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(8, Kyrylo i Mefodii Str., Lviv 79005, Ukraine)**THERMOELECTRIC PROPERTIES  
OF BISMUTH-DOPED TIN TELLURIDE SnTe:Bi**

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*X-ray researches are carried out, and the thermoelectric coefficient  $\alpha$  and the specific conductivity  $\sigma$  are measured for tin telluride specimens doped with bismuth to concentrations of 0–2.0 at.% Bi. Non-monotonic dependences of the unit cell parameter and the electrical parameters on the Bi impurity content are demonstrated. The introduction of bismuth to 1.0 at.% is found to favor an increase in the thermoelectric power  $\alpha^2\sigma$  in SnTe at temperatures  $T > 500$  K as a result of the thermoelectric coefficient growth.*

*Keywords:* tin telluride, doping, thermoelectric properties.

**1. Introduction**

Chalcogenides of metals belonging to the fourth group in the Periodic table, as well as solid solutions on their basis, are widely used in thermoelectric converters of thermal energy [1, 2]. Tin telluride deserves a special attention among those compounds [1–5]. This substance is characterized by a high specific conductance  $\sigma$  and a chemical compatibility with plenty of metals, which determines its usefulness. A shortcoming of thermoelements on the basis of SnTe consists in rather a low thermoelectric (Seebeck) coefficient  $\alpha$ . As a result, the thermoelectric power  $\alpha^2\sigma$ , one of the major operational parameters, also remains rather low. This fact can explain a certain reduction of the attention to SnTe researches in the last years. Nevertheless, the problem of increasing this parameter remains challenging, and its solution will allow the capabilities of thermoelectric generators on the basis of tin telluride to be considerably improved.

One of the ways to modify the thermoelectric parameters of semiconductor crystals is their doping with donor or acceptor impurities. A high value and the  $p$ -type of the tin telluride conductivity are known to result from a considerable concentration of accep-

tor cation vacancies in SnTe crystals. There is a reciprocal relation between the thermoelectric coefficient and the charge carrier concentration. Therefore, by doping a material with donor impurities, it is possible, owing to a reduction in the Hall concentration of holes, to obtain some growth for the thermoelectric coefficient. Since bismuth is one of the most active donors in  $A_4B_6$  compounds, we will study the influence of this impurity on the temperature dependences of the thermoelectric parameters for tin telluride specimens with various concentrations of introduced bismuth atoms.

**2. Experimental Technique**

Tin telluride, both pure and doped with bismuth in concentrations of 1.0, 1.5, and 2.0 at.%, was synthesized by fusing the pure components in quartz ampoules evacuated to a pressure of  $2 \times 10^{-4}$  Pa. The obtained ingots were crushed in an agate mortar. Fractions with particle dimensions of 0.05–0.5 mm were extracted and pressed under a pressure of 1.5 GPa. The obtained cylindrical specimens with the diameter  $d = 5$  mm and the height  $h \approx 8$  mm were annealed in air for 5 h at the temperature  $T = 500$  K.

The thermoelectric coefficient  $\alpha$  and the specific conductance  $\sigma$  were determined by the standard procedure. A specimen was placed between two copper rods in an oven and heated up to a required temperature. The temperature gradient across the specimen

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( $\approx 10^\circ\text{C}$ ) was created with the use of an additional oven mounted on either of the copper rods. The temperature was measured with the help of two chromel-alumel thermocouples located in apertures made in the specimen. The specific conductance was determined by measuring the voltage drop across the specimen. The voltage was generated by an alternating voltage source. One of the wires in each thermocouple was used as a current path.

For X-ray researches, the specimens were ground in an agate mortar. The obtained powder was uniformly deposited with the help of an amorphous glue onto a special amorphous film for X-ray transmission experiments and fixed in a special cuvette with the help of another film.

The arrays of experimental intensities and angles of reflection from the specimens under study were obtained on an automatic diffractometer STOE STADI P (STOE & Cie GmbH, Germany) equipped with a linear position sensitive detector. The measurements were carried out in the transmission mode in a modified Guinier geometry:  $\text{CuK}_{\alpha_1}$  radiation, the concave Johann-type Ge-monochromator (111),  $2\theta/\omega$ -scanning, the interval of angles  $10.000^\circ \leq 2\theta \leq 125.185^\circ$  with a step of  $0.015^\circ$ , a detector step of  $0.480^\circ$ , a scanning time of 100–230 s at every step, the experimental temperature  $T = 297.6 \pm 0.3$  K,  $U = 40$  kV, and  $J = 35$  mA. The linear absorption coefficients were calculated as the logarithmic ratio between the intensities of the primary beam before and after its passage through the background and studied specimens. The equipment was certified making use of standards NIST SRM 640b (Si) and NIST SRM 676 ( $\text{Al}_2\text{O}_3$ ).

The diffraction patterns of the known compounds were calculated in order to identify the phases and to specify the unit cell parameters. The calculations were carried out with the help of software packages STOE WinXPOW (version 3.03) and PowderCell (version 2.4). The crystal structure of phases was specified within the Rietveld method, by applying the pseudo-Voigt profile function with the help of software program FullProf.2k (version 5.30).

### 3. Experimental Results

The results of X-ray researches of the synthesized materials are shown in Fig. 1. Specimens of pure tin telluride and with impurity contents of 1.5 and 2.0 at.%

were found to be single-phase of the NaCl structure type, the spatial group  $Fm-3m$ . The specimen  $\text{SnTe} + 1.0$  at.% Bi additionally contained 1.07(4) wt.% of pure bismuth (Fig. 1,b) of the As structure type.

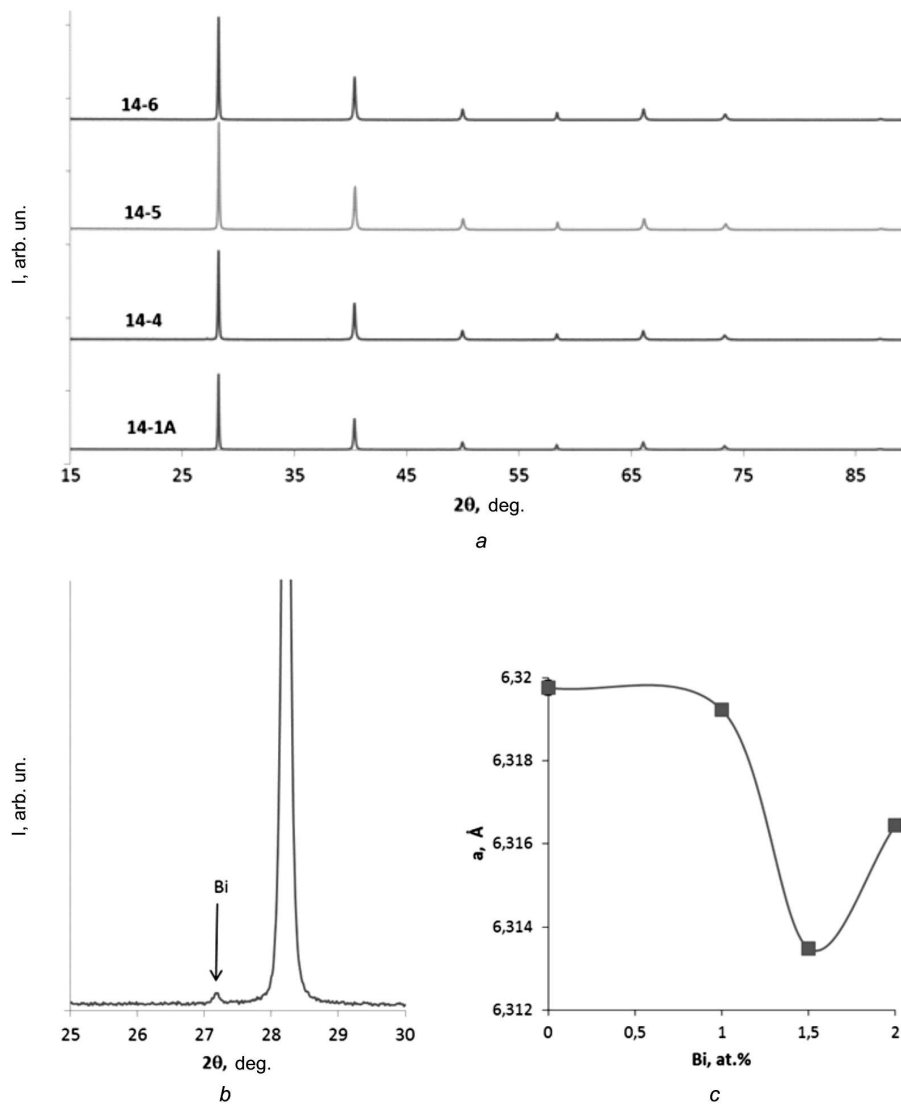
The determined dependence of the lattice constant in bismuth-doped tin telluride on the bismuth content was found to be non-monotonic with minimum in a vicinity of 1.5 at.% (Fig. 1, c).

The results of measurements for the specific conductance and the thermoelectric coefficient are depicted in Figs. 2, a and 2, b, respectively. The results for the thermoelectric power calculated on their basis are shown in Fig. 2, c. All specimens were characterized by the  $p$ -type conductivity, and their dependences  $\sigma(T)$  demonstrated a metallic character. The obtained values for the specific conductivity in pure tin telluride are typical of this substance [1]. The introduction of bismuth to 1.0 at.% insignificantly diminished the specific conductance in the whole temperature interval. On the contrary, the thermoelectric coefficient increased at that, especially at temperatures  $T > 500$  K.

The introduction of Bi to 1.5 at.% resulted in a drastic reduction of the specific conductance of the material to values of about  $200 \Omega^{-1}\text{cm}^{-1}$ . The thermoelectric coefficient of this specimen practically is not changed at high temperatures ( $\approx 600$  K) in comparison with the 1.0 at.% Bi specimen and is substantially increased at low temperatures. A further growth in the amount of introduced bismuth resulted in a relatively insignificant increase of the specific conductance and a reduction of the thermoelectric coefficient.

### 4. Discussion

By comparing the value obtained for the unit cell parameter in pure SnTe with the data presented in work [1], a conclusion can be drawn that the synthesized material contains about 0.2 at.% of superstoichiometric tellurium. The presence of the pure bismuth phase in the SnTe specimen with an impurity content of 1.0 at.% can be associated with the exceeding of the impurity solubility limit or with incorrectly chosen conditions for the synthesis of the substance, at which the impurity did not dissolve uniformly in the matrix. However, those assumptions do not explain why additional phases were not formed in tin telluride specimens with higher bismuth con-

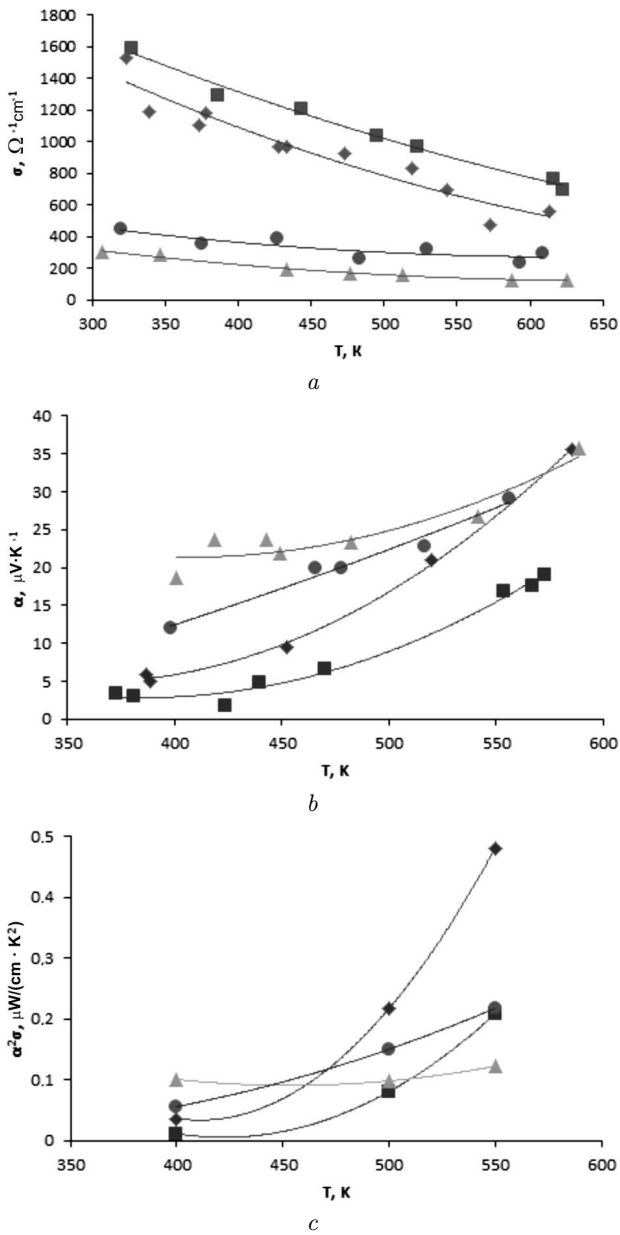


**Fig. 1.** Comparative diffraction patterns of tin telluride specimens with various bismuth impurity contents: 0, 1.0, 1.5, and 2.0 at.% Bi (from bottom to top) (a). Fragment of the diffraction pattern for specimen 14-4 with a bismuth content of 1.0 at.% (b). The arrow marks a reflex from the pure Bi phase. Dependence of the unit cell period in examined SnTe:Bi specimens on the Bi impurity content (c)

concentrations synthesized under the same technological conditions.

This result is evidently a consequence of more complicated interactions between bismuth atoms and intrinsic point defects in the tin telluride crystal lattice than the standard ones. This conclusion is supported by the results of researches of the crystal structure within the Rietveld method. Namely, the bismuth impurity atoms occupy vacant sites in the

cation sublattice, if their concentration does not exceed 1 at.%, and vacant sites in the anion sublattice, otherwise. This concentration of bismuth atoms practically coincides with the highest possible concentration of tin vacancies in SnTe, namely, about 0.8–0.9 at.% [1]. Hence, we may assume that, at a bismuth concentration of about 1 at.%, impurity atoms occupy almost all cation vacancies, which gives rise to a reduction of the Hall carrier concentration and, as a



**Fig. 2.** Temperature dependences of the specific conductance  $\sigma$  (a), thermoelectric coefficient  $\alpha$  (b), and thermoelectric power  $\alpha^2\sigma$  (c) for SnTe:Bi specimens with various Bi contents: 0 (squares), 1.0 (diamonds), 1.5 (triangles), and 2.0 at.% (circles)

consequence, to the experimentally observed drastic reduction in the specific conductance of the material.

However, as one can see from Fig. 2, a, the conductivity is minimum at a somewhat higher bismuth

concentration of 1.5 at.%. In work [6], while studying the influence of the antimony impurity on the SnTe properties, it was found that an increase of the Sb content stimulates the growth of the cation vacancy concentration, maybe owing to the compensation effect. Taking into account that the behaviors of antimony and bismuth impurities in  $A_4B_6$  compounds are almost identical [2], we may assume that a similar situation takes place in SnTe:Bi as well. Hence, the fact that the conductivity minimum is observed at a bismuth concentration of 1.5 at.%, rather than 1.0 at.%, is a result of the growth of the tin vacancy number with the growth of the bismuth concentration, so that the number of Bi atoms required for their filling has to be larger.

The increase of the vacancy concentration can also explain, in particular, the reduction of the unit cell parameter within the impurity concentration interval from 0 to 1.5 at.%. As the impurity concentration increases, the self-compensation processes become more intense, and vacancies are formed more actively, which makes the reduction of  $a$  faster with the growth of the Bi concentration. If vacancies did not emerge at doping, the unit cell parameter would grow, because the ionic radius of  $\text{Bi}^{3+}$  (1.2 Å) exceeds the ionic radius of  $\text{Sn}^{2+}$  (1.02 Å) [7].

The most probably,  $\text{Bi}_{\text{Te}}$  is a singly ionized acceptor. Therefore, the occupation of anion sites by bismuth to concentrations higher than 1.5 at.% stimulates the growth of the hole concentration and, hence, the specific conductance, which is really observed in the experiment (Fig. 2, a). The growth of the unit cell parameter at those impurity concentrations is evidently associated with the fact that the ionic radius of  $\text{Bi}^{3+}$  (2.13 Å) is larger than the ionic radius of  $\text{Te}^{2-}$  (2.1 Å) [7].

In view of the experimentally observed variations of the electrophysical and structural parameters of researched specimens with a variation of the impurity concentration in them, as well as their possible explanations, we may assume that the formation of an additional pure bismuth phase is the most probably associated with a jump-like, rather than smooth, change of the doping mechanism. In particular, up to a concentration of about 1.0 at.%, bismuth atoms fill tin vacancies. When this process becomes energetically disadvantageous, Bi atoms do not transit into the anion sublattice at once, because this is also energetically disadvantageously up to a certain im-

purity concentration. Instead, they are accumulated to form precipitates (the pure bismuth phase). Only when the concentration of Bi atoms reaches a certain critical value, the precipitates are completely dissolved, and impurity atoms start to fill the anion lattice sites.

It is clear that for the confirmation of the adequacy of the proposed doping mechanism, additional researches are required, in particular, the crystallochemical analysis of the defect subsystem; especially for the impurity content within the interval of 1.0–1.5 at.% Bi. However, the results of X-ray researches, as well as the results of specific conductivity and thermoelectric coefficient measurements, unambiguously testify that, in this concentration interval, the mechanism of impurity penetration into the SnTe crystal lattice changes.

## 5. Conclusions

If tin telluride is doped with bismuth to a concentration of 1.0 at.% Bi, impurity atoms occupy sites in the cation sublattice. At higher concentrations, they occupy sites in the anion sublattice. The insertion of the bismuth impurity to a concentration of 1.0 at.% results in the growth of the thermoelectric power ( $\alpha^2\sigma$ ) of tin telluride from approximately  $0.10 \mu\text{W}/(\text{cm K}^2)$  for pure SnTe to approximately  $0.5 \mu\text{W}/(\text{cm K}^2)$  for SnTe + 1.0 at.% Bi at temperatures in a vicinity of 550 K. These values correspond to the parameters of the best thermoelements fabricated on the basis of tin telluride and used in industry. The specific conductance and the thermoelectric coefficient of experimental specimens fabricated by cold pressing and annealing in air are the same as for specimens obtained by hot pressing in vacuum followed by the long-term annealing [2]. This fact is of interest for the optimization of the manufacture technology of thermoelectric materials.

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ТЕРМОЕЛЕКТРИЧНІ  
ВЛАСТИВОСТІ ЛЕГОВАНОГО ВІСМУТОМ  
ТЕЛУРИДУ ОЛОВА SnTe:Bi

Р е з ю м е

Проведено рентгенографічні дослідження та вимірювання коефіцієнта термо-ерс ( $\alpha$ ) і питомої електропровідності ( $\sigma$ ), легovanого вісмутом телуриду олова у діапазоні концентрацій (0–2,0) ат.% Бі. Встановлено немонотонні залежності параметра елементарної комірки та електрофізичних параметрів від вмісту домішки. Показано, що введення вісмуту в кількості 1,0 ат.% сприяє зростанню в інтервалі температур  $T > 500$  К термоелектричної потужності  $\alpha^2\sigma$  SnTe внаслідок збільшення коефіцієнта термо-ерс ( $\alpha$ ) порівняно з нелегованим матеріалом.