Physical Properties of $Bi_2Te_{2.85}Se_{0.15}$ Single Crystals Doped with Cu, Cd, In, Ge, S, or Se

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Abstract—$Bi_2Te_{2.85}Se_{0.15}$ crystals doped with Cu, Cd, In, Ge, S, or Se were grown by the floating-crucible technique. The effective segregation coefficients for the dopants were determined. The thermoelectric power, electrical conductivity, and thermal conductivity of the samples were measured in the temperature range from 77 to 350 K. The effects of the dopants studied on the temperature dependences of the electrical properties and thermoelectric figure of merit were examined. The bending strength of the doped crystals was measured.

INTRODUCTION

$Bi_2Te_{2.85}Se_{0.15}$-based thermoelectric materials of n-type are used in various coolers operating in the temperature range from 200 to 350 K [1]. Doping of $Bi_2Te_{2.85}Se_{0.15}$ with elements of various groups makes it possible to elaborate materials having a high thermoelectric figure of merit in a wide temperature range, which allows one to attain lower temperatures by Peltier cooling. Doping also increases the mechanical strength of $Bi_2Te_{2.85}Se_{0.15}$ [2–7].

Since data on the longitudinal dopant distribution over ingots are of great practical interest, we determined the effective segregation coefficients K_{eff} for various dopants in $Bi_2Te_{2.85}Se_{0.15}$. Besides, it was of interest to assess the electrical activity of various dopants as a function of the alloy composition and doping level.

In this work, we present our results on the doping of $Bi_2Te_{2.85}Se_{0.15}$ with various elements with the aim of enhancing its thermoelectric figure of merit, Z.

EXPERIMENTAL

Undoped and doped $Bi_2Te_{2.85}Se_{0.15}$ single crystals with various carrier concentrations were grown by the floating-crucible technique in the [10$\bar{1}$0] direction. The crystals had the following compositions: $Bi_2Te_{2.85}Se_{0.15}$ doped with Cu to 0.05–0.3 at. %, Ge to 0.2–1.0 at. %, CdTe (0.5–3.0 mol % in the charge), In_2Te_3 (0.2–5.0 mol % in the charge), and In_2Se_3 (0.1–0.3 mol % in the charge); $Bi_2Te_{3-z}S_z$ ($z = 0.06, 0.09$); and $Bi_2Te_{3-y-z}Se_yS_z$ ($y = 0.09, z = 0.06; y = 0.09, z = 0.09$). Since K_{eff} depends on growth conditions, all the crystals were grown under identical conditions. The dopant concentrations in the growth charge, melt, and floating crucible after separation of the crystal were determined by atomic absorption analysis, using procedures fitted for each dopant [2–5]. The sulfur concentration was determined by IR spectroscopy [8].

The thermoelectric power α, electrical conductivity σ, thermal conductivity κ, and Hall coefficient were measured by standard compensation methods.

Bending tests were performed on an Instron machine by the procedure described elsewhere [9], with the load applied along the c axis.

RESULTS AND DISCUSSION

Table 1 lists the values of K_{eff} and octahedral covalent radii r_{oct} for the dopants studied. There is some correlation between K_{eff} and r_{oct}. At the same time, K_{eff} depends not only on r_{oct} but also on the dopant solubility and the character of the forming bonds.

The dopants substituting on Te and Bi sites act as donors (Se, S) and acceptors (Cd, Ge), respectively. In the latter case, Cd'_{Bi} and Ge'_{Bi} acceptors are formed [11, 12]. In $Bi_2Te_{2.85}Se_{0.15}$ doped with CdTe, each Cd atom captures one conduction electron; i.e., increasing the Cd content decreases the electron concentration. Moreover, upon doping with CdTe, charged Te vacancies form, which increases the hole concentration [11]. Ge in $Bi_2Te_{2.85}Se_{0.15}$ acts as an amphoteric impurity. At Ge concentrations less than 0.1 at. %, Ge interacts with antisite defects, decreasing their concentration and acting as a weak donor. At a Ge content above 0.1 at. %, Ge acts as a weak acceptor [12]. The likely reason is that a fraction of the Ge atoms substitute on Bi sites, while the rest enter van der Waals gaps and are not ionized [13]. There is no general agreement regarding the state of indium in the solid solution. According to Pan-

Table 1. Effective distribution coefficients for dopants in $Bi_2Te_{2.85}Se_{0.15}$

Group	Dopant	Type of dopant	Dope additive	r_{oct}, Å [10]	K_{eff}
I	Cu	D	Cu	1.16	0.17
II	Cd	A	CdTe	1.38	0.21
III	In	D	In_2Te_3	1.27	0.51
IV	Ge	D–A	Ge	1.36	0.13
VI	S	D	Bi_2S_3	1.35	0.80
VI	Se	D	Bi_2Se_3	1.45	1.30
VII	I	D	SbI_3	–	0.93

cir *et al.* [14], In atoms substitute on Bi sites and form neutral defects In_{Bi}^x. At low In_2Te_3 concentration, In acts as a donor. At In_2Te_3 concentrations from 2 to 5 mol % (within the solubility limit), In acts as a strong donor due to the essential decrease in the concentration of antisite defects. To control the carrier concentration, we varied the concentration of SbI_3, the dopant ensur-

ing *n*-type conductivity. Dopant atoms produce considerable lattice distortions, which contribute to the scattering of phonons, thereby reducing the lattice thermal conductivity, κ_l. Unlike the above dopants, the group I element Cu resides in interstices, mainly in van der Waals gaps [7]. Since the dopants under consideration occupy different sites, they have different effects on the properties of the solid solution.

Table 2 summarizes the room-temperature electrical and mechanical properties of the best samples.

The concentrations of Cu, In, Ge, S, and Se in the crystals were varied over a wide range corresponding to 300-K values of α from 190 to 280 µV/K. Since Cd acts as an acceptor, the CdTe-doped crystals had a low carrier concentration corresponding to $\alpha = 240–280$ µV/K, with a maximum Z of $(2.8–3.0) \times 10^{-3}$ K^{-1} in the range from 220 to 300 K [3].

Thermoelectric measurements between 77 and 350 K revealed that Z increased upon doping to a certain level. For Cd, In, Ge, S, and Se, this is due to the decrease in κ_l (Table 2, Figs. 1, 2). Doping with small amounts of In_2Se_3 (0.1–0.3 mol % in the charge) has

Table 2. 300-K physical properties of undoped and doped $Bi_2Te_{2.85}Se_{0.15}$ crystals

Composition	$-\alpha$, µV/K	σ, S/cm	$\kappa_l \times 10^3$, W/(cm K)	μ_0, cm^2/(V s)	$Z \times 10^3$, K^{-1}	σ_b, MPa
$Bi_2Te_{2.85}Se_{0.15}$	206	1200	10.7	275	3.1	43
$Bi_2Te_{2.85}Se_{0.15}$ + 0.05 at. % Cu	214	1280	11.0	380	3.4	49
$Bi_2Te_{2.85}Se_{0.15}$ + 0.1 mol % In_2Te_3	214	1080	10.4	250	3.2	52
$Bi_2Te_{2.85}Se_{0.15}$ + 0.1 mol % In_2Se_3	204	1230	10.4	–	3.2	65
$Bi_2Te_{2.85}Se_{0.15}$ + 0.5 at. % Ge	204	1210	10.1	220	3.2	51
$Bi_2Te_{2.82}Se_{0.09}S_{0.09}$	205	1140	10.0	260	3.1	48
$Bi_2Te_{2.85}Se_{0.15}$	273	440	11.4	300	2.5	43
$Bi_2Te_{2.85}Se_{0.15}$ + 2 mol % CdTe	282	470	11.2	280	2.8	50

Table 3. Values of α, K_0, m, and s in the $\alpha = K_0 \ln T$, $\sigma \sim T^{-m}$, and $\kappa_l \sim T^{-s}$ dependences for undoped and doped $Bi_2Te_{2.85}Se_{0.15}$

Composition	$-\alpha$, µV/K	K_0	m	s
$Bi_2Te_{2.85}Se_{0.15}$	206	129	1.35	0.65
$Bi_2Te_{2.85}Se_{0.15}$ + 0.05 at. % Cu	217	123	1.4	0.65
$Bi_2Te_{2.85}Se_{0.15}$ + 0.1 mol % In_2Te_3	220	126	1.25	0.60
$Bi_2Te_{2.85}Se_{0.15}$ + 0.1 mol % In_2Se_3	204	128	1.25	0.60
$Bi_2Te_{2.85}Se_{0.15}$ + 0.5 at. % Ge	204	130	1.3	0.60
$Bi_2Te_{2.82}Se_{0.09}S_{0.09}$	205	127	1.3	0.45
$Bi_2Te_{2.85}Se_{0.15}$	273	131	1.35	0.55
$Bi_2Te_{2.85}Se_{0.15}$ + 2 mol % CdTe	282	132	1.05	0.55

$Z \times 10^3$, K^{-1}

$\kappa_l \times 10^3$, W/(cm K)
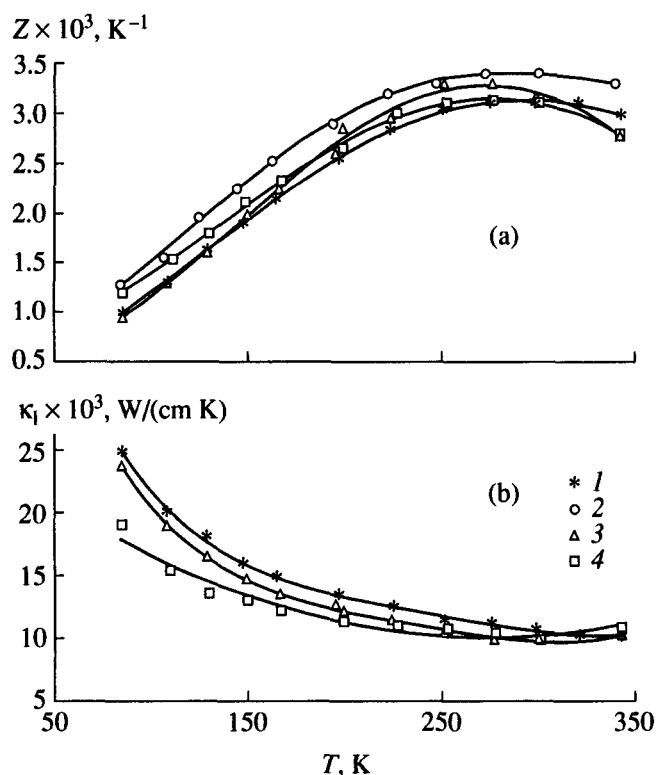
(a)

(b)

* *1*
o *2*
△ *3*
□ *4*

T, K

Fig. 1. Temperature dependences of (a) Z and (b) κ_l for (*1*) $Bi_2Te_{2.85}Se_{0.15}$, (*2*) $Bi_2Te_{2.85}Se_{0.15}$ doped with 0.05 at. % Cu, (*3*) $Bi_2Te_{2.85}Se_{0.15}$ doped with 0.5 at. % Ge, and (*4*) $Bi_2Te_{2.82}Se_{0.09}S_{0.09}$.

virtually no effect on κ_l or Z. Compared to the other dopants studied, sulfur decreases κ_l more effectively because of the essential lattice distortions resulting from the large difference in r_{oct} between Te and S (1.64 and 1.35 Å, respectively) [10]. In the temperature range studied, the κ_l of $Bi_2Te_{2.82}Se_{0.09}S_{0.09}$ is lower than that of $Bi_2Te_{2.85}Se_{0.15}$ (Fig. 1b). The increase in Z upon Cu dop-

ing is due to the increase in carrier mobility μ_0 and, accordingly, σ (Fig. 3, Table 2). One can see in Fig. 1a that, in the range from 250 to 340 K, the Cu-doped crystals exhibit the highest values of Z: (3.2–3.4) × 10^{-3} K^{-1}.

The α, κ_l, and σ data (Table 3) show that increasing the concentration of Cu, Ge, Se, or S has no effect on the $\alpha(T)$ and $\sigma(T)$ dependences, while the $\kappa_l(T)$ dependence becomes weaker. Doping of $Bi_2Te_{2.85}Se_{0.15}$ with CdTe and In_2Te_3 leads to additional scattering from Cd and In atoms. As a result, μ_0 drops [11], and the exponent m in the power-law dependence $\sigma \sim T^{-m}$ for the crystals doped with CdTe and In_2Te_3 (0.5–2 mol % and 0.2–2 mol % in the charge, respectively) decreases from 1.35 to 1.05 and from 1.35 to 0.7, respectively [3, 15].

The effect of doping on the mechanical properties of the crystals is illustrated in Table 2. At the dopant concentrations studied, the crystals doped with In_2Te_3, In_2Se_3, and CdTe retain some plasticity, while the Cu-doped crystals are brittle. The effects of In_2Te_3 and Ge depend on the doping level: as the concentration of In or Ge increases, the bending strength σ_b rises considerably, then decreases, and increases again [5, 6]. In the concentration range studied ($\leq$0.3 mol %), doping with In_2Se_3 strengthens the crystals to a greater extent than does doping with In_2Te_3. The strengthening is due to the elastic stresses developing as a result of the substitution. The anomalous concentration dependences of σ_b at low concentrations of In or Ge are attributable to deviations from stoichiometry, the formation of antisite defects, and their interaction with dopant atoms. We presume that the anomalies in the concentration dependences of mechanical properties are also related to the fact that In, as well as Ge, occupies different lattice sites at low and high concentrations. Similar concentration dependences of σ_b would be expected for other dopants at low concentrations. The strengthening upon

$Z \times 10^3$, K^{-1}
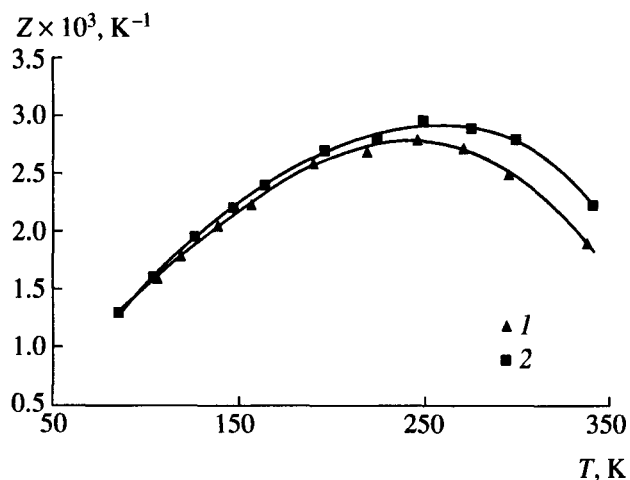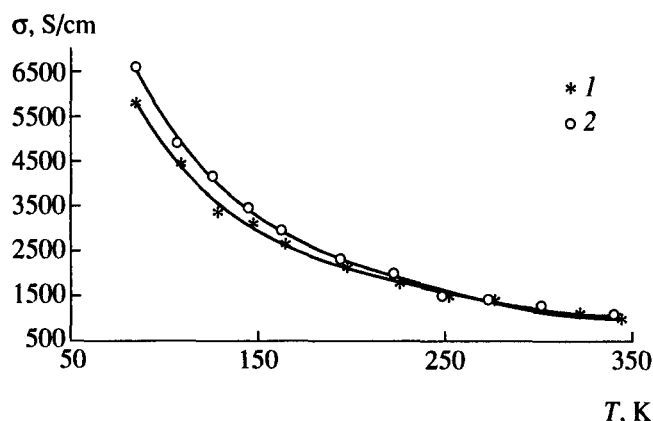

▲ *1*
■ *2*

T, K

Fig. 2. Temperature dependences of Z for (*1*) $Bi_2Te_{2.85}Se_{0.15}$ and (*2*) $Bi_2Te_{2.85}Se_{0.15}$ doped with CdTe (2 mol % in the charge).

σ, S/cm

* *1*
o *2*

T, K

Fig. 3. Temperature dependences of σ for (*1*) $Bi_2Te_{2.85}Se_{0.15}$ and (*2*) $Bi_2Te_{2.85}Se_{0.15}$ doped with 0.05 at. % Cu.

Table 4. Properties of single crystals and thermal converters

Composition of the n-leg	α_n, μV/K	α_p, μV/K	I, A	U, V	T_{max}, K	$Z_{eff} \times 10^3$, K^{-1}
$Bi_2Te_{2.85}Se_{0.15}$	−206	+200	8.90	0.1196	74.4	2.85
$Bi_2Te_{2.85}Se_{0.15}$ + 0.5 at. % Ge	−204	+200	9.52	0.1224	75.3	2.91
$Bi_2Te_{2.82}Se_{0.09}S_{0.09}$	−205	+200	9.52	0.1184	75.2	2.90

Note: The p-leg was prepared from the charge containing 96 mol % $Bi_{0.5}Sb_{1.5}Te_3$ and 4 mol % Bi_2Se_3.

doping with Cu is due to the incorporation of Cu ions into van der Waals gaps, which increases the strength of the bonds between five-layer slabs [7]. Thus, all the dopants under consideration increase the strength of $Bi_2Te_{2.85}Se_{0.15}$ (Table 2).

Thermal converters prepared from single-crystal bismuth and antimony chalcogenides were tested at the Odessa State Academy of Refrigerating Engineering. The p-legs had identical compositions, and the n-legs were prepared from crystals of various compositions (Table 4). The legs had dimensions of $2 \times 2 \times 2.5$ mm. The tests were performed in a vacuum of 10^{-2} Pa at a hot-junction temperature of 303 K. For all the converters, large temperature differences were obtained: $T_{max} = 74.4$–75.3 K, which corresponds to $Z_{eff} = (2.85$–2.91) $\times 10^{-3}$ K^{-1}. The highest values of T_{max} were obtained for the converter prepared from the Ge-doped solid solution (Table 4) (no converters with Cu-doped n-legs were tested).

CONCLUSIONS

$Bi_2Te_{2.85}Se_{0.15}$ single crystals with various carrier concentrations, undoped and doped with Cu, Cd, In, Ge, S, or Se, were grown by the floating-crucible technique. The effective segregation coefficients for the dopants were determined and correlated with r_{oct}. The physical properties of the crystals were studied in the temperature range form 77 to 350 K.

Doping with Cd, In, or Ge was found to decrease the carrier mobility evaluated on the assumption that the scattering from acoustic phonons prevails. Doping with Cu increases μ_0. Compared to the other dopants studied, sulfur decreases κ_l more effectively in the whole temperature range examined.

In the range from 250 to 340 K, the highest figure of merit, $Z = (3.2$–3.4) $\times 10^{-3}$ K^{-1}, was obtained for the Cu-doped crystals. Between 220 and 280 K, the Cd-doped samples show $Z = (2.8$–3.0) $\times 10^{-3}$ K^{-1}.

All of the dopants studied were found to increase the mechanical strength of the material. The thermal converters prepared from single crystals of various compo-

sitions with identical carrier concentrations exhibit high values of T_{max} (74.4–75.3 K).

REFERENCES

1. Semenyuk, V.A., Svechnikova, T.E., and Ivanova, L.D., Single Crystals of Solid Solutions of Chalcogenides of Bismuth and Antimony and Miniature Coolers Based on Them, *J. Adv. Mater.*, 1994, no. 1 (5), pp. 428–434.

2. Svechnikova, T.E., Maksimova, N.M., Polikarpova, N.V., and Konstantinov, P.P., Thermoelectric Properties of Copper-Doped $Bi_2Te_{2.85}Se_{0.15}$ Crystals, *Neorg. Mater.*, 1998, vol. 34, no. 3, pp. 277–280 [*Inorg. Mater.* (Engl. Transl.), vol. 34, no. 3, pp. 210–213].

3. Svechnikova, T.E., Chizhevskaya, S.N., Polikarpova, N.V., et al., Effect of Cadmium Telluride on the Thermoelectric and Mechanical Properties of $Bi_2Te_{2.85}Se_{0.15}$ Crystals, *Neorg. Mater.*, 1992, vol. 28, no. 2, pp. 316–320.

4. Svechnikova, T.E., Chizhevskaya, S.N., and Polikarpova, N.V., Indium Doping of $Bi_2Te_{2.85}Se_{0.15}$ Crystals, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1987, vol. 23, no. 7, pp. 1128–1131.

5. Svechnikova, T.E., Chizhevskaya, S.N., Maksimova, N.M., et al., Doping of the $Bi_2Te_{2.85}Se_{0.15}$ Solid Solution with Germanium, *Neorg. Mater.*, 1994, vol. 30, no. 2, pp. 168–171 [*Inorg. Mater.* (Engl. Transl.), vol. 30, no. 2, pp. 161–164].

6. Chizhevskaya, S.N., Svechnikova, T.E., Geminov, V.N., et al., Mechanical Properties of $Bi_2Te_{2.85}Se_{0.15}$–In_2Te_3 Solid Solutions, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1989, vol. 25, no. 8, pp. 1394–1396.

7. Korzhuev, M.I., Chizhevskaya, S.N., Svechnikova, T.E., et al., Mechanical Properties of Single-Crystal and Polycrystalline Copper-Doped Bi_2Te_3 and $Bi_2Te_{2.85}Se_{0.15}$, *Neorg. Mater.*, 1992, vol. 28, no. 7, pp. 1383–1388.

8. Svechnikova, T.E., Maksimova, N.M., and Konstantinov, P.P., Bi_2S_3 Doping of Single Crystals of Bi_2Te_3-Based Solid Solutions, *Neorg. Mater.*, 1998, vol. 34, no. 3, pp. 302–305 [*Inorg. Mater.* (Engl. Transl.), vol. 34, no. 3, pp. 233–235].

9. Geminov, V.N., Kop'ev, I.M., Svechnikova, T.E., and Chizhevskaya, S.N., Deformation and Fracture of Bi_2Te_3–Bi_2Se_3 Semiconductor Crystals in a Wide Temperature Range, *Fiz. Khim. Obrab. Mater.*, 1985, no. 3, pp. 132–138.

10. Semiletov, S.A., Tetrahedral and Octahedral Covalent Radii, *Kristallografiya*, 1976, vol. 21, no. 4, pp. 752–758.

11. Sher, A.A., Odin, I.N., and Novoselova, A.V., Effects of Cd and Sn Tellurides on the Transport Properties of Bi_2Te_3 and Sb_2Te_3, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1984, vol. 20, no. 8, pp. 1327–1330.

12. Predota, M., Benes, L., and Horak, J., On the Incorporation of Germanium Atoms into the Bi_2Te_3 Crystal Lattice, *Phys. Status Solidi A*, 1987, vol. 100, no. 2, pp. 401–404.

13. Svechnikova, T.E., Korzhuev, M.A., Maksimova, N.M., *et al.*, Anisotropic Hall Coefficient and Electrical Resistivity of Ge-Doped $Bi_2Te_{2.85}Se_{0.15}$ Crystals, *Fiz. Tekh. Poluprovodn.* (S.-Peterburg), 1996, vol. 30, no. 7, pp. 1153–1162.

14. Pancir, J., Horak, J., and Stary, Z., Concentration of Free Carriers in $Bi_{2-x}In_xTe_3$ Mixed Crystals, *Phys. Status Solidi A*, 1987, vol. 103, no. 2, pp. 517–526.

15. Alekseeva, G.T., Konstantinov, P.P., Kutasov, V.A., *et al.*, Kinetic Phenomena in $Bi_{2-x}In_xTe_{2.85}Se_{0.15}$ Solid Solutions, *Fiz. Tverd. Tela* (Leningrad), 1991, vol. 33, no. 12, pp. 3539–3544.