

Thermoelectric properties of Bi₂Te₃ microwires

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We present here a study of electrical and thermoelectric properties of *n*- and *p*-Bi₂Te₃ microwires (*n*-type Bi₂Te₂Se; *p*-type Bi_{0.5}Sb_{1.5}Te₃) with different diameters ($d=10\text{--}20\text{ }\mu\text{m}$). Cylindrical Bi₂Te₃ crystals with glass coating were prepared by the liquid phase casting in a glass capillary. The X-ray studies have shown that the microwire core is in general polycrystal consisting of big disoriented single crystal blocks. Measurements of resistance and thermopower were carried out over a wide range of temperatures (4.2–300 K) and magnetic fields (0–14 T). At 300 K for samples of *n*- and *p*-type the thermopower S and power factor $P_f = S^2\sigma$ were (100–140) $\mu\text{V/K}$, $1.6\times 10^{-3}\text{ W/(K}^2\text{m)}$ and (150–300) $\mu\text{V/K}$,

$4.5\times 10^{-3}\text{ W/(K}^2\text{m)}$, respectively. Magnetic field dependences of Power factor were measured at various temperatures ($T=35, 100, 270\text{ K}$) and different magnetic field orientations. A broad maximum is the dominant feature of the magnetic field dependence of power factor for *p*-type samples, while power factor decreases for *n*-type samples. We have obtained maximum power factor $P_f=6.8\times 10^{-3}\text{ W/(K}^2\text{m)}$ for *p*-type sample at longitudinal magnetic field $B=3\text{ T}$ at $T=100\text{ K}$. Shubnikov de Haas oscillations with equal periods $\Delta B=0.038\text{ T}^{-1}$ both in longitudinal and transverse magnetic fields for carriers with $m_c=0.15m_0$ in *p*-type Bi₂Te₃ microwire were observed. These oscillations could arise from the topological surface states.

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1 Introduction Bismuth telluride (Bi₂Te₃) is a narrow band gap semiconductor, which is well known as one of the best thermoelectric (TE) materials [1]. At room temperature, bulk Bi₂Te₃ and related compounds reveal the highest thermoelectric figures of merit $ZT=TS^2\sigma/k\sim 1$, where S is the Seebeck coefficient, σ is electrical conductivity, T is the temperature, k is the thermal conductivity [2]. Bi₂Te₃ is one of the oldest among the basic materials for high-performance TE elements. Nowadays, the TE parameters of Bi₂Te₃ are optimized by technological factors such as doping and ion substitution [(Bi,Sb)₂(Te,Se,S)₃] [3,4], variation in mesostructure (superlattices, quantum dots, and wires) [5–7], and variation in synthesis conditions [8,9]. Recently, this material has been discovered as a new type of quantum matter, a 3D topological insulator (TI) [10,11]. Due to their many remarkable properties [12,13], topological insulators are now become one of the most ac-

tively researched subjects in condensed matter physics. The bulk of a TI possesses an insulating gap, whereas there exist non-trivial metallic surface states (SS) at the surface. The topological SS are protected by time-reversal symmetry, and therefore cannot be destroyed by perturbations of non-magnetic impurities and small lattice defects. Furthermore, such SS give rise to 2D Dirac fermions with spin-momentum locking and suppressed back scattering, promising a host of new physics and spintronics.

It was shown theoretically that ZT can be drastically improved in thin Bi₂Te₃ films or nanowires with the thickness of just few atomic layers either from confinement-induced increasing of electron density of states near the Fermi level [14] or phonon-boundary scattering [15]. Moreover, at temperatures below 150 K the thermoelectric performance of the TI Bi₂Te₃ thin film is significantly enhanced because of the high ZT of the protected edge states

[16]. At low temperature the bulk contribution is smaller than the surface contribution.

The present paper is concerned with experimental investigations of thermoelectric properties and quantum oscillations in *n*- and *p*-type Bi₂Te₃ microwires in glass coating obtained by the liquid phase casting in a glass capillary. Measurements were carried out over a wide range of temperatures (2–300 K) and magnetic fields (up to 14 T).

2 Samples and experimental details As a thermoelectric materials in the temperature range $T=250\text{--}300\text{ K}$, semiconducting alloys of the compounds Bi₂Te₃, Bi₂Se₃, Sb₂Te₃, Sb₂Se₃ are used. Most frequently for materials of *n*-type conductivity the alloys Bi₂Te_{3-x}Se_x ($x=0.1\div 1$) are utilized. As thermoelectric material of *p*-type conductivity, the alloys (Bi₂Te₃)_{1-x}(Sb₂Te₃)_x commonly used. We have chosen for *n*-type thermoelectric material the alloy Bi₂Te₂Se and for *p*-type thermoelectric material the alloy (Bi₂Te₃)_{0.25}(Sb₂Te₃)_{0.75}. As initial components, materials with a high degree of purity were used: Bi (99.999%), Sb (99.999%), Te (99.999%), Se (99.999%). Synthesis was performed at the temperature of 700–720 °C in cylindrical furnace.

For microwire fabrication on the basis of semiconductor materials with many components and volatile impurities at high temperatures the Taylor–Ulitovsky method with thermal furnace heating has been developed. The main element of a new method was to use as a heater in the Taylor–Ulitovsky installation a furnace with resistive heating and stable temperature regime, which was ensured by a temperature controller with accuracy of $\pm 0.5\text{ }^{\circ}\text{C}$. Before the microwire casting the volatile materials were crushed in the small pieces of polycrystal material with the mass of about 0.3–0.5 g and they were introduced into an ampoule

Table 1 Parameters of the samples.

Sample	d , μm	D , μm	Type	Composition	EDX Analysis, at. %		
N1	16.8	29.9	<i>p</i> -type	Bi _{0.5} Sb _{1.5} Te ₃	Sb L	Te L	Bi M
					32	58.3	9.7
N2	17.3	30.7	<i>n</i> -type	Bi ₂ Te ₂ Se	Se L	Te L	Bi M
					18.24	40.33	41.43

of glass of the molybdenum type. After vacuuming up to $P=10^{-4}\div 10^{-5}$ Torr, the ampoule was soldered and welded to a little glass stick which was used as a holder and was introduced into the feeding mechanism of the installation. After the furnace heating up to the temperature of the glass ampoule softening by slow fall, the ampoule is introduced into the heated furnace zone. As a result of the glass ampoule softening the material introduced into the ampoule melts too and as a result by the capillary stretching a microwire in glass isolation was formed.

The obtained microwire was coiled by the winding drum mechanism into bobbins of different diameters. Changing the furnace temperature and the velocity of the ampoule fall in the heated zone as well as the velocity of the microwire obtaining it was possible to obtain microwires with different diameters of core and glass isolation with necessary parameters.

The results of the measurements have shown that in dependence on the heated furnace temperature, velocity of the ampoule fall into the heated zone and velocity of the microwire obtaining it was possible to change the diameter of the core d and glass isolation D . The smallest obtained diameter was $d=5\text{ }\mu\text{m}$, and the biggest 100 μm . In the range $d\sim 15\div 30\text{ }\mu\text{m}$ the linear dependence between the diameters of the core and isolation of the microwire was practically realized, and the ratio D/d was equal to two. The dependence of the ratio of the isolation diameter on the core diameter may be approximated with formula: $D/d = 3/lgd$, where d is expressed in μm .

A thermal treatment of the obtained microwires at different temperatures (450–520 K) and time intervals (24–72 hours) was performed for improvement of the microwire characteristics. Isothermal annealing of the microwires increases both the thermopower and the resistivity in the samples of *p*-type, and the larger the temperature and annealing time the higher obtained physical parameters. In contrast to the samples of *p*-type, in the samples of *n*-type the thermopower after annealing grows and the resistivity decreases.

The X-ray studies have demonstrated that the microwire core was in general polycrystal consisting of big disoriented single crystal blocks of approximate size 10–15 μm .

As a result of studying of the electrophysical and thermoelectric microwire properties, the dependence of the pa-

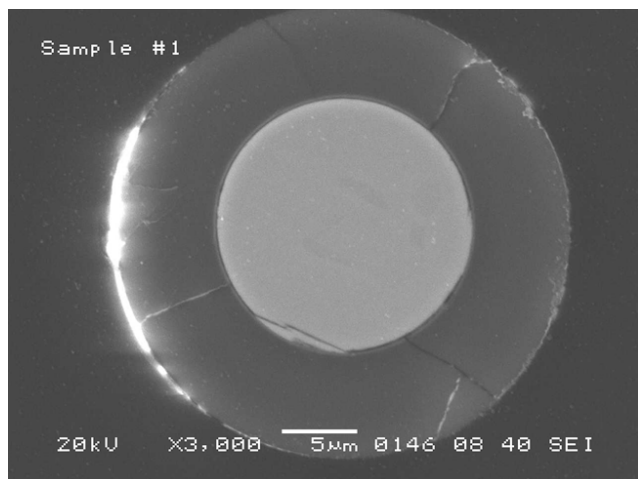


Figure 1 Scanning electron microscope image of cross-sectional view of the sample N1 - Bi_{0.5}Sb_{1.5}Te₃ microwire in glass coating. Outer diameter $D=29.9\text{ }\mu\text{m}$, diameter of the core $d=16.8\text{ }\mu\text{m}$.

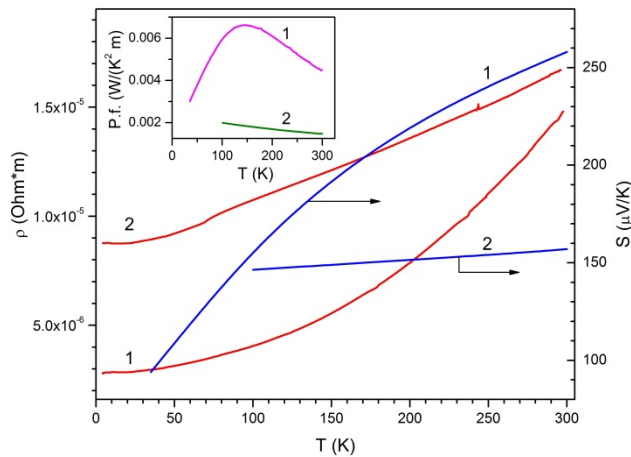


Figure 2 Temperature dependencies of resistivity ρ , thermopower S , and power factor $P.f.$ (shown in the inset) for Bi_2Te_3 microwires: (1) sample N1 ($\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$); (2) sample N2 ($\text{Bi}_2\text{Te}_2\text{Se}$). For convenience, the thermopower of sample N2 was multiplied by -1.

parameter value on the microwire growth conditions it was found that the thermopower for the samples with hole (p) or electron (n) conductivity at the temperature $T=300$ K was correspondingly the following: $S_p=+150\div+300$ $\mu\text{V/K}$, $S_n=-100\div-140$ $\mu\text{V/K}$ while the resistivity had the values $\rho_p=(1\div7)\times 10^{-3}$ $\Omega\text{ cm}$, $\rho_n=(1\div7)\times 10^{-3}$ $\Omega\text{ cm}$.

The samples were cut from long microwires, the length of the samples was 3–5 mm. The main sample parameters are listed in Table 1. Scanning electron microscope image of the $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ microwire in glass coating is shown in Fig. 1. Electrical connections to the microwires were per-

formed using the $\text{In}_{0.5}\text{Ga}_{0.5}$ eutectic. The wires were held in special holders and inserted in a cryostat for low temperature measurements. We employed the arrangement that consists of two copper blocks; the heater is mounted on one of them. Calibrated Cernox thermometers attached to the second block is used for measuring the sample temperature. A differential Cu–Cu(0.05% Fe) thermocouple, which is in thermal contact but electrically insulated from each copper block is used to measure the temperature difference between the hot and cold ends of the sample. The temperature difference was typically 0.5 K to 1.5 K depending on the temperature. Measurement of the Shubnikov de Haas oscillations (SdH) were carried out in longitudinal and transverse magnetic fields up to 14 T in superconducting solenoid at $T=2.1\text{--}4.2$ K in International Laboratory of High Magnetic Fields and Low Temperatures, Wrocław, Poland.

3 Results and discussion Temperature dependencies of resistivity ρ , thermopower S , and power factor $P.f.=S^2/\rho$ for Bi_2Te_3 microwires are shown in Fig. 2. All the investigated samples exhibit a metallic behavior. Power factor for p -type Bi_2Te_3 have a broad maximum (6×10^{-3} $\text{W/(K}^2\text{m)}$) at $T=150$ K.

The magnetic field dependence of the resistivity in our samples follows the classical theory of kinetic phenomena in ideal semiconductors [17]: kinetic coefficients increase according to the square law with magnetic field in weak magnetic fields, and in the fields above 7 T resistance tends to saturate.

We also studied magnetic field effects on the thermopower. Longitudinal magnetic field dependences of thermopower S and power factor $P.f.$ are shown in Fig. 3 for Bi_2Te_3 microwires at different temperatures. It is seen, that the magnetic field has little influence on the thermo-

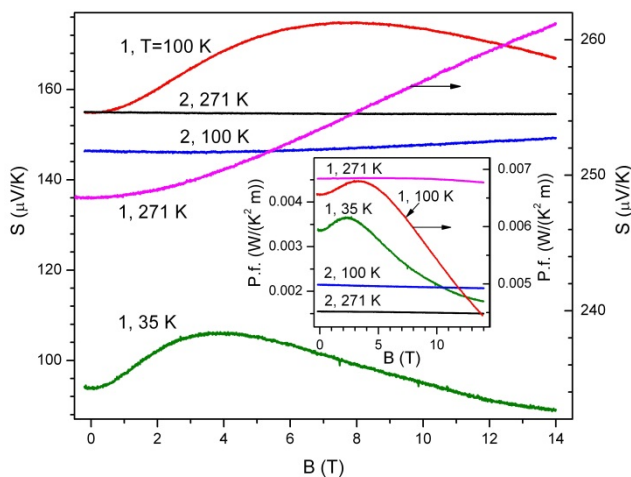


Figure 3 Longitudinal magnetic field dependences of thermopower S and power factor $P.f.$ (shown in the inset) for Bi_2Te_3 microwires at different temperatures. (1) Sample N1 ($\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$); (2) sample N2 ($\text{Bi}_2\text{Te}_2\text{Se}$). For convenience, the thermopower of sample N2 was multiplied by -1.

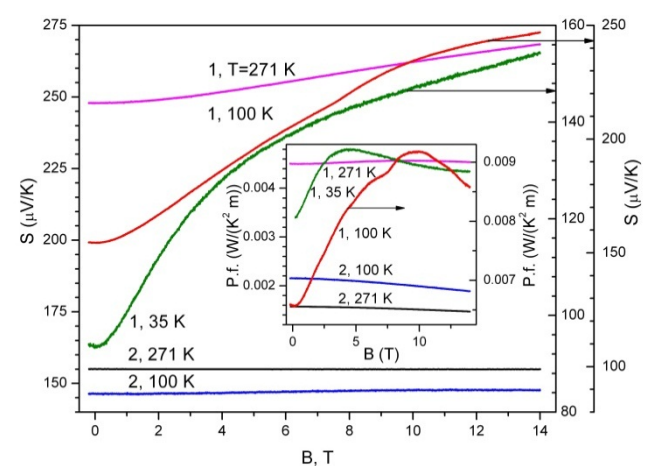


Figure 4 Transverse magnetic field dependences of thermopower S and power factor $P.f.$ (shown in the inset) for Bi_2Te_3 microwires at different temperatures. (1) Sample N1 ($\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$); (2) sample N2 ($\text{Bi}_2\text{Te}_2\text{Se}$). For convenience, the thermopower of sample N2 was multiplied by -1.

electric power and the power factor for a sample of *n*-type Bi₂Te₃, but the magnetic field strongly affects the properties of the *p*-type sample. It should be noted that in dependency of the power factor vs. magnetic field for *p*-type sample there is a significant maximum within the range 2–3 T of the magnetic field, which is important for practical use. Transverse magnetic field dependences of thermopower *S* and power factor *Pf* are shown in Fig. 4. for Bi₂Te₃ microwires at different temperatures. The transverse magnetic field influences the power factor much more strongly.

The maximal absolute value of the power factor that we achieve under transverse magnetic field *B*=9.8 T equals 9.1×10^{-3} W/(K²m) for *p*-type Bi₂Te₃ at temperature *T*=100 K.

In our Bi_{0.5}Sb_{1.5}Te₃ sample we observed SdH oscillations in both longitudinal magnetoresistance and transverse magnetoresistance with the same frequency. Insets in Figure 5 show the derivative of *R* with respect to the magnetic field *B* plotted in 1/*B* coordinates. *dR/dB* is periodic in the inverse magnetic field, indicating the existence of a well-defined Fermi surface. The obtained frequency *F* of 26.2 T, which is directly related to the Fermi-surface cross section *A* via the Onsager relation $F = (\hbar/2\pi e)A$, gives Fermi wave vector $k_F = 0.028$ Å⁻¹, corresponding to the surface carrier density $n_S = k_F^2/4\pi = 0.62 \times 10^{12}$ cm⁻². The experimental data obtained at two different temperatures *T*=4.2 K and 2.1 K give us the possibility to determine the cyclotron mass $m_c = 0.15m_0$, where *m*₀ is the free electron mass, and Dingle temperature *T*_D=5.7 K.

In the SdH oscillations the resistivity oscillates as

$$\Delta R = R(B, T) \cos [2\pi(B_F/B + 1/2 + \beta)], \quad (1)$$

where *R*(*B*, *T*) is the SdH oscillation amplitude, *B*_F is the frequency of SdH oscillations in 1/*B*, and β is associated Berry's phase, arising from the band degeneracy point [18,19] in the range $0 < \beta < 1$. Berry's phase $\beta=0$ (or $\beta=1$) corresponds to the trivial case. A deviation from this value indicates the new physics with $\beta=1/2$, implying the existence of massless Dirac particles [20]. As follows from theoretical prediction [16], the sharp improvement in *ZT* can be achieved in thin Bi₂Te₃ film, provided that the Fermi level is configured to ensure the surface transport and the films are thin enough to open a hybridization gap in the "Dirac cone" dispersion on the surface. Experimentally the phase of the oscillations is obtained from the Landau-level fan diagram, which is shown in Fig. 5 for the SdH oscillations in sample N1 (Bi_{0.5}Sb_{1.5}Te₃) in longitudinal and transverse magnetic fields. The values of 1/*B* corresponding to minima and maxima in *dR/dB* are plotted as a function of the Landau-level number *N*. The least-square fit to the data shown in Fig. 5 gives a finite $\beta = 0.26$ and 0.18 for longitudinal and transverse magnetoresistance oscillations, respectively. According to our data it is difficult to deduce a firm conclusion about the Berry phase.

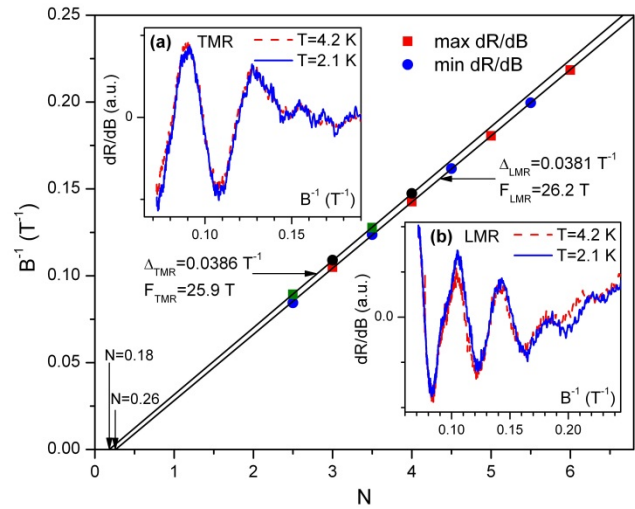


Figure 5 Landau-level fan diagrams for SdH oscillations in *dR/dB* measured at 4.2 K and 2.1 K for sample N1 (Bi_{0.5}Sb_{1.5}Te₃). Insets (a) and (b) show *dR/dB* vs. 1/*B* after subtracting a smooth background for transverse and longitudinal magnetoresistance, respectively.

Assuming that electrons are Dirac type, we can obtain the Fermi velocity $v_F = \hbar k_F/m_c = 2.16 \times 10^5$ m s⁻¹. This *v*_F is consistent with the angle-resolved photoemission spectroscopy (ARPES) data (from ARPES $v_F \sim 4 \times 10^5$ m s⁻¹), affirming the Dirac-fermion assumption. The position of the surface Fermi level measured from the Dirac point can be estimated from $E_F = m c v_F^2$, this yields *E*_F=40 meV. The scattering time τ may be determined from the Dingle temperature $T_D = \hbar/(2\pi k_B \tau)$, where *k*_B is Boltzmann constant, which gives $\tau = 2.13 \times 10^{-13}$ s. Hence we can obtain the mean-free path on the surface $l_S = v_F \tau = 46$ nm and the surface mobility $\mu_S = e l_S/(\hbar k_F) \approx 2500$ cm²V⁻¹s⁻¹. Unfortunately, in our rather thick wires the surface conductivity does not play a decisive role. To achieve noticeable effect of increasing thermoelectric efficiency *ZT* we need to investigate thinner wires.

4 Conclusions Investigations of electrical and thermoelectric properties of *n*- and *p*-Bi₂Te₃ microwires in glass coating (*n*-type Bi₂Te₂Se; *p*-type Bi_{0.5}Sb_{1.5}Te₃) with different diameters (*d*=10–20 μm) were performed. The X-ray studies have shown that the microwire core is in general polycrystal consisting of big disoriented single crystal blocks. Magnetic field dependences of Power factor were measured at various temperatures (*T*=35, 100, 270 K) and different magnetic field orientations. A broad maximum is the dominant feature of the magnetic field dependence of Power factor for *p*-type samples, while Power factor decreases for *n*-type samples. We have obtained maximum Power factor *Pf*= 6.8×10^{-3} W/(K²m) for *p*-type sample at longitudinal magnetic field *B*=3 T at *T*=100 K. SdH oscillations with equal periods $\Delta B = 0.038$ T⁻¹ both in longitudinal

nal and transverse magnetic fields for carriers with $m_e = 0.15m_0$ in *p*-type Bi₂Te₃ microwire were observed. These oscillations could arise from the topological surface states. Assuming that surface electrons are Dirac type, we have obtained the position of the surface Fermi level measured from the Dirac point $E_F = 40$ meV, the mean-free path on the surface $l_s = 46$ nm and the surface mobility $\mu_s \approx 2500$ cm²V⁻¹s⁻¹. Unfortunately, in our rather thick wires the surface conductivity does not play a main role. In order to achieve noticeable effect of increasing thermoelectric efficiency *ZT* it is necessary to investigate thinner samples.

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