

Figure of Merit of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ Single Crystals

C. DRASAR,^{1,4} A. HOVORKOVA,¹ P. LOSTAK,¹ S. BALLIKAYA,^{2,3}
C.-P. LI,² and C. UHER²

1.—Faculty of Chemical Technology, University of Pardubice, Cs. Legii Square 565, 532 10 Pardubice, Czech Republic. 2.—Department of Physics, University of Michigan, Ann Arbor, MI 48109-1120, USA. 3.—University of Istanbul, 34000 Vezneciler, Istanbul, Turkey. 4.—e-mail: cestmir.drasar@upce.cz

We have shown previously that indium doping is beneficial for thermoelectric properties of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$. This effect was ascribed to a change in the magnitude and mechanism of hole scattering and a decrease in thermal conductivity. Since the state-of-the-art material for *p*-type legs in low-temperature applications is the quaternary $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{3-y}\text{Se}_y$, we have attempted to dope this material with In, hoping to improve its properties further. Indeed, the doping enhances the figure of merit of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ by more than 15% compared with the values measured on undoped $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_{2.8}\text{Se}_{0.2}$ below room temperature.

Key words: Chalcogenides, transport coefficients, thermoelectric properties, tetradymite crystals, transport properties

INTRODUCTION

It is well known that properly doped $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$ is used for *p*-type legs of thermoelectric modules working in the vicinity of room temperature and having $ZT = \sigma S^2 T / \kappa$ (where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, and T is absolute temperature) value close to 1. Investigations of ternary and quaternary systems based on Bi_2Te_3 are still an active area of research.^{1–3} We have shown that small concentrations of In can be beneficial for thermoelectric properties of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_3$, enhancing the ZT value by as much as 30% in the low-temperature region [optimal $x \approx 0.02$ in $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_3$].⁴ However, the ZT values of the studied $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_3$ crystals did not reach the magnitudes of the state-of-the-art materials, namely the quaternary system $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{3-y}\text{Se}_y$ used as *p*-type legs at low temperatures.⁵ Therefore, the aim of this work is to examine the influence of In doping on the figure of merit of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{3-y}\text{Se}_y$ single crystals. In this contribution we present and discuss some preliminary results obtained for this system. While most of the

studies have dealt with polycrystalline alloys, we focus on single-crystalline materials due to their reproducibility.

EXPERIMENTAL PROCEDURES

The starting polycrystalline materials of nominal compositions $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ were synthesized from elements of 5 N purity in conical quartz ampoules evacuated to 10^{-3} Pa. Synthesis consisted of heating the reaction mixture at 1073 K for 48 h. The single crystals were grown using a modified Bridgman technique. A conical quartz ampoule, containing the synthesized material, was placed in the upper (warmer) part of the Bridgman furnace, where it was kept at 1000 K for 24 h. The ampoule was then lowered into a temperature gradient of 80 K/cm at a rate of 1.3 mm/h. The single crystals, 60 mm long and 10 mm in diameter, were easily cleavable along the 0001 plane. Orientation of the crystals was performed using Laue back-diffraction technique. Samples of dimensions for measurement were cut from the middle part of single crystals by using a spark erosion machine. The lattice parameters of the single crystals were determined from powdered samples by x-ray diffraction analysis using a D8-Advance diffractometer (Bruker AXE, Germany) in Bragg–Brentano θ – θ

(Received July 7, 2009; accepted March 2, 2010;
published online March 25, 2010)

geometry. The diffraction angles were measured at room temperature from 7° to 80° in 0.02° steps. The lattice parameters were refined using the Fullprof program.

The Seebeck coefficient and thermal conductivity were determined using a longitudinal steady-state technique in a cryostat equipped with a radiation shield. Thermal gradients were measured by means of fine Au:Fe/Chromel thermocouples, and a miniature strain gage served as a heater. For the Seebeck probes, previously calibrated fine copper wires were used, and their thermopower contribution was subtracted from the measured sample thermopower. Electrical conductivity was studied using a Linear Research AC bridge with 16 Hz excitation.

All presented physical parameters are in-plane parameters, i.e., they were measured in perpendicular direction to trigonal axes c . Namely, electrical resistivity $\rho \perp c$, Seebeck coefficient $S(\Delta T \perp c)$, and thermal conductivity $\kappa(\Delta T \perp c)$. Measurements of the electrical resistivity and the Seebeck coefficient have an absolute error of about 1%. Thermal conductivity is measured with an accuracy of 5%.

RESULTS AND DISCUSSION

The x-ray diffraction (XRD) patterns indicated no secondary phases in the samples as documented by the pattern for a sample with the highest content of In (Fig. 1). The results of the measurements of temperature dependence of electrical resistivity ρ , Seebeck coefficient S , and thermal conductivity κ are presented in Figs. 2–4. In Table I we summarize the room-temperature thermoelectric parameters. The increase of the electrical resistivity ρ (Fig. 2) is in accordance with the data published in Ref. 4 for the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_3$ system and is attributed to the decreasing hole concentration and increasing point defect scattering. Indium atoms enter the cation sublattice and form uncharged point defects In_{Me}^x (Me being Bi or Sb) and thus produce neither free electrons nor holes.^{6,7} The decrease of free holes must then be attributed to the interaction of In with native defects, probably due to an increase in bond polarity. The principal point defects in Sb_2Te_3 -based materials are antisite defects $\text{Sb}_{\text{Te}}^{-1}$ producing holes and tellurium vacancies $\text{V}_{\text{Te}}^{+2}$ producing electrons. In particular, the increasing bond polarity implies increasing formation energy of antisite defects and thus decreasing hole concentration. We note that the idea of interaction of impurity atoms with native defects of the host lattice was also used previously to describe free carrier changes in other tetradymite-type crystals.⁸

From Fig. 3 it follows that, in the low-temperature region, the magnitude of the Seebeck coefficient S of all the doped samples (nominal $x = 0.015$ to 0.05) is higher compared with the magnitude for the undoped sample ($x = 0$). This effect is consistent with the observed decrease in the

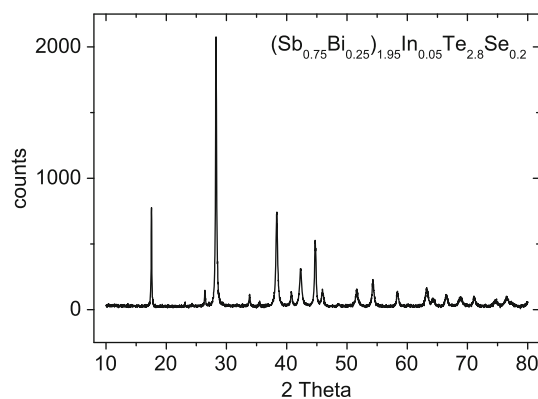


Fig. 1. XRD pattern of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1.95}\text{In}_{0.05}\text{Te}_{2.8}\text{Se}_{0.2}$ single crystal.

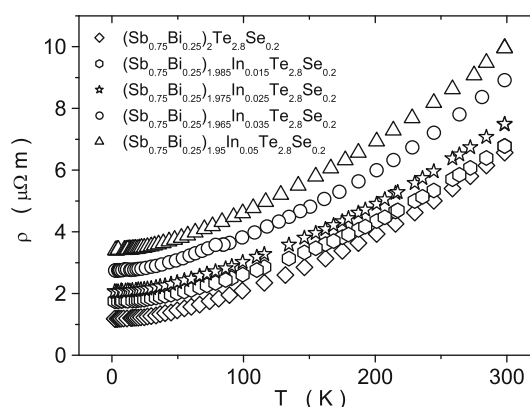


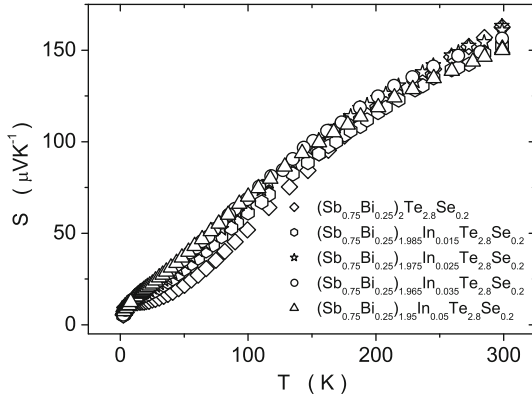
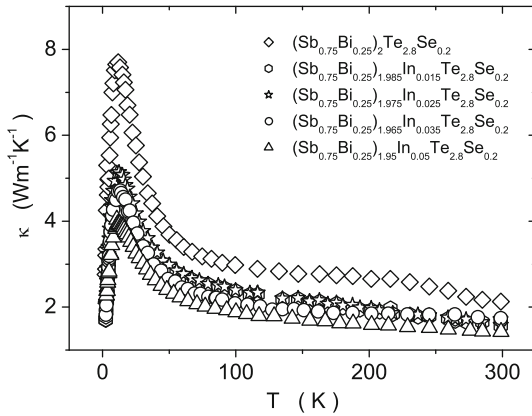
Fig. 2. Electrical resistivity $\rho \perp c$ as a function of temperature for $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ single crystals.

concentration of holes. In Ref. 4, it was shown that a higher concentration of In ($x = 0.15$) changes the scattering mechanism in samples of the related $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_3$ system. Similarly, the change of scattering mechanism from acoustic phonons to point impurities due to In incorporation thus might be another parameter influencing the S values in the $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ system.

From Fig. 4 we can see that, upon doping with In, the thermal conductivity κ decreases in the entire temperature region measured. Generally $\kappa = \kappa_e + \kappa_L$, where κ_e and κ_L are the electronic and lattice parts of the thermal conductivity, respectively. The electronic component of the thermal conductivity κ_e in Table I was computed using the relation $\kappa_e = L\sigma T$, where we used the Lorenz number L in the elastic degenerate limit, i.e., $L = L_0 = \pi^2(k_B/e)^2/3 = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$. Well above the Debye temperature, we argue that this approximation is close enough to reveal the trend.⁹ The observed decrease in κ can be ascribed to a decrease in both κ_e and κ_L (Table I). The former is connected with the decrease in the concentration and mobility of free carriers, while the latter is connected with enhanced point defect scattering on account of the

Table I. Thermoelectric parameters of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ single crystals at $T = 300$ K

Sample	ρ ($\mu\Omega\text{m}$)	S ($\mu\text{V}/\text{K}$)	κ ($\text{W}/\text{m}/\text{K}$)	κ_e ($\text{W}/\text{m}/\text{K}$)	κ_L ($\text{W}/\text{m}/\text{K}$)
$(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_{2.8}\text{Se}_{0.2}$	6.57	162	2.13	1.11	1.02
$(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1.985}\text{In}_{0.015}\text{Te}_{2.8}\text{Se}_{0.2}$	6.78	153	1.57	1.07	0.5
$(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1.975}\text{In}_{0.025}\text{Te}_{2.8}\text{Se}_{0.2}$	7.47	163	1.58	1.02	0.56
$(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1.965}\text{In}_{0.035}\text{Te}_{2.8}\text{Se}_{0.2}$	8.91	156	1.74	0.82	0.92
$(\text{Sb}_{0.75}\text{Bi}_{0.25})_{1.95}\text{In}_{0.05}\text{Te}_{2.8}\text{Se}_{0.2}$	9.97	151	1.42	0.73	0.69

Fig. 3. Seebeck coefficient $S(\Delta T \perp c)$ as a function of temperature for $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ single crystals.Fig. 4. Thermal conductivity $\kappa(\Delta T \perp c)$ as a function of temperature for $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ single crystals.

presence of In. Since indium tends to suppress the concentration of native lattice defects at the same time, the overall effect of In on κ_L is less clear.

The samples with $x \geq 0.025$ actually displayed higher lattice thermal conductivity than the sample with $x = 0.015$. This indicates that the phonon scattering ability (or strength) of an In_{Me}^x defect is lower compared with the scattering strength of native defects. While $\text{Sb}_{\text{Te}}^{-1}$ defects might show enhanced strain field phonon scattering, $\text{V}_{\text{Te}}^{+2}$ defects must show, logically, enhanced strain field as well as mass fluctuation scattering compared with In_{Me}^x . Overall, the decrease in lattice thermal conductivity

is remarkable for samples with lower In content. For such low concentration of In we observe up to 40% drop in κ_L .

The dimensionless figure of merit ZT as a function of temperature is shown in Fig. 5. The data indicate that, in comparison with $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_{2.8}\text{Se}_{0.2}$, ZT values are enhanced upon In doping by more than 15%. This enhancement is realized primarily around $T = 250$ K. Figure 6 indicates that the optimum x lies in the vicinity of 0.02 for low-temperature applications. However, the optimum might lie at $x \geq 0.02$ for higher-temperature applications. The increase in ZT value can be ascribed primarily to the decrease in lattice thermal conductivity as discussed above, and partially also to an increase in the Seebeck coefficient in the low-temperature region. As it turns out, this increase may be due to the change of the free carrier concentration and also due to the change of the carrier scattering mechanism, as evidenced by the temperature dependence of the Hall mobility presented in Ref. 4. Namely, the suppression of scattering of carriers on acoustic phonons in the low-temperature region might account for the increase of S values. On the other hand, in the room-temperature region, S is affected by the decrease of ionized impurity scattering due to the decrease in the number of charged native defects $\text{V}_{\text{Te}}^{+2}$ and $\text{Sb}_{\text{Te}}^{-1}$. We note that ZT values of the studied $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ crystals do not reach previously published magnitudes for excess Te-doped $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{Te}_{2.91}\text{Se}_{0.09}$,⁵ probably due to nonoptimized carrier concentration for the low-temperature region; one perhaps needs lower hole concentration. In spite of this fact, comparison of the set of samples strongly suggests that small amounts of In are beneficial for enhancing thermoelectric performance in the low-temperature region. Such investigations should be continued, since this alloy is used for p -type legs, coupled with n -type Bi-Sb solid solutions for cooling below room temperature.

CONCLUSIONS

Single crystals of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ (nominal $x = 0$ to 0.05) were grown using the Bridgman technique. Property measurements were carried out over the temperature range of 5 K to 300 K. Indium that is incorporated into the host structure enters the cation sublattice and forms uncharged point defects In_{Me}^x . Although nominally

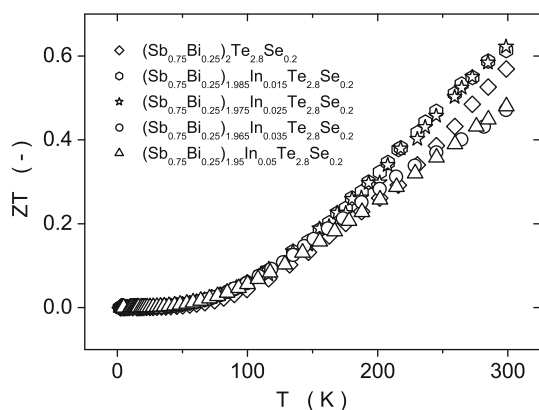


Fig. 5. The dimensionless figure of merit ZT as a function of temperature for $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ single crystals.

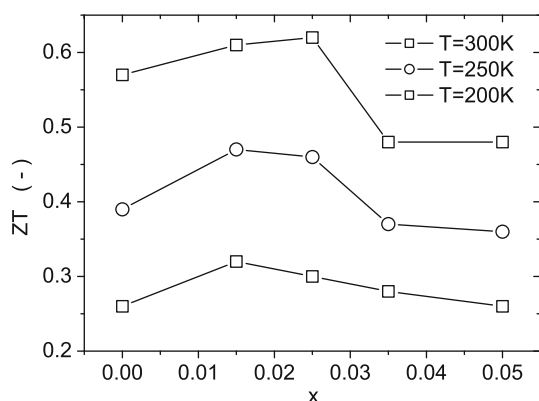


Fig. 6. The dimensionless figure of merit ZT as a function of In content x for $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ single crystals for three temperatures.

electrically inactive, indium causes a change in free hole concentration, probably due to the interaction of indium with native point defects. Therefore In induces a change in the strength and character of charge carrier scattering. Overall, a small concen-

tration of In $x \approx 0.02$ seems to be beneficial for thermoelectric properties, since it enhances the figure of merit of $(\text{Sb}_{0.75}\text{Bi}_{0.25})_{2-x}\text{In}_x\text{Te}_{2.8}\text{Se}_{0.2}$ by more than 15% compared with values measured for undoped $(\text{Sb}_{0.75}\text{Bi}_{0.25})_2\text{Te}_{2.8}\text{Se}_{0.2}$ below room temperature. This increase is primarily due to decreasing lattice thermal conductivity and increasing Seebeck coefficient. Low-concentration doping of tetradymite-type crystals with indium is worthy of further exploration with respect to its potential to improve low-temperature thermoelectric properties through optimization of free carrier concentration and/or selenium content.

ACKNOWLEDGEMENTS

This research was supported by the Ministry of Education, Youth, and Sports of the Czech Republic under Project MSM 0021627501. Work at the University of Michigan is supported as part of the Center for Solar and Thermal Energy Conversion, an Energy Frontier Research Center funded by the US Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0000957.

REFERENCES

1. D. Kusano and I. Hori, *J. Jpn. Inst. Met.* 66, 1063 (2002).
2. P.-W. Zhu, Y. Imai, Y. Isoda, Y. Shinohara, X. Jia, and G. Zou, *J. Phys.: Condens. Matter.* 17, 7319 (2005).
3. P.F.P. Poudeu, J. D'Angelo, H. Kong, A. Downey, J.L. Short, R. Pcionek, T.P. Hogan, C. Uher, and M.G. Kanatzidis, *J. Am. Chem. Soc.* 128, 14347 (2006).
4. C. Drasar, A. Hovorkova, P. Lostak, H. Kong, C.-P. Li, and C. Uher, *J. Appl. Phys.* 104, 023701 (2008).
5. G.S. Nolas, J. Sharp, and H.J. Goldsmid, *Thermoelectrics / Basic Principles and New Material Developments* (Berlin: Springer-Verlag, 2001), p. 128.
6. L. Jansa, P. Lostak, J. Sramkova, and J. Horak, *J. Mater. Sci.* 27, 6062 (1992).
7. F.A. Kroeger, *The Chemistry of Imperfect Crystals* (Amsterdam: North-Holland Publishing Company, 1974), p. 244.
8. J. Horak, P.C. Quayle, J.S. Dyck, C. Drasar, P. Lostak, and C. Uher, *J. Appl. Phys.* 103, 013516 (2008).
9. C. Drasar, M. Steinhart, P. Lostak, H.-K. Shin, J.S. Dyck, and C. Uher, *J. Solid State Chem.* 178, 1301 (2005).