THERMOELECTRIC POWER IN SINGLE CRYSTAL MICROWIRES OF PbTe

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Results of the measurements of thermoelectric properties of thin semiconductor microwires of PbTe (d = 5 ÷ 100 μm) obtained from solution melt by the quartz capillary filling followed by material crystallization are presented for the temperature region 4.2 ÷ 300 K. For the all samples, a sharp peak at the temperature $T \approx 30\ K$ is observed. The value of this peak depends on diameter of microwires. It is supposed that at the temperatures below 40 K the total thermoelectric power is determined to a certain degree by the phonon drag of holes and dependence of the thermoelectric power value is caused by the size effect.

1. Introduction

In recent years, a particular emphasis was placed on 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]. This is due to the fact that in the low dimensional structures it is possible to obtain values of the 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 of 1.5 and more. Solid-state thermoelectric converters at such values of ZT become competitive with traditional refrigerators.

Research of wire crystals of PbTe is of special interest, because PbTe is one of the most effective thermoelectric materials. The researches focused on revealing of new capabilities of increasing parameters defining Z are of high priority.

It is well known [2, 3] that in the region of low temperatures, for single crystals of bulk lead telluride a peak on the temperature dependence of the thermoelectric power is observed. Absolute values of thermoelectric power exceed calculated ones for diffusion thermoelectric power [4]. This behavior of thermoelectric power is explained by phonon drag of carriers. Moreover, in low dimensional crystals (these are the objects connected with the break in the domain of thermoelectricity) an additional dimensional effect for corresponding physical parameters defining thermoelectric efficiency is probable.

The purpose of the given work was to research characteristics of the temperature dependence of thermoelectric power of single crystal microwires of PbTe and to determine the mechanisms leading to these characteristics.

2. Experimental results and discussion

Semiconductor microwires of PbTe (diameter d = 5 ÷ 100 μm, length l ~ 20 cm) were grown by the method similar to that described in work [5]. In the quartz tube (diameter of 15 mm), an initial material with corresponding chemical composition was placed. A bunch of

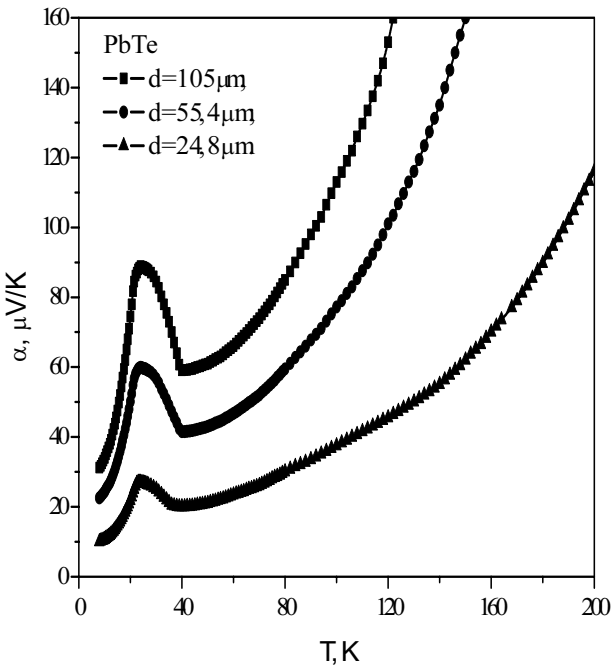

Fig. 1. Temperature dependences of thermoelectric power of PbTe single crystal microwires.

quartz capillaries was situated over the material. The choice of quartz as the material for capillaries was limited by the softening temperature, which 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 a vertical zone furnace, in which the temperature along the whole length of the capillary is the same and higher than the melting temperature of the material ($T_{melt} < T < T_{soft}$). After melting of the material, the capillaries with open lower ends were put down in the melted material. Afterwards, pressure in the tube was increased up to the value at which the capillaries were filled with the melting material. Crystallization of the melting material was realized directly beginning from the soldered ends to the open one by moving the furnace (rate of move may be varied and makes up several centimeters per hour). This method for obtaining of single crystal microwires allows producing samples of high structural perfection with different diameters under the same growth conditions. The structural quality was tested by X-ray diffraction and Laser Microprobe Mass Analyzer (LAMMA).

A sample of corresponding diameter was selected for measurements from the set of prepared crystals. As the initial sample has glass isolation, it was preliminary subjected to selective etching in a solution of HF acid. Reliable electrical and thermal contact was made using eutectic In-Ga. The temperature was determined by means of thermocouple Cu – (Cu + 0.04 at % Fe). This thermocouple makes it possible to carry out high precision experiments in low temperature region.

Temperature dependence of thermoelectric power of the investigated single crystal microwires of undoped lead telluride of p-type conductivity with different diameters is illustrated in Fig. 1.

In the region of temperatures $T \approx 30\ K$ a sharp peak of thermoelectric power is observed. Appearance of this peak can be attributed to the phonon drag contribution to thermoelectric power.

For the region of temperatures $T > 50\ K$, a monotonous dependence of thermoelectric power on temperature is observed, being caused by diffusion of holes under action of a temperature gradient. Similar results for this region of temperatures have been obtained for bulk crystals of p-type PbTe [3, 5]. At the temperatures above 77 K, the thermoelectric power in the field of applicability of one-band models ($p = 10^{18} \div 10^{19} cm^{-3}$), in the assumption of power law dependence of relaxation time on energy and square-law dependence of carrier energy on impulse, the α values can be described by the expression [6]

$$\alpha = \frac{2k^2 T m_d^*}{3e\hbar^2}\left(\frac{\pi}{3p}\right)^{2/3}\left(r + 1 - 3\frac{p}{m_d^*}\frac{dm_d^*}{dp}\right),$$

where m_d^* is the effective mass of density of states; r is the dispersion parameter. This formula

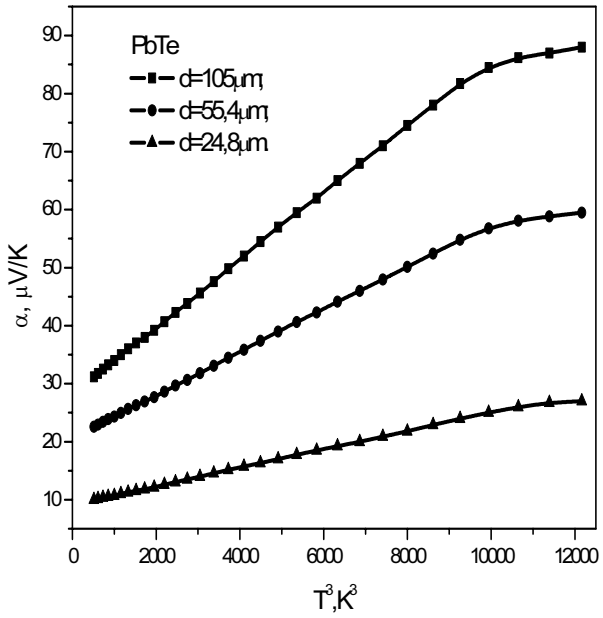

Fig. 2. Temperature dependences of thermoelectric power of PbTe single crystal microwires.

properly describes behavior of thermoelectric power in the investigated single crystal microwires of undoped lead telluride of p-type conductivity at T >77 K. However, for smaller temperatures the given formula is not applicable.

There is a strong drag of electrons by phonons, if phonons dissipate on electrons more strongly than on each other, on defects, and on boundaries of a crystal [7]. This means that $\nu_{pe}/\nu_p \approx 1$, $\nu_{pe} >> \nu_{pp}, \nu_{pd}$. We denoted $\nu_p = \nu_{pe} + \nu_{pp} + \nu_{pd}$ is the full frequency of dispersion of phonons, ν_{pe} is the frequency of dispersion of phonons on electrons, ν_{pp} is the frequency of dispersion of phonons on each other, ν_{pd} is the frequency of dispersion of phonons on defects, impurities, and boundaries.

In the case of degenerate semiconductor, the above 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 [8]. However, it is practically impossible to completely exclude phonon drag due to dispersion of phonons on impurities [9]. Considering that ν_{pe} is commensurable quantity with the frequency of electron energy relaxation ν_e (~$10^8 s^{-1}$ [7]), the condition of phonon drag absence is given by $\nu_{pd} \geq 10^{12} s^{-1}$. If ν_{pd} is defined by dispersion of phonons by deformation field of point defect, then these values of ν_{pd} correspond to concentration of impurity $N \geq 10^{21} cm^{-3}$. Therefore, in the experiments concerned with heat transport in semiconductors it is necessary to consider phonon drag even at rather high levels of impurity doping.

In the case of undoped lead telluride of p-type conductivity, it is practically impossible to obtain concentration of carriers more than $5*10^{18} cm^{-3}$ without special doping. Therefore, phonon drag contribution must be considered to the thermoelectric power at low temperatures.

The peak of phonon thermoelectric power is observed at sufficiently high temperatures. This allows defining the law of $\alpha(T)$ variation at temperatures $T < T_{\max}$. Figure 2 shows dependences of $\alpha(T^3)$ of single crystal microwires of undoped lead telluride of p-type conductivity with different diameters. Analysis of these dependences shows that at the $T < 20\ K$ the decrease of thermoelectric power is proportional to a cube of temperature.

At low temperatures in semimetals and degenerate semiconductors, intervalley transfers are insignificant, only long-wave phonons with impulses interact with charge carriers in case of an isotropic spectrum for $q < 2p_F$ (p_F is Fermi impulse of electrons). In this case a characteristic temperature is not the Debye temperature Θ_D, but the temperature $T_0 = \frac{2 p_F s}{k}$, which is much smaller than Θ_D (s is the sound speed, k is the Boltzmann constant) [10]. In the anisotropic case a role of T_0 is played by the temperatures $T_0^{(\mu^+)}$ and $T_0^{(\mu^-)}$ (μ is the number

of polarization of an acoustic branch of phonons). At $T < T_0$ (in fact, T_0 coincides with $T_{\max}$) thermal phonons interact with carriers; a part of them is of the order of $(sp_F / T)^3$ and is defined by phase volume, which is occupied by long-wave phonons [7]. Therefore, variation of the partial thermoelectric power in these conditions will look like: $\alpha = \frac{k}{e}\left(\frac{T}{T_0}\right)^3$ (freezing of phonons), as it was observed at $T < 20 \div 23\ K$ for single crystal microwires of undoped PbTe of p-type conductivity. Let us estimate value of T_0 in our case. We have: $E = 0,05\ eV$, $\varepsilon_g = 0,17\ eV$, $s^{//}_{k_{100}} = 3,6 * 10^5\ cm/s$, $s^{\perp}_{k_{100}} = 1,26 * 10^5\ cm/s$. Hence, we obtain that the $T_0\left(s^{//}_{k_{100}}\right) = 45\ K$ and $T_0\left(s^{\perp}_{k_{100}}\right) = 16\ K$.

The used approximation properly describes the experimental results obtained for microwires of pure lead telluride.

The increase of carrier current concentration leads to shift of $T_{\max}$ in the region of higher temperatures [9]. It is clear from Fig. 1 that positions of peaks of thermoelectric power on temperature dependences for samples of different diameters practically coincide. This suggests that the concentration of carriers in samples of different diameters is the same; that is, it does not depend on diameter of the sample.

Theoretical consideration of temperature range in which phonon drag is present [10] shows the following variants concerning temperature dependence of thermoelectric power:

1. If the temperature T_I, at which the contribution of ν_{pp} to full frequency becomes small in comparison with the contribution of ν_{pd} and ν_{pe}, exceeds the temperature T_0, then α grows with diminution of temperature at $T > T_I$, it does not depend on temperature in the interval $T_0 < T < T_I$ and decreases with temperature at $T < T_0$.
2. If $T_I < T_0$, then the plateau is absent, α reaches maximum at certain temperature lower than T_0. The size of this maximum is less than in the first case.

It is clear from Fig. 1 that for all the investigated PbTe samples a plateau is not practically shown, and the thermoelectric power peak is observed. However, it is possible to draw a conclusion from Fig. 2 that the cubic temperature dependence is observed up to temperature of the order of 23 K. Further, a deviation from the linear dependence in the chosen coordinates is observed. It allows making a conclusion that in our case T_I is more or of the order of magnitude to the characteristic temperature T_0.

It has been previously shown [9] that in the case of manifestation of phonon drag of carriers, thermoelectric power can reach the theoretical value $k / e (\approx 86\ \mu V / K)$ that considerably exceeds the value of diffusion thermoelectric power of electronic gas $\alpha_D = \frac{k^2 T}{e \varepsilon_F} << \alpha_{ph}$. For the samples having diameter $d \geq 100\ \mu m$ the thermoelectric power in peak is of the order of theoretical limit (Fig. 1). However, for samples having $d \leq 70 \div 80\ \mu m$ there is a strong reduction of thermoelectric power at low temperatures, where phonon drags is actual.

It is known that in the absence of magnetic field, in the temperature gradient the electric field arises, being function of the sizes of the sample a and speed of relaxation of phonons at crystal boundaries [7]

$$u_x = \alpha\Delta T\left[1-\frac{th(ka)}{ka(1+\xi * th(ka)}\right].$$

Analysis of this expression shows that for small values of ξ, which describes the speed of relaxation of phonons on crystal boundaries $(\xi < 3^{-1/2})$, the potential difference u_x at $ka << 1$ is a concave function; at $ka >> 1$, is always a convex function. At $\xi \to \infty$, for a potential difference in the presence of the temperature gradient, an usual expression is obtained: $u_x = \alpha\Delta T$.

It is obvious that the mean free path phonons play a role redeterminating the electro-phonon length of cooling k, on which electrons and phonons equalize their temperatures. We shall estimate mean free path for phonons for single crystal microwires of undoped lead telluride of p-type conductivity in the low temperatures region. Quantities defining the mean free path for phonons are

$$\kappa(5K) = 1,3 * 10^{-1}\ W/cm * K;$$

$$\kappa(10K) = 2,9 * 10^{-1}\ W/cm * K;\ \kappa(15K) = 3,0 * 10^{-1}\ W/cm * K;\ \kappa(20K) = 2,7 * 10^{-1}\ W/cm * K\ [3];$$

$$C_p(5K) = 0,114 * 10^{-3}\ J/g * K;\ C_p(10K) = 1,165 * 10^{-3}\ J/g * K;\ C_p(15K) = 2,949 * 10^{-3}\ J/g * K;$$

$$C_p(20K) = 5,242 * 10^{-3}\ J/g * K\ [11];\ s^{//}_{k_{100}} = 3,6 * 10^5\ cm/s;\ s^{\perp}_{k_{100}} = 1,26 * 10^5\ cm/s\ [4],$$

According to the above, we obtained the following values for the mean free path of phonons in the direction perpendicular to [100]: $l_{ph}(5K) = 270\ \mu m$, $l_{ph}(10K) = 59\ \mu m$, $l_{ph}(15K) = 24,5\ \mu m$, $l_{ph}(20K) = 12,3\ \mu m$, and, accordingly, for the direction parallel to [100] axis: $l_{ph}(5K) = 95\ \mu m$, $l_{ph}(10K) = 20,7\ \mu m$, $l_{ph}(15K) = 8,5\ \mu m$, $l_{ph}(20K) = 4,3\ \mu m$.

Starting from the estimated mean free path of phonons for undoped lead telluride of p-type conductivity (in our case for single crystal microwires), on in the assumption that $k^{-1} \approx 10^{-2} \div 10^{-3}\ cm$ and the length of the sample $l \approx 1\ mm$, we obtained characteristic parameter $ka \approx 10 \div 100 >> 1$. Thus, it is possible to consider that along the crystal axis in the temperature gradient presence $\alpha = \frac{u_x}{\Delta T}$.

The cross-section sizes of the investigated samples ranged within $10 \div 150\ \mu m$. Similar estimation in this case shows that $ka \approx 0,1 \div 10 \approx 1$. Therefore, at occurrence of the temperature gradient on the sample surface in relation to its centre for the bottom limit of diameters, an electric field appears which interacts with carriers drifting along the crystal. This approach is justified, since heat exchange through the surface, which is neglected for bulk samples, becomes sufficient in the case of low dimensional systems. This is caused by relative increase of the sample surface. Studying the thermoelectric and thermal phenomena, we noted that in the temperature region $T < 50\ K$ radiation of heat by the surface is small and is not considered in the specified experiments [12]. In other words, it is possible to state that when the mean free path of phonons is comparable with the cross-section sizes of samples, significant variations in absolute value of thermoelectric power are possible.

3. Conclusions

The analysis of the temperature dependence of thermoelectric power of single crystal microwires of undoped PbTe of p-type conductivity, with different diameters, shows the following.

In the region of low temperatures $T < 20 \div 23\ K$ the appreciable contribution to total thermoelectric power is made by phonon drag. The contribution of phonon drag of carriers to the total thermoelectric power leads to appearance of a maximum on the temperature dependence of thermoelectric power. The maximum position does not depend on diameter of samples (d=5 ÷ 100 μm).

Absolute value of thermoelectric power in the region of low temperatures $T < 20 \div 23\ K$ depends on sizes (diameter) of the samples. With reduction of diameter of the samples, the absolute value of maximum on the temperature dependence of thermoelectric power decreases. This dependence is explained by manifestation of dimensional effect: length of the mean free path of phonons and diameter of the sample become of the same order.

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