ESRF	**Experiment title:** Phase composition of thermoelectric composite materials and structure elucidation of precipitates therein	**Experiment number**: CH-4612
Beamline: ID11	**Date of experiment**: from: 15.06.2016 to: 20.06.2016	**Date of report**: 30.08.16
Shifts: 15	**Local contact(s)**: Vadim Diadkin	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Aim

In thermoelectric materials, low thermal conductivities due to effective phonon scattering can be obtained by the incorporation of nano- to microscale precipitates and in multinary systems with various elements of different element mass. The intention of the experiment was to obtain high quality, possibly single-crystal data from (metastable) microcrystals found as side phases in such heterogeneous thermoelectric materials as done earlier at ID11 (experiment MA-1875) for comparable systems. However, the composite materials to be investigated now contain novel phase combinations with much higher efficiencies. The crystal structure determinations were to be combined with the investigation of the phase composition on an intermediate length scale using a larger beam (multi-crystal and/or powder data). Together with regular powder diffraction experiments and SEM-EDX mappings performed in preparation of the beamtime, these measurements would give insight into the complicated phase relationships in complex systems like Cu/Sb/Ge/Te or Co/Ge/Sb/Te and especially their temperature-dependent behavior. The existence of multiple types of microcrystalline copper telluride precipitates was proven by preliminary TEM-experiments in the Cu/Sb/Ge/Te system; an expected dissolution and reformation in exchange with the copper doped Ge/Sb/Te matrix is correlated with distinct changes of the thermoelectric properties.
In addition, we planned to obtain crystal structure data of new multinary compounds from multi-phase samples in order to achieve a better understanding and optimized synthesis pathways for these single phases. Corresponding samples had been prepared on TEM grids and pre-investigated by electron diffraction and EDX spectroscopy.

Experiments and results

The major part of the project would have involved experiments with high-intensity microfocussed beams at increasing temperatures. This would allow one to determine crystal structures of microcrystalline phases in composite thermoelectrics and their fields of stability. These sample (Ar-ion thinned platelet pre-characterized by TEM) were fixed in argon-filled silica glass capillaries. For the RT experiments, the crystals were spread on TEM grids and mounted on glass fibers. Other small crystals were placed on Kapton foil micro-mounts.

Unfortunately, almost none of the planned measurements could be performed. Much time was lost with alignment of a new experimental setup and evaluating its problems, not all of which could be fixed. In additions, other failures occurred and the heater (gas blower) could not be installed and calibrated in a way that would have enabled reasonable measurements.

description of the course of action

15.06.2016
08:45-16:40 beam alignment and test of the beam size and intensity with a needle-shaped test crystal
17:45-20:00 unsuccessful tests of fluorescence detector
20:00-23:00 technical problem with hexapod, could not be fixed by local contact, need to wait for technician
16.06.2016
08:00-13:30 technician and other scientists fix problem with hexapod, makeshift fix with rubber band
13:30-18:00 trying to obtain data from test crystals, intensity rather weak, rotation axis imprecise; interrupted by problems with goniometer motors (fixed by local contact).
18:00- measurements at room temperature (relatively large crystals from other projects which were suitable for the current setup)
17.06.2016
-08:45 see above
08:45-10:00 measurement of calibration crystal
10:00-14:00 evaluation of calibration crystal data, too imprecise for wavelength determination and calibration
of detector parameters, at the same time measurement of other sample suitable for current setup.
14:00-14:30 measurement CeO_2 for wavelength determination
14:30-16.25 mounting cables and tubes for heater
16:25-18:15 Peltier cooler of detector not working, fixed by local contact
18:15-19:30 beam center realignment
19:30- 0:00 further measurements at RT
18.06.2016
0:00-07:00 unsuccessful attempts to measure small crystallites
07:00-08:40 problem with front end shutter, fixed by local contact
08:40-14:45 unsuccessful attempts to measure small crystallites, intensity too weak
14:45-16:00 changing setup to larger beam (1-2 μm), tests
16:00-23:00 local contact mounts heater, unsuccessful temperature calibration with Ag powder (height of heater differs from height of beam)
23:00 - redetermined beam center, analyzed problems with heater (wrong height, problem with communication with computer – input in software dos not correspond to signal sent to controller), problems cannot be fixed by local contact
19.06.2016
-02:30 see above
02:30-09:30 trying to measure at RT, signals weak
09:30-10:00 beamcenter alignment
10:00-22:00 further unsuccessful attempts to obtain data, users found out that proper centering is not possible due to wrong response of one piezo motor, provisional attempts to compensate that with other motors, local contact tries to fix problems with piezo motors, unsuccessful

22:00 - measurements of large crystals from other projects as setup is not suitable for small samples
20.06.2016
-04:10 see above
04:10-07:00 server problem and front end problem, fixed by local contact
07:00-9:40 further measurements of large crystals from other projects

Note
A significant amount of time was lost because calibration crystals and alignment needles could not be reproducibly mounted on goniometer heads but had to be directly attached to the goniometer, which each time involved time-consuming alignment.
The equipment had not be used before, thus many problems with beamline setup and testing the goniometer occurred during the beamtime and did not allow us to measure samples.

Results

As the heating device could not be put into operation, we were not able to perform the planned measurement. In addition, instability of the goniometer (piezo motors) and low intensity of very small beams did not allow us to measure data from small precipitates.

The following datasets could be obtained with a larger beam at room temperature:

a) crystal of the matrix including endotaxially intergrown precipitates from the system Cu/Ge/Sb/Te:
data of matrix are good, but reflections from precipitates are too weak.

b) microcrystals from the system Sn/Bi/Se at room temperature:
reasonable data from a related system, one good single-crystal dataset

c) larger crystals from other projects measured at times where the setup was not suitable for the proposed project:
- a lithium oxonitridophosphate (new structure, solved)
- a lanthanum oxonitridophosphate with a large unit cell (new structure, not yet solved)
- a strontium oxonotridosilicate (structure not new)
- a lanthanum nitridosilicate (turned out to be $LaSi_3N_5$)

Outlook

Although the local contact tried hard to solve hardware problems, the complete setup could not be put into operation. The hexapod setup turned out to be not stable enough, and it was a major problem that it does not support regular goniometer heads. The setup was new and had not been tested extensively before, it required a whole day for initial yet unsuccessful alignment. Problems with heater setup were not solved and and the control software did not work properly. The proposed project could not be carried out.
However, we tried to make the best out of this situation by measuring a couple of crystals from other projects, and obtained some very few reasonable date.
In general, we are confident that the original project can be a great success at ID11 if we use the setup used in experiment experiment MA-1875 or if the new setup can be put into operation. From the technical point of view, we had already used all equipment successfully in earlier experiments with other samples – chemically very different ones, but very similar concerning the experiment itself.
Therefore, we will re-submit the proposal, including some updates concerning even more interesting, optimized samples. We believe that promising project should not be cancelled because of one unsuccessful attempt. It was unlucky but does not discourage us.