ESRF	**Experiment title:** **Development of Nano-calorimetry accessory for the nano-focus beamlines**	**Experiment number**: SC-3457
Beamline: ID 13	**Date of experiment**: from: 05/10/2012 to: 07/10/2012	**Date of report**: 15/01/2013
Shifts: **2012/II 6**	**Local contact(s)**: Manfred Burghammer	

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This report describes the results obtained during the first four months of our LTP project SC-3457

Introduction:

When materials are confined to nanometer scale they can exhibit unusual properties. Fundamental understanding of these changes is of great importance, both from scientific and technologic points of view. One of the ways to address these changes by measuring the thermal parameters of the materials under confinement is provided by the technique of Nanocalorimetry. The Nanocalorimetry was first introduced by L.H. Allen et al. in 1993, who at first performed thermal analysis of thin films and later extended the technique to other sample geometries such as micron-sized particles and individual polymer single crystals. Thanks to the design of the nanocalorimetric sensor, this technique allows to analyze very small amounts of materials (i.e., nanograms and even hundreds of picograms). The heating and cooling rates employed are much higher than in the classical DSC: they are comprised between 10^3 and 10^6 K/s. As a result, the measurements performed with Nanocalorimetry can be extremely fast (on the order of a few milliseconds).

In collaboration with Russian partners, our group has built a Nanocalorimeter which has competitive technical specifications. For some of the parameters it even exceeds the performance of the Nanocalorimeter very recently commercialized by Mettler-Toledo (the so-called "Flash DSC"). The major advantage of our home-made instrument is that it can be used in combination with optical microscopy in reflection/transmission, AFM and micro-focus synchrotron X-ray diffraction.

Milestones for first Year:

In the first 4 months of the project, in agreement with the milestones established for the first year of the project, a sensor holder compatible with the particular requirements of the ID13 Nano-Hutch experimental stage was installed at the beamline. Moreover, we provided a special home-made flat illuminated aperture using ultra-flat low-power LEDs in the SMD design. Using this installation, first in-situ nanocalorimetric experiments were performed using micro-particles of Indium. During this experimentation, different measuring protocols were tested. The final evaluation of the protocols and the sample stage performance as well as the expansion to other materials is planned for the first halve of the experimental round in 2013. A first publication of the experimental results on Indium is in preparation.

1. Design of the Nano-calorimetric sensor holder

1.1 Sample stage

The strategy in the first period of the project was to develop a novel sensor holder, which will meet the requirements of the experimental sample stage of the EH3 (Nano-hutch) and its application in first experimentations using standard thermal standards. The general sample stage of the experimental hutch consists of a hexapod equipped with a piezo-actuator Cube on top, which allows for precise sample motion in the nanometer range. The use of a piezo-actuator gives strict requirements for the design of the used sensor holder in terms of its weight and rigidity. Additional constraints are given by the extremely short focusing length of the last optical lenses in combination with the mounted optical apertures and collimators giving a final sample space of about 5mm in the upstream direction of the X-ray beam.

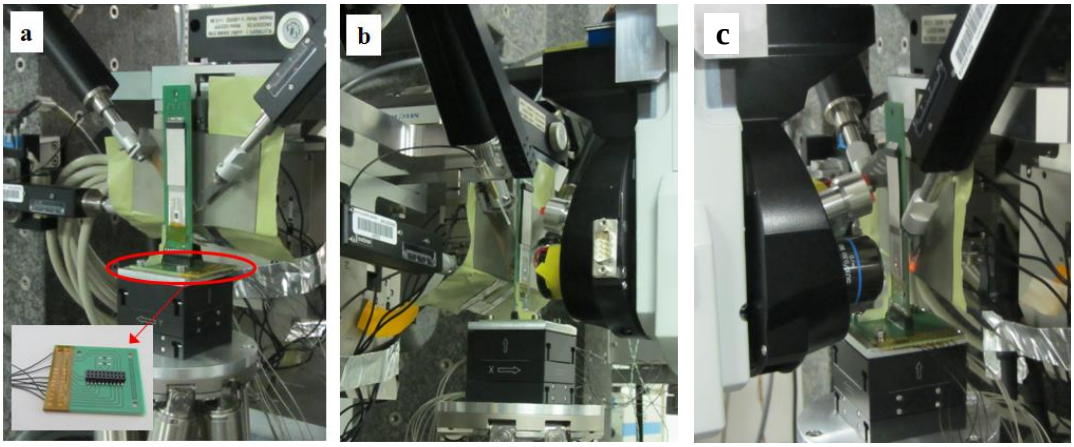

Figure 1. (a) Experimental setup for combined Nanocalorimetry-X-ray scattering using nano-beams. Inset shows image of the mounting socket of the novel sensor stage developed. (b) Geometrical constrains at ID13 EH3 encountered during sample positioning. (c) Sensor holder positioned at the working distance with the online optical microscope and illuminated aperture shield installed.

To meet all the geometrical requirements of the beamline, we have selected a simple approach for design the sensor holder, which is based on the use of standard PCBs (Printed Circuit Board). The modular design of the developed sensor holder allowed for a quick and easy sample exchange with a minimum of manual intervention in the experimental hutch (cf. Figure 1a). Another advantage of this concept is its light weight and rigidity of the used elements, which makes it possible to perform precise and reproducible scanning of the micron-sized sample area. In addition, the wiring for the read-out of the calorimetric signals is easy and requires no additional space. To minimize the interference of the wires with the high-resolution sample motion driven by piezo-actuator, coaxial wires with the outer diameter of 500µm with a capacity of 110pF/m were chosen. The thickness of the newly designed sensor holder is less than 2 mm in the upstream direction providing enough space for the final apertures and collimators of the end-station.

1.1 Illuminated aperture

As mentioned above, the extra-thin design of the sensor holder makes the combined nanocalorimeter/X-ray scattering measurements possible. However, due to confined space imposed by the nano-optics and the need to have the final beam aperture shield close to the sample, the space upstream the sample is very limited. In order to solve this problem, an extra-thin aperture shield was designed and fabricated from extra-thin PCB material (0.5mm) allowing implementation of ultra-flat low-power LED's in SMD design (the height less than 1mm) with high light intensity. The shield including the aperture is shown in Figure 1c. In the center of the shield, a standard TEM aperture with a diameter of 400µm is assembled. This setup allows illuminating the sample around the beam path in transmission while avoiding disturbance of the beam optics by heat. To ensure the absorption of the scattered X-rays upstream the sample, the shield is covered with a thin lead foil making the total thickness of the illuminated aperture shield of about 2 mm. The intensity of the LED illumination is controlled from the computer in the control cabin of the experimental hutch using a simple serial interface protocol.

2. Commissioning of the measurement protocols and first in-situ measurements using Indium micro-particles

One essential part of the experiment preparation is the calibration of the nanocalorimeter sensors. It is noteworthy that without temperature and power calibration, the nanocalorimeter sensors cannot serve for meaningful thermal analysis experiments. The required calibration procedures have been developed by our group in the past. At this stage of the project, these procedures are being adapted for the synchrotron environment. A detailed user´s manual will be written for the final LTP report in order to make the calibration process accessible to the ID13 staff and beamline users.

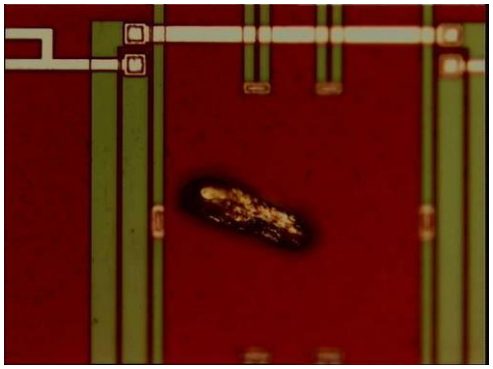

Figure 2. Indium micro-particle deposited on the active area of a nanocalorimetric sensor.

2.1 Absorption mapping of In micro-particles

To perform quantitative experiments with Nanocalorimetry, it is crucial to know the specimen mass. When working with micron-sized specimen, as it is the case here, the estimation of the particle mass can be extremely difficult. A standard approach consists in measuring the geometrical parameters of the particles in order to estimate the volume. However this approach only works for well-defined geometrical shapes such as flat films or spheres. When using specimens of irregular shape, as it is the case of the Indium micro-particles subject of this study, another way to estimate the mass has to be used. In this approach, we can take benefit from the facilities offered by the nano-focus beamline.

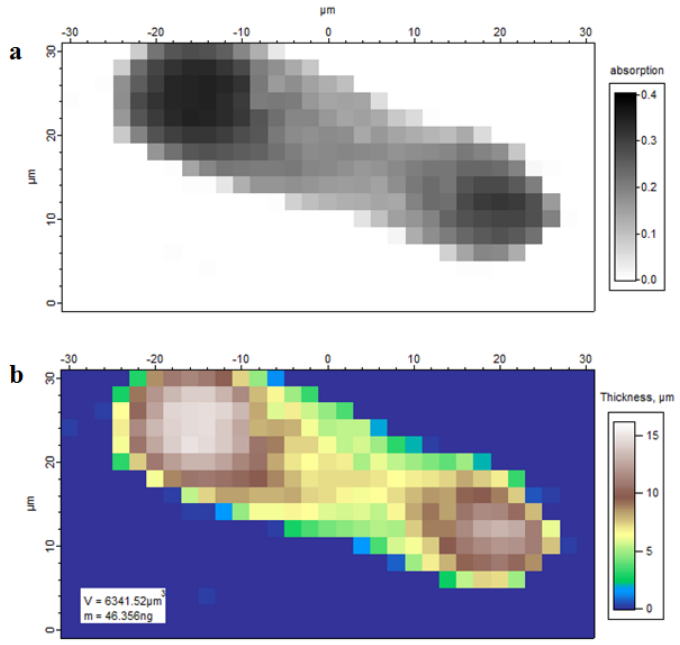

Figure 3. (a) Absorption 2D map displayed for In micro-particle deposited on the active area of a nanocalorimetric chip. (b) Thickness map of the particle obtained from the absorption map.

A common experimentation procedure at the ID13 micro- and nano-branch is generation of two-dimensional sample maps using different methods of detection such as for example absorption maps. In the frame of the first beamsession, the local absorption of the incident X-ray beam was measured with 2µm lateral resolution. A typical Indium micro-particle deposited on the calorimetric sensor chip is given in Figure 2. A two-dimensional representation of the local absorption of the studied Indium micro-particle is given in Figure 3a.

Using the Lambert–Beer law:

$$I_x = I_0 e^{-(\mu/\rho)\rho x} \qquad \text{Eq. 1}$$

where I_0 is the intensity of incoming beam, I_x is the intensity of transmitted beam after passage through the sample of thickness x, ρ is the density of the material and μ/ρ is the mass absorption coefficient, the local thickness of the particle can be derived if the mass absorption coefficient is known. The thickness map of the studied Indium micro-particle is given in Figure 3b. From the thickness map, the mass of the sample can be easily found. In addition, the absorption map of the specimen together with the data derived from the on axis optical microscope can be used for choosing the region of interest on the sample suited best for further studies.

2.2 Temperature mapping of In micro-particles

For preliminary experiments, the sensor chips with an active area of 60x100µm² were used. The suspended Si_xN_y membrane located in the center of the chip serves as substrate for the specimen. The membrane is 900 x 900µm^2 and has a thickness of 1µm. Two pairs of resistive heating elements and a set of six differential thermocouples constitute the active area of the membrane. In this region, the thermal sensitivity of the sensor is the highest. The low heat conductivity and heat capacity of the membrane is essential in order to sense the temperature changes of the specimen deposited on it. The temperature sensitivity of the employed sensor is about 2mV/K at 273K.

When exposed to the incident X-ray beam, the X-ray photons are partially absorbed in the specimen. The energy of the absorbed photons is transformed into heat resulting in the increase of the sample temperature. The sample temperature measured by the differential thermocouples feels the energy of the absorbed photons, as illustrated in Figure 4. Thus, the temperature of the micro-particle almost instantaneously follows the sequence of the exposures resulting in the increase of the particle temperature by about 0.2 K. Using this effect of sample heating due to absorption, a temperature distribution map can be collected.

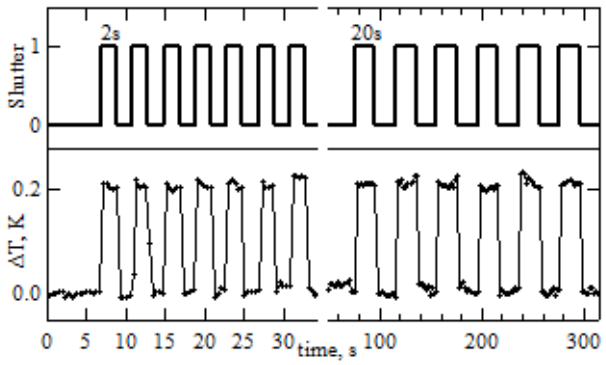

Figure 4. Temperature variation detected on the nanocalorimetric sensor (bottom panel) during exposure of the Indium micro-particle to the incident X-ray beam (top panel).

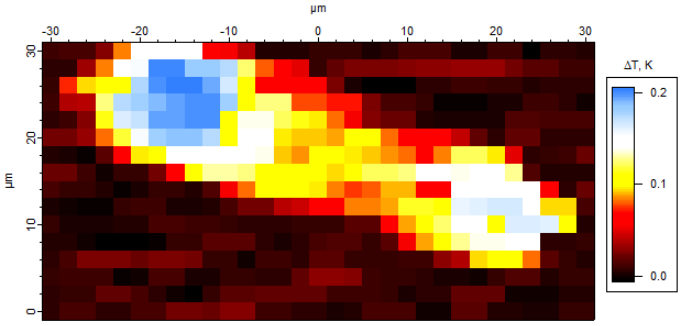

Figure 5. 2D map of temperature variation induced by the incident X-ray beam.

The temperature map of the Indium micro-particle is given in Figure 5. It can be seen that the particle shape calculated from the temperature map correctly reproduces the shape of the particle found in the absorption experiments and visualized optically. In order to validate this procedure and to check whether the nanocalorimetric sensor is sensitive enough to feel the changes in the particle topography, the temperature changes were correlated with the local absorption. The corresponding plot is given in Figure 6 showing a linear correlation of the sample temperature increase with the local absorption.

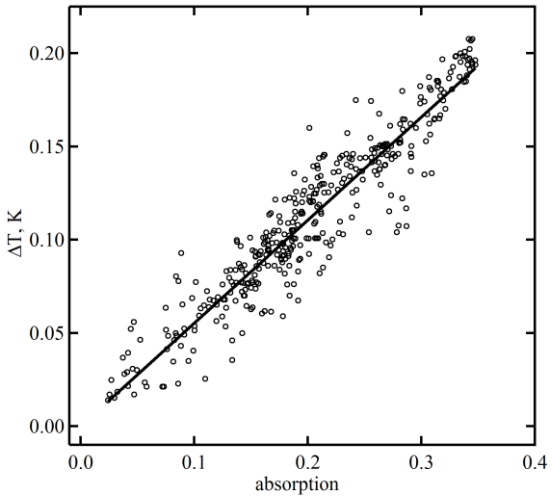

Figure 6. Temperature increase vs. absorption exhibits a linear behavior, showing that the differential thermocouples can nicely detect heating of the micro-particle by the incident X-ray beam.

In conclusion, it can be stated that the nanocalorimetric sensor can be sufficiently sensitive to detect the heat produced by absorption of the incident X-ray photons by the sample. In the first approximation, the effect of the supporting membrane can be neglected.

2.3 In-situ variable temperature experiments using the combined Nanocalorimetry/X-ray scattering setup

2.3.1 Fast heating experiments

The resistive heating elements located at the vicinity of the active area of the nanocalorimetric sensor allow to heat the sample. Due to the small thermal inertia of the system, application of voltage makes it possible to heat the specimen at extremely high heating rates. To perform quantitative heating experiments, a correlation between the temperature in the active area and the applied voltage has to be established for each sensor. However, since the sensitivity of the X-ray detectors is not sufficient to measure in real time the X-ray scattering from such micro-samples, combination of Nanocalorimetry and X-rays for fast temperature ramps is difficult. One possibility to combine the two techniques in this mode is to apply a fast temperature change to the sample and to collect the corresponding diffraction data afterwards. An example of such experiments is given in the text of our LTP proposal (see Figure 5 of the LTP).

2.3.2 Slow heating experiments using AC calorimetry mode

The designed nano-calorimetric device can be also operated in the AC-mode, where a small temperature modulation is added on top of an underlying slow heating ramp. The sensitivity of the sensor to nanogram samples is in this case accounted for by relatively high modulation frequencies, which extend in the kHz-range. The advantage of this operation mode is that, even when the sample mass is small, the thermodynamic transitions are still detectable in slow heating or cooling experiments. For example, Figure 7 displays the amplitude and phase of temperature modulation as a function of temperature for the underlying heating rate of 20K/min. At 95s after the beginning of the heating experiment, the melting of Indium sets in. This event is visible from a drastic decrease of the modulation amplitude. The simultaneously recorded X-ray diffraction signal shows at the same time a transition from the crystalline phase to the melt (cf. Figure 8). When analyzing the intensity of a single crystalline reflection (cf. Figure 9) it appears that the transition detected by the calorimetric sensor corresponds exactly to the change in scattering intensity of the selected single crystal reflection. Thus, it can be seen that, during the whole experiment, the X-ray diffraction intensity was stable and changed only at the observed thermal transition. This proves that heating of the sensor does not affect the final beam optics including the final apertures and collimator setup by the emitted heat. Furthermore, from repeated mapping experiments on the Indium micro-particle conducted before and after the heating experiment no lateral shift of the selected sample region was observed. It is noteworthy that such effects will be inevitable for conventional heating stages due to thermal dilatation.

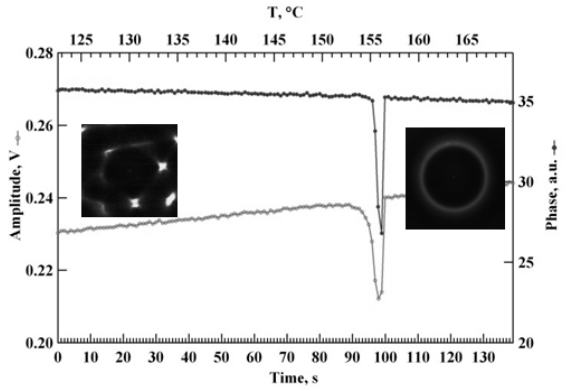

Figure 7. Amplitude and phase of temperature modulation showing the onset of the In melting transition at 95s. The time corresponds to 156.5°C.

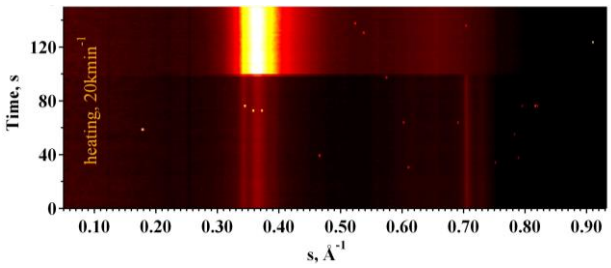

Figure 8. 1D integrated X-ray scattering curves for the Indium particle showing a melting transition after 95s heating.

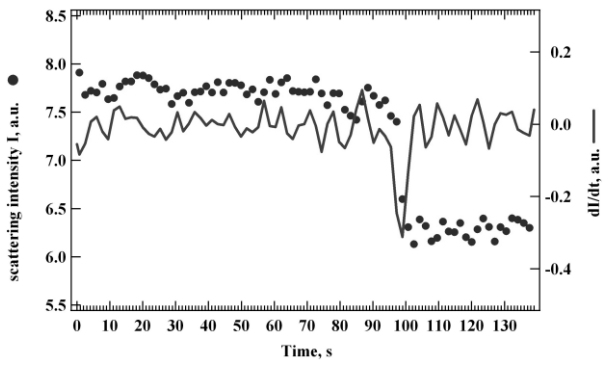

Figure 9. Scattering intensity of a single reflection of Indium as a function of heating time.

The results obtained in different operation modes of the Nanocalorimeter show that both isothermal high-temperature and variable-temperature experiments are possible in combination with the nano-focus setup in the EH3 of the ID13 beamline. This also proves that the developed nanocalorimetric sensor holder is suitable for the beamline. Even more, using the AC-mode of the calorimeter, thermodynamic transitions can be studied simultaneously with the nano-focus X-ray diffraction. Using the X-ray absorption mapping it is possible to characterize the shape and size of the studied specimen providing useful information for the analysis of the calorimetric parameters.

It is however clear that the described experimentation is only applicable to materials, which do not suffer much from the beam damage in the course of a repeated X-ray exposure. Moreover, at present time the selection of In is due to its relatively high X-ray absorption, which is higher than for most of organic materials. Therefore, a refinement of the experimental method to make it applicable for polymeric and other organic materials is planned for the second half of the first year and the second year of the LTP. One possibility, which will be considered, is continuous scanning of the beam position by submicron steps during heating experiments. To this end, the effect of the beam damage has to be evaluated. Also here the calorimetric device will serve as a useful tool to quantify the locally absorbed photon energy and the effects of the beam damage.

2. Conclusions

In agreement with the milestones defined for the first year of the LTP, a novel sensor holder was successfully installed at the nano-focus EH3 of the ID13 beamline. The flat design of the sensor holder meets the specific requirements of the nano-focus beamline, while its modular design allows easy exchange of sample with a minimum of manual intervention in the experimental hutch. In addition, an ultra-flat illuminated aperture was developed and installed. The power of the illumination can be controlled from the control cabin using common serial interface protocols. In the first experiments on micron-sized Indium particles different measuring protocols were successfully applied. A first publication summarizing the results of the measurements is in preparation.