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ENHANCEMENT OF POWER FACTOR OF THERMOELECTRIC ELEMENT UNDER PRESSURE

*The objective of creating a thermoelectric element with improved characteristics using high-pressure impact is considered. The search for *p*- and *n*-type thermoelectrics whose thermoelectric parameters are improved under pressure has been performed. The measurements have been carried out using an automated set-up with both diamond and hard alloy anvils. The results obtained for some compounds indicate the possibility of creating a thermoelectric element containing both *n*- and *p*-type legs with enhanced characteristics within the same pressure range. The power factor of the element has been estimated for specific values of applied pressure with respect to normal conditions. Various variants of using high pressure in thermoelectric devices have been discussed. The work is partly supported by the Program of the RAS Presidium.*

Key words: thermoelement, high pressures, Bi_2Te_3 based compounds, thermoelectric power.

Introduction

The improvement of thermoelectric (TE) parameters, namely, the power factor $\alpha = S^2/\rho$ and the figure of merit $Z = S^2/(\rho\lambda)$, where S is the thermopower, ρ is the electrical resistivity, λ is the thermal conductivity, is still the primary objective in the research of thermoelectric materials [1, 2]. Bismuth telluride compounds are the most promising among the basic materials for high-performance low-temperature thermoelements. Along with traditional *n*-type Bi_2Te_3 -based TE compounds, *p*-type materials of similar structure are also much-in-demand for TE industry [3-6]. The TE parameters of Bi_2Te_3 are usually optimized by “technological factors” such as (I) doping and ions substitution [5-8], (II) variation in mesostructure (nanostructures, superlattices, quantum dots and wires) [3, 9-15], and (III) variation in synthesis conditions [15-18]. A permanent search for alternative medium-temperature TE materials is under way [19]. High pressure-related enhancement of TE properties of *p*- Bi_2Te_3 has been found recently [20, 21].

In the present paper, measurements of thermopower S and electrical resistance R of the ternary and quaternary chalcogenides based on $Bi_2(Sb_2)Te_3$ crystals possessing high initial TE parameters under normal conditions have been performed. The purpose of the work is searching for the possibility to enhance zero-pressure TE parameters (α , Z) of both *n*- and *p*-type crystals for creation of high-performance thermoelement.

Details of experiment

The $S(P)$ and $R(P)$ dependences were measured by an automated high-pressure setup allowing simultaneous registration of several properties of a microsample at high pressure [22]. Two different anvil cells were employed for pressure generation: one of the Bridgman type, made of synthetic diamonds with

a working diameter $d \sim 0.6$ mm, and another one of toroidal shape, made of tungsten-carbide hard alloy with a working diameter of the central semispherically concave anvils $d \sim 1$ mm [23, 24].

Table 1

TE parameters of samples under normal conditions

No.	Compound	Thermopower S , $\mu\text{V}\cdot\text{K}^{-1}$	Conductivity σ , $\Omega^{-1}\cdot\text{cm}^{-1}$	Power α , $10^{-5}\text{W}\cdot\text{cm}^{-1}\cdot\text{K}^{-2}$
2	$\text{Bi}_2\text{Te}_{2.73}\text{Se}_{0.27}$	-227	938	4.83
3	$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$	-225	882	4.47
4	$\text{Bi}_2\text{Te}_{2.82}\text{Se}_{0.09}\text{S}_{0.09}$	-216	987	4.60
6	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	205	1216	5.11
7	$\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$	209	998	4.36
8	$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$	220	1037	5.02

A sample of $\sim 200 \times 200 \times 30$ and $200 \times 200 \times 250 \mu\text{m}^3$ was placed into a hole of a container made of the lithographic stone in the Bridgman and toroidal cells, respectively [23, 24]. The pressure values were determined to an accuracy of $\sim 10\%$ from a calibration “force-pressure” curve based on the registration of phase transitions in Bi , PbS , PbSe , CdSe , etc. [25]. Applied force was measured by a digital dynamometer with resistive-strain sensors [23]. The anvils were characterized by a high electrical conductivity, and, therefore, were used as electrical contacts to a sample. In the thermopower measurements the upper anvil was heated. The temperature difference along the sample ΔT was determined at the fixed points of the anvils using copper-constantan thermocouples. Calculations of temperature distribution inside the “anvils-container-sample” system were performed in [22, 25]. Several measurement cycles (up to 5) were performed for each sample with pressure increase/decrease.

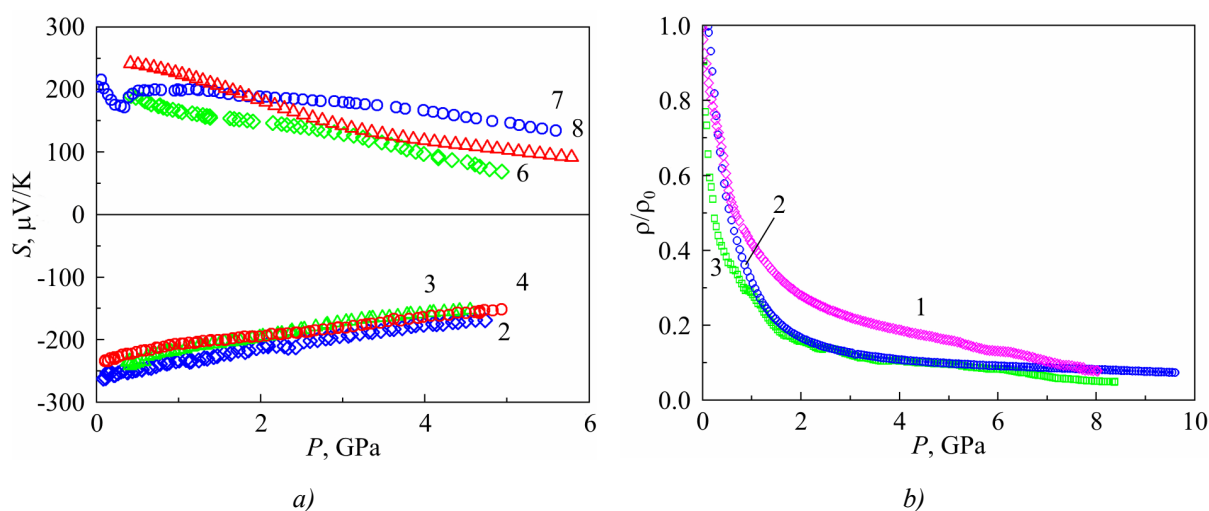


Fig. 1. Pressure P dependences of the thermoelectric power S (a) and normalized resistance ρ/ρ_0 (b) for samples listed in Table 1. Curve numbers correspond to sample numbers [26].

Results of thermoelectric testing and discussion

The ternary and quaternary $Bi_2(Sb_2)Te_3$ -based crystals of both p - and n -type possessing high TE parameters under normal conditions (see Table 1) were taken for investigation. The characteristics of the samples are shown in Table 1. As Bi_2Te_3 and compounds on its basis are known to suffer structural transition at a pressure above 6 – 8 GPa [27, 28], the upper limit of applied pressure was restricted to $\sim 5 - 6$ GPa for checking the reversibility of TE properties at pressure variation.

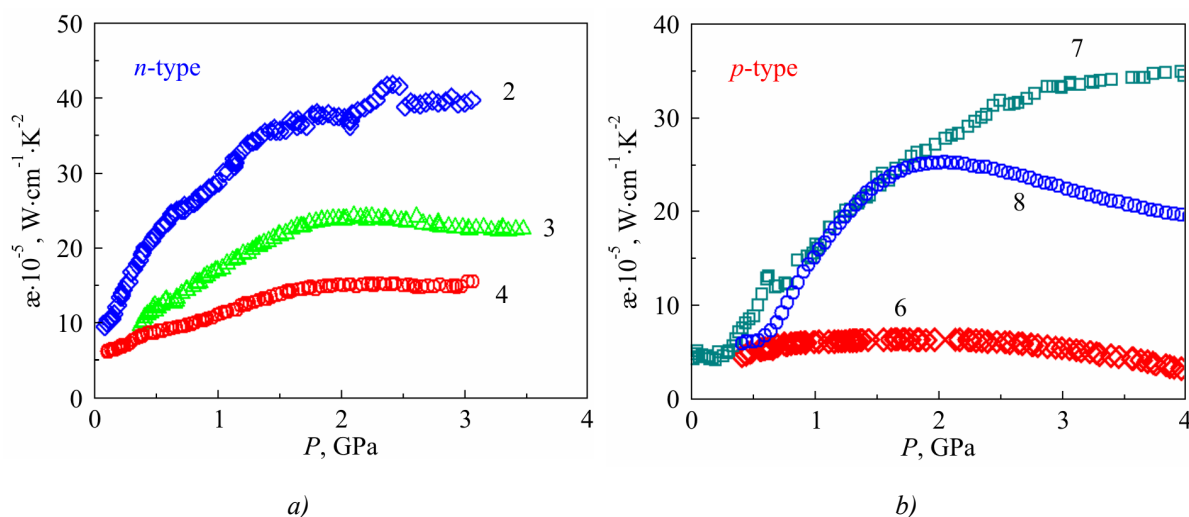


Fig. 2. Pressure P dependencies of the power factor α for samples 2, 3, 4 (a) and 6, 7, 8 (b) listed in Table 1. Curve numbers correspond to sample numbers [26].

The gradual decrease in thermopower S (in absolute values) with pressure increase was observed both for n - and p -type samples (Fig. 1). The electrical resistance also drops with pressure increase, as in the case of a binary compound Bi_2Te_3 (Fig. 1) [20]. The calculated values of power factor obtained using the experimental $S(P)$ and $R(P)$ data for p -type compounds have a non-monotonic dependence on P with a maximum in the region of ~ 2 to 4 GPa (Fig. 2), whereas for n -type compounds they reach maximal values at ~ 2 GPa and then remain unchanged with pressure increase (see Fig. 2). The non-monotonic dependence of α on P is obviously due to pressure-driven electron structure variation [20, 27-29]. With regard to experimental results, it seems possible to choose the pairs of n - and p -type compounds having maximal values of α at the same pressure range, e.g. samples No. 2 – 4 (n -type) and sample No. 7 (p -type) at $\sim 3 - 5$ GPa, or samples No. 2 – 4 (n -type) and sample No. 8 (p -type) at ~ 2 GPa, and samples No. 2 – 4 (n -type) and sample No. 6 (p -type) at $\sim 2 - 3.5$ GPa. The highest values of α are achieved for the pair “sample 3 or 4 (n -type) – sample 7 (p -type)” near $P \sim 4$ GPa (see Fig. 2). Decompression cycles showed the reversibility of pressure-induced α -enhancement effect. Thus, manufacture of high-performance TE element containing both p - and n -type legs seems to be feasible due to retention of pressure ~ 2 to 4 GPa in small devices or strained films. A variant of autonomous synthetic diamond chamber used in magnetic field measurements [21] may be a suitable device, as synthetic diamonds possess both excellent thermal conductivity and high electrical conductivity, to provide the input/output of thermal flows as well as electrical connection in TE-element.

The observed enhancement of power factor under pressure is related to a moderate decrease in the absolute value of S and a more rapid drop of electrical resistance. In a binary compound Bi_2Te_3 the semiconductor gap $E_g = 0.17$ eV decreases with pressure increase which explains the behavior of S and

R. In the ternary and quaternary $Bi_2(Sb_2)Te_3$ -based chalcogenides the value of E_g is somewhat modified by chemical substitution in the lattice, so the “optimal” semiconductor gap [21], hence the highest TE parameters, are achieved at different values of P (Fig. 2).

From the general expression for the electrical conductivity σ , and thermoEMF $S: \sigma = \int \sigma(E)(-\partial f / \partial E) dE$ and $S = (k / |e|) \int [(E - E_F) / (kT)] [\sigma(E) / \sigma] (-\partial f / \partial E) dE$ (where f is the distribution function, E_F is the Fermi energy, E is the electron energy, k is Boltzmann’s constant, and e is the electron charge), the equation for the Seebeck coefficient of a semiconductor with one additional hole band may be obtained as follows [20]:

$$\frac{S}{k / |e|} = \left\{ \sum_i \frac{\sigma_{pi} - \sigma_{ni}}{\sigma} \times (r + 2) + \sum_i \frac{(\sigma_{pi} - \sigma_{ni})}{\sigma} \frac{E_g}{2kT} + \frac{3}{4} \ln \frac{m_p^*}{m_n^*} + \frac{\Delta E_v}{kT} \frac{\sigma_{p2}}{\sigma} \right\}, \quad (1)$$

where $\sigma = \Sigma (\sigma_{ni} + \sigma_{pi})$ is the total conductivity and r is the scattering parameter of carriers. The index i corresponds to the electron and the hole bands and to the additional hole band ($i = 2$). According to recent calculations [30], the topmost valence band in Bi_2Te_3 lies along the $Z-U$ direction in the Brillouin zone and exceeds the second band in energy by $\Delta E_v \approx 3.8$ meV ($\Delta E_v \approx 40$ meV in [31]). The second valence band is important in achieving high values of TE properties both in a binary Bi_2Te_3 compound [20, 29] and in Bi_2Te_3 -based ternary and quaternary chalcogenides. The energy gap between the hole bands ΔE_v increases with pressure ($dE_v/dP \sim +30$ meV/GPa [32]), whereas the forbidden gap is reduced at a rate of 20/60 meV/GPa below/above $P \sim 3$ GPa [28]. Since pressure application leads to narrowing of the forbidden gap, and therefore, to the increase in the carrier concentration, it eventually brings about the intrinsic conductivity increase. The above equation makes it possible to explain the complex behavior of S versus P for these compounds.

It is also interesting to evaluate the behavior of figure of merit ZT under pressure (where T is temperature). Under normal conditions for n - and p -type materials the figure of merit ZT is ~ 0.9 . The experimental data of [33-35] on thermal conductivity variation at high pressures 1.6 – 10 GPa for Bi_2Te_3 and Sb_2Te_3 compounds show the maximal increase of thermal conductivity λ by a factor of 2 under a pressure of 4 GPa. Thus, the attainable figure of merit values for the samples under study may be roughly estimated to be $ZT \approx 3$. This value is close to that of the advanced bulk $Bi_2(Sb_2)Te_3$ based thermoelectrics [1-3]. This value may be overestimated to a certain extent due to unknown contribution of electron component of thermal conductivity in the samples under study, which ought to rise due to a strong decrease in resistivity.

High-pressure thermoelement testing

In the framework of this work the high-pressure thermoelement has been created and tested. The schematic of this device represents a miniature high-pressure chamber with insulating boron nitride anvils of the Bridgman type (Fig. 3). p -type and n -type pellets (legs) of the element made of samples No. 8 and No. 2 (Table 1) were placed into a container similar to the above described experimental setups (Fig. 3). The diameter of working tips of the anvils was 2.0 mm. Thin bronze tapes were used to provide the electrical contacts to each thermoelement leg and to electrical outputs of the entire thermoelement. According to experimental data represented in Fig. 2 the highest TE power factor for this thermoelement is achieved at a pressure of $\sim 2 - 3$ GPa. The device has a hold-down-nut which permits high pressure retention after thermoelement unloading.

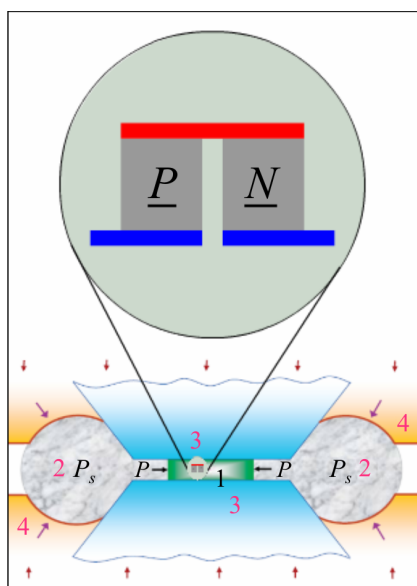


Fig. 3. Schematic of the high-pressure thermoelement: 1 – thermoelement, 2 – container, 3 – anvils, 4 – plungers.

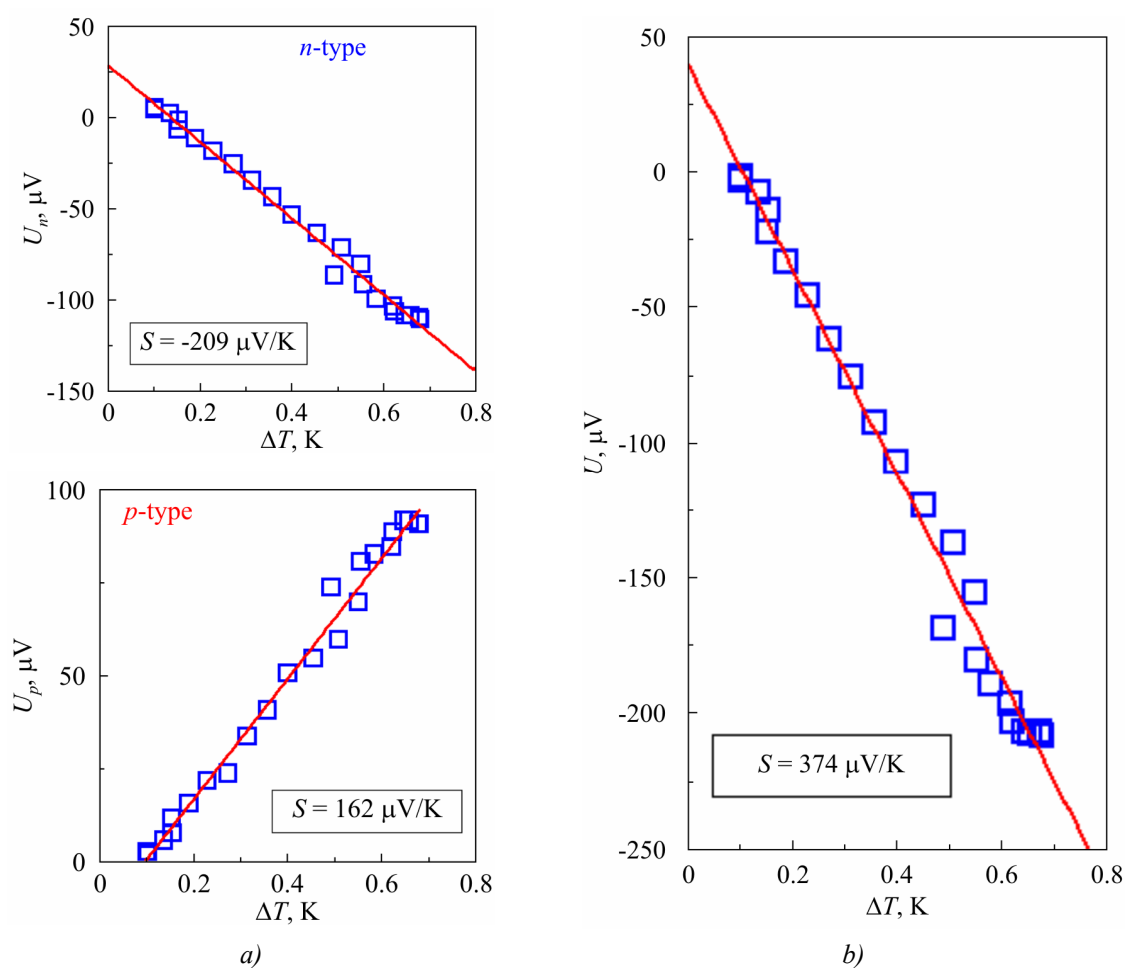


Fig. 4. Experimental data of the thermoelectric measurements for each leg (a) and for the entire thermoelement (b) at a pressure of ~ 2.5 GPa. The plots represent experimental dependences of TE signal on the temperature difference (marked as squares). The Seebeck coefficient S was determined from the linear slope of the dependences (straight lines).

High pressure ~ 2.5 GPa was generated in the TE device by using a hydraulic press, following which the pressure was fixed for TE measurements. Results of TE measurements allowed estimating the TE power factor of high-pressure thermoelement (Fig. 4). Using the data on the pressure dependences of electrical resistance (not shown) and thermoelectric power (Fig. 4), the $\sim 3.4 \pm 0.9$ -fold increase in thermoelectric power factor was observed for each leg and for the entire thermoelement. To the authors' knowledge, this is the first testing of the entire thermoelement at high pressures up to ~ 2.5 GPa.

Conclusion

To summarize, pressure application was established to lead to a significant improvement in the TE figure of merit of *p*- and *n*-samples of the ternary and quaternary $Bi_2(Sb_2)Te_3$ -based chalcogenides possessing high initial TE parameters under normal conditions. The effect exceeds the values reported previously [36].

The working model of thermoelement has been created and tested at a pressure of ~ 2.5 GPa. The $\sim 3.4 \pm 0.9$ -fold increase in thermoelectric power has been achieved for each leg and for the entire thermoelement. There are several ways for high pressure retention under normal conditions, including: I) miniature synthetic diamond (boron nitride) anvils; II) retention of pressure in strained films; III) generation of pressure due to creation of thermal gradient by using materials with high temperature expansion coefficient (water at low temperatures, some polymers, etc.).

It should be noted that a search for high TE parameters is usually restricted to normal pressure. However, the best parameters obtained at present for the known thermoelectrics are by no means related to normal temperature. Thus, for some Bi_2Te_3 -based compounds the optimal temperature range lies below room temperatures, whereas for *PbTe*-based compounds and *SiGe* alloys the optimal values of TE parameters are achieved at much higher temperatures, namely $\sim 600 - 1000$ K. The variation of chemical composition of these materials does not cause a shift of the optimal temperature range to normal temperature. Using this analogy, one may suggest that at least for the above mentioned materials the optimal pressure range for the highest TE parameters may also lie far from the normal conditions (at atmospheric *P*), and so, from this point of view the sufficient increase in power factor under pressure obtained in the present work for a thermoelement comes as no surprise.

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