ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т.1, №1 (2000) С.135-138

PHYSICS AND CHEMISTRY OF SOLID STATE
V.1, №1 (2000) P.135-138

PACS 72.15.E

Thermoelectric properties of PbTe-SnTe: In

P.Melnyk, L.Mezhylovska, R.Zapukhlyak, M.Kalyniuk, R.Mykhajlonka
Precarpathian University, Shevchenko 57, 76000 Ivano-Frankivsk, Ukraine

The analysis of the dependencies of thermoelectric properties of the solid solution $(Pb_{0.8}Sn_{0.2})_{1-X}In_XTe$ upon In content ($0.02 \le x \le 0.15$) at the temperatures 77-300 K has been conducted. It has been proved that at temperatures higher than 250 K the thermo-emf coefficient is negative for all compositions. At lower temperatures (77-200 K), the samples with $0.02 \le x \le 0.05$ also have negative thermo-emf coefficients, while for the samples with $x \ge 0.05$ exhibit inversion of the sign of the thermo-emf coefficient. The power factor ($\alpha^2\sigma$) has maximal values for x=0.02.

Keywords: PbTe-SnTe solid solutions; doping with In; thermoelectric characteristics.

Paper received 21.11.1999; accepted for publication 27.11.1999

I. Introduction

$A^{IV}B^{VI}$ compounds are prospective thermoelectric materials that function at temperature up to 800 K [1]. The effectiveness of their use is determined by the possibility to obtain the high values of the thermoelectric characteristics, such as coefficient of the thermo-emf (α) and power factor ($\alpha^2\sigma$) [2]. Thermoelectric characteristics of the semiconductor depend on the position of the Fermi level, concentration (n), mobility (μ) and effective mass of the charge carriers, and upon the mechanisms of their scattering. Using solid solutions and doping processes. It is possible to successfully control the above-mentioned parameters of the material, and therefore to control its thermoelectric characteristics [1,3]. In publications [3-6] it has been shown that the energy levels of indium in $A^{IV}B^{VI}$ compounds substantially depend on the composition of the basic matrix. In PbTe at low temperatures they are situated amongst the levels in In conduction band, while in $Pb_{1-Y}Sn_YTe$ solid solution with increasing Sn composition up to $y \approx 0.2$, they shift in the direction of the valence band. The dependence of the position of the doping In energy levels upon the In concentration in SnTe-PbTe solid solutions has been discussed in [7].

We have analyzed the dependencies of the thermoelectric characteristics of the solid solution $(Pb_{0.8}Sn_{0.2})_{1-X}In_XTe$ upon the content of indium ($0.02 \le x \le 0.15$). The solid solution $Pb_{0.8}Sn_{0.2}Te$ is interesting for analysis because its width of forbidden zone is about zero, and its alloying for In x=0.02-0.05 causes considerable changes of the structure of forbidden zone [7].

II. Experimental procedure and results

The high purity Pb, Sn, Te, In (with dashes < 10^{-4} %) were used as starting materials for composition synthesis. The samples were prepared using cermet technology followed with homogenization at 920 K for 100 hours. The thermoelectric characteristics of the material were measured in the temperature interval 77-300 K by compensation method in ***dc*** and ***H*** fields.

We have been established that the dependence of the thermoelectric characteristics of $(Pb_{0.8}Sn_{0.2})_{1-X}In_XTe$ upon the content of indium is determined by the temperature (fig. a, curve 1). At temperatures higher than 250 K the thermo-emf coefficient is negative for all compositions (fig. a, curve 2). At lower temperatures (77-200 K), the samples with $0.02 \le x \le 0.05$ also have negative thermo-emf coefficients, while for the samples with $x \ge 0.05$ exhibit inversion of the sign of the thermo-emf coefficient (fig. a, curve 1). It should be also noted that in both regions (with negative and positive thermo-emf coefficient), an increase of the indium content leads to a decrease in the absolute value of the thermo-emf (fig. a). The conductivity (σ) of the solid solution grows with increasing indium content (fig. b). While the power factor ($\alpha^2\sigma$) for $0.02 \le x \le 0.05$ drops, and the becomes almost

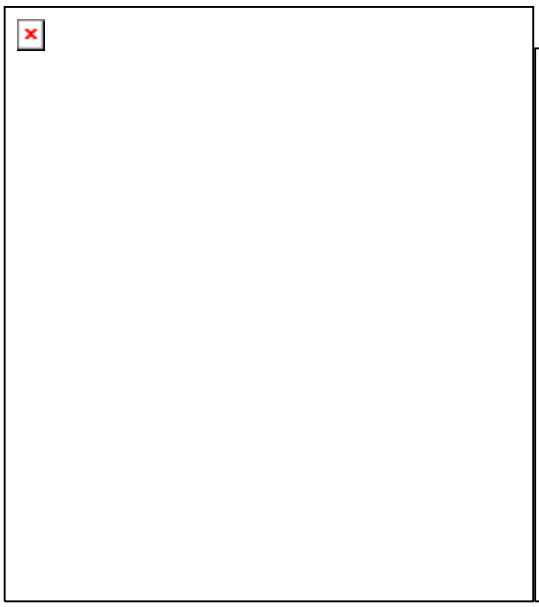

fig.a

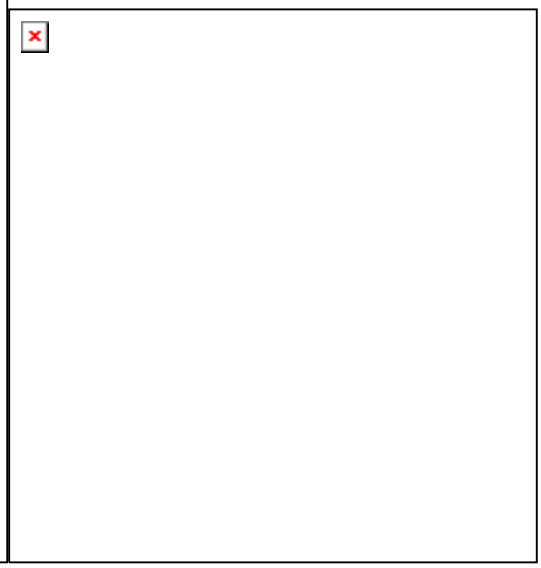

fig.b

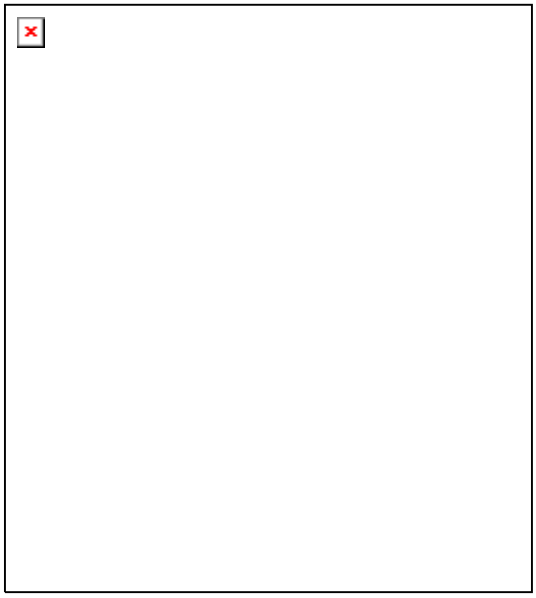

fig.c

Dependency of the coefficient of the thermo-emf (α - a), of specific conductivity (σ - b), thermoelectric power ($\alpha^2\sigma$ - c) of solid solution $(Pb_{0.8}Sn_{0.2})_{1-X}In_XTe$ upon In content at temperatures T, K: 1 - 100, 2 – 300.

insensitive to the indium contents (fig. c).

III. Discussion

From published [3,5-7] it is known that In impurities in PbTe and in PbTe-SnTe solid solutions act as donors. When the content of In in $(Pb_{0.78}Sn_{0.22})_{1-Z}In_ZTe$ is small (less than 5 atomic %), the impurity levels are situated in the forbidden gap near the conduction band [7]. In this case there is an energy gap between the conduction band and the impurity levels. As the content of In grows (5-15 atomic %) the impurity band expands and partially overlaps the conduction band. The energy gap disappears and becomes a pseudo-gap. There exist energy intervals where the energy derivative of the density of states has both negative and positive signs [8]. The fact that the number of states in the impurity band is twice the number of electrons that come from In atoms [3] explains the asymmetry of the impurity band relative the maximum of the density of states. Over half of the impurity levels are situated above this maximum. The increase of the In content in the samples leads to the grown of the concentration of electrons as measured by the Hall Effect, reaching values common for metals ($\sim 10^{22}$ cm^{-3}).

Considering the above described model of the energy structure it can be inferred that when the content of In in the solid solution is small, the main role in the transport phenomena is played by the carriers of the impurity band that are ionized and partly separated from the conduction band. The increase of In content in this range ($0.02 \leq x 0.05$) results in the growth of the concentration of the electrons, and this in its turn leads to the growth of the specific conductivity (σ) (fig.b) and to the decrease of the thermo-emf coefficient (α) (fig.a).

When the content of In is substantial and the temperatures are low, the Fermi level is situated in the region of the negative values of the energy derivative of the density of impurity states. This cause the change of the sign of the thermo-emf coefficient to the normal (i.e. positive) one (fig.a, curve 1). At high temperatures, the fermi level is situated in the region with the positive sign of the derivative, the therefore the thermo-emf of the materials adopts its usual (i.e. negative) sign (fig.a, curve 2).

[1] N. X. Abrikosov, L. E. Shelimova. *Semiconductor materials based on compounds $A^{IV}B^{VI}$*. M. Nauka. 196, pp. (1975).

[2] L.I. Anatychuk. *Thermoelements and thermoelectric devices*. K. Naukova dumka. 768, pp. (1979).

[3] V.I.Kajdanov, Y.I. Ravich // *Achievements of physical sciences*. 145, pp. 51 (1985).

[4] Y.I Ravich, B.A. Yefimova, I.A. Smirnov. *Methods of investigation of semiconductor materials applied to lead chalcogenides PbTe, PbSe, PbS*. M. Nauka. 384, pp. (1968).

[5] A.J. Rosenberg, R. Crierson, J.C.Wooley, P.Nicolic // *Trans. of AIME*. 230, pp. 342 (1964).

[6] A.J. Rosenberg, F.Wald // *J. Phys.Chem.Sol*. 26, pp. 1079 (1965).

[7] S.A. Nemov, Y.I. Ravich, A.V. Berezin, V.E. Gasumyanz, M.K. Zhitinskaja, V.I. Proshin // *Physics and Technology of Semiconductors*. 27, pp. 299 (1993).

[8] S.N. Lykov, Y.V. Ravich, I.A.Chernik // *Physics and Technology of Semiconductors*. 11, pp. 1731 (1977).

Термоелектричні властивості PbTe-SnTe: In

П.Мельник, Л.Межиловська, Р.Запухляк, М.Калинюк, Р.Михайльонка

Проведено аналіз залежностей термоелектричних властивостей твердого разчину $(Pb_{0.8}Sn_{0.2})_{1-X}In_XTe$ від складу ($0.02 \le x \le 0.15$) при температурах 77-300 K. Доведено, що при температурах вище ніж 250 K коефіцієнт термо-ЕРС негативний для всіх складів. При нищих температурах (77-200 K), зразки з $0.02 \le x \le 0.05$ також мають негативний коефіцієнт термо-ЕРС, тоді як для зразків з $x \ge 0.05$ спостерігається інверсія знаку коефіцієнта термо-ЕРС.

Коефіцієнт ($\alpha^2\sigma$) має максимальне значення при x=0.02.

Ключові слова: PbTe-SnTe тверді розчини; термоелектричні характеристики.