ELECTRONIC PROCESSES IN THE $Pb_{0.75}Sn_{0.25}Te<Pb>$ SOLID SOLUTION AND IN THE METAL-SEMICONDUCTOR STRUCTURE BASED ON IT

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Single crystals of with 0.0÷1.0 at.% superstoichiometric lead were grown and their electrical conductivity σ, thermopower α and Hall coefficients R_x in the range of 77÷300K were studied. It was found that annealing significantly affects the values and temperature dependences of these parameters, as well as the signs of α and R_x. The results obtained are explained by the appearance of electroactive structural defects during growth in crystals, which are healed by annealing, the compensation of these defects by excess lead atoms, the existence of impurity centers with an activation energy of ~0.06–0.11 eV in the samples, and an increase in the contribution of heavy holes to conductivity with temperature. $Pb_{0.75}Sn_{0.25}Te<Pb>$-(In-Ag-Au) structures were fabricated and their electrical properties were studied.

Keywords: solid solution, metal-semiconductor structure, contact resistance, intermediate phase
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INTRODUCTION

$Pb_{0.75}Sn_{0.25}Te$ solid solutions are materials potentially to be utilized for infrared detectors and lasers, as well as thermoelectric converters [1-3]. However, these materials crystallize with a deviation from stoichiometry in the cation sublattice with a concentration of up to ~10^{20} cm^{-3}, which complicates their practical application. It was found that the introduction of superstoichiometric lead or tin atoms makes it possible to control the concentration of electroactive cationic vacancies and, accordingly, concentration (and mobility) of current carriers in PbTe, SnTe and some of their solid solutions [4–6]. The best thermoelectric properties in the PbTe-SnTe system are alloys containing 25-30 mol. % SnTe [3].

$Pb_{1-x}Sn_xTe$ solid solutions have the same crystal structure and up to x~0.4 retain the structure of the valence band similar to PbTe. It can be assumed that in the crystals of the $Pb_{0.75}Sn_{0.25}Te$ solid solution, excess of Pb or Sn atoms, changing the concentration of cationic vacancies, will lead to a decrease in the concentration of current carriers.

In this work, single crystals of $Pb_{1-x}Sn_xTe$ with 0.0; 0.01; 0.05; 0.1; 0.5; 1.0 at.% Pb of superstoichiometry are developed and their electrical conductivity σ, thermopower α and Hall coefficients R_x in the temperature range 77÷300 K before and after annealing were studied. To identify the role of structural defects arising during the preparation of resealed crystals and the preparation of research samples from them, experiments were carried out on annealed samples and on the same samples annealed at 673 K for 120 hours.

EXSPERIMENTAL TECHNIQUES

The compositions were synthesized in quartz ampoules evacuated to ~10^{-2} Pa by co-fusion of the initial components at 1245 K. Lead grade C-0000, tin grade ОВЧ-000, tellurium grade Т-сЧ (99.999) were used for synthesis, taken in a stoichiometric ratio with an accuracy of 0.0001 g.

The initial components (Pb, Sn, Te) were previously purified from the surface oxide film and possible impurities. Single crystals were grown by the Bridgman method from the synthesized material in the same quartz ampoules in which the composition was synthesized. The inner surface of the quartz ampoules intended for the synthesis and growth of single crystals was preliminarily graphitized. When growing, the temperatures of the hot and cold zones of the heater were setup as 1245 and 1145 K. The temperature gradient at the crystallization front was ~15 deg/cm and the crystal growth rate was 2 mm/h.

The single crystalline of the grown ingots was confirmed by the X-ray method. The lattice parameter in the case of a pure (without excess lead) and with an excess of lead crystal was equal to a=6.399 Å.

The homogeneity of the ingots of single crystals was checked by measuring the electrical resistance in separate sections along the ingot. Samples in the form of rectangular parallelepipeds with dimensions of 3x6x12 mm were cut from a homogeneous part of the ingots using an electric spark installation. The removal of the damaged layer formed on the surface and ends of the samples during cutting was carried out by electrochemical etching. After removing the damaged layer, the samples were annealed in an atmosphere of spectrally pure argon at 673 K for 120 hours.

The electrical parameters were measured on the same samples before and after annealing process. Electrical conductivity σ, thermopower α and Hall coefficients R_x were measured in direct current by the probe method along the ingot with an error not exceeding ~5 %.

RESULTS AND ANALYSES

Experiments have shown that the temperature dependences of electrical conductivity σ for all samples that have not undergone annealing are metallic in nature (Figure 1a). As a result of annealing, the conductivity of the samples significantly (up to ~ 6 times) decreases and, by $\sigma(T)$ of pure (without excess Pb) and containing 0.01÷0.5 at.% excess lead, samples in the range of ~100÷210 K, semiconductor (activation) sites (Figure 1b).
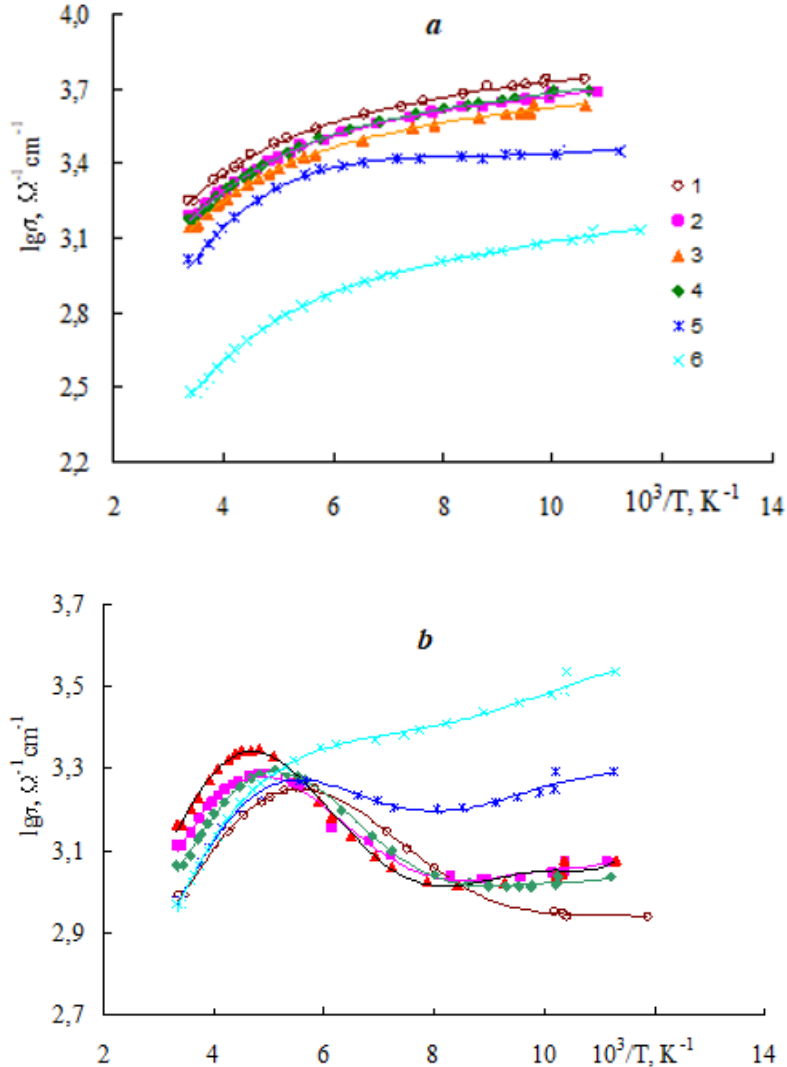

Fig. 1. Temperature dependences of the electrical conductivity before (a) and after annealing (b) crystals of the Pb$_{0.75}$Sn$_{0.25}$Te solid solution with an excess of lead. Curves 1-6 refer to samples 1-0; 2-0.01; 3-0.05; 4-0.1; 5-0.5; 6-1.0 at.% excess lead, respectively.

The absolute values of α and R_x of annealed samples at 77 K become larger than those of annealed samples, and the sign of the coefficient R_x for annealed samples at low temperatures (up to ~190–200 K) is positive (with a negative sign of α). For a sample with 1.0 at.% excess Pb, the sign of R_x is positive over the entire temperature range (Figure 2a,b).

Thus, annealing at 673 K for 120 hours radically changes the values, sign, and temperature dependences of the electrical parameters of Pb$_{0.75}$Sn$_{0.25}$Te solid solution crystals with overstoichiometric lead atoms.

As in the case of unannealed samples, in annealed samples the sign of the coefficient α at 77 K is negative, with increasing temperature α of the samples (except for the sample with 1.0 at.% excess Pb, in which no semiconductor region is observed on $\alpha(T)$) change their sign from negative to positive, and increases with temperature (Figure 2a).

The values of the power factor $\alpha^2\sigma$ of some annealed and unannealed crystals with excess lead exceed the values of the power factor of the composition Pb$_{0,75}$Sn$_{0,25}$Te. So, for example, the power factors of an unannealed crystal with.

See designations in Fig.1 0.5 at.% Pb at 300 K ~ 1.7; 8.2 and 30 times, and for a crystal with 0.05 at.% Pb at 300 K is 1.5 times higher than the power factor of a pure crystal.
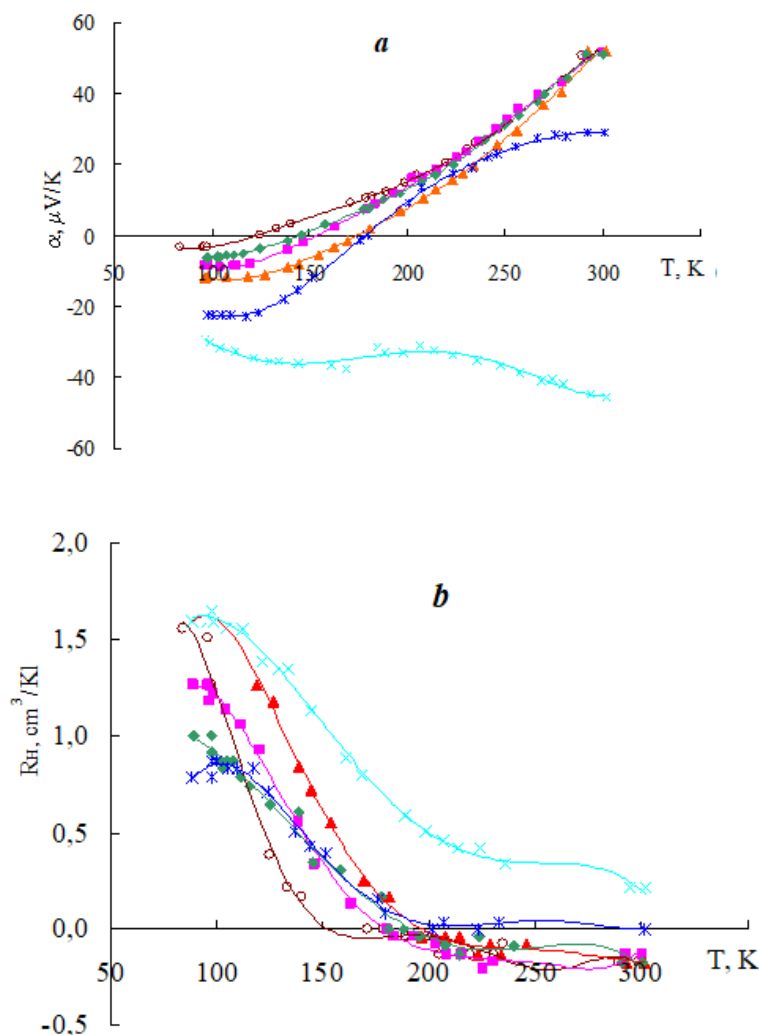
Fig. 2. Temperature dependences of thermopower (a) and Hall (b) coefficients of Pb$_{0.75}$Sn$_{0.25}$Te solid solution crystals with lead excess after annealing.

These data show that in the studied unannealed Pb$_{0.75}$Sn$_{0.25}$Te crystals, in addition to vacancies in the cation and anion sublattices, there are various acceptor and donor type structural defects. Excess lead atoms, compensating for acceptor defects, lead to a decrease in the concentration of holes and σ. Excess Pb atoms can also form electrically neutral complexes with free tellurium atoms in the crystal. Therefore, at concentrations of 0.5 and 1.0 at.% excess lead, α crystals of Pb$_{0.75}$Sn$_{0.25}$Te at ~77K have positive signs.

The data on the values of R$_x$ and σ (Figures 1 and 2b) at 77 K indicate that annealing heals structural defects (except for cationic and anionic vacancies), which leads to a decrease in the concentration of current carriers and electrical conductivity, as well as to an increase in the absolute value of the thermopower coefficient at 77K. As a result of the healing of structural defects of an acceptor nature, the introduced excess lead atoms with a low concentration create new donor centers in the crystal, increasing the concentration of the current carriers, the absolute values of the thermoelectric coefficient and electrical conductivity. At the same time, with an increase in the concentration of excess lead, the value of the positive Hall coefficient at low temperatures will decrease.

In PbTe-SnTe solid solutions, the electron mobility varies from 1600 for pure PbTe to 200 cm^2/V·sec, for SnTe, having a minimum value of ~80 cm^2/V·sec for compositions containing 70 mol.% SnTe. The hole mobility at the content of SnTe (up to 30 mol.%) slightly changes depending on the composition and is equal to ~500÷400 cm^2/V·sec [3]. Apparently, in the Pb$_{0.75}$Sn$_{0.25}$Te crystals studied by us, the values of μ$_n$ are somewhat lower than the hole mobility, which leads to a discrepancy between the sign of R$_x$ and the sign of the thermopower coefficient. The filling of cationic vacancies with excess of Pb atoms, as well as the formation of electrically neutral complexes vacancy-excess of Pb atoms, should lead to a weakening of the scattering of current carriers from vacancies and an increase in their mobility. Indeed, such an increase in the mobility of the current carriers, calculated from μ= R$_x$σ, is observed in samples with a low content (up to 0.05-0.10 at.%) of lead.

9

In addition, the semiconductor dependence σ(T) in the temperature range of ~100÷210 K in samples with 0 ÷ 0.1 at. % excess lead indicates that there are donor centers in the $Pb_{0.75}Sn_{0.25}Te$ solid solution with an activation energy of 0.06-0.11 eV. The ionization of these centers leads to an increase in the electron concentration and a change in the sign of R_x to negative. Indeed, the sign reversal of R_x occurs at temperatures corresponding to the semiconductor region σ(T) and it is not observed in samples with 0.5 and 1.0 at. % excess Pb, in which there is no semiconductor region on σ(T).

In PbTe and $Pb_{0.75}Sn_{0.25}Te$ crystals, the valence band consists of two subbands, and with increasing temperature, the light hole band shifts towards the heavy hole zone, and the contribution of heavy holes to the conductivity and the thermopower coefficient

increase. As a result, the decrease in the electrical conductivity of crystals above ~180 K increases with temperature, and the thermopower coefficient α, increasing, changes its sign from negative to positive.

The table shows the thermoelectric parameters of $Pb_{0.75}Sn_{0.25}Te<Pb>$ crystals, structures (In-Ag-Au) - $Pb_{0.75}Sn_{0.25}Te<Pb>$. The table also shows the real thermoelectric efficiency of a thermoelement based on p- $Pb_{0.75}Sn_{0.25}Te<Pb>$ and n- $Pb_{0.75}Sn_{0.25}Te< 1,0at.\%Pb >$, determined by [7]

$$Z_r = (T - T_{0min})/T_{0min}^2$$

at T=300K. Here $T_{0min} -$ is the minimum temperature of the cold junction of the thermoelement when the optimal current passes through it.

Table

Electrical conductivity σ($\Omega^{-1}cm^{-1}$), thermopower coefficients α(μV/K) and thermal conductivity χ·10^2(W/cm·K) of $Pb_{0.75}Sn_{0.25}Te<Pb>$ crystals, and contact resistance r_k·10^3 (Ω· cm^2), thermoelectric efficiency of a real thermoelement Z_r.

Content of excess Pb in solid solution $Pb_{0.75}Sn_{0.25}Te<Pb>$, at %	σ	α	χ	r_k	Z_r.
0,0	773,2	109,8	2,06	0,39	
0,01	1210,9	36,0	2,56	0,24	
0,05	1212,1	-13,1	2,50	0,15	
0,5	1123,6	-48,6	3,37	0,46	
1,0	1026,3	-160,1	1,57	0,38	0,81·$10^{-3}K^{-1}$

CONCLUSIONS

The results show that the $Pb_{0.75}Sn_{0.25}Te$ crystals after growth contain structural defects predominantly of an acceptor nature, which are healed by annealing at ~ 673 K. The dependences of the electrical parameters of the unannealed and annealed samples of these crystals on the content of excess lead, annealing, and temperature are satisfactorily explained by the assumptions of partial filling and compensation of structural defects (cationic vacancies) at low lead

concentrations, the creation of new donor levels by Pb atoms, the existence of donor centers in the crystals, and unequal a decrease in the mobility of electrons and holes during the formation of this solid solution and an increase in the contribution of heavy holes in the valence band to the conductivity with temperature.

The real thermoelectric efficiency of a termoelementmade on the basis of the studied is equal to 0,81·$10^{-3}K^{-1}$ at 300K.

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