1. Introduction

Thermoelectric (TE) materials are able to directly convert thermal energy into electrical energy and vice versa. To determine the quality of a TE material, the dimensionless figure of merit \( ZT = S^2 T / \rho \sigma \) is used, with \( S \) the Seebeck coefficient or thermopower, \( T \) the temperature, \( \rho \) the electrical resistivity, and \( \sigma = \rho^{-1} \) the total thermal conductivity, consisting of the electronic part \( \sigma_e \) and the phonon part \( \sigma_{ph} \). The electronic part of the thermal conductivity is linked to the electrical resistivity via the Wiedemann-Franz law, \( \sigma_e \sim L_0 T / \rho \), with the Lorenz number \( L_0 \). Therefore one way to increase \( ZT \) is to decrease \( \sigma_{ph} \), which is possible by enhancing the scattering of the heat carrying phonons, on various lattice defects like point defects including vacancies, dislocations, and grain boundaries. Not only a high \( ZT \) value at a certain temperature is important, but also a high average \( ZT, (ZT)_a \) over a wide temperature range, to maximize the so-called thermo-electric conversion efficiency

\[
\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + (ZT)_a} - 1}{\sqrt{1 + (ZT)_a} + \frac{T_c}{T_h}}
\]

including the Carnot efficiency, where \( T_h \) and \( T_c \) are the temperatures on the hot and cold side respectively.

“Bottom-up” methods like ball-milling (BM) followed by hot-pressing (HP) achieve materials with a grain size of the order of micrometers and (especially with high energy ball-milling, HBM) in the range of 100 nanometers and less. It was found that the smaller the grain size the higher is the thermoelectric performance due to a reduction in the phonon part of the thermal conductivity. Another method to reduce the grain and/or crystallite size and concomitantly to increase the density of lattice defects in general and, thereby, further increase the scattering of heat carrying phonons, is to apply severe plastic deformation (SPD) in its various forms. SPD methods produce materials with grains in sub-micrometer or even nanometer range. Because of the presence of high hydrostatic pressure, SPD methods provide
extremely large strains, almost without changing the sample’s geometry. Therefore SPD not only achieves very fine grains with high and small angle boundaries, but also vacancies, dislocations and other defects.\textsuperscript{5,9,21-25} 

There exist many techniques to sustain plastic strains as described in an overview article by Valiev.\textsuperscript{18} Of course, they all have advantages and disadvantages.

A very effective method is high-pressure torsion (HPT).\textsuperscript{26-30} Using HPT, the sample’s shape remains almost unchanged by the deformation, a finer grain structure is achieved but damage and fracture are suppressed. The technique is essentially based on the use of a Bridgman anvil-type device: the thin sample (disk shaped) is subjected to a torsional strain under a high pressure between two anvils. Additionally it is possible to process under various temperatures, using cooling or heating with an inductive coil. As in some cases it is necessary to prevent the sample from oxidation, a modified version of the HPT equipment with a tight “cage” for inert gas can be applied.

Using HPT one has to take into account that the processed samples are not completely homogeneous as the shear strain, \( \gamma \), is increasing from the center of the sample to the rim according to \( \gamma = (2\pi r / h) n \), where \( n \) is the number of revolutions, \( r \) is the radius and \( h \) is the thickness of the sample; however, as Pippan \textit{et al.}\textsuperscript{30} demonstrated, even in the center (\( r = 0 \)) the strain is not zero.

For measuring the electrical resistivity as well as the Seebeck coefficient, the equipment requires samples with cubic shape with the dimensions of at least \( 8 \times 2 \times 1 \text{ mm}^3 \). The thermal conductivity is measured perpendicularly to the resistivity and the Seebeck coefficient. As the HPT-processed samples are discs with 10 mm in diameter and about 1 mm in thickness, some inhomogeneities of the samples must be accepted. More details of the measurement techniques can be found in Refs. 5, 6, 9, 15).

The influence of the processing parameters (number of revolutions, applied pressure, temperature) as well as of the starting conditions (grain size of the powder before HP)\textsuperscript{7} and various annealing processes\textsuperscript{5} on the structural and physical properties have been studied systematically for a p-type skutterudite (\( \text{DD}_{0.6} \text{Fe}_3 \text{CoSb}_{12} \), DD stands for didymium) by Rogl \textit{et al.}\textsuperscript{10} It was found that processing at room temperature produced very brittle samples, almost unserviceable, therefore all further experiments were performed at 600–670 K. Independent of all above-mentioned conditions, after HPT the lattice parameter was enlarged, the relative density decreased, the crystallite size became much smaller (up to forty times), and the dislocation density increased by about ten times. Independent of the applied pressure (2–8 GPa) and the number of revolutions (1–5), the HPT-processed skutterudite samples were not completely homogeneous and more or less strewn with microcracks.\textsuperscript{10} These observations are in contrast to those of Masuda \textit{et al.}\textsuperscript{17} claiming that HPT-processing HP Heusler alloys at room temperature with 5 GPa and 10 revolutions yielded homogeneous and crack-free samples.

Whilst the Seebeck coefficient, independent of the composition and processing parameters, in almost all cases is in the range of the materials’ state before HPT, the electrical resistivity, due to introduced defects such as dislocations, vacancies and/or micro cracks, is dependent on the processing parameters and more or less enhanced. The thermal conductivity, out of the above-mentioned reasons, is decreased. The net effect usually is positive, i.e. as a result, ZT is higher for all HPT-processed samples.

For a short introduction into the solid state physics of thermoelectrics, into the various methods of severe plastic deformation as well for a comprehensive summary on HPT-processed skutterudites the reader is referred to an earlier review article by G. Rogl \textit{et al.}\textsuperscript{9} 

2. Skutterudites

Since 2010 the influence of HPT on structural, physical, mechanical and magnetic properties of p- and n-type skutterudites has been investigated, and the results were published by the authors as a review article\textsuperscript{9} and in various journals.\textsuperscript{3-8,10,11,13-16} It could be shown that after HPT-processing skutterudites do not exhibit any secondary phases and/or impurities but microcracks and pores, an enhanced number of dislocations and of other defects as well as smaller grains. These observations were confirmed via transition electron microscopy (TEM): as depicted in Figs. 1 and 2, where grain boundaries and dislocations are clearly visible.

The lattice parameter is larger, the density lower. During measurement-induced heating or deliberate annealing, the grains grow, the major part of the cracks fuse to pores or disappear, the dislocation density becomes smaller, but all these temperature induced changes do not restore the state as it has been before HPT. These changes are reflected in the

![Fig. 1 Superimposed energy-filtered TEM image of HP+HPT-processed Sr$_0.07$Ba$_{0.1}$Yb$_{0.85}$Co$_6$Sb$_{12}$, showing grain boundaries and dislocation structure.](image1)

![Fig. 2 TEM image of a selected area of CP+HPT-processed DD$_3$Fe$_3$CoSb$_{12}$, exhibiting a close up of dislocations and grain boundaries.](image2)
changes of the physical properties, mainly in the electrical resistivity and thermal conductivity right after HPT-processing and during the annealing process. Although the electrical resistivity even after annealing is higher for the HPT sample, the thermal conductivity is lower, resulting in a positive net effect in respect of ZT, generally with enhancements of 13–28%.

As the scheme is the same for all p-type (mainly DD filled, Fe/Co or Fe/Ni substituted) and n-type (multifilled) skutterudites, one of them was exemplarily selected for demonstration.

To evaluate the X-ray diffraction data in terms of line profile analysis, models for the crystallite size and its distribution as well as of the dislocations density were applied, using the CMWP-fit software. For example for p-type, DD$_{0.6}$Fe$_3$CoSb$_{12}$, BM, the crystallite size was reduced by means of HPT from 152 nm to 53 nm, and the dislocation density of $2.8 \times 10^{13}$ m$^{-2}$ was ten times larger. Although for the Sb/Sn substituted BM DD$_{0.7}$Fe$_2$Co$_{12}$Sb$_{11.8}$Sn$_{0.2}$, the crystallite size through HPT was reduced from 336 nm to 95 nm, it grew back to 256 nm during the annealing process, but the residual strain was about 2.5 times higher after HPT. For n-type Sr$_{0.1}$Ba$_{0.1}$Yb$_{0.1}$Co$_{4}$Sb$_{12}$, the HPT induced structural changes were less spectacular, showing a crystallite size reduction from 36.5 nm to 30 nm, and an enhancement of the dislocation density from $1.4 \times 10^{14}$ m$^{-2}$ to $1.8 \times 10^{14}$ m$^{-2}$. Multiple filled p- and n-type skutterudites, (Sr,Ba,DD,Yb)$_{4}$Fe$_{1-x}$Ni$_{x}$Co$_{4}$Sb$_{12}$ with ZTs $\sim 1$ attracted interest because tuning the band structure and the location of the Fermi level adjusted both p- and n-type materials to exhibit the same thermal expansion coefficient and mechanical properties. After HPT-processing, ZT was enhanced by 20% for the p- and 38% for the n-type skutterudite.

For DD$_{0.64}$Fe$_2$Co$_{10.9}$Sb$_{12}$ the changes after HPT and annealing were investigated employing not only transition electron microscopy but also Raman spectroscopy and texture measurements. Raman spectra of HP, HPT and HPT-annealed DD$_{0.64}$Fe$_2$Co$_{10.9}$Sb$_{12}$ showed almost the same peak position, with a move to the lower energy side in the higher frequency range, indicating a softening of the vibration modes. The spectrum for the HPT sample exhibited additional softening in the high-energy region as well as peak broadening, denoting that the vibration modes related to the shorter Sb–Sb bonds in the Sb$_4$ rings are more affected than those with longer Sb–Sb bonds. After annealing, these features were not visible anymore and the HPT-annealed skutterudite spectrum is indistinguishable from the HP spectrum. Anbalagan et al. gained the same results for Raman spectroscopy investigations of the double-element-substituted unfilled skutterudite Fe$_{0.05}$Co$_{0.95}$Sb$_{2.875}$Te$_{0.125}$.

Texture measurements of DD$_{0.4}$Fe$_2$Co$_{10.9}$Sb$_{12}$, comparing a HP sample with a HPT-processed (for the latter performed on a plane perpendicular to the HPT pressing direction) did not show any changes in the orientation distribution of the crystallites. However, for Fe$_{0.05}$Co$_{0.95}$Sb$_{2.875}$Te$_{0.125}$ Anbalagan et al. found changes in the crystallographic texture, which indicated strengthening of the (112), (102) poles and weakening of the 28 (123) pole of the HPT-processed sample.

The temperature and phase stability of p-type skutterudites DD$_{0.7}$Fe$_2$Co$_{0.9}$Sb$_{12}$, HP and HPT-processed, have been studied by means of thermal analysis (TA) and Knudsen effusion mass spectrometry (KEMS). The difference in the mass loss per day at 800 K, due to antimony evaporation (into vacuum), of the HP (3–4%) and the HPT-processed sample (5–6%) is marginal. For the sample, DD$_{0.7}$Fe$_2$CoSb$_{12}$, for which commercial powder (TIAG, Austria) was simply hot-pressed (labeled as HP), the lowest mass loss (<1%) was found, however, as soon as the same powder was cold pressed (CP) and HPT-processed, the highest mass loss was detected (9–10%). This high mass loss for the CP+HPT sample can be attributed to the fact that during CP, in contrary to HP, the surplus of antimony, used as densification aid (DA), is not squeezed out of the sample.

For a better imagination, physical properties are exemplarily depicted and explained for p-type DD$_{0.6}$Fe$_3$CoSb$_{12}$ and n-type Sr$_{0.08}$Ba$_{0.1}$Yb$_{0.05}$Co$_{4}$Sb$_{12}$ (data and figures are adapted from Refs. 10 and 13) respectively. Basically all processed skutterudites follow the presented scheme. Measuring the physical properties of the HPT-processed skutterudite a second or third time, reveals the same results as for the first measurement with decreasing temperature; thus it appears that during only one measurement-induced heating already all possible recovery processes have been run.

Figure 3 shows that for p-type DD$_{0.4}$Fe$_2$CoSb$_{12}$ as well as for n-type Sr$_{0.08}$Ba$_{0.1}$Yb$_{0.05}$Co$_{4}$Sb$_{12}$ the electrical resistivity of the HP sample is metallic as $\rho(T)$ is increasing with increasing temperature. After HPT, due to a higher density of dislocations, other lattice defects and presumably also because of fine cracks, the electrical resistivity is quite higher in comparison to the reference sample. In addition one can see (Fig. 3) that $\rho(T)$ of the HPT sample is increasing almost linearly in parallel to $\rho(T)$ of the HP sample till almost 600 K, but that after a plateau-like maximum $\rho(T)$ is decreasing rather rapidly with further temperature increase. Obviously during the measurement-induced heating and annealing at elevated temperatures the crystallites grow, the cracks fuse together, recrystallization occurs, which altogether cause a reduction of $\rho(T)$. For the measurement with decreasing temperature, the annealed sample still shows an enhanced...
ρ(T) but metallic behavior without anomalies. The temperature dependent thermal conductivity, λ(T), as displayed in Fig. 4, due to the smaller grains and the defects discussed above, introduced during HPT, is much lower for the HPT sample and hardly changes after annealing. The lattice thermal conductivity in all cases is very low.

Comparing the p- and n-type skutterudite in Figs. 3 and 4, one can also see for the HP samples that the lower ρ(T), the higher is λ(T). After HPT and after annealing, the relative increase in ρ(T) is much higher for $\text{Sr}_{0.09}\text{Ba}_{0.11}\text{Yb}_{0.05}\text{Co}_{4}\text{Sb}_{12}$ than for $\text{DD}_{0.6}\text{Fe}_{3}\text{CoSb}_{12}$ and this behavior is reflected in λ(T), with a much bigger downsizing for $\text{Sr}_{0.09}\text{Ba}_{0.11}\text{Yb}_{0.05}\text{Co}_{4}\text{Sb}_{12}$ than for $\text{DD}_{0.6}\text{Fe}_{3}\text{CoSb}_{12}$.

The illustration (Fig. 5) defines the temperature dependent Seebeck coefficient, S(T), which is positive for $\text{DD}_{0.6}\text{Fe}_{3}\text{CoSb}_{12}$, indicating holes as main carriers, but is negative for $\text{Sr}_{0.09}\text{Ba}_{0.11}\text{Yb}_{0.05}\text{Co}_{4}\text{Sb}_{12}$, as electrons are the main carriers. Figure 5 informs that neither HPT-processing nor annealing for the p- as well as for the n-type samples has an influence on S(T), as all S(T) curves are, within the error bar, alike. With a more or less completely unchanged Seebeck coefficient after HPT and annealing, but a higher electrical resistivity in both cases, the power factor, $\text{pf} = S^2T/\rho$ becomes lower, therefore both HP samples exhibit the highest values (Fig. 6).

Figure 7 summarizes the figure of merit, ZT. The increase of ZT is higher for $\text{DD}_{0.6}\text{Fe}_{3}\text{CoSb}_{12}$ by 41% for the HPT sample (from $\text{ZT} = 1.1$ at 823 K) and 30% (to $\text{ZT} = 1.5$) than for $\text{Sr}_{0.09}\text{Ba}_{0.11}\text{Yb}_{0.05}\text{Co}_{4}\text{Sb}_{12}$ with 19% for the HPT sample (from $\text{ZT} = 1.6$ to $\text{ZT} = 1.9$ at 838 K) and 12% (to $\text{ZT} = 1.8$). These ZT enhancements can vary individually: dependent on the starting material and the composition of the skutterudite, so far for all HP skutterudites, ZT was higher after HPT-processing. The thermo-electric conversion efficiency increased for $\text{DD}_{0.6}\text{Fe}_{3}\text{CoSb}_{12}$ from $\eta = 13.9\%$ (HP) to $\eta = 14.6\%$ (HP+HPT), for $\text{Sr}_{0.09}\text{Ba}_{0.11}\text{Yb}_{0.05}\text{Co}_{4}\text{Sb}_{12}$ from $\eta = 15.0\%$ (HP) to $\eta = 16.0\%$ (HP+HPT).

Enhancing ZT via HPT-processing does not only work for filled p- and n-type skutterudites, but also for unfilled skutterudites and filled skutterudites substituted at the Sb-site. Mallik et al.\textsuperscript{11) reported for $\text{Fe}_{0.5}\text{Co}_{3.5}\text{Sb}_{11.1}\text{Te}_{0.5}$ that ZT increased from $\text{ZT} = 1.06$ to $\text{ZT} = 1.3$, which equals an enhancement of 23%.
Rogl et al.\(^{16}\) HPT-processed Sb-substituted DD\(_{0.54}\)Fe\(_{2.7}\)-Co\(_{1.3}\)Sb\(_{11.9}\)Ge\(_{0.1}\) and DD\(_{0.7}\)Fe\(_{2.7}\)Co\(_{1.3}\)Sb\(_{11.8}\)Sn\(_{0.2}\). Whilst ZT of DD\(_{0.54}\)Fe\(_{2.7}\)Co\(_{1.3}\)Sb\(_{11.9}\)Ge\(_{0.1}\) after HPT was not much higher, for DD\(_{0.7}\)Fe\(_{2.7}\)Co\(_{1.3}\)Sb\(_{11.8}\)Sn\(_{0.2}\) ZT = 1.3 at 780 K of the HP sample could be topped with ZT = 1.45 at 773–813 K of the HPT-processed sample. Both ZT values, for a processed and a HP p-type skutterudite are, to our knowledge, so far the highest ZTs. The values of \(\eta \approx 14.6\%\) before and after HPT are about the same.

Recently, SPD via HPT at elevated temperatures and in protective gas atmosphere was used to directly consolidate and plastically deform commercial p-type (DD\(_{0.7}\)Fe\(_{3}\)CoSb\(_{12}\))\(^{34}\) and n-type ((Mm,Sm)\(_{y}\)Co\(_{4}\)Sb\(_{12}\))\(^{35}\) skutterudite powder from TIAG, Austria, into a dense thermoelectric solid. Applying this method, not only time and energy consuming steps like ball milling and especially hot pressing could be eliminated, but in addition this method is much faster as it takes about 15 to 25 minutes, dependent on the number of revolutions during HPT, instead of several hours (about 10). For both, the p- and n-type skutterudite, the structural, physical and mechanical properties (see chapter 6) of the cold pressed (CP) and HPT-processed sample (referred to as CP+HPT–1r or CP+HPT–5r, dependent on the number of revolutions) were compared with those of a reference sample (referred to as HP), which was traditionally consolidated in the hot press. It should be noted that cold compacting (CP) of the powder is only necessary in order to easily place the right amount of powder between the anvils of the HPT equipment.

Whilst the calculated lattice parameters (Fig. 8, top) for both, p- and n-type, are lower for the homogeneous HP sample than for the starting powder, they are higher after CP+HPT. After measurement-induced annealing they “shrink” to the size of those of the starting powders. Interestingly, the lattice parameters for the n-type skutterudite, HPT-processed by five revolutions are slightly lower than those processed with one revolution.

Figure 8 (bottom) compares the measured relative density in % with the calculated X-ray density (\(d_\text{X} = (ZM)/(NV)\), where M is the molar mass, Z is the number of formula units per cell, N is Loschmidt’s number, and V is the volume of the unit cell). For the p- as well as for the n-type skutterudite the CP+HPT sample has a much lower density than the HP sample. The reason is that defects like vacancies and small cracks are introduced during HPT-processing. After annealing the density further decreases for DD\(_{0.7}\)Fe\(_{3}\)CoSb\(_{12}\), whereas for (Mm,Sm)\(_{y}\)Co\(_{4}\)Sb\(_{12}\) a slight increase occurs.

The crystallite size (Fig. 9) was evaluated from the X-ray pattern via line profile analysis. The crystallite size of both HP samples (p-type: 76 nm, n-type: 78 nm) is practically the same and much smaller after HPT-processing (44 nm and 45 nm, respectively, for one revolution, 39 nm for five revolutions). During measurement-induced annealing the grains grow, but remain still smaller in comparison to the HP samples. The results of the profile analysis for the dislocation density is depicted in Fig. 9. Especially for the sample processed with five revolutions the dislocation density is ten times higher than for the HP sample, for the other two samples about four times \((3.6 \times 10^{14} \text{m}^{-2} \text{ and } 3.3 \times 10^{14} \text{m}^{-2})\). During the physical properties’ measurements many defects anneal out, but not completely so that finally for the annealed samples the dislocation density is still about three times higher in comparison to that of the HP sample.

The temperature dependent electrical resistivity \(\rho(T)\) for both, p- and n-type CP+HPT (see Fig. 10), is much higher than for the HP counterpart, descending from various defects and cracks. For the p-type, after a maximum, \(\rho(T)\) decreases, undergoes a low minimum and slightly increases.

![Fig. 8 Lattice parameter, a (top) and relative density, d rel (bottom) of DD\(_{0.7}\)Fe\(_{3}\)CoSb\(_{12}\) (left column) and (Mm,Sm)\(_{y}\)Co\(_{4}\)Sb\(_{12}\) (right column).](image)

![Fig. 10 Electrical resistivity, \(\rho\) of DD\(_{0.7}\)Fe\(_{3}\)CoSb\(_{12}\) and (Mm,Sm)\(_{y}\)Co\(_{4}\)Sb\(_{12}\) prepared via HP and CP+HPT vs. temperature, T.](image)
This behavior was backed by in situ synchrotron measurements for DD$_{0.7}$Fe$_3$Co$_8$Sb$_{12}$, which were performed in a temperature range of 300 to 825 K in steps of 50 K, in order to evaluate the changes in grain size and dislocation density of the CP+HPT samples before, during and after annealing. With increasing temperature the size of the crystallites ($\sim 44$ nm) decreases slightly ($\sim 38$ nm) but above about 500 K it increases ($\sim 60$ nm), but even at 800 K the crystallite size is smaller than that of the HP sample ($\sim 78$ nm). It was confirmed that at room temperature the grains at the rim are smaller than in the center, and that this proportion is independent of the heat treatments and inversely proportional to the dislocation density. Below about 600 K the dislocation density ($3.5 \times 10^{14}$ to $4.2 \times 10^{14}$ m$^{-2}$) is not affected by the heat treatment but is decreasing almost linearly above 600 K. Beyond that temperature, it is then bisected but still two times larger than the dislocation density of the HP sample. Further heat treatments do neither affect the crystallite size nor the dislocation density. These changes are in parallel with the changes in the electrical resistivity for the first measurement with increasing temperature.

The thermally stable $\rho$ (T)-curve is higher than for the HP sample but has the same curvature. For the n-type sample for the first measurement with increasing temperature, about the same behavior occurs, but for decreasing temperature, $\rho$ (T) increases, instead of decreasing, especially for the sample processed with five revolutions. This performance indicates a change from metallic to semiconducting behavior during measurement-induced annealing, which could be explained via the change of lattice distortion and its influence on the band gap. All further resistivity measurements confirmed semiconducting behavior.

Thermal conductivity (Fig. 11) for all three CP+HPT samples is much lower than for the HP reference sample. After annealing, the thermal conductivity does not change much, but whilst the thermal conductivity becomes slightly lower for the annealed CP+HPT n-type sample it becomes slightly higher for the p-type. This feature is not surprising, as thermal conductivity acts reciprocal to the electrical resistivity. Lattice thermal conductivities are very low, indicating that the lower limit of the possible thermal conductivity reduction is reached.

The temperature dependent Seebeck coefficient is displayed in Fig. 12. For DD$_{0.7}$Fe$_3$Co$_8$Sb$_{12}$ and for (Mm,Sm)$_{2}$Co$_4$Sb$_{12}$, the difference between HP and CP+HPT is marginal; also annealing hardly influences the Seebeck coefficient. The power factor (Fig. 13) reaches the highest values for the HP samples, due to high and very high electrical resistivities and because of almost no change in the Seebeck coefficient.

All ZT values (Fig. 14) are remarkable. With CP+HPT the goal is, of course, to get high ZTs, but they should not compete with the ZTs of the HP+HPT samples as one always has to consider the sustainability and energy-saving preparation procedure of the CP+HPT samples. The highest ZT with ZT $\geq 1.44$ at 823 K could be achieved for the thermally stable (Mm,Sm)$_{2}$Co$_4$Sb$_{12}$ (5 revolutions). DD$_{0.7}$Fe$_3$Co$_8$Sb$_{12}$ has ZT $\geq 1.3$ at 783 K. In addition the thermo-electric conversion efficiencies for the CP+HPT samples are in the range of $\eta = 12.2$–15.7%.

L. Zhang et al. compared the magnetic behavior of Pr$_{0.67}$Fe$_3$Co$_8$Sb$_{12}$ before and after HPT. Despite the fact that
after HPT a long-range magnetic order for $T < 5.6$ K could not be detected in the temperature dependent electrical resistivity curve, the susceptibility indicates anti-ferromagnetism, even though diminished, revealing that the magnetic order at $T < 5.6$ K is just superposed by high residual resistivity. Before HPT the effective magnetic moment is 4.18 $\mu_B$, after HPT it amounts to 4.07 $\mu_B$, accompanied by a metamagnetic transition in the isothermal magnetization curves. The field dependent transitions considerably smear out as a consequence of the nanograined structure.

For all skutterudites, HPT-processing is a great tool to either enhance ZT of HP samples or to directly produce fast and easily high-ZT thermoelectric materials.

3. Clathrates

Yan et al. investigated the influence of HPT on type I clathrate $\text{Ba}_8\text{Cu}_{3.5}\text{Ge}_{41}\text{In}_{1.5}$, prepared via high frequency melting followed by BM and HP (for details see Ref. 12). All features, typical of HPT-processed samples (4 GPa, 1 revolution at 673 K), like reduced grain size, but enhanced residual strain, dislocation density, point defects and cracks, accompanied by a lower density, turned up. As a consequence, compared with the BM+HP sample, the HPT-processed sample had a higher electrical resistivity and Seebeck coefficient but a lower charge carrier concentration, lower Hall mobility and thermal conductivity so that finally no essential improvement of ZT in the investigated temperature range occurred (Fig. 15).

Only one clathrate $\text{Ba}_8\text{Cu}_{3.5}\text{Ge}_{41}\text{In}_{1.5}$ was investigated. The enhanced electrical resistivity was balanced by a reduced thermal conductivity and slightly higher Seebeck coefficient, therefore ZTs of the HP and HP+HPT sample were alike.

4. Heusler Alloys

Kourov et al.2) HPT-processed a rapidly quenched Heusler-type alloy $\text{Ni}_{12.16}\text{Mn}_{0.84}\text{Ga}$ (2 and 5 revolutions, under a pressure of 3 and 5 GPa), and studied the crystalline structure and behavior of electrical resistivity, thermoelectric power, thermal expansion, and magnetic properties. After HPT of the sub-microcrystalline alloy, a mixture of amorphous and nanocrystalline (90 vol%) phases was formed, however, after annealing at $T > 600$ K the structure changed first to nanocrystalline and later back to a submicrocrystalline one. SPD was made responsible for the facts that (i) the temperature dependent electrical resistivity exhibits a negative temperature coefficient (ii) the long-range magnetic order underwent a transition to a magnetically ordered state accompanied with a significant drop in the magnitude of magnetization (iii) the temperature dependent Seebeck coefficient is proportional to the temperature in the magnetically ordered state, but that (iv) the absolute value of S drops drastically when the magnetic order vanishes and that (V) the thermal expansion coefficient is remarkably increased. All these observations indicate a rearrangement of the electronic band structure near the Fermi level caused by the HPT treatment.

Whilst the thermoelectric properties helped to get insight into the electronic behavior of $\text{Ni}_{12.16}\text{Mn}_{0.84}\text{Ga}$, the investigation of Heusler alloys from the system $\text{V}–\text{Fe}–\text{Al}$ focused on the thermoelectric performance.

Masuda et al.17) HPT-processed Heusler alloys, $\text{VTa}_{0.95}\text{Fe}_{2}\text{Al}_{0.05}$ and $\text{V}_{1.02}\text{Fe}_{2}\text{Al}_{0.95}$, at room temperature with 5 GPa and 10 revolutions, and observed neither cracks nor differences in hardness between the center and the rim area. The structural and physical properties of the so obtained samples were compared with the respective arc-melted samples before HPT and after it plus annealing at 873 K. They observed some grain size reduction after HPT, which almost vanished after the annealing process. The lattice parameters of both processed alloys measured as a function of temperature were enhanced right after HPT but decreased with increasing temperature during the measurement.

The electrical resistivities after HPT are enhanced and show a rather sharp peak with a decrease due to recovery and grain growth during measurement-induced heating, similar to the behavior of HPT-processed skutterudites. After recurrence, above 800 K, resistivities are in line with those of the arc-melted samples as well as with those of annealed ones. The absolute values of the Seebeck coefficient of the HPT samples were lower in comparison to the arc-melted ones but increased after annealing. Thermal conductivity is almost...
bisected (about 5 W/m) after processing and hardly changes during annealing. Element mapping revealed that Ta atoms segregated at the grain boundaries, and it seems that they were able to retard the grain boundary migration and this way suppress grain growth during recrystallization. Therefore VTa$_{0.05}$Fe$_2$Al$_{0.95}$ even after annealing exhibited a grain size of about 80 nm, whereas in non-doped V$_{1.05}$Fe$_2$Al$_{0.95}$ the grains grew back to 270 nm, being a disadvantage for the thermal conductivity. Therefore ZT (Fig. 16) of the annealed V$_{1.05}$Fe$_2$Al$_{0.95}$ is lower than that of the arc-melted counterpart, however, ZT of the annealed, HPT-processed VTa$_{0.05}$Fe$_2$Al$_{0.95}$ reaches ZT $\approx$ 0.3 at around 500 K because of the low thermal conductivity even after annealing in parallel with the restoration of the rather large power factor.

For the Heusler-type Ni$_{2.16}$Mn$_{0.84}$Ga the comparison of the behavior of the thermolectric power, electrical resistivity, and magnetic properties indicated a significant rearrangement of the electronic band structure near the Fermi level due to the HPT treatment of the alloy. Whilst for VTa$_{0.05}$Fe$_2$Al$_{0.95}$ a higher ZT after HPT was detected, this was not the case for non-doped V$_{1.05}$Fe$_2$Al$_{0.95}$ because during annealing the grains grew back to original size.

5. Half-Heusler Alloys

Although Half-Heusler (HH) alloys reveal increasing interest as thermoelectric materials, severe plastic deformation has been applied only recently. Particularly the group of Rogl et al. $^{37}$ investigated the influence of HPT on p-type (NbFeSb) and n-type (Ti$_{0.15}$Nb$_{0.85}$FeSb) Half-Heusler (HH) alloys. All HP samples were processed at 650 K, applying 4 GPa and 1 revolution under argon to prevent oxidation. X-ray diffraction patterns revealed peak broadening for all HPT samples, indicating finer grains and/or an enhanced dislocation density. After measurement-induced heating the peaks became slimmer. Lattice parameters became larger after HPT, whereas the relative density became lower. For skutterudites, the second measurement for increasing temperature showed all physical properties being similar to those measured in the first measurement with decreasing temperature; for HH alloys, however, at least three times cycling is necessary to gain a thermally stable, annealed sample, indicating that for HH alloys the introduced defects and structure changes seem to be more resistant against heat treatments.

Both samples NbFeSb and Ti$_{0.15}$Nb$_{0.85}$FeSb were prepared as described in detail in Ref. 38). ZTs of processed and annealed samples were enhanced (Figs. 17 and 18, respectively).

Interestingly, the HPT-processed NbFeSb exhibits an electrical resistivity lower than that of the HP sample, already for the first measurement; at room temperature the annealed sample has a resistivity of about five times lower than that of the HP; but at 823 K the values are about the same. Seebeck coefficient of the HP sample exhibits a crossover from negative to positive values at around 455 K and after undergoing a maximum (at 623 K), it changes back to negative values at around 505 K (insert in Fig. 17). These changes are also present after severe plastic deformation via HPT. As the Seebeck coefficient of the HPT annealed sample is slightly lower in comparison with the HP sample, and the thermal conductivity is almost three times lower, ZT at 623 K reaches ZT = 0.00043. This is, as absolute value, very low, but as relative value double the ZT-value of the HP sample.
Ti$_{0.15}$Nb$_{0.85}$FeSb behaves like a typical HPT-processed alloy. Electrical resistivity is - right after HPT - much higher, shows a maximum and decreases. After annealing the resistivity is only slightly higher than after hot-pressing. The Seebeck coefficient does not change within the error bar, but thermal conductivity is much lower, so that ZTs of the HPT sample at 823 K are higher than the ZT of the HP (ZT = 0.68) sample with ZT = 0.71 and ZT = 0.74 (for the first measurement and the annealed sample, respectively).

Figures 19–22 summarize the thermoelectric properties for all three investigated n-type HH alloys, Ti$_{0.5}$Zr$_{0.5}$NiSn, Ti$_{0.5}$Zr$_{0.5}$NiSn$_{0.98}$Sb$_{0.02}$ and Ti$_{0.5}$Zr$_{0.5}$NiSn$^{+}$DA, however, not all measured temperature-dependent curves are presented: only the graphs of the HP (the reference), of the HPT-processed (first measurement, temperature increasing) and the additionally annealed sample (after cycling) are presented. All samples, arc-melted, annealed, BM and HP, were prepared as described in detail in Ref. 39). For all three HH alloys (Fig. 19), the electrical resistivity after HPT is very high, presents a maximum between 500 and 600 K and is further decreasing with increasing temperature. For Ti$_{0.5}$Zr$_{0.5}$NiSn$_{0.98}$Sb$_{0.02}$ and Ti$_{0.5}$Zr$_{0.5}$NiSn$^{+}$DA after three times cycling, $\mu$ (T) of the annealed and of the HP sample are showing the same curvature with higher values for the annealed one. For these two compounds, the absolute values of the Seebeck coefficient after HPT and cycling are lower than those for the HP sample. The undoped sample Ti$_{0.5}$Zr$_{0.5}$NiSn without DA, displays an extremely high resistivity right after HPT-processing, but after measurement-induced heating it is even lower than for the HP sample. The absolute values of the Seebeck coefficient of Ti$_{0.5}$Zr$_{0.5}$NiSn after HPT and annealing are about 60% lower than those for the HP sample (Fig. 20).

For all three HH alloys, the thermal conductivity (Fig. 21) is decreased although not by the same extent. The highest enhancement of ZT (see Fig. 22), almost 20%, is exhibited by Ti$_{0.5}$Zr$_{0.5}$NiSn with ZT = 0.81 at 773 K. For Ti$_{0.5}$Zr$_{0.5}$NiSn$^{+}$DA, however, the HP sample has a higher ZT than the as-processed one, mainly because of a rather low Seebeck coefficient.

For p- and n-type HH alloys, at least three temperature cycles are necessary to gain a thermally stable state, indicating that obviously the introduced defects and structure changes are more resistant against heat treatments than in case of skutterudites. For both p-type HH alloys investigated, as well as for two of the three n-type HH alloys, ZT was enhanced after HPT in comparison to the HP counterparts. SEM images (Fig. 23), exemplarily shown for the HH alloy system Ti$_{0.15}$Nb$_{0.85}$FeSb, compare the microstructure of the fracture surfaces of the HP, HP+HPT and the HP+HPT...
annealed samples. Grain sizes of the HP sample ranging from 0.1 to about 10 µm are reduced to less than 2 µm after HPT. However, during annealing the grains grow and show a rather homogeneous size. TEM images (Fig. 24) confirm these findings and show that the dislocation density in the HPT sample is enhanced by almost two orders of magnitude (for details on the thermoelectric HH phase TixNb1-xFeSb, please see Ref. 37).

6. Bismuth Tellurides

This type of non-skutterudite alloys belongs to the group of semiconductors and shows its maximum of the figure of merit ZT typically around T = 400–500 K, mainly due to the maximum of thermoelectric power and the minimum of phonon thermal conductivity at this temperature.

Attempts to improve ZT mainly concern macroscopic deformation processes. Already with elastic deformation, some tuning of the band gap is possible especially when the deformation induces a phase transition. The paper of Ovsynnianikov et al.40 is an example the effects of which can follow from applying elastic hydrostatic pressures between 2–25 GPa in Bi2Te3 and Sb2Te3: whilst pressures till 4 GPa already enhance the power factor PF due to a transition from semiconductor to metal characteristics, the rhombohedral R3m phase of these compounds undergoes a phase transition into a monoclinic C2/m lattice. This transition, however, deteriorates PF in case of p-type Bistellurides, while it increases it continuously till pressures of 25 GPa in case of Se-doped n-type tellurides because of a continuous increase of electrical conductivity. Biswas et al. also present a simple technical model with diamond anvils for a compact thermoelectric high-pressure module, which provides both a permanent pressure and a heat sink.40

First ideas for applying plastic deformation for the sake of improvement of ZT in those alloys were to re-orient the TEs’ crystal lattice by plastic deformation for the sake of increasing the electrical conductivity i.e. achieve a texture along (00f) and thus maximize conductivity. The first real experiments with application of plastic deformations go back to the nineteen-nineties when Seo et al.41 applied hot extrusion (HE) to p-type Te-doped Bi0.5Sb1.5Te3 and n-type Sb1-doped Bi2Te2.85Se0.15 thermoelectric compounds, within 573–713 K. Besides the improvement by doping with Te and Sb, the figure of merit could be improved by a factor 3, by applying HE and increasing the HE temperature, arriving at ZT = 0.87 at RT, probably mainly due to the increase of electrical conductivity.

One of the first works trying generation of lattice defects (i.e. grain boundaries by nanocrystallization) in these semiconductor materials was that by Yu and colleagues in 200942 who reached a ZT = 0.94 at 398 K and/or at least...
$ZT = 0.7$ between $325\text{--}525\text{K}$, through BM, cold pressing and sintering between $473\text{--}773\text{K}$. This ZT was markedly higher than the former record-figure-of-merit achieved by Zone Melting (ZM)\(^{43}\) being $ZT \approx 0.75$ only.

A significant increase of $ZT$ in these materials was presented also in 2008 by Poudel et al.\(^{44}\) and Ma et al.\(^{45}\) who reached a peak $ZT = 1.4$ at $373\text{K}$ in p-type $\text{Bi}_2\text{Sb}_2\text{Te}_3$ bulk ternary alloys through reductions in thermal conductivity by means of nanocrystallization and defect generation. The latter was achieved by suitable ball milling and high pressure consolidation.

The first real use of an SPD method has been done by Im et al.\(^{46}\) in 2004 who chose a multi-pass ECAE (called also ECAP) method at a temperature of $773\text{K}$. However, the ZT values reached by Seo et al.\(^{41}\) could not be overcome. The same is true with the ECAE experiments performed by Fan et al.\(^{47}\) in 2008, as well as by Hayashi et al. carried out in 2006\(^{48}\) and 2010\(^{49}\) although in the latter work they tried to optimize the ECAE route with regard to a (001) texture for the sake of maximizing the electrical conductivity. In 2008 another treatise concerning ECAE processed $\text{Bi}_0.5\text{Sb}_1.5\text{Te}_3$ compound was undertaken by Lim et al.\(^{50}\) at temperatures $653\text{--}733\text{K}$ arriving at a still considerable grain size of about $10\ \mu\text{m}$ which explains that the figure of merit reached the same values as did the previous ECAP works i.e. $ZT = 0.9$ at RT.

A much better ZT value could be achieved by the group of Sun et al.\(^{51}\) in 2008 who chose a multi-pass ECAE (called also ECAP) method at a temperature of $773\text{K}$. However, the ZT values reached by Seo et al.\(^{41}\) could not be overcome. The same is true with the ECAE experiments performed by Fan et al.\(^{47}\) in 2008, as well as by Hayashi et al. carried out in 2006\(^{48}\) and 2010\(^{49}\) although in the latter work they tried to optimize the ECAE route with regard to a (001) texture for the sake of maximizing the electrical conductivity. In 2008 another treatise concerning ECAE processed $\text{Bi}_0.5\text{Sb}_1.5\text{Te}_3$ compound was undertaken by Lim et al.\(^{50}\) at temperatures $653\text{--}733\text{K}$ arriving at a still considerable grain size of about $10\ \mu\text{m}$ which explains that the figure of merit reached the same values as did the previous ECAP works i.e. $ZT = 0.9$ at RT.

The second SPD method applied to V-VI and/or V2-VI3 alloys has been High Pressure Torsion (HPT), by M. Ashida et al.\(^{52,53,55}\) and T. Hamachiyo et al.\(^{54}\). Investigations have been done with the stoichiometric alloy $\text{Bi}_0.5\text{Sb}_1.5\text{Te}_3$ produced by ball milling (BM) or Vertical Bridgman Method (VBM), sintered by hot pressing at $673\text{K}$, and then HPT-processed at $473\text{K}$ under a pressure of $6\ \text{GPa}$ and rotated by speeds of $0.1\text{--}1\ \text{rpm}$. A combination of VBM and HPT using high HPT rates yielded power factors (PFs) as low as $4 \times 10^{-3}\ \text{Wm}^{-1}\text{K}^{-2}$. However, modifying the processing route by starting with BM followed by a low-rate HPT of $0.1\ \text{rpm}$ provided a power factor being around $6 \times 10^{-3}\ \text{Wm}^{-1}\text{K}^{-2}$ within a temperature interval from $320\text{--}470\text{K}$\(^{55}\) (see also Fig. 26). This increase of PF could be attributed partially to the low-rate HPT’s texture evolution which proceeded along (001), and partially to the enhanced Seebeck coefficient,\(^{55}\) Fig. 26. Unfortunately, the works\(^{52-55}\) did not present the thermal conductivity, which is necessary to reliably estimate the ZT-value resulting from these experiments. According to the authors’ promising experiences from Skutterudites (see this article) and from the results from other techniques of plastic deformation applied to the tellurides mentioned above,\(^{44,45,51}\) one can hope that HPT could be very successful in further enhancing the ZT value through the generation of lattice defects acting as additional scattering centers for further decreases of the thermal conductivity.
conductivity and thus increases of ZT. Among the numerous methods of plastic deformation, HPT seems to provide the highest number of advantages: (1) HPT is the most powerful method achieving a maximum of lattice defects, not at least thanks to the enhanced pressure which allows for very large strains without developing cracks and failures; (2) HPT can achieve bulk nanocrystalline samples directly from powders; (3) HPT does not introduce a strong texture or – under certain conditions – can achieve (00ℓ) textures at elevated processing temperatures and low processing rates which maximize the electrical conductivity in those Te-composites.

There have been done also some but only few treatises to improve ZT in PbTe, e.g. by Biswas et al. in 2012,56) who doped this alloy with Na, or with SrTe and Na, and applied processing by Spark Plasma Sintering (SPS) where the sample is quickly molten and sintered under pressure. With this processing technique, small scale second phase particles were formed with both phase boundaries for small particles with strain fields around them, as well as with misfit boundary dislocations at the larger ones could be generated. Such defects have been intentionally produced in order to provide additional scatterers for phonon scattering thus giving a minimum of lattice thermal conductivity. In the best case, values of figure of merit till $ZT = 2.2$ at 900 K were reached.

In what follows, more recent developments are described which concern the specific scattering properties of the various lattice defects. A marked step herein was given by the paper of Kim et al.57) which emphasizes the high scattering power of dislocations (especially closely neighboured ones): In contrast to point defects as well as grain boundaries which preferably scatter high and low frequency phonons, respectively, the dislocations cover the broad intermediate range of phonons with medium frequency (see Fig. 27). By aimed introduction of such dislocations through liquid phase compacting process of melt-spun eutectic compound of stoichiometric Bi$_0.5$Sb$_1.5$Te$_3$ with pure Te, Kim et al. showed that the ZT value can be increased up to $ZT = 1.89$ (Fig. 27) compared to $ZT = 0.91$ of the ingot or BM initial material and to $ZT = 1.4$ reported by the works of Poudel44) and Ma45) using BM and Hot Pressing (HP) for these p-type BiSbTe compounds. It has been shown by the authors of this article56) that a nanostructure with a regular dislocation array in the grain boundaries indeed gives the lowest lattice thermal conductivities possible (near to the theoretical minimum) thus enabling records in ZT of 1.5 for p- and almost 2.0 for n-type skutterudites. That arrangement has been achieved by high temperature HPT. In a paper of Park & Lee,58) published one year after that of Kim,57) they recommend to apply this SPD technique also to BiSeTe compounds. Recently an extensive work on n-type V$_2$VI$_3$ alloys was published by Hu et al.59) who for the first time report the optimization of TE properties by applying a special way of hot deformation (HD, called “progressive”). By choosing a large number of HD counts but not too high HD temperatures (at maximum 723 K) to account for a low electrical conductivity as well as for a sufficient number of lattice defects including dislocations and grain boundaries, at a grain size of only 60 nm, they reached record values of $ZT = 1.3$ in Sb-doped n-type Bi, at $T = 470$ K (Fig. 28).

Fig. 27  A: Spectral lattice thermal conductivity $\kappa_a(f)$ with different contributions of phonon scattering. Dislocation scattering is operative over the whole frequency range, in contrast to boundaries and point defects which mainly scatter phonons with low or high frequencies, respectively. B, C: Lattice thermal conductivity $\kappa_l$ (left bottom, B) and figure of merit $zT$ (right, C) for melt-solidified (BM), solid-phase compacted (S-MS), and liquid-phase compacted (Te-MS) Bi$_0.5$Sb$_1.5$Te$_3$ alloys. Only the latter contains dislocations embedded in grain boundaries which cause a large overall phonon scattering, thus minimizing the lattice thermal conductivity and maximizing the figure of merit (from Kim et al., Ref. 57)).
7. Mechanical Properties of Skutterudites and Half-Heusler Alloys

So far for many HPT-processed materials, mechanical properties have been measured. The details about the equipments, measurements and evaluations of the data are described in Refs. 3, 60, 61). Here only room temperature data are discussed, and only examples, typical of the general behavior, are presented here.

The values of the elastic moduli, independent of the preparation steps (HP + HPT, CP + HPT, CP + HPT-annealed or HP + HPT-annealed) of HPT-processed skutterudites are not much different from those of the respective HP ones. Also a slight change in the samples’ density has not much influence. For example, all Young’s moduli (E) for HP, CP + HPT and CP + HPT-annealed p-type DD0.7Fe3CoSb12 are in the range of 136 GPa ≤ E ≤ 144 GPa;34) for ball-milled and HP DD0.8Fe3CoSb12, E = 150 GPa, after HPT one gets E = 153 GPa, which is practically the same value considering 3% uncertainty. Also for (Mm,Sm)Co4Sb12 there is no change in E within the error bar, independent of the number of revolutions, with all values 142 GPa ≤ E ≤ 145 GPa.35)

The values of hardness of HP skutterudites and of HH alloys are, besides the composition, strongly dependent on the density. As shown in Fig. 29, generally n-type HP skutterudites are harder than p-type skutterudites for a large variation of density. After HPT-processing, the grains are much smaller and, as a consequence of the Hall-Petch relation, hardness must be higher, which is indeed the case for the p- and n-type skutterudites, independent of the preparation method HP + HPT or CP + HPT. Hardness of HPT samples also depends on the processing conditions, i.e. samples processed with more than one revolution have much higher values, especially prominent for (Mm,Sm)Co4Sb12 prepared by five revolutions (sample CP + HPT-5r). As HPT-processed samples exhibit a gradient in strain along the radius, the hardness depends on the distance from the sample’s center as depicted in Fig. 30. For example, DD0.6Fe3CoSb12, with an overall density of 97% after HPT (4 GPa, 1 revolution, 623 K) exhibited a hardness of HV = 498 in the center section of the sample and HV = 522 at the rim.5) It is interesting to note that (i) the hardness of HH alloys generally is much higher than that of skutterudites and (ii) the difference in HV between center and rim area is larger for the HH alloys. These observations are in contrast to those of Masuda et al.,17) as they claimed that no difference in the hardness between rim and center occurred when they measured their HP + HPT-processed (5 GPa, 10 revolutions) Heusler alloys.

Besides all these facts, for HP + HPT samples the starting conditions play a role. Hand milled (HM) and ball milled samples of DD0.44Fe2.1Co1.9Sb12 were HPT-processed under the same conditions (4 GPa, 1 revolution, 623 K). The HM + HP sample had a density of 95.2%, and HV = 393, which changed to 94% and a much higher hardness HV = 479 (rim) after HPT resulting in an enhancement of 22%. The BM + HP sample had a density of 98.3% and HV = 410. After HPT, HV was increased to 562 (rim), which equals 37%, Ref. 7).

Generally after HPT and HPT annealing, no noticeable changes in the elastic moduli occurred. Due to the changing strain from the center to the rim of a circular sample, hardness values are higher in the rim than in the center area but in any case higher than those of the HP sample although their density is lower.
8. Thermal Expansion of Skutterudites

Thermal expansion exhibits a quite unusual behavior after HPT-processing, related to the behavior of the temperature dependent electrical resistivity. As all temperature dependent curves of the thermal length change exhibit the same features, exemplarily the thermal expansion of DD$_{0.6}$Fe$_3$CoSb$_{12}$ is shown (Fig. 31) and discussed.

In the low temperature range (4.2–300 K), no anomalies for the HPT sample are visible, however, above 300 K the curve is not strictly linear anymore, and at ~443 K instead of further expanding, the sample contracts. At about 470 K the expansion continues. The anomaly occurs in about the same temperature window in which the electrical resistivity starts to decrease after a maximum; obviously the ‘shrinking’ of the sample is connected with the annealing of defects and/or disappearance of cracks. As can be seen in Fig. 31, with decreasing temperature as well as for a second run with increasing temperature, no anomalies appear. It should be added that thermal expansion was not only measured in the pressing direction as imaged in Fig. 31, but also perpendicular to it, showing the same behavior. All thermal expansion coefficients of HPT-processed samples hardly differ from those of the HP samples and are listed in Ref. 9).

9. Conclusions

This article is to show that SPD-processing of thermoelectrics can provide values of figure of merit (ZT) higher than 1.2, and thus gets highly attractive for materials which enable sustainable generation of electric power. These high values arise from the ultrafine grained microstructure in combination with a high level of point, linear and surface lattice defects which significantly enhances the scattering of the phonons, thus leading to a minimum of thermal conductivity and therefore to exceptional values of ZT. The extent of SPD-induced enhancement depends on the special thermoelectric materials. So far, the following thermoelectrics have been tried to get improved by SPD processing:

1) From all thermoelectrics, n- and p-type skutterudites benefit most from SPD-processing especially if one applies high pressure torsion (HPT) to already hot-pressed or still powdered materials thus producing thermoelectric bulks. Significant enhancements of figure-of-merit ZT for n-type skutterudites from 1.6 to almost 2, and for p-type skutterudites from 1.15 to almost 1.5 at 825 K could be achieved.

2) HPT-processing of Heusler and Half-Heusler phases yields about the same relative improvement of ZT (0.22 to 0.3) as skutterudites, although the absolute values still appear limited. However, SPD-induced increases of ZT achieved in Clathrates were found to be nearly negligible.

3) Low temperature thermoelectrics like Bismuth Tellurides of type V$_1$(VI)$_1$ and/or V$_2$(VI)$_3$ (with V, VI representing the group elements) show a considerable potential in SPD-induced increases of ZT. Already with high temperature pressure after ball milling, ZT could be enhanced from ZT $\sim$ 1.0 up to ZT $\sim$ 1.4 at T $\sim$ 373 K, at least by ensuring a high electrical conductivity while considering the strong anisotropy in these materials. Therefore the choice of the best SPD-processing technique includes the careful optimization of texture, but also that of the processing rate and temperature. Recent investigations underline the importance of the lattice defects’ specific phonon scattering efficiencies - especially those of dislocations - and their generation in sufficiently high densities, thus reaching enhancements of p-type Bi-Tellurides up to ZT = 1.9.

As concerns the mechanical properties of SPD-skutterudites and Half-Heusler-alloys, the application of SPD methods significantly raises the strength while the elastic moduli remain unchanged unless new phases have been formed.

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