Electrical properties of rapidly solidified of heavily doped alloys $(Bi_{91} - Sb_9)_{100-x}\ Sn_x$

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Abstract **- We report the measurement of microstructure and transport properties in pure $Bi_{91}Sb_9$ and heavily doped with Sn (0.8at%, 1.2at%, 2.4at%) foils prepared by the high velocity crystallization ≈ $5\cdot10^5$ K/s. The foil thickness was 30-100 μm. It is shown that the rapidly solidified alloys $(Bi_{91}\text{-}Sb_9)_{100-x}Sn_x$ has a microcrystalline structure and contains the dispersed tin particles. Their average size increases with increasing concentration of tin in the alloys and does not exceed 0.3 μm. The rapidly solidified foils have a microcrystalline structure and texture (10$\underline{1}$2).**

It is shown that the electrophysical properties of the alloys $(Bi_{91}\text{-}Sb_9)_{100-x}Sn_x$ (x = 0,8 - 2,0) are determined mainly by holes. The foils are characterized by a high positive Peltier coefficient value and can be used for manufacturing the thermoelectric devices, working at the temperatures below room temperature.

Index Terms **– thermoelectricity, foils, semiconductor alloys, high velocity crystallization.**

I. INTRODUCTION

The new ideas about topological phases in condensed matter have been realized in $Bi_{1-x}Sb_x$ alloys, in the insulating regime 0.07 < x < 0.22) (topological insulator) [1-3]. The angle resolved photoemission spectroscopy studies on its cleaved (111) trigonal surface have revealed that the energy dispersions of the surface states possess the distinctive character to qualify this material as a topological insulator [4, 5]. On the other hand bismuth-antimony alloys are thermoelectric materials [6]. To produce the *p*-branch of thermoelements Hor Y.S. and Cava R.J have been proposed to use the bismuth-antimony alloys with tin-doped additionally and traditional techniques [7]. However, the formation of cellular or dendryt structure in ingot during crystallization under small and medium cooling rates of the melt impairs its thermoelectric parameters. Eliminating dendryt structure requires a long annealing at temperatures close to the melting temperature of the alloy [8]. In recent decades, actively conducting research on the synthesis of thermoelectric materials by high crystallization [9-11], in which it is possible to avoid the formation of the dendryd structure. In this regard, results of investigation of the electrical properties of rapidly solidified foils alloys Bi - 9 at. % Sb, additionally doped tin from 0.8 to 2.0 at. %, are presented.

II. SAMPLES AND EXPERIMENT.

The ternary alloys of the system $(Bi_{91} - Sb_9)_{100-x}Sn_x$ (x = 0,8 - 2,0) were obtained with melting the components in quartz ampoules. The alloy foils were obtained by crystallization of a thin layer of the melt on the inside polished surface of a rapidly rotating copper cylinder. The cooling rate of the liquid phase ≈ $5\cdot10^5$ K/s. Measurements of the electrical resistivity ρ and differential thermoelectromotive force α are performed in the temperature range 77 - 300 K.

The rapidly solidified alloys $(Bi_{91}\text{-}Sb_9)_{100-x}Sn_x$ have a microcrystalline structure and contain the dispersed tin particles. Their average size increases with increasing concentration of tin in the alloys and does not exceed 0.3 μm [12]. The rapidly solidified foils have a microcrystalline structure and texture (10$\underline{1}$2).

Image of cross-sectional microstructure of the foil of Bi – 9at. % Sb - 1.2 at. % Sn alloy, obtained by scanning electron microscopy, is shown in Fig. 1. Thereon are observed dispersed tin particles having a dark color. They are predominantly equiaxed shape and are located at grain boundaries of the solid solution of bismuth - antimony.

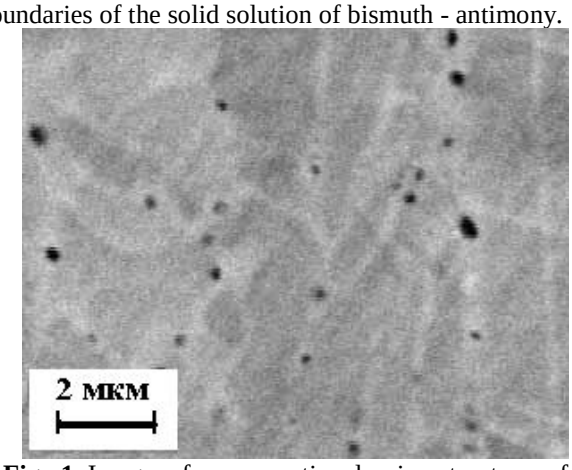

Fig. 1 Image of cross-sectional microstructure of the rapidly solidified foil of Bi – 9at. % Sb - 1.2 at. % Sn alloy.

Doping bismuth with antimony up to 9at.% causes an increase in the microhardness of about 2 times that due to the effect of solid solution hardening mechanism and strengthen the covalent bonding forces in the solid solution of bismuth - antimony by replacing the atoms of bismuth with antimony atoms. Graphs of the dependences of microhardness of bulk samples of Bi – 9at.% Sb - x at. % Sn alloys, obtained at a cooling rate of fluid ≈10^2 K/s and rapidly solidified foils of the same alloy of concentration of tin are shown in Fig. 2.

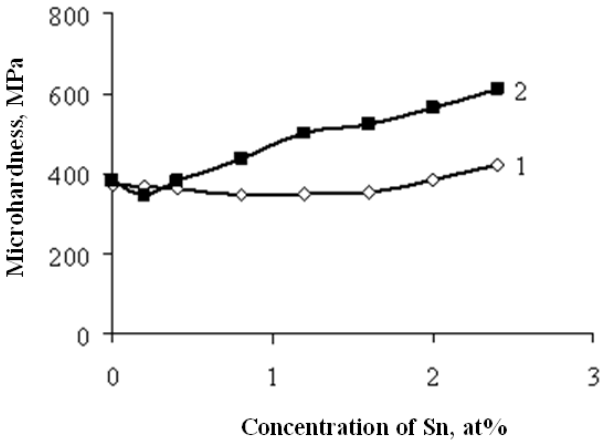

Fig. 2 The microhardness dependences of bulk samples (1) and rapidly solidified foils (2) vs concentration of Sn in Bi – 9at.% Sb – x at.%Sn alloy.

Microhardness of rapidly solidified foils of the investigated alloys with increase of concentration of tin is decreases slightly, then at x > 0.4at%Sn is grow.

III. RESULTS AND DISSCUSIONS.

The temperature dependences of the electrical resistivity and thermoelectromotive force of rapidly solidified alloy foils $(Bi_{91}\text{-}Sb_9)_{100\text{-}x}Sn_x$ (x = 0,8, 1,2 and 2,0) are shown in Fig. 3 and 4. With the increasing temperature *ρ(T)* increases monotonically in the temperature range of 77 - 300 K: at the first in a linear fashion, then at temperatures, close to room temperature, the deviation from linearity. Dependence of *α(T)* for each alloy has a maximum whose position is determined by the concentration of tin. Positive sign *α* are coursed the facts that transport processes in the studied alloys are defined with holes.

The appearance of the maximum in *α(T)* and the deviation from linearity in the dependence *ρ(T)* are coursed with the appearance of electrons in the conduction band due to thermal excitation of electrons from the valence band [13, 14]. It should be noted that the maximum differential thermopower of investigated ternary alloys are superior to module differential thermoelectromotive force of pure bismuth.

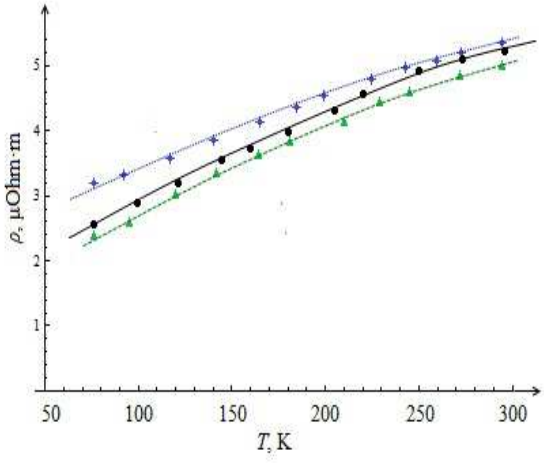

Fig. 3 Temperature dependences *ρ(T)* (+– *x* = 0.8, ● – *x* = 1.2, ▲ – x =2.0).

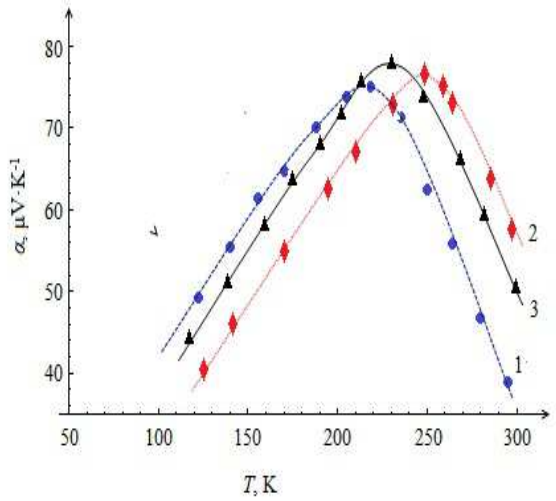

Fig. 4 Temperature dependences *α(T)* (1– *x* = 0.8, 2 – *x* = 1.2, 3 – x = 2.0).

Calculations of the thermoelectric power factor $Y = \alpha^2/\rho$ rapidly solidified alloys $(Bi_{91}\text{-}Sb_9)_{100\text{-}x}Sn_x$. are performed. The temperature dependences of *Y(T)* have maxima. The maximum values of *Y* (≈ 0,12 mA m^{-1} K^{-2}) for the alloys containing 0.8, 1.2, and 2.0 at % Sn are achieved at temperatures 210, 230 and 235 K respectively.

Thus, the electrophysical properties of the alloys $(Bi_{91}\text{-}Sb_9)_{100\text{-}x}Sn_x$ (x = 0,8 - 2,0) are determined mainly by holes.

The calculations of the Peltier coefficient *Π* rapidly solidified alloys were performed; graphics of the temperature dependences *Π(T)* are shown in Fig. 5.

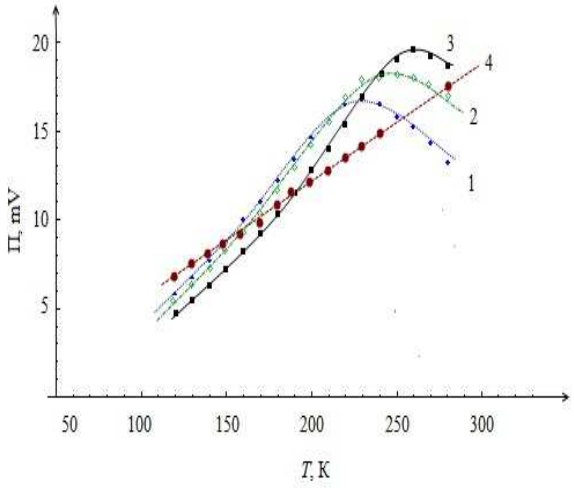

Fig. 5 Temperature dependences *Π(T)* (1– *x*=0.8, 2 – *x* = 1.2, 3 – x = 2.0, 4 – Bi).

The dependencies *Π(T)* have maximuma, the appearance of which are coursed with the thermal excitation of electrons from the valence band to the conduction band. The meaning of Peltier coefficient for the rapidly crystallization of ternary alloys $(Bi_{91}\text{-}Sb_9)_{100\text{-}x}Sn_x$, containing 0.8, 1.2 and 2.0 at % Sn, are more meanings of Peltier coefficient of bismuth in the temperature ranges 150 - 255, 170 - 275 and 195 - 285 K, respectively. These data indicate the possibility of using the foils of rapidly solidified ternary Bi - Sb - Sn alloys for producing *p*-

branch multistage thermoelectric devices working on the Peltier effect at temperatures below room temperature.

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