

Structure and Thermoelectric Properties of Nanostructured $Bi_{1-x}Sb_x$ Alloys Synthesized by Mechanical Alloying

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We report on the synthesis of $Bi_{1-x}Sb_x$ alloys and the investigation of the relationship between their structural and thermoelectric properties. In order to produce a compound that will work efficiently even above room temperature, $Bi_{1-x}Sb_x$ alloys were chosen, as they are known to be the best suited *n*type thermoelectric materials in the low-temperature regime (200 K). Using a top-down method, we produced nanostructured $Bi_{1-x}Sb_x$ powders by ballmilling in the whole composition range of 0 < x < 1.0. Nanostructuring of $Bi_{1-x}Sb_x$ alloys increases the band gap and thus results in an enlargement of the semiconducting composition region $(0 \le x \le 0.5)$ compared to its bulk counterpart (0.07 $\leq x \leq$ 0.22). The enhancement of the band gap strongly affects the transport properties of the alloys, i.e. the electrical conductivity and the Seebeck coefficient. Moreover, nanostructuring reduces the thermal conductivity through the implementation of grain boundaries as phonon-scattering centers, leading to a significant enhancement of the thermoelectric properties. The highest figure-of-merit observed in this study is 0.25 which was found for Bi_{0.87}Sb_{0.13} at 280 K.

Key words: Thermoelectrics, bismuth, antimony, structure, mechanical alloying, synthesis

INTRODUCTION

Thermoelectric devices are used to convert temperature differences into voltage or to generate a temperature difference if an external voltage is applied. The efficiency of this conversion depends on the dimensionless figure-of-merit, ZT, of the materials employed,¹ which is proportional to the

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electrical conductivity σ , the square of the Seebeck coefficient, S^2 , and inverse to the thermal conductivity, κ , of the material used ($ZT = S^2 \sigma T/\kappa$). The best conventional thermoelectric bulk materials exhibit ZT values of about 1, which is not sufficient for large-scale commercial applications because the conversion rate is too low. The limitation of the ZTvalues is mainly caused by the fact that the parameters which define ZT cannot be optimized independently, and an improvement of, e.g., the electrical conductivity would also increase the thermal conductivity and reduce the Seebeck coefficient. However, as the thermal conductivity is composed of an electronic and a lattice part, and only the electronic part is basically connected to the electrical conductivity by the Wiedemann–Franz law,² one possibility to increase the thermoelectric ZT of a material is to reduce its lattice thermal conductivity.³ Different pathways for this reduction have been established. The thermoelectric properties of Skutterudites^{4,5} and Clathrates⁶ have been improved by the introduction of heavy atoms into their structures, which causes localized vibrational modes and, thus, increases the scattering rate of extended phonon modes. Also, solid solutions of different materials⁷ or materials containing inclusions⁸ reveal an increased phonon scattering.

Another approach to improve the thermoelectric properties of well-established thermoelectric materials is nanostructuring, which affects the electronic band structure and leads to an increased amount of interfaces, which may act as additional scattering centers for phonons. Most recent investigations of nanostructured thermoelectric materials aim at improving the thermoelectric performance at room temperature and above for waste heat recovery. Although this approach has been proved to be effective for such materials, the most promising results should be obtainable for low-temperature materials for thermoelectric cooling. At low temperatures, the critical issues of sintering and the lack of long-term stability of nanostructured materials are much less pronounced.

For applications at temperatures below 200 K, $Bi_{1-x}Sb_x$ alloys^{9,10} are the most suitable thermoelectric materials. Both elements are semimetals with a rhombohedral crystal structure in the space group *R*-3m. They form a complete series of solid solutions without a miscibility gap.¹¹ Their thermoelectric properties show a strong dependence on the composition, which is the result of changes in the band structure with varying antimony content, as schematically shown in Fig. 1. For low Sb concentrations, single crystals of $Bi_{1-x}Sb_x$ alloys show semimetallic behavior due to an overlap between the T and the L bands. With increasing the Sb content, the top L band and the T band shift down relative to the bottom L band leading to a gapless state at x = 4%. At 7%, the overlap between the *L* and the T bands disappears (semimetal-semiconductor transition), and for higher Sb content the alloy exhibits an indirect band gap and semiconducting behavior. A direct band gap occurs for an Sb content between 9% and 15% in bulk $Bi_{1-x}Sb_x$ alloys. In the composition range between 12% and 15%, a maximum band gap of about 20 meV is found.¹⁴⁻¹⁶ For higher Sb concentrations, the H bands shift up in energy, again resulting in an indirect band gap. Finally, at Sb concentrations higher than 22%, the H bands shift above the L band, resulting in a semiconductor-semimetal transition of the alloy.¹³ There are also a few studies of the changes in band structure

with varying Sb content for microcrystalline samples. $^{17-20}$

Numerous efforts have been made to improve the thermoelectric properties of $\text{Bi}_{1-x}\text{Sb}_x$ alloys by nanostructuring. Most of the approaches for nanostructured $\text{Bi}_{1-x}\text{Sb}_x$ alloys use single crystalline BiSb nanowires.^{21–23} The thermoelectric properties of other $\text{Bi}_{1-x}\text{Sb}_x$ nanostructures, such as superlattices,²⁴ thin films or nanoparticles,^{25–27} have been studied comparatively less often. Nevertheless, some synthetic approaches, especially to create BiSb-nanoparticles, and investigations of their thermoelectric properties have been published in recent years, but mainly in a restricted composition range of 0.1 < x < 0.3.^{28–33}

In order to further investigate the effect of nanostructuring on the thermoelectric properties of $Bi_{1-r}Sb_r$ alloys, we synthesized nanopowders over the whole composition range of 0 < x < 1 using a top -own approach and carried out composition-dependent thermoelectric measurements. In samples consisting of $Bi_{1-x}Sb_x$ nanoparticles with diameters below 100 nm, we observed significantly increased band gaps compared to bulk material. Throughout the series of these nanostructured $Bi_{1-x}Sb_x$ samples, the band gaps increased with x up to x = 14%, where a band gap of about 40 meV was reached and then decreased again becoming semimetallic at about x = 50%.³⁴ The enhancement of the band gap strongly affects the electrical transport properties, such as electrical conductivity, thermal conductivity and the Seebeck coefficient, which results in an enhancement of the thermoelectric properties.

EXPERIMENTAL

 $Bi_{1-x}Sb_x$ nanoparticles were synthesized by mechanical alloying. First, Bi and Sb powders were mixed in the desired ratio, put into a steel beaker, and sealed under argon atmosphere. Then, the powder mixture was ball-milled for 20 h at a speed of 450 rpm and a ball-to-powder ratio (BPR) of 7.5:1. After the milling process, the product was annealed for 17 h at 250°C under inert atmosphere (argon). Afterwards, it was pressed into pellets, which were again annealed for 17 h at 200°C.^{30–32} The pressing procedure was carried out by uniaxial cold pressing with a pressure of 390 MPa at room temperature for 30 min, resulting in disk-shaped pellets with a thickness of about 1 mm. A schematic scheme of the synthesis route is shown in Fig. 2.

The composition and microstructure of the samples were studied by powder x-ray diffraction (XRD) and transmission electron microscopy (TEM)/energy-dispersive x-ray spectroscopy (EDX) before the pressing procedure on a Stoe StadiP and a Philips CM 30 with an acceleration voltage of 300 kV and an EDAX-PV 9900 EDX detector. The Seebeck coefficient (S) and electrical conductivity (σ) of the pressed pellets were studied using



Fig. 1. Schematic representation of the changes in the band structure of $Bi_{1-x}Sb_x$ alloys with changing antimony content. *SM* semimetal, *SC* semiconductor, *SMSC* semimetal–semiconductor transition, *SCSM* semiconductor–semimetal transition.



Fig. 2. Schematic scheme of the synthesis route to prepare diskshaped pellets of $Bi_{1-x}Sb_x$ alloys in the whole composition range.

homebuilt equipment. S was determined by the direct measurement of the obtained voltage for a given temperature difference³⁵ and σ by using the Van der Pauw method, both between 100 K and 300 K. At 280 K, Hall measurements were performed at 1 T to determine the carrier concentration and their mobilities. The thermal conductivity (κ) was measured between 30 K and 300 K using three different methods to cover the whole temperature range. For high temperatures between 173 K and 300 K, κ was calculated from the thermal diffusivity data, α , the specific heat, C_p , and the material density, ρ , using the relationship:

$$\kappa = \alpha \rho C_p \tag{1}$$

The diffusivity was determined by the laser flash method using an Anter Flashline 3000 as well as a Linseis XFA 500 system to minimize experimental errors. The specific heat, C_p , was measured in the temperature range from 1.8 K to 300 K with a PPMs device using a relaxation-type technique.

For temperatures below 200 K, κ was obtained in a steady state heat flow experiment using a homebuilt setup.³⁶ Above 100 K, the data obtained with this method have to be corrected for radiation losses. Those were determined by comparing the data in the overlapping temperature range (173– 200 K) with data on the same samples measured by the laser flash method. The relative uncertainties of the thermoelectric measurements are 2–3% for the electrical conductivity, 5–7% for the Seebeck coefficients, and about 10% for the thermal conductivity.

RESULTS AND DISCUSSION

Microstructure

The XRD patterns and lattice parameters of samples with different x are shown in Fig. 3. With increasing x, the reflections are shifted to higher 2θ values, indicating a smaller unit cell. This observation is also confirmed by the lattice parameters which decrease with x following Vegard's law, as shown in Fig. 3b).

Figure 4 shows TEM images of the prepared $Bi_{1-x}Sb_x$ nanoparticles which exhibit an inhomogeneous distribution of particle shape and size. The average particle size is around 70 nm according to the TEM images, showing particle sizes between 40 nm and 100 nm. With the Scherrer equation, we can estimate particle sizes of 30-110 nm for the different samples, which are in good agreement with the TEM data. The particle sizes decrease linearly with increasing antimony content (see supplementary Fig. S1). EDX measurements show a very homogeneous particle composition within each sample. The high-resolution (HR) TEM images and the electron diffraction patterns show the high crystallinity of the material. The lattice planes in the HRTEM image correspond to the (012) plane of Bi_{0.85}Sb_{0.15}. The density of all samples is between 90% and 98% of the theoretical density. The composition does not show a systematic influence on the density of the pellets.

Thermoelectric Properties

Electrical Conductivity

In Fig. 5a, the electrical conductivity of different samples is shown as a function of x for different temperatures. The temperature dependence of the electrical conductivities, σ , of selected compositions is shown in supplementary Fig. S2. It can be seen that the electrical conductivity of the samples with x < 0.50 increases with increasing temperature, which is a typical behavior of semiconductors, while σ decreases with increasing T for higher x; i.e., these samples show a semimetallic behavior.

As mentioned above and shown in Fig. 1, the electronic structure of the $\text{Bi}_{1-x}\text{Sb}_x$ system strongly depends on x. Single crystals of $\text{Bi}_{1-x}\text{Sb}_x$ are semiconducting in the range 0.07 < x < 0.22 and semimetallic for all other compositions.^{12,13} As pure bulk bismuth is a semimetal, its electrical conductivity is expected to decrease with increasing temperature. However, for nanostructures of Bi, such as nanowires²³ or thin films,^{38,39} a semimetal–semiconductor transition (SMSC) was shown to occur below a certain wire diameter (~ 50 nm) or film thickness (~ 28 nm), respectively. Also, in the case of $\text{Bi}_{1-x}\text{Sb}_x$ nanowires, it was predicted that the semiconducting region is broadened due to quantum confinement and depends on the wire diameter, e.g., for a diameter of 65 nm, the semiconducting region



Fig. 3. (a) XRD patterns of ball-milled $Bi_{1-x}Sb_x$ samples with varying *x*. Data taken from Ref. 31. (b) Lattice parameters *a* (left axis) and *c* (right axis) of different samples from the XRD patterns compared with the lattice parameters of single crystals. Data taken from Ref. 37.



Fig. 4. (a) Low- and (b) high-resolution TEM images of Bi_{0.85}Sb_{0.15} particles after annealing and before pressing of the pellet, and (c) the corresponding electron diffraction pattern. (Reproduced with permission,³¹ Copyright 2013, Springer).



Fig. 5. (a) Electrical conductivity of $Bi_{1-x}Sb_x$ ($0 \le x \le 0.6$) alloys as function of x at three different temperatures. (b) Carrier concentration and Hall mobilities at 280 K as a function of x.

range is 0.03 < x < 0.27.²³ Thin films of $\text{Bi}_{1-x}\text{Sb}_x$ alloys with x = 0.035 and x = 0.051 were also found to be semiconducting.^{25,38,39} The semiconducting behavior for $x \le 0.5$ in our alloys can therefore be attributed to the nanostructuring of the material, resulting in a shift of the semiconductor-semimetal (SCSM) transition to much higher antimony content than reported previously. The shift of the SCSM transition to higher Sb content is also confirmed by the change in carrier concentration as shown in Fig. 5b, which was determined by Hall measurements. For an Sb content higher than x = 0.4, the carrier concentration significantly increases due to a vanishing band gap caused by the overlap of the Hand the L bands. According to TEM and Scherrer analysis, the particle size of the $Bi_{1-x}Sb_x$ particles studied here is between 40 nm and 100 nm. Obviously, this particle size is sufficiently small to induce the SMSC in the case of mechanically alloyed nanoparticles. Further details can be found in Ref. 34.

The nanostructured alloys with the lowest conductivity are obtained in a composition range of 0.12 < x < 0.17. The lowest conductivity and carrier concentration correlates with the largest band gap of the alloy system, which was determined in a previous work.³⁴ In this respect, our data are also in a good agreement with earlier reports on single crystals, which showed a maximum band gap between $x = 0.12^{15}$ and x = 0.15.¹² For other nanostructures, various values have been reported. A maximum band gap was found for x = 0.09 in thin films²⁵ and for x = 0.15 in nanowires.²¹

Interestingly, the nanostructured alloys show a second minimum in the conductivity, which is not observed for bulk $\operatorname{Bi}_{1-x}\operatorname{Sb}_x$.⁴⁰ This second minimum again arises due to the energetic shift of the different bands with increasing Sb content. As mentioned above, at x > 0.4 the *H* band starts to overlap with the *L* band. Thus, the transport is also determined by the hole carriers in the *H* band. As holes have a significantly higher mass than electrons, the mobility drops by more than one order of magnitude, as shown in Fig. 5b, resulting in a reduced conductivity. It is worth noting that all the

electronic transport properties of the Bi-Sb system⁴¹ have to be described in the framework of a two-band model, accounting for the presence of the two types of carriers of different carrier density and different mobility. However, further analysis going beyond the scope of this paper is required to quantitatively describe the observed complex behavior of the transport properties.

The electrical conductivity of our ${\rm Bi}_{0.85}{\rm Sb}_{0.15}$ sample is in the range of $0.6-1.6 \times 10^5 \,\Omega^{-1} \,{\rm m}^{-1}$. For other mechanically alloyed ${\rm Bi}_{0.85}{\rm Sb}_{0.15}$ samples, values between $1.4 \,\Omega^{-1} \,{\rm m}^{-1}$ and $4.5 \times 10^5 \,\Omega^{-1} \,{\rm m}^{-1}$ have been reported for uniaxial pressed¹⁸ and extruded microcrystals,⁴² both in the temperature range between 100 K and 300 K. However, an improvement of the pressing conditions may lead to a further increase of the electrical conductivity of our samples.

Seebeck Coefficient

The sign of the Seebeck coefficients of coldpressed alloys with x < 0.67 is negative (*n*-type), while for $x \ge 0.67$, the Seebeck coefficient has a positive sign (p-type). This behavior was also found for single crystalline Bi-Sb alloys.¹⁴ Figure 6 shows the Seebeck coefficient values of different samples versus x. The temperature dependence of the Seebeck coefficient of selected compositions is shown in supplementary Fig. S3. The highest absolute values at all temperatures were obtained for x = 0.16, which corresponds to the maximum band gap of the alloy system. This result is in quite good agreement with the results of the electrical conductivity, where the minimum electrical conductivity was obtained for 0.12 < x < 0.17. The samples with positive Seebeck coefficients exhibit similar values. while the samples with negative Seebeck coefficients show a strong dependence on x. The differences in the temperature dependence of the Seebeck coefficient shown in supplementary Fig. S3 affirm the conclusions drawn from the electrical conductivity with respect to the SCSM transition. While the Seebeck coefficient for alloys with $x \ge 0.67$ show a monotonic temperature dependence typical for semimetals, the alloys with smaller x show a maximal Seebeck coefficient in the temperature dependence. indicating their semiconducting nature.²⁵

Thermal Conductivity

The composition dependence of the thermal conductivity κ at room temperature is shown in Fig. 7. As described in the "Experimental" section, the data below room temperature were determined with the steady-state method and at room temperature with the laser flash method. The steady-state data were corrected for radiation. Specific heat was measured from 2 K to 300 K on a cold-pressed Bi_{0.67}Sb_{0.33} sample and a hot-pressed Bi_{0.85}Sb_{0.15} sample (see supplementary Fig. S4). Within experimental



Fig. 6. Seebeck coefficients of $\text{Bi}_{1-x}\text{Sb}_x$ ($0 \le x \le 1$) alloys versus x. Inset zoom of the Sb region, where the highest Seebeck coefficient is observed.



Fig. 7. Thermal conductivity of $Bi_{1-x}Sb_x$ ($0 \le x \le 1$) alloys as a function of *x* at room temperature.

resolution, both curves coincide. Thus, to calculate the thermal conductivity from the thermal diffusivity, we also used this specific heat for other samples.

The results of the thermal conductivity for the nanostructured $\text{Bi}_{1-x}\text{Sb}_x$ matrix material show a clear trend with composition. For low Sb content, κ decreases nearly linearly to approximately 2.5 W m⁻¹ K⁻¹ for the Bi_{0.80}Sb_{0.20} pellet and remains nearly constant for higher Sb content. Thus, the nanostructured pellets show a reduced thermal conductivity not only compared to single crystals, which exhibit values of κ between 6 W m⁻¹ K⁻¹ and 9 W m⁻¹ K⁻¹ for 0.04 < x < 0.12,⁴³ but also compared to polycrystalline alloys with grain sizes ranging between 300 μ m and 500 μ m, which show thermal conductivity values ranging between 300 μ m between 300 K.⁴⁴ Due to the clear dependence of κ on the composition, the random variation of the density of the pellets seem to play a minor role and the reduction of κ is mainly caused by the nanostructuring indicating

that the grain boundaries between the nanoparticles act as efficient phonon scattering centers.

Although the lowest values of κ at room temperature ($\kappa_{\min} = 2.0 \text{ W m}^{-1} \text{ K}^{-1}$ for x = 0.17) were obtained within a very broad composition range (0.13 < x < 0.67), the Seebeck coefficient and the electrical conductivity have their optima in the range 0.10 < x < 0.30. Alloys with a higher xexhibit electrical conductivities and Seebeck coefficients (Figs. 5 and 6) too low to provide high *ZT* values.

Figure of Merit

The *ZT* values as a function of *x* at 280 K are shown in Fig. 8. The highest value of 0.25 was obtained for $Bi_{0.88}Sb_{0.13}$, which is in good agreement with the optimal composition for single crystals.^{14,16} The highest *ZT* value for x = 0.13 compared to the



Fig. 8. The ZT of $Bi_{1-x}Sb_x$ ($0 \le x \le 1$) alloys at 280 K as function of x.

other compositions is due to the high Seebeck coefficient.

The temperature dependence of ZT is shown in Fig. 9. Compared to microcrystalline samples, the temperature where the highest ZT value is observed is slightly shifted to higher temperatures and heavily shifted compared to single crystals. For $Bi_{0.5}Sb_{0.5}$, a maximum ZT value can be found in the temperature range between 240 K and 260 K. This behavior was also found for extruded microcrystalline samples.⁴² $Bi_{0.85}Sb_{0.15}$ and $Bi_{0.67}Sb_{0.33}$, on the other hand, seem to reach a plateau of their ZTvalues at about 280 K. These results reveal that, due to the reduction of particle size, a shift of the $ZT_{\rm max}$ values to higher temperatures occurs. This shift of ZT_{max} can be attributed to the changes of the band gap caused by nanostructuring. The ZT value of a material depends on its electrical conductivity as well as its Seebeck coefficient, which both depend on the carrier concentration. Thus, a maximum ZToccurs for a certain optimal carrier concentration. Due to nanostructuring, the band gap increases and higher temperatures are needed to excite the optimal amount of carriers, resulting in the observed shift of ZT_{max} .

CONCLUSIONS

 $\operatorname{Bi}_{1-x}\operatorname{Sb}_x$ nanoparticles with sizes between 30 nm and 110 nm were synthesized by mechanical alloying. Pure Bi particles were found to be semiconducting, which indicates that a semimetal to semiconductor transition occurs when reducing the particle size. Bi-Sb nanoalloys were found to be semiconducting for all x < 0.50, while single crystals are semiconducting in the range of $0.07 \le x \le 0.22$ only. The maximum absolute value of the Seebeck coefficient was obtained for a nanostructured Bi_{0.84}Sb_{0.16} sample. The room-temperature thermal



Fig. 9. Temperature dependence of the ZT of $Bi_{1-x}Sb_x$ (0.15 $\le x \le 0.5$). Data for microcrystalline uniaxially pressed (data taken from Ref. 18) and extruded (data taken from Ref. 42) $Bi_{0.85}Sb_{0.15}$ samples are added for comparison.

conductivity is reduced compared to polycrystalline samples over a broad composition range of composition (0.14 < x < 0.67) with values between 2.0 W m⁻¹ K⁻¹ and 2.5 W m⁻¹ K⁻¹. At lower temperatures, the alloys even exhibit thermal conductivities as low as $1.25 \text{ W m}^{-1} \text{ K}^{-1}$. A significant decrease of the total thermal conductivity compared to single crystals and microcrystalline samples is therefore obtained due to the nanostructuring. The highest ZT value (0.25) was obtained at 280 K for x = 0.13. This is consistent with the optimum composition for $Bi_{1-x}Sb_x$ alloys in earlier reports on single crystals. Compared to microcrystalline alloys with ZT values between 0.15 and 0.3, the ZT values reported here are slightly smaller, which is mainly caused by a lower electrical conductivity. However, the thermal conductivity was successfully reduced compared to the reported samples while the Seebeck coefficients are comparable. Thus, an enhancement of the electrical conductivity by optimizing the pressing conditions, i.e., by increasing the density of the pellets prepared, should lead to an improvement of the ZT values compared to microcrystalline materials. The optimum temperature range of $Bi_{1-x}Sb_x$ alloys for thermoelectric applications can also be shifted to higher temperatures by the reduction in particle size.

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AUTHOR CONTRIBUTIONS

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ELECTRONIC SUPPLEMENTARY MATERIAL

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