ESRF	**Experiment title:** Time-resolved in situ SAXS/WAXS studies of nucleation and growth of inorganic nanoparticles synthesized in supercritical fluids	**Experiment number**: SC-2389
Beamline: ID02	**Date of experiment**: from: July 23rd 2008 to: July 27th 2008	**Date of report**: Sept. 1st 2009
Shifts: 12	**Local contact(s)**: Michael Sztucki	*Received at ESRF:*

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Report:

The specific properties of supercritical fluids have been exploited in the last five years for synthesizing functional nanostructured materials, especially in the field of inorganic and hybrid materials. It is known that the control of the physicochemical properties of nanomaterials (size, morphology, structure and composition) can be achieved by choosing specific operating parameters. Many important results have been obtained in materials science in the last few years using supercritical fluids [1]. Due to the use of high pressure and high temperature, the reactor of nanomaterials synthesis is often considered as a "black box".

In these conditions, there is a crucial need of *in situ* experiments to better understand and model the nucleation and growth of nanostructures in supercritical fluids. To meet this requirement we have developed a pressure cell allowing us to study the formation and growth of nanoparticles using small and wide angle X-ray scattering (SAXS/WAXS) [2]. The specific objectives of the beamtime were:

i) Study of mechanism of nucleation and growth in supercritical alcohol ($Ba_xSr_{1-x}TiO_3$ ($0<x<1$) – 14 experiments) [3]
ii) Coupling *in situ* SAXS/WAXS experiments to *in situ* fluorescence spectroscopy (Case; ZnO – 2 experiments)
iii) Determination of a new phase (Case of Nd_2NiO_4 - 8 experiments),
iv) Validation of the modelling of the nucleation and growth of copper nanoparticles [4] (Case of copper – 0 experiment due to a technical problem).
v) The formation kinetics and crystal phase evolution of $Ce_xZr_{1-x}O_2$ (6 experiments) [5]
vi) Study of the early stages of zirconia crystallization in aqueous solution [6] using three different zirconium precursors (8 experiments)

More than 38 experiments were performed during the beamtime as specified in the list. The study of the nucleation and growth of copper nanoparticles in supercritical CO_2 was not performed due to technical problems with the high pressure CO_2 pump and this study could be an important objective for a forthcoming

beamtime at ESRF, since this study could validate the first model on nucleation and growth of metal nanoparticles in supercritical fluids [4].

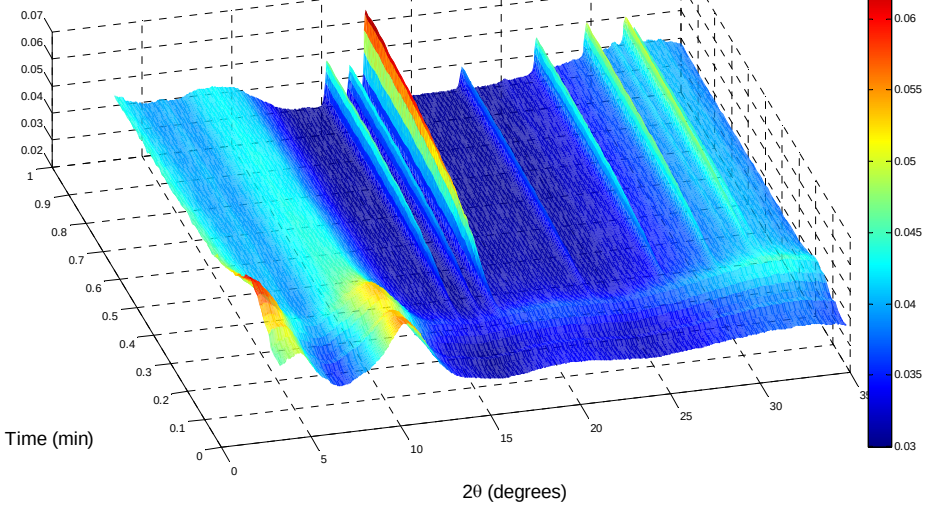

Figure 1. Diffraction data collected on the formation of zinc oxide nanoparticles in supercritical ethanol (235°C and 250 bar).

Regarding the beamline instrumentation the quality of SAXS data collected at ID02 is of very high quality. The high photon intensity and the fast detector allowed us to reach subsecond time-resolution, which is ideal for our experiments. However, the wide-angle X-ray scattering part has not been optimized to the same degree as the SAXS at ID02 and apparently serves mainly to detect crystallinity and is not intended for detailed diffraction analysis (Rietveld refinement). The resolution of the diffraction data is poor and size determination based on diffraction peak broadening is limited to very small nanoparticles. Furthermore, the tilted positioning of the WAXS detector easily leads to angular distortions, which cannot be modeled accurately using the standard displacement parameters available in Rietveld refinement software. It is unfortunate that none of this information was provided by the beamline staff at an earlier stage. However, as discussed during the beamtime with the local contact, this part of the setup is planned to be upgraded and this would be desirable for future beamtimes. Fortunately many of the systems studied do form very small nanoparticles and size determinations are possible.

As an example figure 1 shows diffraction data collected on ZnO nanoparticle formation at 60 frames per minute illustrating the rapid formation of ZnO nanocrystals in supercritical ethanol. Currently, publications including kinetical data on the formation of $Ce_xZr_{1-x}O_2$ [5] and the pure ZrO_2 data [6] are in preparation, while the data analysis of the other systems are still in progress.

References

[1] F. Cansell and C. Aymonier, Design of functional nanostructured materials using supercritical fluids, J. Supercrit. Fluids, 2009, 47, 508-516.

[2] Bremholm, M; Jensen, H; Iversen, SB, Iversen, BB: J. Supercriti. Fluids, 2008, 44 385-390

[3] H. Reveron, C. Aymonier, A. Loppinet-Serani, C. Elissalde, M. Maglione, F. Cansell, Single-step synthesis of well-crystallized and pure barium titanate nanoparticles in supercriticals fluids, Nanotech., 2005, 16(8), 1137 – 1143; H. Reveron, C. Elissalde, C. Aymonier, M. Maglione, F. Cansell, Continous synthesis of well-crystallized BST nanoparticles under supercritical conditions and its ferroelectric properties, J Nanosci. Nanotech. 2005, 5(10), 1741-1744; H. Reverón, C. Elissalde, C. Aymonier, C. Bousquet, M. Maglione and F. Cansell, Continuous supercritical synthesis and dielectric behaviour of the whole BST solid Solution, Nanotech., 2006, 17, 3527-3532.

[4] A. Erriguible, F. Marias, F. Cansell, C. Aymonier, Monodisperse model to predict the growth of inorganic nanostructured particles in supercritical fluids through a coalescence and aggregation mechanism, J. Supercrit. Fluids, 2009, 48, 79-84; S. Marre, A. Erriguible, A. Perdomo, F. Cansell, F. Marias, C. Aymonier, Kinetically-controlled formation of supported nanoparticles in low temperature supercritical media for the development of advanced nanostructured materials, J. Phys. Chem. C, 2009, jp-2008-09533n.R1.

[5] C. Tyrsted, J. Becker, P. Hald, M. Bremholm, J. S. Pedersen,J. Chevallier, S. B. Iversen, B. B. Iversen, Crystalline $Ce_xZr_{1-x}O_2$ Nanoparticles Synthesized in Supercritical Water, *in preparation*

[6] M. Bremholm, J. Becker, J. S. Pedersen, B. B. Iversen, Kinetically controlled nucleation of zirconia polymorphs probed by time-resolved *in situ* X-ray scattering in sub- and supercritical water (working title), *in preparation*