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ELECTRICAL PROPERTIES OF LEAD TELLURIDE SINGLE CRYSTALS DOPED WITH Gd

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Abstract–*Temperature dependences of electric conductivity, free carrier concentration and mobility in single-crystalline PbTe:Gd samples with a varied impurity content are investigated. 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 exist in different charge states.*

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

1. INTRODUCTION

Lead telluride single crystals doped with rare earths and transition metals have attracted a great interest in the recent years due to changes in electrophysical properties. It was observed that group III doped $A^{IV}B^{VI}$ compounds acquire new properties which are not characteristic of undoped compounds, such as: Fermi level pinning, enhanced photosensitivity at low temperatures, remanent behaviour of the photoconductivity at low temperatures [1 – 4]. But so far there are relatively few data 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 the above mentioned group III impurities, leads to Fermi level pinning in the valence and conduction band, respectively [5–7] in addition to a decrease in the concentration of native defects.

It was observed that Gd-doped lead telluride are of *n*-type and exhibit an improvement in thermoelectric efficiency, and 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 explained 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.

2. EXPERIMENTAL

Samples. Lead telluride single crystals were grown by the Bridgman method. A GdTe compound 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 are of 10^6 cm^{-2} which are 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 Hall measurements data. 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.

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3. RESULTS

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

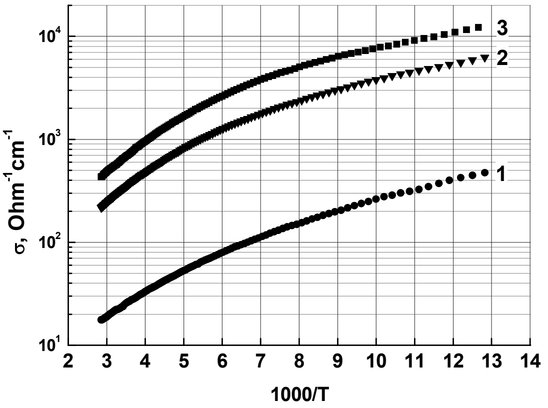

Fig. 1. Measured temperature dependences of the electric conductivity of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

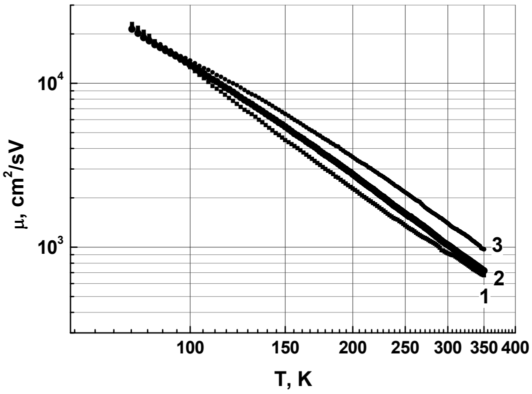

Fig. 2. Measured temperature dependences of the concentration of free carriersl conductivity of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

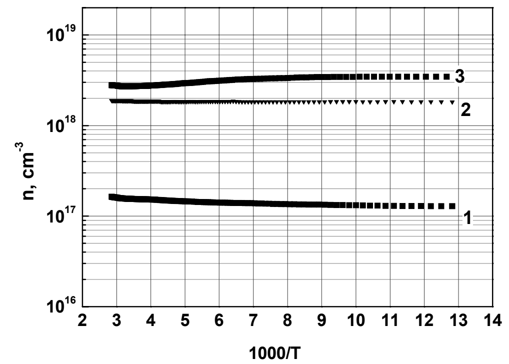

Fig. 3. Measured temperature dependences of the electric mobility of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

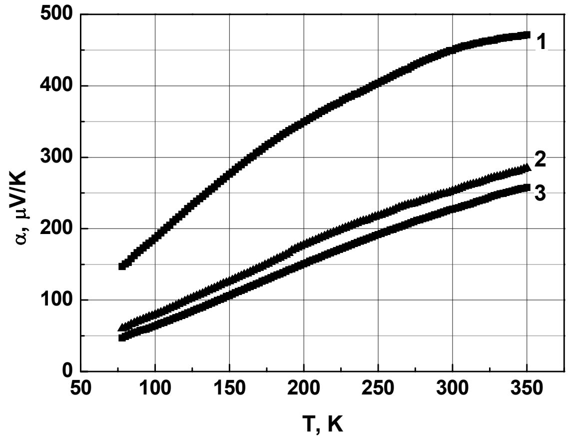

Fig. 4. Measured temperature dependences of the Seebeck coefficient of: (1) PbTe; (2) PbTe:Gd<1%>; (3) PbTe:Gd<2%>.

Table 1. 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}	$1{,}56\cdot10^{17}$	$1{,}85\cdot10^{18}$	$2{,}71\cdot10^{18}$
α^{2}σ, 10^6	4,68	21	31,3

It is evident from Figs. 1a and 1b that the electric conductivity σ(1000/T) in PbTe:Gd decreases with increasing temperature.

The free-carrier mobility follows a dependence $T^{2.35}$ for undoped PbTe and $T^{-2.2}$ for PbTe:Gd, which indicates that the diffusion is related to the acoustic phonons. The deviation of the diffusion coefficient from its theoretical value is conditioned by the temperature dependence of the effective mass. 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 Hall measurements data. Figure 2 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 electrical 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 electron concentration resulting in an increase in electric conductivity. But there is no direct relation between Gd and free carrier concentrations in the PbTe:Gd crystals.

The important result from the Seebeck coefficient measurements is that the thermoelectric power factor increases significantly. Measurements of the 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 for undoped PbTe α = 450 μV/K. However, free-carrier mobilities are higher and along with 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 better 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 better values at higher temperatures which provide better thermoelectric efficiency.

MS measurements at temperatures ranged within 4.2 and 300 K were carried out for doped samples mentioned above. Figure 5 shows the MS measurements for the samples under study. 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):

$$\chi = \chi_0 + \frac{C}{T-\theta}$$

$$\chi = \frac{N_{Gd} p_{eff}^2 \mu_B^2}{3k_B T}$$

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.

It should be noted that undoped lead telluride is also paramagnetic with very weak temperature independent MS $\chi_g \sim 4{,}5\text{-}5\cdot10^{-7}$ emu/g. 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. It means that impurities exist in different charge states (the derived effective magnetic momentum does not correspond to the Gd^{2+} or Gd3+ charge states) and the ratio between these charge states depends on doping level [8-11].

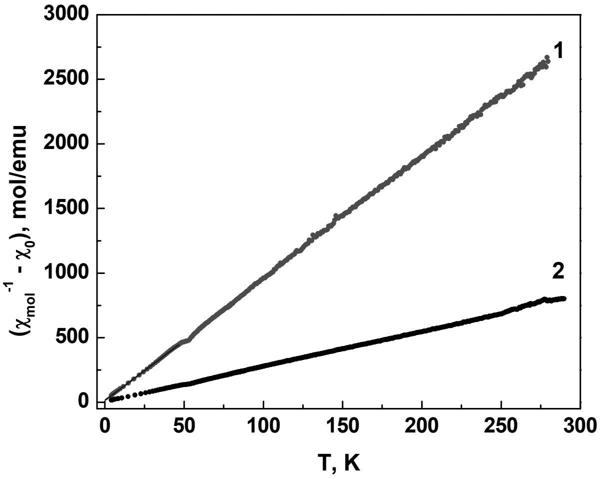

Fig. 5. Temperature dependences of the inverse molar MS of (1) PbTe:Gd<1%> and (2) PbTe:Gd<2%>.

Experimental data shown in Fig. 5 can be extrapolated by lines which intersect the abscissa at a negative temperature (θ=–1,8 K). This fact indicates the presence of weak antiferromagnetic interaction between the magnetic centers.

4. CONCLUSIONS

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

The MS measurements at low temperatures permit us to suggest that Gd ions exist in different charge states and the ratio between these charge states depends on doping level.

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