ESRF	**Experiment title: "Determination of Sb-Te distribution in phase-change and thermoelectric materials of the system Ge-Sb-Te by single crystal diffraction using anomalous scattering techniques"**	**Experiment number**: HS-3785
Beamline: ID11	**Date of experiment**: from: 25.09.2009 to: 29.09.2009	**Date of report**: 26.02.2009
Shifts: **12**	**Local contact(s)**: Gavin Vaughan, Jonathan Wright	*Received at ESRF:*

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Report:

Aim

Metastable crystalline phases of multinary antimony tellurides are important as phase-change materials for optical and electrical data storage. The corresponding stable crystalline modifications can be regarded as candidates for thermoelectrics. Although some of these materials are already applied in technical devices, questions regarding structure-property relationships are still open, because many structural details have remained unclear.[1-5] This includes on the real-structures of the materials, e.g. short-range defect ordering, anti-site defects and concentration modulations in long-range ordered crystals. However, Sb and Te show similar diffraction contrast for conventional X-ray methods, and many interesting phases contain additional elements with similar form factors (e.g. In or Sn). Hence, the aim of our experiments at the ESRF beamline ID11 was to enhance the scattering contrast making use of anomalous dispersion effects at the K absorption edges of these elements (29.2 – 31.8 keV, i. e. 0.42 - 0.38 Å). The comparison of room-temperature and high-temperature data promises insight into diffusion processes associated with phase transitions.

Experiments and Results

In one part of the experiments, we obtained various high-resolution datasets of the two similar phases $Ge_{\sim 0.6}Sb_{\sim 0.4}Te$ and $Ge_{\sim 0.8}Sb_{\sim 0.2}Te$ at the Sb and Te edges as well as far away from the edges (30.49 keV, 31.81 keV, 28.65 keV). The excellent experimental conditions and good crystal quality allowed to collect complete datasets at various tremperatures containing Bragg reflections as well as pronounced diffuse intensities of a slightly distorted rocksalt type structure. The diffuse streaks vanish at temperatures around 300 °C. High temperature data sets at all interesting wavelengths were collected at 500 °C. The data indicate an order-disorder transition from a slightly distorted rocksalt type with partially 2D ordered cation defects to an idealized rocksalt type structure with random disorder of Ge, Sb and vacancies on cation positions. In this context, due to the high intensity of the X-ray source, we were also able to gain first in situ observations of

this temperature dependent order-disorder transition, however, only by snapshot exposures for single crystals fixed in one position, as shown in Figure 1. These data are preliminary, however, the complete data sets collected are very promising. Work on the structural characterization including simulation of the diffuse scattering and the observed phase transition is still in progress, however, the atom distribution in the average rocksalt type structure has already been refined including data measured at different energies. The data obtained at the ESRF promise further insight into the structural nature of phase-change materials which is especially interesting since the compositions of the single crystals investigated is close to the composition used for Blu-Ray disc data storage media.

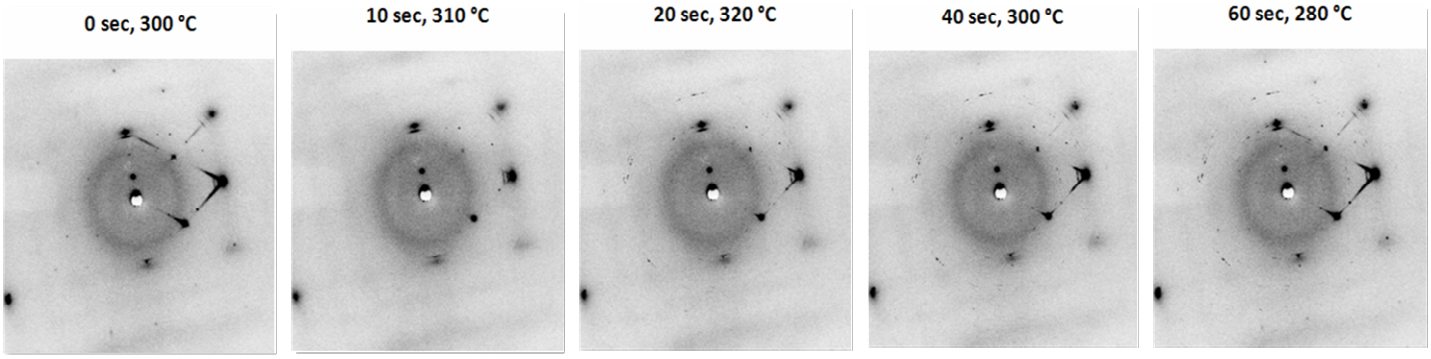

Figure 1: Temperature dependent investigation of the change of intenisty distribution by snapshot exposures of a single crystal fixed in one position (1° oscillation per exposure) in the temperature range around 300 °C. Diffuse scattering disappears during heating of the sample and reappears when recooled (rate 1 °C/s)

In the other part of our experiments, we obtained high-resolution resonant scattering data of several long-range ordered phases at the Sn-, Sb- and Te-edges (29.20 keV, 30.49 keV, 31.81 keV)and at wavelengths far away of the edges. These data allow for a simultanous refinement of site occupancies with anisotropic displacement parameters. The principal element distribution in long-periodically ordered structures is clearly revealed. For 21*R*-$SnSb_2Te_4$,[6,7] the structure of which has been controversially discussed, we refined the anomalous scattering factors f' and f'' with JANA.[8] A joint refinement of all datasets using SHELX [9] ($R\,\bar{3}m$, a = 4.2916(4) Å, c = 41.496(7) Å, $R1$ = 0.0277) reveals that there is no significant amount of Sb-Te or Sn-Te anti-site defects in the layered structure. However, mixed site occupancy with Sn and Sb on the cation positions depends on the location of the position with respect to neighbouring Te layers (cf. Figure 2). A publication of these results will shortly be submitted.

The refinement for $SnSb_2Te_4$ was successfully used to "calibrate" f' and f'' values for the determination of the exact structure of the much more complex phase $GeSb_{10}Te_4$ and the isotypic compound $SnSb_{10}Te_4$ based on similar multi-wavelength datasets that did not allow for a stable refinement of the dispersion correction parameters. Preliminary results demonstrate that these phases exhibit a 39*R*-type trigonal structure. The long-periodic structure ($SnSb_{10}Te_4$: $R\,\bar{3}m$, a = 4.285(1) Å, c = 75.50(1) Å) shows interdependent concentration modulations of the site occuopancies of anion and cation positions accompanied by positional displacements. Thermoelectric properties have been measured for both phases, which represent ideal model systems to gain further insight on the exact influence of Ge and Sn and the concentration gradients on the materials properties, which was investigated during our experiments at the ID11 beamline.

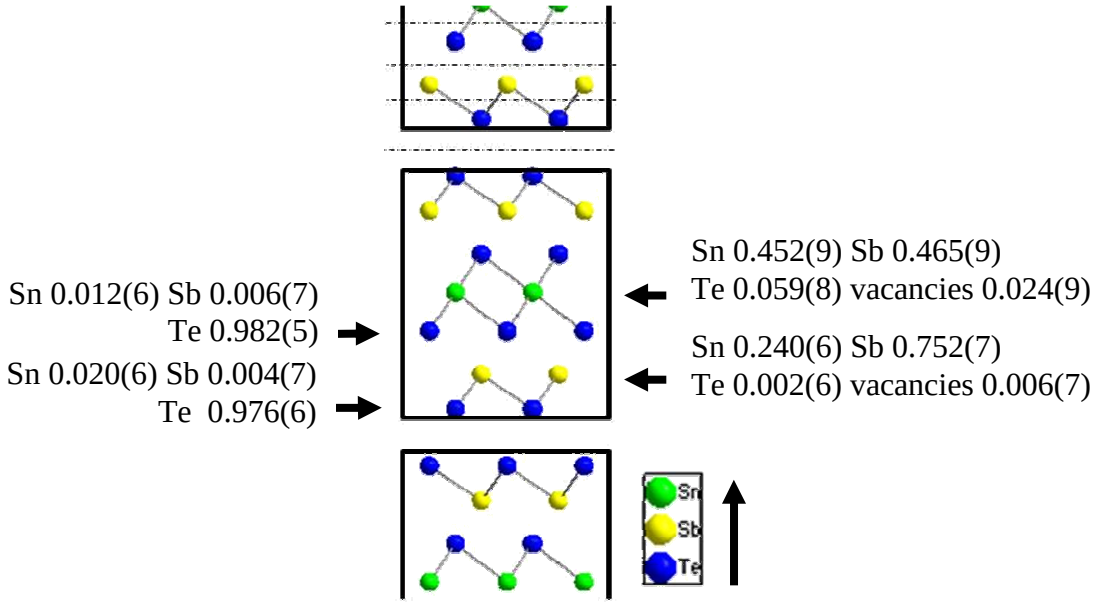

Figure 2: Elemental distribution in the crystal structure of 21*R*-$SnSb_2Te_4$ determined by multi-wavelength dataset refinement

As the effect of anomalous dispersion is rather small if the energy is not set very close to the edges but strongly depends on the exact wavelengths used as well as the environment of the elements if it is set very close to the edge, a problem that limits the precision of our results is the fact that the refined f' and f'' values are not very accurate. Although we were able to refine them on the "calibration phase" 21*R*-$SnSb_2Te_4$, it seems reasonable to establish more exact values for completely ordered phases measured at each monochromator setting before the actual data collection in order to obtain exact refined values for f' and f''. Another way might be the direct measurement of scattering factors from absorption/fluorescence experiments.

Although integrated datasets could finally be obtained, the procedure was tedious as although the program packages provided by the beamline are well established (SMART, SAINT, FABLE…), problems occured during integration for disordered materials which show diffuse scattering or long-periodically ordered structures which show very strong reflections of the average structure and extremely weak reflections of the superstructure. This situation was complicated by the fact that image headers were corrupted after a lightning stroke lead to a shutdown. However, the problem with the data was solved in cooperation with the very helpful beamline staff.

Outlook

The data obtained demonstrate the possibilities of the method and allow to investigate the elemental distribution in multinary antimony tellurides at various temperatures. The results obtained will be published soon. In addition we will apply for additional beamtime not only to further optimize the technique for multinary antimony tellurides, but also to investigate further interesting long-range ordered phases at moderate temperatures. Another interesting idea based on the results of our experiments will be a detailed structural in situ investigation of reversible order-disorder transitions of the materials. The allocated beamtime for our experiments was successfully used and did not only yield very interesting results but also initiated new ideas for further experiments.

References

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