ESRF	**Experiment title:** Pair Distribution Function analysis of size-stabilised high temperature phases of ZrO2 and TiO2	**Experiment number**: HS-3611
Beamline: ID31	**Date of experiment**: from: 25/2/2008 to: 29/02/2008	**Date of report**: 22/09/08
Shifts: 12	**Local contact(s)**: Dr. Irene Margiolaki	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Monica Dapiaggi* Università di Milano

Giulio Borghini* Università di Milano

Filippo Maglia* Università di Pavia

Report:

Recently, the stabilization of the high-temperature phase, as a general phenomenon in nano-sized materials, has attracted much attention.

Zirconia (ZrO_2) primarily exists in three different polymorphs at ambient pressure: monoclinic (room temperature-1175 °C), tetragonal (1175-2370 °C), and cubic (2370-2680 °C). The room-temperature monoclinic phase has no practical applications since its formation during cooling from the high temperature tetragonal phase is associated with the volume expansion, which results in crumbling of the ceramic components. On the other hand, the high-temperature ZrO_2 phases are suitable for various industrial applications such as solid electrolytes in solid oxide fuel cells1 and sensors, as a catalyst/catalyst support, and as membranes and dispersed phase in composite materials. Hence, traditionally high temperature ZrO_2 phases have been stabilized at room temperature by doping trivalent cations in the ZrO_2 lattice.

The high-temperature tetragonal phase can also be stabilized at room temperature without doping any trivalent impurities, provided ZrO_2 is synthesized in its nanocrystalline form with size less than a critical nanosize. In the case of nanopowders, the existence of a critical crystallite size has been determined, above which the material reverts to the stable monoclinic phase. This critical crystallite size is about 20–30 nm for pure ZrO_2.

Five different samples of size-stabilised ZrO2 were measured in a total scattering experiment at ID31. The sample compositions were (0%, 0.5%, 1%, 2%, 4% in Y atoms). The wavelength chosen for the experiments was of 0.399946 Å, with X-rays of sufficient energy to get a high momentum transfer Q, necessary to provide proper total scattering data. Those have to be normalised and then Fourier transformed in order to

provide the Pair Distribution Function (PDF) for the chosen structure. For this reason, high angle data are necessary, together with a very good counting statistics. This can be achieved by counting more on the data at higher angles. Together with those data, it is necessary to get the data for normalisation, i.e. The empty container, the empty environment, and so on.

The data collected allowed us to produce the PDFs for the 5 samples, from which it was possible to get information on both the local and the average structure. With PDF, in fact, it is possible to get information from the diffuse scattering data, and not only from Bragg peaks. In this way, one can check if, for example, the local structure is different from the average 'crystallographic' one. This is particularly useful when dealing with highly disordered samples, such as those with a finite spatial coherence, like the nanocrystalline ones. In all our samples, it was possible to note that the local structure, up to an r of 8 Å, is different from the average one, with domains that probably belong to a different crystal system (see the figure for an example).
This was out first total scattering experiment at ID31, and unfortunately, the statistics at high angle was not enough to provide a good resolution in the real space. The total counting time for each sample was about 4 hours: a good-enough statistics at high angle would mean at least to double the time spent at higher angles, with a total counting time of about 6-7 hours. This will be taken into account for while planning the next experiment.