

# Melt spinning preparation of Bismuth Telluride and partially alloying with IV-VI compounds for thermoelectric application

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## Abstract

Intrinsic p- and n-doped Bismuth Telluride samples are compared with respect to the evolution of their thermoelectric material parameters like thermal and electrical conductivity. The Seebeck coefficient is discussed in dependence on the melt spinning fabrication technique. The melt spinner used is only able to produce small thin ribbon shaped specimens, some as thin as 10 micron. This limits melt spinning to mainly production of research specimens for alloys with high critical cooling rate, which are difficult to fabricate with other techniques. Therefore this method was combined with spark plasma sintering (SPS) to produce wafer sized samples from the melt spinning flakes. Additional parameters are alloying or doping of the base material by comparing the properties as prepared to different annealing conditions. The intrinsic p- and n-doped material was alloyed with up to 0.5% lead telluride by rapidly cooling the bulk material to improve the thermoelectric properties analysed from RT up to about 600 K. A Seebeck coefficient of well above 200  $\mu\text{V}/\text{K}$  could be obtained for p- and n-type materials. For annealed melt spin prepared material with the composition  $[(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3]_{0.97}\text{PbTe}_{0.03}$  a compaction and the formation of a nanocomposite structure was obtained resulting a high powerfactor of about  $34\mu\text{W}/\text{K}^2\text{cm}$ .

## Introduction

The preparation of thermoelectric compounds of doped bismuth telluride and its alloys has recently gained increasing interest due to their structural features showing increased values for the thermoelectric figure of merit (ZT) [1, 2].

One promising approach to improve the thermoelectric properties is to manufacture nanocomposite materials exhibiting lower thermal conductivities and higher ZT values. The use of nanostructured materials has led to recent breakthroughs in the thermoelectric field [1–3].

Beside the possibility to grow nanoscaled materials by epitaxial methods, it is attractive to produce much cheaper bulk materials with a nanoscaled structure exhibiting similar profits for thermoelectric applications. Mainly two basic methods are described. One is based on mechanical alloying and subsequent sintering of those mixtures [4], the other one is based on rapid cooling of melted materials exhibiting miscibility gaps in the phase diagram, which will form

nanoscaled precipitations in a bulk sample under these conditions. [5-9]

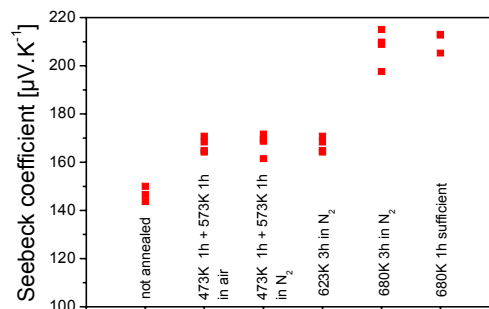
Melt spinning, developed for rapid cooling of liquids like metal melts, is used to develop materials that require extremely high cooling rates in order to form, such as metallic glasses or nanocomposites. The cooling rates achievable by melt-spinning are on the order of  $10^1$ - $10^7$  Kelvin/s.

The multi component system of  $\text{PbTe}/\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3/\text{Bi}_2\text{Se}_3$  is of special interest being composed of good thermoelectric materials on the one hand but with a restricted miscibility in the phase diagram e.g.  $\text{PbTe}/\text{Bi}_2\text{Te}_3$ . The miscibility in phase diagrams may even differ severely for different authors, also indicating a high uncertainty of the crystalline fine structure on the nanoscale. [10-14]. Nanocomposites of „ $\text{V}_2\text{VI}_3$ “ with  $\text{PbTe}$  bulk quenched material will be compared to the corresponding melt spin material.

## Melt spin n/p-“ $\text{Bi}_2\text{Te}_3$ “

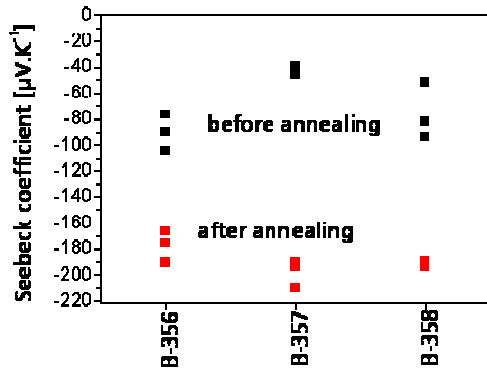
For the melt spinning process parameters like the rotation speed, extrusion pressure, casting temperature, distance nozzle to cooling wheel as well as the pressure and kind of gas in the recipient were varied.

The obtained samples of the melt spin process were flakes with a size of about 2 mm by 2 mm and a thickness of 30 to 100  $\mu\text{m}$ . The flakes are highly oriented with the c-axis showing in the direction perpendicular to the surface, determined by oriented XRD-experiments. The specimens are very fragile. There was no difference in the composition



**Figure 1:** Improvement of Seebeck coefficient of p-type  $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$  prepared by the melt spinning method due to different annealing conditions.

of the samples measured with EDX between before or after Growth.

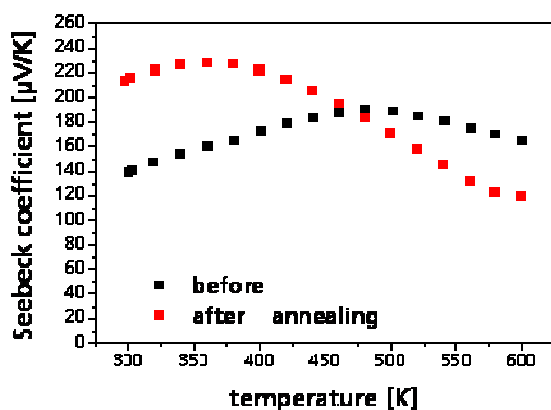


**Figure 2:** Seebeck coefficients of n-type Bi<sub>2</sub>(Se<sub>0.1</sub>Te<sub>0.9</sub>)<sub>3</sub> prepared by the melt spinning method due to different preparation conditions of the sample. Annealing conditions were 1h at 680 K.

Measuring the thermoelectric properties of those samples results in a Seebeck coefficient for p-type material of about 140 µV/K. It is remarkable that no influence was observed from the variation of all the melt spinning process parameter mentioned above and that the variation of this value remained within the experimental error of less than 10 %. For n-type material the Seebeck coefficient became as low as -40 µV/K (fig. 2) and again there was also no evident influence of the process parameters to be seen.

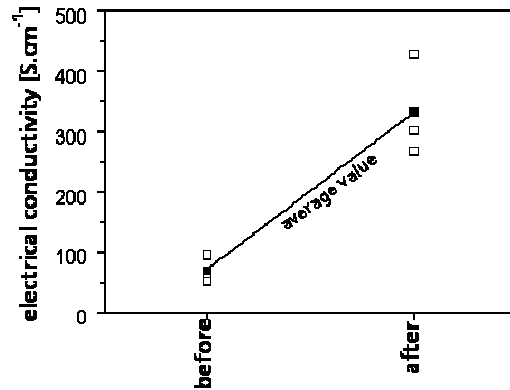
A substantial improvement could be obtained for the thermoelectric properties by annealing of the samples. The annealing conditions were varied according to figure 1 in a temperature range from 473 K to 680 K and the annealing time between 1 and 3 hours.

Best conditions were found to be an annealing time of 1



**Figure 3:** Influence of the annealing procedure on the temperature dependence of the Seebeck coefficient for p-type (Bi<sub>0.2</sub>Sb<sub>0.8</sub>)<sub>2</sub>Te<sub>3</sub> prepared by the melt spinning method. Annealing 1h at 680 K improves the thermal power only up to 450 K. For higher temperatures the thermoelectric properties of the not annealed sample give better results.

hour at 680 K under Nitrogen atmosphere. No influence was found of oxygen on the annealing process. The conditions hold as well for p-type material as they do for n-type material.



**Figure 4:** Improvement of the electrical conductivity of n-type Bi<sub>2</sub>(Se<sub>0.1</sub>Te<sub>0.9</sub>)<sub>3</sub> prepared by the melt spinning method due to annealing 1h at 680 K.

For both materials we end up with Seebeck coefficients giving an absolute value as high as 210 µV/K (figure 2: for n-type material). It is remarkable that the initial value of the Seebeck coefficient for n-type material is only about half of that for p-type and that the n-type material shows a higher standard deviation for the as-grown material as well as for the annealed one which implies, that the n-material is less reproducible and might show a higher degree of disorder.

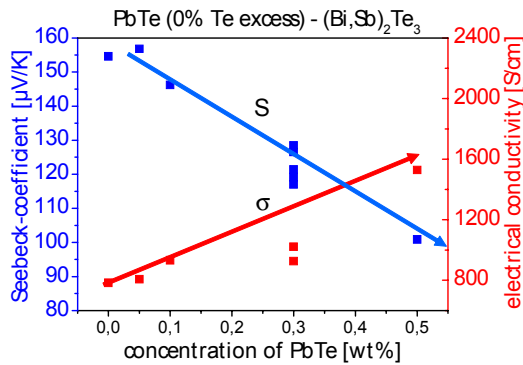
The temperature dependence of the Seebeck-coefficient (figure 3) shows improvement only for temperatures close to room temperature. Above 450 K the as grown material exhibits better values of the Seebeck-coefficient. This might be due to the different micro- or nanostructure of the as grown material which influences the mobility and concentration of the charge carriers as well as the heat conductivity. But the conditions are evidently not stable for the as grown material, since during measuring its temperature dependence an annealing effect is observed leading to irreproducible results. Figure 3 shows only the data of the first measurement for the not annealed sample. A second scan exhibits lower values for high temperatures and higher thermopower at room temperature.

Regarding the electrical conductivity of the melt spin samples we observe a similar behavior. While the p-material shows only a minor change of the electrical conductivity of initially 400 S/cm connected with a reduced standard deviation after annealing (+/-100 reduced to +/-10), we observe for the n-type material an increase of the electrical conductivity of more than 300% (figure 4). The drawn line indicates the increase of conductivity as a guide for the eye.

#### **Alloying of (Bi, Sb)<sub>2</sub>Te<sub>3</sub> with PbTe**

To further improve the thermoelectric properties of the material we started to alloy the Bi<sub>2</sub>Te<sub>3</sub> compounds with PbTe as a promising possibility to form nanocomposites. The concentration of PbTe was varied between 0.05 at% and

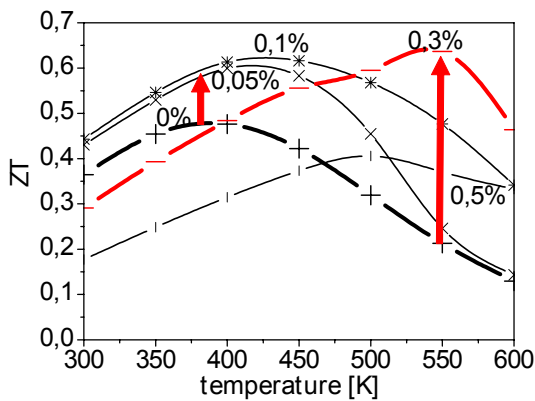
0.5 at%, which is still in a range where some authors predict miscibility of these compounds [10].



**Figure 5:** Influence of the amount of PbTe alloying on the thermoelectric properties of in water quenched p-type  $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$ . Lines are guides to the eye.

The samples were prepared by melting the starting materials with appropriate initial weight in a quartz ampoule together; the ampoules were quenched in cold water. The microscopic inspection of the samples showed no evidence of any precipitation or inclusions down to the sub-micron range. Also annealing of the samples did not produce any precipitation in that range. TEM inspection of the material is still in preparation and will be published later on.

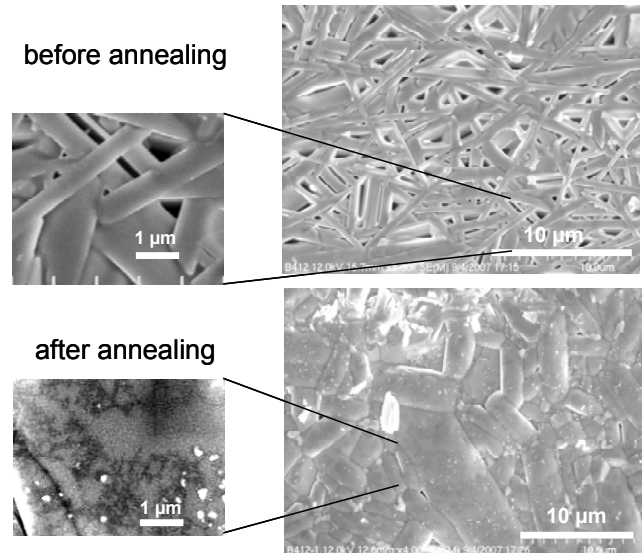
The thermoelectric properties are shown in figure 5. By increasing the amount of PbTe the Seebeck coefficient is reduced from about 160 to 100  $\mu\text{V}/\text{K}$  while the electrical conductivity is increased from about 800 to 1600  $\text{S}/\text{cm}$ , which might be explained by a doping effect due to the



**Figure 6** Figure of merit ZT for p-type  $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$  with different concentrations of PbTe depending on measuring temperature. A clear improvement of ZT is observed for low concentrations of PbTe close to RT and for higher concentrations at elevated temperature up to 600 K, indicated by red arrows.

PbTe. The thermoelectric properties were analysed parallel to the surface at room temperature (RT) for p-type samples with PbTe up to 0.5%. The thermal conductivity of these samples shows a minimum for a concentration of 0.1% PbTe at temperatures from RT to 600 K. This leads to an improvement of the figure of merit ZT at RT of about 20%

( $ZT = 0.45$ ) compared to the samples without PbTe (fig. 6). While that improvement at RT is most likely due to the improved electrical and reduced thermal conductivity, the increase by a factor of 3 at 550 K for alloys with 0.3% PbTe might be due to a combination of increased Seebeck coefficient and a substantially reduced thermal conductivity. That leads to the highest ZT value of 0.64. Further increase of the ZT seems to be possible due to annealing of the materials.

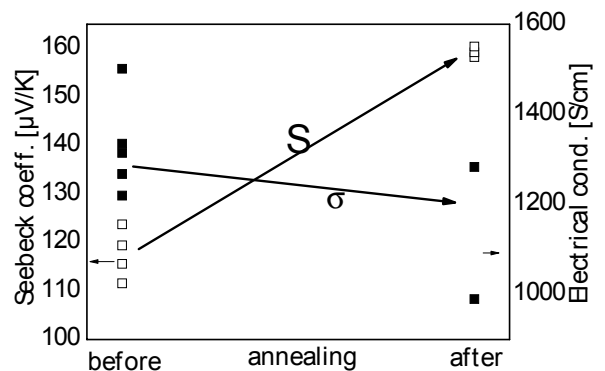


**Figure 7** Scanning electron micrographs indicating the improvement of the melt spin prepared p-type material  $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$  with 0.3 at% of PbTe by annealing 1h at  $680^\circ\text{C}$  under nitrogen.

For comparison, samples with a concentration of PbTe of about 0.3 at% were analyzed, which were prepared by the melt spinning process.

Figure 7 exhibits a SEM picture of the surface of such a sample before and after annealing. The as-grown material exhibits a network-like structure of needles with a diameter of about 1  $\mu\text{m}$ . After annealing this structure has become more compact and the magnification in the inset shows clearly structures of precipitations in the nm-range.

That change of the structure is also reflected in the thermoelectric properties of the material, shown in figure



**Figure 8** Improvement of the electrical conductivity for p-type  $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$  prepared by the melt spinning method due to annealing 1h at 680 K.

8. The electrical conductivity remains more or less the same after annealing (1000 – 1300 S/cm) and is slightly higher compared to the in water quenched material (about 1000 S/cm). More interesting is the substantial improvement of the Seebeck coefficient from about 120  $\mu\text{V/K}$  (the quenched and the meltspin material are the same) to about 160  $\mu\text{V/K}$  by annealing the melt spin material. By this a power factor of  $\sim 34 \mu\text{W/K}^2\text{cm}$  was obtained by annealing. It seems, that the nanocomposite structure improves the thermopower and eventually the thermal behaviour offering the chance of  $ZT > 1$ , which is still under investigation. These results will be published elsewhere.

### Conclusions

It could be demonstrated that melt spin fabrication can exhibit relatively high Seebeck coefficients of more than 200  $\mu\text{V/K}$  at RT after annealing. Although the process parameters of the melt spinning process do not remarkably influence the properties of the material, both p- and n- $\text{Bi}_2\text{Te}_3$  are improved after annealing substantially to exhibit higher Seebeck coefficients and better electrical conductivity. In general, n-type material seems to remain more unstable even after annealing.

For temperatures above RT the results are still not convincing and further experiments are necessary to obtain better effects. Alloying with PbTe is another promising possibility to produce nanocomposites due to the incomplete miscibility of the materials.

For  $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$  alloyed with up to 0.5% PbTe and quenched after melting in water the properties could already be improved for temperatures higher than RT. The thermal conductivity is significantly reduced and Pb-rich precipitations at grain boundaries of layered material could be observed. An improvement for ZT of nearly 30% was obtained at RT and for temperatures of about 550 K a factor of 3 was obtained for the improvement giving values for ZT of about 0.64. Further enhancement seems to be possible due to annealing of the material. While the properties of in water quenched material and for melt spin material are more or less the same, a substantial improvement of the thermoelectric properties was observed due to annealing of melt spin material, resulting a power factor as high as  $\sim 34 \mu\text{W/K}^2\text{cm}$ . The nanocomposite structure was shown by SEM for the best material with a composition of  $[(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3]_{0.97}\text{PbTe}_{0.03}$  after annealing, accompanied with a substantial compaction of the material. This material offers the chance for  $ZT \gg 1$ .

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### References

1. R. Venkatasubramanian *et al.*, “Thin-film thermoelectric devices with high room-temperature figures of merit”, *Nature* Vol. 413 (2001), 597

2. T.C. Harman *et al.*, “Quantum Dot Superlattice Thermoelectric Materials and Devices”, *Science* Vol. 297 (2002), 2229
3. K.F. Hsu *et al.*, “Cubic  $\text{AgPb}_m\text{SbTe}_{2+m}$ : Bulk Thermoelectric Materials with High Figure of Merit”, *Science* Vol. 303 (2004), 818.
4. Jing Liu *et al.*, “ $\text{Bi}_2\text{Te}_3$  and  $\text{Bi}_2\text{Te}_3/\text{nano-SiC}$  Prepared by Mechanical Alloying and Spark Plasma Sintering”, *Key Engineering Materials* Vols. 280-283 (2005), 397.
5. H. Y. Chen *et al.*, “Microstructures and thermoelectric properties of  $\text{Fe}_{0.92}\text{Mn}_{0.08}\text{Six}$  alloys prepared by rapid solidification and hot pressing”, *Journal of Applied Physics* Vol. 94 (2003), 6621.
6. E. Koukharenko *et al.*, “Electrical properties of  $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$  materials obtained by ultrarapid quenching”, *Journal of Alloys and Compound* Vol. 327 (2001), pp. 1-4.
7. V.M. Glazov *et al.*, “Thermoelectric properties of semiconducting solid solution,  $\text{Bi}_2\text{Te}_{2.4}\text{Se}_{0.6}\text{Bi}_{0.52}\text{Sb}_{1.48}\text{Te}_3$  prepared by ultrafast cooling of melts”, *Izv. Akad. Nauk, SSSR, Neorg. Mater.* Vol. 22, No. 1 (1986), pp 36-40.
8. E. Kukharenka *et al.*, “Electrical and microstructural properties of  $\text{Bi}_{2-x}\text{Sb}_x\text{Te}$  and  $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_2$  foils obtained by ultrarapid quenching process”, *Journal of Materials Science: Materials in Electronics* Vol. 14 (2003), pp. 383-388.
9. X. Tang *et al.*, “Preparation and thermoelectric transport properties of high-performance p-type  $\text{Bi}_2\text{Te}_3$  with layered nanostructure”, *Applied Physics Letters* Vol. 90 (2007), 012102.
10. T. Hirai *et al.*, “The pseudo-binary  $\text{V}_2\text{VI}_3\text{-IV VI}$  compounds systems,  $\text{Bi}_2\text{Te}_3\text{-PbTe}$ ,  $\text{Bi}_2\text{Te}_3\text{-SnTe}$ ,  $\text{Sb}_2\text{Te}_3\text{-PbTe}$ ,  $\text{Sb}_2\text{Te}_3\text{-SnTe}$  and  $\text{Bi}_2\text{Se}_3\text{-SnSe}$ ”, *Journal of Less-Common Metals* Vol. 13 (1967), pp. 352-356,
11. E.I. Elagina *et al.*, “An investigation of the  $\text{PbTe-Bi}_2\text{Te}_3$  and the  $\text{SnTe-Sb}_2\text{Te}_3$  systems”, *Russian Journal of Inorganic Chemistry* Vol. 4, No. 7 (1959), pp. 738-740.
12. D. Kusano *et al.*, “Effects of PbTe Doping on the Thermoelectric Properties of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$ ”, 21<sup>st</sup> *International Conference on Thermoelectrics* (2002), pp. 13-16.
13. P-W. Zhu *et al.*, “High thermoelectric properties of PbTe Doped with  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$ ”, *Chinese Physics Letter* Vol. 28, No. 8 (2005), pp. 2103-2104
14. P. Zhu *et al.*, “Composition-Dependent Thermoelectric Properties of  $(\text{PbTe})_{100-x}(\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3)_x$  ( $0.1 \leq x \leq 5$ )”, *Materials Transactions* Vol. 46, No. 4 (2005), pp. 761-764.