ESRF	**Experiment title:** Temperature-dependent structure determination by resonant X-ray scattering at germanium antimony tellurides and Tl/Pb/Bi chalcogenides	**Experiment number**: CH-4131
Beamline:	**Date of experiment**: from: 04.12.2014 to: 09.12.2014	**Date of report**:
Shifts:	**Local contact(s)**: Nicholas Harker	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Oliver Oeckler* (Leipzig University)

M.Sc. Frank Heinke* (Leipzig University)

M. Sc. Peter Schultz* (Leipzig University)

B.Sc. Lennart Staab* (Leipzig University)

Report:

Aim

Multinary chalcogenides are a promising class of materials for thermoelectric applications. This is due to a high degree of disorder in their complex structures. These can exhibit various dimensionalities. The main aspect of this experiment was the determination of the distribution of cations that lack scattering contrast with conventional X-rays, especially the differentiation between Pb and Bi. Among classes of compounds investigated, "sulfosalt"-like phases of the systems Sn/Bi/Se, Ag/Bi/Pb/Se and Cu/Bi/Pb/Se are the most complex, they consist of various arrangements of tilted NaCl-type slabs. In addition, the focus was on layered compounds $(PbS)_n(Bi_2Te_2S)$ derived from the tetradymite structure.[1] Laboratory data were inconclusive concerning the element distribution and, especially in the system Sn/Bi/Se, many analyses suggested the presence of vacancies on the cation positions. The project aimed at the exact determination of the cation distribution in these compounds in order to more deeply understand their thermoelectric porperties. Therefore, resonant x-ray scattering on previously characterized crystals was used. It is often assumed that in copper chalcogenide compounds the copper mobility increases at high temperatures, thereby enhancing the thermoelectric performance. Therefore, high-temperature single crystal x-ray scattering experiments were also attempted. In addition, a part of the project focused on the structure determination of small particles in multiphasic samples to discover new classes of materials for thermoelectric and other applications.

Experiments and results

The project consisted of three major parts. For resonant scattering experiments, the crystals were mounted on glass fibers or, for the high-temperature experiments, in silica glass capillaries under argon atmosphere. Samples which for experiments with microfocussed synchrotron radiation were placed on micro-mounts.

Except for the small crystallites for part 3, all crystals had been previously tested at our laboratory single crystal diffractometer to confirm good crystal quality.

Part 1: Resonant x-ray scattering experiments

For the resonant scattering experiemts, data were collected near the K edges of Bi (90.48 keV, 0.13703 Å), Pb (87.95 keV, 0.14097 Å), Sn (29.19 keV = 0.42482 Å) and far from the edges (80.00 keV, 0.15498 Å). We were able to gather datasets of three samples:
$Pb_2Bi_2S_3Te_2 = (PbS)_2(Bi_2Te_2S)$ (Pb-edge, Bi-edge, off-edge)
$Cu_2Pb_8Bi_{10}Se_{24}$ (Pb-edge, Bi-edge, off-edge)
$Sn_2Bi_2Se_5$ (Sn-edge, Bi-edge, off-edge)

All datasets could be indexed and accurate cell parameters were obtained. The intensity was rather low, which was compensated by long exposure times. However, no datasets for structure refinements could be obtained as unfortunately all datasets were corrupted in a way that the integration did not yields reliable intensities. This was probably due to problems with the shutter control and discovered only after the beamtime. Even with great effort of the beamline staff, this problem could not be solved.

Note: For this reason, we received an additional day of beamtime in our experiment CH4318.

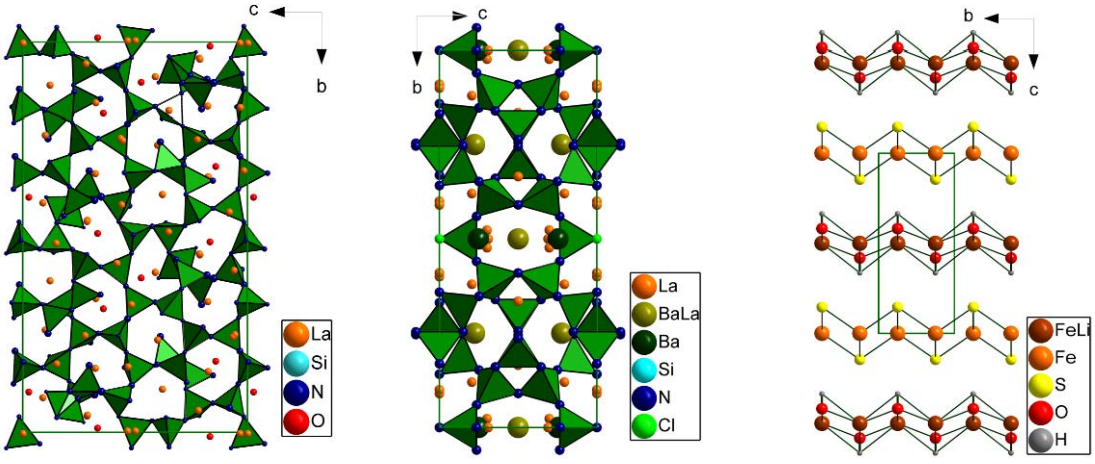
These new data could be interpreted without problems and yield the element distribution. Pb and Bi are almost ordered in the structures, only a small degree of mixed sites was observed. In $Sn_2Bi_2Se_5$, disordered defects as well as disordered cations could be clearly confirmed. Detailed investigations are being performed. Due to this additional beamtime, the most important aspects of part 1 could be successfully completed.

Part 2: High-temperature scattering experiments

The datasets for all temperatures were gathered with radiation of 0.15498 Å (80.00 keV). $Cu_2Pb_8Bi_{10}Se_{24}$ was investigated at 4 different temperatures (room temperature, 100 °C, 250 °C, 400 °C). All the datasets showed the same problem described in part 1.

Part 3: Microfocussed scattering experiments:

After the problem with low intensity and shutter as well as transfocator motors was solved, only little beamtime remained. This was not enough to perform the measurements of parts 1 and 2 again. Therefore, a few hours of beamtime, beyond the original scope of the project, we applied for collecting synchrotron data of very small crystallites for structure determination of nitridosilicates and a sulfide oxide. All datasets were collected at a wavelength of 0.3099 Å (40 keV). The structures of three compounds were determined and will lead to several publications.



Structures of $La_{88}Si_{104}N_{216}O_{16}$, $La_{29.51}Ba_{10}Si_{44}N_{92}Cl_{1.67}$ and $Li_{1.64}Fe_{2.36}S_2O_2H_{1.64}$ (from left to right)

$La_{88}Si_{104}N_{216}O_{16}$ crystallizes in a new structure type with a network of corner-sharing Q^4- and Q^2 type SiN_4 tetrahedra (space group: *Cmc*2_1, *a* = 9.507 Å, *b* = 32.063 Å, *c* = 18.508 Å, R_{int} = 0.034, *R*1(obs) = 0.028). The large cavaties are partially filled with OLa_4 tetrahedra or isolated La cations. The structure resembles those of clathrates.
$La_{29.51}Ba_{10}Si_{44}N_{92}Cl_{1.67}$ crystallizes in the $(Ba_2Nd_7Si_{11}N_{23})$[1] structure type. It consists of a zeolite-like network of corner-sharing Q^4- and Q^2 type SiN_4 tetrahedra (space group: *Cmmm*, *a* = 10.987 Å, *b* = 23.214 Å, *c* = 9.687 Å, R_{int} = 0.037, *R*1(obs) = 0.017).
$Li_{1.64}Fe_{2.36}S_2O_2H_{1.64}$ crystallizes in space group *P4/n* (*a* = 3.670 Å, *b* = 3.670 Å, *c* = 8.790 Å, R_{int} = 0.035, *R*1(obs) = 0.029). The structure consists of alternating layers of FeS and $Fe_{1-x}Li_xOH_x$ and is a high-temperature superconductor.[2] Reconstructed reciprocal space sectons show diffuse streaking, whose evaluation is still in progress.

Outlook

It should be noted that beamline staff tried hard to resolve the problems with the low intensity and were very helpful when we tried to evaluate the corrupt data. Much of the problem was solved by allocations one day of additional beamtime during our next project. Fortunately, this made the whole project a successful one. Also, the beamtime of CH-4131 at least yielded datasets of some new structures during the last hours of the beamtime after the problems were fixed.
The method of resonant x-ray scattering was applied to determine the cation distribution in multinary chalcogenides. In the future, dispersion correction terms should be determined by measuring energy-dependent fluorescence. A further enhancement would be the in-situ resonant x-ray scattering at high temperatures to evaluate possible order-disorder phenomena. This would be especially interesting for compounds with highly mobile cations. Such results would provide valuable insight in thermoelectric materials and give rise to new approaches for the enhancement of thermoelectrics.
Resonant x-ray scattering is also an interesting method for heterostructured materials. These are composite materials obtained by annealing high-temperature phases at lower temperatures. Due to miscibility gaps, the materials decompose into two or more phases. As the crystals are very small, the combination of the structure determination with microfocussed synchrotron radiation and the elucidation of the cation distribution with resonant x-ray scattering would provide an excellent approach to understand the exsolvation process. By applying a elevated temperatures to the material one could even study the kinetic of this process as well as intermediate phases and their composition.

[1] H. Huppertz, W. Schnick, *Angew. Chem.* **1997**, *109*, 2765; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2651.
[2] U. Pachmayr, F. Nitsche, H. Luetkens, S. Kamusella, F. Brückner, R. Sarkar, H.-H. Klauss, D. Johrendt, *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 1.