



## 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.

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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> Combinations of microfocused, resonant and in-situ diffraction for the characterization of the element distribution and diffusion processes in chalcogenide thermoelectrics	<b>Experiment number:</b> MA-1875	
<b>Beamline:</b> ID11	<b>Date of experiment:</b> from: 30.01.2014 to: 04.02.2014	<b>Date of report:</b>  <i>Received at ESRF:</i>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Gavin Vaughan	

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**Report:**

**Aim**

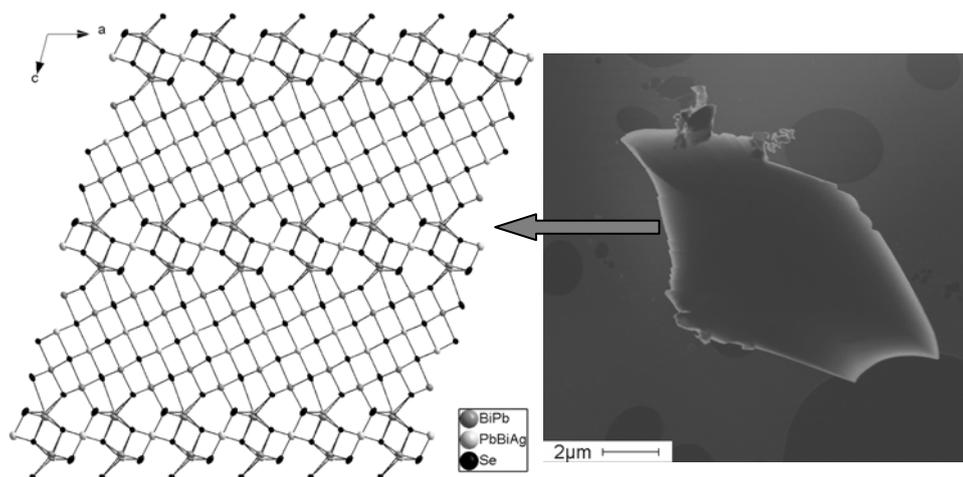
Syntheses aiming at new thermoelectric materials often involve quenching melts. This approach often results in microcrystalline, inhomogeneous samples. The main aspect of the present experiment was the determination of new complex "sulfosalt"-like chalcogenides. Novel phases obtained from neither single crystals suitable for conventional laboratory X-ray equipment nor homogeneous powder samples for structure elucidation. The aim of this project was to show how this problem can be successfully overcome by combining the advantages transmission electron microscopy (TEM), i. e. selected-area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX), with highly brilliant, microfocussed synchrotron radiation as available at ID11. Based on experience from previous experiments (project HS4625), much more challenging samples were selected and pre-characterized by TEM on carbon-film-coated finder grids. The same crystallites that were investigated by TEM were to be placed in the synchrotron beam and single-crystal data should be measured. In addition, Ga- and As-containing crystallites embedded in polycrystalline alloy matrices were located by fluorescence and diffraction scans on thinned samples, and single-crystal data were acquired.

**Experimental progress and results**

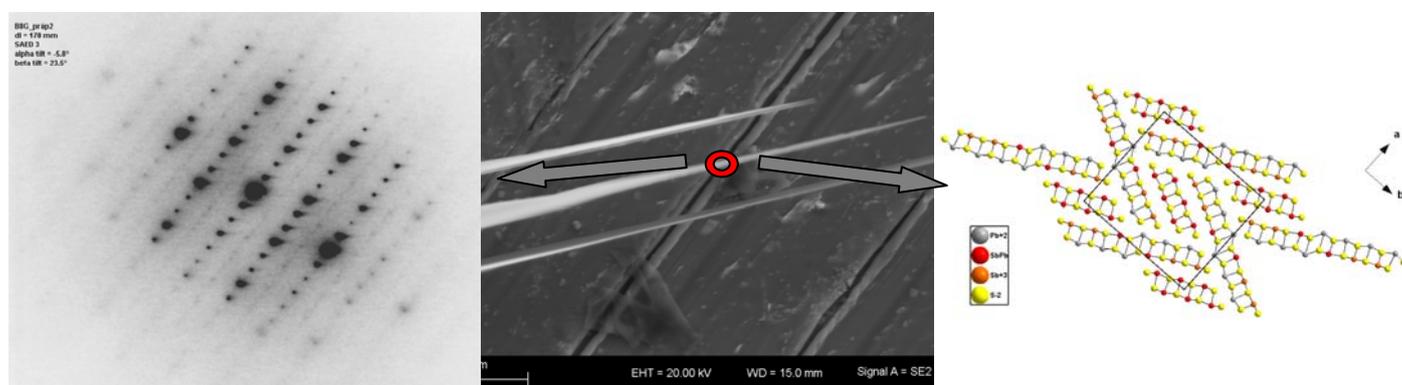
One part of the samples was prepared by drop-casting a suspension of microcrystalline powders in ethanol on carbon-film-coated copper TEM grids. In contrast, samples of heterostructured bulk samples were cut, thinned, polished and treated by Ar-ion etching until very small holes were obtained. At the resulting edges around the holes crystallites of minority phase and/or the matrix alloys could be characterized. In addition, thin needles of sulfides with chain structured were investigated in space-resolved fashion by taking series of diffraction pattern along the needles, some of them also Ar-ion thinned. All samples were characterized in the TEM, the chemical composition was measured by EDX and SAED patterns were used to determine unit-

cell metrics, indicative of new phases. The grids were then glued onto pins and further investigated at ID11. We used a beam energy of 36.99 keV to keep the absorption minimal, as many samples contain a large fraction of heavy elements such as Sb, Te, Pb or Bi. The crystallites were re-located approximately by a telescope with large magnification and then precisely located and centered in the beam by fluorescence scans. The beam size was varied between  $1.2 \times 3 \mu\text{m}$  and  $0.2 \times \sim 1.5 \mu\text{m}$ , depending on the individual samples' morphologies. It was possible to obtain single-crystal diffraction data from various pre-characterized crystallites as well as from additional ones found by diffraction scans in other samples. Resonant diffraction and in-situ heating experiments were not included in this experiments; the title originates from a proposal for a long-term project converted into MA-1875, i. e. a sub-project dealing with microfocus diffraction. The following samples were examined in our experiments:

**a)** Multinary sulfides often consist of NaCl-like building blocks derived from PbS and chain-like elements derived from  $\text{Sb}_2\text{S}_3$ ; this combination leads to a plethora of complex structures.<sup>[1]</sup> Although such structure types appear ideal for thermoelectrics, sulfides usually lack reasonable electrical conductivities although they exhibit low thermal conductivities and high Seebeck coefficients. In order to overcome the low electrical conductivity, the substitution of S by Se is a promising approach towards new thermoelectric materials.<sup>[2]</sup> In the present case, TEM-EDX and SAED data revealed that a multi-phase sample of the nominal composition  $\text{Ag}_{0.68}\text{Pb}_{0.61}\text{Bi}_{2.28}\text{Se}_5$  contained a new quaternary phase with unknown lattice parameters. Excellent microfocus diffraction data lead to a straightforward structure solution. The refinement yielded a monoclinic structure derived from pavonite ( $\text{AgBi}_3\text{S}_5$ ). The new compound (cf. Fig. 1) corresponds to  $\text{Ag}_3\text{Pb}_4\text{Bi}_{11}\text{Se}_{22}$  and consists of distorted NaCl-like slabs interconnected by chain-like elements (space group  $C2/m$ ,  $a = 13.853(3) \text{ \AA}$ ,  $b = 4.2108(8) \text{ \AA}$ ,  $c = 19.721(4) \text{ \AA}$ ,  $\beta = 104.57(3)^\circ$ ,  $R_{\text{int}} = 0.029$ ,  $R1(\text{obs}) = 0.032$ ).



**Figure 1:** Refined structure of  $\text{Ag}_3\text{Pb}_4\text{Bi}_{11}\text{Se}_{22}$  (left), STEM dark-field image of the examined sample (right).



**Figure 2:** Local SAED pattern (left), selected spot on a crystalline needle (center) and crystal structure (right) of  $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ .

**b)** We further examined lead/antimony sulfides, especially ones with the nominal composition  $\text{Pb}_5\text{Sb}_4\text{S}_{11}$  (“boulangerite”). These are interesting due to the complicated real-structure effects present. Different models concerning cation-ordering phenomena were proposed but are not well understood.<sup>[3,4]</sup> We derived a unified structure description for all models using an orthogonal cell (space group  $B2_1/d$ , unconventional setting of

No. 14,  $a = 42.57 \text{ \AA}$ ,  $b = 23.53 \text{ \AA}$ ,  $c = 8.04 \text{ \AA}$ ,  $\beta = 90^\circ$ ). At ID11, space-resolved datasets from several sites on various needle-shaped crystals were measured. Refinements reveal that 12 out of 18 cation positions are disordered and indicate (presumably polysynthetic) reflection twinning along (010). Weak superstructure reflections ( $l = 2n+1$ ) and diffuse scattering with varying intensity that interconnects these reflections shows partial cation ordering and stacking disorder which had been suggested based on OD theory.<sup>[5]</sup> ID11 data yield a clear overview over the structural variations present and enable unambiguous refinements.

c) In the system Ga/Ge/Sb/Te, we were able to locate a suitable crystallite of a new quaternary compound by diffraction scans. Data were collected, structure solution and refinement reveal a structure closely related to that of GaGeTe<sup>[6]</sup> (space group  $R\bar{3}m$ ,  $a = 4.055 \text{ \AA}$ ,  $c = 35.337 \text{ \AA}$ ,  $R_{\text{int}} = 0.023$ ,  $R1(\text{obs}) = 0.097$ ). The distribution of Ga and Ge could not yet be determined due to their lack in scattering contrast. The structure refinement renders approximately 10% of Ge being substituted by Sb.

d) Germanium antimony tellurides (GST phases) are well known as phase-change materials for data storage and also exhibit promising thermoelectric properties.<sup>[7]</sup> We successfully measured data from inhomogeneous, heterostructured samples with various precipitates. For the first time, data of the As-substituted compound  $(\text{GeTe})_n(\text{Sb}_{2-x}\text{As}_x\text{Te}_3)$  could also be obtained, their evaluation is in progress.

e) In addition and beyond the original scope of the project, we applied the method of TEM-pre-characterization and collecting synchrotron data directly from crystallites in finder TEM grids for luminescent nitridosilicates. A novel framework type was found in a straightforward way and the corresponding publication is already in preparation: The oxonitridosilicate  $\text{La}_3\text{BaSi}_5\text{N}_9\text{O}_2$  crystallizes in a yet unknown structure type (space group  $Pmn2_1$ ,  $a = 9.5505(8) \text{ \AA}$ ,  $b = 19.0778(16) \text{ \AA}$  and  $c = 12.1134(9) \text{ \AA}$ ,  $R_{\text{int}} = 0.052$ ,  $R1(\text{obs}) = 0.035$ ) with *dreier* and *sechser* rings. The three-dimensional tetrahedra network  $\{3.6^3.7^2\}_2\{3\}\{6^6\}_2$  hosts La and Ba cations and upon doping with  $\text{Ce}^{3+}$  exhibits intense yellow luminescence.

## Outlook

The method of combined TEM and synchrotron microfocus examination for the determination of otherwise inaccessible crystal structures of microcrystalline, heterogeneous samples was developed so that it can almost routinely be applied. A broad range of different structures were elucidated and will enable several publications. A next step concerning this procedure, especially in the field of thermoelectrics, would be the combination with resonant scattering and/or in-situ heating experiments, both on micro- to nanometer-sized crystallites. This will enable experimentalists to avoid the disadvantages of powder diffraction in case of lacking scattering contrast in compounds present in inhomogeneous samples, even minority phases. Space-resolved X-ray diffraction analysis along needle shape were also performed and enables us to correlate compositional gradients with structural changes. After the successful structure determination of a microcrystalline nitridosilicate phosphor, we also plan to continue this work on further interesting, luminescent oxonitridophosphates and oxonitridosilicates at ID11.

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