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# Preparation and some electrophysical properties of the compound $Sn(Pb)SbBiS_4$ and solid solutions based on $SnSbBiS_4$

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When studying the ternary system $Sb_2S_3$-Sn(Pb)S-$Bi_2S_3$, it was established that in the Sn(Pb)$Sb_2S_4$-Sn(Pb)$Bi_2S_4$ sections a quaternary compound with the composition $SnSbBiS_4$ and $PbSbBiS_4$ is formed. And in the $SnSbBiS_4$-SnS system, solid solutions are formed based on the initial components. Their electrical conductivity and temperature dependence of thermoelectric properties have been studied over a wide range. The results of measuring the temperature dependence of electrical conductivity, the samples have a semiconductor conductivity throughout the entire temperature range. It was established that all samples are n-type semiconductors. The compound $SnSbBiS_4$ and $PbSbBiS_4$ have high photosensitivity in the IR region of the spectrum. At operating voltage 10-20 V, $R_d / R_l$ $1.1 \cdot 10^3 \div 1.4 \cdot 10^3$.

**Keywords:** solid solutions, electrical conductivity, $SnSbBiS_4$, photosensitivity, thermoelectric, Phase diagram, $PbSbBiS_4$.

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## Introduction

Currently, ternary semiconductors based on tin, antimony and sulfur elements $Sn(Pb)_aSb(Bi)_bS(Se,Te)_c$ have been presented as interesting materials in some technological applications such as solar cells [1-9], thermoelectric conversion energy [10] and sensors [11-14].

Moreover, these compounds could open up new opportunities for materials for solar energy and thermionics. Applications because they are abundant and stable compounds with easily controlled both surface and bulk properties. Among them, $SnSb_2S_4$ has been studied as a captivating sulfosel. Material as previously reported [15-18]. However, its electrical as well as thermal properties have not been widely studied. Compounds of type and, as well as complex solid solutions based on them, are the best thermoelectric materials, having a high thermoelectric effect at 300-900 K.

Using complex methods of physicochemical analysis, we studied the systems $SnSb_2S_4$–$SnBi_2S_4$, $PbSb_2S_4$–$PbBi_2S_4$ and $SnSbBiS_4$–SnS in a wide concentration range. It has been established that in the $SnSb_2S_4$–$SnBi_2S_4$ section it is characterized by the formation of one quaternary compound of the composition $SnSbBiS_4$ and narrow regions of solid solutions based on the ternary sulfide $SnBi_2S_4$ (Fig. 1) [19,20]. The quaternary compound SnSbBiS4 melts congruently at 880 K.

The $SnSbBiS_4$–SnS system is a quasi-binary section of the quasi-ternary system $Sb_2S_3$–SnS–$Bi_2S_3$; its phase diagram is of the eutectic type (Fig. 2). The section is characterized by narrow areas of homogeneity based on the initial components[21].

The $PbSb_2S_4$–$PbBi_2S_4$ section is a partially quasi-binary section of the $Sb_2S_3$–PbS–$Bi_2S_3$ quasi-ternary system (Fig. 3). When the ratio of the initial components is 1:1, a quaternary compound of the composition $PbSbBiS_4$ is formed, which melts congruently at 870 ± 5 K [22].

# I. Experimental part

Previously, electrophysical properties of solid solutions containing $(SnSbBiS_4)_{1-x}(SnS)_x$ (x = 0.01; x = 0.03; x = 0.05), $SnSbBiS_4$ and $PbSbBiS_4$ compounds were not studied. In order to measure physical properties, 1, 3 and 5 mol.% SnS samples, $SnSbBiS_4$ and $PbSbBiS_4$ compounds were re-synthesized based on $SnSbBiS_4$ cross-section $SnSbBiS_4$-SnS by complex methods of physico-chemical analysis. The synthesis of the samples was carried out by the direct synthesis method in a heat-resistant quartz ampoule with air sucked up to 0.133 Pa. The temperature of the synthesized ampoule was heated up to 900K at a rate of 100/K per hour and kept at that temperature for 3 hours. During the synthesis process, the samples were mechanically mixed several times for complete chemical interaction. The obtained alloys were placed in the furnace at a temperature of 600-650 K for 50-55 hours. To measure the electrophysical properties, solid solution alloys based on $SnSbBiS_4$, samples of $SnSbBiS_4$ and $PbSbBiS_4$ compounds were cut in the shape of a parallelepiped of ~3x4x10 mm in an electric spark device. In order to remove the damaged layer formed on the surface after cutting, the surface of the alloys was electrochemically etched in $KOH+C_6H_6O_6+H_2O$ solution at room temperature (300K) after cutting. The wear time was 20-23 seconds, and the density of the current flowing through the sample was 0.5 A/cm$^2$. Electrical contacts (mass %): drawn using (47Bi+53Sn) composition $ZnCl_2+NH_4Cl+NiCl_2+H_2O$ size. Electrical conductivity (σ) and thermo-e.h.q. of solid solution alloys based on $SnSbBiS_4$. (α) values were measured by potentiometric method.

# II. Results

The electrical properties of $(SnSbBiS_4)_{1-x}(SnS)_x$ and the compounds $SnSbBiS_4$ and $PbSbBiS_4$ were studied over a wide temperature range. The results of measuring the temperature dependence of their electrical conductivity are presented in Fig. 4. 5. The measurement showed that all the studied samples have a semiconductor conductivity

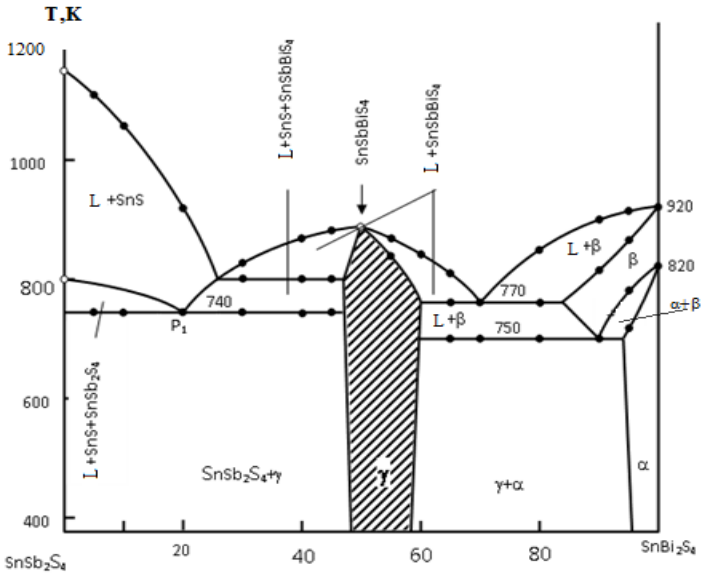


**Fig. 1.** Phase diagram of the $SnSb_2S_4$–$SnBi_2S_4$ system [19,20].

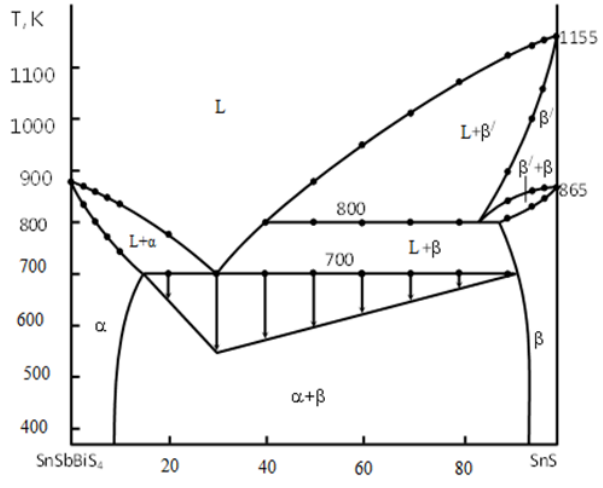


**Fig. 2.** Phase diagram of the $SnSbBiS_4$–SnS system [21].

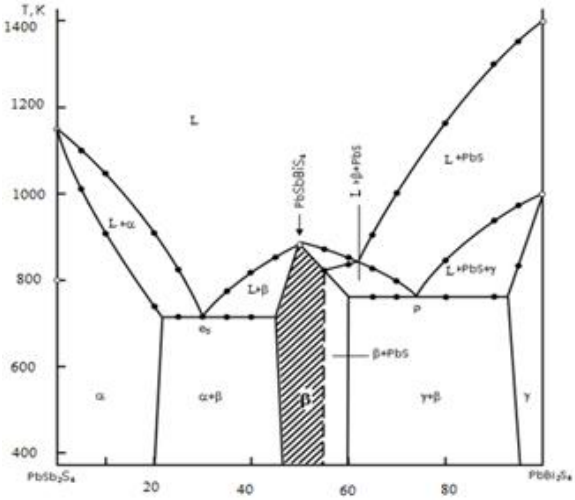


**Fig. 3.** Phase diagram of the $PbSb_2S_4$–$PbBi_2S_4$ system [22].

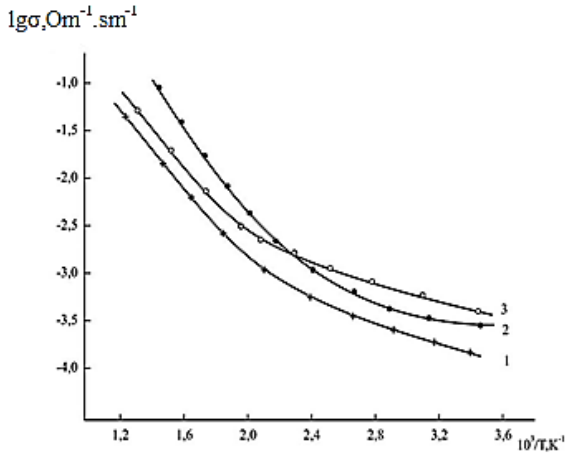


**Fig. 4.** Temperature dependence of electrical conductivity of solid solutions $(SnSbBiS_4)_{1-x}(SnS)_x$: 1 – x = 0.03; 2 – x = 0.05 and 3 – x = 0.01.

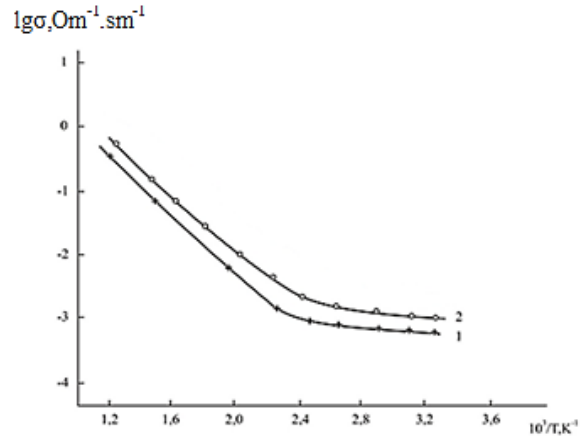


**Fig. 5.** Temperature dependence of electrical conductivity of compounds $PbSbBiS_4$ (1), $SnSbBiS_4$ (2).

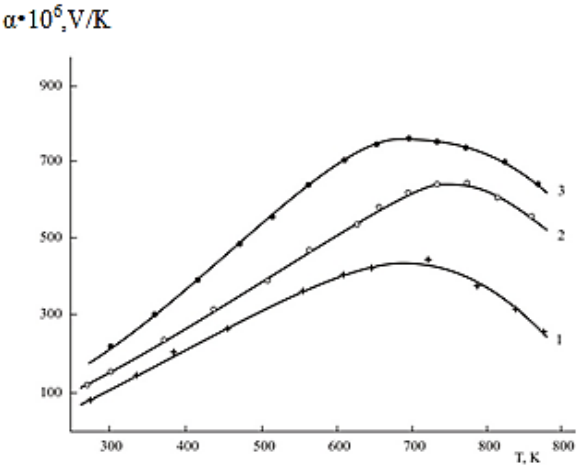


**Fig. 6.** Temperature dependence of thermo-emf of solid solutions $(SnSbBiS_4)_{1-x}(SnS)_x$: 1 – x = 0.03; 2 – x = 0.05; 3 – x = 0.01.

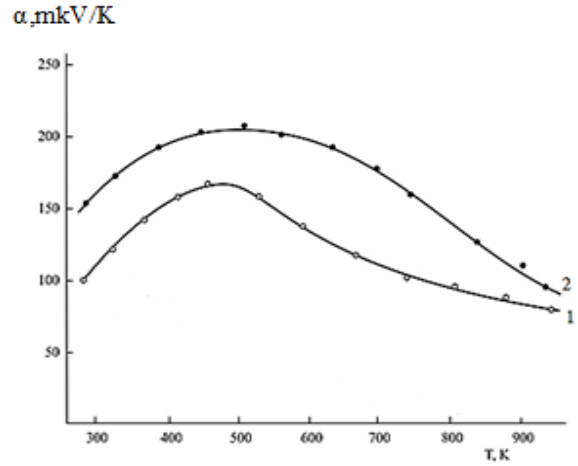


**Fig. 7.** Temperature dependence of thermo-emf of compounds $PbSbBiS_4$ (1), $SnSbBiS_4$ (2.)

throughout the entire temperature range.

All compositions are initially characterized by a region of impurity conductivity. Then, starting from 500 K for the $(SnSbBiS_4)_{1-x}(SnS)_x$ alloys, a stronger increase in electrical conductivity with temperature is observed, associated with the appearance of intrinsic conductivity.

The study showed that the replacement of tin with bismuth and stibium in the SnS crystal lattice leads to a decrease in ΔE values.

The temperature dependences of the thermo-emf coefficient of solid solutions are shown in Fig. 6. For all samples they have the same character, typical for compounds of the $A^{IV}B^{VI}$ type and solid solutions based on them, i.e. at the beginning α increases linearly with temperature, then passes through a gentle maximum, after which its monotonic decrease is observed. This behavior of the thermo-emf coefficient is most likely associated both with the appearance of carriers of the second sign in the main valence band and with the approaching region of intrinsic conductivity.

The results of the study allow us to make the assumption that the complex band structure characteristic of chalcogenides of elements of the germanium subgroup and solid solutions based on them also occurs in the materials studied, which is why such a complex change in kinetic coefficients is observed depending on temperature. In Figure 7, the temperature dependence of the of thermo-emf (α) for $PbSbBiS_4$ and $SnSbBiS_4$ compounds is presented. It was found that in both samples, with increasing temperature, the thermoelectric power factor initially increases, reaching its maximum in the range of 400–500 K, and then shows a tendency to decrease. For the $PbSbBiS_4$ compound, the maximum value of α is approximately 160 mkV/K, while for the SnSbBiS4 compound this value reaches 210–220 mkV/K. The decrease of the thermoelectric power factor in the high-temperature region for both compounds can be explained by the increase in carrier concentration. A comparison shows that the $SnSbBiS_4$ compound possesses higher thermoelectric parameters, which proves its promising potential. The results clearly demonstrate that the thermoelectric power factor strongly depends on both the composition of the materials and the temperature range. This dependence highlights the importance of selecting the optimal temperature region for the efficient application of thermoelectric materials.

A study of the temperature dependence of the

compound $SnSbBiS_4$ and $PbSbBiS_4$ (Fig. 5) showed that the temperature dependence of electrical conductivity is semiconductor in nature. The calculated band gaps for $SnSbBiS_4$ and $PbSbBiS_4$ are 1.20 and 0.94 eV, respectively. Based on the sign of the thermo-emf, it was determined that these compounds are semiconductors with n-type conductivity. The spectral dependences of the photocurrent of the $SnSbBiS_4$ and $PbSbBiS_4$ compounds on the light wavelength were also studied (Fig. 8). As can be seen from the figure, the $PbSbBiS_4$ and $SnSbBiS_4$ compounds have high photoconductivity in the IR region of the spectrum.

Their maximum photoconductivity λ max shifts to the region of short waves and amounts to 1.00 and 1.08 μm. The band gap of $SnSbBiS_4$ and $PbSbBiS_4$, calculated from the maximum photocurrent at 300 K, is ΔEop.=1.24 and 1.17 eV, respectively.

The spectral sensitivity range of the $SnSbBiS_4$ and $PbSbBiS_4$ compounds is in the region of 0.7÷1.4 μm. The $SnSbBiS_4$ compound, compared to $PbSbBiS_4$, has a higher sensitivity.

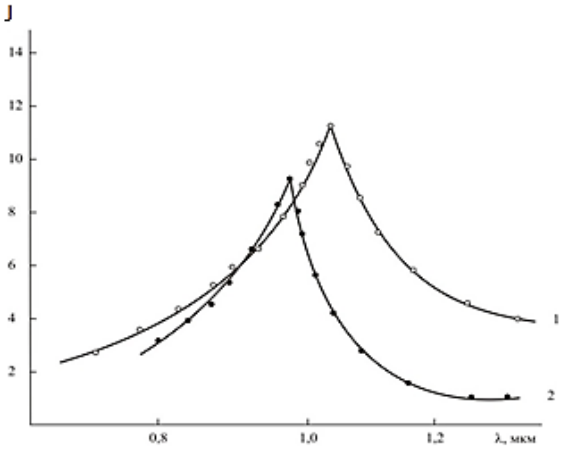


**Fig. 8.** Spectral dependence of the photocurrent of $SnSbBiS_4$ (1) and $PbSbBiS_4$ (2) single crystals on the shaft length at 300 K.

At room temperature, $SnSbBiS_4$ dark and light resistances have the values $R_t=9.2\cdot10^9\div4.5\cdot10^9$, $R_c=1.3\cdot10^7\div0.8\cdot10^7$ at an operating voltage of 10-20 V and illumination of $3.5\cdot10^{-1}$ lux. This connection has $R_d/R_l = 1.1\cdot10^3\div1.4\cdot10^3$, which is suitable for the development of photoresistors and can be used in the manufacture of energy converters. The compound $SnSbBiS_4$ and $PbSbBiS_4$ are characterized by high photosensitivity in the near and long IR regions of the spectrum. Their photosensitivity is many times higher than $Sb_2S_3$, used in optical devices, in particular, in vidicons. These materials are recommended for use in the manufacture of photoresistors used in energy converters.

## Conclusions

1. When studying the ternary system $Sb_2S_3$-Sn(Pb)S-$Bi_2S_3$, it was established that in the Sn(Pb)$Sb_2S_4$-Sn(Pb)$Bi_2S_4$ sections, with a ratio of initial components of 1:1, a quaternary compound with the composition $SnSbBiS_4$, $PbSbBiS_4$ is formed.
2. In the $SnSbBiS_4$-SnS system, solid solutions are formed based on the initial components.
3. Measurements of the temperature dependence of electrical conductivity; samples have a semiconductor conductivity throughout the entire temperature range. It was established that all samples are n-type semiconductors.
4. The compound $SnSbBiS_4$ and $PbSbBiS_4$ have high photosensitivity in the IR region of the spectrum. At operating voltage 10-20 V, $R_D/R_L=1.1\cdot10^3\div1.4\cdot10^3$.
5. These materials ($SnSbBiS_4$ and $PbSbBiS_4$) are recommended for use in the manufacture of photoresistors used in energy converters.

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# Отримання і деякі електрофізичні властивості сполуки Sn(Pb)SbBiS$_4$ та твердих розчинів на основі SnSbBiS$_4$

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У процесі вивчення потрійної системи $Sb_2S_3$-Sn(Pb)S-$Bi_2S_3$ було встановлено, що в областях Sn(Pb)$Sb_2S_4$-Sn(Pb)$Bi_2S_4$ формується четвертинні сполуки складу SnSbBiS$_4$, PbSbBiS$_4$. А у системі SnSbBiS$_4$-SnS утворюються тверді розчини на основі вихідних компонентів. Було досліджено їх електропровідність та температурну залежність термоелектричних властивостей у широкому діапазоні. Результати вимірювань температурної залежності електропровідності показали, що зразки мають напівпровідниковий характер провідності в усьому дослідженому температурному інтервалі. Встановлено, що всі зразки є напівпровідниками n-типу. Сполуки SnSbBiS$_4$ і PbSbBiS$_4$ характеризуються високою фоточутливістю в ІЧ-області спектра. При робочій напрузі 10-20 В, відношення $R_d/R_l$ становить $1{,}1\cdot10^3 \div 1{,}4\cdot10^3$.

**Ключові слова:** тверді розчини, електропровідність, SnSbBiS$_4$, світлочутливість, термоелектрика, фазова діаграма, PbSbBiS$_4$.