Effect of magnetic Gd impurities on the electrical properties of PbTe single crystals

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Under investigation are temperature dependences of electric conductivity, free carrier concentration and mobility in single-crystalline PbTe:Gd samples with varied impurity content. The features of electron transport in PbTe:Gd may be caused by a variable gadolinium valence. The striking result from the Seebeck coefficient measurements is that the thermoelectric power factor increases dramatically. Measurements of the magnetic susceptibility at low temperatures permit us to suggest that Gd ions may exist in different charge states.

Keywords: narrow-gap semiconductors, lead telluride single crystals, rare earths, magnetic susceptibility.

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INTRODUCTION

Lead telluride single crystals doped with rare earths and transition metals have attracted great interest in recent years due to changes in their electrophysical properties. It was noticed that group III doped $A^{IV}B^{VI}$ compounds acquire new properties, not characteristic of undoped compounds, such as: Fermi level pinning, enhanced photosensitivity at low temperatures, persistent photoconductivity at low temperatures [1–4]. But so far there is insufficient information on the influence of rare earth impurities on the electrophysical properties of PbTe. It is well known that lead telluride could be used in thermoelectric and optoelectronic applications. A high deviation from the stoichiometric composition results in a high concentration (10^{18}–10^{19} cm^{-3}) of native defects. The concentration of free carriers can be controlled by doping of PbTe with group III elements, in particular, doping with In, Ga or Tl. Doping of PbTe with Yb and Gd in a certain range, as well as with the above-mentioned group III impurities, leads to Fermi level pinning in the valence and conduction bands, respectively [5–7], in addition to a decrease in the concentration of native defects.

It was revealed that Gd-doped lead telluride compounds are of *n*-type and have improved thermoelectric efficiency, while Yb-doped single crystals are of *p*-type and are photosensitive to IR radiation at low temperatures. Moreover, there is no direct relationship between the doping range and concentration of the free carriers. This fact could be accounted for by Ytterbium and Gadolinium mixed-valence charge states in PbTe:Yb and PbTe:Gd single crystals [6–7].

In this paper, we present the results of research of the influence of Gd impurity on the electrical and thermoelectric properties of PbTe.

EXPERIMENTAL METHOD

Samples

Lead telluride single crystals were grown by the Bridgman method. The compound of GdTe was used as a source of the doping element during synthesis. The concentration of the doping element C_{Gd} was selected to be 1 and 2 at %. The resulting samples had a single-phase composition of lead telluride confirmed by powder X-ray diffraction. Chemical etching was used to estimate the concentration of dislocations, and its values were of 10^6 cm^{-2}, which is typical for the selected crystal growth technique. Samples of dimensions of 1×1.5×5 mm^3 were cut parallel to the <100> direction of the ingot. Electrical contacts to the *n*-type samples were soldered with an indium alloy.

Characterization

Magnetic susceptibility (MS) measurements were carried out by the standard Faraday method using a CAHN 1000 electrobalance. MS measurements were performed in a temperature range of 4.2–300 K under magnetic fields up to 0.3 T. The concentration of free carriers was obtained from the data of Hall measurements. DC electric conductivity measurements were performed using a standard 4-probe method in a temperature range of 77–300 K. The samples were chemically polished in a HBr + 5% Br_2 solution.

RESULTS AND DISCUSSION

Temperature dependences of electric conductivity, concentration of free carriers, electric mobility, and thermoelectric coefficient are shown in Figs. 1–4. The basic experimental data are presented

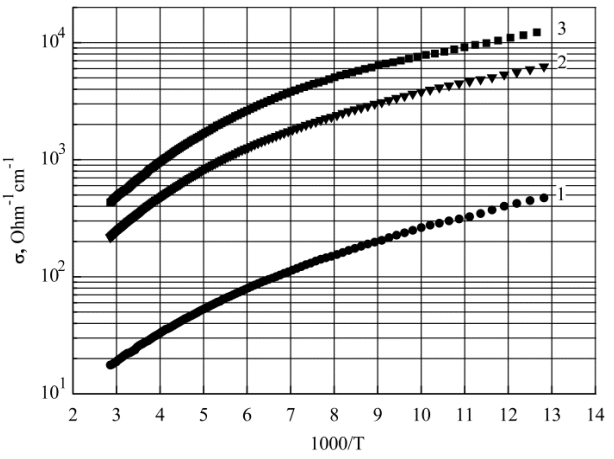

Fig. 1. Measured temperature dependences of electric conductivity of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

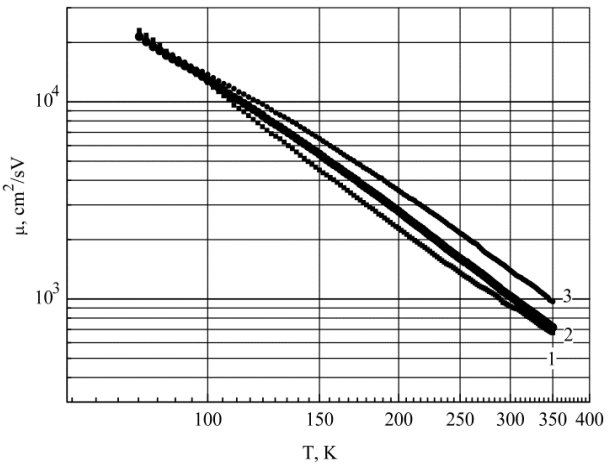

Fig. 2. Measured temperature dependences of electric mobility of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

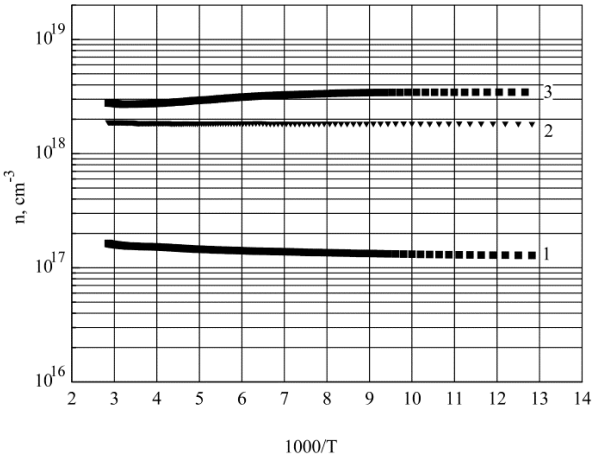

Fig. 3. Measured temperature dependences of concentration of free carriersl conductivity of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

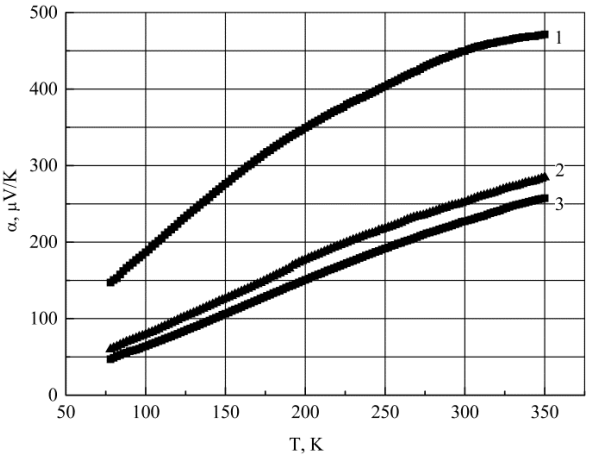

Fig. 4. Measured temperature dependences of Seebeck coefficient of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

in the table. The maximal concentration of Gd was selected to be 1 and 2 at %.

As is evident from Fig. 1, the electric conductivity σ(1000/T) in PbTe:Gd decreases with the increase of temperature.

Table. Basic experimental parameters of PbTe:Gd

	T = 300K		
	PbTe	C_{Gd}=1at%	C_{Gd}=2 at%
σ, Ohm^{-1}cm^{-1}	23	325	606
α, μV/K	451	253	227.3
μ, cm^2/V·s	931	1050	1392
n, cm^{-3}	$1.56\cdot10^{17}$	$1.85\cdot10^{18}$	$2.71\cdot10^{18}$
$\alpha^2\sigma$, 10^6	4.68	21	31.3

Temperature dependences of mobility in Fig. 2 demonstrate regularities $\mu \sim T^{-2.2}$ for PbTe:Gd and $T^{-2.35}$ for undoped PbTe, which is somewhat different from the standard law $\mu \sim T^{-3/2}$ that characterizes the scattering of carriers to the acoustic phonons. As was pointed out in [8, p.60], in certain semiconductors with a narrow band gap (for example, PbTe and PbSe) a significant contribution to the law $\mu \sim T^{-3/2}$ can give a variation of the effective mass on temperature and therefore the dependence of the mobility on temperature may be stronger than $\mu \sim T^{-3/2}$ [8]. For example, the authors in [9, p.96] indicate the dependence $\mu(T) \sim T^{-5/2}$ for PbTe samples. Thus, a fairly high coefficient of the degree of temperature in dependence $\mu \sim T^{-2.2}$ and $T^{-2.35}$, obtained in our experiment, is consistent with the statement above, and we may suppose that the mechanism of scattering in the present case also is related to the acoustic phonons.

The maximal value of the mobility $\mu \approx 1400$ cm^2/(V·s) at room temperature is typical of the conduction band electrons in this temperature range. The concentration of free carriers was obtained from the data of Hall measurements. Fig. 3 presents temperature dependences of the carrier concentration in PbTe:Gd and undoped PbTe crystals. The samples of Gd doped PbTe exhibit the same temperature dependences of the concentration of free carriers. The samples are degenerated and electrically active Gd impurities show a pronounced donor action in the PbTe crystals (part of Pb^{2+} ions is replaced by Gd^{3+}). An increase in the Gd impurity concentration leads to an increase in the free elec-

tron concentration resulting in an increase in electric conductivity. But there is no direct relationship between the concentration of Gd and free carrier concentrations in the PbTe:Gd crystals.

An important outcome from the Seebeck coefficient measurements is that the thermoelectric power factor increases significantly. Measurements of the temperature dependences of thermoelectric properties show that the Seebeck coefficients α = 253 μV/K and α = 227 μV/K for PbTe:Gd<1%> and PbTe:Gd<2%>, respectively, are not stronger than those for undoped PbTe α = 450 μV/K. However, free-carrier mobilities are higher and along with the increased concentration of electrons provide a considerable thermoelectric power factor at room temperature. Assuming that the main thermal conductivity features could not be affected due to weak changes in electronic contribution to the thermal conductivity, an improvement in the figure of merit is expected. It is known that lead telluride compounds achieve a larger figure of merit at 500–600˚C, and room temperatures are not of great interest. Thus, the power factor/figure of merit estimated at room temperature could achieve higher values at higher temperatures, which provides higher thermoelectric efficiency.

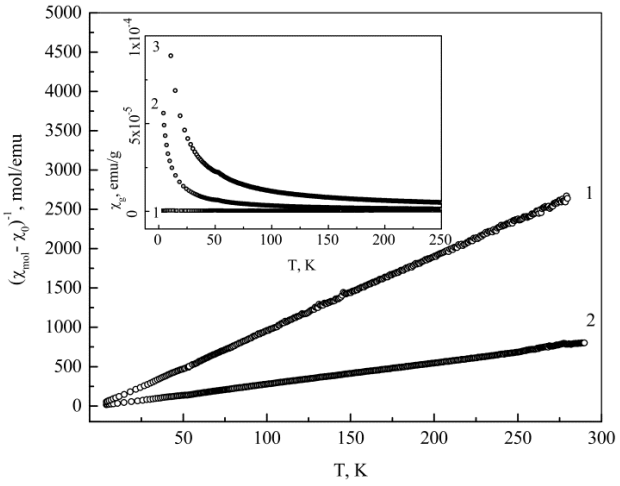

Fig. 5. Temperature dependences of inverse molar MS of (1) PbTe:Gd<1%> and (2) PbTe:Gd<2%>. In inset: temperature dependences of magnetic susceptibility for: 1 – PbTe; 2 –PbTe:Gd<1%>; 3 – PbTe:Gd<2%>.

MS measurements at temperatures ranged within 4.2 and 300 K were carried out for doped samples mentioned above (see Fig. 5). MS data show that the paramagnetic Gd impurities are present in the two investigated samples and exhibit the standard Curie-Weiss dependence at low temperatures (T < 60 K):

$$\chi = \frac{C}{T - \Theta}. \qquad (1)$$

In order to correctly interpret the magnetization measurements it was necessary to know the susceptibility contribution of the host material χ_0 that may be diamagnetic for pure PbTe, as was shown in [9, 10]. However, in the investigated PbTe samples the magnetization was very small and with positive sign, which suggests a paramagnetic contribution. In analyzing data for PbTe:Gd samples we denote experimental measured magnetic susceptibility as:

$$\chi^* = \chi_0 + \frac{C}{T - \theta} \equiv \chi_{exp}. \qquad (2)$$

The magnetic susceptibility of single PbTe crystals with electron concentrations of $1.5 \cdot 10^{-17}$ cm^{-3} was measured at temperatures from 4.2 to 300 K in magnetic fields up to 0.3 T. The found value of $4.5–5 \cdot 10^{-7}$ emu/g is practically independent of temperature (inset in Fig. 5, curve *1*). Really it is very difficult to determine properly the contribution from the host lattice to the susceptibility of the investigated PbTe:Gd crystals, since the initial electron concentration of PbTe changed when changing the Gd content. Thus, the characterizing host material parameter χ_0 in the sample of PbTe:Gd may be slightly different from that in pure PbTe.

Nevertheless, while analysing our data for PbTe:Gd and PbTe we have found out that the magnetic susceptibility in the magnetic field up to 0.3 T may be well described by the fitting parameter $\chi_0 = 4{,}5–5 \cdot 10^{-7}$ emu/g.

We have noticed that there is no relationship between χ_0 and the material parameters of Gd from Eq. (3).

The Curie constant values calculated from the line slopes of inverse molar susceptibility were used to estimate charge states of the magnetic centers. We obtained the following values: C_m = 0.11 and C_m = 0.38 for PbTe:Gd<1%> and PbTe:Gd<2%>, respectively.

Taking into consideration the expression of magnetic susceptibility for paramagnetic materials:

$$\chi_p = \frac{N_{Gd}\, p_{eff}^2 \mu_B^2}{3 k_B T} \qquad (3)$$

where N_{Gd} and p_{eff} are the concentration of paramagnetic atoms or ions and their effective magnetic momentum, respectively; μ_B is the Bohr magneton; and k_B is the Boltzmann constant, an effective magnetic momentum that does not correspond to the Gd^{2+} or Gd^{3+} charge states was derived. It means that there are Gd impurities in different charge states and that the ratio between those charge states depends on the doping level [11–14].

Experimental data in Fig. 5 can be extrapolated by lines that intersect the abscissa at a negative temperature (θ = -1.8 K). This fact testifies to the presence of weak antiferromagnetic interaction between magnetic centers.

CONCLUSIONS

Lead telluride single crystals doped with gadolinium exhibited high power factor, electric mobility and considerable electric conductivity. This fact permit us to assume that lead telluride based compounds can be used in energy conversion systems.

The MS measurements at low temperatures suggest that there are Gd ions in different charge states and that the ratio between those charge states depends on the doping level.

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Реферат

В работе исследованы температурные зависимости электрической проводимости, концентрации свободных носителей и подвижности в монокристаллических образцах PbTe:Gd с примесями в различной концентрации. Наблюдаемые особенности, обнаруженные в результате измерения коэффициента Зеебека, состоят в существенном увеличении коэффициента термоэлектрической мощности. Измерения магнитной восприимчивости при низких температурах позволяют предположить, что ионы гадолиния могут находиться в различных зарядовых состояниях.

Ключевые слова: узкозонные полупроводники, монокристаллы PbTe, редкоземельные элементы, магнитная восприимчивость.