

# Growth by Czochralski Technique and Thermoelectric Properties of the $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$ Solid Solutions

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## Abstract

In the present work,  $(\text{Bi}_2\text{Te}_3)_{0.90}(\text{Sb}_2\text{Te}_3)_{0.05}(\text{Sb}_2\text{Se}_3)_{0.05} \langle \text{SbI}_3 \rangle$  and  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03} \langle \text{Te}, \text{SbI}_3 \rangle$  solid solution alloys (SS-alloys) of the n- and p-type conductivity respectively were grown by Czochralski technique. The n-type homogeneous material doped with  $\text{SbI}_3$  is characterized by thermoelectric figure of merit  $Z_{\text{max}}=3.1 \cdot 10^{-3} \text{K}^{-1}$  at  $\sim 350 \text{K}$ . The p-type SS alloy doped with Te and  $\text{SbI}_3$  is characterized by thermoelectric figure of merit  $Z_{\text{max}}=2.6 \cdot 10^{-3} \text{K}^{-1}$  at  $375 \text{K}$ . Functionally graded TE materials (FGTM) based on  $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$  solid solutions were prepared by Czochralski method by varying concentration and nature of doped impurities in the seed and the charge. In such a manner, considerable Seebeck coefficient gradient is created at narrow range of the length near the interface between the seed and grown crystal.

## Introduction

Pseudo-ternary  $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$  solid solutions (SS-alloys) are attractive thermoelectric (TE) materials of n- and p-type conductivity for the 270-450 K temperature range [1-3]. The thermal conductivity of the alloys could be lowered with solid solution alloying without degrading the electrical properties, thus improving the overall figure of merit. The energy gap of solid solutions can be increased by adding  $\text{Sb}_2\text{Se}_3$  to  $\text{Bi}_2\text{Te}_3$ - $\text{Sb}_2\text{Te}_3$  alloys what favours to expanding operating temperature range of the materials. Solid solution alloys were prepared earlier by crystallization from the melt using either the Bridgman or zone-levelling technique [1-3]. Czochralski technique was not used earlier for pulling single crystals of the solid solutions  $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$ .

In Ref. [1], the best thermoelectric properties were reached for n-type  $(\text{Bi}_2\text{Te}_3)_{0.90}(\text{Sb}_2\text{Te}_3)_{0.05}(\text{Sb}_2\text{Se}_3)_{0.05}$  alloy doped with  $\text{SbI}_3$  grown by Bridgman technique. This alloy has electrical resistivity ( $\rho$ ) of about  $1.1 \cdot 10^{-3} \Omega\text{-cm}$ . It is characterized by  $Z=3.2 \cdot 10^{-3} \text{K}^{-1}$  at  $300 \text{K}$ . The lattice thermal conductivity of the SS-alloy is  $\kappa_{\text{ph}}=10 \cdot 10^{-3} \text{W/cm K}$  which in comparison with  $\kappa_{\text{ph}}$  for  $\text{Bi}_2\text{Te}_3$  is lower by almost 40 %.

The best thermoelectric properties are characteristic for p-type Te-compensated  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03}$  alloy. A maximum Z value  $3.4 \cdot 10^{-3} \text{K}^{-1}$  was obtained at  $\rho=1.1 \cdot 10^{-3} \Omega\text{-cm}$  [1]. The lattice thermal conductivity of the excess Te-compensated  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03}$  alloy is  $\kappa_{\text{ph}}=9.6 \cdot 10^{-3} \text{W/cm K}$ . The superior thermoelectric properties of

the SS-alloys were attributed to (1) the low lattice thermal conductivity and its small temperature dependence as a result of alloy-disorder scattering of phonons, and (2) the increase in the band gap with addition of  $\text{Sb}_2\text{Se}_3$  which avoids an ambipolar contribution to the thermal conductivity.

Thermoelectric  $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$  alloys have been fabricated usually by Bridgman method and zone growth in Ref. [2,3] using double doping technique. In Ref. [3], the preparation of p-type functionally graded and n-type segmented  $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$  alloys was optimized for operation over the temperature range 223-423 K. The material efficiency of the thermocouple over this temperature gradient is estimated in Ref. [3] to be 10 % compared with 8.8 % for standard  $\text{Bi}_2\text{Te}_3$ -based materials.

The objective of the present work was to grow by Czochralski technique the  $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$  solid solution alloys n- and p-type conductivity for thermoelectric power generation, to study thermoelectric properties of homogeneous SS-alloys and to prepare functionally graded thermoelectric materials based on SS-alloys.

## Experimental

The crystals of the n-type  $(\text{Bi}_2\text{Te}_3)_{0.90}(\text{Sb}_2\text{Te}_3)_{0.05}(\text{Sb}_2\text{Se}_3)_{0.05}$  solid solutions doped with  $\text{SbI}_3$  and the p-type  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03}$  solid solutions doped with Te and  $\text{SbI}_3$  were grown by the Czochralski technique with replenishment of the melt from the liquid phase from a floating crucible. FGTM based on SS-alloys were prepared by Czochralski technique by varying concentration and nature of doped impurities in the seed and in the melt charge. The gradient at narrow range of the crystal length near the interface between the seed and grown crystal was determined by Seebeck micro-thermoprobe method.

Seebeck coefficient, electrical and thermal conductivity of homogeneous SS-crystals were measured in the temperature range from 300 to 600 K. As rule, the samples were cut from the middle portion of the crystals at a distance of 40-50 mm from the seed.

## Results and discussion

### Thermoelectric properties of homogeneous SS-alloys

Thermoelectric properties were measured for two p-type  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03}$  samples with different level of doping by Te and  $\text{SbI}_3$  and, therefore, different carrier

concentration. Seebeck coefficients at 300 K are equal to:  $S=160 \mu\text{V/K}$  and  $S=182 \mu\text{V/K}$  for the samples N1 and N 2 respectively (Table 1). Equally with the properties of p-type samples, thermoelectric properties of the n-type  $(\text{Bi}_2\text{Te}_3)_{0.90}(\text{Sb}_2\text{Te}_3)_{0.05}(\text{Sb}_2\text{Se}_3)_{0.05} \langle \text{SbI}_3 \rangle$  sample (N 3) with  $S= -176 \mu\text{V/K}$  at 300 K are also presented in Table 1.

Table 1. Thermoelectric properties of the homogeneous SS-alloys at room temperature

	Type conductivity	S, $\mu\text{V/K}$	$\sigma$ , S/cm	$\kappa_{\text{tot}} \cdot 10^3$ , W/cm K	$\kappa_{\text{ph}} \cdot 10^3$ , W/cm K	$Z \cdot 10^3$ , 1/K
1	p-	160	1900	19.3	9.6	2.4
2	p-	182	1290	15.2	8.8	2.8
3	n-	-176	1710	19.0	10.4	2.8

- 1-  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03} \langle \text{Te, SbI}_3 \rangle$
- 2-  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03} \langle \text{Te, SbI}_3 \rangle$   
(concentration of  $\text{SbI}_3$  in the sample N 2 is greater than that in the sample N 1)
- 3-  $(\text{Bi}_2\text{Te}_3)_{0.90}(\text{Sb}_2\text{Te}_3)_{0.05}(\text{Sb}_2\text{Se}_3)_{0.05} \langle \text{SbI}_3 \rangle$

The sample N 1 with larger carrier concentration compared to that for the sample N 2 has electrical and thermal conductivity greater than those for the sample N 2. Both samples are characterized by lattice thermal conductivity lower than that of  $\text{Bi}_2\text{Te}_3$  obtained in Ref. [1] ( $14 \cdot 10^{-3} \text{ W/cm K}$ ). This is because of alloying introduces in the lattice short-range distortions which greatly enhance the scattering of phonons but are much less effective in scattering charge carriers.

Temperature dependencies of thermoelectric properties for the sample N 1 are presented in Fig. 1 and Fig. 2. The  $S=f(T)$  dependence (Fig. 1a) has a broad maximum near 450 K. A steep decreasing Seebeck coefficient at the temperatures higher than 450 K is related to the onset of intrinsic conductivity. Electrical conductivity (Fig. 1b) decreases with enhancement of temperature. By analogy with results obtained in Ref. [1], it is possible to suggest that the temperature variations in  $\sigma$  may be due to the changes in the carrier mobility with temperature. Temperature dependencies of total and lattice thermal conductivity are presented in Fig. 2a. In the temperature range of extrinsic conduction, i.e. from 400 K to 300 K,  $\kappa_{\text{tot}}$  increases at decreasing temperature. The  $\kappa_{\text{ph}}=f(T)$  dependence is done in Fig. 2a by the dotted curve in the range of extrinsic conduction. The small temperature dependence  $\kappa_{\text{ph}}=f(T)$  is a strong indication that alloying scattering is predominant in this temperature range. A steep rise of total thermal conductivity in the range from 400 K to 600 K is related to enhancing the ambipolar contribution to the thermal conductivity as intrinsic behavior develops

Temperature dependence of figure of merit of the sample N 1 is presented in Fig. 2b. The highest Z value is reached at 375 K and it is equal to  $Z=2.6 \cdot 10^{-3} \text{ K}^{-1}$ .

Thermoelectric properties of N 2 sample are presented in Table 2 as a function of temperature. This sample is characterized by rather high thermoelectric properties near 300 K. Thermal conductivity is weakly dependent on temperature as it is characteristic for heavily doped semiconductors.

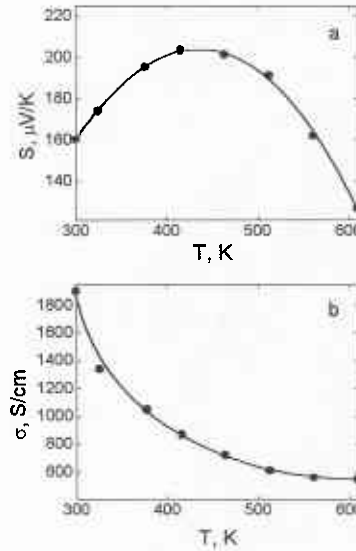


Fig. 1. Temperature dependencies of Seebeck coefficient (a) and electrical conductivity (b) for the sample N 1.

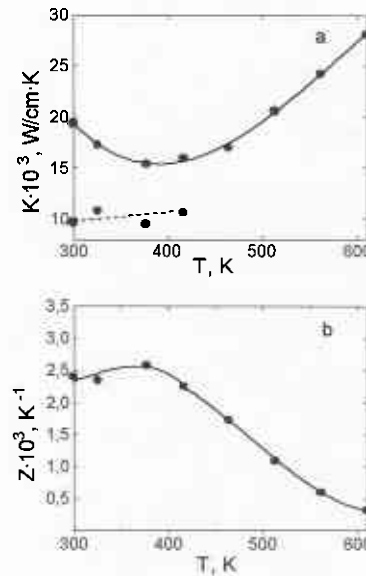


Fig. 2. Temperature dependencies of total and lattice (dotted curve) thermal conductivity (a) and thermoelectric figure of merit Z (b) for the sample N 1.

Table 2. Temperature dependencies of thermoelectric properties for the sample N 2

T, K	S, $\mu\text{V/K}$	$\sigma$ , S/cm	$\kappa_{\text{tot}} \cdot 10^3$ , W/cm K	$\kappa_{\text{ph}} \cdot 10^3$ , W/cm K	$Z \cdot 10^3$ , 1/K
300	182	1290	15.2	8.8	2.8
342	201	942	14.5	9.3	2.6
362	208	797	14.2	9.6	2.4
382	215	772	14.3	9.6	2.5
402	218	624	14.5	10.5	2.0

Temperature dependencies of thermoelectric properties for n-type SS-alloy (N 3 in Table 1) are presented in Fig. 3, 4.

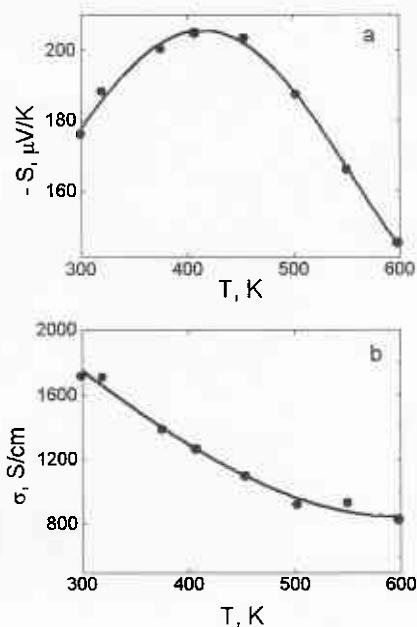


Fig.3. Temperature dependencies of Seebeck coefficient (a) and electrical conductivity (b) for the n-type SS-alloy (N 3).

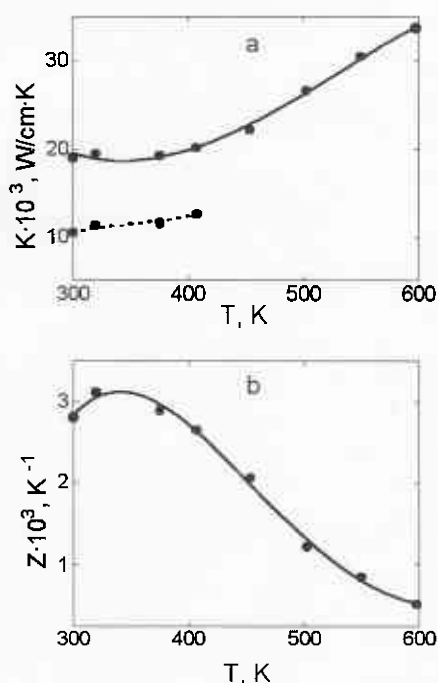


Fig. 4. Temperature dependencies of total and lattice (dotted curve) thermal conductivity (a) and  $Z$  (b) for n-type SS-alloy.

The character of the  $S=f(T)$ ,  $\sigma=f(T)$ ,  $\kappa=f(T)$  and  $\kappa_{\text{ph}}=f(T)$  dependencies (Fig. 3,4) is similar to that which is described for p-type SS-alloy (Fig. 1,2). The n-type SS-alloy is characterized by rather high thermoelectric figure of merit:  $Z_{\text{max}}=3.1 \cdot 10^{-3} \text{ K}^{-1}$  at  $\sim 350 \text{ K}$ . The dimensionless figure of merit is presented in Fig.5 as a function of temperature for n- and p-type alloys (samples are N 3 and N 1 in Table 1, respectively).

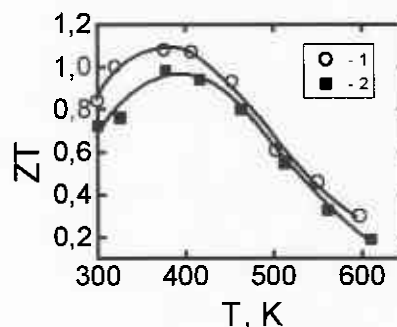


Fig. 5. Temperature dependencies of  $ZT$  values for n-type (1) and p-type (2) SS-alloys.

$ZT$  values are equal to  $ZT=1.08$  and  $0.98$  near  $400 \text{ K}$  for n- and p-type SS-alloys correspondingly. As seen from Fig. 5, these SS-alloys can be used as n- and p-type effective TE materials at least up to  $400\text{--}450 \text{ K}$ .

#### Functionally graded TE materials (FGTM) based on the $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$ solid solutions

Czochralski method was used for growing the FGTM of n- and p-type conductivity based on SS-alloys. The FGTM were prepared by varying level of doping and the nature of doped impurities in the seed and the charge. In such a manner, considerable Seebeck coefficient gradient is reached in narrow range of the length near the interface between the seed and grown crystal.

**FGTM of n-type conductivity.** A fragment of the n-type crystal near the interface between the seed and the grown crystal is presented in Fig.6.

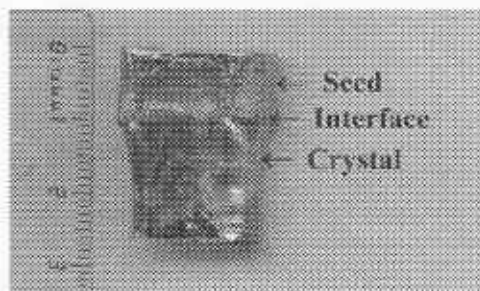


Fig.6. A fragment of n-type crystal near the interface between the seed and grown crystal.

The seed for drawing FGTM has the composition of the traditional n-type  $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15} \langle \text{SbI}_3 \rangle$  alloy [4]. It is characterized by high Seebeck coefficient:  $S= -250 \mu\text{V/K}$  at room temperature (low temperature end of n-type FGTM). The charge corresponds to the  $(\text{Bi}_2\text{Te}_3)_{0.90}(\text{Sb}_2\text{Te}_3)_{0.05}(\text{Sb}_2\text{Se}_3)_{0.05} \langle \text{SbI}_3 \rangle$  SS-composition ( $S=-180 \mu\text{V/K}$ ). Thus, the  $\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}/\text{SS}$ -alloy stacked structure is considered to be two-stage segmented TE material. The results of Seebeck scan by micro-thermoprobe method are presented in Fig. 7. Seebeck scan was performed along the growth direction and perpendicular to the cleavage planes. As seen, a steep gradient of Seebeck coefficient takes place near the interface between the seed and grown crystal. The gradient is about  $40 \mu\text{V/K}$  on the length about  $1 \text{ mm}$ .

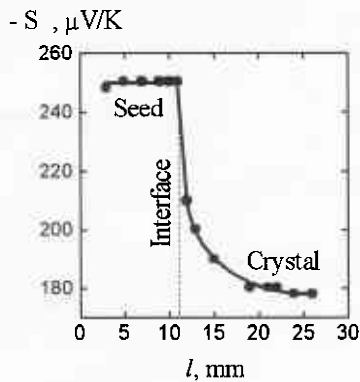


Fig. 7. The distribution of Seebeck coefficient along the growth direction across the interface for n-type FGTM.

#### FGTM of p-type conductivity

A fragment of the p-type crystal near the interface between the seed and grown crystal is presented in Fig. 8.

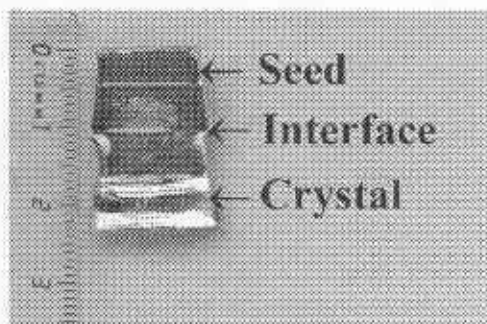


Fig.8. The origin part of the p-type crystal near the interface between the seed and grown crystal.

The seed for pulling p-type crystal has the composition of the following solid solution:  $(\text{Bi}_2\text{Te}_3)_{0.25}(\text{Sb}_2\text{Te}_3)_{0.72}(\text{Sb}_2\text{Se}_3)_{0.03} \langle \text{Te}, \text{SbI}_3 \rangle$ . It is characterized by Seebeck coefficient  $S=180-185 \mu\text{V/K}$  at room temperature (low temperature end of p-type FGTM). The charge corresponds to the same base composition but it is distinguished from the seed by lower content of Te and  $\text{SbI}_3$ . Seebeck coefficient for the charge is found to be  $S \sim 150 \mu\text{V/K}$  at room temperature (high temperature end of p-type FGTM).

The results of Seebeck coefficient scan by micro-thermoprobe method are presented in Fig.9. As seen from Fig. 9, a steep gradient of Seebeck coefficient (about  $30 \mu\text{V/K}$  on the length  $\sim 1 \text{ mm}$ ) is noted for p-type FGTM

#### Conclusions

The single crystals of pseudo-ternary solid solutions  $(\text{Bi}_2\text{Te}_3)_{1-x-y}(\text{Sb}_2\text{Te}_3)_x(\text{Sb}_2\text{Se}_3)_y$  were grown by Czochralski technique with melt supply through a floating crucible. Thermoelectric properties of SS-alloys have been measured in the range from 300 to 600 K. It is found that SS-alloys are promising materials of n- and p-type conductivity for thermoelectric power generation at least up to 400-450 K.

Functionally graded thermoelectric materials (FGTM) were fabricated by Czochralski technique by varying the

concentration of doped impurities in the seed and in the charge. Seebeck scan by micro-thermoprobe method was

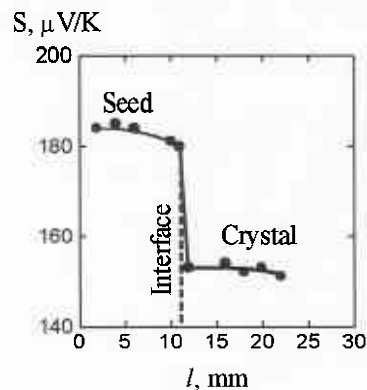


Fig.9. The distribution of Seebeck coefficient along the growth direction across the interface for p-type FGTM.

performed near the interface between the seed and grown crystal. The steep gradient of Seebeck coefficient was discovered in narrow range of the length near the interface.

The n-type  $(\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}/\text{SS-alloy})$  stacked structure represents two-stage segmented combination. Joining segments can directly contacted because of the closeness of their physicochemical nature. The necessity in soldering and metallic interconnects to bond the segments falls off in this case.

#### Acknowledgments

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