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*ELECTROPHYSICAL PROPERTIES OF THE $Bi_{2-X}Se_{3-X}$• X SmSe ALLOYS AS THERMOELECTRIC CONVERTER OF n-TYPE**

SUMMARY. The paper presents the research of the electrophysical properties of the Bi_2Se_3-based alloys containing 0.5 – 5.0 mol. % SmSe at 27 – 110 °C. The as-cast samples are synthesized by the ampoule method. The thermoelectric Q-factor of these alloys is determined according to the $\alpha^2*\sigma$ value. All the investigated alloy samples are semiconductive.

When the SmSe content increases to 1.5 mol. %, inclusive, the decrease in resistance and the increase in the thermoelectric power are registered at indoor temperature. The $\alpha^2*\sigma$ values for the samples of this range composition are commeasurable. The increase in the temperature does not result in the change of the values of electrical conductivity and thermoelectric power in the sample containing 98.5 mol. % Bi_2Se_3. The increase in the SmSe content from 2 to 5 mol. % in the samples results in natural decrease in the $\alpha^2*\sigma$ value, that correlates with the second phase occurrence in the samples. The microhardness of the samples naturally increases from about 500 to 750 MPa when the SmSe content increases from 0.5 to 5 mol. %. The value of the SmSe solubility in Bi_2Se_3 under the standard conditions (25 °C) is 1.5 mol.% SmSe.

KEY WORDS. Bismuth selenide, alloying with samarium monoselenide, electrophysical properties, microhardness, thermoelectric materials.

The possibility of using the alloys based on bismuth selenide (Bi_2Se_3) as a thermoelectric material in the macro- and nanostructures is being extensively studied [1-4]. The ways of obtaining thin films of bismuth selenide by the thermal spraying [5] and electrodeposition [6] methods as well as by cultivation on various substrates [7-8] have been developed.

The Bi_2Se_3 compound is the n-type thermoelectric converter with the electron carrier concentration of 8×10^{17} cm^{-3}. The Seebeck coefficient varies from -60 μV/K at 7 K to -190 μV/K at 300 K. The thermal conductivity at 300 K is about 1.55 W/K*m. The resistance varies from about 0.4 mΩ*cm at temperatures about 0 K to 2 mΩ*cm at 300 K. The thermoelectric Q-factor of ZT increases with the increase in temperature reaching about 0.1 at 300 K [3].

The crystal structure of Bi_2Se_3 can be described as a cubic densest packing of Bi and Se atoms. The layers formed by Bi and Se atoms pack up along the *c* axis in the

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form of five layered Se-Bi-Se-Bi-Se packets, forming quintet layer and being connected to each other by weak van der Waals forces [1], [7] [9-11] (Fig. 1).

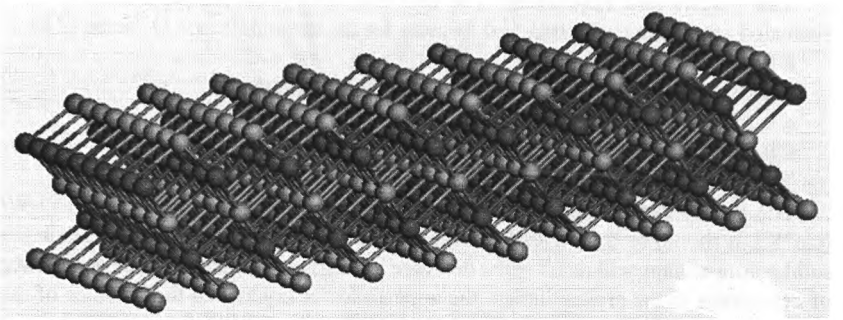

Fig.1. The crystal structure of Bi_2Se_3

In SmSe samarium selenide, as in SmSe samarium monosulfide, Sm $4f^6 5d^0 6s^2$ donates its $6s^2$-electrons to a Se atom. The last of the $4f^6$-electrons is localized on a samarium atom, therefore the SmSe formula unit contains one 4f-electron which is energetically located in the conduction band [12-16].

Some authors suppose [17] that alloying Bi_2Se_3 by the SmSe compound should result in the increase in the number of charge carriers to the optimum values of 10^{19} cm^{-3} order and in the increase in the thermoelectric Q-factor of materials in the solid-solution range.

There are no data published on the electrophysical properties of the phases formed in the Bi_2Se_3-SmSe system.

The purpose of this paper is to determine the phase composition of the Bi_2Se_3 alloys doped up to x=0.05 mol. of SmSe and to specify their electrophysical properties.

The experiment. To prepare the samples (the compositions are specified in Table 1), the accurately weighed portions of *Vi-0000* Bi, *OSCh 17-4* Se, and *M-1* Sm were placed into a quartz ampoule vacuum-processed to the residual pressure of 0.1 Pa and sealed up.

The ampoule was cured in the furnace at t = 400 – 500 °C during 24 hours, then the temperature was raised to ≈ 850 °C and it was cured during 2 hours, then the furnace was cooled in the shutdown mode. The cast samples were obtained.

The electrical conductivity and thermoelectric power were measured with the appliance described in [18]. Before measuring, the cylindrical sample with the strictly parallel upper and lower faces 8-12 mm in height was made from the alloys obtained. The sample was placed between the two clips of the working chamber of the appliance. It was heated by the gradient heater until the temperature of the hottest clip reached 155 °C. The data were accumulated on the appliance by the algorithm described in detail in [19]. The graphs showing the change in temperature of the hot clip (T_2, °C) and cold clip (T_1, °C), the resistance (R, Ohm), the electromotive force (U, mV) were displayed in real-time mode and then exported to *Excel* and processed.

The microhardness was measured on the *PMT-3M* microhardness tester with the accuracy of 7%.

The results and discussion. The thermoelectrical properties of alloys were evaluated according to the standard formula for the thermoelectric Q-factor (ZT):

$ZT = \alpha^2*\sigma*T/\kappa$,

where $\sigma=1/\rho$ is specific electrical conductivity, $Ohm^{-1}*m^{-1}$;

α is the Seebeck coefficient, V/K (or V/deg.);

κ is the lattice thermal conductivity, W/(m*K);

T is the absolute temperature, K.

The Bi_2Se_3 thermal conductivity amounts the value of the order of 0.0155 W/(cm*K). It should be theoretically assumed that any complication of contents in the solid-solution range will result in the decrease in thermal conductivity. The occurrence of new atoms in the crystal lattice, the appearance of crystals in the samples of the second phase will result in dispersing thermal phonons on the areas of the structure discontinuity.

The thermoelectric efficiency was evaluated by the $\alpha^2*\sigma$ value on the assumption of the decrease in thermal conductivity in the solid-solution range.

All the samples synthesized are of the semiconductor conductibility type: when the temperature increases, the resistivity decreases (Table 1, Fig. 2), and the Seebeck coefficient of low-alloyed samples tends to increase (Table 1, Fig. 3).

The results demonstrate that the increase in the SmSe content to 1.5% results in the decrease in the resistance and the increase in the thermoelectric power at indoor temperature. The $\alpha^2*\sigma$ value is by an order of magnitude greater when the temperature increases up to 110 °C. The $\alpha^2*\sigma$ values for samples 1, 2, and 3 are commeasurable. The values of conductivity and thermoelectric power of the sample containing 98.5% Bi_2Se_3, remain virtually unchanged with the temperature increasing.

Table 1

The electrophysical properties of the samples under study

No.	Composition		Temperature, °C								
			27			60			110		
	Mol.% Bi_2Se_3	Mol.% SmSe	ρ, Ohm*m	α, mV/deg.	$\alpha^2*\sigma$,	ρ, Ohm*m	α. mV/deg.	$\alpha^2*\sigma$	ρ, Ohm*m	α. mV/deg.	$\alpha^2*\sigma$
1	99.5	0.5	0.165	0.026	0.004	0.079	0.089	0.100	0.079	0.098	0.121
2	99	1	0.102	0.035	0.012	0.072	0.085	0.100	0.086	0.093	0.101
3	98.5	1.5	0.094	0.108	0.124	0.098	0.086	0.075	0.077	0.094	0.115
4	98	2	0.161	0.101	0.063	0.099	0.088	0.078	0.107	0.100	0.093
5	97	3	0.193	0.122	0.077	0.097	0.082	0.069	0.093	0.09	0.087
6	95	5	0.325	0.054	0.009	0.119	0.074	0.046	0.104	0.083	0.066

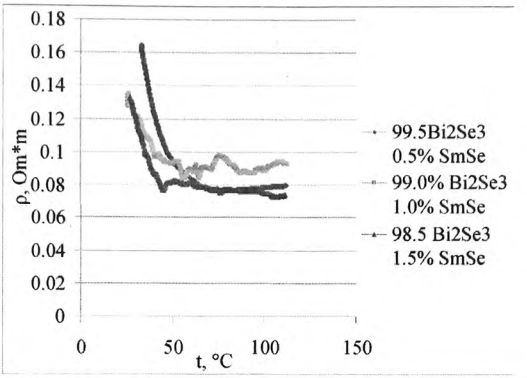

Fig.2. The dependence of the resistivity on the temperature

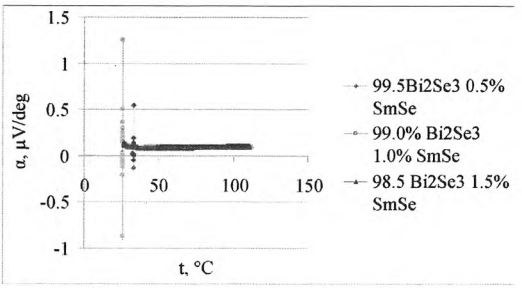

Fig.3. The dependence of the Seebeck coefficient on the temperature

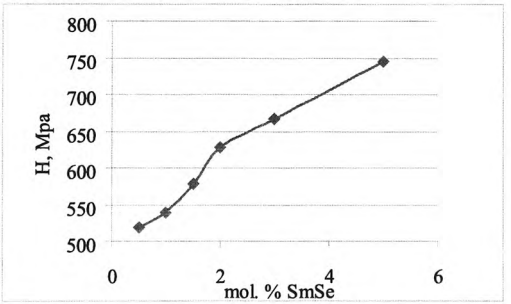

Fig.4. The dependence of microhardness on the SmSe mole fraction

When the SmSe content increases from 2 to 5%, the $\alpha^2*\sigma$ value naturally decreases, which correlates with the appearance of the second phase in the samples. According to the MSA data, the second phase appears in the form of needle segments, the sizes of which increase from a few microns to about 15-20 microns.

The microhardness of the samples regularly increases (Fig. 4). The non-occurrence of the eutectic per se in the samples suggests that based on Bi_2Se_3-SmSe in the section, a solid solution is formed, and its isothermal solubility increases significantly with the increase in temperature.

Based on Bi_2Se_3 a solid solution is formed. The solubility value under the standard conditions (25 °C) is 1.5 mol. % SmSe. While doping Bi2Se3 0.5-1 mol. % SmSe, the thermoelectric properties of the alloys increase.

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