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THERMOELECTRIC FIGURE OF MERIT OF $TlIn_{1-x}Yb_xTe_2$ ($0 \le x \le 0.10$)

On the basis of the temperature dependences of the electrical conductivity σ, the Seebeck coefficient α and total thermal conductivity χ_{tot} in the solid solutions $TlIn_{1-x}Yb_xTe_2$ ($0 \le x \le 0.10$) thermoelectric figure of merit Z have been calculated in the temperature range of 80 – 1000 K. It was established that the maximum thermoelectric figure of merit $Z \approx 3\ K^{-1}$ reaches at 800 K for the solid solution of $TlIn_{0.9}Yb_{0.1}Te_2$. It is shown that the growth of Z is mainly due to increasing of the hole mobility and concentration of defects in the samples.

Key words: thermoelectric figure of merit, thermopower, solid solution, thermoelectric efficiency, thermal conductivity.

Introduction

Sufficiently intensive studies of electrical and thermoelectric properties of $TlIn_{1-x}Yb_xTe_2$ solid solutions [1 – 6] are connected primarily with the use of these materials in a variety of energy converters and, particularly in the manufacture of thermoelectric transducers operating at high temperatures.

According to [1] the solubility region of $TlYbTe_2$ in $TlInTe_2$ at room temperature is up to 10 %. Transition from $TlInTe_2$ to $TlIn_{1-x}Yb_xTe_2$ is accompanied by the increasing of hole concentration. The increasing of hole concentration is connected with arising of various structural imperfections, vacancies and anti-structure defects in these alloys; emerging intrinsic defects, mainly vacancies, are electroactive.

Synthesis of Samples

The synthesis of $TlInTe_2 - TlYbTe_2$ solid solutions was conducted by fusing the initial components taken in stoichiometric ratio. For the synthesis high purity materials (99.999 – 99.992 %) were used. According to the constitution diagram [1], a minor deviation from stoichiometry in any direction may result in heterophase samples. Therefore, the batch was added up to 0.05 mass % of tellurium over the stoichiometric requirement. The synthesis was carried out in the evacuated to 10^{-2} Pa, and sealed quartz ampoules in the following way: the temperature of the heater with quartz ampoules containing substance, was raised at a rate of 20 – 25 K/h up to 750 K. The samples were kept for 3 – 4 hours at this temperature and then were heated to 1100 K and kept for another 4 hours. After homogenization lasting for 20 – 25 hours at 1250 K the ampoule was moved with the speed of 2 – 3 mm/h through the zone with a temperature gradient of 50 K/cm.

The obtained ingots were cooled slowly (2 K/hr) to 1000 K and then down to 500 K at a rate of 4 K/h, following which the furnace was turned off. As a result, single crystals and large-block polycrystalline p-$TlIn_{1-x}Yb_xTe_2$ were obtained. The measurements were performed on polycrystalline samples.

Results and discussion

According to A.Ioffe [7], increasing the value of μ / χ_{ph} (χ_{ph} – phonon part of the heat conductivity, mobility of charge carriers) leads to an increase in Z. It means that a quantitative decrease in phonon scattering is fully compensated by an increase in scattering by defects [8]. As the wavelength of electrons is greater than that of phonons, it leads to total increase in μ / χ_{ph}. The thermoelectric peculiarities of the $TlIn_{1-x}Yb_xTe_2$ solid solutions show that these materials can provide rather high thermoelectric figure of merit.

It is known that the efficiency of a thermoelectric transducer is determined by the following formula:

$$Z = \alpha^2\sigma/\chi_{tot}, \quad (1)$$

here $\alpha^2\sigma$ – thermoelectric power, χ_{tot} – total heat conductivity.

The temperature dependences of the measured electrical conductivity σ and thermopower coefficient α for $TlIn_{1-x}Yb_xTe_2$ ($0 \le x \le 0.10$) solid solutions in the temperature range of 80 – 1000 K are shown in Fig. 1 and 2, respectively.

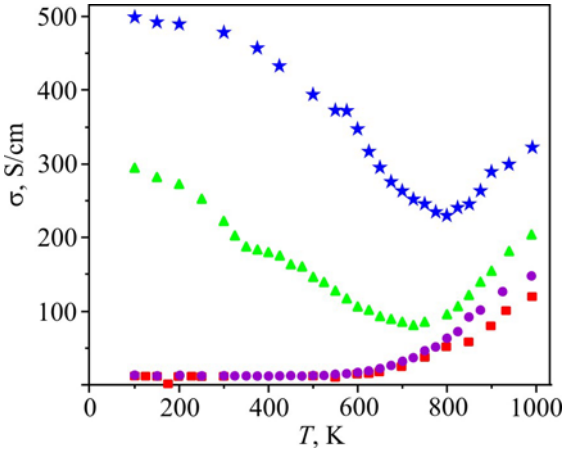

Fig. 1. Temperature dependences of electrical conduction in $TlIn_{1-x}Yb_xTe_2$;
■ – *(x = 0)*, ● – *(x = 0.02)*, ▲ – *(x = 0.05)*, ★ – *(x = 0.10)*.

As seen from Fig. 1, the $\sigma(T)$ dependences for different compositions of the solid solutions are essentially unlike. The region of intrinsic conduction for the initial compound $TlInTe_2$ begins at the temperature ~ 700K while the intrinsic region shifts towards higher temperatures with increase in relative content of ytterbium in $TlIn_{1-x}Yb_xTe_2$ solid solutions.

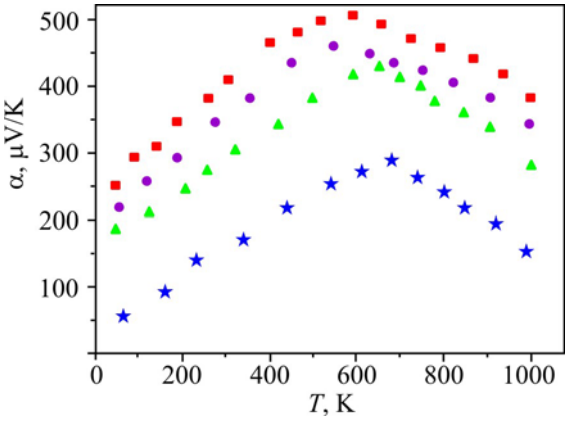

Fig. 2. Temperature dependences of thermopower coefficient in $TlIn_{1-x}Yb_xTe_2$. Markers describing experimental points correspond to the values of x as in Fig. 1.

As seen from Fig. 2, the $\alpha(T)$ dependences have similar character – $\alpha(T)$ grows linearly up to $T \sim 650$ K and then decreases in the intrinsic region – for all compositions and the sign of thermopower coefficients in the investigated temperature range is positive that proves that conduction occurs by holes in $TlIn_{1-x}Yb_xTe_2$ solid solutions.

Total heat conductivity is determined as the sum of phonon χ_{ph} and hole χ_h heat conductivities. Taking into account that $\chi_h = L_0\sigma T$, where $L_0 = (\pi^2/3)\cdot(k/e)^2 = 2.44\cdot10^{-8}$ W·Ω/K (we assume elastic scattering of holes [9]), we get

$$\chi_{tot} = \chi_{ph} + L_0\sigma T. \tag{2}$$

According to the theoretical calculations of G.I.Leibfried and E.Schlömann [10], at temperatures $T > \theta$ phonon conductivity is determined as

$$\chi_{ph} = \frac{12}{5}\cdot\left(\frac{k}{h}\right)^3\cdot\frac{\bar{M}\delta\theta^3}{\gamma_0^2 T} = 5,7\frac{\bar{M}\delta\theta^3}{\gamma_0^2 T} \tag{3}$$

here γ_0 is Grüneisen constant; it is usually on the order of 2 for the most solid state materials; θ is the Debye temperature, $\bar{M}$ is the average mass of the compound atoms, δ is cube root of the volume per atom. For the solid solutions of $TlIn_{1-x}Yb_xTe_2$ $\bar{M}$ can be calculated from $\bar{M} = \left[(1-x)\bar{M}_{TlInTe_2} + x\bar{M}_{TlInTe_2}\right]/2$, where $\bar{M}_{TlInTe_2} = 143.60$, $\bar{M}_{TlInTe_2} = 158.15$; $\theta = 200$K [11]; $\delta = \sqrt[3]{\Omega_0 / N}$, where $\Omega_0 = a^2c$ is the volume of the tetragonal unit cell, N is the number of atoms per unit volume [12]. By substituting the data into Eq. (3), we get the values for χ_{ph}, which are presented in the Table. The values of χ_{tot}, calculated on the basis of Eq. (2) are also given in the Table. Having the values of χ_{tot}, the values of Z can be calculated according to Eq. (1) (see the Table).

Table

Main parameters influencing the figure of merit for $TlIn_{1-x}Yb_xTe_2$ solid solutions

Samples	T	m_n^*	m_p^*	χ_{ph}	χ_{tot}	ΔW_i	Γ
$x = 0$	100	0.040	0.55	0.98	0.98		
	300	0.040	0.53	0.95	0.95		
	500	0.040	0.53	0.79	0.80		
	600	0.039	0.52	0.73	0.78		
	700	0.038	0.51	0,68	0.75		
	800	0.037	0.51	0.62	0.76		
	900	0.036	0.50	0.60	0.78		
$x = 0.02$	100	0.036	0.52	0.86	0.87	14	2.9
	300	0.036	0.52	0.82	0.83	16	
	500	0.035	0.51	0.64	0.67	29	
	600	0.035	0.51	0.60	0.66	50	
	700	0.034	0.50	0.58	0.68	58	
	800	0.033	0.49	0.54	0.70	69	
	900	0.032	0.48	0.47	0.74	78	
$x = 0.05$	100	0.034	0.48	0.76	0.83	29	7.1
	300	0.034	0.47	0.63	0.78	35	
	500	0.033	0.47	0.58	0.72	49	

Table (continued)

Samples	T	m_n^*	m_p^*	χ_{ph}	χ_{tot}	ΔW_i	Γ
	600	0.032	0.46	0.56	0.70	58	
	700	0.031	0.45	0.55	0.72	69	
	800	0.030	0.45	0.51	0.74	76	
	900	0.029	0.44	0.46	0.78	84	
$x = 0.10$	100	0.031	0.47	0.66	0.78	49	12.3
	300	0.031	0.47	0.42	0.75	133	
	500	0.030	0.46	0.37	0.76	143	
	600	0.029	0.46	0.32	0.78	183	
	700	0.028	0.46	0.30	0.85	200	
	800	0.027	0.45	0.29	0.88	237	
	900	0.026	0.45	0.24	0.94	255	

Here, m_n^* and m_p^* are effective masses of electrons and holes, correspondingly [16]; χ_{ph} 10^{-2} ($W \cdot cm^{-1} \cdot K^{-1}$) is coefficient of phonon thermal conductivity; $\chi_{tot} \cdot 10^{-2}$ ($W \cdot cm^{-1} \cdot K^{-1}$) is coefficient of total thermal conductivity; ΔW_i ($cm \cdot K \cdot W^{-1}$) is coefficient of thermal resistance; $\Gamma \cdot 10^3$ is parameter of disorder.

For taking into consideration the influence of disorders in the lattice thermal conduction we used the theory of Klemens [13], which takes into account scattering phonons by point defects in addition to the Umklapp scattering processes.

$$\chi_{ph} = \chi(\omega_0 / \omega_d)\mathrm{arctg}(\omega_d / \omega_0), \tag{4}$$

where, $(\omega_0 / \omega_d) = k / (2\pi^2 \chi_V \omega_d A)$ and $A = (1/4V^2 N)\Gamma$. Here, χ_V is heat conductance of the stoichiometric compound in the absence of defects influence, $\omega_d = \theta \cdot k/\hbar$ is maximum frequency in the Debye model (Debye frequency), ω_0 is the frequency at which the value of relaxation times due to U-processes and scattering on defects are equal, v is average sound velocity in the crystal, N is the number of atoms in a unit volume, Γ is the parameter of disorder which is equal to

$$\Gamma = x(1-x)\left[(\Delta\overline{M} / \overline{M})^2 + \varepsilon(\Delta\delta/\delta)^2\right], \tag{5}$$

and takes into consideration simultaneous influence of a local change in density and elastic properties, ε – characterizes elastic properties of medium and $\Delta\overline{M} / \overline{M}$ is a relative change in mass when basic atoms are replaced by impurity atoms, which can be expressed as:

$$\Delta\overline{M}/\overline{M} = \frac{\overline{M}_{TlYbTe_2} - \overline{M}_{TlInTe_2}}{(1-x)\overline{M}_{TlInTe_2} + x\overline{M}_{TlYbTe_2}}$$

According to [14] a value of Δδ/δ can be computed from the difference of parameters of elementary cell of matrix a_{mat} and impurity a_{imp} as:

$$\frac{\Delta\delta}{\delta} = \left(\frac{a_{TlInTe_2} - a_{TlYbTe_2}}{a_{TlInTe_2}}\right)\frac{\eta}{1+\eta}, \tag{6}$$

where, $\eta = (1+\nu)/\left[2(1-2\nu)\right]$, ν is Poisson`s ratio. All parameters necessary for calculations (v, ε, ν, θ, N etc.) were taken from [5, 11 – 12; 15] and linearly extrapolated for $TlIn_{1-x}Yb_xTe_2$ solid solutions as $P = (1-x)P_{TlInTe_2} + xP_{TlYbTe_2}$, where P is the necessary parameter for calculation thermal conductivity of the solid solutions.

It should be noted that the values of $\chi_{ph}(T)$ calculated by expressions (3) and (4) insignificantly differ. The values of the Γ parameter for various x in the $TlIn_{1-x}Yb_xTe_2$ are presented in the Table. From the comparison of stoichiometric compound $TlInTe_2$ with the solid solutions of $TlIn_{1-x}Yb_xTe_2$ it is clear that the parameter of disorder Γ changes by nearly 4.3 times at room temperature. It means that for other parameters being equal, thermal resistance arising in the solid solutions due to disorder must be much more than in $TlInTe_2$. It gives a reason that the determined values of Γ are true reflection of real relation of the basic factors responsible for additional scattering of phonons by point defects. It leads to the additional thermal resistance as in [14]:

$$\Delta W_i = 1/\chi_{ph} - 1/\chi_{\nu}.$$

Calculated data for ΔW_i are also presented in the Table.

Having all necessary data set in the Table allows us to analyze the thermoelectric peculiarities of the $TlIn_{1-x}Yb_xTe_2$ solid solutions more precisely for getting rather high thermoelectric figure of merit. The dependence of Z on the content of Yb in $TlIn_{1-x}Yb_xTe_2$ solid solutions for fixed temperatures 300, 500 and 800 K is described in Fig. 3. As is seen from the figure, Z increases both with temperature and the content of Yb in the solid solutions; Z has its minimal value for $x = 0$ at $T = 300$ K and maximal value for $x = 0.1$ at 800 K.

It is clear that increasing α, σ and decreasing χ_{lot} lead to an increase in the values of thermoelectric power ($\alpha^2\sigma$) and thermoelectric figure of merit (Z). Strong influence of the content of Yb atoms on Z in the investigated solid solutions is connected with high content of intrinsic defects in the materials [8].

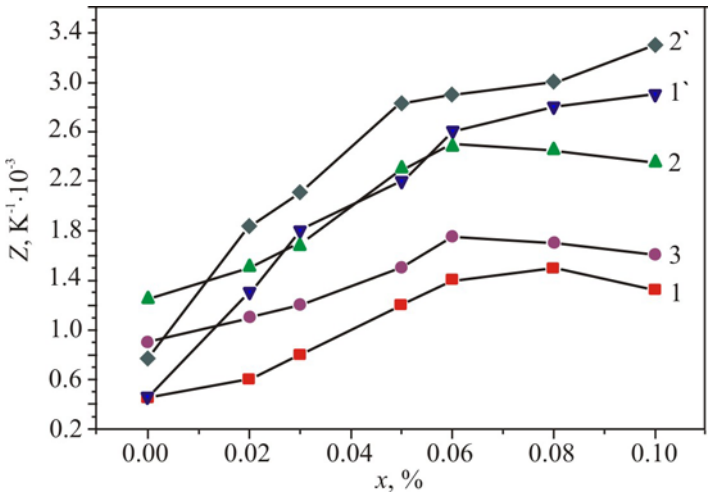

Fig. 3. The dependence of the thermoelectric figure of merit on the content of Yb in $TlIn_{1-x}Yb_xTe_2$ solid solutions at the temperatures ■ – 300 K, ● – 500 K and ▲ – 800 K.

The peculiarities of temperature dependence of χ_{ph} also may be explained by high concentration of defects in the materials [8]. It should be noted that for the $TlIn_{1-x}Yb_xTe_2$ solid solutions always $\chi_{ph} > \chi_h$, in spite of χ_h rising, but χ_{ph} decreasing with temperature in the temperature range where the material keeps its solid state.

As seen from Fig. 1 and 2, σ is decreasing, but α increasing in the temperature range of 300 – 700 K. Therefore the decreasing of σ with temperature in the abovementioned temperature range is connected to decreasing mobility of holes. The decreasing of hole mobility with temperature occurs mainly due to scattering of holes on thermal lattice vibrations and on defects according to $\mu_h \sim T^{-0.7}$ [1, 4]. The defects arise in the $TlIn_{1-x}Yb_xTe_2$ solid solutions mainly due to vacancies of In and *Yb*, and *Yb* atoms vacancies have more effect than In ones. The latter is connected with the large value of screening of *Yb* atoms ("crystal" ionic radii of $R(Yb^{3+})$ = 100.8 pm, $R(In^{3+})$ = 94 pm [16]) in the $TlIn_{1-x}Yb_xTe_2$. At the same time phonon-phonon and phonon-defect scattering effects bring to decreasing of χ_{ph} with temperature as $\chi_{ph} \sim T^{-1.2}$. With increasing of *Yb* atoms content in the solid solutions the values of χ_{ph} and index n in the expression of $\chi_{ph} \sim T^{-n}$ also decreases. As a result, for $x \ge 0.05$ we have the following relation $\mu_h/\chi_{ph} \sim T^{0.5}$. Thus, the increasing of Z up to ~ 700 K is due to linear increasing of $\alpha(T)$ (Fig. 2).

As seen from the Table, for the temperatures $T > 700$ K the rise in x leads to increasing of $\chi_{tot}(T)$. It is connected with high contribution of bipolar thermal conductivity (χ') into the total heat conductivity. So, for the temperatures $T > 700$ K its contribution to the total heat conductance is more than 40 %. Thus, at that case the expression (2) may be rewritten as $\chi_{tot} = \chi_{ph} + \chi'$, where $\chi' = (\sigma_n + \sigma_h) L_0 \cdot T$.

Conclusion

It is shown that the solid solutions of $TlIn_{1-x}Yb_xTe_2$ at $x \ge 0.05$ are promising materials for practical use in the thermoelectric transducers operating at high temperatures. The following features of those materials have been established:

- the wavelength of holes is greater than wavelength of phonons and this fact leads to higher values of Z;
- due to the peculiar defect structure of the $TlIn_{1-x}Yb_xTe_2$ solid solutions, the condition of $\mu_h / \chi_{ph} >> 1$ for the charge carriers and phonons is fulfilled, which resultы in gaining higher values for Z;
- the increasing of the level of submission of In atoms with *Yb* ones leads to an increase in the values of thermoelectric power ($\alpha^2\sigma$) and thermoelectric figure of merit (Z);
- the maximum thermoelectric figure of merit $Z \approx 3$ K^{-1} is reached at 800 K for the solid solution of $TlIn_{0.9}Yb_{0.1}Te_2$.

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