

# Thermoelectric Properties of Single Crystals of Bismuth-Arsenic-Tellurium Solid Solutions

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The thermoelectric properties of single-crystal samples of bismuth-arsenic-tellurium solid solutions  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  ( $0 \leq x \leq 0.10$ ) synthesized by the Bridgman method were studied in the temperature range  $77 < T < 330$  K. It was found that the conductivity decreases, and the Seebeck coefficient initially increases significantly and then decreases in  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  solid solutions with increasing  $x$ . The thermal conductivity of samples with As decreases compared to the original bismuth telluride at  $T < 250$  K and increases slightly at  $T > 250$  K. As a result, the maximum thermoelectric figure of merit  $ZT$  shifts from temperature of 300 K to temperature of 250 K with an increase in the As content.

**Keywords:** Seebeck effect, thermoconductivity, thermoelectrical figure of merit, bismuth telluride.

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## 1. Introduction

Thermoelectric materials (TEM) are distinguished by a very high practice-oriented potential, however, their use is currently restricted because of their low efficiency. Efficiency of TEM-based devices is defined by a dimensionless figure of merit  $ZT = S^2 T \sigma / \kappa$ , where  $S$  — Seebeck coefficient (thermal emf),  $\sigma$  — conductivity,  $\kappa$  — thermal conductivity of material,  $T$  — absolute temperature.

In theory it was found that the whole class of semiconductors  $\text{Bi}_2\text{Se}_3$ ,  $\text{Bi}_2\text{Te}_3$ ,  $\text{Sb}_2\text{Te}_3$  are the topological insulators [1]. It turned out that it is due to accounting for the spin-orbit interaction in these crystals that results in the inversion of the two near-Fermi level zones of different parity which allows them being classified as having a non-trivial topology. The existence of topological surface states in crystals  $\text{Bi}_2\text{Te}_3$ ,  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$  was discovered in various experiments [2–6]. On the other hand,  $\text{Bi}_2\text{Te}_3$ ,  $\text{Bi}_2\text{Se}_3$ ,  $\text{Sb}_2\text{Te}_3$  — are well-known thermoelectric compounds used at room temperature. Variation of transport properties, namely  $\sigma$ ,  $S$  and  $\kappa$  of the thermoelectric materials is crucial for attaining the best thermoelectric characteristics.  $\text{Bi}_2\text{Te}_3$ ,  $\text{Sb}_2\text{Te}_3$  materials and the like are thoroughly investigated to understand their thermoelectric properties and relation to structure, point defects, concentration of charge carriers [7–10]. In semiconductors of  $\text{Bi}_2\text{Te}_3$  type there exist valence bands (light and heavy holes) and two conduction bands (light and heavy electrons) [11,12].

Solid solutions, i.e. crystals like  $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$  or  $\text{Sb}_2\text{Te}_{3-y}\text{Se}_y$ , are of high interest because of large values of their thermoelectric efficiency  $ZT$ . Solid solutions are featuring high thermoelectric characteristics at near room temperature compared to  $\text{Bi}_2\text{Te}_3$  [13,14]. Depending

on concentration of the charge carriers maximal value  $ZT$  is commonly observed at a near room temperature.

Arsenic telluride is attributed to the same group of metals.  $\text{As}_2\text{Te}_3$  has two allotropic modifications:  $\alpha$  and  $\beta$ - $\text{As}_2\text{Te}_3$ , among which only the latter one is crystallized in the same rhombohedral structure as  $\text{Bi}_2\text{Te}_3$  [15].  $\beta$ - $\text{As}_2\text{Te}_3$  belongs to a family of semiconductors like  $\text{Bi}_2\text{Te}_3$  — a well-known class of thermoelectric materials effective at room temperature. Metastable  $\beta$ - $\text{As}_2\text{Te}_3$  ( $R\bar{3}m$ ,  $a = 4.047$  Å and  $c = 29.492$  Å at 300 K) is isostructural to  $\text{Bi}_2\text{Te}_3$  and is known as a good thermoelectric material at temperatures of 400 K. Crystallization of  $\text{As}_2\text{Te}_3$  gives rise to multiphase samples, while  $\beta$ - $\text{As}_2\text{Te}_3$  can actually be synthesized with high phase purity by melt quenching.  $\beta$ - $\text{As}_2\text{Te}_3$  undergoes a phase transition and is converted into stable  $\alpha$ - $\text{As}_2\text{Te}_3$  ( $C2/m$ ,  $a = 14.337$  Å,  $b = 4.015$  Å,  $c = 9.887$  Å and  $\beta = 95.06^\circ$ ) at 480 K [16].

It is known that As may be substituted by Bi in  $\text{As}_{2-x}\text{Bi}_x\text{Te}_3$  system up to  $x = 0.035$ . Solid solutions  $\text{As}_{2-x}\text{Bi}_x\text{Te}_3$  have reduced resistivity while preserving the same thermal conductivity  $< 1$  W/m · K within the temperature range  $5 < T < 300$  K. In these materials  $ZT \sim 0.2$  was obtained at room temperature [15]. Additionally, defects of solid solutions was studied  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  [17].

In this study the thermoelectric properties of single-crystals  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  ( $0 \leq x \leq 0.1$ ) within the temperature range  $77 < T < 330$  K were investigated.

## 2. Samples and experimental procedure

For preparing the solid solutions  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  Bi, Te and  $\text{As}_2\text{Te}_3$  were placed in the quartz tubes. Arsenic telluride was synthesized earlier. All materials were placed according

to the required composition  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  ( $x = 0.00-0.1$ ). Single crystals were grown by the modified Bridgman method [18]. Arsenic contents in samples was indicated when loading the initial components and basically may slightly differ from the indicated values in the studied samples. According to the X-ray diffraction analysis all samples were single-phase. On the electrical erosion machine the samples 5 mm long and  $1.5 \times 1.5$  mm in cross-section were cut from the ingot.

Electrical resistance of samples was measured by DC current four-probe method. The current passed through the sample and generated by a stabilized power source generally was 10 mA. Current flow direction was along the axis  $C_2$ . Current and voltage in sample were measured by digital multimeters, respectively. Seebeck coefficient for all samples was measured in temperature range  $77 < T < 330$  K with temperature gradient along the cleaved planes complying with method described in Ref. [19].

### 3. Measurement results and discussion

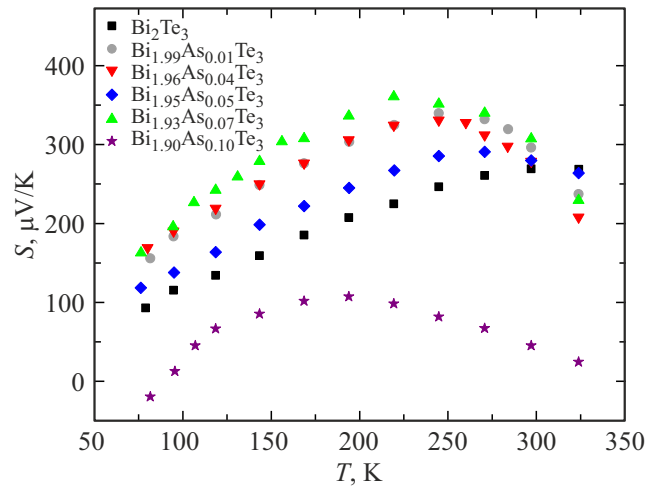
It was found that Seebeck coefficient  $S$  is positive in  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  ( $x = 0.00-0.1$ ) which corresponds to  $p$ -type of conductivity, and  $S$  increases sufficiently when Bi is substituted by As to values  $x = 0.07$ , and at  $x = 0.10$  it goes down (Figure 1).

The studies of conductivity  $\sigma$  of  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  ( $0 \leq x \leq 0.1$ ) single-crystal samples in the temperature range  $77 < T < 330$  K demonstrated that  $\sigma$  for all samples rises with the decrease of temperature and goes down with the increase of arsenic content as shown in Figure 2. A singularity in the temperature dependence of conductivity at  $T \approx 150$  K is attributed to the reversible phase transition [16].

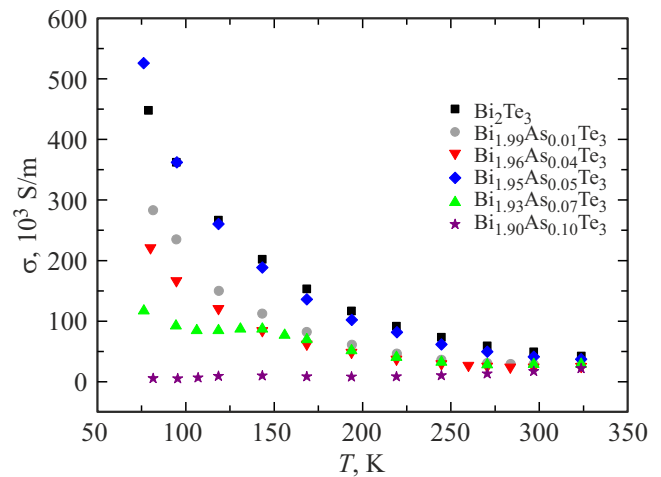
Thermal conductivity  $\kappa$  with the growth of arsenic content at room temperature rises, yet staying  $< 2.5$  W/m·K. However, at  $T < 250$  K thermal conductivity goes down when arsenic is added (Figure 3).

If bismuth is substituted by arsenic in  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  single-crystals, it generally results in decrease of conductivity, i.e. arsenic acts here as a donor. Such behavior can be explained by lower number of point charged defects in bismuth telluride with the growth of arsenic content. With stoichiometric loading of bismuth telluride components the crystals with a slight excess of bismuth are obtained. Extrinsic stacking faults of Bi are positioned in tellurium places forming the substitution faults. Since they have negative charge,  $\text{Bi}_2\text{Te}_3$  crystals, that grew under stoichiometric loading of components, always have a conductivity of  $p$ -type and a significant holes concentration.

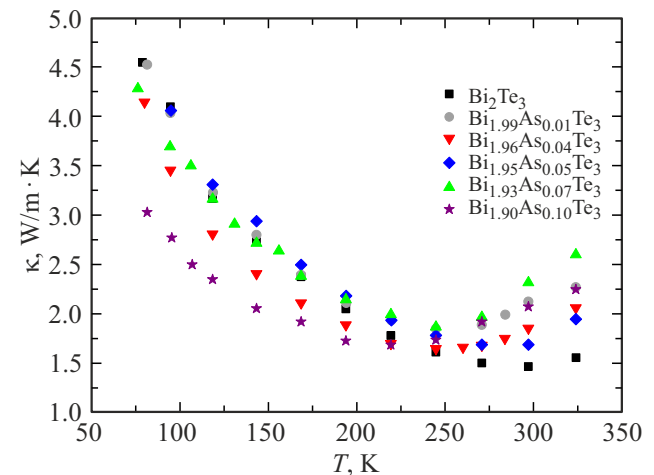
Dimensionless thermoelectric figure of merit  $ZT$  reaches the value of 0.7, while its maximum is displaced from the room temperature to  $T \approx 250$  K when arsenic content grows in the solid solutions of  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$ , as shown in Figure 4.



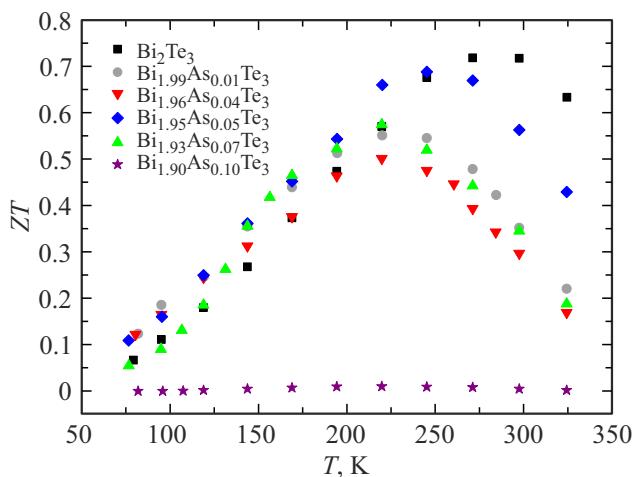
**Figure 1.** Seebeck coefficients versus temperature for samples  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$ .



**Figure 2.** Conductivity  $\sigma$  of  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  single-crystal samples versus temperature.



**Figure 3.** Thermal conductivity  $\kappa$  of  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  single-crystal samples versus temperature.



**Figure 4.** Dimensionless thermoelectric efficiency  $ZT$  of  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  single-crystal samples versus temperature.

#### 4. Conclusion

It was found that Seebeck coefficient  $S$  is positive in  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$  ( $x = 0.00-0.10$ ) which corresponds to  $p$ -type of conductivity, and  $S$  increases sufficiently when Bi is substituted by As to values of  $x = 0.07$ . Electric conductivity goes down with adding of arsenic, i.e. arsenic here acts like a donor. Thermal conductivity with the growth of arsenic content at room temperature rises insufficiently, yet staying  $< 2.5 \text{ W/m}\cdot\text{K}$ . Dimensionless thermoelectric efficiency  $ZT$  reaches the value of 0.7, while its maximum is displaced from the room temperature to  $T = 250 \text{ K}$  when arsenic content grows in the solid solutions of  $\text{Bi}_{2-x}\text{As}_x\text{Te}_3$ .

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#### Conflict of interest

The authors declare that they have no conflict of interest.

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