THERMOELECTRIC FIGURE OF MERIT OF $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ AND $Hg_{1-x}Mn_xTe_{1-z}S_z$ CRYSTALS

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- *In this paper, we report on the results of research on the temperature dependences of the electric conductivity and thermoEMF, as well as estimate the value of thermoelectric figure of merit Z of $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ crystals prior to and after thermal treatment of samples in component vapors. Based on the resulting values of Z it can be concluded that the afore-referenced materials can be used in thermoelectric devices.*

Introduction

Semimagnetic semiconductor solid solutions $Hg_{1-x}Mn_xS$, with the region of existence ($0 < x \le 0.375$) [1], $Hg_{1-x-y}Mn_xFe_yS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ that we prepared by the Bridgman method possess *n*-type conduction (electron concentration $n \sim 10^{18}$cm^{-3}). In this paper, the value of thermoelectric figure of merit *Z* of $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ crystals is estimated. Based on the resulting values of *Z* it can be concluded that the afore-referenced materials can be used in thermoelectric devices.

Experiment and its results

Investigations of the kinetic effects at $T = 77$–300 K were conducted at direct current.

For the manufacture of samples we used washers cut perpendicular to crystal growth axis. The samples were cut such that each of them comprised only one block and had the shape of a parallelepiped with the sides: $l \sim 8$ mm; $a \sim 1.2$ mm, $b \sim 1$ mm. Grinding was done on a flat glass using an emulsion of grinding powders, with a consecutive reduction of powder grain size from 28 to 5 μm. After grinding, the samples were polished on silk cloth using diamond pastes, and then washed with alcohol.

For the measurements, two pairs of Hall probes are soldered to the sample surface. Indium, for instance, serves as contact material, current contacts must cover completely the sample ends, potential contacts must be arranged in a plane perpendicular to direction **H**, and the distance between them must satisfy the inequality $(c/r) >> 1$, where *r* is radius of contacts, *c* is the distance between their centres. The sample composition was controlled by magnetic susceptibility method.

Investigation of the kinetic properties of crystals has shown that thermoEMF |α| of $Hg_{1-x-y}Mn_xFe_yS$ crystals (Fig. 1) (just as $Hg_{1-x}Mn_xS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ crystals [2, 3, 4]) grows with a rise in temperature, as long as with increasing *T*, the degree of electron gas degeneracy in the samples is reduced. The electric conductivity (σ) of $Hg_{1-x-y}Mn_xFe_yS$ samples (Fig. 2) (just as of $Hg_{1-x}Mn_xS$ samples [2, 3]) prior to an after thermal treatment in *S* and *Hg* vapor is of metallic nature, i.e. grows with a decrease of temperature, whereas in $Hg_{1-x}Mn_xTe_{1-z}S_z$ it is of semiconductor nature [4]. After thermal treatment in mercury and sulfur vapor the electric conductivity of $Hg_{1-x-y}Mn_xFe_yS$ samples at low temperatures is considerably reduced (Fig. 2). Moreover, annealing in mercury vapor reduces the concentration of electrons and increases their mobility, whereas annealing in sulfur vapor increases the concentration of electrons and reduces their mobility.

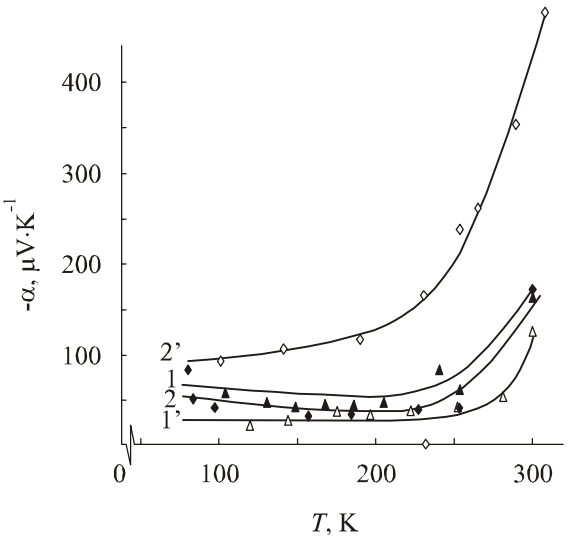

Fig. 1. Temperature dependence of the thermoEMF of $Hg_{1-x-y}Mn_xFe_yS$ samples.

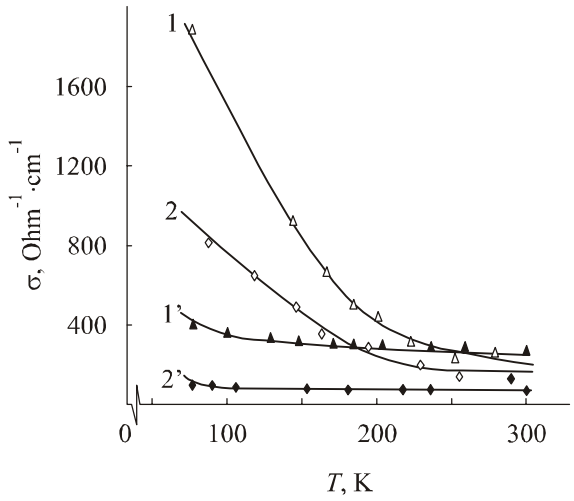

Fig. 2. Temperature dependence of the electric conductivity of $Hg_{1-x-y}Mn_xFe_yS$ samples.

1, 1' – (x + y) = 0.06; 2, 2' – (x + y) = 0.1; 1 – prior to annealing in S vapor; 1' – after annealing in S vapor; 2 – prior to annealing in Hg vapor; 2' – after annealing in Hg vapour.

Having performed the measurements of the thermoEMF α of crystals, the specific electric conductivity σ and knowing the thermal conductivity λ, one can determine the thermoelectric figure of merit $Z = \frac{\alpha^2 \cdot \sigma}{\lambda}$ of $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ crystals, as well as estimate the possibility of their use as material for thermoelectric devices.

Due to the absence of data in the literature on the value of thermal conductivity λ of $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ and *HgS* solid solutions, for the estimation of *Z* we used the value of λ the same as that of *HgSe*. The point is that for chalcogenides with sphalerite structure the values of lattice thermal conductivity $\lambda_p \approx 0.02$ W/cm·K [5] for *HgTe*, and for *HgSe* $\lambda_p \approx 0.019$ W/cm·K [5]. As long as the values of λ_p for *HgTe* and *HgSe* differ very little, it can be assumed that for *HgS* (with sphalerite structure) λ_p will be about the same (or even lower). Taking also into account that, after all, *HgS* is closer in its properties to *HgSe*, we, therefore, assume $\lambda(Hg_{1-x-y}Mn_xFe_yS) \approx \lambda(Hg_{1-x}Mn_xS) = \lambda_p(HgS) \approx \lambda_p(HgSe) = 0.019$ W/cm·K, where $\lambda_p(HgSe)$ is lattice thermal conductivity of *HgSe* (at $T \approx 300$ K). Account of the electron thermal conductivity λ_e would increase $\lambda(Hg_{1-x}Mn_xS) \approx \lambda_p(HgS)+\lambda_e$, and account of the specific feature of lattice thermal conductivity of solid solutions that consists in considerable reduction of its value as compared to the initial components [5], would lead to reduction of λ by $\Delta\lambda_p$ and then $\lambda(Hg_{1-x}Mn_xS) \approx \lambda_p(HgS)-\Delta\lambda_p+\lambda_e$. Taking into account that $\Delta\lambda_p$ and λ_e are equal in magnitude, but opposite in sign, we assume for $Hg_{1-x}Mn_xS$ and $Hg_{1-x-y}Mn_xFe_yS$ that $\lambda(Hg_{1-x-y}Mn_xFe_yS) \approx \lambda(Hg_{1-x}Mn_xS) \approx \lambda_p(HgS) \approx \lambda_p(HgSe) = 0.019$ W/cm·K (for small compositions "*x*" close to *HgS*).

The thus obtained *Z* values (at $T \approx 300$ K) are represented in Table 1 for $Hg_{1-x}Mn_xS$ samples, in Table 2 – for $Hg_{1-x-y}Mn_xFe_yS$ and in Table 3 – for $Hg_{1-x}Mn_xTe_{1-z}S_z$. From Tables 1 – 3 it is seen that annealing leads to increase of thermoelectric figure of merit, and introduction of *Fe* atoms into a solid solution also brings about a drastic increase of *Z* (Tables 1 and 2, $x = 0.12$ and $(x + y) = 0.1$).

Table 1

Thermoelectric figure of merit of $Hg_{1-x}Mn_xS$ crystals (T = 300 K)

x	$n\cdot10^{-18}$, cm^{-3}	σ, $Ohm^{-1}cm^{-1}$	-α, μV/K	$Z\cdot10^3$, K^{-1}	Annealing
0.017	1.1	184	200	0.37	prior to annealing
0.027	0.9	76	155	0.09	prior to annealing
0.03	2.7	49	79	0.15	prior to annealing
	2.7	594	78	0.18	annealing in mercury vapor
0.03	12	488	95	0.22	prior to annealing
	2.4	593	154	0.7	annealing in sulfur vapor
0.03	2.5	119	92	0.05	prior to annealing
	4.9	88	60	0.02	annealing in sulfur vapor
0.046	0.9	69	120	0.05	prior to annealing
0.069	0.5	25	210	0.06	prior to annealing
0.12	5.9	78	180	0.13	prior to annealing

Table 2

Thermoelectric figure of merit of $Hg_{1-x-y}Mn_xFe_yS$ crystals (T = 300 K)

$(x + y)$	$n\cdot10^{-18}$, cm^{-3}	σ, $Ohm^{-1}cm^{-1}$	-α, μV/K	$Z\cdot10^3$, K^{-1}	Annealing
0.037	14	464	50	0.06	prior to annealing
0.06	1.6	360	120	0.26	prior to annealing
	2.1	320	160	0.41	annealing in sulfur vapor
0.1	42	120	450	1.22	prior to annealing
	2.1	72	170	0.1	annealing in sulfur vapor

Sample compositions x and $(x + y)$ were obtained on the basis of $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ magnetic susceptibility measurements [2, 4, 6].

Growth of sulfur content in $Hg_{1-x}Mn_xTe_{1-z}S_z$ increasing the electron component of kinetic coefficients, and thermal treatment of samples in sulfur vapor result in the growth of the thermoelectric figure of merit reaching high values ($Z \sim 2.1 \cdot 10^{-3}$ K^{-1}) non-typical of other solid solutions based on mercury chalcogenides.

Table 3

Thermoelectric figure of merit of $Hg_{1-x}Mn_xTe_{1-z}S_z$ crystals ($x \sim 0.001$)

y	T, K	α, μV/K	σ, 1/Ohm·cm	λ W/cm·K	$Z \cdot 10^3$, K^{-1}	Annealing
0.01	100	30	100	0.092	0.001	prior to annealing
	300	-120	750	0.02	0.540	
0.05	100	-25	144	0.092	0.001	prior to annealing
	300	-137	750	0.02	0.704	
0.05	100	-20	130	0.092	0.0005	prior to annealing
	300	-120	830	0.02	0.598	
	100	-70	530	0.092	0.026	annealing in mercury vapor
	300	-100	1440	0.02	0.720	
	100	-80	590	0.092	0.038	annealing in sulfur vapor
	300	-120	1700	0.02	1.224	
0.1	100	20	90	0.092	0.0004	prior to annealing
	300	-140	650	0.02	0.637	
	100	50	270	0.092	0.007	annealing in sulfur vapor
	300	-200	1070	0.02	2.140	
0.1	100	-60	260	0.092	0.010	prior to annealing
	300	-110	2150	0.02	1.300	
	100	-80	1260	0.092	0.088	annealing in mercury vapor
	300	-140	2600	0.02	2.550	
	100	70	990	0.092	0.053	annealing in sulfur vapor
	300	-145	2500	0.02	2.628	

Conclusions

In conclusion it bears repeating that the resulting high values of thermoelectric figure of merit Z of $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ crystals (non-typical of other solid solutions based on mercury chalcogenides) are of evaluative nature, the real Z values could be obtained with the experimental results of research on thermal conductivity λ of $Hg_{1-x}Mn_xS$, $Hg_{1-x-y}Mn_xFe_yS$ and $Hg_{1-x}Mn_xTe_{1-z}S_z$ crystals, and they would be even greater for the reasons stated above.

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