ESRF	**Experiment title:** In situ time-resolved high energy SAXS/WAXS and PDF studies of nanoparticle formation and growth in supercritical fluids	**Experiment number**: **CH-2733**
Beamline: ID15B	**Date of experiment**: from: April 1st 2009 to: April 7th 2009	**Date of report**: March 1st 2009
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Report:

In recent years, the specific properties of supercritical fluids have been exploited for synthesizing functional nanostructured materials, especially in the field of inorganic and hybrid materials. It is well 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". There is therefore 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 experimental setups allowing us to study the formation and growth of nanoparticles under sub- and supercritical conditions, using small and wide angle X-ray scattering (SAXS/WAXS) and the pair distribution function (PDF) [2].

The objectives of the beam time were:

1) Studies of the mechanism of the formation and growth of TiO_2 and ZrO_2 in supercritical water using SAXS/WAXS and PDF.
2) Studies of the mechanism of the formation and growth of Li_2TiO_3 and $Li_4Ti_5O_{12}$ in supercritical water using SAXS/WAXS and PDF.
3) PDF studies of the mechanism of the formation of Fe_3O_4 on which we have obtained high quality SAXS/WAXS data from a previous beamtime [3]
4) SAXS/WAXS studies of the formation of manganese oxide nanoparticles, investigating the role of the synthesis conditions on the oxidation state of manganese
5) SAXS/WAXS studies of the formation of Na_xCoO_2 under hydrothermal conditions
6) PDF studies of the formation of $LiFePO_4$ in sub- and supercritical water in order to understand the formation of the compound
7) SAXS/WAXS studies of the formation of CeO_2 nanoparticles, with and without the addition of adipic acid surfactants in different concentrations.

8) PDF studies of samples of nanoparticles, synthesized in our home laboratory.

The high photon intensity and the fast detector allowed us to reach sub-second time resolution, which is ideal for our purposes. Unfortunately, doing simultaneous SAXS/WAXS studies proved unfeasible due to the limited beam focusing. SAXS was therefore sacrificed in favor of WAXS. This meant that we could only extract information on the crystallite phase and crystallite size. Without the SAXS data, particle size distributions and information about any amorphous phases could unfortunately not be obtained. In hindsight, ID15A would have been more appropriate for our experiments, due to the option of microfocusing the beam. The data analysis of the WAXS and PDF data is ongoing. The WAXS data quality is sufficient to do Rietveld refinement and obtain information on crystal phase, unit cell and particle sizes. As an example of the data obtained, figure 1 shows the formation of Na_xCoO_2 from CoOOH, and the subsequent transformation into Co_3O_4. The data obtained allowed us to understand the formation mechanism, and thereby finding a way to hydrothermally synthesize phase pure nanocrystalline Na_xCoO_2. [4]

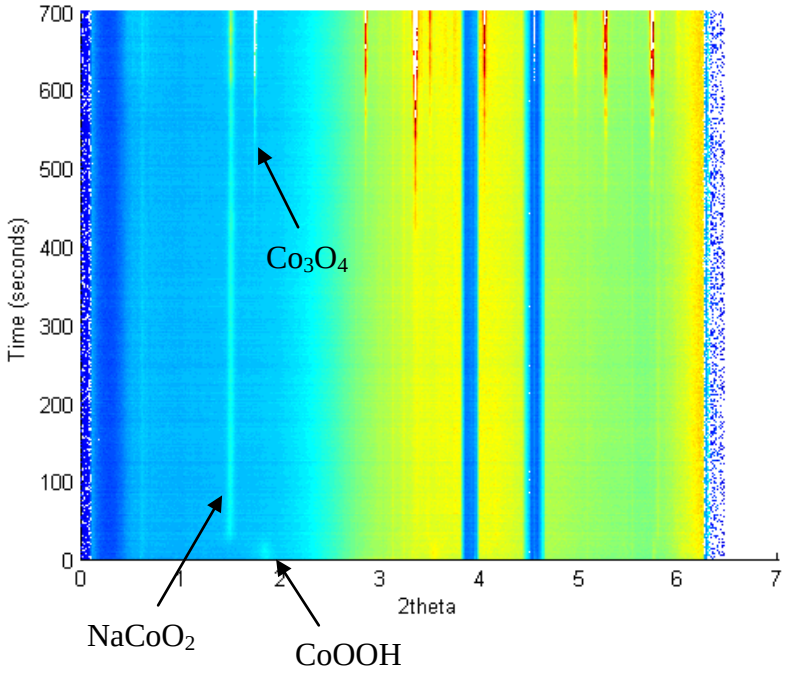

Figure 1. The transformation of CoOOH into phase pure $NaCoO_2$ under hydrothermal conditions. Formation of Co_3O_4 is observed after approximately 400 seconds demonstrating that short residence time is a requirement for phase pure $NaCoO_2$.

[1] F. Cansell and C. Aymonier, J. Supercrit. Fluids, 2009, 47, 508-516.
[2] M. Bremholm et al, J. Supercritit. Fluids, 2008, 44, 385-390.
[3] M. Bremholm et al, Angew. Chem. Int. Ed., 2009, 48, 4788-4791.
[4] K. M. Jensen et al, in preparation.