

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> “Temperature- and time-dependent phase transitions and diffusion processes in multinary germanium antimony tellurides investigated by resonant X-ray scattering“	<b>Experiment number:</b> CH-4020
<b>Beamline:</b>	<b>Date of experiment:</b> from: 24.07.2014 to: 29.07.2014	<b>Date of report:</b>
<b>Shifts:</b>	<b>Local contact(s):</b> Nicholas Harker	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):  
**Prof. Dr. Oliver Oeckler\*** (University of Leipzig, Leipzig)  
**Stefan Schwarzmüller\***, M. Sc. (University of Leipzig, Leipzig)  
**Daniel Souchay\***, M. Sc. (University of Leipzig, Leipzig)  
**Matthias Grotevent\***, B. Sc. (Ludwig Maximilian University, Munich)

## Report:

### Aim:

Substitution variants of germanium antimony tellurides (GST materials) with Na, Mn, In and heterogeneous samples with e.g. skutterudite-type precipitates were synthesized and their thermoelectric properties were investigated. In addition, the related compounds  $Tl_9BiTe_6$ ,  $Tl_4PbTe_3$  and  $Tl_{8.5}Bi_{0.5}PbTe_6$  as well as samples in the system  $(Ag_2Ga_2Te_4)_x(CdGa_2Te_4)_{x-1}$  were investigated. The study aimed at the detailed structural characterization of these phases as a function of temperature. Some characteristic temperature-dependent features of thermoelectric properties may often be explained as due to phase changes or decomposition reactions of the materials. More complicated phenomena are attributed to the formation or dissolution of small amounts of precipitates or to element and vacancy ordering phenomena. Reflections originating from long-range ordered superstructures or from nano- to microscale precipitates typically exhibit very low intensities. Conventional powder X-ray diffraction is not suitable to trace the occurrence of such phases as a function of time and temperature. Tracing the distribution of elements with similar electron counts at different temperatures must rely on anomalous dispersion. Therefore, setting special wavelengths is essential and only provided by synchrotron radiation. From the time and temperature resolved tracing of phase transitions, decompositions, precipitate formation as well as element and vacancy ordering, a correlation with our thermoelectric measurements in particular and a deeper understanding of thermoelectric materials in general is aimed at.

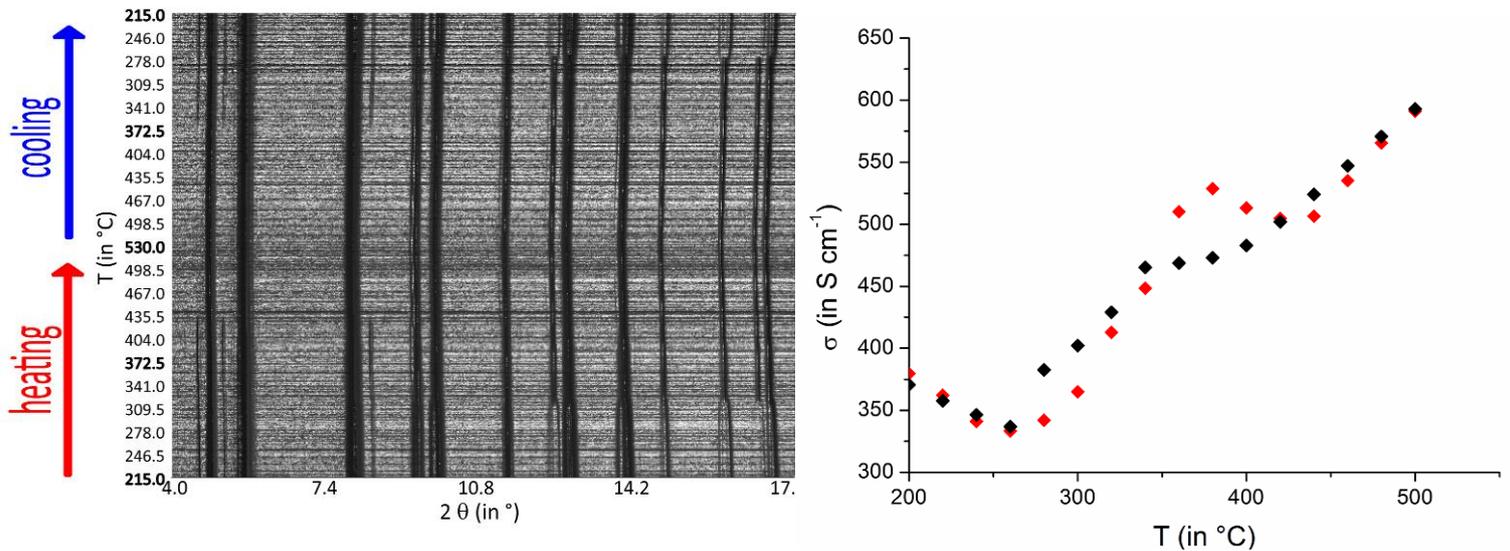
### Experimental details and results:

For the corresponding measurements, the frequent change of samples, temperatures, heating rates and switching between various beam energies (between 25.515 and 90.561 keV) proved as crucial as challenging. Owing to a well planned time management and the great experience of the beamline staff at ID11, all measurements could be performed as previously planned. Samples were ground and sealed in silica tubes

with diameters between 0.2 and 1.0 mm according to their absorption coefficients in order to avoid problems with absorption corrections. For resonant measurements, the absorption edges were detected by means of wavelength-dependent fluorescence measurements;  $\Delta f''$  was calculated directly from the fluorescence measurements and  $\Delta f'$  via the Kramers-Kronig transform, based on experience from earlier beamtimes.<sup>[1]</sup>

The detector distance and tilt were calibrated with LaB<sub>6</sub> reference samples using the program Fit2D.<sup>[2]</sup> Powder diffraction patterns were corrected for flux changes, spatial distortion and detector background effects.<sup>[3-5]</sup> Integration was done with the program TwoTheta,<sup>[6]</sup> where the intensity distribution of powder rings was fitted with a Poisson distribution, in this process, single-crystal-like reflections in spotty rings were automatically excluded. An incident beam correction was applied as described in the literature.<sup>[7]</sup> The following samples were examined in our experiments:

**a)** Materials with the nominal composition Cu<sub>2</sub>Ge<sub>11</sub>Sb<sub>2</sub>Te<sub>15</sub> turned out to consist of a Cu-doped GST matrix with Cu<sub>2</sub>Te precipitates, which are endotactically intergrown in the matrix (according to HRTEM). The thermoelectric properties of such composites are promising with a figure of merit ZT of 1.6. The explanation of the temperature dependence of these properties must rely on very weak reflections of the Cu<sub>2</sub>Te precipitates, which cannot be traced with laboratory methods. Yet, the excellent brilliance of synchrotron beam and the fast read-out time of the FRELON detector yielded well resolved diffraction patterns, also during fast and continuous heating. Initially, the heating rate was kept with 2 K/min, i.e. the same as in the measurement of physical properties. The hysteresis of the electrical conductivity between 260 and 310 °C (cf. Fig. 1) can be attributed to the expected phase change from trigonal to cubic. In addition, a correct interpretation of the hysteresis between 350 and 420 °C is provided, for the first time, by the the temperature dependent data obtained at ID11: Cu<sub>2</sub>Te precipitates dissolve in the matrix upon heating and are formed again during subsequent cooling. In a second series of measurements, a heating rate of 8K/min was applied in order to investigate the time dependence of the observed phenomena; however, no difference was detected. This means that the measurements predominantly show temperature-dependent effects.



**Figure 1:** left: temperature-dependent powder diffraction patterns of Cu<sub>2</sub>Ge<sub>11</sub>Sb<sub>2</sub>Te<sub>15</sub> (beam energy: 42 keV); right: corresponding measurement of the electrical conductivity (red: heating; black: cooling).

**b) and c)** In a similar way as for copper-doped GST as described above, it was possible to trace small amounts of In<sub>2</sub>Te<sub>3</sub> precipitates in Ge<sub>12</sub>In<sub>2</sub>Te<sub>15</sub> as well as both skutterudite-type and CoGe precipitates in [CoSb<sub>2</sub>(GeTe)<sub>0.5</sub>]<sub>1</sub>(GeTe)<sub>10.5</sub>Sb<sub>2</sub>Te<sub>3</sub> and correlate them with the thermoelectric behaviour of these materials. These data are not yet completely evaluated, but no problems are expected.

**d)** In the thermoelectric material Ge<sub>3</sub>MnSb<sub>2</sub>Te<sub>7</sub>, the effects of a phase transition at 300 °C associated with partial decomposition can also be seen in the electrical and thermal conductivity measurements. With the new synchrotron data, the phase transition could be explained in terms of the formation of a long-range ordered superstructure.

e) The temperature-dependent behavior of the phase changes in the thermoelectric material  $\text{NaGe}_{5.5}\text{Sb}_2\text{Te}_9$  was investigated and correlated with the thermoelectric measurements. In this case, the synchrotron data confirmed previous laboratory measurements and allow us to exclude further “weak” effects.

f) Concerning the solid solution series  $(\text{Ag}_2\text{Ga}_2\text{Te}_4)_{x-1}(\text{CdGa}_2\text{Te}_4)_x$ , three samples were measured at the Ag-K, Cd-K and Te-K absorption edges and at an energy away from the edges (42 keV):  $\text{Cd}_{0.2}\text{Ag}_{1.6}\text{Ga}_2\text{Te}_4$ ,  $\text{Cd}_{0.4}\text{Ag}_{1.2}\text{Ga}_2\text{Te}_4$  and  $\text{Cd}_{0.6}\text{Ag}_{0.8}\text{Ga}_2\text{Te}_4$  ( $x = 0.2, 0.4, 0.6$ ). Measurements were performed at three different temperatures (RT, 270 °C, 525 °C). All of these solid solutions crystallize in the chalcopyrite structure type of  $\text{AgGaTe}_2$  (space group  $I 42d$ ). First results of joint refinements for the room temperature measurement of  $\text{Cd}_{0.4}\text{Ag}_{1.2}\text{Ga}_2\text{Te}_4$  show that the anion position  $8d$  is fully occupied by Te and one cation position  $4b$  is fully occupied by Ga, while the other cation position  $4a$  is shared by Ag, Cd and vacancies. Whereas at 270 °C no significant changes are present, at 525 °C  $4b$  is occupied by Ag and Ga and  $4a$  by Ag, Cd, Ga and vacancies indicating a higher mobility of Ag and Ga at elevated temperatures.

g)  $\text{Tl}_9\text{BiTe}_6$ , and  $\text{Tl}_4\text{PbTe}_3$  were measured at the Tl-K and Bi-K edges and at 42 keV. Again, all measurements were performed at three different temperatures (RT, 225 °C, 395 °C). For  $\text{Tl}_{8.5}\text{Bi}_{0.5}\text{PbTe}_6$ , the detector channels for fluorescence measurements could not be calibrated due to the overlap of the Tl, Bi and Pb signals; in this case database values must be used. Detailed data evaluation for  $\text{Tl}_9\text{BiTe}_6$ ,  $\text{Tl}_4\text{PbTe}_3$  is currently in progress.

h) Chalcogenide glasses exhibit exordinarly low thermal conductivities which render them an interesting class of materials for portential thermoelectric application. As the electrical conductivities are too low, the combination of glasses and crystalline materials seems reasonable. Such materials are accessible in the temperature region where glasses begin to crystallize. Therefore, the temperature and time dependent crystallization of amorphous  $\text{GeSb}_2\text{Se}_4$  was studied from 300 °C until the melting point at 490 °C. Two different heating rates of 2 K/min and 8 K/min were applied. The crystalline phase undergoes different phase changes and decompositions leads to the binary phases  $\text{Sb}_2\text{Se}_3$  and GeSe.

## Outlook

Small amounts of impurities and/or vacancies are a well established way of increasing the performance of thermoelectric materials. Usually their time and temperature dependent interaction with the host system is not investigated and hence poorly understood. Our investigations present an effective method for tracing the time and temperature dependent behaviour of both precipitates and ordering phenomena and correlate them with thermoelectric measurements. The broad variety of systems investigated lead to many new insights and will result in several publications. Whereas powder diffraction offers straightforward access to the temperature and time dependence of known phases as well as dissolution and precipitation phenomena, the possibilities for detailed structure analysis of embedded precipitates with unknown crystal structures and temperature dependent changes thereof are very limited. Therefore, the next step will be to extend this methods in related thermoelectric materials to temperature-dependent single crystal or multi-grain diffraction at ID11.

## References

- [1] S. Welzmler, P. Urban, F. Fahrnbauer, L. Erra, O. Oeckler, *J. Appl. Crystallogr.* **2013**, *46*, 769.
- [2] A. P. Hammersley, *ESRF Internal Report*, **1997** ESRF97HA02T, “FIT2D: An Introduction and Overview”.
- [3] A. P. Hammersley, S. O. Svensson, A. Thompson, H. Graafsma, Å. Kvick, J. P. Moy, *Rev. Sci. Instr.* **1995**, *66*, 2729.
- [4] J.-P. Moy, A. P. Hammersley, S. O. Svensson, A. Thompson, K. Brown, L. Claustre, A. Gonzalez, S. McSweeney, *J. Synchrotron Rad.*, **1996**, *3*, 1.
- [5] A. P. Hammersley, K. Brown, W. Burmeister, L. Claustre, A. Gonzalez, S. McSweeney, E. Mitchell, J.-P. Moy, S. O. Svensson, A. Thompson, *J. Synchrotron Rad.*, **1997**, *4*, 67.
- [6] S. Vogel, L. Ehm, K. Knorr, G. Braun, *Adv. X-Ray Anal.* **2001**, *45*, 31.
- [7] G. Wu, B. L. Rodrigues, P. Coppens, *J. Appl. Crystallogr.* **2002**, *35*, 356.