THERMOELECTRIC PROPERTIES OF SOLID SOLUTION OF $TlIn_{1-x}Yb_xTe_2$ ($0 \le x \le 10$)

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According to the temperature deoendences of the electrical conductive (σ), the Hall coefficient (R), thermo power (α) and thermoelectric figure of merit (Z) over a wide temperature range and hole concentration in $TlIn_{1-x}Yb_xTe_2$ solid solutions. It is established that, increasing number of yttrium atoms up to x = 0.10 substituting indium atoms leads to rising of Z in $TlIn_{1-x}Yb_xTe_2$. In comparison with $TlInTe_2$ mainly due to the scattering of phonons and holes on defects, as well as increasing the hole mobility of them when replacing ytterium to indium.

Keywords: electrical conductivity, thermal conductivity, thermoelectric figure of merit, effective mass of charge carriers, scattering on defects.
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According to the Ioffe criteria [1], increasing μ/χ_{ph} (μ - mobility of charge carriers, χ_{ph} - is the phonon fraction of thermal conductivity) is caused change in the kinetic properties of materials, which based on an additional number of defects are formed during the process of crystal lattice distortion. Such objects are characterized by interesting physical processes: high mobility of charge carriers, low phonon thermal conductivity and functioning prospects over a wide temperature range [2]. This means that decreasing the intensity of phonon scattering on phonons is fully compensated by the increasing scattering on impurities (or defects) [2]. Since the electron wavelength is longer than the phonon wavelength, this leads to an overall increasing of μ/χ_{ph}.

These features can provide a very high thermoelectric figure of merit Z in $TlIn_{1-x}Yb_xTe_2$ solid solutions at high temperatures. It is known [1] that the efficiency of a thermoelectric transformer is determined:

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

Where, χ_{tot} – is total thermal conductivity. In the calculation of temperature dependence of χ_{tot} error, the integral radiation of heat flux was taken into account. The experimental data on $\chi_{tot}(T)$ are given in [3].

From the above formulas (1), it can be seen that a high-quality thermoelectric material must simultaneously have high electrical conductivity, high thermoelectrical power and low thermal conductivity. Thermoelectric power and electrical conductivity are determined only by the electronic properties of the material, and therefore they are often combined into a quantity $P = \alpha^2 \sigma$ that is called "power factor". In this aspect, one of the fundamental parameters of the electron spectrum of semiconductor is a band gap E_g. Another important parameter of formula of thermoelectric figure of merit (Z) is the effective mass of charge carriers m^*. The relationship between E_g and m^* is very weak. Increasing of Z is associated with a high value of α, and is obtained due to the large effective mass of charge carriers, and a large m^* leads to decreasing σ (high mobility of charge carriers cannot be obtained with a large effective mass). Therefore, the implementation of all these conditions in one material is difficult. In general, the dependence of Z on temperature and charge carrier concentration is more difficult. However, at a certain approximation, the relationship between Z_{max} and parameters of charge carriers is described as [1]

$$Z'_{\max} = 1{,}2 \cdot 10^{-7} \frac{\left(m^*\right)^{3/2} \left(\frac{T}{T_0}\right)^{3/2}}{\chi_{ph}} \cdot e^r \qquad (2)$$

where, T_0 =300K. r – parameter of scattering mechanism.

For $TlInTe_2$ compound and solid solutions based on its $TlIn_{1-x}Yb_xTe_2$ occurs p-type material [3]. The temperature dependences of the electrical conductivity (σ), the Hall coefficients (R), and the thermo power (α) are shown in [3]. As can be seen from Fig. 1, when x=0÷0.02 σ(T) increases with x, and at x=0.05÷0.10, first σ(T) decreases to T~700K, and after T~700K it increases. Therefore, a decrease in σ(T) to T~700 K occurs due to a decrease in the mobility of charge carriers, and after T~700 K an increase in σ(T) is associated with an increase in the concentration of charge carriers with the appearance of intrinsic conductivity. In [3], it was established that in $TlIn_{1-x}Yb_xTe_2$ the valence band is parabolic. As is known in this model of the energy spectrum, there is no connection between the effective mass of the

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charge carriers and the band gap. In this case, the temperature and concentration dependence of the effective hole mass almost remains constant. The values of the band gap E_g [3] to T~700K in $TlIn_{1-x}Yb_xTe_2$ do not exceed k_0T. This leads to the fact that at such a band gap the Fermi level lying near the top of the valence band, the concentration of minority carriers and their contribution to transport become negligible. And this leads to increasing thermopower to T~700K.

In order to determining the effect of pointless defects on χ_{ph}, the Clemens theory was used [4], taking into account three-phonon redelivery processes and phonon scattering on spotty defects, according to which

$$\chi_{ph} = \chi_{tot}(\omega_0/\omega_d)arctg(\omega_d/\omega_0) \qquad (3)$$

where, $\omega_0/\omega_d = k_0/\left(2\pi^2\chi_{tot}\omega_d A\right)$ and

$$A = \left(1/4V^2N\right)\cdot\Gamma$$

Here, χ_{tot} is thermal conductivity of stoichiometric equality in the absence of influence of defects, $\omega_d = \theta k_0/\hbar$ is Debye phonon frequency, ω_0- frequency, which is the value of the relaxation time for U – processes and scattering on defects, V is the average sound of velocity in the crystal, Γ is the disorder parameter, equal to [4].

$$\Gamma = x\cdot(1-x\left[\left(\Delta\overline{M}/\overline{M}\right)^2 + \varepsilon\left(\Delta\gamma/\gamma\right)^2\right] \qquad (4)$$

and taking into account the combined effect of local changes of density and elastic properties. In (8), ε-characterizes the elastic properties of the medium, $\Delta\overline{M}/\overline{M}$ is the relative change in mass when replacing the atoms with impurity atoms.

When estimating Γ, the number of atoms in a unit volume of the corresponding composition N is determined by formulas (6). Since in the solid solutions studied by us

$$TlIn_{1-x}Yb_xTe_2 \rightarrow Tl\left[\sum InTe_2\right]_{1-x}\cdot\left[YbTe_2\right]_x \rightarrow \left[TlInTe_2\right]_{1-x}\cdot\left[TlYbTe_2\right]_x$$

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

According to [4], the value of Δγ/γ can be calculated from the difference of the parameters on the base of elementary cell a_{TlInTe_2} and a_{TlYbTe_2}:

$$\frac{\Delta\gamma}{\gamma} = \left[\left(a_{TlInTe_2} - a_{TlYbTe_2}\right)/a_{TlInTe_2}\cdot\left(\eta/(1+\eta)\right)\right], \qquad (5)$$

where, $\eta = (1+\nu)/[2(1-2\nu)]$, ν – Poisson's coefficient.

It is known that increasing of α, σ and decreasing in χ_{tot} lead to increasing the power factor P and Z, however, self-doping of Yb strongly influences the Z value, undoubtedly this is due to the change in the number of intrinsic defects [2]. At the same time, $\chi_{tot}(T)$ is characteristic for more defective materials [2]. If we compare the change of thermal conductivity and its hole component in $TlIn_{1-x}Yb_xTe_2$ has a common pattern, since in $TlIn_{1-x}Yb_xTe_2$ in a solid state is always $\chi_{ph}>\chi_n$. However, the hole thermal conductivity increases with temperature, and $\chi_{ph}(T)$ decreases.

Fig.4 indicates calculation of Z values in solid solutions $TlIn_{1-x}Yb_xTe_2$ which calculated on the base of experimental values of σ(T) , α **(T)** and $\chi_{tot}(T)$ at temperatures of 300, 500 and 800K, respectively. As can be seen from the table, increasing of x in solid solutions $TlIn_{1-x}Yb_xTe_2Tl$ leads to increasing Z. From Fig.4, it can be seen that Z (T) for all samples increases with claiming temperature. Z(T) also increases with decreasing hole concentration. It was found that the sample with x = 0 at T = 300K has the minimum value of Z [5]. .

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It is mentioned that [3], the total thermal conductivity is sensitive to the replacement of indium atoms by ytterbium atoms. This may be due to the fact that the replacement of In atoms with Yb atoms by hole thermal conductivity increases more rapidly than the phonon fraction of thermal conductivity decreases. Such a strong dependence of χ_{ph} from the concentration of defects indicates the possibility of their participation in heat transfer as scattering centers.

As can be seen from Fig.1,3, in the temperature range 300-700K σ decreases, but α increases by rising temperature. And the hole concentrations for all samples in the specified temperature range change slightly (Fig.2) [3]. This means that in this temperature range by increasing temperature, decreasing of σ occurs mainly due to a decreasing the hole mobility μ_h (T).

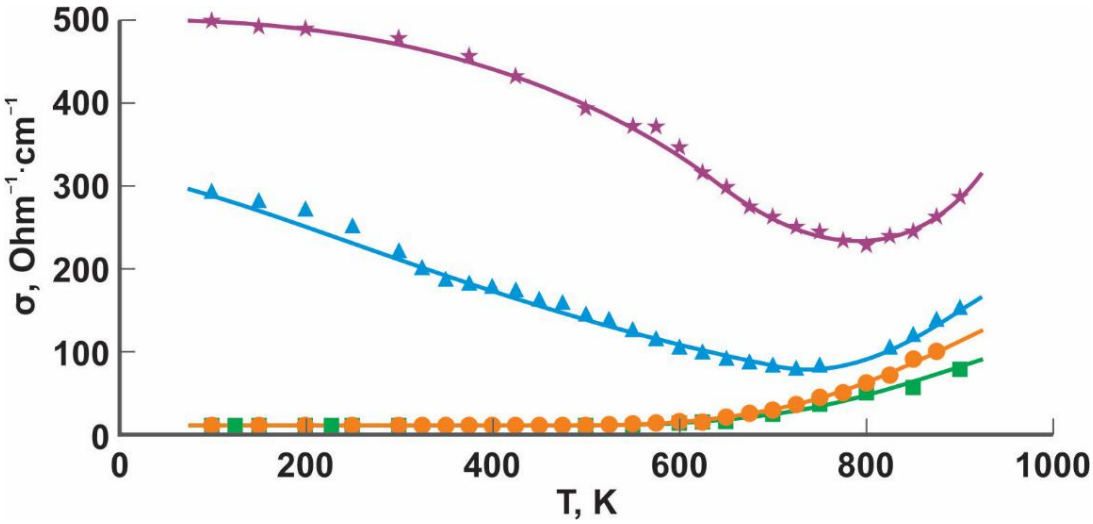

Fig.1. Temperature dependence of electrical conductivity in $TlIn_{1-x}Yb_xTe_2$; green line - (x=0), orange line- (x=0.02), blue line- (x=0.05), purple line- (x=0.10) [3].

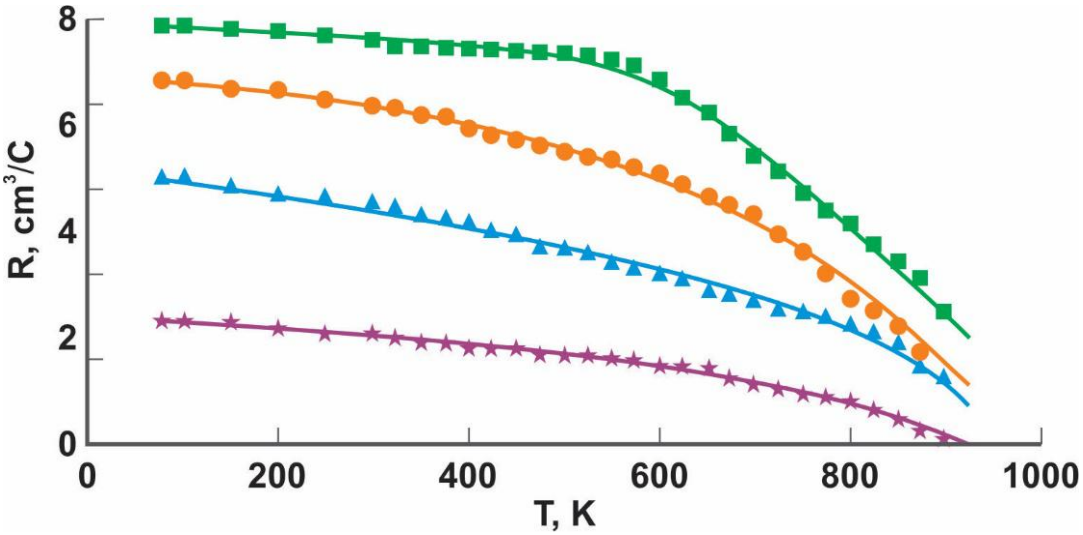

Fig.2. Temperature dependence of coefficient Hall in $TlIn_{1-x}Yb_xTe_2$; The designation is the same as in Fig.1. [3].

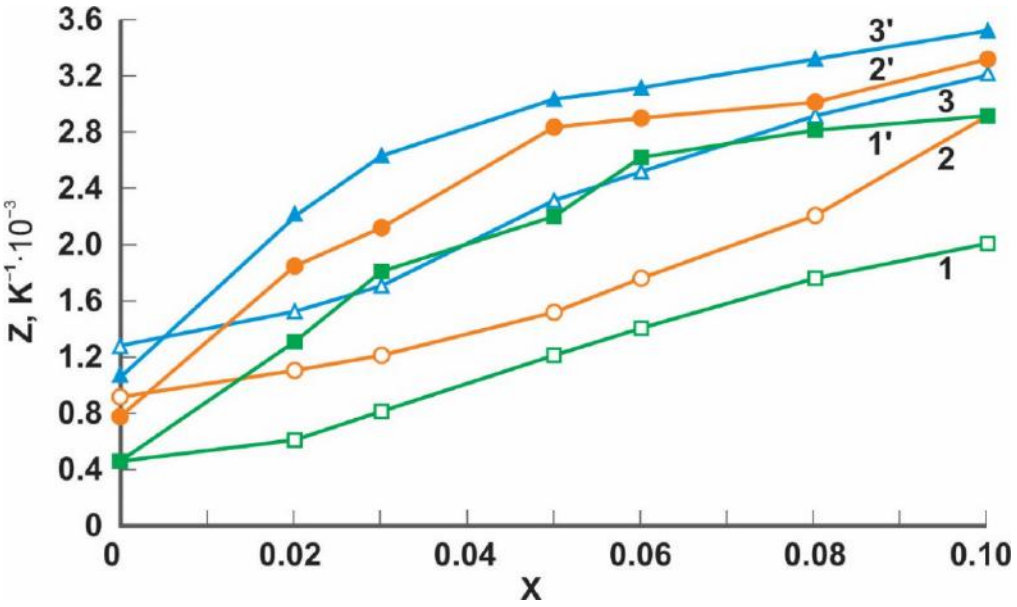

Fig.3. Temperature dependence of thermo power in $TlIn_{1-x}Yb_xTe_2$; The designation is the same as in Fig.1. [3].

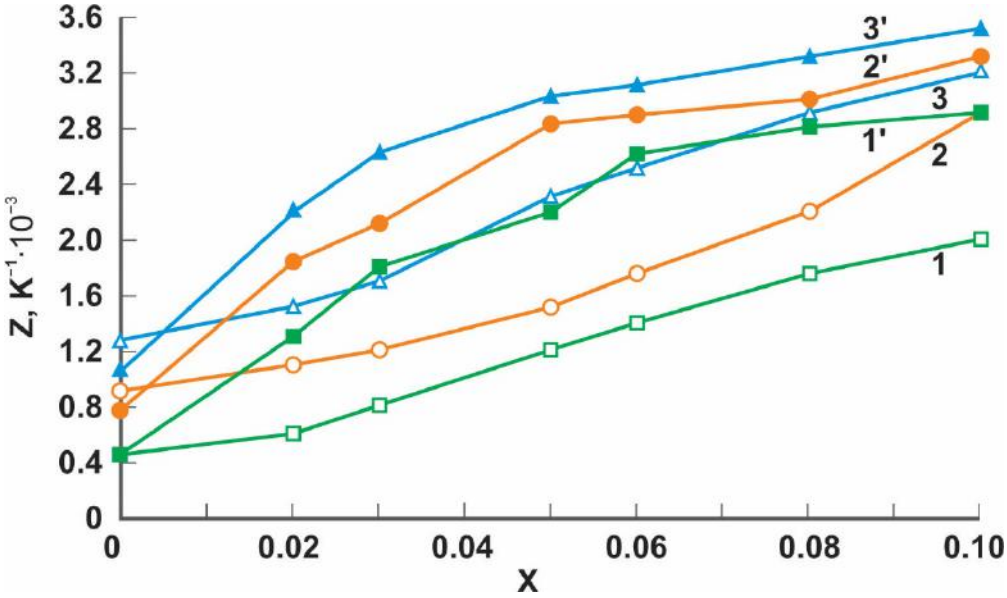

Fig.4. Temperature dependence of thermoelectric figure of merit in various samples $TlIn_{1-x}Yb_xTe_2$ at different temperatures. The designation is the same as in Fig.1.

But decreasing of μ_h (T) occurs due to the scattering of holes on the thermal vibrations of the lattice and on defects according to the law $\mu_h \propto T^{-0,7}$ [3].

In these crystals, vacancies of Yb atoms are larger than vacancies of In atoms. The reason of this is the large screening of Yb atoms (ionic radius R_{Yb} = 1.93A°, R_{In} = 1.57A°) in $TlIn_{1-x}Yb_xTe_2$. Therefore, due to phonon-phonon and phonon-defect scattering, χ_{ph} is reduced as $\chi_{ph} \propto T^{-1.2}$. By increasing x decreases the value of χ_{ph} and the exponent n' ($\chi_{ph} \propto T^{-n'}$). As a result, when x≥0.05 μ_h/χ_{ph} by increasing temperature changes according to the law $\mu_h/\chi_{ph} \propto T^{0.5}$. Therefore, up to T∝700K, increasing of Z with temperature occurs only due to a linear increasing of α(T) (Fig. 3). And after T∝700K, increasing of Z is associated with the onset of its peculiar region, since rising of conductivity with temperature is stronger than the total thermal conductivity χ_{tot}.

So, for use in practice as a promising material with high efficiency $TlIn_{1-x}Yb_xTe_2$ meet the following conditions:

1. In $TlIn_{1-x}Yb_xTe_2$ solid solutions, the hole wavelength is longer than the phonon wavelength. This leads to an overall increasing of Z.

2. To achieve maximum Z, it provides propagation conditions for charge carriers and phonons to obtain $\mu_h/\chi_{ph} >> 1$.

3. The growth of substitution of indium atoms by ytterbium atoms leads to rather high values of Z.

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