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**ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА**
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# Temperature Dependencies of Electrical Properties of Thin Films Based on Solid Solutions PbSnAgTe

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The electrical properties of thin polycrystalline films of solid solutions $Pb_{18}Ag_2Te_{20}$, $Pb_{16}Sn_2Ag_2Te_{20}$ and $Pb_{14}Sn_4Ag_2Te_{20}$ (LATT) on mica-muscovite substrates have been investigated. The temperature dependencies of concentration and mobility of charge carriers for these condensates are researched. Predominant scattering mechanisms are established. These are scattering on ionized impurities and acoustic phonons at low and high temperatures respectively.

**Keywords:** lead telluride, solid solution, electrical property, thin films, LATT.

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## Introduction

Semiconductors of the $A_4B_6$ group are widely used to create on their basis heat-to-electricity converters operating in the temperature range (500 - 800) K [1-2]. Their main advantage over other alternative energy sources is reliability and long service life. In addition, thermoelectric converters can be used in large enterprises, where much of the thermal energy of a variety of devices is dissipated into the environment.

The main obstacle in this way is the relatively low efficiency of heat generators. This is due to the interconnection of the main thermoelectric parameters of the material, improving one of which we degrade another. One way to solve this problem is to modify the properties of the materials used for the converters by creating solid solutions or switching to nanosized materials [3-5]. The introduction of impurities and the creation of a significant number of intergranular boundaries allow relatively independently improving the required parameters of the material.

In [6-10], the possibility of achieving a high thermoelectric figure of merit for materials based on lead telluride with impurities of antimony and silver AgPbSbTe (LAST) was demonstrate. Such materials are multiphase, and their properties are highly sensitive to technological factors of production, which complicates the reproduction of the material with predetermined properties.

Solid solutions of PbSnAgTe (LATT) have been proposed as materials for p-branches of heat generators in [11]. According to [11], they, like LAST, are multiphase, which ensures the achievement of the required for practical use of low values of thermal conductivity. In [12, 13] solid solutions of PbSnAgTe obtained by thermal evaporation in vacuum were studied.

In this paper, the interpretation and analysis of the dependences obtained in [13] are perform. Due to the significant number of electrically active defects in the samples, as well as the temperature range of the researches, we used the model of scattering of free charge carriers on ionized defects and acoustic phonons.

## I. Analysis of experimental dependences

In [13] for mica-deposited polycrystalline films (~ 0.5 μm) of $Pb_{18}Ag_2Te_{20}$ n - type, it shown that Ag atoms cause a weak acceptor effect without the transition of conductivity to p-type. When introducing additional Sn ($Pb_{16}Sn_2Ag_2Te_{20}$, $Pb_{14}Sn_4Ag_2Te_{20}$), a p-type conductivity was obtain. Moreover, with increasing tin content, the concentration of current carriers increases.

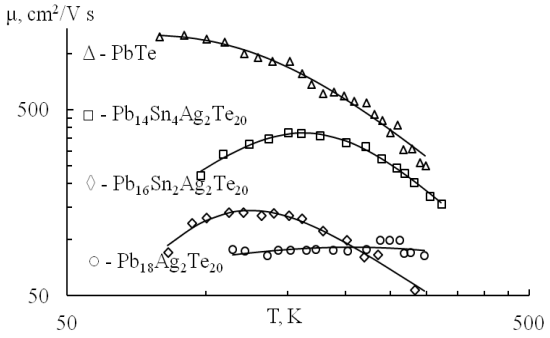


**Fig. 1.** Temperature dependence of mobility for films of different compositions. There are present experimental points and approximation curves by the formula (1). Experiment – [13].

X-Diffraction analysis of the films revealed a predominant orientation (111), indicating partial epitaxial growth. Temperature dependences of specific electrical conductivity and Hall mobility of the studied films turned out to be nonmonotonic with maxima, the coordinates of which depend on the chemical composition of the material.

These nonmonotonic temperature dependences of the mobility of charge carriers (Fig. 1) were approximated according to the Matissen rule by a function:

$$\mu = 1/((A/T)^{\alpha} + (T/B)^{\beta}), \qquad (1)$$

which containing two components that are responsible for the increase and decrease of mobility depending on temperature. Indicators α and β will indicate the scattering mechanism. The optimal parameters obtained from the approximation of the experimental dependences are presented in Table. 1. Units of measurement of parameters A and B are expressed through the following units: V, cm, s, K in power that depend on α and β. In the following, a formula with convenient units will be given.

From the table 1 shows that α is close to the value 1.75 = 7/4, which corresponds to scattering on ionized impurities, and β is close to the value 2.25 = 9/4, which corresponds to scattering on acoustic phonons [14-16]. Based on this, the temperature dependences of the mobility of charge carriers later were approximated by a function:

$$\mu = 1/(a/T^{7/4} + bT^{9/4}), \qquad (2)$$

where the first term is responsible for scattering on ionized defects, and the second on acoustic phonons. It is known that $b \sim E_{ac}^2/C_1$, where $E_{ac}$ is the deformation potential constant, $C_1$ is the average propagation velocity of acoustic oscillations; $a \sim N_I$, $N_I$ - the total number of ionized defects of both donors and acceptors [14, 16].

Let's perform linearization of dependence (1):

$$T^{7/4}/\mu = a + bT^4. \qquad (3)$$

Units of measurement of a and b has the same disadvantages as units of A and B, but it is easy to determine the parameters of convenient dimension from them: $T_{max}$ in K and $\mu_{max}$ in cm²/V s. These values are determined by formulas:

$$T_{max} = (7a/9b)^{1/4}, \ \mu_{max} = T_{max}^{7/4}/(a + bT_{max}^4). \qquad (4)$$

Optimal parameters obtained from the approximation of experimental dependences in coordinates $T^{7/4}\mu$ - $T^4$ (Fig. 2), presented in Table 2.

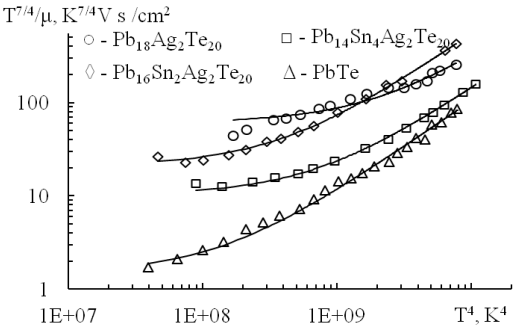


**Fig. 2.** Temperature dependence of mobility for films of different compositions:
Δ – PbTe, □ – $Pb_{14}Sn_4Ag_2Te_{20}$, ◊ – $Pb_{16}Sn_2Ag_2Te_{20}$, ○ – $Pb_{18}Ag_2Te_{20}$. There are present experimental points and approximation curves by the formula (3). Experiment – [13].

We present the dependence (1) in the form with parameters that have convenient units of measurement:

$$\mu = \mu_{max}(\alpha+\beta)/(\beta(T_{max}/T)^{\alpha} + \alpha(T/T_{max})^{\beta}). \qquad (5)$$

**Table 1**

Optimal parameters of approximation of experimental dependences μ(T) by function (1)

| Compound | A | B, $10^4$ | α | β |
|---|---|---|---|---|
| PbTe | 0.48 | 0.80 | 1.5 | 1.74 |
| $Pb_{18}Ag_2Te_{20}$ | 0.067 | 0.66 | 0.62 | 1.86 |
| $Pb_{16}Sn_2Ag_2Te_{20}$ | 4.18 | 0.14 | 1.58 | 2.39 |
| $Pb_{14}Sn_4Ag_2Te_{20}$ | 5.48 | 0.29 | 1.93 | 2.33 |

**Table 2**

Optimal parameters of approximation of experimental dependences μ (T) by functions (3, 4) and (6)

| Compound | a | b, $10^{-8}$ | $T_{max}$, K (3, 4) - (6) | $\mu_{max}$, $cm^2/V\ s$ (3, 4) - (6) |
|---|---|---|---|---|
| PbTe | 1.44 | 1.04 | 102 – 99 | 1261 – 1227 |
| $Pb_{18}Ag_2Te_{20}$ | 60.9 | 2.66 | 205 – 196 | 103 – 103 |
| $Pb_{16}Sn_2Ag_2Te_{20}$ | 20.9 | 5.28 | 132 – 130 | 139 – 141 |
| $Pb_{14}Sn_4Ag_2Te_{20}$ | 10.2 | 1.35 | 156 – 161 | 378 – 369 |

**Table 3**

Optimal parameters of approximation of experimental dependences n (T) by formula (8)

| Compound | $n_i(300)$, $10^{18}$ $cm^{-3}$ | $E_g(300)$, eV | $N_D^+(A^-)$, $10^{18}$ $cm^{-3}$ | γ, $10^{-4}$ eV |
|---|---|---|---|---|
| PbTe | 0.46 | 0.235 | 0.86 | 8.0 |
| $Pb_{18}Ag_2Te_{20}$ | 0.42 | 0.23 | 0.096 | 4.1 |
| $Pb_{16}Sn_2Ag_2Te_{20}$ | 0.59 | 0.22 | 0.59 | 4.0 |
| $Pb_{14}Sn_4Ag_2Te_{20}$ | 0.58 | 0.25 | 1.67 | 4.0 |

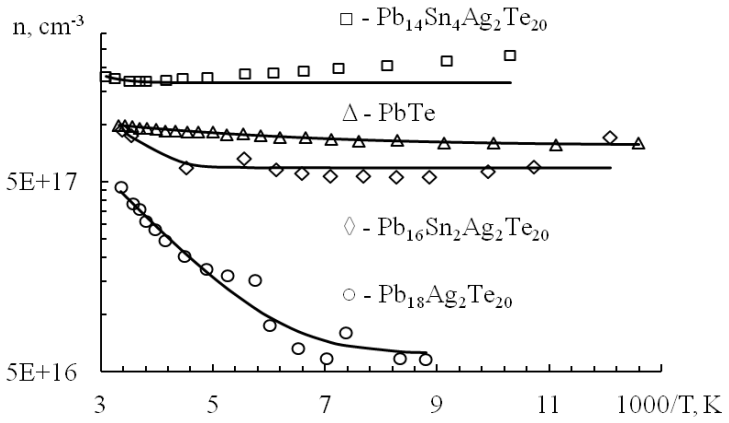


**Fig. 3.** Temperature dependence of Hall concentration for films of different compositions. There are present the experimental points and approximation curves by the formula (8). Experiment – [13].

Given the values of the parameters α and β, we rewrite (5) as follows:

$$\mu = \mu_{max}/(9/16(T_{max}/T)^{7/4} + 7/16(T/T_{max})^{9/4}). \quad (6)$$

The optimal parameters obtained from the approximation of the experimental data of Figs. 2 by dependence (6), are presented in Table. 2. The difference in the values of identical parameters, determined by different methods of approximation, indicates the error of these values, as well as the adequacy of the proposed model with experimental data.

If we enter a replacement $y = \mu/\mu_{max}$ and $x = T/T_{max}$, then we get a convenient dependence for analysis:

$$y = 16/(7x^{2.25} + 9/x^{1.75}). \quad (7)$$

The temperature dependences of the charge carriers concentration obtained in [13] can be explained by the change in the concentration of donor (acceptor) levels of $N_D^+(A^-)$ from the composition of the components and the contribution of the own conductivity at high temperatures. The temperature dependences of the concentration n(T) or p(T) (according to the type of sample) are obtained from the equation of electrical neutrality [17, 18].

$$n = N_D^+ + n_i^2(300)\exp(-(E_g(T)-E_g(300)T/300)/(kT))/n,$$

$$p = N_A^- + n_i^2(300)\exp(-(E_g(T)-E_g(300)T/300)/(kT))/p, \quad (8)$$

where the width of the forbidden zone:

$$E_g(T) = E_g(300) - \gamma\cdot(300 - T)\ eB, \quad (9)$$

$n_i(300)$ – own concentration of charge carriers at a temperature of 300 K. The concentration of donor levels $N_D^+$, (respectively acceptor levels $N_A^-$) is determined from the approximation of the experimental temperature dependences of the concentration of charge carriers (Fig.

3), given in Table. 3. The Table 3 shows that of the four parameters of the approximation significantly change the concentration of impurity levels, other parameters can be considered the same.

It should be noted that the concentration of silver atoms in solid solutions is 10 at. %, which corresponds to a concentration of ~ $10^{21}$ $cm^{-3}$ and is much higher than the concentration of ionized centers presented in table 3. Thus, we can assume that most silver atoms are in the electrically neutral state, most likely in the precipitates. This conclusion is consistent with the data on the solubility of silver impurities in PbTe, which according to [19] is in the range of 0.5 at.%.

## Conclusions

1. Based on the analysis of the results of measuring the mobility of charge carriers, it was found that for thin films of solid solutions p-$Pb_{14}Sn_4Ag_2Te_{20}$, p-$Pb_{16}Sn_2Ag_2Te_{20}$ and n-$Pb_{18}Ag_2Te_{20}$, as well as PbTe in the region of nitrogen temperatures, scattering on ionized impurities dominates. As the temperature increases, the role of this mechanism decreases, and scattering by acoustic phonons increases. The temperature of change of the dominant scattering mechanism depends on the chemical composition of the samples.

2. The concentration of carriers in the region of nitrogen temperatures is determined by the concentration of ionized impurities, and with increasing temperature for the interpretation of experimental dependences it is necessary to take into account their own carriers. In this case, the vast majority of silver atoms in the investigated solid solutions are in neutral state.

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# Температурні залежності електричних властивостей тонких плівок на основі твердих розчинів PbSnAgTe

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Розглянуто електричні властивості тонких полікристалічних плівок твердих розчинів $Pb_{18}Ag_2Te_{20}$, $Pb_{16}Sn_2Ag_2Te_{20}$ і $Pb_{14}Sn_4Ag_2Te_{20}$ (LATT) осаджених на підкладки із слюди. Досліджено температурні залежності концентрації та рухливості носіїв заряду наведених тонких плівок. Встановлено домінуючі механізми розсіювання носіїв заряду - розсіювання на іонізованих домішках та акустичних фононах при низьких та високих температурах відповідно.

**Ключові слова**: плюмбум телурид, тверді розчини, електричні властивості, тонкі плівки, LATT.