Electrical Properties of Pb and Sn Doped Crystals of the $Pb_{0.75}Sn_{0.25}Te$ Solid Solution and Thermoelements Based on Them

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Abstract. Single crystals of $Pb_{0.75}Sn_{0.25}Te$ with additions of Pb and Sn up to 1.0 at.% were grown, thermoelement legs were created on their basis, and their electrical properties were studied in the range of ~ 77–300 K. It was shown that atoms of additional Pb or Sn at low contents, being located in cation vacancies of crystals, lead to a decrease in the hole concentration, a change in the conductivity type, an increase in the specific resistance ρ and contact resistance r_k of the thermoelement legs, and at high contents, creating donor centers in the crystals, they reduce ρ and r_k. The specific contact resistance of the legs, as well as their temperature dependences, are also determined by the diffusion of the connecting alloy components into the near-contact region of the crystals. The thermoelectric figure of merit of the studied crystals with a 1.0 at.% Pb additive and the legs of thermoelements based on them reach values of 1.7×10^{-3} K^{-1} and $1.16\times10^{-3}K^{-1}$, respectively, at ~300 K.

Keywords: solid solution, crystal, vacancy, additive, thermoelectric figure of merit.

1 Introduction

$Pb_{1-x}Sn_xTe_x$ solid solutions, like their constituents PbTe and SnTe, crystallize in face-centered cubic lattices of the NaCl type. These materials are used to fabricate various medium-temperature thermoelectric generators and infrared photovoltaic converters [1-5]. The best thermoelectric figures of merit for $Pb_{1-x}Sn_xTe$ solid solutions in the temperature range of ~ 400-700 K are those with x=0.25–0.30 [4, 5]. PbTe and SnTe compounds and their solid solutions crystallize with deviations from stoichiometry and contain electroactive vacancies in the cation sublattice on the order of 10^{18}–10^{20} cm^{-3}. This concentration of cation vacancies, leading to a high concentration of holes in the crystals, limits their range of application. It has been found that the introduction of superstoichiometric Pb and Sn atoms, respectively, can reduce the concentration of cation vacancies in PbTe and SnTe single crystals [6, 7].

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Based on this, in this work, in order to clarify the patterns of influence of super-stoichiometry additives of Pb and Sn on the electrical properties of crystals of the $Pb_{0.75}Sn_{0.25}Te$ solid solution and thermoelements based on them, their single crystals with Pb and Sn additives up to 1.0 at.% were grown by the Bridgman method, and branches of thermoelements were created on their basis using a commutation solder of the eutectic wt.% 57Bi+43Sn and their electrical properties were studied in the temperature range of ~77÷300 K.

2 Experiments and Discussion of Results

The synthesis of $Pb_{0.75}Sn_{0.25}Te$ with additives of 0; 0.01; 0.05; 0.10; 0.50; 1.0 at.% lead or tin was carried out in quartz ampoules evacuated to 10^{-3} Pa by joint fusion of the starting components (lead grade C-0000, tin grade ОСЧ-000, tellurium grade Т-сЧ) at ~1245 K for 6 hours. The starting components lead, tin, and tellurium were pre-cleaned to remove any possible surface oxide film by passing their melts through narrow necks in quartz ampoules evacuated to a vacuum of ~10^{-3} Pa. Tellurium was further purified from any possible initial impurities using zone melting. During the synthesis, the melt was continuously stirred by shaking the furnace in the vertical plane. Single crystals were grown in the same ampoules in which the synthesis of the compound was carried out, using the mode described in [8]. The inner surface of quartz ampoules used for component purification and solid solution synthesis was pre-graphitized. Rectangular parallelepiped-shaped samples measuring 3x5x10 mm, as well as thermoelement branches measuring 3x3x5 mm, were cut from the grown $Pb_{0.75}Sn_{0.25}Te$<Pb,Sn> single crystal ingots using an electric spark cutting system. During electric spark cutting of the ingot samples and branches, a damaged polycrystalline layer ~15÷20 μm thick, contaminated with cutting products, was formed on the cut surface of the samples. This damaged layer was removed by electrochemical etching in solutions of 1 L H_2O + 83 g KOH + 67 g $C_4H_6O_6$ for p-type samples and 1 L H_2O + 90 g NaOH + 55 g $C_4H_6O_6$ for n-type samples at a current density of ~0.5 A/cm^2 for ~50 s. The grown crystals were annealed at ~773 K for 120 hours in an argon atmosphere. The single-crystal nature of the grown crystals of the $Pb_{0.75}Sn_{0.25}Te$ <Pb, Sn> compositions were confirmed by X-ray diffraction. The lattice parameter of the $Pb_{0.75}Sn_{0.25}Te$ crystals was found to be 6.399 Å. The homogeneity and single-phase nature of the ingots were confirmed by microstructural analysis and resistivity measurements of individual ingot sections. The specific electrical conductivity σ, coefficients of thermo-emf α and Hall coefficient R_x of the crystals, and the specific contact resistance r_k of the thermocouple legs in the connecting alloys were studied.

The experiments showed that the temperature dependence of σ is metallic for all samples. Moreover, starting from temperatures of ~190÷200 K, the slope of the σ(T) dependence increases slightly. The sign of α for the stoichiometric composition is positive over the entire temperature range, while for samples with lead additives of up to 0.5 and 0.1 at.% at temperatures below ~180 K and for samples with tin additives of up to 1.0 at.% over the entire temperature range from (~77÷300 K), it is negative. The

absolute values of the Seebeck coefficient for all compositions increase with temperature. The Hall coefficients of $Pb_{0.75}Sn_{0.25}Te$ samples with lead and tin additives show opposite signs compared to their Seebeck coefficients (Figure 1, a, b, c).

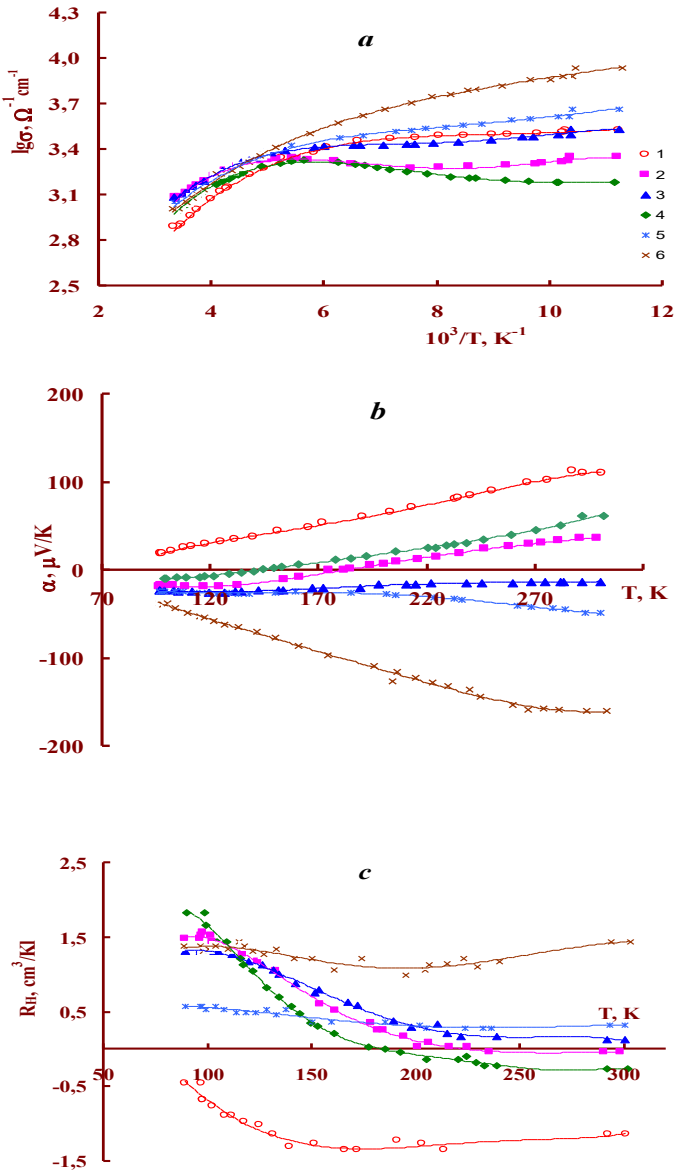

Fig. 1. Temperature dependences of electrical conductivity σ (a), coefficients of thermo-emf α (Seebeck coefficient) (b) and Hall coefficient (c) of $Pb_{0.75}Sn_{0.25}Te$ crystals with lead additives. Curves 1-6 refer to samples with 0; 0.01; 0.05; 0.10; 5; 1.0 at.% lead additives, respectively.

With an increase in the concentration of excess tin to 0.1 at.%, the contact resistance r_k of the (Bi+Sn)- $Pb_{0.75}Sn_{0.25}Te$ structure at ~77 K, decreasing from a value of 3.1×10^{-4} Ω·cm^2, reaches a value of 3.1×10^{-6} Ω·cm^2, and then increases and at 1.0 at.% of excess tin becomes equal to 1.94×10^{-4} Ω·cm^2. At 300 K, the r_k values of the structure are $Pb_{0.75}Sn_{0.25}Te$ and $Pb_{0.75}Sn_{0.25}Te$<1.0 at.% Sn> crystals are 7.2×10^{-4} Ω·cm^2 and 5.4×10^{-4} Ω·cm^2, respectively. For all structures, r_k increases with temperature (Figure 2 a, b).

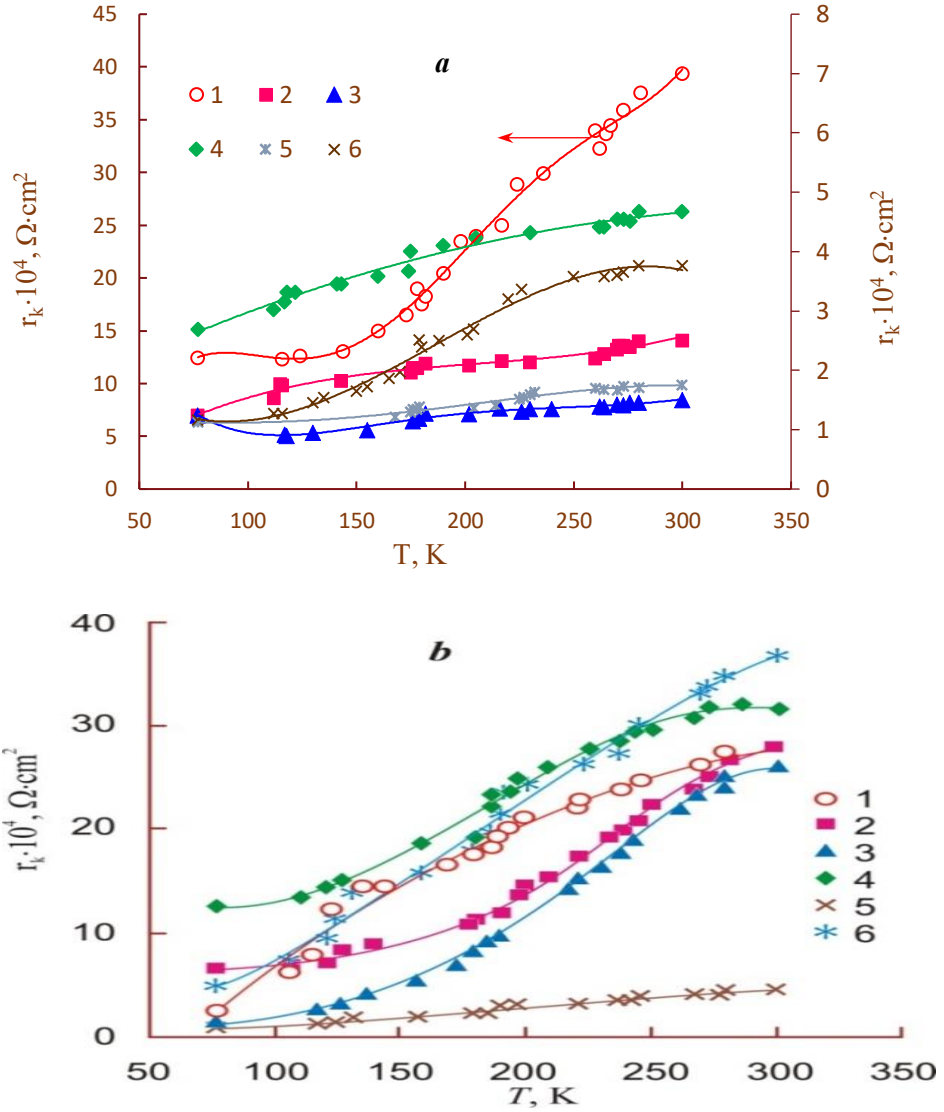

Fig. 2. Temperature dependences of the switching contact resistance r_k of the metal-semiconductor structures (Bi+Sn)-$Pb_{0.75}Sn_{0.25}Te$<Pb>(a) and (Bi+Sn)-$Pb_{0.75}Sn_{0.25}Te$<Sn>(b). Curves 1-6 correspond to samples with 0; 0.01; 0.05; 0.10; 0.5; and 1.0 at.% lead (a) and tin (b), respectively.

In $Pb_{0.75}Sn_{0.25}Te$ crystals, the charge carrier concentration is primarily determined by vacancies in the cation sublattice (each cation vacancy produces two holes). Therefore, a sample without added Pb and Sn exhibits hole conductivity in the temperature range of 77-300 K. Additional lead or tin atoms introduced into the sample at low concentrations (up to 0.01-0.1 at.%), by occupying these cation vacancies, reduce the hole concentration, resulting in an increase in the resistivity of the crystals and the contact resistance of the structures based on them. At higher concentrations, some of the added lead or tin atoms not located in cation vacancies, creating new donor centers, increasing the concentration of free electrons and decreasing the resistivity of the crystals and the contact resistance r_k of the structures.

The valence band of the $Pb_{0.75}Sn_{0.25}Te$ solid solution, like that of PbTe and SnTe crystals, is complex and consists of subbands of light and heavy holes [9, 10]. With increasing temperature, the light-hole zone shifts toward heavy holes, and the role of heavy holes in the electrical properties increases. As a result, in the studied crystals of the $Pb_{0.75}Sn_{0.25}Te$<Pb, Sn> solid solutions, the σ(T) dependence at temperatures above ~190 K is somewhat enhanced.

When tinning the ends of crystals with a commutation alloy (Bi+Sn) to create thermocouple legs, some diffusion of this alloy's components into the near-contact region of the crystals occurs. Diffusing Bi and Sn atoms, creating new impurity centers in this region, increasing the carrier concentration and decrease r_k. The solid solution $Pb_{0.75}Sn_{0.25}Te$crystallizes with an excess of tellurium. Therefore, when Bi and Sn diffuse into the near-contact region of the crystal, intermediate phases such as Bi_2Te_3 and SnTe can form in this region, which also affects r_k.

Based on the values of enthalpy changes ΔHi295 and entropy changes ΔS^0 i295 of compounds under standard conditions, the following relation was used:

$$\Delta G^0 = \sum n_i \left(\Delta H^0{}_{i295} - T\Delta S^0{}_{i295}\right)_{fin} - \sum n_i \left(\Delta H^0{}_{i295} - T\Delta S^0{}_{i295}\right)_{init}$$

Based on the reactions Sn+Te=SnTe, 2 Bi+3Te=Bi_2Te_3, the Gibbs free energy values ΔG^0 were obtained to be -61.9 and -78.1 kJ/mol, respectively. The sufficiently high negative values of ΔG^0 indicate that the above reactions occur and that SnTe and Bi_2Te_3 crystals are formed in the near-contact region.

As Bi and Sn diffuse into the near-contact region of the crystal, intermediate phases such as Bi_2Te_3 and SnTe can also form in this region, which also affects r_k. In these metal-semiconductor alloy contacts, Bi and Sn atoms diffusing into the near-contact region can also deposit along imperfection lines in the crystal, forming shunts that short-circuit the space charge layer. In this case, current flows through the metal shunts at the metal-semiconductor contact, and r_k increases with temperature [11,12]. The increase in r_k for $Pb_{0.75}Sn_{0.25}Te$<Pb,Sn> structures with temperature is also associated with an increase in the resistivity of $Pb_{0.75}Sn_{0.25}Te$<Pb,Sn> crystals.

The thermoelectric efficiency Z_k of $Pb_{0.75}Sn_{0.25}T$<Pb, Sn>crystals and thermocouples Z_T based on them were calculated at 300K using the expressions [13,14]

$$Z_k = \frac{\alpha^2}{\rho\chi}, \quad Z_T = Z_k/(1+2r_k\sigma/l)$$

respectively.

Here, χ - is the thermal conductivity of the crystals, and l - is the length of the thermocouple branches.

The highest Z_k at 300 K were found in n-$Pb_{0.75}Sn_{0.25}Te$<1.0 at.% Pb> and n-$Pb_{0.75}Sn_{0.25}Te$<1.0 at.% Sn> crystals, equal to 1.7×10^{-3} K^{-1} and 0.34×10^{-3} K^{-1}, respectively.

The table shows the measured values of σ,α, χ of the solid solution crystals and the switching contact resistance rk of the structures (thermoelement branches) (Bi-Sn) - $Pb_{0.75}Sn_{0.25}Te$<Pb>and (Bi-Sn) - $Pb_{0.75}Sn_{0.25}Te$<Sn>.

Table. Electrical conductivity σ ($\Omega^{-1}cm^{-1}$), thermoelectric power coefficients α (μV/K) and thermal conductivities $\chi\cdot10^{-2}$ (W/cm·K) of $Pb_{0.75}Sn_{0.25}Te$<Pb,Sn>crystal samples, as well as specific switching contact resistance $r_k\cdot10^{-3}$($\Omega\cdot cm^2$) of thermoelement branches based on these crystals.

Content of additional lead in $Pb_{0.75}Sn_{0.25}Te$, at.%	**σ**	**α**	**χ**	**r_k**
0,0	773,2	109,8	0,39	2,06
0,01	1210,9	36,0	0,24	2,56
0,05	1212,1	-13,1	0,15	0,50
0,5	1123,6	-48,6	0,46	3,37
1,0	1026,3	-160,1	0,38	1,57
Content of additional tin in $Pb_{0.75}Sn_{0.25}Te$, at.%	**σ**	**α**	**χ**	**r_k**
0,0	773,2	109,8	0,71	2,06
0,01	1139,4	-81,3	1,35	3,06
0,05	2467,8	-87,6	0,16	2,97
0,5	4213,0	-60,0	0,98	3,96
1,0	3584,2	-71,1	0,44	3,60

3. Conclusion

It was found that in the crystals of the $Pb_{0.75}Sn_{0.25}Te$ solid solution, annealed at 773 K after growth, the atoms of additional lead and tin at low contents, being located mainly in cation vacancies, lead to a decrease in the hole concentration and a change in the type of conductivity from pto n, an increase in the specific resistance of both the crystals themselves and the specific contact resistance of the metal-semiconductor structures based on them. Added lead and tin atoms at high concentrations create new donor centers in $Pb_{0.75}Sn_{0.25}Te$ crystals, reducing their resistivity ρ and the contact resistance of the (Bi-Sn)- $Pb_{0.75}Sn_{0.25}Te$<Pb,Sn> structures. The values and temperature dependence of r_k for the structures are also determined by the diffusion of the components of the connecting alloy (Bi+Sn) into the near-contact region of the crystals. Crystals of the $Pb_{0.75}Sn_{0.25}Te$ solid solution with 1.0 at.% Pb and thermoelement legs based on them have thermoelectric efficiencies of 1.7×10^{-3} K^{-1} and 1.16×10^{-3} K^{-1}, respectively. In the case of a crystal with an addition of 1.0 at.% Sn, these parameters are 0.34×10^{-3} K^{-1} and 0.23×10^{-3} K^{-1}, respectively.

Conflict of Interest

The authors of this work declare that they have no conflicts of interest.

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