

# Anisotropy of the Seebeck Coefficient Detected by the Seebeck Scanning Microprobe

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## Abstract

Many thermoelectric materials with non-cubic unit cell show anisotropy of their thermoelectric parameters. Usually this effect is detectable on single or highly textured crystals by measurement of integral parameters of a bulk sample. From our study, the scanning Seebeck microprobe as a tool for the determination of local values of the thermoelectric power at any position on a sample surface with a resolution down to 10  $\mu\text{m}$  turns out to be a suitable instrument for a rough orientation analysis on single crystalline or coarse-grained thermoelectric samples.

The principle behind is that for a flat thermal contact area between of the sample and the probe similar in size or larger than the information area, the temperature gradient is preferentially directed perpendicular to the surface. This direction is heavier weighted in the obtained Seebeck value than the lateral one.

Thus, not only information about inhomogeneities, phase changes or grading of material becomes visible with this tool, but also an anisotropy in the Seebeck coefficient can be detected spatially resolved.

## The Scanning Seebeck Microprobe

A scanning Seebeck microprobe is a device for measuring the Seebeck coefficient on a samples surface spatially resolved to achieve information especially on the homogeneity or distribution of the components.

A heated probe tip is positioned onto the surface of a sample. The probe is connected with a thermocouple (in this case type T, Cu-CuNi) measuring the temperature  $T_1$ . The sample is in good electrical and thermal contact with a heat sink and also connected with a thermocouple measuring  $T_0$ . The probe tip heats the sample in the vicinity of the tip leading to a temperature gradient (see fig. 1).

Combining the Cu-Cu and the CuNi-CuNi wires of the thermocouples a voltage  $U_0$  and  $U_1$  is measured yielding the Seebeck coefficient  $S$  according to equations:

$$U_0 = (S_S - S_{Cu}) \cdot (T_1 - T_0) \quad (1)$$

$$U_1 = (S_S - S_{CuNi}) \cdot (T_1 - T_0) \quad (2)$$

Combining the Eqs. (1) and (2) we get

$$S_s = \frac{U_0}{U_1 - U_0} (S_{Cu} - S_{CuNi}) + S_{Cu}, \quad (3)$$

which is the Seebeck coefficient of the sample at the position of the probe tip [1]. Mounting the pointed probe to a three dimensional micro-positioning system allows the determination of the individual thermopower of each single sample position for a certain temperature, the easiest case room temperature (see Fig.2). The result is a two dimensional image of the Seebeck coefficient of the sample surface. The system is fully automatised, so that a computer controls the position of the probe as well as the measuring equipment and data. With this tool it is possible to get information about inhomogeneities, phase changes, anisotropy in the Seebeck coefficient, as well as about the grading of the material.

Recent improvement of the measuring device by the implementation of a cooling/heating system led to an expansion of the sample temperature ranging between about 30 K below and above room temperature and enables computer controlled repeated scans on the sample surface at different stabilised temperatures set in user defined steps. In this way, along with the sample homogeneity, the temperature dependence of the Seebeck coefficient near room temperature can be determined at different locations of the sample. A stainless steel vacuum recipient can be installed to protect the sample and the measurement equipment from external influences as there are moisture and ice forming on the sample's surface or thermal fluctuation due to ambient temperature changes, when using this option to measure temperature dependent scans[2].

An important condition of the measuring principle is that temperature difference between the probe and the sample must amount reproducibly to a few K. Thus, the gradient has to be adjusted by controlling the temperature of both probe and sample separately but simultaneously which has to be provided over the whole temperature range. Peltier elements were integrated for heating and cooling the probe head and the sample. Another Peltier cooler is attached to a heat sink. During operation of the facility the power supply for each cooling device is linked to a PID-controller. Since one data point is measured in about 4-5 seconds, the scanning of a regular sample with sufficient resolution takes a couple of hours for one temperature. Then, the next temperature point is automatically adjusted.

Different sample holders have been developed for an easy change of samples. A further option has been implemented to the apparatus, that several samples mounted into the heat sink can be measured in one run.

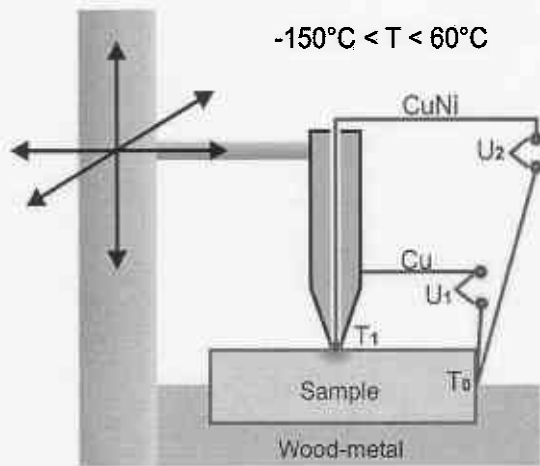


Figure 1. Principle of the spatially resolved Seebeck coefficient measurement. A small heated probe tip is set onto the surface of the sample that is embedded in a heat sink. Both, tip and heat sink are temperature controlled and can be moved via linear stages.

The thermal conductivity of the samples has a strong influence on the temperature gradient formed in the material and thus leading to the Seebeck voltage. Different probe tips have been developed to compensate this effect.

The Seebeck Microprobe meets the following specifications:

- Positioning accuracy: 1  $\mu\text{m}$
- Travel: x-direction 150mm, y-direction 50mm
- Local resolution: up to 10  $\mu\text{m}$ , depending on the thermal conductivity of the sample
- Measuring time: < 8s (typically 4s) per one data point;
- Reproducibility: better than 3% of the Seebeck coefficient
- Seebeck accuracy: better than 10% (for  $\text{Bi}_2\text{Te}_3$ -related materials)



Fig. 2: Set-up of the Seebeck Microprobe. Linear stages in x-, y- and z-direction allow for a scanning of the sample. The measurement is computer controlled and fully automatized.

## Anisotropy detecting with the SMP

Many material show an anisotropic behaviour in the electrical and thermal conductivity. Also several materials show an anisotropy in the Seebeck coefficient. Depending on the crystal geometry the Seebeck coefficient varies for example in  $\text{Sb}_2\text{Te}_3$  for about 20% in two directions, the c-axis and the axis perpendicular to the c-axis, the growing direction [3].

## Experiments

A  $\text{Zn}_4\text{Sb}_3$  ingot was prepared and the composition distribution was measured by Electron Probe Micro Analysis yielding an almost constant composition over the whole area of the ingot [4] whereas the Seebeck scans image different grains as very homogeneous areas which differ from each other by small but significant values. Adjacent faces of the sample with a common edge were scanned close to the edge by the Seebeck microprobe. Line structures of the sample allow for identifying the location of individual grains.

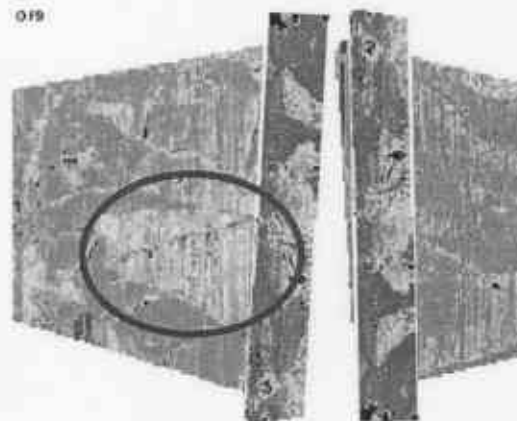


Fig. 3: SMP measurement of the same  $\text{Zn}_4\text{Sb}_3$  sample at different positions. The red marked area indicates a crystallite with different orientation and thus different  $S$  in the direction perpendicular to the top plane.

Fig. 3 shows a spatially resolved measurement of the Seebeck coefficient for the  $\text{Zn}_4\text{Sb}_3$  sample. The smaller bars are the measurements of the side face, perpendicular to the top face (left) and bottom face (right). Several individual crystal grains could be distinguished where the face perpendicular to the growth direction shows a different mean value of the Seebeck coefficient from the face parallel to the growth direction. The red circle indicates such a crystallite. As a conclusion, the difference in the values is due to the difference in crystalline orientation.

An Electron Probe Micro Analysis yields an almost constant composition over the whole area of the ingot, but still different structures are visible at a polished sample. Fig. 4 (top) shows an optical micrograph at another slide of the sample. The red marked part was also scanned with the Seebeck Microscope. This measurement

is shown in Fig. 4 (bottom). The different areas are clearly visible, in the optical micrograph as well as in the Seebeck coefficient.

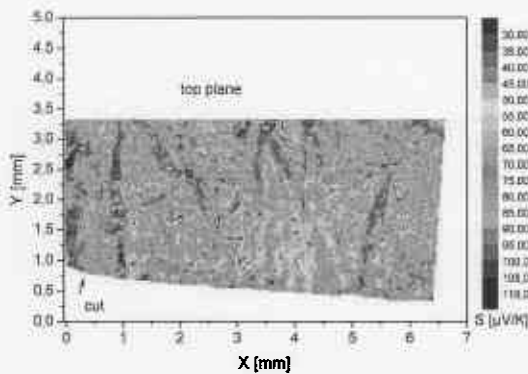


Fig. 4: Optical micrograph and SMP scans of a  $Zn_4Sb_3$  sample. The microscopy shows a structure that is clearly visible also in the Seebeck scan (see red marked area).

To confirm the results of the Electron Probe Micro Analysis (EPMA) an Energy Dispersive X-Ray analysis has been performed at the same position of the sample. The result is shown in Fig. 5. The material is completely homogeneous regarding the Zn part (lower diagram) as well as the Sb (upper diagram). Thus, this analysis provides no information about textures.

Obviously the behaviour shown in Fig. 4 is caused by an anisotropy of the crystals regarding the Seebeck coefficient. This is also confirmed by the fact of a different averaged Seebeck coefficient of top and bottom planes and base faces, respectively. These Seebeck scans are shown in Fig. 6 and Fig. 7. The side face again shows a different averaged Seebeck coefficient as the top and bottom faces. Furthermore a different structure becomes visible.

Since the thermo-voltage detected is a volume average over the information area, this direction is heavier weighted in the obtained Seebeck value than the lateral one. However, the anisotropy itself as the ratio of the Seebeck values along different crystal directions cannot be resolved because the value measured from differently



Sb La1



Zn Ka1

Fig. 5: EDX scans of the same area (red marked in Fig. 4) of the  $Zn_4Sb_3$  sample. The EDX analysis results in a completely homogeneous material, regarding the Zn part (lower diagram) as well as the Sb (upper diagram). Thus this analysis provides no information about textures.

oriented surfaces on a crystal contains in any case a mixture of contributions in normal and lateral direction, according to the shape of the spreading temperature gradient.

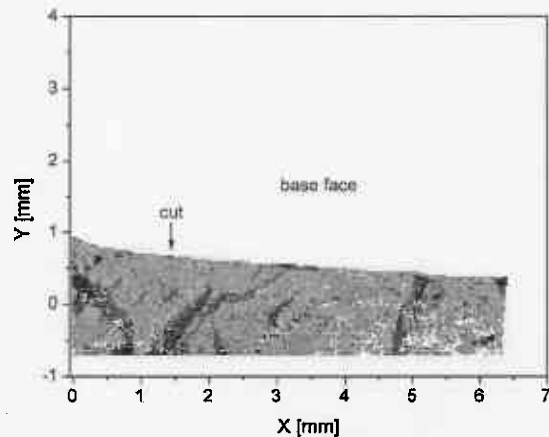


Fig 6: The side face shows a different averaged Seebeck coefficient as the top and bottom faces.

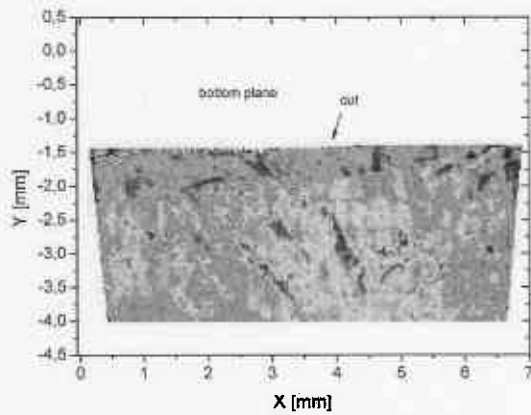


Fig 7: Bottom face of the same sample as in Figs. 4-6.

### Sb<sub>2</sub>Te<sub>3</sub> single crystal

Sb<sub>2</sub>Te<sub>3</sub> single crystals show an anisotropy of about 20 % of the c-axis and the axis perpendicular to the c-axis [3]. Thus a single crystal of Sb<sub>2</sub>Te<sub>3</sub> has been analysed with the Seebeck Microscope. The measurement scan of the cleavage plane is shown in Fig 8 (upper part).

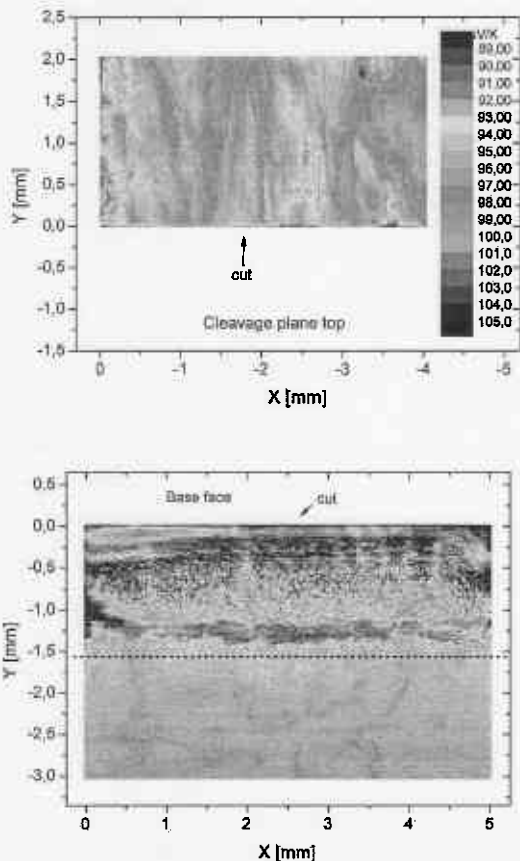


Fig. 8a and b: SMP measurement of a Sb<sub>2</sub>Te<sub>3</sub> single crystal. The SMP tip damaged the upper part of the base face perpendicular to the cleavage plane (2nd fig., b), the lower part shows a different orientation and was not affected.

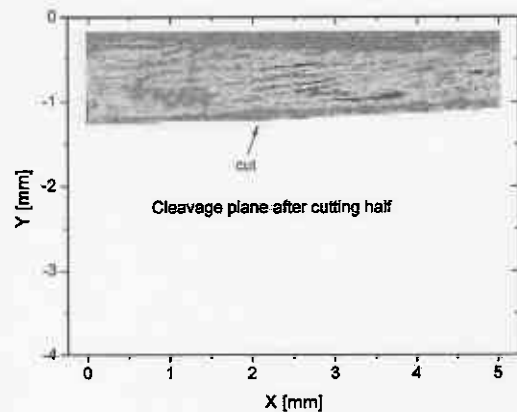


Figure 8c: The crystal was cut below the damaged part (see dotted line in the middle fig.) and the top plane was measured again. The crystal orientation has changed, the measurement is now perpendicular to the cleavage plane, also proven by the damages. The insert shows the orientation of the planes.

The Seebeck scan shows a light variation of the Seebeck coefficient leading to the structure visible in Fig 8 (upper part). Measuring the base face perpendicular to the cleavage plane the probe tip caused a mechanical damaging of this side. The tip went inbetween the layers causing a variation in the Seebeck coefficient. But the lower part of the sample was not damaged at all – in the same measurement. The Seebeck coefficient shows a very good homogeneity similar as in the measurement of the cleavage plane. Obviously the orientation has changed due to some reason during the growing process.

To compare this measurement with the Seebeck coefficient of the perpendicular side, the damaged part of the sample was removed (cut indicated by the dotted line) and again the same plane as in Fig. 8a (upper diagram) was measured. The result is shown in Fig 8c. The plane perpendicular to the homogeneous plane was again damaged mechanically and the Seebeck coefficient is more inhomogeneous.

This “single crystal” consists of different parts, where the growing direction has changed, proved by the Seebeck Microscope.

Theoretical analysis will be performed to characterise the degree of anisotropy more quantitative.

Anyway, these results provides experimental evidence that the Scanning Seebeck Microprobe is a suitable tool to detect the anisotropy of the Seebeck coefficient.

### Other applications

Fig. 9 (b) shows the local distribution of the Seebeck coefficient in a Czochralski grown single crystal (Fig. 9a) as described in [5]. The crystal was functionally graded during the growing process. The scale indicates the Seebeck coefficient surface distribution within the scanned area. Fig 9c shows the same measurement, but the Seebeck coefficient is also indicated by the magnitude of the z-axis to demonstrate the sharp edges. Fig 9 (d) shows

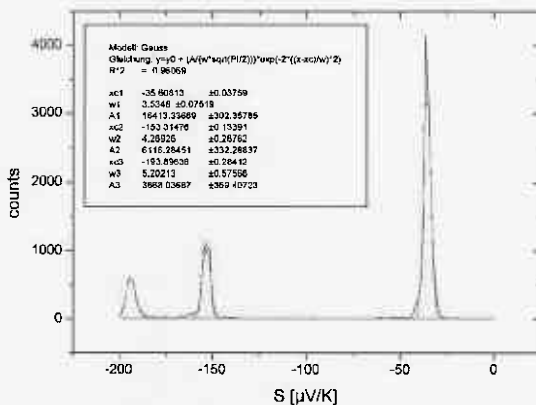
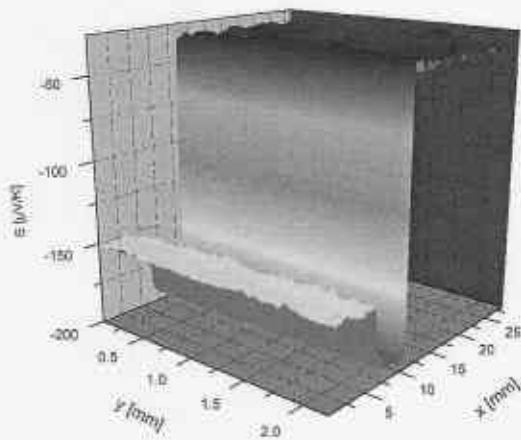
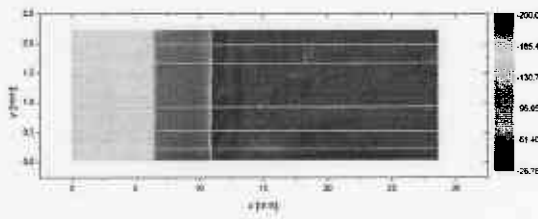
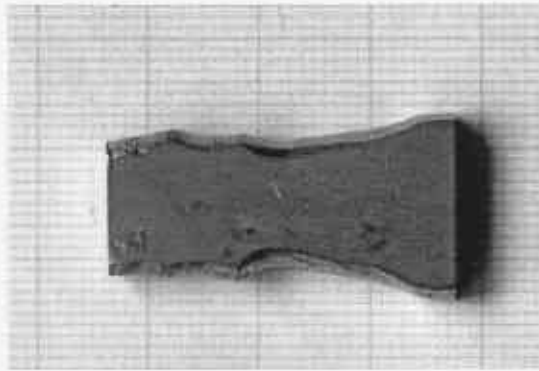


Fig. 9 a-d: The spatial (surface) distribution of the Seebeck coefficient in Bi<sub>2</sub>Te<sub>3</sub> based graded material. The quantitative analysis of the Seebeck coefficient value distribution, indicating three main peaks. The FWHM (full width at half maximum) gives a number for the homogeneity of the material.

the quantitative analysis of the measurement data, i.e. the Seebeck coefficient value distribution. Three peaks more or less broadened indicate the inhomogeneity of the sample. Hence, the material is composed more likely of three single materials than to be true graded. With these results the Czochralski process can be improved in order to optimise the functional grading of the sample.

## Conclusion

The scanning Seebeck Microprobe, also called “Seebeck Microscope”, and also a scanning electrical potential probe (to be published) are an elegant and important tool for the control of inhomogeneities, phase changes or grading of material and also for detecting anisotropies in the Seebeck coefficient. Even interdiffusion between single layers of stacked material can be detected to determine degradation.

## Outlook

For the year 2005 it is planned to commercialise the Seebeck Microscope and make it available as a product. For further information contact PANCO, Physics technology, development and Consulting, [www.panco.de](http://www.panco.de), email to [info@panco.de](mailto:info@panco.de).

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