Phase Relations and Thermoelectric Properties of Alloys in the Bi_2Te_3–Bi_2Se_3 System

O. B. Sokolov[a], S. Ya. Skipidarov[a], N. I. Duvankov[a], and G. G. Shabunina[b]

[a] Nord Specialized Design & Technology Bureau, ul. Peschanyi kar'er 3, Moscow, 109383 Russia
[b] Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia
e-mail: info@sctbnord.ru

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Abstract—Using differential thermal analysis and x-ray diffraction, we have shown that the Bi_2Te_3–Bi_2Se_3 system contains a continuous series of solid solutions in a narrow temperature range and a compound of composition Bi_2Te_2Se below the solidus line. The liquidus and solidus lines determined using zone-melted samples differ little from those reported in the literature for equilibrium samples. The $Bi_2Te_{3-x}Se_x$ solid-solution phase extends to ≈ 14 mol % Bi_2Se_3 ($Bi_2Te_{2.58}Se_{0.42}$). The thermoelectric power of the alloys drops sharply near the boundary of the two-phase region. Within the homogeneity range of Bi_2Te_2Se (33.3 mol % Bi_2Se_3), the thermoelectric power factor has a minimum, while the thermoelectric power has a small maximum.

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INTRODUCTION

Bi_2Te_3–Bi_2Se_3 alloys containing ≤ 30 mol % Bi_2Se_3 are of considerable interest as low-temperature n-type materials for thermoelectric generators and coolers [1]. According to most reports, Bi_2Te_3 and Bi_2Se_3 form a continuous series of solid solutions, which undergo ordering on cooling to form the compound Bi_2Te_2Se below 500°C [2, 3]. Dumas et al. [4] reported a peritectic phase diagram with limited solid solubility and a two-phase region from 22 to 48 mol % Bi_2Se_3. The compound Bi_2Te_2Se is missing in their phase diagram.

The purpose of this work was to investigate the composition range in question in greater detail than in earlier studies [2, 3] in order to clarify the melting relations in the Bi_2Te_3–Bi_2Se_3 system.

EXPERIMENTAL

The starting materials used were $\approx 99.99\%$-pure bismuth, tellurium, and selenium. Bi_2Te_3–Bi_2Se_3 samples were synthesized at 1072 K in silica tubes pumped down to 0.1 Pa. Next, the samples were processed by vertical zone melting at 1130 K in the same tubes. The specific free volume was 0.314 cm³/g.

We prepared samples in the composition range 0 to 100 mol % Bi_2Se_3. The composition of the bismuth-telluride-rich samples was varied in 2 mol % steps. In phase-diagram studies, we used samples containing 4, 6, 8, 10, 15, 20, 25, 33.3, and 40 mol % Bi_2Se_3. In addition, to obtain enhanced-performance n-type materials, we prepared Bi_2Te_3–Bi_2Se_3 samples doped with C_6Br_6.

The Bi_2Te_3–Bi_2Se_3 samples were characterized by differential thermal analysis (DTA) and x-ray diffraction (XRD). DTA was performed using an NTR-72 pyrometer and Pt/Pt–Rh thermocouple. The samples were heated to 900°C and cooled in silica Stepanov vessels pumped down to 0.1 Pa. The sample weight was 1 g. Al_2O_3 was used as a reference substance. The positions of the solidus and liquidus lines were determined from the heating and cooling curves, respectively. XRD patterns were collected on a DRON-1 powder diffractometer (Ni-filtered CuK_α radiation, $2\theta \leq 100°$) and were indexed using ICDD Powder Diffraction File (PDF) data. Both DTA and XRD were performed on samples free from halogens. Lattice parameters were refined by least squares fitting. The estimated error of determination was ± 0.004–0.007 Å.

Thermoelectric power was measured in a thermostated cell composed of two independently heated copper blocks. The temperature difference between the blocks was on average 20 K. The thermoelectric power of the sample was measured with a digital voltmeter to within $\pm 2\%$ accuracy.

RESULTS AND DISCUSSION

Figure 1 shows a partial liquidus diagram (≤ 40 mol % Bi_2Se_3) of the Bi_2Te_3–Bi_2Se_3 join. The present experimental data, coupled with earlier results [2, 3], indicate the existence of a continuous series of solid solutions in a narrow temperature range and the compound Bi_2Te_2Se below the solidus line. The melting point of the Bi_2Te_3 sample prepared by zone melting (589°C)
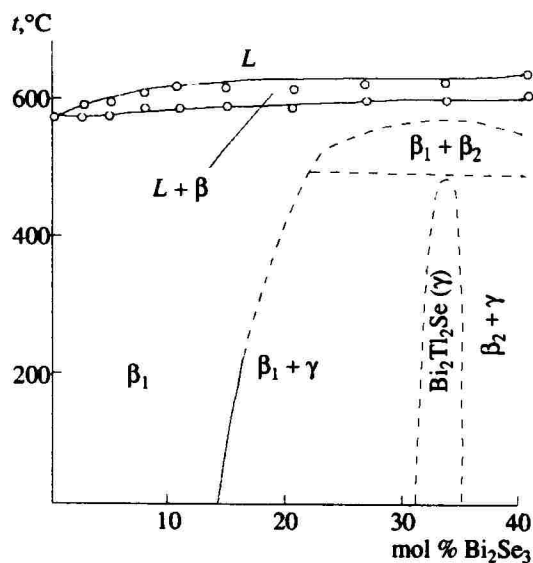
Fig. 1. Partial phase diagram of the Bi_2Te_3–Bi_2Se_3 system.

coincides with that reported earlier (585°C [2, 3]) to within experimental uncertainty. The solidus and liquidus temperatures also agree with earlier data [2, 3] (within ±5°C), except for the sample containing 20 mol % Bi_2Se_3, whose liquidus temperature is slightly lower than the literature value.

In the studies reported by Bankina and Abrikosov [2] and Chizhevskaya et al. [3], the lattice parameters of Bi_2Te_3–Bi_2Se_3 alloys varied across the two-phase region, and its boundaries could not be determined from the composition dependences of lattice parameters. Chizhevskaya et al. [3] calculated the extent of the two-phase region β_1 + $Bi_2Te_2Se(\gamma)$ at the phase-separation temperature. Extrapolating their data to room temperature, they obtained 20–33.3 mol % Bi_2Se_3.

In this study, the range of $Bi_2Te_{3-x}Se_x$ solid solutions (β_1) was determined by XRD. At 20 mol % Bi_2Se_3 (assumed boundary of the two-phase region [3]), the sample consisted of two phases: a Bi_2Te_3-based solid solution (β_1) and a significant amount of Bi_2Te_2Se (γ)

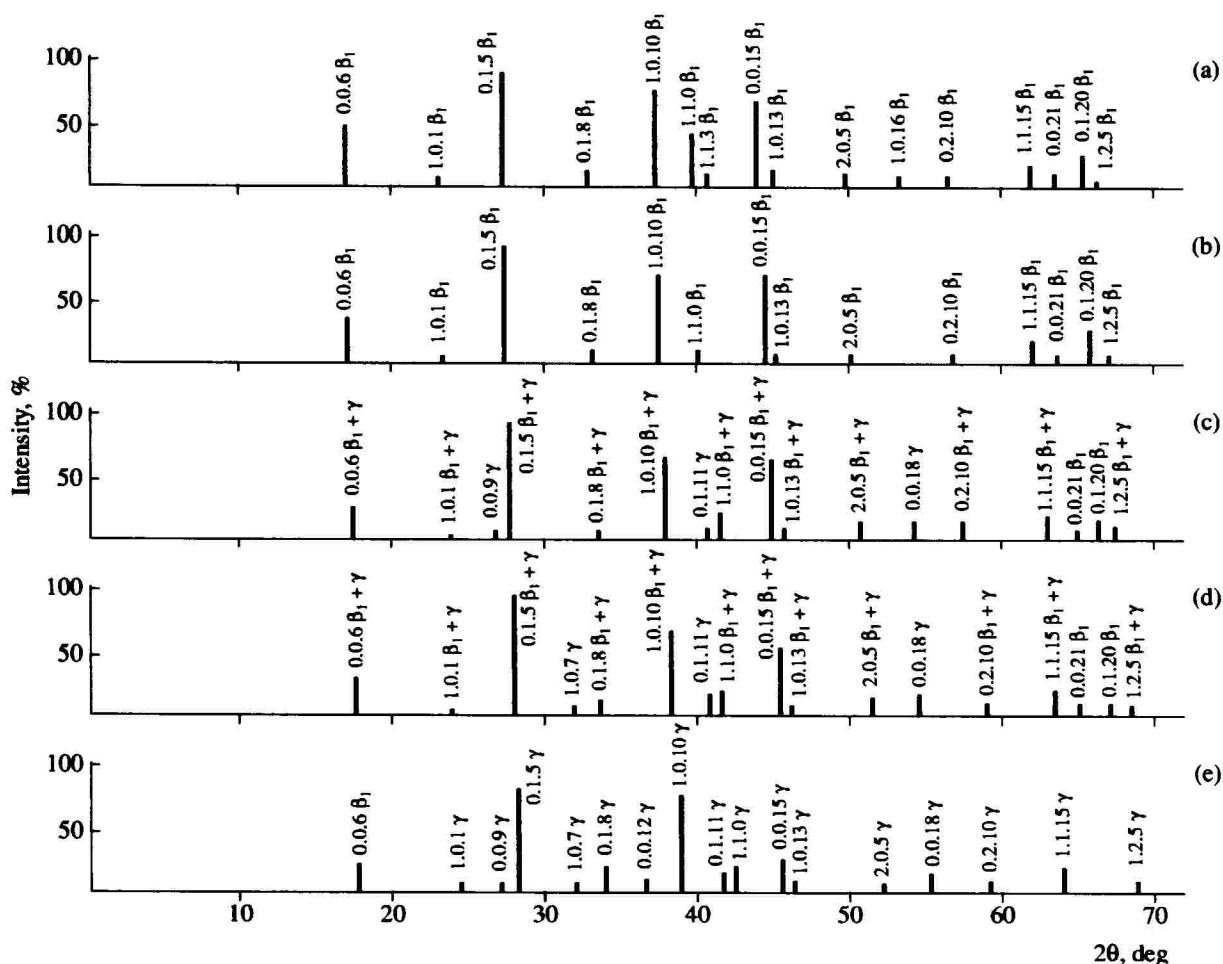Fig. 2. Schematic XRD patterns of zone-melted Bi_2Te_3–Bi_2Se_3 samples: (a) Bi_2Te_3, (b) 10 mol % Bi_2Se_3, (c) 15 mol % Bi_2Se_3, (d) 20 mol % Bi_2Se_3, (e) Bi_2Te_2Se (γ).
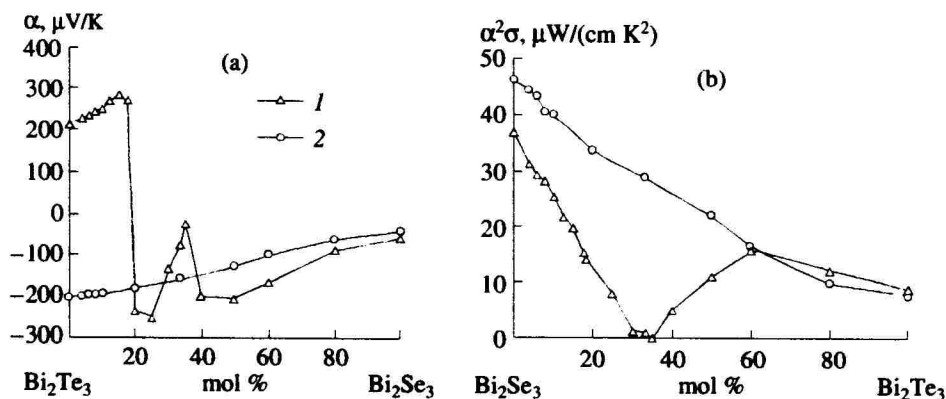
Fig. 3. (a) Thermoelectric power and (b) power factor as functions of Bi_2Se_3 content for Bi_2Te_3–Bi_2Se_3 samples: (*1*) undoped, (*2*) doped with 0.053 wt % C_6Br_6.

(Fig. 2d). Therefore, according to our data, the two-phase is broader.

Bi_2Te_3 and Bi_2Te_2Se are known to crystallize in rhombohedral symmetry. Their XRD patterns differ in that the one of Bi_2Te_2Se shows a number of weak lines: 009, 107, 0.0.12, 0.1.11, 0.0.18, and others (PDF data).

The XRD data for the samples containing 0–33.3 mol % Bi_2Se_3 (Fig. 2) demonstrate that the lattice parameters of the solid solutions (table) decrease with increasing Bi_2Se_3 content across the entire two-phase region, as in earlier studies [2, 3]. At the same time, the weak reflections characteristic of Bi_2Te_2Se are present down to 15 mol % Bi_2Se_3 (Fig. 2c) and are missing in the XRD pattern of the sample containing 10 mol % Bi_2Se_3 (Fig. 2b). It seems likely that, under the conditions of this study, the $\gamma + \beta_1$ two-phase region extends from ≈13–14 to 33.3 mol % Bi_2Se_3. The XRD data for the sample containing 33.3 mol % Bi_2Se_3 confirm the existence of the compound Bi_2Te_2Se at room temperature (Fig. 2e). The interplanar spacings in its structure coincide with PDF data for equilibrium samples. The lattice parameters of Bi_2Te_2Se, refined by least squares fitting ($a = 4.283$ Å, $c = 29.846$ Å), also agree well with literature data ($a = 4.18$–4.28 Å, $c = 29.66$–29.86 Å).

The discrepancy between the lattice parameters of the γ phase reported in the literature is probably related to different sample preparation procedures. In most studies, the γ phase was prepared by very slow cooling from its melting point or by annealing at the phase-separation temperature (500°C) or slightly lower temperatures, and the preparation conditions of this phase differed from those of other Bi_2Te_3–Bi_2Se_3 samples. In this study, all of the alloys were prepared under identical conditions.

Note that the thermoelectric power of our samples varies steadily with composition in the single-phase regions (0–14 and 53–100 mol % Bi_2Se_3) and shows sharp changes (Fig. 3) in the two-phase regions (14–33.3 and 33.3–53 mol % Bi_2Se_3). In particular, α drops from 285 to –250 μV/K near 20 mol % Bi_2Se_3.

This behavior of α is characteristic of solid solutions containing two carrier types [5–7]. In the composition range 33–35 mol % Bi_2Se_3 (Bi_2Te_2Se phase region), α has another maximum, while the thermoelectric power factor drops to a minimum level. The thermoelectric power and power factor of the C_6Br_6-doped Bi_2Te_3–Bi_2Se_3 alloys vary steadily over the entire composition range.

CONCLUSIONS

The partial (0–40 mol % Bi_2Se_3) Bi_2Te_3–Bi_2Se_3 phase diagram constructed in this study shows a continuous series of solid solutions in a narrow temperature range and a compound of composition Bi_2Te_2Se below the solidus line.

The boundary between the $Bi_2Te_{3-x}Se_x$ solid solution and $Bi_2Te_{3-x}Se_x + Bi_2Te_2Se$ two-phase region has been located experimentally for the first time.

The thermoelectric power of the alloys studied has maxima at the boundaries of the single- and two-phase regions. Within the homogeneity range of Bi_2Te_2Se, the

Lattice parameters of Bi_2Te_3–Bi_2Se_3 solid solutions

mol % Bi_2Se_3	a, Å	c, Å	Phase composition
0	4.378	30.440	Bi_2Te_3 (β_1)
6	4.364	30.400	β_1
10	4.361	30.323	β_1
15	4.348	30.221	$\beta_1 + \gamma$
20	4.330	30.169	$\beta_1 + \gamma$
33.33	4.283	29.846	Bi_2Te_2Se (γ)

thermoelectric power has a maximum, while the thermoelectric power factor drops to a minimum level.

REFERENCES

1. Gol'tsman, B.M., Kudinov, V.A., and Smirnov, I.A., *Poluprovodnikovye termoelektricheskie materialy na osnove Bi₂Te₃* (Bi_2Te_3-Based Semiconducting Thermoelectric Materials), Moscow: Nauka, 1972.

2. Bankina, V.F. and Abrikosov, N.Kh., System Bi_2Te_3–Bi_2Se_3, *Zh. Neorg. Khim.*, 1964, vol. 9, no. 4, pp. 931–936.

3. Chizhevskaya, S.N., Shelimova, L.E., Kosyakov, V.I., and Shestakov, V.A., Critical Evaluation and Optimization of Data on the Bi–Te–Se Phase Diagram and Crystal Structure of Bi_2Te_3–Bi_2Se_3 Alloys, *Neorg. Mater.*, 1997, vol. 33, no. 8, pp. 907–911 [*Inorg. Mater.* (Engl. Transl.), vol. 33, no. 12, pp. 757–764].

4. Dumas, F., Brun, G., Liautard, B., et al., New Contribution in the Study of the Bi_2Te_3–Bi_2Se_3 System, *Thermochim. Acta*, 1987, vol. 122, no. 1, pp. 135–139.

5. Gordyakova, G.N., Kokosh, G.V., and Sinani, S.S., Thermoelectric Properties of Bi_2Te_3–Bi_2Se_3 Solid Solutions, *Zh. Tekh. Fiz.*, 1958, vol. 28, no. 1, pp. 3–17.

6. Sokolov, O.B., Skipidarov, S.Ya., and Duvankov, N.I., The Variation of the Equilibrium of Chemical Reactions in the Process of $(Bi_2Te_3)(Sb_2Te_3)(Sb_2Se_3)$ Crystal Growth, *J. Cryst. Growth*, 2002, vol. 236, pp. 181–190.

7. Sokolov, O.B., Skipidarov, S.Ya., Duvankov, N.I., and Shabunina, G.G., Chemical Reactions on the Bi_2Te_3–Bi_2Se_3 Section in the Process of Crystal Growth, *J. Cryst. Growth*, 2004, vol. 262, pp. 442–448.