Electrophysical properties of PbTe doped with CdSe

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Abstract. The temperature dependences of electrical conductivity, thermoelectric power and thermoelectric power factor of solid solutions of the PbTe system doped with up to 3 mol% CdSe have been studied in the present work. The dependences show that these parameters reach their maximum values at a CdSe concentration of 3% in the temperature range of 420-450 K with \( \alpha = 310 \, \mu \text{V/K} \), \( \sigma = 210 \, (\text{Ohm} \cdot \text{cm})^{-1} \) and \( P = 15.1 \, \mu \text{W/(cm} \cdot \text{K}^2) \).

1. Introduction

To form thermoelectric converters with high figure of merit in low and medium temperature ranges and infrared receivers of wide range, semiconductor compounds based on lead chalcogenides (IV–VI), in particular PbTe–based ones, are used [1–5]. Using solid solutions based on PbTe as thermoelectric converters requires dopants which can increase its thermoelectric efficiency. It is of particular interest to study the behavior of impurities whose physical and chemical nature is similar to that of the initial component of a certain chemical compound. Doping of PbTe with Tl up to 2 at% [6] increases the thermoelectric figure of merit ZT of the material and is mainly used at low temperatures. Doping with nanoparticles of Na up to 1 at% [7] also increases ZT at high temperatures, and doping with In [8] improves sensitivity of photodetectors of thin films in the terahertz spectral range. Within the temperature range of 600 – 800 K, it is most technologically and economically advantageous to use impurities of semiconductor compounds, in particular of cadmium selenide, in lead telluride.

Peculiarities of the phase diagram of lead telluride make it significantly difficult to prepare homogeneous crystals that are similar in composition to the stoichiometric ones [1]. The maximum melting temperature of lead telluride is shifted towards that of chalcogen, and during solidification of lead telluride its composition changes as follows: first p–type crystals precipitate (with excess of tellurium), then the crystal composition changes towards a higher lead content and a transition from a p-type to an n-type conductivity can be observed. Only at a certain composition of the solid solution, which corresponds to the maximum melting temperature, the liquid phase retains its composition during solidification («invariant point»). Only for this composition, homogeneous crystals can be prepared by any method of crystallization from the melt. At all other compositions, including the stoichiometric one, a gradual change in crystal composition occurs during solidification.

The present work studies effects of doping lead telluride with cadmium selenide in the range of solid solutions (up to 3 mol% CdSe [9]) on temperature dependence of electrical conductivity and thermoelectric power in the temperature range of 300 – 480 K.

2. Experiment

For our investigations, we prepared samples of lead telluride with different molar concentrations of CdSe impurity (0.5, 1, 2, 3 mol%). As the starting components, we used lead of high purity (99.999 %), tellurium of high purity (99.999 %) and cadmium selenide of high purity as a disperse powder with a particle size of 28 – 35 \( \mu \text{m} \). The synthesis process was performed under the high temperature flux in atmospheric environment at 1183 K. The resulting melt was subjected to continuous mixing by acoustic waves of 22 kHz and 400 W. Then, the melt was kept for 15 minutes at
Next, the melt was cooled at a rate of 130 K/min to \( T = 823 \) K, after which it was subjected to homogenizing annealing for 8 hours.

The studied samples had the shape of a disk of 14–17 mm in diameter and 3–4 mm thick, which we then carefully polished using diamond paste and etched in the solution of \( \text{CrO}_3 \) (3g) + \( \text{H}_2\text{SO}_4 \) (25ml) + \( \text{H}_2\text{O} \) (75ml) for 3 minutes.

We studied electrical conductivity and thermoelectric power of the resulting semiconductor compounds in the temperature range of 300 – 480 K.

3. Results and discussion

We used the four-probe method to measure the specific electrical conductivity, \( \sigma \), of the semiconductor materials. The resulting temperature dependences of specific electrical conductivity for the PbTe–CdSe system show that in the temperature range of 300 – 350 K the undoped lead telluride compound has the highest value of \( \sigma \), equal to \( \sim 250 \) (Ohm·cm\(^{-1}\)) at \( T = 340 \) K (figure 1, line 1).

Adding small amounts of cadmium selenide (up to 2 mol\%) results in a decrease of the specific electrical conductivity in the same temperature range, showing the values \( \sigma = 110 \) (Ohm·cm\(^{-1}\)) for the sample with 1 mol\% CdSe (line 3) at \( T = 340 \) K, and \( \sigma = 72 \) (Ohm·cm\(^{-1}\)) for the sample with 2 mol\% CdSe (line 4) at \( T = 340 \) K. For the solid solution containing 0.5 mol\% CdSe (line 2), it is characteristic to have a slight change of the specific electrical conductivity over the entire temperature range. We got the maximum value of the specific electrical conductivity at a CdSe concentration of 3 mol\% at \( T = 470 \) K, that is \( \sigma = 210 \) (Ohm·cm\(^{-1}\)) (line 5).

![Figure 1](image-url)

Figure 1. Temperature dependences of electrical conductivity of PbTe doped with CdSe at different concentrations: 1 – 0 mol\%, 2 – 0.5 mol\%, 3 – 1 mol\%, 4 – 2 mol\%, 5 – 3 mol\%.

We used the standard differential method to measure the temperature dependence of thermoelectric power, \( \alpha \), in vacuum with a pressure of \( 1 \times 10^{-4} \) mmHg in the temperature range of 300 – 380 K. Figure 2 presents the obtained results.
Figure 2. Temperature dependences of thermoelectric power of PbTe doped with CdSe at different concentrations: 1 – 0 mol%, 2 – 0.5 mol%, 3 – 1 mol%, 4 – 2 mol%, 5 – 3 mol%.

The data obtained show that for all the compounds under study an increase in temperature leads to an increase in the thermoelectric power coefficient. The maximum value for the starting undoped lead telluride compound (line 1) is $\alpha = 275 \, \mu V/K$ at $T = 410 \, K$. When we added about 0.5 mol% CdSe (line 2), we observed a decrease in the thermoelectric power, and its maximum value shifts to higher temperatures ($\alpha = 236 \, \mu V/K$ at $T = 450 \, K$).

The thermoelectric power increases with temperature at CdSe concentrations of 1 mol% (line 3) and 2 mol% (line 4). The maximum values of the thermoelectric power are the following: $\alpha = 262 \, \mu V/K$ at $T = 470 \, K$ and $\alpha = 270 \, \mu V/K$ at $T = 430 \, K$. With increasing cadmium selenide concentration to 3 mol% (line 5), the thermoelectric power reaches the maximum value $\alpha = 310 \, \mu V/K$ at $T = 450 \, K$, which is highly important for devices operating in the high temperature range.

Using the obtained experimental values of the specific electrical conductivity and thermoelectric power for all the compounds under study, we calculated the specific thermoelectric energy (thermoelectric power factor), $P$, in the temperature range of 300 – 450 K by the formula

$$P = \alpha^2 \sigma.$$

Figure 3 presents the dependences of the thermoelectric power factor of the studied solid solution on the content of cadmium selenide. Analysis of the concentration dependences of the thermoelectric power factor of the investigated semiconductor compounds shows that at $T = 450 \, K$ (line 5) the maximum corresponds to the solid solution containing 3 mol% of cadmium selenide, $P = 15.1 \, \mu W/(cm\cdot K^2)$, while for the starting undoped compound of lead telluride $P = 5.6 \, \mu W/(cm\cdot K^2)$, which is almost 3 times lower. In our opinion, this result is highly important in terms of practical use.
We believe that to explain this character of temperature dependences of the investigated kinetic coefficients, one can use the so-called model of two valence bands [10]. According to this model, at low temperatures the band of heavy holes is lower than the edge of the band of light holes with a splitting $\Delta \varepsilon \approx 0.17$ eV. Therefore, at low temperatures only light holes play a dominant role. The bandgap $\varepsilon_g$ increases with increasing temperature, and the splitting $\Delta \varepsilon$ decreases. When the temperature reaches 400–500 K, the splitting completely disappears, and the tops of the bands of light and heavy holes coincide with each other. Yet further increase in temperature lowers the band of light holes even more, while the distance between the conduction band and the band of heavy holes does not change. Thereby, at high temperatures the valence band edge is the edge of the band of heavy holes, and the one of light holes can be disregarded in the electrical conductivity. As a result, the average hole effective mass increases, which leads to increasing of thermoelectric power coefficient. Apparently, adding CdSe changes the character of temperature and concentration dependences of the thermoelectric power factor. In this case, light holes stop dominating in the temperature range of 300–340 K, and the valence band edge is formed by the heavy holes. Thus, figure 3 shows decrease in the power factor at 300–340 K, while at higher temperatures the power factor increases.

4. Conclusions
Thus, the study of temperature dependences of electrical conductivity, thermoelectric power and thermoelectric power factor of solid solutions of PbTe–CdSe system has showed that they have maximum values at a CdSe concentration of 3 mol% in the temperature range of 420–450 K with $\alpha = 310$ $\mu$V/K, $\sigma = 210$ (Ohm·cm)$^{-1}$ and $P = 15.1$ $\mu$W/(cm·K$^2$).

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