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Thermoelectric Properties of Solid Solutions PbSnAgTe

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The phase composition and thermoelectric properties of solid solutions $\text{Pb}_{16}\text{Sn}_2\text{Ag}_2\text{Te}_{20}$ and $\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$ are researched. Biphasic structure of the samples is installed, which providing to low values of thermal conductivity. Best samples have values of dimensionless thermoelectric figure of merit $ZT \approx 0,55$.

Keywords: lead telluride, solid solutions, thermoelectric properties.

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Introduction

The main feature of thermoelectric generators among all other alternative sources of electric energy is their autonomy and significant lifetime [1]. To produce active elements TEG operating in the temperature range 300-500 °C is the most widely used materials on the basis of lead telluride. One of the main ways to improve their thermoelectric parameters in order to increase efficiency is doping and creating of solid solutions. Thus, it is necessary to increase the electrical conductivity of the material and the Seebeck coefficient and simultaneously reducing the thermal conductivity.

In particular, in recent years system $\text{Pb}_{18}\text{Ag}_1\text{Sb}_1\text{Te}_{20}$ are actively investigated [2-3]. In our studies [4-5], attention was focused on the system Pb-Ag-Te, where established composition in which the thermal conductivity $\approx (0,002-0,003) \text{ W / (cm C)}$. For undoped PbTe this value in 2-3 times more. The reason for such low values of k is biphasic structure of the samples is caused by the formation of micro and nano inclusions of argentum telluride. This paper presents the results of research aimed at improving material conductivity investigated in [4-5] by optimization of technological conditions and additional introduction into the solution of tin.

I. Methods of experiment

The synthesis of the materials carried out in evacuated to a residual pressure of 10^{-4} Pa quartz ampoules. The resulting ingots ground in an agate mortar and separated fraction size (0.05 - 0.5) mm compressed

under pressure (1-2) GPa. The resulting cylindrical samples with $d = 5 \text{ mm}$ and $h \approx 8 \text{ mm}$ subjected to annealing in air.

Phase composition and structure of synthesized ingots and samples examined X-diffraction methods on an automatic diffractometer STOE STADI P. Array of experimental diffraction was performed using the software package STOE WinXPOW (version 3.03) and PowderCell (version 2.4).

Seebeck coefficient α , specific conductivity σ and thermal conductivity k were determined as described in [6, 7] methods.

II. Results and Discussion

For research conducted the synthesis of solid solutions of composition $\text{Pb}_{16}\text{Sn}_2\text{Ag}_2\text{Te}_{20}$ and $\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$. Phase composition similar to previous studies materials system Pb-Ag-Te (Fig. 1): the main phase PbTe, structural type NaCl; additional phase is $\text{Ag}_{10,6}\text{Te}_7$. For samples with lower tin content the unit cell is 6.4402 (2) Å, and with more content - 6.4413 (3) Å.

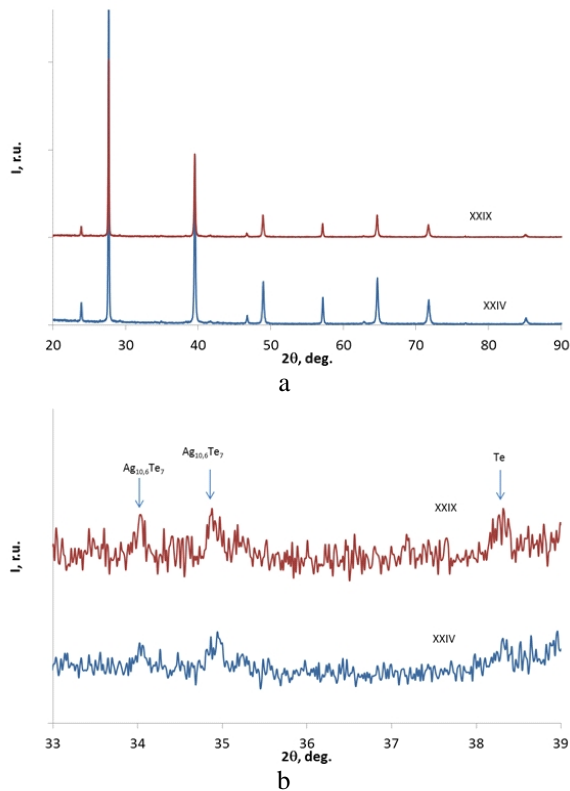
Technological factors prepare samples for measuring thermoelectric parameters presented in the table 1 and the results of measurement - Fig. 2 and 3. Based on their analysis found that as a result of isovalent replacement of lead atoms on stannum atoms the carrier concentration increases from the values $\approx (1-3) 10^{18} \text{ cm}^{-3}$ for samples $\text{Pb}_{18-x}\text{Ag}_{2+y}\text{Te}_{20}$ ($x, y = 0..1$) to values $(3-7) 10^{19} \text{ cm}^{-3}$ for samples in this study. During this conductivity increases not much but Seebeck coefficient value decreases from 300 mV/K for $\text{Pb}_{18}\text{Ag}_2\text{Te}_{20}$ to 200 mV/K for

Table 1

Technological conditions of preparation of test samples of solid solutions $\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$.

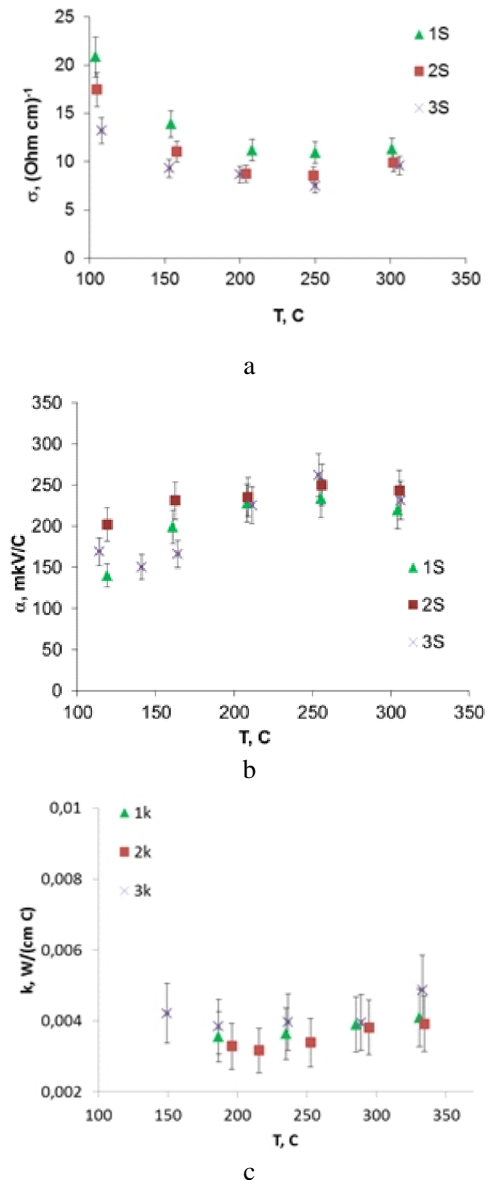
Sample	Pressure pressing, P, GPa	Time pressing, t, min	Annealing temperature*, T, °C	Annealing time, t, h	Fractions, mm
1S, 1k	2	15	228	5	0.05-0.5
2S, 2k	2	30	320	2	0.05-0.5
3S, 3k	2	60	320	2	0.05-0.5
16-20	1,0	30	500	0,25	0.05-0.5
16-21	1,0	30	500	0,25	0.05-0.5

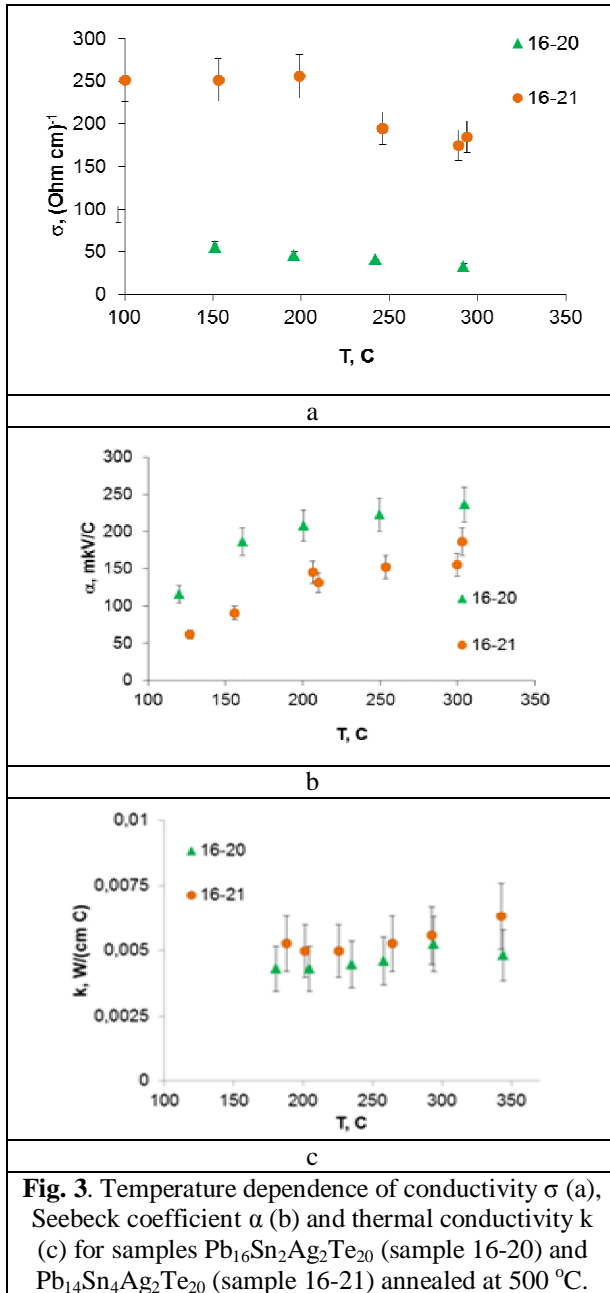
* - annealing was performed on air.


Fig.1. The diffraction of solid solutions $\text{Pb}_{16}\text{Sn}_2\text{Ag}_2\text{Te}_{20}$ (XXIV) and $\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$ (XXIX) (a) and fragment of diffraction where found reflections of additional phases (b).

$\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$. Increase of pressing time and annealing temperature to 320 °C does not improve significantly the basic parameters of thermoelectric material.

Qualitative improvement of the thermoelectric characteristics of the investigated materials achieved by reducing the pressing pressure up to 1.0 GPa and the increasing of the annealing temperature up to 500 °C (Fig. 3). In the composition with a high content of tin the specific conductivity at 300 °C is $\approx 180 (\text{Ohm cm})^{-1}$, the Seebeck coefficient $\approx 180 \text{ mV/K}$, and the coefficient of thermal conductivity is $\approx 0.006 \text{ W}/(\text{cm K})$, which provides thermoelectric figure of merit $ZT \approx 0,55$. The holes concentration for this sample is $3.5 \cdot 10^{19} \text{ cm}^{-3}$, which is in the range of optimal carrier concentrations for thermoelectric materials.


Fig. 2. Temperature dependence of conductivity σ (a), Seebeck coefficient α (b) and thermal conductivity k (c) for samples $\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$ obtained by various technological factors (see. Table 1).



It is clear that the main factor determining the low thermal conductivity in material with argentine

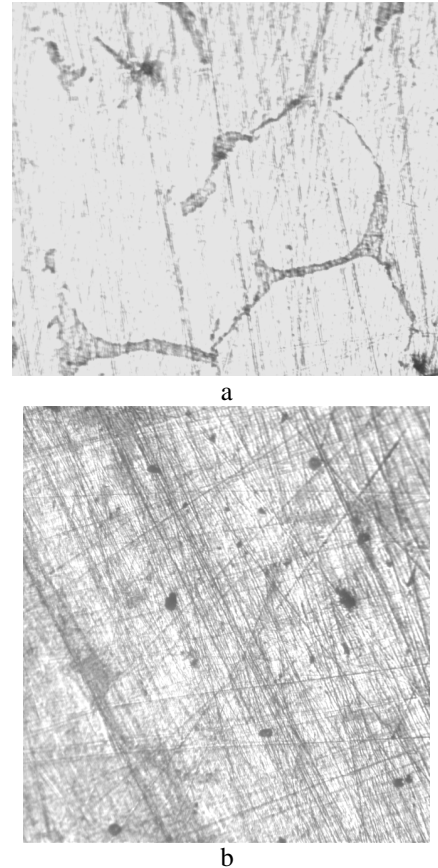


Fig. 4. Photomicrographs of sample 16-20 surface with 100x fold increase: before annealing (a) and after annealing at 500 °C.

inclusions is due to of additional phases. Another factor affecting the thermal conductivity of the pressed samples is its density ($k \sim \rho$). Table 2 shows that with content increasing of argentine and especially of tin the density of samples (determined by Archimedes method) decreases. It should be noted that the X-ray density during this growing. And if in the first case, changes are observed in the first decimal place, then the second - the second sign. Reducing the density of pressed samples was caused by increasing of their microhardness with addition of tin and silver, which reduces the possibility of further growth of density during compaction. So for unannealed samples 16-20 ($\text{Pb}_{16}\text{Sn}_2\text{Ag}_2\text{Te}_{20}$)

Table 2

The dependence of the samples density from chemical composition and technological factors receipt *

Material	Sample №	Pressure of pressing, GPa	Time pressing, t, min	Annealing temperature T, °C	Annealing time, h	Density g/cm ³	X-ray density, g/cm ³
PbTe	1Sb	2	15	230	5	8.19	8.268
$\text{Pb}_{17}\text{Ag}_3\text{Te}_{20}$	1Sa	2	15	230	5	7.90	8.2517
	1Sb	2	15	230	5	7.90	
$\text{Pb}_{16}\text{Sn}_2\text{Ag}_2\text{Te}_{20}$	1Sa	2	15	230	5	7.88	8.3250
	1S	2	15	230	5	7.75	8.3207
$\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$	2S	2	30	320	2	7.79	
	3S	2	60	320	2	7.87	
$\text{Pb}_{14}\text{Sn}_4\text{Ag}_2\text{Te}_{20}$	1	1	30	500	0.25	7.05	

* - for all samples with fractions - (0.05-0.5) mm.

microhardness of 1033 MPa, whereas undoped PbTe (XV) - \approx 350 MPa (load measurements were performed at 300 gf, loading time 10 sec.). It should be noted also reduce microhardness of sample after annealing in air at 500 °C for 15 minutes to a value of 935 MPa. A similar pattern is typical for density (Table 2.). But the increase in porosity surface on the photomicrographs of the sample not observed (Fig. 4).

Conclusions

Replacement in crystal systems Pb-Ag-Te the lead to the tin of causes increases in thermoelectric figure of merit of the material. For samples Pb₁₄Sn₄Ag₂Te₂₀ which obtained by pressing (pressure load is 1 GPa) and

followed by annealing (annealing temperature - 500 oC); this technological factors made the dimensionless thermoelectric figure of merit $ZT = 0.55$ at 300°C.

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Термоелектричні властивості твердих розчинів PbSnAgTe

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Досліджено фазовий склад і термоелектричні властивості твердих розчинів Pb₁₆Sn₂Ag₂Te₂₀ Pb₁₄Sn₄Ag₂Te₂₀. Встановлена двофазність отриманих зразків, що забезпечує отримання низьких значень коефіцієнта теплопровідності. Для найкращих зразків досягнуто значень безрозмірної термоелектричної добротності $ZT \approx 0,55$.

Ключові слова: телурид свинцю, тверді розчини, термоелектричні властивості.