EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** In-Situ Synthesis of AlOOH nanoparticles	**Experiment number**: CH-4609
Beamline: ID31	**Date of experiment**: from: 06.07.2016 to: 08.07.2016	**Date of report**: 15.10.2016
Shifts: 6	**Local contact(s)**: Maria Valeria Blanco	

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Report:

The aim of the proposal referred to, was to study the nucleation and formation of ultra small AlOOH nanoparticles with the Pair Distribution Function (PDF) Technique.

In preparation for the project we refined a commonly chosen synthesis route for boehmite nanoparticles in such a way that it could be monitored at a beamline with our in-situ cell equipment at ambient as well as non-ambient conditions. The experimental setup and all sample measurements were executed as scheduled. Data analysis with PDF shed light on the first few hours of crystal growth of AlOOH.

Figure 1 depicts a capillary data set of a completed synthesis of AlOOH prepared in advance as reference for PDF analysis. Taking into account instrumental resolution parameters, an excellent fit of these fully aged particles was achieved in the course of the data analysis.

The averaged nanoparticle sizes were found to be 3.2 x 2.2 x 1 nm. As boehmite crystallises in Cmcm these values correspond to orthorhombic platelets consisting of 4 layers in average. The layer distances are found to be 10% larger than reported for boehmite single crystal structures.

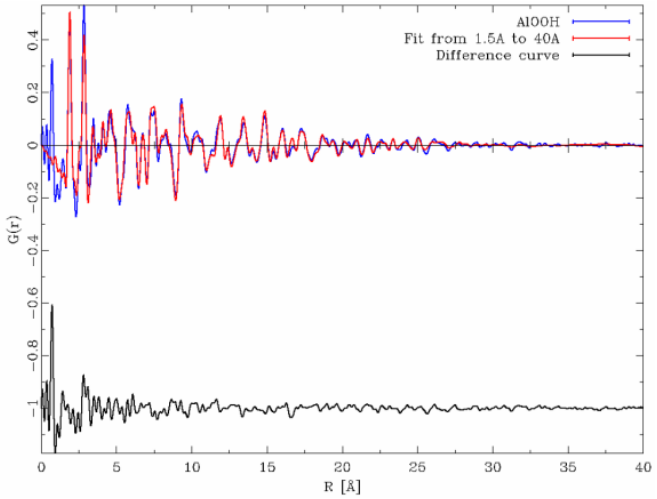

Fig. 1: Accurate fit (red, R_w=26%) of fully aged nanoparticles (blue), which are the major product of the in-situ synthesis.

PDF data collected during time-resolved in-situ measurements were processed similarly and were found to show the following behaviour (Fig. 2a/b).

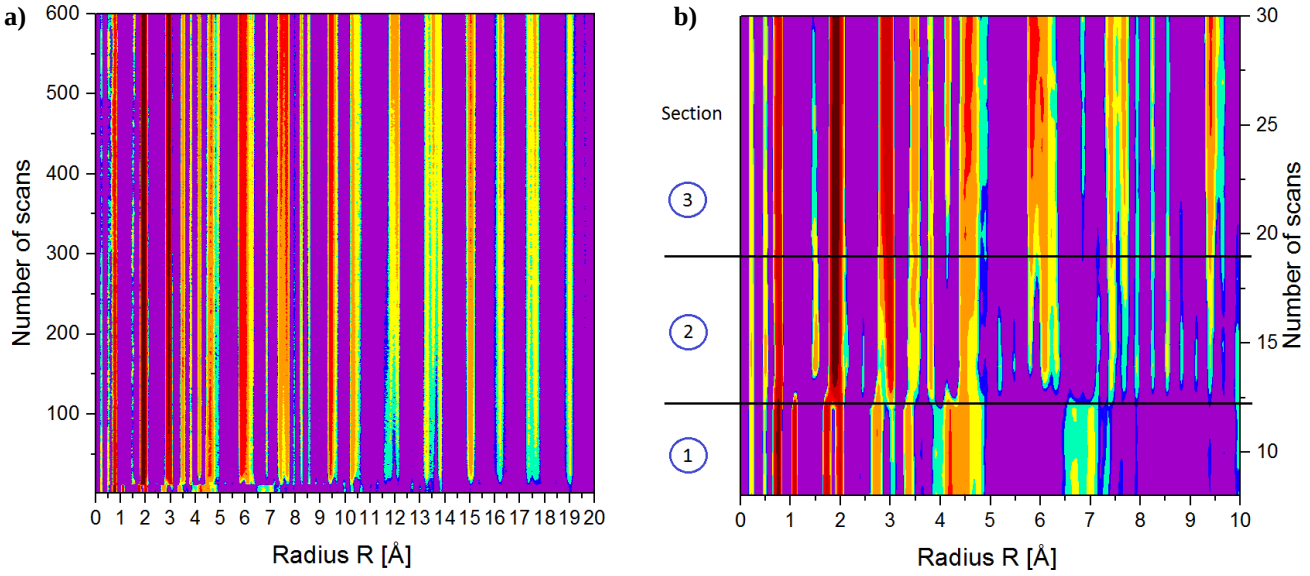

Fig. 2: a) Full PDF data set of one measurement during 2.5h; b) PDFs of the first five minutes indicating at least one precursor species dissapearing and the assembly of two single layers.

Data was collected within two hours and reveal that the reaction process can be divided in three sections. The first section refers to one reactant in solution and a few early scans right after the addition of the second reactant which determines the start of the reaction. The second section shows a vanishing precursor and the first polynuclear clusters of the reactant monomers until the first stacking of distinct layers of the crystal structure. At that point (start of section 3) the boehmite consists of two layers and a diameter of 5.0 nm in ac direction. Further growth of the nanoparticles can be monitored as time progresses until in b direction a size of 2.5 nm is reached which corresponds to nanoparticles consisting of four layers.
The significantly changing data was collected in the first few minutes of the synthesis and could not be resolved in detail due to a time resolution of 10s per output file. It appears that rapid changes in the molecular structure are averaged and, hence, accurate fits incorporating several species attempted yet to fail.

In addition, ligands used during the further AlOOH syntheses also lead to drastic changes in that early part of the measurement. To complement the study on the boehmite with focus on the nucleation phase of the nanoparticles, measurements with higher time resolution are aimed at for a successive beamtime.