Influence of Phase Composition on Thermoelectric Performance of $CoSb_3$ Skutterudites

C. Stiewe[1], M. Toprak[2], D. Platzek[1], E. Müller[1], M. Muhammed[2]

[1] German Aerospace Center (DLR), Inst. of Materials Research, D-51170 Cologne, Germany
[2] Royal Institute of Technology, Materials Chemistry Division, SE-10044 Stockholm, Sweden
e-mail: christian.stiewe@dlr.de, phone: +49 2203 601-2662, fax +49 2203 961215

Abstract

Recently, nano-structured Skutterudite materials have been prepared following a newly developed route of chemical co-precipitation. This technique has the advantage of relatively low preparation temperatures compared to conventional metallurgical methods, thus retaining the nano-structure of small-grained powders. Furthermore, the low process temperature makes this technique more attractive for industrial use because of shorter time consumption for preparation and easier upscaling.

Up to now highest figure of merit was measured on samples with a certain level of Nickel and Tellurium substitution for Cobalt and of Antimony, respectively. A specific phase composition of $CoSb_3$, $CoSb_2$ and Sb was observed in these samples by means of powder X-ray diffraction (XRD) followed by Rietveld refinement. This composite showed up to have better thermoelectric properties than single-phase $CoSb_3$.

In order to get a better insight of how the phase composition affects the TE properties, a series of Ni- and Te-doped $CoSb_3$ samples with various percentage of phase impurities have been prepared, characterized and evaluated with regard to their thermoelectrical properties and their behaviour under the influence of external magnetic fields.

Introduction

The Skutterudite material is a very promising candidate for a so-called phonon glass electron crystal (PGEC [1]), because of its low specific resistance which is related to covalent bonding and low thermal conductivity, caused by the large number of atoms per unit cell [2]. The Skutterudite structure has the space group $Im\bar{3}$ and can be seen as cubic Co frame building eight formula units in the primitive cell, six of which are occupied by Sb atoms, forming almost square planar Sb_4 rings. The remaining two voids are usually filled with rare earth atoms, so called "rattlers", acting as point defect scattering centers for the heat carrying phonons, thus reducing the thermal conductivity. Fig. 1 shows the structure of such a filled Skutterudite.

However, the thermal conductivity of these systems is still too high for a good thermoelectric material. Several attempts have been made to increase the efficiency of this material, indexed by the figure of merit ZT, by reducing the thermal conductivity and raising the electrical conductivity at the same time [3].

Increasing the concentration of grain boundaries as a further approach is expected to lower the thermal conductivity already in unfilled skutterudites, due to scattering of the heat carrying phonons. In this work powders with very small grain sizes have been prepared and compacted to pellets for evaluation of the TE properties.

The expected influence of boundary scattering on the charge carriers, resulting in an as well reduced electrical conductivity was counter-balanced by the addition of Ni and Te atoms, respectively. This also offers the opportunity of achieving charge balance when filling the voids with rare earth atoms. Combined substitutions of Ni and Te have been tested, too.

We have reported earlier about the investigations on the most suitable doping level of Ni and Te [4] with up to now largest ZT values of unfilled Skutterudite 0.67 at 680 K. These samples revealed a significant content of $CoSb_2$ leading to the question how additional phases affect the thermoelectric properties.

Experimental

$CoSb_3$ precursors with 8% Ni substitution on the Co sites and 3% Te substitution on Sb sites, respectively, were prepared as oxalates by chemical co-precipitation from aqueous solution [5]. Subsequent thermal treatment formed the desired skutterudite phase and yielded in powders with grain sizes of about 40 nm [6], forming $Co_{0.92}Ni_{0.08}(Sb_{0.97}Te_{0.03})_3$. Two powder batches have been prepared and various amounts of pure Sb and $CoSb_2$, respectively, and combinations of both have been added afterwards (see Tab. 1). All powders were kept under hexane during transport and handled in a glove box under nitrogen atmosphere to rule out contamination of oxygen. Pellets for evaluation of the thermoelectric properties were produced by hot uniaxial pressing (HUP) of the powders at 853 K under 100 MPa for 30 min.

X-ray powder diffraction analysis (XRD) and Rietveld refinement were performed to reveal the phase composition of the samples and for calculating the lattice parameter.

Measurements of the Hall coefficient between 25 and 300 K gave information about the kind of charge carriers, their temperature dependend concentration and mobility.

The temperature dependence of the electrical and thermal conductivity as well as the Seebeck coefficient and the figure of merit were investigated in the range from room temperature up to 500 °C under vacuum using various facilities both commercial and self-built ones. The electrical conducitivity was measured by the Hall effect device in the low temperature region and by a simple 4-point-probe setup above room temperature, respectively. Seebeck coefficient investigation was performed by a differential technique applying several temperature gradients for each data point. Thermal conductivity has been calculated from measurements of the thermal diffusivity by Laser Flash Apparatus (LFA) and heat capacity determined by Differential Scanning Calorimetry (DSC).

Table 1: Overview of two batches of nano-structured Skutterudite samples $Co_{0.92}Ni_{0.08}(Sb_{0.97}Te_{0.03})_4$ with different content of Sb and $CoSb_2$ phases (percentages are vol.-%)

add. Phases	**2,61% Sb 0% $CoSb_2$**	**1.29% Sb 0% $CoSb_2$**	**0.13% Sb 1.55% $CoSb_2$**
Batch 1 Labels	2207 – D122	1904 - D110	1905 - D111
Density [g/cm³]	7.23	7.26	7.46
% theor. Density	94.6	95	97.7
Lattice const. [Å]	9.0444	9.0454	9.0443

add. Phases	**1.87% Sb 0% $CoSb_2$**	**0.22% Sb 3.88% $CoSb_2$**	**0.43% Sb 5.25% $CoSb_2$**	**0.08% Sb 4.77% $CoSb_2$**
Batch 2 Labels	2136 - D113	2141 - D119	2138 - D120	2140 - D121
Density [g/cm³]	7.34	7.36	7.07	7.21
% theor. Density	96.1	96.4	92.6	94.4
Lattice const. [Å]	9.0448	9.0441	9.0467	9.0438

Results and Discussion

Skutterudites are very sensitive to slight deviations from stoichiometry. This way the thermal and electrical properties are likely to change between different batches of preparation because of self doping and even if the nominal composition is the same. For this reason the two prepared and measured batches are interpreted independently in order to separate the effect of phase composition from doping.

The 1st batch samples contain either about 1% $CoSb_2$ or pure Sb as impurity phase to the $CoSb_3$ one. With the 2nd batch one sample (D113) had additional Sb phase while for the other specimen (D119 to D121) the content of $CoSb_2$ has been varied. No significant Sb was detected here.

Figures 1 and 2 display the temperature dependence of the electrical and thermal conductivity and Seebeck coefficient for these samples.

The thermal condutivity shows room temperature values of approx. 5 W/(m·K) decreasing with increasing temperature for all samples investigated. There is hardly any dependence on the phase composition or variation in carrier concentration among the samples, proving the reducing effect of the nano-structuring on the heat conduction compared to usual polycrystalline samples (approx. 10 W/(m·K) at r.t. [7]). The reduction in κ with increasing temperature up to 400 °C is due to increased phonon-phonon scattering and Umklapp processes.

All samples exhibit metallic behaviour in their electrical conductivity at low temperatures. A minimum in the σ(T) dependence indicates the transition to an intrinsic semi conductor with increasing conductivity at higher temperatures. The temperatures for these minima vary among the samples.

The electrical conducitvity is about 300 to 400 S/cm and differs slightly between the specimens, thus showing only small variations in doping, except for the sample D110, exhibiting high conducitivity of 900 S/cm at 25 K decreasing to approx. 550 S/cm above room temperature. This causes an exceptionally large electrical contribution to the thermal conductivity in this sample, which is evident from Fig. 1. When the lattice thermal conductivity is reduced at higher temperatures the electrical part becomes more effective,

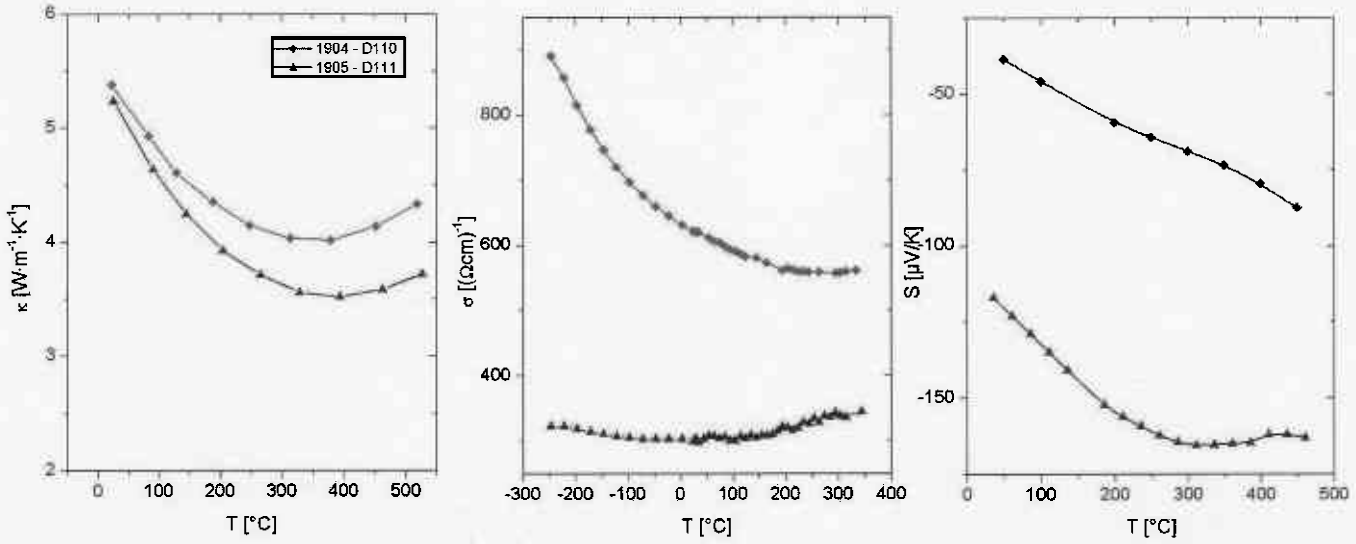

Fig. 1: Thermal, electrical conductivity and Seebeck coefficient of batch 1 Skutterudite samples. Note the different temperature ranges.

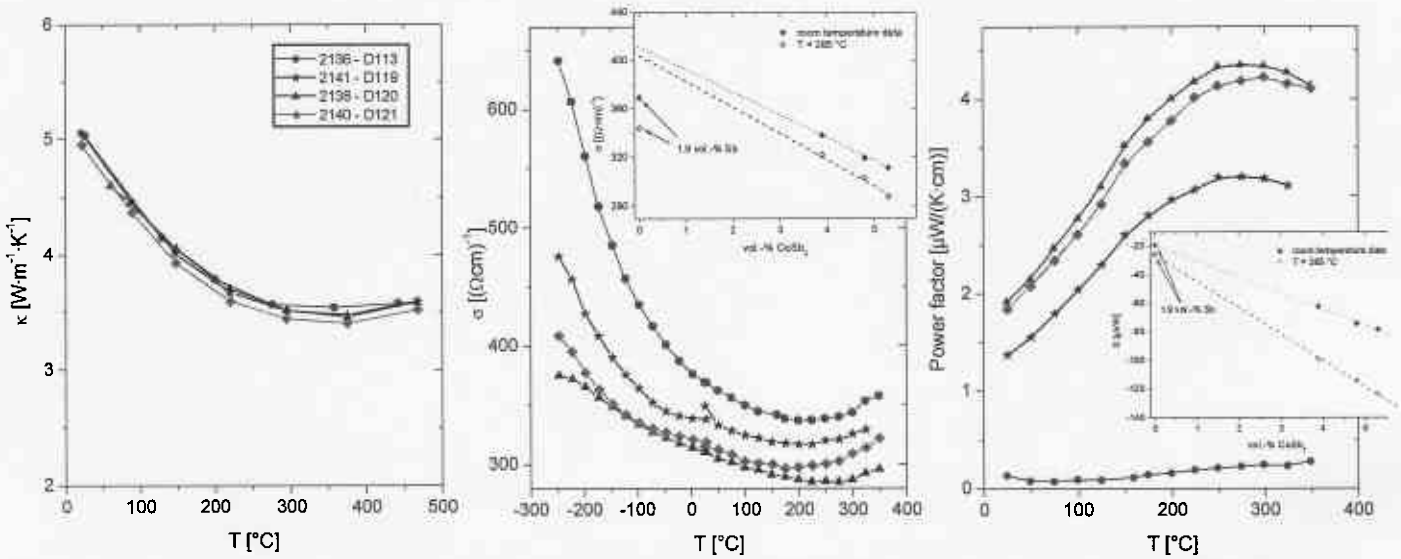

Fig. 2: Thermal and electrical conductivity and power factor of the 2nd batch Skutterudite samples. Note the different T ranges. Insets show data for σ and S with varying phase composition at room temperature and 285 °C, respectively.

especially in the sample D110, while the samples of the 2nd batch exhibit similar electrical and the very same thermal condutivity, see Fig. 2. The insulating $CoSb_2$ reduces σ directly proportional to the actual content percentage (see inset in Fig. 2). Linear extrapolation to the 0 %, i.e. to pure $CoSb_3$ results in higher values for σ compared to the Sb added sample. This might lead to the assumption of phase clean samples having the best performance. But the results of the Seebeck coefficient measurements contradict this picture, showing the inverted behaviour. While the undoped $CoSb_3$ sample is p-type with positive Seebeck coefficient, all doped samples exhibit negative S values, confirming the electrons as major charge carriers due to the doping with Ni and Te. The absolute values of S scale with the amount of $CoSb_2$ content and, if linearily extrapolated to 0 % $CoSb_2$, match the values obtained on the Sb added samples. These are reduced in the whole temperature range to values as low as S = -40 μV/K at r.t. for 1.29 at.-% Sb and -20 μV/K at r.t. for 1.87 at.-% Sb, respectively.

The measurement of Hall effect on these samples revealed not only a strongly non-linear relation between the voltage U_H and the magnetic field B, but an unsymmetry in the direction of B. The origin of this unexpected result is twofold and can be explained after a separation of the measured Hall voltage into an odd and an even part, see Fig. 3. A missalignment of the electrical contacts used for Hall voltage pickup usually causes a constant offset. In case of the nano-structured Skutterudites a variation of the electrical conductivity with the magnetic field has been found. This magneto resistance causes a varying voltage offset, being the even contribution to U_H. Fig. 4 shows the temperature dependence of $\Delta\sigma/\sigma_0$ with σ_0 the conductivity when no external field B is applied. The largest value of 17.5% reduction at 25 K was observed for the doped sample with Sb addition, whereas $CoSb_2$ addition seems to be able to reduce the magneto resistance from approx. 7 to 4%. This can be explained using Landau curves for the charge carriers in a magnetic field that are longer and thus more effective in samples of high charge carrier mobility compared

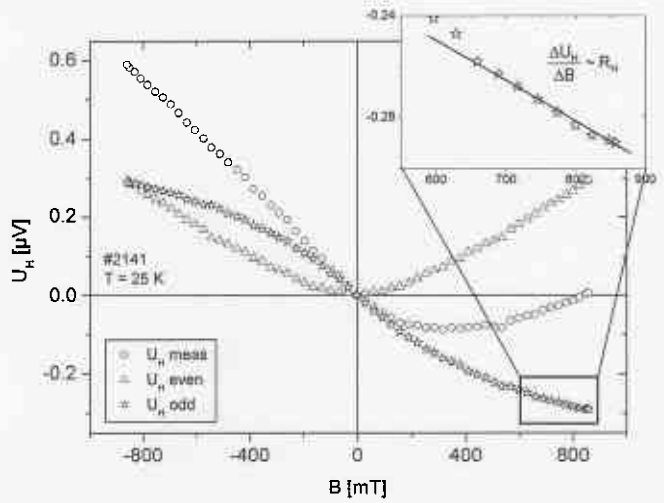

Fig. 3: Hall voltage measurement, even and odd contribution at 25 K. The even part is corrected for the offset at B=0. Inset shows area used for calculation of R_H.

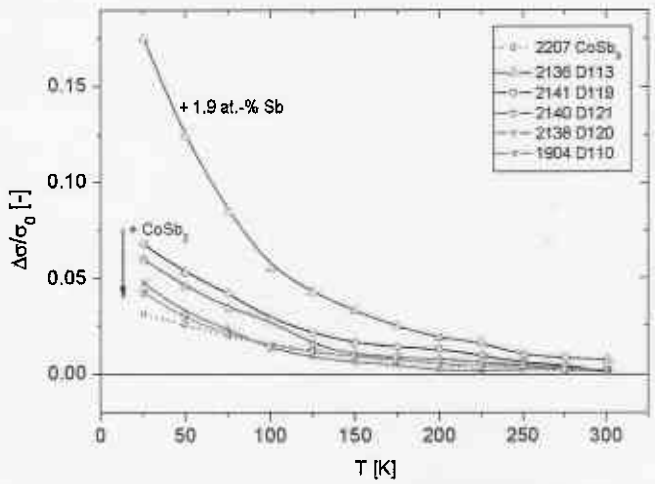

Fig. 4: Magneto resistance in Ni and Te doped Skutterudites containing various phase impurities.

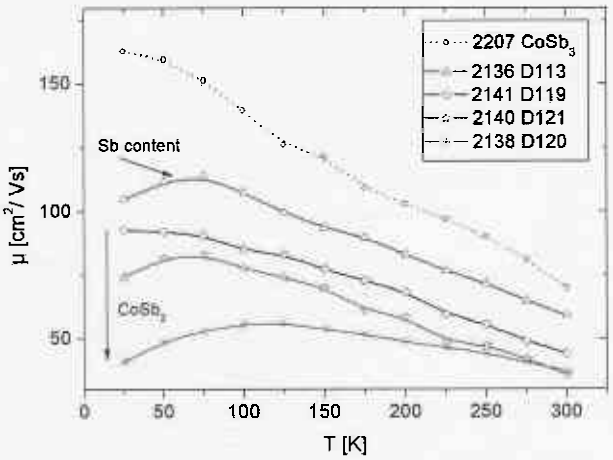

Fig. 5: Charge carrier mobility of Ni and Te doped Skutterudites containing various levels of phase impurities.

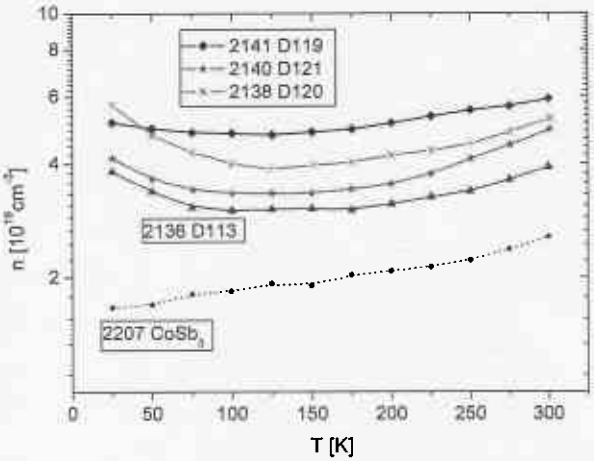

Fig. 6: Charge carrier density of nanostructured Skutterudites.

to the reduced mobility in the $CoSb_2$ containing specimens. Fig. 5 displays mobility data of these samples, showing largest values at low temperature, decreasing to higher temperature because of increasing scattering with phonons. When electron phonon scattering takes over the influence of $CoSb_2$ vanishes.

The odd part of the Hall voltage (see Fig. 3) shows a significant deviation from linearity, suggesting a strong magnetic behaviour of the material. The reference measurement on undoped $CoSb_3$ did not show such magnetic effects. For this reason the Ni has to be adressed. Indeed $CoSb_3$ has been found diamagnetic whereas the addition of Fe or Ni changes the material to paramagnetic [8]. In order to get the correct values of the Hall coefficient only the Hall voltages around the maximum magnetic field have been used for the calculation. Here the Hall voltage varies nearly lineary with magnetic field strength. For technical reasons this strength could not be increased further in order to be sure of the linearity. The inset in Fig. 3 shows the procedure and gives evidence for the assumption of linearity.

From the Hall coefficient the charge carrier density n was calculated assuming a single parabolic band using $n=-(R\cdot e)^{-1}$ where e is the charge of the carrier. Fig. 6 provides the data obtained this way. All investigated samples exhibit densities in the range of heavily doped semi conductors, including the nominally undoped specimen. This fact might be due to the exess antimony, detected by XRD. For the Ni/Te doped samples the carrier density is raised for both Sb and $CoSb_2$ added material, but no clear dependence on phase composition can be seen.

Conclusions

Nanostructured $CoSb_3$ Skutterudites doped with Ni and Te containing various amounts of Sb and $CoSb_2$ as additional phases have been prepared and investigated due to their thermoelectric properties and charge carrier concentration and mobility.

Evidences have been found that both excess Sb and $CoSb_2$ reduces the electrical conductivity slightly. While Sb addition leaves the Seebeck coefficient almost unchanged the absolute values of S scale linearily with $CoSb_2$ amount, thus providing an opportunity of improving the performance of a material already adjusted to the best doping level. Thermal conductivity has been found strongly reduced compared to literature data of highly annealed samples and very similar for all samples under investigation. Hardly any influence by doping and Sb or $CoSb_2$ addition could be seen, proving that the reduction in κ is caused by the nano-structuring.

As the most interesting result the materials' behaviour under the influence of an external magnetic field was found to be unsymmetric in field direction. This could be explained by two superimposing effects: 1.) A magnetoresistance together with an intended mismatch in the electrical contacts leading to an even offset to the Hall voltage depending on the magnetic field strength. 2.) The remaining odd part in the voltage measurement is affected by the magnetic behaviour of Ni. Its additional electron compared to Co is not for all temperatures transferred into the conduction band but is retained in a $3d^7$ state at low temperatures leading to the spin state S=1/2. This unpared spin changes the field dependence of the Hall voltage until saturation. So only the slopes of $U_H(B)$ at strongest magnetic fields were taken into account for calculating the charge carrier density.

Acknowledgments

This work was supported by European Community under contract number G5RD-CT2000-00292, NanoThermel project. Special thanks go to all partners in this project, i.e. to L. Bertini and C. Gatti (ISTM, Italy), to M. Rowe (NEDO Lab., U.K.), to M. Christensen and B. Iversen (University of Aarhus, Danmark), to A. Saramat, A. Palmqvist (Chalmers University of Technology, Göteborg, Sweden), to G. Noriega (CIDETE, Spain), L. Holmgren (LEGELAB, Sweden).

Very special thanks to S. Williams for technical and scientific discussions.

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