Hopping Conductivity and Negative Magnetoresistance of the Bulk Nanograined Bi$_2$Te$_3$ Material

O.N. Ivanov, R.A. Lyubushkin, M.N. Yaprintsev, I.V. Sudzhanskaya

Belgorod State University, 85, Pobedy St., 308015 Belgorod, Russia

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The bulk nanograined Bi$_2$Te$_3$ material was prepared by the microwave assisted solvothermal method and cold isostatic pressure method. It was found that above T* = 190 K the temperature dependence of the specific electrical resistivity of material is of metallic type, while below this temperature a semiconductor conductivity takes place. Within the temperature ΔT = 90 K-35 K interval the electrical conductivity of material can be described by the variable-range hopping conductivity mechanism. Negative magnetoresistance was observed at the same temperature interval.

Keywords: Bulk nanograined materials, Hopping conductivity, Magnetoresistance.

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1. INTRODUCTION

It is known that the nanograined materials are disordered and inhomogeneous materials [1-3]. As a rule, such kind of materials consists of numerous conducting or semiconducting grains separating by insulating interfaces [4, 5]. Specific mechanisms of the electrical conductivity can take place in electrically inhomogeneous solid. In particular, hopping conductivity of various types is predicted for disordered and inhomogeneous semiconductors at low temperatures [6, 7]. It is important to note that unusual physical properties including negative magnetoresistance can also observed the hopping conductivity phenomenon [8].

The aim of this paper is to find out and analyze the features of the specific electrical conductivity of the bulk nanograined Bi$_2$Te$_3$ material.

2. EXPERIMENTAL PROCEDURE

Microwave-solvothermal synthesis (closed reactor ERTEC model 02-02) was applied to prepare the nanosized Bi$_2$Te$_3$ powder. As is known, compared with the conventional methods, the microwave-assisted heating technique has the advantages of very short time of synthesis, simplicity and energy efficiency, small particle size of the products, narrow particle size distribution and high purity [9].

Analytically pure chemicals were used for the synthesis from LANHIT-LTD (bismuth oxide Bi$_2$O$_3$ with 99.9 % purity, tellurium oxide TeO$_2$ with 99.9 % purity and L-cysteine (cys ≥ 97 %), Ethylene glycol (EG 99.8 % purity), nitric acid (HNO$_3$ 70 % with purity) and N,N-dimethylformamide (DMF anhydrous 99.8 % purity), were purchased from Sigma-aldrich.

Oxides of bismuth and tellurium taken in a stoichiometric ratio was dissolving in concentrated nitric acid, resulting solution was mixed in a ratio of 1 : 1 of ethylene glycol and cosolvent (DMF or DMSO or CAN). Then 4.2 mmol of L-cysteine was added to resulting solution with stirring for 30 min.

The microwave-assisted reaction was carried out in an ERTEC 02-02 microwave reactor, with a power of 300 W at 2.45 GHz working frequency. Synthesis was carried out for 20 min at temperature of 453 K and pressure of 40 bar.

The powder after synthesis was cold isostatically pressed under pressure 2800 bar. Then, the pressured powder was calcined at 623 K for 2 h in Ar atmosphere.

X-ray diffraction (XRD) analysis was performed for the phase and crystal structure determination by using a Rigaku Ultima IV diffractometer with CuKα - radiation (a step width of 0.03° and a counting time of 1.6 s/step). Transmission electron microscope (TEM), JEM-2100, was applied to study morphology of the powders (for an accelerating voltage of 200 kV). Scanning electron microscope (SEM), Nova NanoSEM, was used to examine the grain structure of the bulk material (for an accelerating voltage of 2 kV).

The specific electrical resistivity, ρ, was measured by four-probed method at 0.1 mA dc current using the sintered samples with Ag electrodes. Magnetic field up to 5 T directed perpendicular to the electrical current can be applied to the sample during the ρ measurements.

3. RESULTS AND DISCUSSION

XRD-analysis confirmed that the synthesized powder is the single-phase Bi$_2$Te$_3$ compound (space symmetry group is R3m).

TEM-image in Fig. 1 shows a typical morphology of the powder. It is seen that the powder mainly consists of irregularly shaped nanoparticles of 20-50 nm in size.

The bulk Bi$_2$Te$_3$ material has dense, homogeneous and porous structure (Fig. 2). Nano- and microsized grains having a crystal faceting can be taken as evidence of intense sintering of the nanopowder.

The temperature dependence of the specific electrical resistivity for the sample under study taken for the 2-300 K interval is shown in Fig. 3.

One can see that this dependence is rather complicated and can be divided into two temperature fields. Above the temperature T* = 190 K, the resistivity decreases at cooling. Such kind of behavior is typical for metals or degenerate semiconductors having T-independent concentration of charge carriers. Below T* the resistivity increases as temperature decreases. This ρ(T) dependence is characteristic for semiconductors.
A few mechanisms of the electrical conductivity could lead to the $\rho(T)$ dependence like the dependence presented in Fig. 3 below $T^*$. One can see that this dependence is rather complicated and can be divided into two temperature fields. Above the temperature $T^* \approx 190$ K, the resistivity decreases at cooling. Such kind of behavior is typical for metals or degenerate semiconductors having $T$-independent concentration of charge carriers. Below $T^*$ the resistivity increases as temperature decreases. This $\rho(T)$ dependence is characteristic for semiconductors.

A few mechanisms of the electrical conductivity could lead to the $\rho(T)$ dependence like the dependence presented in Fig. 3 below $T^*$. First of all, it should be noted that temperature $T^*$ is low enough to generate of charge carries via transitions of electrons from valence band into conduction band.

Typical mechanism of the electrical conductivity of semiconductors is the thermal activation of the charge carriers from shallow impurity levels to the conduction or valence band. In this case, the $\rho(T)$ dependence will satisfy the law

$$\rho(T) = \rho_0 \exp\left(\frac{E_a}{kT}\right),$$  \hspace{1cm} (1)

the $\rho_0$ is the prefactor, $k$ is the Boltzmann constant and $E_a$ is the activation energy.

It was found that the experimental $\rho(T)$ dependence cannot be described by the expression (1). So, another mechanism of the electrical conductivity explaining the experimental data should be applied. As was mentioned above the hopping conductivity can take place in the bulk nanograined materials.

The hopping conductivity can be realized via different mechanisms given by a universal equation [10]

$$\rho(T) = DT^p \exp\left(\frac{T_0}{T_T}^p\right),$$  \hspace{1cm} (2)

where $D$ is a constant, $T_0$ is a characteristic temperature and $p$ is an exponent depending on regime of the localized electrons hopping.

The case of $p = 1$ corresponds to the regime of nearest-neighbor hopping (NNH) conductivity and $p = 1/4$ and $1/2$ to the Mott [11] and the Shklovskii-Efros [12] types of variable-range hopping conductivity, respectively.

It was established that the best fitting by the expression (2) can be achieved at $p = 1/4$ for the temperature interval from $T_1 \approx 90$ K down to $T_2 \approx 35$ K (Fig. 4).
So, within the temperature $\Delta T = T_1 - T_2$ interval the variable-range hopping conductivity can takes place in the bulk nanograined Bi$_2$Te$_3$ material.

As was mentioned above, negative magnetoresistance can take place within the the temperature interval of the variable-range hopping conductivity.

Negative magnetoresistance was really observed for the sample under study as is shown in Figure 5 as an instance. This Figure demonstrates the change in the specific electrical resistivity, $\Delta \rho(B)/\rho(0) = (\rho(B) - \rho(0))/\rho(0)$ under external magnetic field, $B$, for the temperature of 60 K.

![Graph](image)

**Fig. 5** – The $\Delta \rho/\rho(0)$ vs. $B$ for the bulk nanograined Bi$_2$Te$_3$ material at 60 K

One can see that the $\Delta \rho(B)/\rho(0)$ value first decreases as $B$ increases up to $\sim 1.7$ T. This behaviour is corresponding to the negative magnetoresistivity.

Under higher magnetic field $\Delta \rho(B)/\rho(0)$ vs. $B$ dependence shows usual positive behaviour of the magnetoresistivity.

Further experiments should be done to examine negative magnetoresistivity in material under study phenomenon in detail.

4. CONCLUSIONS

The bulk nanograined Bi$_2$Te$_3$ material was prepared by the microwave assisted solvothermal method and cold isostatic pressure method. It was found that the temperature dependence of the specific electrical resistivity can be divided into metallic conductivity interval and semiconductor conductivity interval. Within the temperature $\Delta T = 90$ K-35 K interval the variable-range hopping conductivity takes place in material under study. Negative magnetoresistivity was observed at the same temperature interval.

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