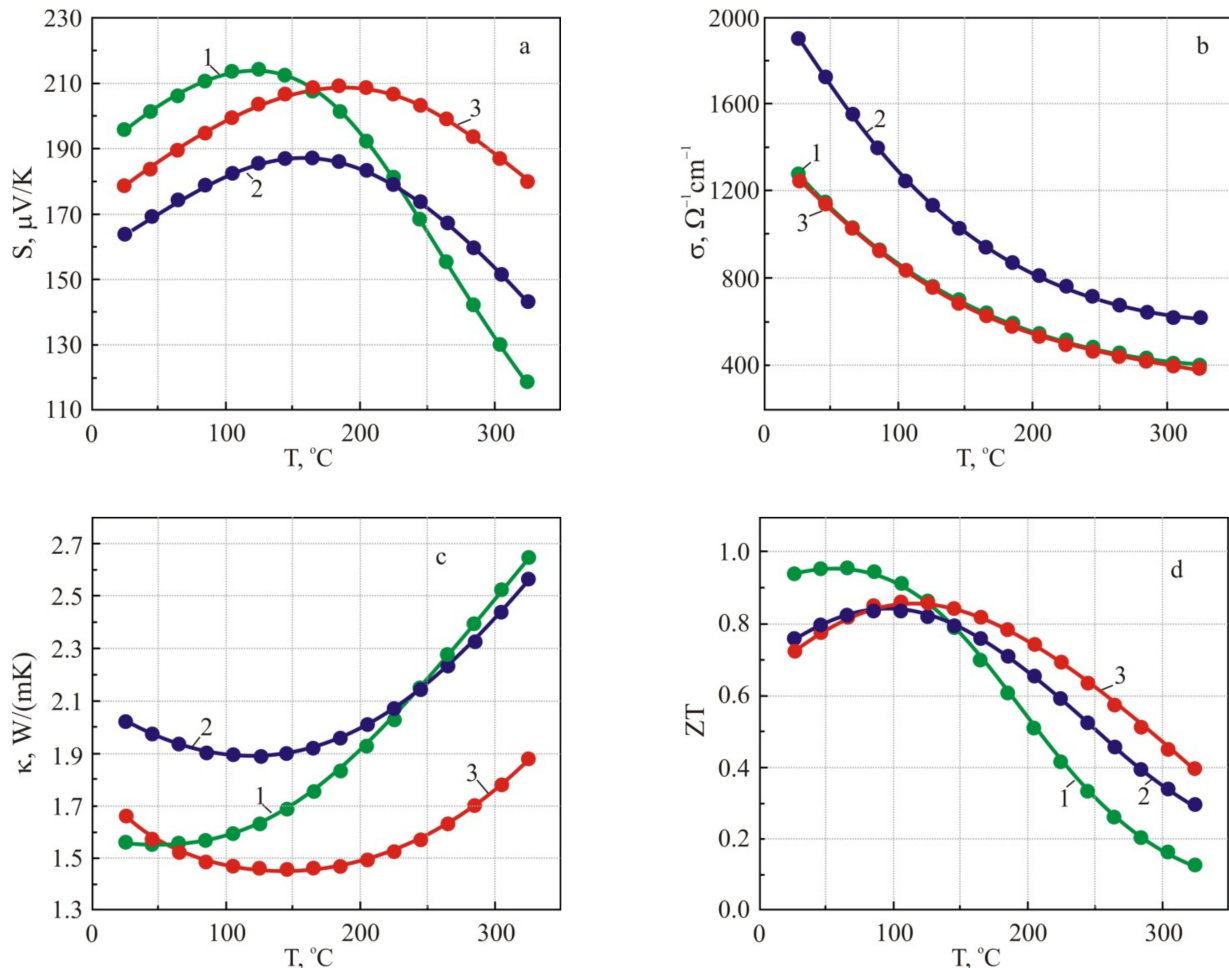


Figure 9. The temperature dependence of Seebeck coefficient (a), electrical conductivity (b), thermal conductivity (c), and the dimensionless figure of merit ZT (d) over 30–300 °C temperature range for p -Type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ fabricated by hot extrusion. 1—stoichiometric $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (conventional orientation). 2— $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 + 0.5$ wt.% Pb (conventional orientation). 3— $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 + 0.5$ wt.% Pb (parallel to C axis).

The Seebeck coefficient S (Figure 9a) reaches the maximum for all specimens and then decreases with an increase in temperature. As shown in [14,17], this S behavior is connected with the appearance of electrons, which have a negative S coefficient value. In this case, S is determined as [17]:

$$S = \frac{(S_p\sigma_p + S_n\sigma_n)}{\sigma_n + \sigma_p} \quad (5)$$

where indices n and p describe the parameters for electrons and holes, respectively.

The electron mobility is higher than the hole mobility [14], and electron concentration exponentially increases with temperature. In this case, we can observe a sharp decrease in S . According to Equation (5), the Seebeck coefficient becomes anisotropic at high temperatures due to the presence of opposite-sign charge carriers. As shown in [14], the negative effect of minority charge carriers is minimized with crystals prepared by hot extrusion, with a parallel orientation to axis C. The increased thermal conductivity κ at $T > 200$ °C (Figure 9c) is due to the appearance of the ambipolar thermal conductivity of electron–hole pairs,

which is weak for samples with the lowest mobility minority carriers (electrons) [14]. In this case, $T > 200$ °C values of the dimensionless figure of merit ZT is higher for samples where the orientation parallel to axis C is higher (Figure 9d).

5. Middle-Temperature Thermoelectric Materials (Operating Temperature 300–600 °C)

Lead telluride (PbTe) is an effective thermoelectric material for applications at middle temperatures of up to 600 °C [46]. It has a high melting point of ~900 °C and good chemical stability. Its high ZT allowed for its use in NASA space programs [47]. In our latest papers, indium- (effective donor impurity)-doped n -type PbTe specimens, prepared by SPS technique, were optimized to improve TE efficiency [28,29]. However, while the ZT for different impurities-doped, p -type PbTe has a very high value, at 300–500 °C [48–52], it has poor mechanical properties and is unreliable for use for real applications in thermoelectric energy devices [43,44]. Therefore, the p -type, GeTe-based compound is a real candidate for p -type thermoelectric materials in a 300–600 °C temperature range. In our recent paper, Bi-solid-solution, $\text{Ge}_{1-x}\text{Bi}_x\text{Te}$ -doped, p -type GeTe specimens prepared using SPS technique were thoroughly investigated to improve their thermoelectric efficiency up to 600 °C, which is the maximal temperature for real applications in gas thermoelectric generators [36].

5.1. Middle-Temperature n -Type Thermoelectric Material Based on In and I-Codoped PbTe semiconductor Compound

The maximal value of the figure of merit Z as a function of electron density depends on the location of Fermi level E_F relative to the bottom of the conduction band E_C . It was shown that indium dopant in PbTe produces the optimal location for Fermi levels due to the creation of an indium quasi-local level in the conduction band. This leads to the so-called pinning of the Fermi level [53–56]. The indium level is a source of electrons, which mitigates the influence of the minority carriers (holes). This effect makes the average figure of merit $(ZT)_{av}$ significantly higher over a wider temperature range. An additional improvement in $(ZT)_{av}$ was achieved by co-doping PbTe with iodine, which is a well-known donor in PbTe [31,57].

The temperature dependence of the Seebeck coefficient (a), electrical conductivity (b), thermal conductivity (c), and the dimensionless figure of merit ZT (d) over 300–600 °C temperature range for n -type $\text{Pb}_{1-x}\text{In}_x\text{Te}_{1-y}\text{I}_y$ specimens prepared by SPS are presented in Figure 10. The maximum value of ZT is close to 1.3 at $T = 450$ °C for $\text{Pb}_{0.999}\text{In}_{0.001}\text{Te}_{0.999}\text{I}_{0.001}$ composition, which is one of highest ZT values for n -type PbTe.

5.2. Middle Temperature p -Type Thermoelectric Material Based on GeTe Compound

The temperature dependence of the Seebeck coefficient (a), electrical conductivity (b), thermal conductivity (c), and the dimensionless figure of merit ZT (d) over 300–600 °C temperature range for p -type $\text{Ge}_{1-x-y}\text{Bi}_x\text{Pb}_y\text{Te}$ prepared by SPS are presented in Figure 11.

The $\text{Ge}_{0.96}\text{Bi}_{0.04}\text{Te}$ specimen has the lowest value of $\kappa \approx 2$ W/mK at 300 °C, which is more than twice as low as that of the GeTe specimen, and this trend is observed up to $T = 600$ °C (Figure 11c). The dimensionless figure ZT for $\text{Ge}_{0.96}\text{Bi}_{0.04}\text{Te}$ specimen reaches the value of ~2.0 at $T = 450$ °C and remains virtually constant up to 600 °C, which is more than twice the value of ZT for pristine GeTe. The average thermoelectric figure of merit for $\text{Ge}_{0.96}\text{Bi}_{0.04}\text{Te}$ specimen $(ZT)_{av} \sim 1.3$ was obtained for the operating temperature difference of $\Delta T = 300$ K ($T_c = 300$ °C, $T_h = 600$ °C).

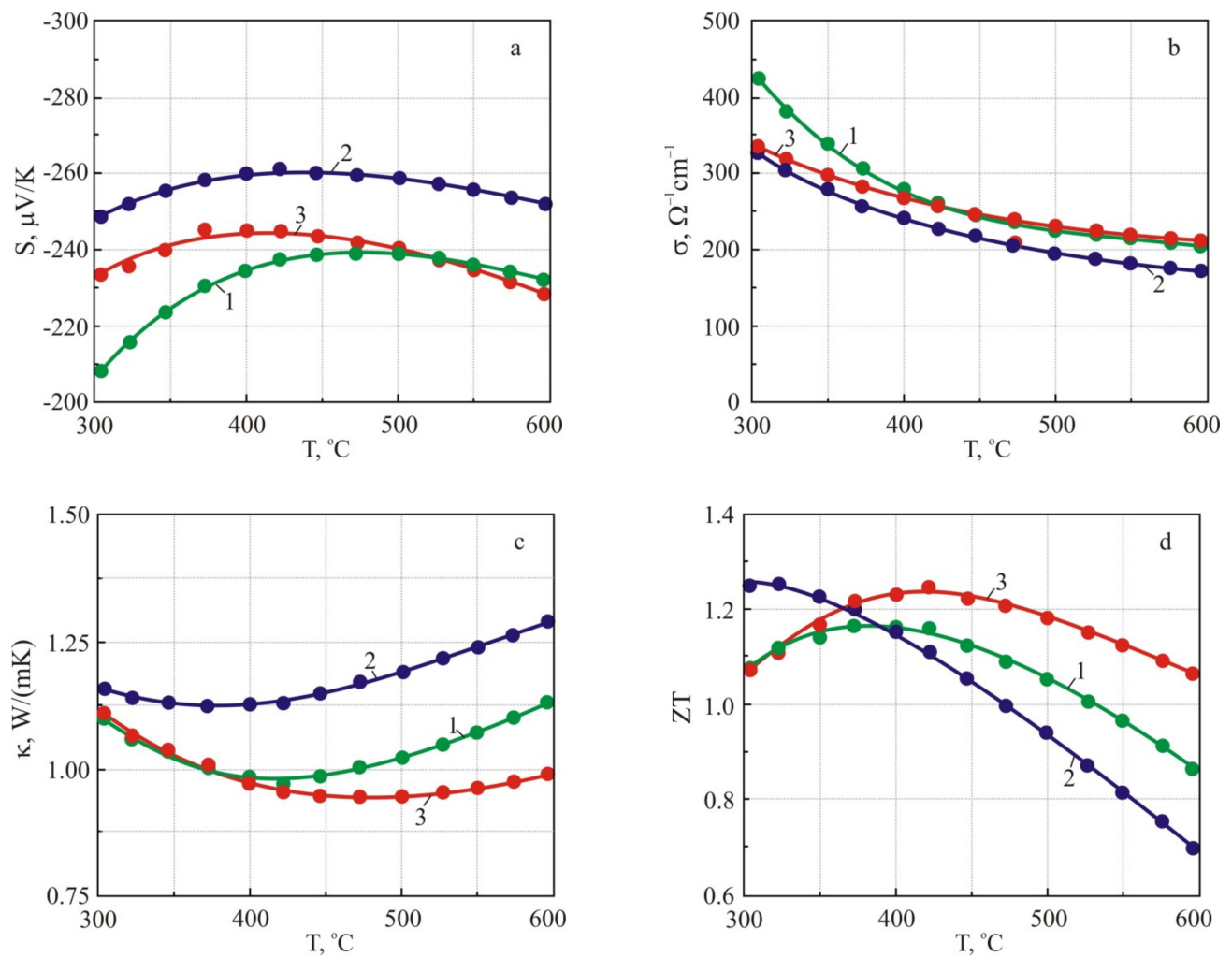


Figure 10. The temperature dependence of Seebeck coefficient (a), electrical conductivity (b), thermal conductivity (c), and the dimensionless figure of merit ZT (d) over 300–600 °C temperature range for n -type $\text{Pb}_{1-x}\text{In}_x\text{Te}_{1-y}\text{I}_y$ fabricated by SPS. 1— $\text{Pb}_1\text{Te}_{0.999}\text{I}_{0.001}$. 2— $\text{Pb}_{0.9995}\text{In}_{0.0005}\text{Te}_{0.9995}\text{I}_{0.0005}$. 3— $\text{Pb}_{0.999}\text{In}_{0.001}\text{Te}_{0.999}\text{I}_{0.001}$.

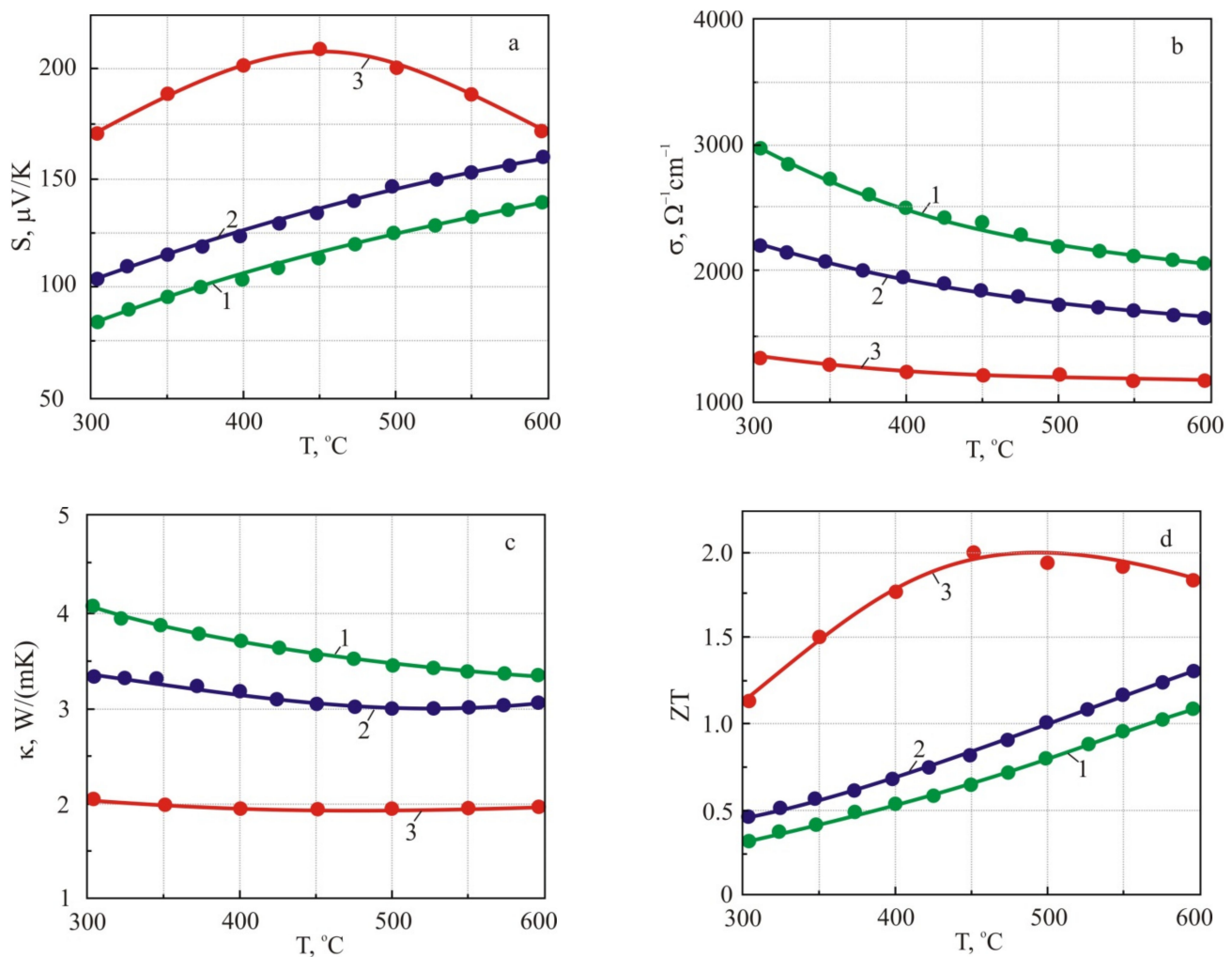


Figure 11. The temperature dependence of Seebeck coefficient (a), electrical conductivity (b), thermal conductivity (c), and the dimensionless figure of merit ZT (d) over 300–600 °C temperature range for p -Type $\text{Ge}_{1-x-y}\text{Bi}_x\text{Pb}_y\text{Te}$ prepared by SPS. 1— GeTe . 2— $\text{Ge}_{0.94}\text{Pb}_{0.06}\text{Te}$. 3— $\text{Ge}_{0.96}\text{Bi}_{0.04}\text{Te}$.

6. Applications

6.1. Thermoelectric Module

To obtain maximum TE efficiency, we propose fabricating composite TE modules (TEMs) from multilayer uncouples designed for given temperature gradients, following the suggestion of Prof. Z. Dashevsky [33]. Each stage should be made of a different material layer. Each material should be selected such that its ZT is maximal in the temperature range prevailing in the corresponding stage (Figures 7–11).

Figure 12 presents the structure of a multilayer TE uncouple designed for the temperature range of 50–600 °C. The first-layer material should be selected from low-temperature TE materials (the temperature interval: 50–300 °C) based on n -type and p -type Bi_2Te_3 materials, fabricated by hot extrusion (layers 2 and 5). The second-layer materials should be selected from middle-temperature materials, n -type $\text{Pb}_{0.999}\text{InTe}_{0.999}\text{I}_{0.001}$ (4) and p -type $\text{Ge}_{1-x}\text{Bi}_x\text{Te}$ (6), prepared by Spark Plasma Sintering (SPS). They should be joined by hot-pressing using thin Bi foils ~0.1 mm (3) between the two layers in each leg.

Several two-layer uncouples were fabricated, and their efficiency was measured using the setup described in Section 3.3. The very first experiment has shown that the energy conversion efficiency reaches a high value of $\eta \sim 14$ –15% when operated between the hot temperature $T_h = 600$ °C and cold temperature $T_c = 50$ °C.

Fabrication of the proposed thermoelectric module (TEM) (Figure 13) may proceed with the following steps:

- Assembly of the developed TE uncouples and enclosing/placing cold side plates into an aluminum cassette.
- Sintering of the cassette under pressure.
- Formation of a sequential chain of thermoelements.
- Assembly of the TE module in a protective case of stainless-steel thin sheet.
- Sealing of the module, including welding of the cover, rollbacks and argon filling.

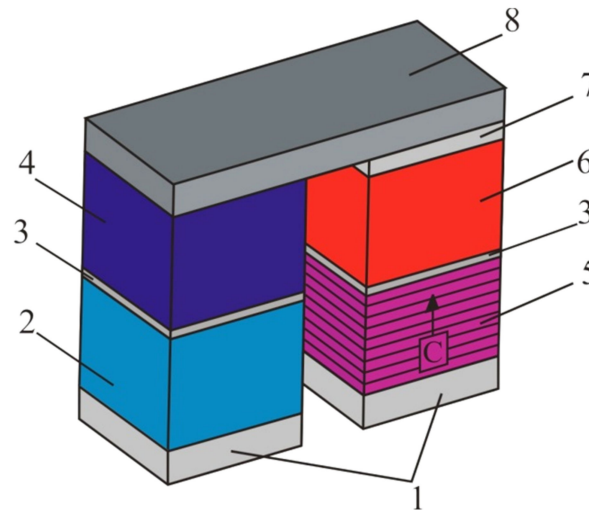


Figure 12. Design of multilayer thermoelectric generator uncouple (for the temperature range $T_c = 50\text{ }^{\circ}\text{C}$ and $T_h = 600\text{ }^{\circ}\text{C}$); 1—metallic contact from Co + 6 wt% Bi. 2—*n*-type TE layer made by hot extrusion of $n\text{-Bi}_{2.7}\text{Se}_{0.3}\text{Te}_3$. 3—thin Bi foil. 4—*n*-type TE layer made by SPS of $n\text{-Pb}_{0.999}\text{InTe}_{0.999}\text{I}_{0.001}$. 5—*p*-type TE layer made by hot extrusion based on $p\text{-Bi}_{0.5}\text{Sb}_{0.5}\text{Te}_3$, oriented along C axis. 6—*p*-type TE layer made by SPS of $p\text{-Ge}_{0.96}\text{Bi}_{0.04}$. 7—thin, heavily doped *p*-type SnTe layer for improving ohmic contact. 8—Fe metal contact on the hot side.

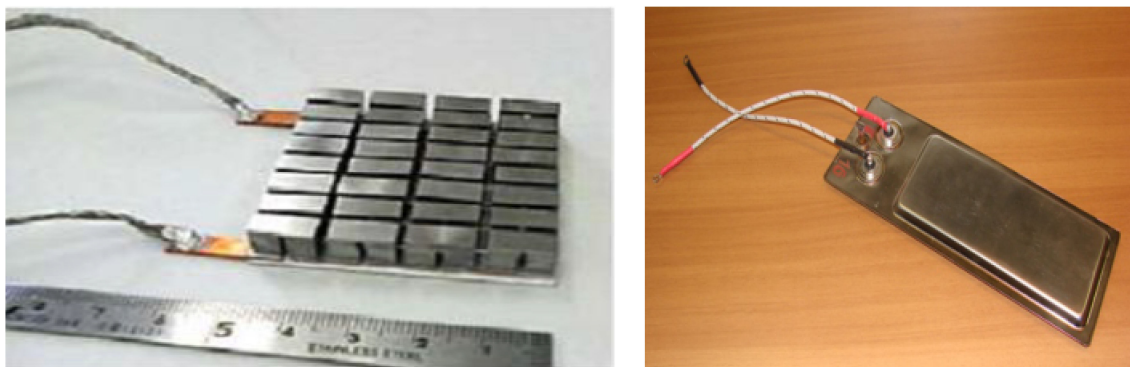


Figure 13. Photos of multistage thermoelectric module and capsulated module in Argon.

6.2. Gas Thermoelectric Generator (TEG)

The first design of a gas TEG with the electric power of 170 W was developed in the laboratory of Prof. Z. Dashevsky in 1993 [58]. Rib aluminum radiators (sic units) with a weight of ~50 kg were proposed for heat collection from the cold side of thermoelectric modules. These TEGs have a high reliability and long operative time of ~15–20 years.

A schematic view of a novel gas TEG is presented in Figure 14a. The gas burner (1) evenly heats up the heat exchanger (2), to which the design of the gas burner (1) is presented in Ref. [1]. A screen with flue gas outlet holes is placed around the gas burner to optimize the heating of the heat exchanger (2). It is made of cast iron and has extra-lateral

ribs to increase the heating area. The thermoelectric converters (modules) (3) are attached to the heat exchanger (2). Some of the thermal energy is converted into electrical energy due to the temperature difference ΔT between the gas burner and radiators (4) on the cold side of the modules. In an ordinary TEG, the cooling radiators dissipate most of the thermal energy to the environment [10]. However, it is suggested that TEGs should be used in domestic gas burners, such that the heat generated by gas burning would pass through TEGs, in which a small part of the thermal energy (up to 15%) would be converted to electric power while the rest of the thermal energy would be utilized for domestic heating and the supply of hot water at the exit temperature of the TEGs (Figure 14b,c). We expect that the prototype of such a hybrid system could produce ~400–500 W of electrical energy and 1700–2000 W of heat energy for domestic heating and hot water supply.

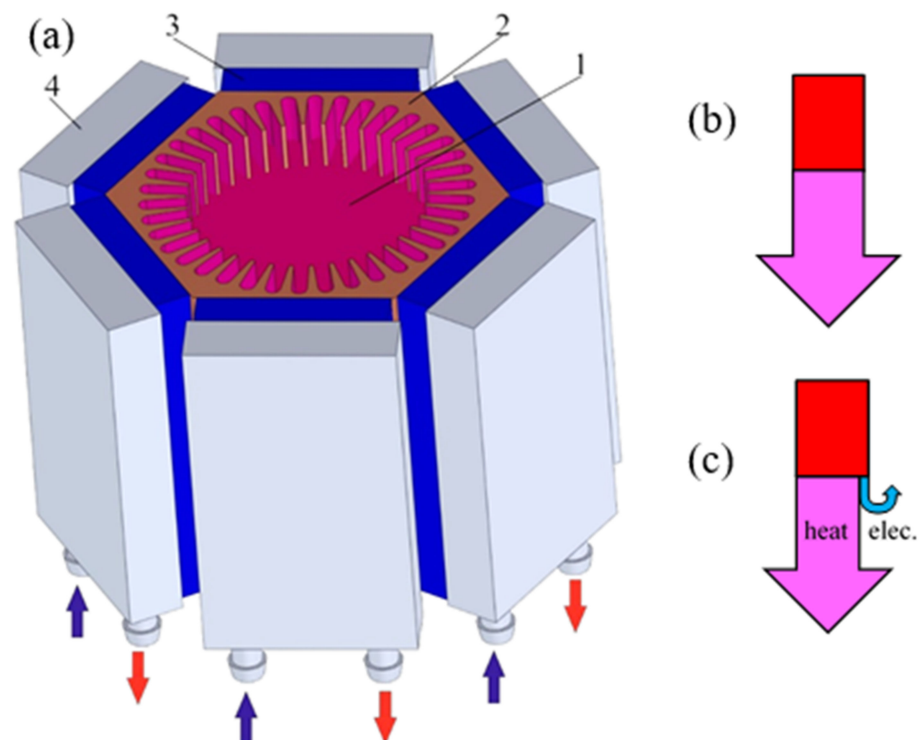


Figure 14. (a)—Schematic view a gas thermoelectric generator (TEG); General view of a gas TEG; (b,c)—Schematic energy flow diagram of a common gas burner and a hybrid TEG boiler; 1—fuel furnace; 2—heat exchanger; 3—TE module; 4—water sink.

7. Conclusions

For the first time, we discovered:

- (a) A unique design for a multilayer (multistage) TE uncouple, which is the main part of the thermoelectric energy module, is developed. Two types of thermoelectric materials were selected: the *n*- and *p*-type low-temperature TE materials (with an operating temperature range of 50–300 °C) based on Bi₂Te₃ compounds with an optimal crystal orientation provided by hot extrusion, and the middle-temperature TE materials (with an operating temperature range of 300–600 °C), which uses the SPS technique to prepare *n*-type TE material based on PbTe and *p*-type TE material based on GeTe. The TE outstanding energy conversion efficiency $\eta \sim 15\%$ was measured for the TE uncouple with a temperature difference $\Delta T = 550\text{ °C}$ ($T_h = 600\text{ °C}$), which is practically the maximum efficiency for TE modules of gas TEGs.
- (b) The possibility of extracting this amount of electrical power from the heat generated for domestic warming, and using the waste heat for water-heating. We suggest using this high-efficiency TEG design in a system combining TEG and a gas boiler into one autonomous source of electrical energy and heat for domestic use. We expect that

the prototype of this hybrid system can produce ~400–500 W of electrical energy and 1700–2000 W of heat energy for heating and hot water supply.

Author Contributions: Z.D.—principal investigator; A.J.—XRD investigation. Data curation; Y.U. mechanical property investigation. Methodology; B.D.—Investigation and visualization; F.G.—project management and conceptualization; R.Z.S.—supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Patient consent was waived.

Data Availability Statement: The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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