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THERMOELECTRIC PROPERTIES OF $Pb_{0.85}Ge_{0.15}Te$ SOLID SOLUTION

A.I. Vahanyan, E.M. Baghiyan, V.K. Abrahamyan, H.G. Demirkhanyan,

Yerevan State University, E-mail: aivahanyan@yahoo.com

A.H. Yepremyan

Sonics Armenia Holdings Inc., Armenian Branch, 41 Arshakunyats St., Yerevan 0026

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1. Introduction

Solid solutions of $Pb_{1-x}Ge_xTe$ are considered as perspective materials for creation of thermo elements and cooling systems. We investigated thermoelectric properties of the composition with x = 0.15. Obtained experimental results and their analysis are reported in this paper.

2. Experiment and discussion of results

Temperature dependences of coefficients of the thermal e.m.f. $\alpha(T)$, electrical conductivity $\sigma(T)$, and thermal conductivity $\chi(T)$ in the 120-500 K temperature range were measured. Measurement results of the thermal e.m.f. coefficient in the mentioned temperature range are given in Fig. 1. As can be seen from Fig. 1, the thermal conductivity coefficient sharply decreases from about 120 K to 170 K, then the constant and low enough value [~0.8×10^{-2} W/(cm·K)] is kept in a wide temperature range (170–360 K) which is a premise for obtaining high values of figure-of-merit for this material. Later on $\chi(T)$ decreases again, reaching the value of 0.35×10^{-2} W/(cm·K) at 500K.

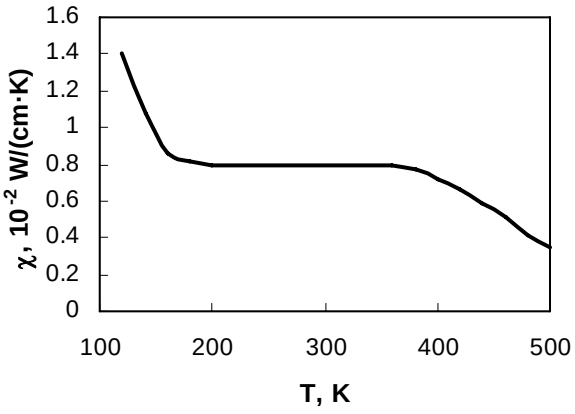

Fig. 1

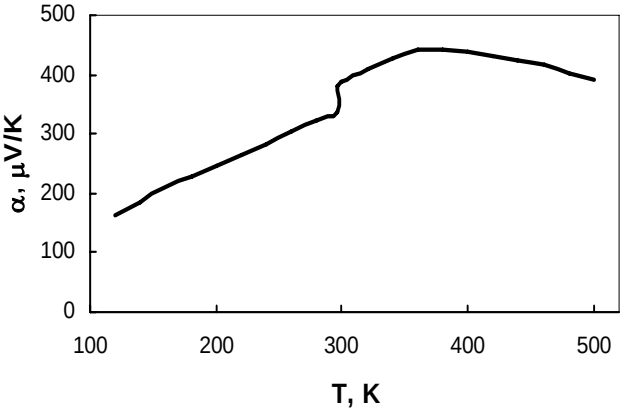

Fig. 2

The temperature dependence of the thermal e.m.f. coefficient is shown in Fig. 2. As follows from Fig. 2, a nearly linear change of $\alpha(T)$ is observed up to 295 K, then a jump of the thermal e.m.f. coefficient from 337 to 380 μV/K occurs at 297 K.

The temperature dependence of the electrical conductivity coefficient is presented in Fig. 3. As seen in Fig. 3, the electrical conductivity increases, reaching its maximal value 180 $\Omega^{-1}\cdot cm^{-1}$ at the temperature of 170 K, then decreases, undergoing a small but abrupt fall at 297 K. The mentioned jump in the dependence $\alpha(T)$ and the abrupt decrease in the dependence $\sigma(T)$ at the same temperature (at 297 K) indicate the presence of a phase transition.

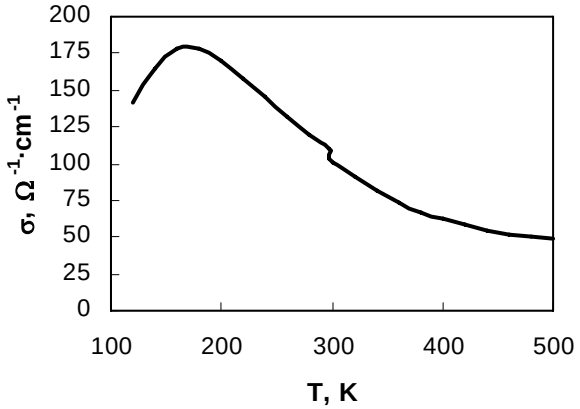

Fig. 3

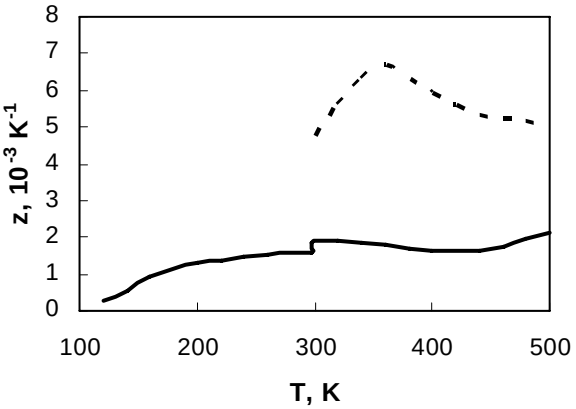

Fig. 4

There are some experimental data in literature pointing out that phase transitions with a change of structure are observed in similar solid solutions [1, 2]. In our opinion, we also have a phase transition as in some solid solutions of such type, and the crystalline lattice structure changes from rhombic to cubic.

It is known that the figure-of-merit of a material is defined by the expression

$$z = \frac{\alpha^2 \sigma}{\chi}. \qquad (1)$$

The temperature dependence of the figure-of-merit $z(T)$ is calculated on the basis of $\alpha(T)$, $\sigma(T)$, and $\chi(T)$ (Fig. 4, solid line). As can be seen from Fig. 4, the values of the figure-of-merit are low enough up to the temperature 180K. Then the values of z increase up to the phase transition temperature, where a jump of the value of z from $1.56\times10^{-3}K^{-1}$ to $1.95\times10^{-3}K^{-1}$ occurs. Thereafter the values of the figure-of-merit slowly decrease up to $1.64\times10^{-3}K^{-1}$ at 420K, and then increase again, reaching the value of $2.3\times10^{-3}K^{-1}$ at 500K. According to Ref. [1], the valence band of $Pb_{1-x}Ge_xTe$ solid solutions has a two-valley structure. Having the values of energy gaps for initial materials (Pb, Ge, and Te), the following expression is obtained for the $Pb_{0.85}Ge_{0.15}Te$ solid solution, using the linear approximation

$$\delta E = 0.1875 - 3\times 10^{-4} T\,. \tag{2}$$

Effective masses of light and heavy holes of the investigated material are also defined, using the linear approximation ($m_1 = 0.486m_0$, $m_2 = 1.695m_0$). As the valley of light holes in the valence band consists of 4 L-maxima and the valley of heavy holes consists of 12 Σ-maxima [1], the ratio of relative occupancies of the heavy and light holes can be presented by the expression

$$\frac{c_2}{c_1} = \frac{p_2}{p_1} = M\left(\frac{m_2}{m_1}\right)^{3/2} e^{-\frac{\delta E}{kT}}\,. \tag{3}$$

The temperature dependences of $c_1(T)$ and $c_2(T)$ can be determined, using (3) and taking into account that $c_1 + c_2 = 1$. Having the values of relative occupancies of the valleys, it is possible to determine the separate concentrations of light and heavy holes. And for doing this we need to have the temperature dependence of the total concentration of holes. For that purpose, the temperature dependence of the Hall coefficient is measured in the 300–500K temperature range. The choice of temperature range is connected with the presence of comparatively high values of the figure-of-merit at temperatures higher than the temperature of phase transition.

Note that the Hall coefficient in two-valley case is defined by the expression

$$R = \frac{p_1u_1^2 + p_2u_2^2}{e(p_1u_1 + p_2u_2)^2} = \frac{c_1b^2 + c_2}{ep(c_1b + c_2)^2}\,, \tag{4}$$

where *b* is the ratio of mobilities of light and heavy holes. As we do not have the actual values of mobilities for light and heavy holes, we accepted the following approximate value for the ratio of mobilities:

$$b = \frac{u_1}{u_2} \approx \frac{m_2}{m_1}\,. \tag{5}$$

Using (4), we can determine the total concentration of holes $p(T)$ by the expression

$$p = \frac{c_1b^2 + c_2}{eR(c_1b + c_2)^2}\,, \tag{6}$$

and, consequently, also separate the concentrations of light holes $p_1(T)$ and heavy holes $p_2(T)$ (Fig. 5) by the formulas

$$p_1(T) = c_1(T)\,p(T)\,, \qquad p_2(T) = c_2(T)\,p(T)\,. \tag{7}$$

In Ref. [6] it is shown that the valence band of a multi-valley semiconductor can be replaced by the equivalent one-valley band. In such a band the observed effective mass of holes is not constant and changes with temperature due to the transitions of holes from one valley to another. According to Ref. [3],

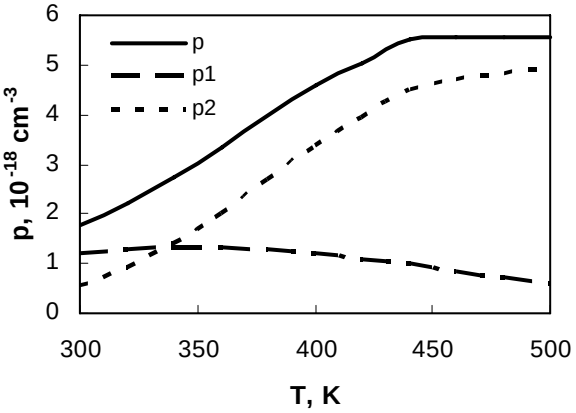

Fig. 5

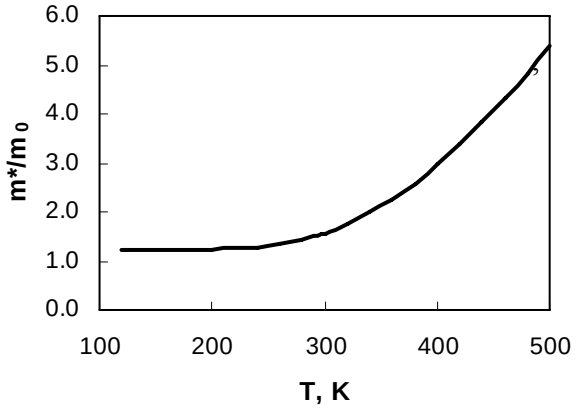

Fig. 6

$$(m^*)^{3/2} = \frac{M}{c_1}(m_1)^{3/2}, \tag{8}$$

where M is the number of equivalent maxima in the valence band, c_1 is the relative occupancy of the valley of light holes, and m_1 is the effective mass of holes in this valley. The calculated curve of the temperature dependence of the observed effective mass of holes is given in Fig. 6.

The expression for maximal value of the figure-of-merit [2] was used to estimate the maximal resources of the investigated solid solution:

$$z_{\max} = \frac{(\alpha^2\sigma)_{\text{opt}}}{\chi} = 4\left(\frac{k}{e}\right)^2 ep_0\left(\frac{m^*}{m_0}\right)^{3/2}\left(\frac{T}{T_0}\right)^{3/2}\frac{u}{\chi_L}e^r, \tag{9}$$

where r is the scattering parameter. After replacing u by σ/ep we obtain

$$z_{\max} = 4\left(\frac{k}{e}\right)^2 p_0\left(\frac{m^*}{m_0}\right)^{3/2}\left(\frac{T}{T_0}\right)^{3/2}\frac{\sigma}{\chi_L p}e^r, \tag{10}$$

where σ and p are the experimental values of the electrical conductivity and total concentration of holes, respectively.

On the basis of the Pisarenko formula, using the values of $\alpha(T)$ and $m^*(T)$, it is possible to determine r from the formula [4]

$$r = \frac{\alpha}{k/e} - 2 - \ln\frac{2(2\pi m_0 kT_0)^{3/2}}{h^3} - \frac{3}{2}\ln\left(\frac{m^*}{m_0}\right) - \frac{3}{2}\ln\left(\frac{T}{T_0}\right) - \ln p\,. \tag{11}$$

Having the temperature dependences $r(T)$, $m^*(T)$, $\sigma(T)$, $p(T)$, and $\chi_L(T)$, we can calculate the temperature dependence $z_{\max}(T)$ which is given in Fig. 4 (dashed line). From Fig. 4 it follows that the resources of the given material significantly exceed obtained results, although our experimental data is high enough compared with data available in literature.

3. Conclusions

Reported results and estimations of the figure-of-merit of the investigated material showed that the expectations from solid solutions $Pb_{1-x}Ge_xTe$ near the chosen composition x = 0.15 are not exhausted and it is possible to obtain better results by changing the composition, by doping, or by using various technological techniques.

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