Thermoelectric Properties of Tl-Doped PbTe Microwires

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Abstract

Results of the measurements of thermoelectric properties of thin monocrystal wires of $Pb_{1-x}Tl_xTe$ (x=0.00 ÷ 0.02, d = 5 ÷ 100 μm) in the temperature region 4,2 ÷ 300 K, which were obtained from solution melt by the filling of quartz capillary with the following crystallization of material are presented. For the samples corresponding to chemical composition with concentration of thallium 0,0025 < x <0,005 double change of the sign of thermoelectric power is observed. In samples with thallium concentration more than 1 at.% thermoelectric power, it is positive in the whole temperature range. In the undoped samples the sharp peak at the temperature T≈30K is observed. The value of this peak depends on the diameter of microwires. Various mechanisms which can lead to observable anomalies, including Kondo-like behavior of a non-magnetic degenerate two-level system and phonon drag of holes are discussed. Obtained experimental results let suppose that the observed anomalies for doped wires can be interpreted on the basis of model of an impurity with mixed valences. For pure PbTe wires it is supposed, that at the temperatures below 40 K the total thermoelectric power to a marked degree is determined by the phonon drag of holes and dependence of value of thermoelectric power is caused by the size effect.

Introduction

In recent years there has been particular attention to investigation of traditional thermoelectric materials, which can be efficient for energy conversion based on the Peltier effect for cooling and the Seebeck effect for power generation [1]. It is caused by that in the low dimensional structures it is possible to receive values of figure of merit ZT ($ZT = \frac{\alpha^2 \sigma}{K_l + K_e} T$, where α, σ T, K_l and K_e are the Seebeck coefficient, electrical conductivity, absolute temperature, lattice thermal conductivity and electronic thermal conductivity, respectively) of the order 1,5 and more. Solid state thermoelectric converters at such values of ZT become competitive with traditional refrigerators.

Research of wire crystals of semiconductor compounds of type A_4B_6 represents special interest. It is caused by that PbTe itself is one of the most effective thermoelectric materials. And the researches directed to revealing of new opportunities of increase of parameters, defining Z, are rather actual. By that is explained the interest to such materials and, in particular, to semiconductor compound $Pb_{1-x}Tl_xTe$ as to the most striking example in which a lot of unique properties have been observed.

Specific action of thallium consists in the following: the thallium impurity generates on the range of the permitted band states of a valence band an impurity band that leads to essential change of density of band states. It leads to essential change of transport characteristics which are determined by density of states, by the form of the impurity band and by the relative position of the Fermi level [2, 3]. On the other hand, thallium is an impurity element of the IIIrd group in the compounds connections A_4B_6 which show a mixed valence [4]. It means that thallium can have the valence from 1 to 3, and the most unstable is the state with a bivalent impurity. In such case they should dissociate as [5]: $2Tl^{2+} \rightarrow Tl^{1+} + Tl^{3+}$. Theoretical description of that assumes existence of the centers with negative correlation energy U: $U_n = (E_{n+1} - E_n) - (E_n - E_{n-1}) < 0$, where valence number n takes the values 1, 2, 3.

Theoretically it has been predicted, that the presence of the U-centers can lead to those features in electro physical properties which were observed in the system $Pb_{1-x}Tl_xTe$ [5]. Such a behavior of an impurity of thallium in PbTe is similar to Kondo effect in metals and should be manifests in particular on the thermoelectric properties of this compound.

On the other hand, it is well known [6, 7], that in the region of low temperatures on monocrystals of bulk lead telluride on temperature dependence of thermoelectric power the characteristic peak is observed. Absolute values of thermoelectric power reach values which surpass calculated values for diffusion thermoelectric power [8]. Such a behaviour of thermoelectric power is explained by phonon drag of carriers. Besides that, in low dimensional crystals (just with such objects is connected the break in the domain of thermoelectricity) it is probably in addition manifestation of dimensional effect for the corresponding physical parameters which defining thermoelectric efficiency of material.

The purpose of the given work was carrying out of research of features of temperature dependence of thermoelectric power of single crystal microwires of $Pb_{1-x}Tl_xTe$ and determination of the mechanisms leading to the given features.

Experimental Results and Discussion

Semiconductor microwires of $Pb_{1-x}Tl_xTe$ (diameter d = 5 ÷ 100 μm, length l ~ 20 sm) were grown by the method similar to described in work [9] in the following way (see Fig.1.). In the quartz tube (diameter - 15 mm) initial material with corresponding chemical composition was placed. The bunch of quartz capillary is situated over the material. The choice of quartz as the material for capillaries is limited by the high temperature of softening one, that must be higher than the melting temperature of material. The tube was

evacuated up to residual pressure $10^{-2} \div 10^{-3}$ Pa and placed in vertical zone furnace, in which the temperature on the whole length of the capillary is the same and higher than the melt temperature of material ($T_{melt} < T < T_{soft}$). After melting of material the capillaries with open lower ends were put down in the melt material. Afterwards in the tube rise pressure under which capillary were filled by the melting material. Crystallization of melting material was realized directly beginning from soldered ends to open one at the expense of move of furnace (rate of move may be changed and make up several centimeters per hour). Given method of obtaining of monocrystal microwires allows producing samples with different diameters under the same grown conditions with high structural perfection. The structural quality was tested by X-ray diffraction and Laser Microprobe Mass Analyzer (LAMMA).

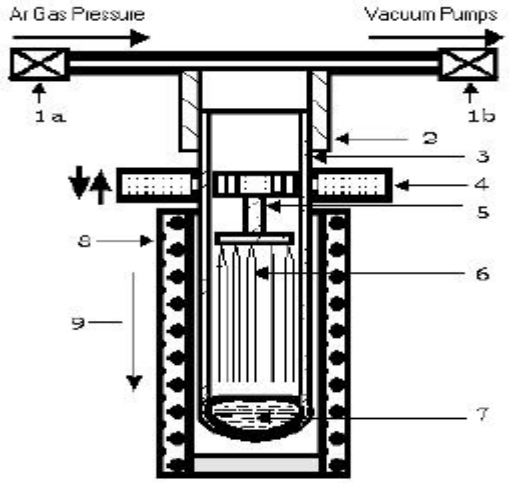

Fig.1. Sketch of the laboratory-scale apparatus for fabrication of thin glass-coated semiconducting wires using the high-pressure injection and directional crystallization method.
1a, 1b - vacuum valves; 2 - metallic tube; 3 - quartz tube; 4 - permanent-magnet system to move capillaries; 5- support for capillaries; 6 - glass capillaries; 7 - molten material; 8 - electric furnace; 9 - direction of furnace movement durina wire crvstallization.

The samples for the measurements were prepared in the following mode. The sample of the corresponding diameter was chousen from the set of crystals obtained in that way for carrying out the measurements. As the initial sample has glass isolation, it was preliminary subjected to selective etching in a solution of acid HF. Reliable electrical and thermal contact was made using eutectic In-Ga. Measurements of temperature were carried out by means of thermocouple Cu – (Cu + 0,04 at % Fe). Such a thermocouple make it possible to carry out experiments with high precision in low temperature region.

Temperature dependence of thermoelectric power of investigated samples of single crystal microwires of undoped lead telluride of p-type conductivity with different diameters is illustrated in Fig.2.

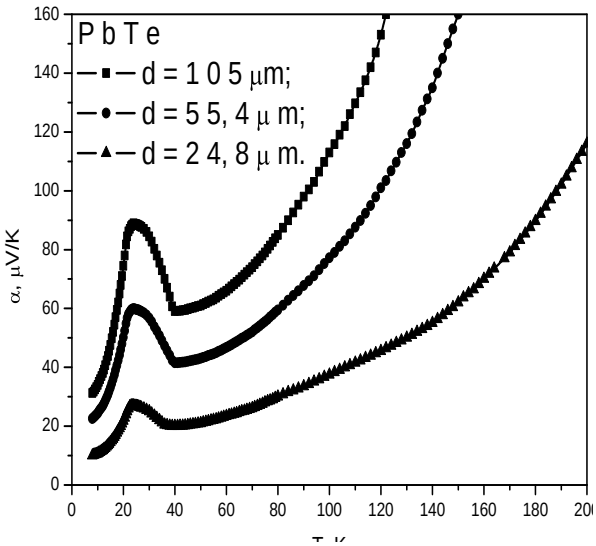

Fig. 2. Temperature dependences of thermoelectric power of monocrystal microwires of PbTe.

In the region of temperatures T≈30K the sharp peak of thermoelectric power is observed. Appearance of this peak can be connected with the contribution of phonon drag thermoelectric power to total value of thermoelectric power.

For the region of temperatures T>50K monotonous dependence of thermoelectric power on temperature which is caused by diffusion of holes under action of a temperature gradient is observed. Similar results for this region of temperatures have been obtained for bulk crystals of p-PbTe [7, 8].

It is known [10], that the strong drag of electrons by phonons takes place, if phonons dissipate on electrons more strongly, than on each other, on defects and on boundaries of a crystal, i.e. $v_{pe}/v_p \approx 1$, $v_{pe} >> v_{pp}, v_{pd}$, where $v_p = v_{pe} + v_{pp} + v_{pd}$ is full frequency of dispersion of phonons, v_{pe} is frequency of dispersion of phonons on electrons, v_{pp} is frequency of dispersion of phonons on each other, v_{pd} is frequency of dispersion of phonons on defects, impurities, boundaries.

In case of degenerate semiconductor realization of the above resulted conditions for observation of phonon drag effects can be broken due to increasing of frequency of dispersion of phonons on defects and impurities at low temperatures [10]. However it is practically impossible to exclude completely phonon drag due to dispersion of phonons on impurities [10]. Considering, that v_{pe} is commensurable quantity with the frequency of electrons energy relaxation v_e ($\sim 10^8 s^{-1}$ [10]), the condition of phonon drag absence is reduced to $v_{pd} \geq 10^{12} s^{-1}$. If v_{pd} is defined by dispersion of phonons by deformation field of point defect, then such values of v_{pd} correspond to concentration of an impurity $N \geq 10^{21} sm^{-3}$. Therefore in the experiments connected with heat transport in semiconductors it is necessary to consider phonon drag even at rather high levels of doping by impurities.

In case of undoped lead telluride of p-type conductivity it is practically impossible to obtain concentration of carriers more than $5*10^{18} sm^{-3}$ without special doping. Therefore

phonon drag is necessary to consider at carrying out of thermoelectric measurements at low temperatures.

The peak of phonon thermoelectric power is observed at the enough high temperatures. It allows to define the law of change of α(T) at temperatures$T<T_{max}$. Analysis of this dependence shows that at the T<20K decrease of thermoelectric power is proportional to a cube of temperature. This is in agreement with assumption about freezing of phonons, as it was observed at T<20÷23K on investigated samples of single crystal microwires of undoped PbTe of p-type conductivity. Estimations for T_0 in our case are – $T_0\left(\overset{//}{k_{100}}\right)=45K$ and $T_0\left(\overset{\perp}{k_{100}}\right)=16K$.

The obtained approximation shows that the experimental results obtained on microwires of pure lead telluride are in a good agreement with the assumption made above.

Earlier it has been shown [11], that in case of manifestation of phonon drag of carriers thermoelectric power can reach theoretical value k/e≈86μV/K, that considerably exceeds value of diffusion thermoelectric power of electronic gas. In Fig.2 one can see, that for the samples having diameter d≥100μm value of thermoelectric power in peak under the order of size is close to a theoretical limit. However for samples having diameter d≤70÷90μm is observed strong reduction of thermoelectric power by value in the field of low temperatures where phonon drag is actual.

Explanation of such dependence is the following [10]. Estimation of length of mean free path for phonons in a direction perpendicular to [100] give: l_{ph}(5K)=270μm, l_{ph}(10K)=59μm, l_{ph}(15K)=24,5μm, l_{ph}(20K)=12,3μm, and accordingly for a direction parallel to an axis [100]: l_{ph}(5K)=95μm, l_{ph}(10K)=207μm, l_{ph}(15K)=8,5μm, l_{ph}(20K)=4,3μm.

The cross-section sizes of the investigated samples were within the limits of 10÷150μm. Therefore at occurrence of a gradient of temperatures on a surface of the sample in relation to its centre for the bottom limit of diameters an electric field appears which interact with carriers drifting along the crystal. Legitimacy of such approach is justified, as heat exchange through a surface by which in case of bulk samples it is neglected, in case of low dimensional systems becomes essential. This is caused by relatively essential increase of the sample surface. In other words it is possible to state, that when mean free path for phonons under the order of value is comparable with the cross-section sizes of samples significant variations of absolute value of thermoelectric power are possible.

On the Fig.3,4 temperature dependences of thermoelectric power of monocrystals wires of $Pb_{1-x}Tl_xTe$ are presented. The analysis of temperature dependences of thermoelectric power shows, that on the doped samples thermoelectric power manifested anomalous character - at low temperatures this dependence becomes essentially no monotonic. For $Pb_{1-x}Tl_xTe$ (x=0,0025; 0,005) thermoelectric power changes a sign twice, and for other compounds on temperature dependence the bend without change of a sign is shown. At higher temperatures (T > 100K) dependence of thermoelectric power vs temperature shows usual behavior, characteristic for strongly doped lead telluride, and numerical value of thermoelectric power in this region are comparable with the data resulted in [12].

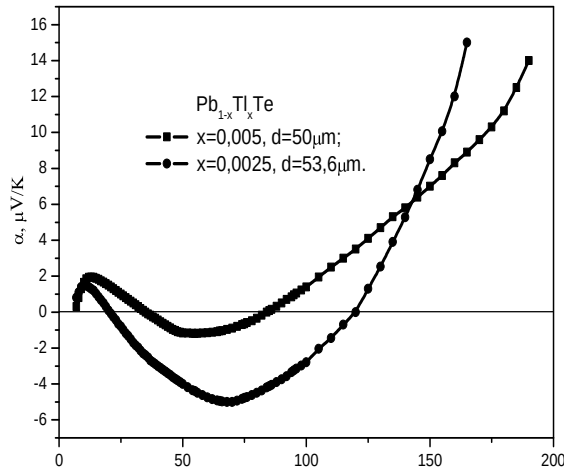

Fig.3. Temperature dependences of thermoelectric power of monocrystal wires of $Pb_{1-x}Tl_xTe$.

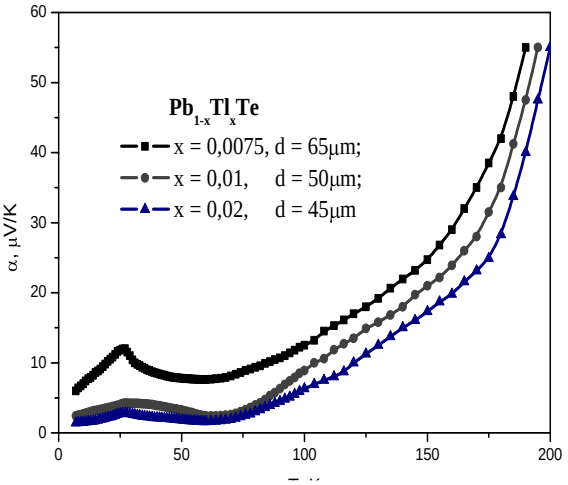

Fig.4. Temperature dependences of thermoelectric power of monocrystal wires of $Pb_{1-x}Tl_xTe$.

The change of a sign of thermoelectric power in the dependence of concentration of an impurity of thallium at temperatures above the temperature of liquid nitrogen in lead telluride was found out earlier [2] and was interpreted within the limits of features of resonant scattering of carriers. On dependence of thermoelectric power from concentration of thallium the deep minimum down to change of its sign [2] is observed. However as follows from the received experimental data besides the high temperature change of a sign of thermoelectric power is observed and low temperature. Furthermore the resonant scattering of carriers is not a process of activation type. It means, that at $k_0T << \Gamma$ (Γ - width of impurity band) time of a relaxation does not depend on temperature. Therefore the anomaly behavior of thermoelectric power at low temperatures cannot be connected with features of resonant scattering.

The reason of low temperature changes of a sign of thermoelectric power can be electron-phonon drag. It was observed earlier for pure lead telluride at T <20K (p =

$10^{18}sm^{-3}$) [7]. However in monocrystal wires of $Pb_{1-x}Tl_xTe$ where concentration of carriers more than on the order larger than in samples investigated in [7] electron-phonon drag cannot cause low temperature change of a sign of thermoelectric power.

The assumption of the mixed mechanism of scattering of carriers also does not allow explaining no monotonic temperature dependence of thermoelectric power.

The analysis of temperature dependences of thermoelectric power of monocrystal wires of $Pb_{1-x}Tl_xTe$ in all spectrum of concentration of a doping impurity in the field of low temperatures shows, that presence of a maximum is characteristic. It is known [13] that in systems with magnetic impurity presence of low temperature maximum of thermoelectric power specifies on interaction of the magnetic moments of impurities. Isolated kondo-impurity gives the negative contribution in thermoelectric power and as a first approximation does not depend neither on temperature, nor from concentration of the kondo-centers. From concentration of an impurity depends only the temperature at which thermoelectric power starts to deviate the law characteristic for metals. Such picture is observed until then while the temperature will not go down to Kondo temperature where thermoelectric power starts to decrease quickly on the module, tends to zero value at $T \rightarrow 0K$.

Conclusions

On the basis of the executed researches of temperature dependence of thermoelectric power of single crystal microwires of $Pb_{1-x}Tl_xTe$ ($x=0.00 \div 0.02$, $d = 5 \div 100$ μm) of p-type conductivity it is possible to draw the following conclusion:

- ✓ In the region of low temperatures $T<20\div23K$ the essential contribution to total thermoelectric power of single crystal microwires of undoped PbTe is made by a phonon drag thermoelectric power;
- ✓ The contribution of phonon drag of carriers in the total thermoelectric power of single crystal microwires of undoped PbTe leads to occurrence on temperature dependence of thermal e.m.f. a characteristic maximum;
- ✓ Position of a maximum on temperature dependences of thermoelectric power of single crystal microwires of undoped PbTe of p-type conductivity does not depend on diameter of samples ($d=5 \div 100$ μm);
- ✓ Absolute value of thermoelectric power of single crystal microwires of undoped PbTe of p-type conductivity in the region of low temperatures $T<20\div23K$ depends on the sizes (diameter) of the samples;
- ✓ With reduction of diameter of the samples absolute value of thermoelectric power of single crystal microwires of undoped PbTe in the region of a maximum decreases. Such dependence is explained by manifestation of dimensional effect - length of mean free path of phonons and diameter of the sample become the same order;
- ✓ For all investigated samples of single crystal microwires of $Pb_{1-x}Tl_xTe$ in the low temperature region anomalies on temperature dependence of thermoelectric power are observed;
- ✓ For the samples of single crystal microwires of $Pb_{1-x}Tl_xTe$ corresponding to chemical composition with concentration of thallium $0,0025 < x < 0,005$ double change of the sign of thermoelectric power is observed. In samples with thallium concentration more than 1 at.% thermoelectric power it is positive in the whole temperature range;
- ✓ Such dependences of thermoelectric power of single crystal microwires of $Pb_{1-x}Tl_xTe$ is explained by charge Kondo effect associated with skip valences of Tl manifested in the PbTe

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