

Influence of Group IV-Te Alloying on Nanocomposite Structure and Thermoelectric Properties of Bi_2Te_3 Compounds

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Thermoelectric compounds based on doped bismuth telluride and its alloys have recently attracted increasing interest. Due to their structural features they show increased values of the thermoelectric figure of merit (ZT). A promising approach to improve the thermoelectric properties is to manufacture nanocomposite materials exhibiting lower thermal conductivities and higher ZT . The ZT value of compounds can be shifted reasonably to higher values (>1) by alloying with IV-Te materials and adequate preparation methods to form stable nanocomposites. The influence of PbTe and Sn on the thermoelectric properties is studied as a function of concentration and preparation methods. Melt spinning and spark plasma sintering were applied to form nanocomposite materials that were mechanically and thermodynamically stable for applications in thermoelectric devices. The structural properties are discussed based on analysis by transmission electron microscopy and x-ray diffraction.

Key words: Melt spin, spin casting, spark plasma sintering, nanocomposite, Bi_2Te_3 -compounds, PbTe, SnTe

INTRODUCTION

For several years, efforts have been undertaken to obtain large figures of merit with nanostructured bulk materials,¹ especially with regard to the high values found in superlattices.^{2,3} This is motivated by the possibility of obtaining useful electrical power from waste heat based on thermoelectric technology. Efficient and cost-effective thermoelectric materials are required in the temperature range from 300 K to 800 K to apply this technology to industrial applications.

It is well known that it is possible to produce a large quantity of bulk microcomposites when two thermoelectric materials with different crystal

structures are mixed, melted, and then quenched in water. The materials system Bi_2Te_3 -PbTe was studied in the 1950s and 1960s, but no efficient thermoelectric materials were found at that time.⁴⁻⁷ Considering the large number of different phase diagrams available for this particular materials system, it can be concluded that the link between cooling rate and microstructure has not been studied sufficiently to date. Recently, Kusano et al. reported a very good figure of merit ($ZT > 1$) for the material with the chemical composition $(\text{Bi,Sb})_2\text{Te}_3$ with 0 wt.% to 0.5 wt.% PbTe.⁸ The material was produced by mechanical alloying. At a temperature higher than 420 K, the thermal conductivity was undoubtedly lower than that of pure $(\text{Bi,Sb})_2\text{Te}_3$. The link between the transport properties and the microstructure was not investigated in that publication.

(Received August 18, 2008; accepted April 22, 2009;
published online May 7, 2009)

A further material system consisting of a solid solution based on Bi₂Te₃ with the addition of Sn is also promising because of the so-called Fermi-pinning effect. The literature on the Fermi-pinning effect is not abundant, but it is claimed that there is a Fermi-level pinning effect in (Bi,Sb)₂Te₃ doped with Sn or in PbTe doped with In^{9,10} due to the formation of an impurity band in the band gap at high doping levels. At a pronounced position of the impurity band, the edge of the valence (or conduction) band and the position of the chemical potential (approximately the Fermi level at 0 K) are fixed, and carriers with a comparatively low energy ($\varepsilon - \mu < 0$) are strongly scattered while more energetic ones ($\varepsilon - \mu > 0$) show higher mobility. These types of materials are particularly useful for thermoelectric applications due to their relatively high Seebeck coefficients with reduced temperature dependence.

In this study, the transport properties of (Bi,Sb)₂Te₃-PbTe and Bi₂(Te,Se)₃-Sn have been investigated up to 2 mol.% PbTe and 1% Sn, respectively. Several methods of synthesis have been used to see the influence of cooling rate on the microstructure and transport properties. The morphology of the sample was examined with transmission electron microscopy and x-ray diffraction. Considerably larger *ZT* values are presented here compared with currently reported values for microcomposites.^{11,12} Most of the material consists of nanostructured materials with a feature size not larger than 10 nm.

EXPERIMENT

Materials Synthesis and Measurement of Transport Properties

Quartz ampoules previously cleaned with HF were filled with commercial (Bi,Sb)₂Te₃ and elemental Pb and Te. The ampoules were evacuated, sealed, and put in a rocking furnace at a predetermined temperature for 24 h. The materials were subsequently quenched into water. The prepared materials were either directly compacted by spark plasma sintering (SPS)¹³ or melted again and quenched on a rotating copper wheel (melt spinning). Relatively small flakes were obtained and sintered subsequently. The material was then cut and measured with a highly accurate homemade measurement system for the power factor (IPM-SR1).¹⁴ The thermal conductivity was measured with the laser flash method (LFA457) from Netzsch. The heat capacity was measured by the differential scanning calorimetric method (DSC204F1) from Netzsch. Bi₂(Te,Se)₃-Sn was prepared by quenching these materials, measuring them before and after an additional annealing step. The remaining materials were melt-spun, and the Seebeck coefficient was measured in the same manner to study the influence of annealing.

Transmission Electron Microscopy

Melt-spun (Bi,Sb)₂Te₃-0.3 wt.%PbTe was examined by transmission electron microscopy before and after annealing. The samples were glued (glue Gatan G1) on a 3-mm Cu ring. The samples were thin enough to start directly with the ion-milling procedure (Baltec RES 101, two Ar⁺ guns, voltage varied between 3 kV and 5 kV, current between 1.5 mA and 5.5 mA). Transmission electron microscopy was performed with a Philips CM30 microscope.

RESULTS

Transmission Electron Microscopy

A transmission electron micrograph of melt-spun (Bi,Sb)₂Te₃-0.3 wt.%PbTe is shown in Fig. 1a before annealing. The grain size is clearly in the submicrometer range. Some kind of modulations (fringes) can be seen in particular grains. This type of modulation has already been reported elsewhere.¹⁵⁻¹⁷ This type of modulation does not provide evidence of nanostructure of the materials. The reason for the appearance of the modulation in only some grains is due to the different orientation of these specific grains, which is close to [100], [010] or [110]. After annealing (407°C, 1 h), clear grain growth is observed, but the size of the grains remains much smaller than that of usual bulk materials (Fig. 1b). The grain size for quenched material is typically in the millimeter range. High-resolution imaging of the annealed sample was carried out. Some kind of modulation in the contrast is visible within some grains. The modulation is random and is due to strain in the material, which could be increased by the addition of PbTe.

In order to study the strain field produced by dislocations, high-resolution images were Fourier-transformed and lattice fringes were generated by the inverse Fourier transformation. With this procedure, it is possible to recognize the source of the strain field. For the two insets (left and right) of Fig. 1c, the dislocation edge is easy to recognize on the lattice fringes (*arrows*). There is a clear link between the location of the dislocation and the contrast. The domain size within the grains is smaller than 10 nm. However, it remains unclear how this strain modulation influences the thermoelectric properties. Strain may locally change the interatomic distances, the effective masses, and the band gap.^{18,19} The phonons may be reflected and scattered because of the local change in the density of the material.

Transport Property Measurements

The figures of merit measured in the materials system (Bi,Sb)₂Te₃-PbTe are shown in Fig. 2a. High figures of merit (above 1) over a broad temperature range have been measured. The best performances are obtained with material quenched in water and

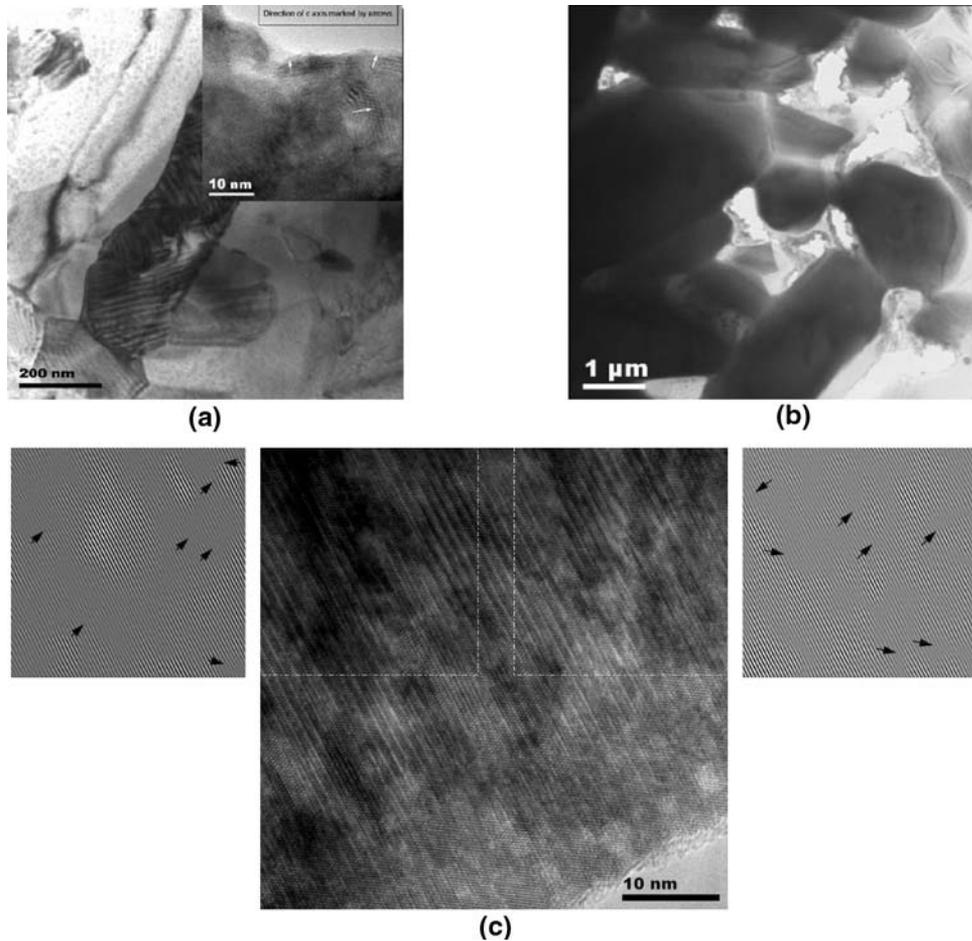


Fig. 1. Transmission electron imaging of melt-spun $(\text{Bi,Sb})_2\text{Te}_3\text{-0.3 mol.\%PbTe}$: (a) before annealing, (b) after annealing, and (c) after annealing, larger magnification. Left and right: strain fields and marked region with stacking fault; center: high-resolution transmission microscopy.

subsequently sintered (curve c). These results confirm the potential of the material system investigated first by Kusano.⁸ Compared with Kusano, our maximum figure of merit is shifted to higher temperatures. The Seebeck coefficient measured by us is lower in the temperature range between 300 K and 450 K, and our measurement system was specially designed for that temperature range. Since the method of fabrication of the material differs, it is difficult to draw a final conclusion. Thermal coupling, thermal guarding, and the gage of the thermocouple are very important in order to obtain accurate temperature measurement at temperatures below 450 K.¹⁴

The performance of melt-spun materials subsequently sintered (curves 1, 2, 4–5) seems to be lower and conforms much more to what is expected for material based on Bi_2Te_3 . However, it should be stressed that the thermal conductivity and the electrical properties reported in this article were not measured in the same direction within the material. The thermal properties were measured in the direction perpendicular to the electrical properties. Since the electrical conductivity, the Seebeck

coefficient, and the thermal conductivity of material based on Bi_2Te_3 are known to be anisotropic and since sintered materials are textured,²⁰ the measuring procedure adopted here could overestimate the figure of merit. It was also found that the anisotropy of the transport properties in sintered material is a strong function of the grain size.²⁰ Since the grain size of melt-spun materials is particularly small, the transport properties of melt-spun and subsequently sintered material may be much more isotropic than that of water-quenched material after sintering.

It is remarkable to note that the figure of merit of the melt-spun sintered $(\text{Bi,Sb})_2\text{Te}_3\text{-0.3 mol.\%PbTe}$ (curve b) is higher than that of the melt-spun sintered $(\text{Bi,Sb})_2\text{Te}_3$ (curve a) even at room temperature. In fact, the electrical conductivity of the melt-spun sintered $(\text{Bi,Sb})_2\text{Te}_3\text{-0.3 mol.\%PbTe}$ is much larger than that of the melt-spun sintered $(\text{Bi,Sb})_2\text{Te}_3$. The thermal conductivity is almost the same for both chemical compositions over the entire temperature range. This may indicate a lower lattice thermal conductivity in $(\text{Bi,Sb})_2\text{Te}_3\text{-0.3 mol.\%PbTe}$, if we are assuming that anisotropy is

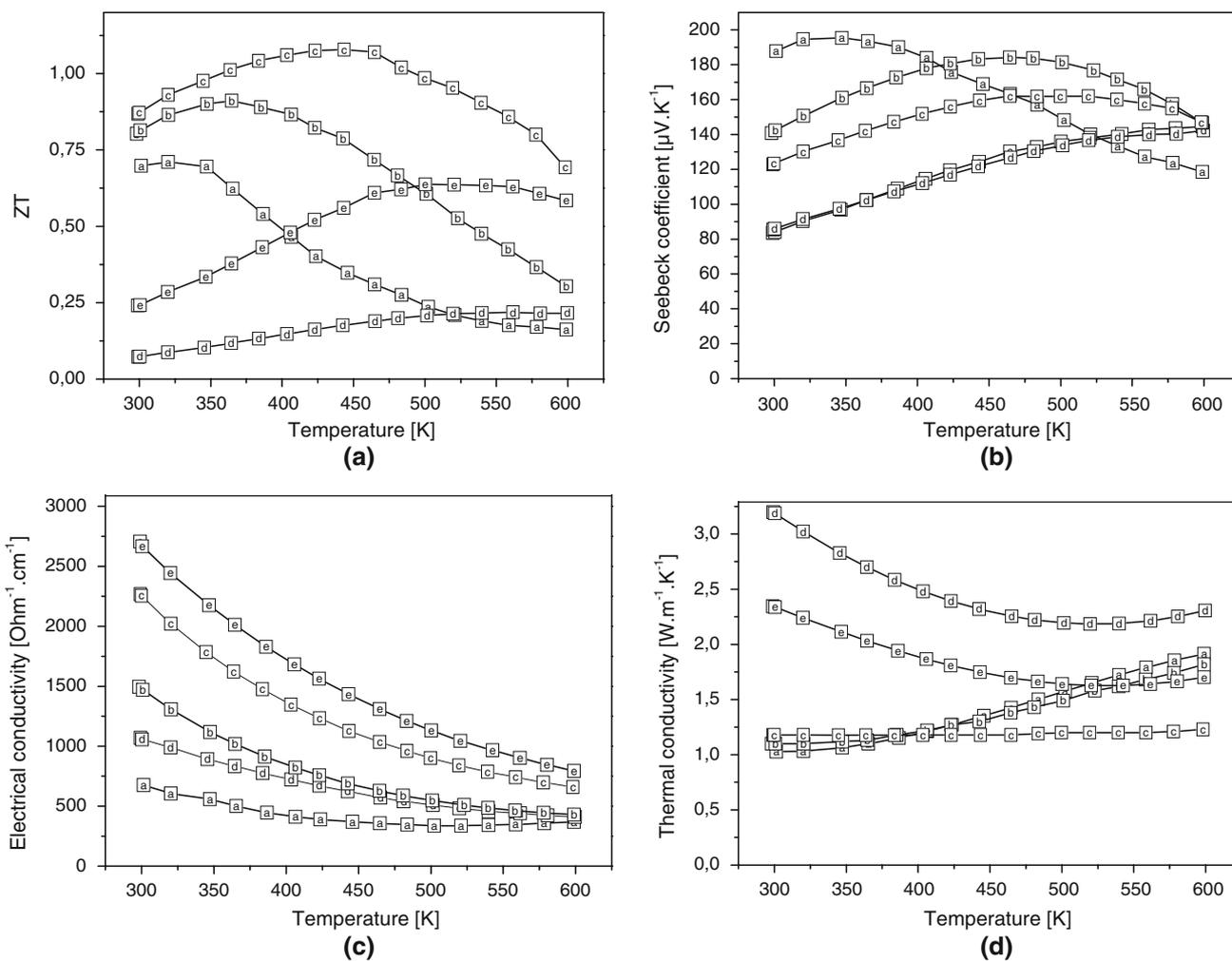


Fig. 2. Transport properties in the materials system $(\text{Bi,Sb})_2\text{Te}_3\text{-PbTe}$: (a) Melt-spun and spark plasma sintered $(\text{Bi,Sb})_2\text{Te}_3$, (b) melt-spun, spark plasma sintered $(\text{Bi,Sb})_2\text{Te}_3\text{-0.3 mol.\%PbTe}$, (c) melt-spun, annealed, and spark plasma sintered $(\text{Bi,Sb})_2\text{Te}_3\text{-0.3 mol.\%PbTe}$, (d) quenched in water and spark plasma sintered $(\text{Bi,Sb})_2\text{Te}_3\text{-2 mol.\%PbTe}$, and (e) quenched in water and spark plasma sintered $(\text{Bi,Sb})_2\text{Te}_3\text{-2 mol.\%PbTe}$ with excess tellurium.

not a function of doping concentration. A pole figure (Fig. 3) obtained on a material quenched in water and subsequently sintered suggests that at least this sample was relatively isotropic.

Two samples with 2 mol.% PbTe were measured (Fig. 2, curves d and e). The first sample contains slightly more Te (Fig. 2, curve e). Both samples are made of melt-spun, subsequently sintered materials. The figure of merit of the sample with an addition of Te is much larger. The reason is the larger electrical conductivity and the lower thermal conductivity of the material with an addition of Te. An explanation for this result is not evident and has to be found. The change in the thermal conductivity with temperature for all materials can be qualitatively well explained by the decrease of the electrical conductivity with temperature and the increase of the bipolar contribution at high temperature.²¹

From the results in Fig. 2a-d it can be deduced that the addition of 0.3 mol.% PbTe increases the ZT value substantially due to improved electrical

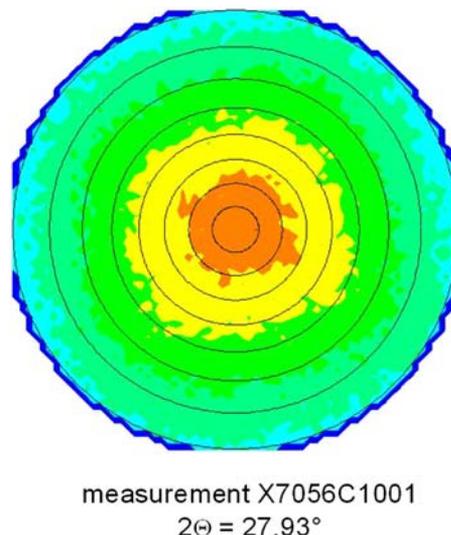


Fig. 3. X-ray pole figure of $\text{Bi}_2(\text{Te,Se})_3$ quenched in water and subsequently sintered ($\text{CuK}_{\alpha 1}/0^\circ < \chi < 80^\circ$).

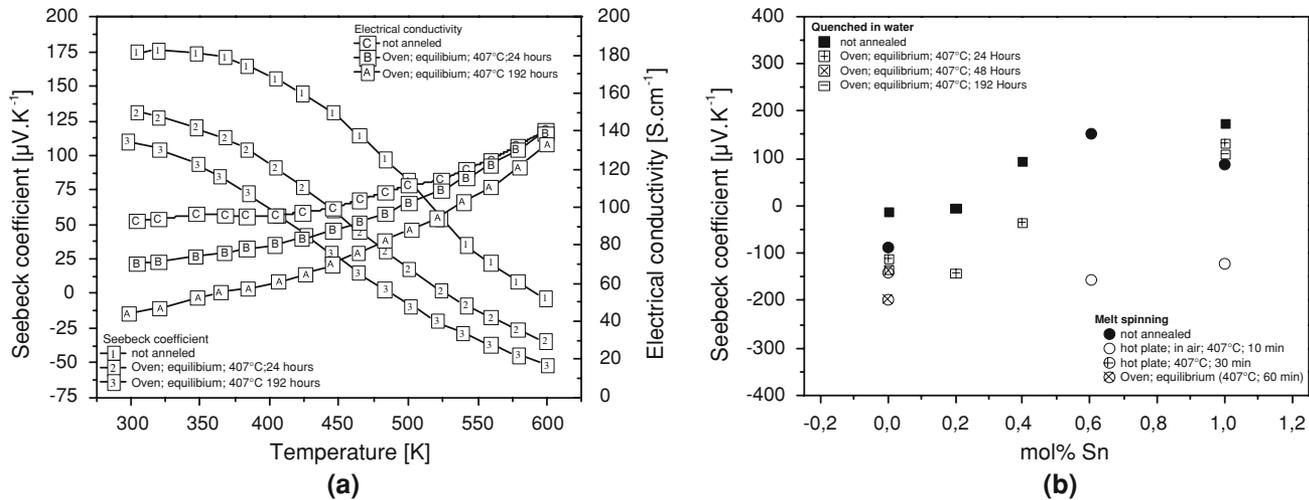


Fig. 4. Transport properties in the $\text{Bi}_2(\text{Te,Se})_3\text{-Sn}$ material system: (a) $\text{Bi}_2(\text{Te,Se})_3-1 \text{ mol.}\% \text{Sn}$ quenched in water, and (b) comparison between melt-spun and quenched materials containing up to 1 mol.% Sn annealed up to 192 h in various environments.

conductivity and higher Seebeck coefficient for temperatures above 400 K. For this concentration of PbTe the thermal conductivity is influenced only slightly in the case of unannealed samples. Annealing improves the thermal conductivity particularly at elevated temperatures above 400 K. The transmission electron microscopy (TEM) results confirm a rearrangement of the structural properties due to the annealing process. Although the electrical conductivity is improved by increasing the PbTe amount to 2 mol.%, a decrease of the ZT value is observed, because this effect is overruled by decreased Seebeck coefficient and increased thermal conductivity. The latter may indicate a changed structure of the material with larger grains or a different mechanism to support thermal conductivity, which is confirmed by the influence of excess Te (reducing thermal conductivity).

The transport properties of $\text{Bi}_2(\text{Te,Se})_3$ with 1 mol.% Sn and subsequently quenched in water have been measured before and after annealing (Fig. 4a). Whereas $\text{Bi}_2(\text{Te,Se})_3$ is usually n -type, $\text{Bi}_2(\text{Te,Se})_3$ with 1 mol.% Sn quenched in water is p -type and its electrical conductivity is very low. Annealing decreases the Seebeck coefficient and increases the electrical conductivity. The material is a compensated semiconductor with no or little prospect for thermoelectric application. The most important thing to note is that the material is not at thermodynamic equilibrium after 192 h of annealing at a temperature of 407°C. The annealing time required to bring a melt-spun material into thermodynamic equilibrium is much shorter. This is nicely illustrated in Fig. 4b. The Seebeck coefficients of melt-spun flakes ($\sim 3 \text{ mm} \times 3 \text{ mm} \times 0.1 \text{ mm}$) made of $(1-x)\text{Bi}_2(\text{Te,Se})_3-x\text{Sn}$ ($0 < x < 1 \text{ mol.}\%$) were measured with IPM-SR1 along with material quenched in water.¹⁴ The Seebeck coefficient of melt-spun $\text{Bi}_2(\text{Te,Se})_3$ can be very high when the material

is annealed in a proper manner to prevent the loss of tellurium or selenium (“equilibrium” annealing condition). However, it is more important that, even if melt-spun materials are annealed on a hotplate and in air, it takes less than 10 min to bring the material into thermodynamic equilibrium. This feature can be used to optimize quickly the thermoelectric properties of materials (rapid thermoelectric materials prototyping). Surprisingly, it was impossible to get n -type material containing 1% Sn. Only with annealing in air for 10 min at 407°C does the melt-spun material become n -type, when the Seebeck coefficient reaches slightly less than $-150 \mu\text{V K}^{-1}$.

CONCLUSIONS

A strong influence on the thermoelectric properties is observed due to the alloying of $(\text{Bi,Sb})_2\text{Te}_3$ with Te compounds of group IV elements. While improved thermoelectric performance is observed when adding 0.3 mol.% PbTe compared with the pure compound, the properties degrade in the case of higher concentration of PbTe or adding Sn instead. In all cases, the annealing step could improve the properties again, which might form part of the optimized SPS process.

Nanostructured materials from the $(\text{Bi,Sb})_2\text{Te}_3\text{-PbTe}$ materials system can be easily obtained by the melt-spinning method. The nanostructure survives the annealing process, resulting in good thermoelectric properties. Even if large grain growth is observed, the grain sizes are much closer to that found in thin films rather than in bulk materials. Even if the best materials contain just 0.3 mol.% PbTe, nanostructures are observed in this material. High-resolution TEM imaging shows that the material is nanostructured, with most of the characteristic features down to 10 nm. Micro or

nano-inclusions are not observed at the grain boundaries. Random modulation of the strain field at the atomic level is observed. This modulation of the strain field may contribute to the measured reduction in thermal conductivity. Measurements of the transport properties suggests that fine-tuning of the chemical composition (addition of small quantity of tellurium) may drastically improve the electrical conductivity and at the same time decrease the thermal conductivity. This interesting feature has been observed solely on melt-spun spark plasma sintered materials. The Bi₂(Te,Se₃)-Sn material system seems to be less promising due to the reduced properties of a compensated semiconductor. The material containing (1% Sn) that was quenched in water was *p*-type. The Seebeck coefficient was very small after annealing, but the Seebeck coefficient was never negative even after 192 h of annealing at 407°C, except for annealing in an oxygen-containing ambient. Applying annealing durations of less than 10 min brought the melt-spun materials to thermodynamic equilibrium at the same annealing temperature. Short annealing time is a very interesting feature of the melt-spun material that can considerably speed up the characterization of new thermoelectric materials. However, the reported *ZT* values may be overshadowed by the fact that the thermal conductivity and the electrical conductivity have not been measured in the same direction. New measuring systems are required to measure the thermal conductivity in both directions in small and thin samples.

ACKNOWLEDGEMENTS

This work was supported by the FhG Internal Programs under Grant No. WISA 815 020. The preparation of PbTe-alloyed samples is also acknowledged and was performed by the group of the LPM in Nancy, France, (Dr. Bertrand Lenoir) and by BASF in Ludwigshafen, Germany (Dr. Frank Haass).

REFERENCES

1. H. Böttner and J. Nurnus, patent number EP1891688 (27 February 2008).
2. H. Beyer, J. Nurnus, H. Böttner, A. Lambrecht, T. Roch, and G. Bauer, *Appl. Phys. Lett.* 80, 1216 (2002). doi:10.1063/1.1448388.
3. J. Koenig; A. Jacquot, U. Vetter, H. Böttner, and A. Lambrecht, *Proceedings of the 25th International Conference on Thermoelectrics*, Vienna, Austria, 6–10 August 2006.
4. E.I. Elagina and N.Kh. Abrikosov, *Russ. J. Inorg. Chem.* 4, 738 (1959).
5. N.S. Golovanova, V.P. Zlomanov, and O.I. Tananaeva, *Izv. Akad. Nauk. SSSR Neorg. Mater.* 19, 740 (1983).
6. T. Hirai, Y. Takeda, and K. Kurata, *J. Less-Common Met.* 13, 352 (1967). doi:10.1016/0022-5088(67)90143-9.
7. K.S.V.L. Narasimhan, *J. Indian Pure Appl. Phys.* 5, 261 (1966).
8. D. Kusano and Y. Hori, *Proceedings of the 21st International Conference on Thermoelectrics* (2002), pp. 13–16.
9. M.K. Zhitinskaya, S.A. Némov, and T.E. Svechnikova, *Phys. Solid State* 40, 1297 (1998). doi:10.1134/1.1130548.
10. Y. Gelbstein, Z. Dashevsky, and M.P. Dariel, *Physica B* 363, 196 (2005). doi:10.1016/j.physb.2005.03.022.
11. H. Böttner, D. Ebling, A. Jacquot, J. König, L. Kirste, and J. Schmidt, *Phys. Stat. Sol. (RRL)* 1, 235 (2007).
12. D. Ebling, A. Jacquot, M. Jägler, H. Böttner, U. Kühn, and L. Kirste, *Phys. Stat. Sol. (RRL)* 1, 238 (2007).
13. D.G. Ebling, A. Jacquot, J. König, H. Böttner, J. Schmidt, and P. Spies, *Proceedings of the 26th International Conference on Thermoelectrics*, Jeju, Korea, June 2007.
14. A. Jacquot, J. König, and H. Böttner, *Proceedings of the 25th International Conference on Thermoelectrics*, Vienna, Austria, 6–10 August 2006, p. 184.
15. D. Maier, *Solid State Commun.* 122, 565 (2002). doi:10.1016/S0038-1098(02)00142-4.
16. N. Peranio and O. Eibl, *Phys. Stat. Sol. A* 204, 3243 (2007). doi:10.1002/pssa.200622579.
17. N. Peranio, O. Eibl, and J. Nurnus, *J. Appl. Phys.* 100, 114306 (2006).
18. A. Jacquot, *Proceedings of the 5th Europe Conference on Thermoelectrics*, Odessa, Ukraine, 10–12 September, 2007.
19. A. Jacquot, *Proceedings of the 6th Europe Conference on Thermoelectrics*, Paris, France, 2–4 July, P1-15 (2008), p. 1.
20. J. Jiang, L. Chen, S. Bai, Q. Yao, and Q. Wang, *Mater. Sci. Eng. B* 117, 334 (2005).
21. T.M. Tritt, ed., *Thermal Conductivity, Theory, Properties and Applications* (New York: Kluwer Academic/Plenum Publishers, 2004).