ELECTRICITY AND HEAT TRANSFER IN TIN TELLURIDE SINGLE CRYSTALS WITH DIFFERENT CATION VACANCY CONCENTRATION

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Single crystals of tin telluride containing up to 1.0 at. % over stoichiometry of tin were grown by the Bridgman method, and their electrical conductivity σ, thermoelectric power α and thermal conductivity χ coefficients were investigated in the range of ~ 90-305 K. The lattice χ_l and electronic χ_e components of thermal conductivity and thermal resistances created by cation vacancies have been determined. It is shown that the Sn atoms introduced over stoichiometry at low (up to ~ 0.05 at. %) concentrations create electrically neutral complexes with cation vacancies, which leads to a decrease in the concentration of current carriers, σ, χ_l and χ_e, and at high concentrations, filling these vacancies, as well as creating new impurity levels, they lead to an increase in the indicated parameters. The dependences of the thermopower coefficient of the samples on the concentration of excess tin and temperature are satisfactorily explained by the model of two valence bands.

Keywords: single crystal, thermal conductivity, valence band, vacancy.
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1. INTRODUCTION

Tin telluride, especially its solid solutions are promising materials for thermo and photoelectric converters.

These compounds have a one-sided homogeneity region shifted towards excess tellurium and are characterized by a high concentration (~ 10^{20} cm^{-3}) of intrinsic defects (mainly a vacancy in the tin sublattice) [1-5]. Electroactive tin vacancies in SnTe should affect the concentration of current carriers, on scattering of electrons and phonons, i.e. on the mobility of current carriers, lattice and electronic components of the thermal conductivity, which determine the effectiveness of the material for application. However, in the literature, there are almost no works devoted to the study of the influence of these cation vacancies on the indicated parameters of SnTe single crystals.

The concentration of cation vacancies in SnTe can be varied by introducing into the melt of the stoichiometric composition excess (over stoichiometry) tin atoms. In order to elucidate the effect of tin vacancies on the electrical properties and thermal conductivity of tin telluride crystals, in this work SnTe single crystals containing 0, 0.01, 0.05, 0.1, 0.5 and 1.0 at.% excess over the stoichiometry tin atoms were grown by the Bridgman method, and their electrical conductivity σ, thermoelectric power α and thermal conductivity χ coefficients have been investigated in the range of ~ 90-305*K*.

2. EXPERIMENTAL TECHNIQUE

The synthesis of SnTe samples from a stoichiometric batch mixture (from a batch mixture containing 50 at. % Sn a nd 50 at. %Te) and SnTe samples from a batch mixture of stoichiometric composition (batch) to which an excess of up to 1.0 at.% tin was additionally added, was carried out by direct fusion corresponding amounts of initial components in quartz ampoules evacuated to ~ 10^{-2} *Pa*, at a temperature of ~1135*K* for 6 hours.

Tin of grade *OVCh*-000 and tellurium of grade *T-SCh* (99.999) were used.

The studies were carried out on single-crystalline samples annealed in spectrally pure argon at 773 K for 120 hours.

Diffraction patterns obtained on XRD Bruker D8 ADVANCE diffractometer confirmed the high level of crystallinity of the samples under study. The refined unit cell parameters for tin telluride turned out to be 6.318 (1)$\mathring{A}$ (space group $Fm\bar{3}m$).

The length of single crystal ingots with a diameter of 13-14*mm* was ~25*mm*. The homogeneity of the single-crystalline ingots was also checked by measuring the electrical resistance at various sections along the ingot.

Samples in the form of a cylinder with a diameter of 13-14*mm* and a height of ~10*mm* were cut from single-crystalline ingots on an electric spark installation.

The disturbed layers formed at the ends of the samples during cutting was removed by electrochemical etching.

The electrical parameters and thermal conductivity of the samples were measured by the methods described elsewhere [6] in the direction of the length of the ingots.

The measurement error of these parameters in the entire temperature range did not exceed 5%.

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3. RESULTS AND DISCUSSION

Experiments have shown that the temperature dependences of σ for all samples have a metallic character (figure1a) With an increase in the concentration of excess tin up to 0.05 at. %, σ of the sample at a given temperature decreases, and then with an increase in the concentration of tin, σ increases and approaches σ of the stoichiometric composition. $\alpha(T)$ curves for stoichiometric samples and samples with 0.01 and 1.0 at.% excess tin have minima at ~190 ÷220*K*.

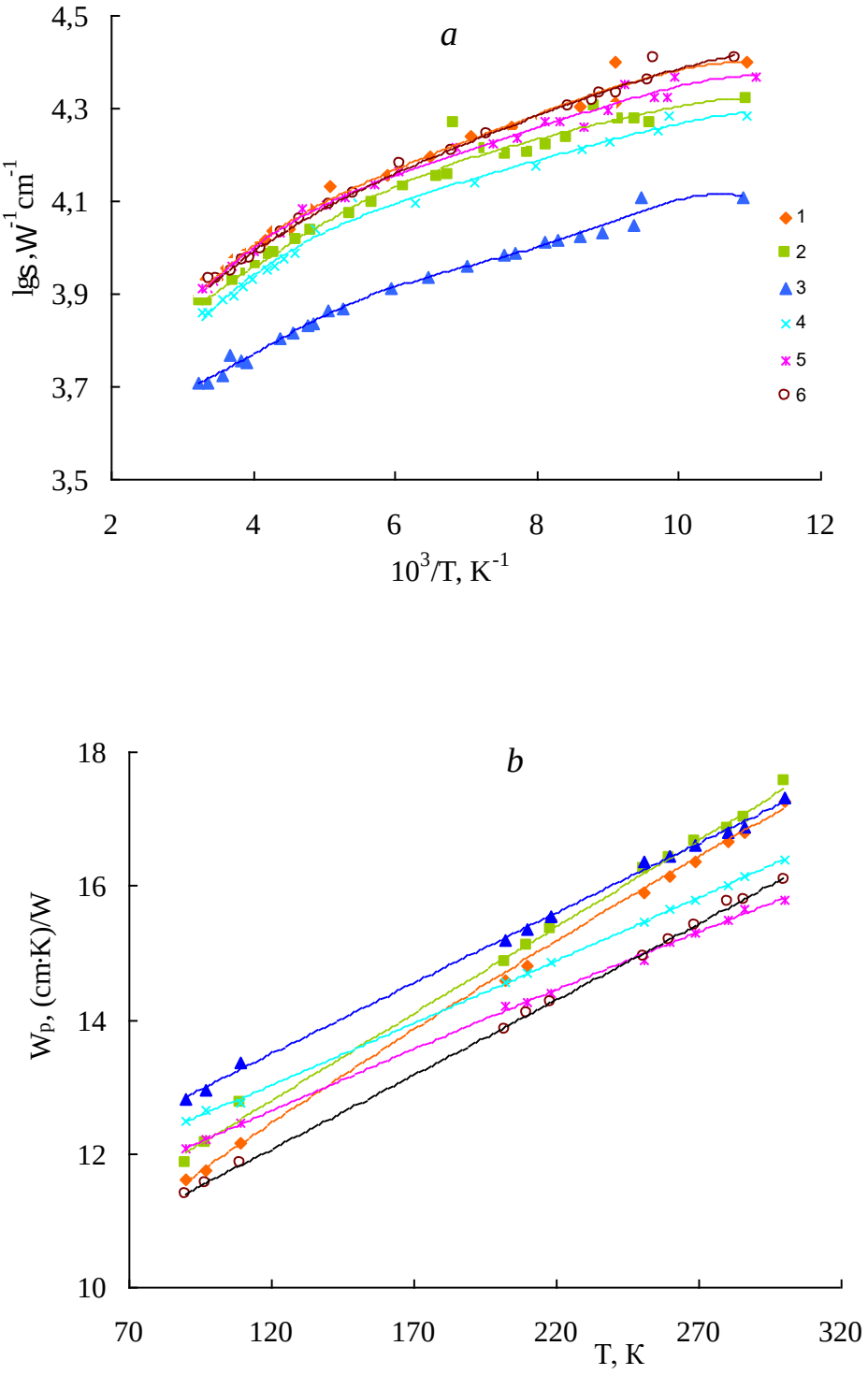

Fig.1. Temperature dependences of electrical conductivity (1a) and of the thermal resistance of SnTe samples with the addition: 0 (1); 0.01 (2); 0.05(3); 0.1 (4);0.5(5) and 1.0(6) at. % Sn over stoichiometry, annealed at 773*K* for 120 hours.

In the region of impurity conductivity, in the case when the semiconductor is opaque in the infrared region, its thermal conductctivity can be expressed in the form [7, 8]

$$\chi = \chi_l + \chi_e = \chi_l + L\sigma T$$

For semiconductors with a parabolic band in the case of arbitrary degeneracy and elastic scattering of current carriers $L = A\,(k/e)^2$ and $\chi_e = A\,(k/e)^2\,\sigma T$ where k is the Boltzmann constant, e is the electronic charge, and A is a parameter depending on the scattering parameter. The value of A was determined from the experimental values of the thermo-e.m.f. coefficient α of samples we measured using a curve $A = f(\alpha)$ [7, 8].

The measured values of χ, as well as the calculated values of χ_l and χ_e, at 90 and 305K are given in the Table. The Table also shows the values of σ and α of the samples at 90 and 305K. From the data in the Table it follows that heat in the studied samples is transferred mainly by lattice vibrations. The electronic component of the thermal conductivity of the samples does not exceed ~ 30% of the total thermal conductivity.

In single-crystalline SnTe samples with an increase in the concentration of excessively introduced tin to 0.05 at. % the lattice thermal conductivity decreases both at ~90 and at 305K, and increases above 0.05 at.%.

Fig. 1b shows the temperature dependences of the lattice thermal resistance ($W_l = 1/\chi_l$) of SnTe samples with excessively introduced tin. The rectilinear character of the $W_l(T)$ dependences shows that thermal resistance is created mainly due to phonon-phonon scattering.

Tin vacancies in SnTe create phonon scattering point defects. The thermal resistance of a material with point defects can be represented as [7]

$$W_l = Wo + D/c^2$$

where W_o is the thermal resistance of the material without defects, D and c are constants. It is seen that point defects make a temperature-independent contribution to the thermal resistance. This was experimentally observed in PbTe doped with iodine [9], as well as in $Pb_{1-x}Mn_xTe$ [10] and $Sn_{1-x}Mn_xTe$ crystals [11, 12]. In this regard, the value of the additional thermal resistance ΔW_o caused by defects can be determined by extrapolating the linear dependence of the lattice part of the thermal conductivity W_l on temperature at low temperatures. When extrapolating the linear dependence of W_l on T in the region of low temperatures, a segment equal to the thermal resistance created by defects in the studied SnTe samples is cut off on the axis of thermal resistance at $T = 0K$. The ΔW_o values are also shown in the Table.

Table 1.

Electrical conductivity σ, coefficient of thermo-e.m.f. α, lattice (χ_l), electronic (χ_e) components of thermal conductivity and additional thermal resistance ΔW_0, of SnTe samples with excessively introduced tin

Content of Excessively introduced tin, at.%	At ~90K temperature				At ~305K temperature				
	σ, $\Omega^{-1}\cdot cm^{-1}$	α, μV/K	χ_l, W/m·K	χ_e, W/m·K	σ, $\Omega^{-1}\cdot cm^{-1}$	α μ V/K	χ_l, W/m·K	χ_e W/m·K	ΔW_0, m·K/W
0	21875	8,7	10,35	4,23	7086	5,6	5,77	5,12	6,3
0,01	20951	22,8	9,23	3,30	7649	22,3	5,62	4,02	7,7
0,05	12861	20,8	8,80	2,03	5112	19,7	5,55	2,68	8,7
0,1	19282	21,3	10,80	3,04	7249	20,0	6,23	3,81	8,5
0,5	23392	23,7	10,61	3,68	8187	35,5	6,33	4,17	8,2
1,0	25557	8,5	9,41	4,60	8519	6,5	5,66	5,11	8,0

It is assumed that Sn atoms at low concentrations (up to 0.05 at. %) being distributed over the SnTe sample create donor centers [13]. These donor centers, compensating for doubly charged cation vacancies in SnTe create electrically neutral complexes with them. Compensation for doubly charged cation vacancies leads to a decrease in the hole concentration and accordingly to a decrease in electrical conductivity σ and an increase in the thermo-e.m.f. α. Electrically neutral complexes of vacancy-tin atoms, scattering phonons, reduce the lattice part of the thermal conductivity. With a further increase in the excess tin content, additional donor centers created by tin lead to an increase in the electron concentration in the sample, i.e. to the growth of σ and χ_e. At high contents of excessively introduced tin, some of the tin atoms also located in the tin vacancies decrease the concentration of structural defects (vacancies), which ends with an increase in χ_l. This is also evidenced by the fact that at high concentrations of excessively introduced Sn (more than 0.5 at.%) the value of the thermoelectric power strongly decreases. This assumption is in good agreement with the data on the dependence of the additional thermal resistance ΔW_o on the concentration of excessively introduced tin. It was shown elsewhere [14-16] that the features in the electrical parameters of SnTe can be explained on the basis of the model of two valence bands separated by an energy gap in the presence of interband scattering. According to this model, the valence bands of tin telluride at ~100K are

separated by an energy gap of $0.03eV$. Light holes have an effective mass of $0.4m_0$, a mobility of ~3500 $cm^2/V{\cdot}s$, and heavy holes have an effective mass of $3m_0$, and a mobility of ~ 50 $cm^2/V{\cdot}s$. With increasing temperature, the gap between the two maxima of the valence bands decreases. Up to the temperature corresponding to the minimum on the $\alpha(T)$ dependence light holes play the main role in the conductivity. A decrease in the gap with increasing temperature between the subbands of light and heavy holes is accompanied by an increase in the contribution of heavy holes to the conductivity and the Seebeck coefficient.

Apparently, starting from the temperature corresponding to the minimum on the $\alpha(T)$ curve, the contribution of heavy holes to σ and α gradually becomes decisive, as a result of which α increases with temperature, and the decrease in σ of the samples increases with temperature. It can be seen that the two-band model also satisfactorily explains the temperature dependences of the Seebeck coefficient of SnTe single crystal samples with an excess of Sn.

4. CONCLUSION

Single crystals of the SnTe compound with superstoichiometric tin up to 1.0 at.% were grown by the Bridgman method, their electrical conductivity σ and thermoelectric power α and thermal conductivity χ coefficients were investigated in the temperature range from 90 to 305K. The electronic χ_e and lattice χ_l components of the thermal conductivity, as well as the thermal resistance caused by structural defects (mainly by cation vacancies) have been calculated. It is shown that tin atoms introduced over stoichiometry up to 0.05 at. % create as donor centers electrically neutral complexes with cation vacancies, as a result of which the concentration of current carriers decreases and the scattering of electrons and phonons increases, leading to a decrease in σ and χ_l and an increase in α. After 0.05 at. %, Sn atoms filling cation vacancies and creating new current carriers lead to an increase in σ and χ_l, and a decrease in α. Heat in the studied SnTe samples with excessively introduced tin atoms is transported mainly by lattice vibrations, and the electronic component of thermal conductivity in them does not exceed ~30% of the total thermal conductivity. Structural cation vacancies play a significant role in the thermal resistance in samples. The dependences of α on the concentration of excess Sn and temperature are well explained by the two-band model.

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