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**Electrotechnical Model of Conductivity of Lead Telluride, Obtained  
by Method of Powder Pressing**

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The results of study of thermoelectric properties of lead telluride obtained by method of powder pressing are presented. A modified electrical model for interpreting the empirical dependences  $\sigma(T)$  is proposed, according to which the compressed sample is represented by a system of crystallites with intergranular boundaries whose properties differ along and across the compression axis.

**Keywords:** Lead telluride, doping, pressing, thermoelectric figure of merit.

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## Introduction

The urgency of the search and research of effective thermoelectric materials is determined by a number of significant advantages of thermoelectric generators over other types of alternative energy sources [1-2]. First of all, this relates to high reliability and a significant period of uninterrupted operation of such devices. The efficiency of materials used in thermoelectric converters is determined by the magnitude of the thermoelectric figure of merit  $Z$ , which is directly proportional to the specific electrical conductivity, the square of the Seebeck coefficient, and the inversely proportional to coefficient of thermal conductivity.

A promising direction is the study of thermoelectric samples obtained by method of powder pressing, which provides a large area of intergranular boundaries and, accordingly, low values of the coefficient of thermal conductivity [1, 7]. There are two main types of pressing: cold pressing under pressure of 4-10 t / cm<sup>2</sup> followed by sintering in vacuum, argon, water, fine graffiti; and hot pressing of powder [1, 7]. It is worth noting that the parameter  $Z$  for pressed samples may exhibit a dependence on the geometric dimensions of the sample [1, 8]. According to [8], this dependence is particularly significant for samples > 5 mm long.

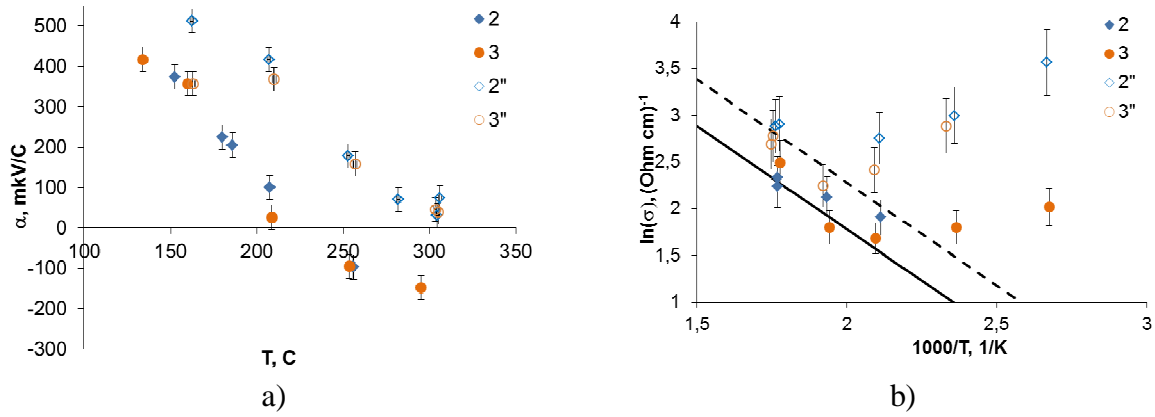
According to [9], the formation of a connection between different grains of a powder is possible in two ways: the formation of a Van der Waals connection and the formation of a stable chemical connection, which is several orders of magnitude stronger than previously mentioned. The main obstacle to the formation of

connection is the contamination of the surface of crystallites, which is practically impossible to avoid. Impurity atoms on the surface saturate the torn connection of the atoms of the matrix and hinder the direct interaction of atoms from different crystallites. However, under the pressure of the order GPa, the grains are crushed to form free surfaces that can form strong chemical connection [10].

During the realization of the metal-ceramic method without a special protective atmosphere, the possibility of significant oxidation of samples increases, especially in the case of highly dispersed fractions [9]. Also, oxygen will almost always be present in the pores, which closed when pressed [9]. This leads to the formation on the surface of crystals of oxide non-conductive films, which reduce the electrical conductivity of the material. In particular, oxidation processes are limited the temperature of hot pressing of chalcogenides at the air to 700 K [9].

Theoretically, the air from the pores can be completely displaced under the conditions of very slow pressing. Quantitative estimates of pressure of pressed air are usually in order different from experimentally determined, which indicates the complexity of this process. Typically, the experimental values of  $P$  are lower [10]. It should be borne in mind that with increasing pressure, the solubility of gases in crystals will increase, which may affect the air pressure in the pores [10].

The purpose of this work is to determine the effect of atmospheric oxygen on the temperature dependence of the specific electrical conductivity and the Seebeck



**Fig. 1.** The dependence of the Seebeck coefficient on temperature (a) and the dependence of the logarithm of conductivity on the inverse temperature (b) for pure PbTe samples obtained by pressing the powder (0.05 - 0.5) mm at a pressure of 2 GPa. Samples 2, 3 are non-annealed, 2'', 3'' are annealed at 773 K. Directs on Fig. 1.(b), corresponding  $\ln(\sigma) = -0,38/2kT+A$ .

coefficient of samples of lead telluride, obtained by compressing powder in the air.

## I. Experiment results

The method of obtaining samples and their research is described in detail in [11]. Synthesis of lead telluride was carried out in vacuum-sealed tubes of quartz glass at a temperature of 1020  $^{\circ}\text{C}$ . The phase composition and element cell parameter were determined by X-diffraction methods at the STOE STADI P. The samples for research were obtained by pressing the powder in air at pressures 1.5-2.0 GPa. The Seebeck coefficient was determined by measuring the magnitude of the thermoelectric force on the sample at a temperature gradient at its ends  $\approx 10$   $^{\circ}\text{C}$ . The electrical conductivity was determined by measuring the voltage drop across the specimen when passing through the alternating current.

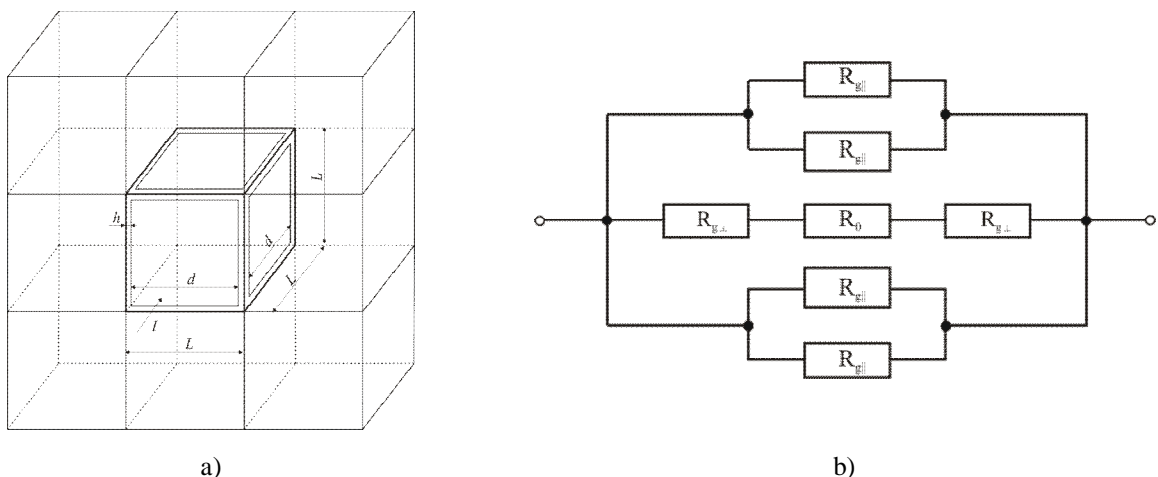
## II. Experiment results

On the basis of X-ray studies, it was found that synthesized ingots and the powder samples produced on their basis are single-phase and have structural type

NaCl. The elementary cell parameter for the synthesized polycrystalline ingots is  $a_{\text{ing}} = 6,4577 \pm 0,0010$   $\text{\AA}$ , and for the pressed and annealed sample - ( $a_{\text{sam}} = 6,4564 \pm 0,0010$   $\text{\AA}$ ).

Typical temperature dependences of thermoelectric parameters of pure lead telluride are shown in Fig. 1. Non annealed samples at temperatures below 200  $^{\circ}\text{C}$  show a p-type conductivity. The Seebeck coefficient at 100  $^{\circ}\text{C}$  is  $\approx 400$   $\mu\text{V}/\text{K}$ . With the temperature rise in the vicinity of 200  $^{\circ}\text{C}$ , the conductivity changes to the n-type conductivity and at 300  $^{\circ}\text{C}$   $\alpha \approx 200$   $\mu\text{V}/\text{K}$ . The temperature dependence of the electrical conductivity for all samples is nonmonotonic with a minimum at the temperature which corresponds to p-n-junction. Annealing at 500  $^{\circ}\text{C}$  leads to a significant increase in the electrical conductivity of the material, which exhibits only p-type conductivity in the studied temperature range.

The reason for a qualitative change in the electrical conductivity of the material after annealing can be as a grain gradient restraint, fixed in the study of the surface structure of samples [11], and modification of defective subsystem. However, according to [12-13], the defective subsystem PbTe practically completely tempered at significantly higher temperatures than 500  $^{\circ}\text{C}$ . Thus, the reduction of the resistance between the grains from which the sample is compressed is the most probable



**Fig. 2.** Model of polycrystal (a), and its equivalent electrical circuit (b) [14].

reason for the growth of the value  $\sigma$ .

If we represent the measured dependencies of the specific electrical conductivity on the temperature in the coordinates  $\ln(\sigma)-1/T$ , then in the high temperature range the inclination of the experimental dependences corresponds to the activation energy of 0.38 eV, which corresponds to width of the band gap PbTe. After the annealed the slope of the investigated dependence does not change, although the free member of the dependence  $\ln(\sigma)=-E_g/2kT+A$  increases.

In order to explain the nature of the dependences of thermoelectric parameters at temperatures below 200 °C, the most logical, given that the compression of samples is carried out in the air, is a model for the formation of a near-surface layer of p-type conductivity, due to the interaction of the grain surface with atmospheric oxygen.

An electrotechnical model can be used to calculate the conductivity of polycrystalline pressed samples with a near-surface layer whose properties differ from the properties of the central part of the grains [14]. As a result of the calculations, some parameters of the near-surface layer, in particular its thickness can be established.

According to [14], a polycrystalline sample can be represented as a system of crystallites of cubic shape with a length of the edge  $L$  having intergranular boundaries of thickness  $h$  (Fig. 2, a). Accordingly, the linear size of the monoblock grain itself will be equal  $d=L-2h$ , and its resistance,  $R_0=\rho_0 d^{-1}$  where  $\rho_0$  is the specific monoblock grain resistance. In addition, such an electrotechnical cell will have four resistances  $R_{g\parallel}$  intergranular boundaries included in parallel and two resistance series to  $R_0$  (Fig. 2, b):

$$R_{g2} = \frac{1}{4} R_{g\parallel} = \rho_g \frac{1}{L^2 - d^2}, \quad (1)$$

$$R_{g1} = 2R_{g\perp} = \rho_g \frac{L-d}{d^2}. \quad (2)$$

Where  $\rho_g$  – specific resistance of the area between grain boundaries.

Taking into account the equivalent scheme (Fig. 2, b), the total capacity of crystals with inter-grain boundaries of  $R_e$  will be determined by the ratio [14]:

$$\frac{1}{R_e} = \frac{1}{R_0 + R_{g1}} + \frac{1}{R_{g2}}, \quad (3)$$

$$R_e = \frac{R_{g2}(R_0 + R_{g1})}{R_0 + R_{g1} + R_{g2}}. \quad (4)$$

Knowing the resistance of the electrotechnical cell of the film, one can determine its equivalent specific resistivity [14]:

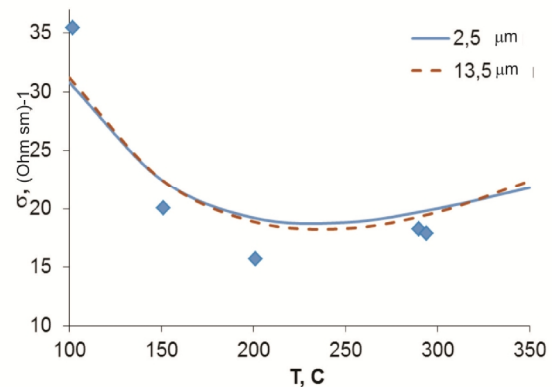
$$\rho_e = R_e L = \frac{R_{g2}(R_0 + R_{g1})L}{R_0 + R_{g1} + R_{g2}}. \quad (5)$$

Using the results presented in the third section, and assuming that the specific electrical conductivity is determined by the p-type conductivity of the surface layer and at high temperatures by the central part with the n-type of conductivity, the temperature dependence of the conductivity of the p-layer is determined as  $\sigma = 10^{0.2} T^{-3.4}$  (annealed), and the temperature dependence of the conductivity n-layer

$$\sigma = \exp\left(6,6 - \frac{0,38}{2kT}\right) \text{ (annealed sample).}$$

Taking the average grain size near 200  $\mu\text{m}$ , and varying the thickness of the surface layer, no just only qualitative agreement of the calculated curve  $\sigma(T)$  with experimental data failed. Obviously, some model representations for pressed samples and thin films, for which the model and developed, will be different. So, with the growth of a polycrystalline film, the structure of the intergranular boundaries should be the same for different directions. At the same time, for pressed samples, the pressure acting on the grains along and across the pressing axis, is different, which determine the different parameters in near-surface layers and, above all, their conductivity.

If the compression pressures are different in along and across the compression axis, then probably the resistance of the formed contacts will be different. That is, in formulas (1) and (2), instead of the value of the specific resistance  $\rho_g$ , it is necessary to enter separately  $\rho_{g1}$  and  $\rho_{g2}$ . The results of this calculation are presented in Fig. 3. In this case, satisfactory correlation with the experiment can be achieved for two sets of model parameters. In the first case it is assumed that the resistance of the near-surface layers along the compression axis is  $\sigma_1 = 10^{0.2} T^{-3.4}$ , while the resistance of the other four, and the thickness of the near-surface layer was varied. The most optimal values are  $\rho_{g2} = 5\rho_{g1}$ ,  $h = 2.5$  microns. Another model envisaged  $\sigma_2 = 10^{0.2} T^{-3.4}$ , and the other parameters witch set by fitting are  $\rho_{g1} = 30\rho_{g2}$ ,  $h = 13.5$   $\mu\text{m}$ . However, such a thickness of the near-surface layer seems ungrounded, and therefore the first option (a set of parameters) is more logical. It is worth paying attention to the fact that in both cases an assumption is required about the growth of conductivity of one of the layers. That is, it can be assumed that the lower compression pressures in the direction



**Fig. 3.** Dependence of the specific electrical conductivity of PbTe obtained by the method of compression of the powder from the temperature for annealed sample at 500 °C, calculated on the basis of the modified electrotechnical model. Parameters of calculation: solid curve -  $\rho_{g2}=5\rho_{g1}$ ,  $h=2,5$  microns; dashed curve -  $\rho_{g1}=30\rho_{g2}$ ,  $h=13,5$   $\mu\text{m}$ .

perpendicular to the compression axis will be much less destroying the near-surface layer, which results in higher values of its conductivity.

## Conclusions

1. The temperature dependences of the properties of the investigated materials are determined by the peculiarity of the structure of the grains obtained by the grinding of the synthesized ingot, namely, by the near-surface layer formed by the interaction of oxygen with the surface PbTe and its central part, which is characterized by its own conductivity.

2. Directional pressing at pressures of 1.0-2.0 GPa of thermoelectric materials based on the lead telluride

results in different properties of intergranular boundaries parallel and perpendicular to the compression axis. The ratio of the values of their specific conductivity is  $\sigma_{\parallel}/\sigma_{\perp} \approx 5$ .

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## Електротехнічна модель провідності плюмбум телуриду, отриманого методом пресування порошку

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Представлено результати дослідження термоелектричних властивостей плюмбум телуриду отриманого методом пресування порошку. Запропоновано модифіковану електротехнічну модель для інтерпретації емпіричних залежностей  $\sigma(T)$ , згідно якої пресований зразок представляється системою кристалітів з міжзерненними межами, властивості яких відрізняються вздовж та впоперек осі пресування.

**Ключові слова:** плюмбум телурид, легування, пресування, термоелектрична добротність.