

Thermoelectric Figure of Merit in Solid Solution of $TlIn_{1-x}Yb_xTe_2$ ($0 \leq x \leq 10$).

Aliyev F.F.¹, Eminova V.I.¹, Zarbaliev M.M.², Agayeva U.M.², Ismailov M.H.²
1- Institute of Physics of ANAS, c. Baku, Javid av. 131, Az-1143,
2- Sumgait State University, Azerbaijan, Az-5000.
Corresponding Author: Aliyev F.F

Abstract.: According to temperature dependences of the electrical conductivity (σ), the Hall coefficient (R), thermo power (α) and thermal conductivity (χ), the thermoelectric figure of merit (Z) and its dimensionless combination (ZT) were calculated 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 and ZT 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, thermoelectric figure of merit, scattering on defects.

Date of Submission: 06-04-2019

Date of acceptance: 26-04-2019

I. Introduction

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:

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

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 the table. More often use the form of a dimensionless combination

$$ZT = \frac{\alpha^2 \sigma T}{\chi_{tot}} \quad (2)$$

From the above formulas (1) and (2), 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]

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

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 $x=0 \div 0.02$ $\sigma(T)$ increases with x , and at $x=0.05 \div 0.10$, first $\sigma(T)$ decreases to $T \sim 700K$, and after $T \sim 700K$ it increases. Therefore, a decrease in $\sigma(T)$ to $T \sim 700 K$ occurs due to a decrease in the mobility of charge carriers, and after $T \sim 700 K$ an increase in $\sigma(T)$ 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 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 $T \sim 700K$ 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 $T \sim 700K$.

The total thermal conductivity is determined by the sum of the phonon χ_{ph} and the hole thermal conductivity χ_h , where $\chi_h=L_0\sigma T$ (где $L_0=(\pi/3)(k_0/e)^2 = 2,44 \cdot 10^{-8} W \cdot Ohm/K$).

$$\chi_{tot} = \chi_{ph} + L_0\sigma T \quad (4)$$

According to theoretical calculations by Leibfried and Haazen [4] at a temperature T , the phonon thermal conductivity

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

Where γ_0 is Gruneisen constant. Gruneisen constant, which, as usual for most solids of order;

$$\bar{M} = \frac{(1-x)\bar{M}_{TlInTe_2} + x\bar{M}_{TYbTe_2}}{2} - \text{average mass of atoms of the compound (where } \bar{M}_{TlInTe_2}=143.60,$$

$\bar{M}_{TYbTe_2}=158.15$), δ - cubic root of the average volume of atom, θ -Debye temperature. For solid solutions of

$$TlIn_{1-x}Yb_xTe_2 \theta=200K [5], \delta = \sqrt[3]{\frac{\Omega_0}{N}}. \text{ Here } N \text{ is determined by radiographic, so } N = d_{xr} / \bar{M} = az\Omega_0$$

(6), The z is a number of formula units, and a is a number of atoms in it, $\Omega_0 = a^2c$ is the volume of tetragonal cells [5]. Substituting these values into (5), we obtained $\chi_{ph}(T)$ for samples $TlIn_{1-x}Yb_xTe_2$ ($0 \leq x \leq 0,10$) (table).

Table
Zonal and thermal parameters in solid solutions of $TlIn_{1-x}Yb_xTe_2$

Samples	α_1	E_{g_0}	T	E_g (T)	m_n^*	m_p^*	χ_{ph}	χ_{tot}	ΔW_i	Γ
X=0	1.2	0.70	100	0.70	0.040	0.55	0.98	0.98		
			300	0.66	0.040	0.53	0.95	0.95		
			500	0.64	0.040	0.53	0.79	0.80		
			600	0.63	0.039	0.52	0.73	0.78		
			700	0.62	0.038	0.51	0.68	0.75		
			800	0.60	0.037	0.51	0.62	0.76		
			900	0.59	0.036	0.50	0.60	0.78		

X=0,02	1.23	0.66	100	0.65	0.036	0.52	0.86	0.87	14	2.9
			300	0.62	0.036	0.52	0.82	0.83	16	
			500	0.60	0.035	0.51	0.64	0.67	29	
			600	0.59	0.035	0.51	0.60	0.66	50	
			700	0.57	0.034	0.50	0.58	0.68	58	
			800	0.56	0.033	0.49	0.54	0.70	69	
			900	0.55	0.032	0.48	0.47	0.74	78	
X=0,05	1.28	0.62	100	0.61	0.034	0.48	0.76	0.83	29	7.1
			300	0.58	0.034	0.47	0.63	0.78	35	
			500	0.56	0.033	0.47	0.58	0.72	49	
			600	0.54	0.032	0.46	0.56	0.70	58	
			700	0.53	0.031	0.45	0.55	0.72	69	
			800	0.52	0.030	0.45	0.51	0.74	76	
			900	0.50	0.029	0.44	0.46	0.78	84	
X=0,10	1.3	0.54	100	0.53	0.031	0.47	0.66	0.78	49	12.3
			300	0.52	0.031	0.47	0.42	0.75	133	
			500	0.50	0.030	0.46	0.37	0.76	143	
			600	0.48	0.029	0.46	0.32	0.78	183	
			700	0.46	0.028	0.46	0.30	0.85	200	
			800	0.44	0.027	0.45	0.29	0.88	237	
			900	0.42	0.026	0.45	0.24	0.94	255	

In order to determining the effect of pointless defects on χ_{ph} , the Clemens theory was used [7], taking into account three-phonon redelivery processes and phonon scattering on spotty defects, according to which

$$\chi_{ph} = \chi_{tot} (\omega_0/\omega_d) \text{arctg}(\omega_d/\omega_0) \quad (7)$$

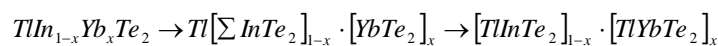
где, $\omega_0/\omega_d = k_0 / (2\pi^2 \chi_{tot} \omega_d A)$ и $A = (1/4V^2N) \cdot \Gamma$

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 [7].

$$\Gamma = x \cdot (1-x) \left[\left(\frac{\Delta \bar{M}}{\bar{M}} \right)^2 + \varepsilon (\Delta \gamma / \gamma)^2 \right] \quad (8)$$

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, $\Delta \bar{M}/\bar{M}$ 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



$$\text{То } \frac{\Delta \bar{M}}{\bar{M}} = \frac{\bar{M}_{TlYbTe_2} - \bar{M}_{TlInTe_2}}{(1-x)\bar{M}_{TlInTe_2} + x\bar{M}_{TlYbTe_2}}$$

According to [7], the value of $\Delta \gamma / \gamma$ can be calculated from the difference of the parameters on the base of elementary cell a_{TlInTe_2} and a_{TlYbTe_2} :

$$\frac{\Delta\gamma}{\gamma} = \left[\left(a_{TlInTe_2} - a_{TlYbTe_2} \right) / a_{TlInTe_2} \cdot (\eta / (1 + \eta)) \right], \quad (9)$$

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

The parameters required for the calculation for the components were taken from (ν, ϵ, ν) [5] and $(a_{TlInTe_2}, a_{TlYbTe_2})$ [6] and were linearly extrapolated for $TlIn_{1-x}Yb_xTe_2$. The data obtained for $\chi_{ph}(T)$ by formulas (5) and (7) differ slightly. The calculated values of the parameter Γ for $TlIn_{1-x}Yb_xTe_2$ for $x = 0.02, 0.05, \text{ and } 0.10$ are given in the table. Comparing the stoichiometric composition $TlInTe_2$ and the compositions $TlIn_{1-x}Yb_xTe_2$, it turns out that at room temperature due to the value of the disorder parameter Γ , the value of χ_{ph} from the dependence of x decreases almost 1.3 to 4.3 times. This indicates that with other parameters being equal, the thermal resistance arising due to the disorder in $TlInTe_2$ should be much less than in $TlIn_{1-x}Yb_xTe_2$. This suggests that the value of Γ found correctly reflects the actual ratio of the main factors responsible for the additional phonon scattering (scattering on defects) [2]. This leads to additional thermal resistance, defined as [8].

$$\Delta W_i = \frac{1}{\chi_{ph}} - \frac{1}{\chi_v}$$

The data obtained for ΔW_i is given in the table. As can be seen from the table, an increasing of concentration of defects leads to the diminished ΔW_i and Z . As noted above, increasing of concentration of defects occurs only due to the replacement of indium atoms with ytterbium atoms in $TlIn_{1-x}Yb_xTe_2$. This gives grounds to say that thermal conductivity along with other kinetic properties is determined by the nature of its own defects and the nature of their behavior [2].

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 $\sigma(T)$, $\alpha(T)$ 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 $TlIn_{1-x}Yb_xTe_2$ 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 .

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.

As can be seen from the table, 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 $\mu_h(T)$. But decreasing of $\mu_h(T)$ 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 $R_{Yb} = 1.93\text{\AA}$, $R_{In} = 1.57\text{\AA}$) 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 $x \geq 0.05$ μ_h/χ_{ph} by increasing temperature changes according to the law $\mu_h/\chi_{ph} \propto T^{0.5}$. Therefore, up to $T \approx 700K$, increasing of Z with temperature occurs only due to a linear increasing of $\alpha(T)$ (Fig. 3). And after $T \approx 700K$, 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} .

The particular interest is shown dimensionless value of ZT in these solid solutions (Fig. 5). As is known, at room temperature, the value of ZT for most thermoelectric materials does not exceed unity [9]. It has materials, which in them ZT reaches 2-3 [11]. Samples of these solid solutions for $x=0.10$ ZT at a temperature of $T \approx 800K$ reaches up to ~ 3.4 (Fig. 5). This is consistent with the data of [10]. With the exception of high temperature, principle of $ZT \geq 2$ can be for two reasons: 1) at a temperature range of 700÷1000K, the effective hole mass decreases by temperature, which indicates that the valence band is not parabolic, since parabolicity in

strongly degenerate samples does not lead to significant temperature growth of the effective mass $m_p^* \propto T^{-0.20}$. In the same temperature range, due to the onset of the intrinsic conductivity region, the total thermal conductivity increases according to the law $\chi_{tot} \propto T^{0.15}$. It is clear from these arguments that the temperature behavior of the effective mass $m_p^*(T)$ in $TlInYb_xTe_2$ solid solution indicated temperature range does not weaken and leads to increasing of ZT in the form of $ZT \propto T^{1.2}$. Therefore, the version due to the dependence of ZT at high temperatures that goes to growth does not justify itself; 2) the second version is that at $T > 700K$ due to the onset of its own conduction region, due to the band transitions of electrical conductivity increases with increasing temperature as $\sigma \propto T^{1.5}$, and the thermo power decreases according to the law $\alpha \propto T^{-0.7}$. At the same time, due to phonon-phonon and phonon-defect scattering, $\chi_{ph}(T)$ decreases in the form of $\chi_{ph} \propto T^{-1.2}$. As a result, at $x \geq 0,5$ and $T > 700K$ ZT by increasing temperature changes according to the law $ZT \propto T^{1.3}$. So from the above two versions, it follows that due to the band transitions of charge carriers, increasing of $\sigma(T)$ and decreasing of $\chi_{ph}(T)$ leads to increasing ZT at $T > 700K$.

From Fig. 4-5, it can be seen that for the studying temperature range studied, calculations using formulas (1-3) differ from Z and ZT. The reason for this may be due to the fact that in these materials: 1- has a large error when determining the value of the effective mass of holes; 2- the parameter of scattering mechanism is not determined univocal.

From the table it can be seen that in the temperature range of 80-700K, decreasing of x introduces less thermal resistance than the same amount of $TlYbTe_2$. This is probably due to phonon scattering on disorder fusions. The table also shows that, at $T > 700K$, increasing of x leads to increasing of $\chi_{tot}(T)$. The reason of this is the predominant role of thermal conductivity of bipolar component of thermal conductivity (χ'). At a temperature $T > 700K$, depending on composition, it increases from 18% up to 60% from χ_{tot} , then by formulas (4), the total thermal conductivity has the form $\chi_{tot} = \chi_{ph} + \chi'$, where $\chi' = (\sigma_n + \sigma_h)L_0T$.

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 $\mu_h/\chi_{ph} \gg 1$.
3. The growth of substitution of indium atoms by ytterbium atoms leads to rather high values of Z and ZT.

II. Literature

1. A.Ф. Иоффе. Semiconductor thermo elements. Izd. AN USSR, Moscow 1960 (in Russian).
2. V.S. Oskotskiy, I.I. Smirnov. Defects in crystals and thermoconductivity. Nauka, Leningrad 1972 (in Russian).
3. F.F. Aliyev, U.M. Agaeva, M.M. Zarbaliev. Fiz. Tech. Poluprovodn. 10, 50, 1297 (2016).
4. G.I. Ieibfzied, P. Haasen. Zum mechanismus der plastischen verformune. J.Phys, 137, 67 (1954).
5. V.A. Gadjiev, M.M. Gurbanov and etc. Neorg. Mater. 26, 1325 (1990) (in Russian).
6. M.M. Zarbaliev. Neorg. Mater. 35, 560 (1999) (in Russian).
7. P.G. Klemens. Phys.Rev. 119, 5 (1960).
8. B. Abdes. Phys.Rev. 131, 1906 (1963).
9. G.S. Nolas, I. Sharp, H.I. Goldsmid. Fiz. Thermoelectric. Springer, Berlin, 45, 78 (2002).
10. H. Ohta. Materials Today, 10, issue 10, 44 (2007).

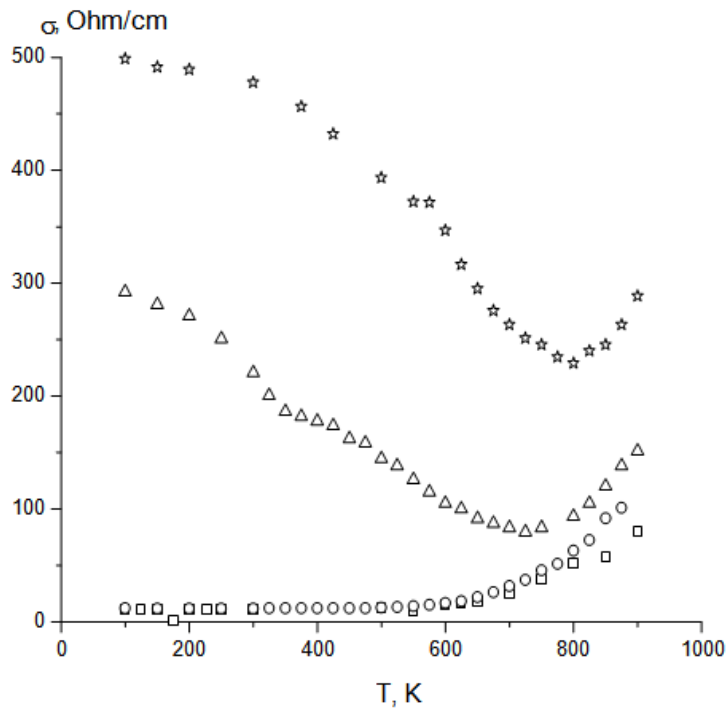


Fig.1. Temperature dependence of electrical conductivity in $TlIn_{1-x}Yb_xTe_2$; \square - ($x=0$), \circ - ($x=0.02$), Δ - ($x=0.05$), $*$ - ($x=0.10$) [3].

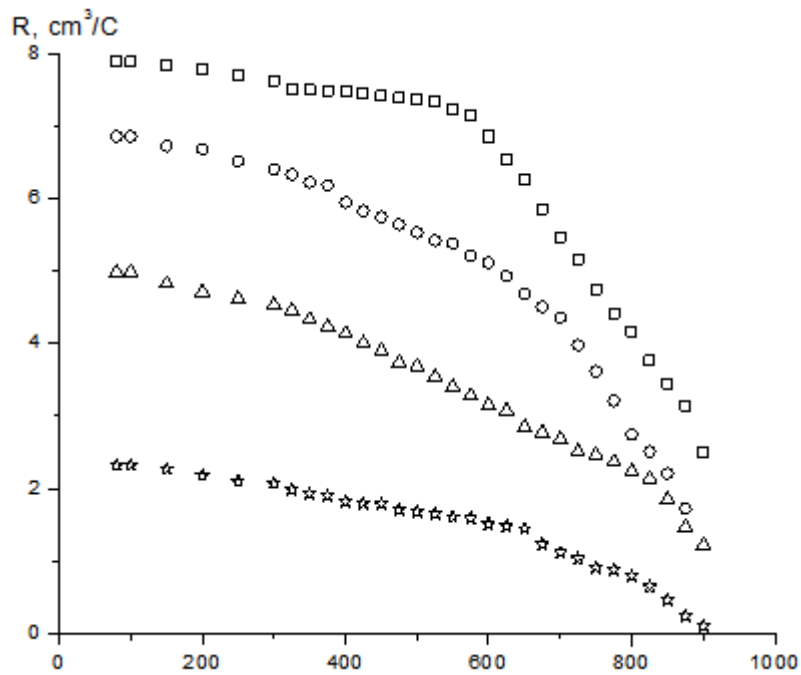


Fig.2. Temperature dependence of coefficient Hall in $TlIn_{1-x}Yb_xTe_2$; ($H=1200A/m$). The designation is the same as in Fig.1. [3].

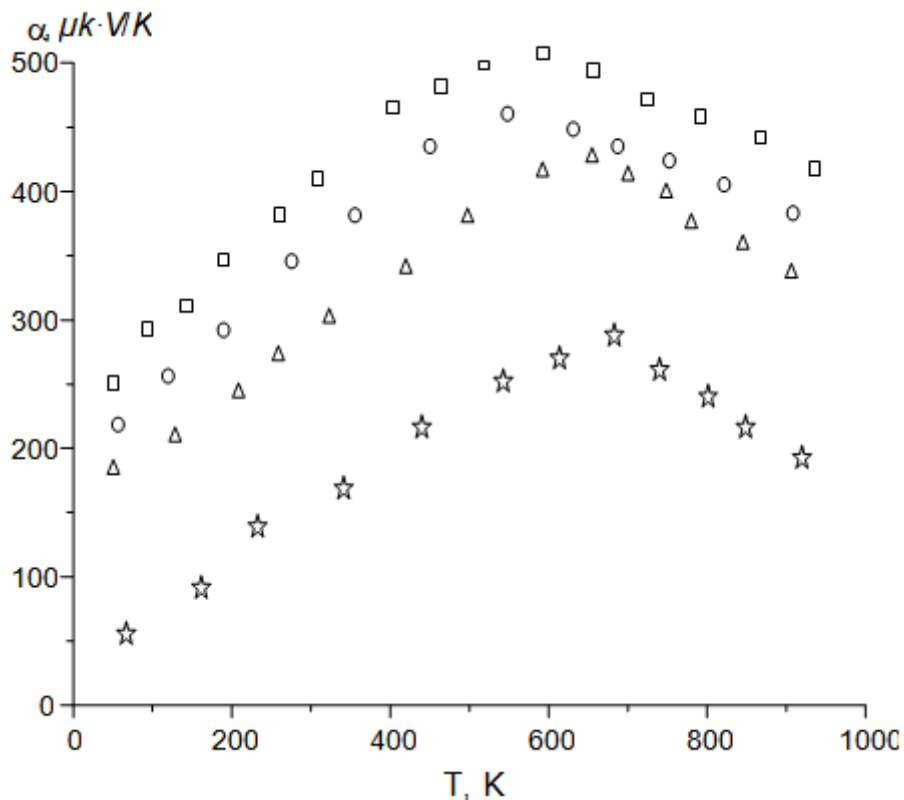


Fig.3. Temperature dependence of thermo power in $TlIn_{1-x}Yb_xTe_2$; ($H=1200A/m$). The designation is the same as in Fig.1. [3].

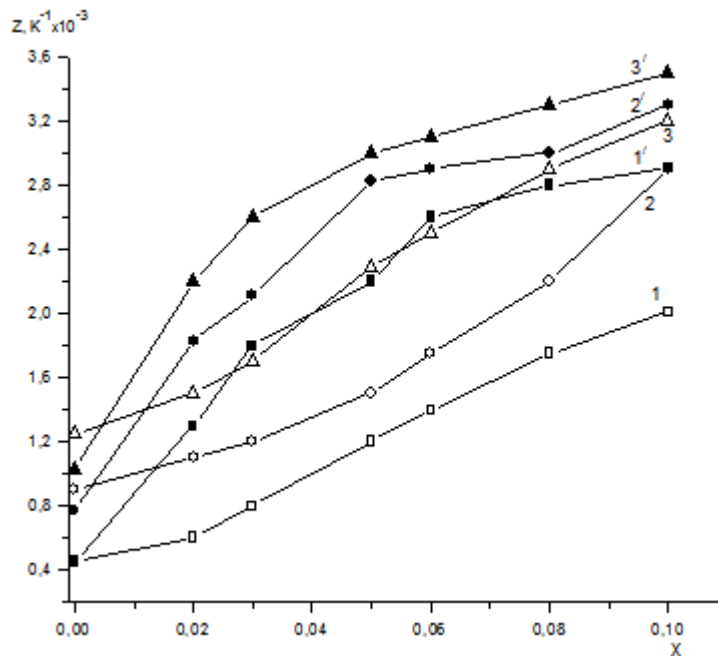


Fig.4. Temperature dependence of thermoelectric figure of merit in various samples $TlIn_{1-x}Yb_xTe_2$ at different temperatures. Calculations 1-3 by formula (1), but 1'-3' by formulas (3) (1,1'-300; 2,2'- 500; 3,3'-800K). The designation is the same as in Fig.1.

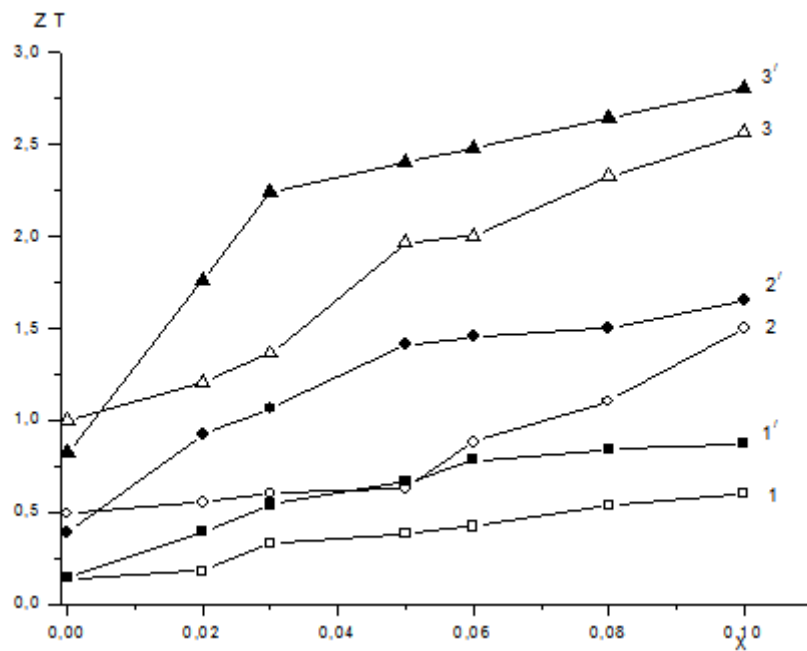


Fig.5. Temperature dependence of dimensionless thermoelectric figure of merit in $TlIn_{1-x}Yb_xTe_2$; ($H=1200A/m$). The designation is the same as in Fig.1.

Aliyev F.F" Thermoelectric Figure of Merit in Solid Solution of $TlIn_{1-x}Yb_xTe_2$ ($0 \leq x \leq 10$)."
 International Journal of Engineering Science Invention (IJESI), Vol. 08, No. 04, 2019, PP 60-67