



	Experiment title: Pair Distribution Function (PDF) of the Precursor of ZnO Nuclei in Nanoparticle Synthesis via in-situ XRD	Experiment number: SC- 3602
Beamline: ID-15-B	Date of experiment: from: 19 th June 2013 to: 21 st June 2013	Date of report:
Shifts: 9	Local contact(s): Simon Kimber	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): M. Zobel * R. B. Neder * Institute of Crystallography and Structural Physics Friedrich-Alexander Universität Erlangen-Nürnberg		

Report:

The aim of the proposal was to study the whole process of dissolution, precursor formation and nucleation of ZnO nanoparticles in sol-gel processes in ethanol in order to shed light onto the nucleation mechanism.

Initially it was planned in the proposal to run the synthesis only in ethanol, since this is the commonly published synthesis route. However, we ran a multitude of test experiments in our laboratories in the solvent methanol, since methanol seemed to have a multitude of advantages: i) it shows less background correction problems in the PDF, because ethanol molecules possess a higher number of intramolecular atomic distances and furthermore feature a stronger intermolecular ordering effect in solution in comparison to the smaller methanol molecules; ii) the solubility limit of our zinc source, i.e. zinc acetate dihydrate, is way higher (ca. 5-fold) in methanol, allowing higher turnover rates and hence increased scattering contrast.

We carried out several synthesis prior to the beamtime in methanol and ethanol in order to check whether our planned syntheses can as well be studied in methanol due to similar results with respect to ZnO crystallinity and particle size. In-house XRD experiments indicated this. Fig. 1 shows the PDFs of ZnO powders, which were produced prior to the experiment and measured during our beamtime at ID-15-B: once in methanol (blue) and once in ethanol (red). The nanoparticles synthesized in methanol are slightly larger, but structurally identical.

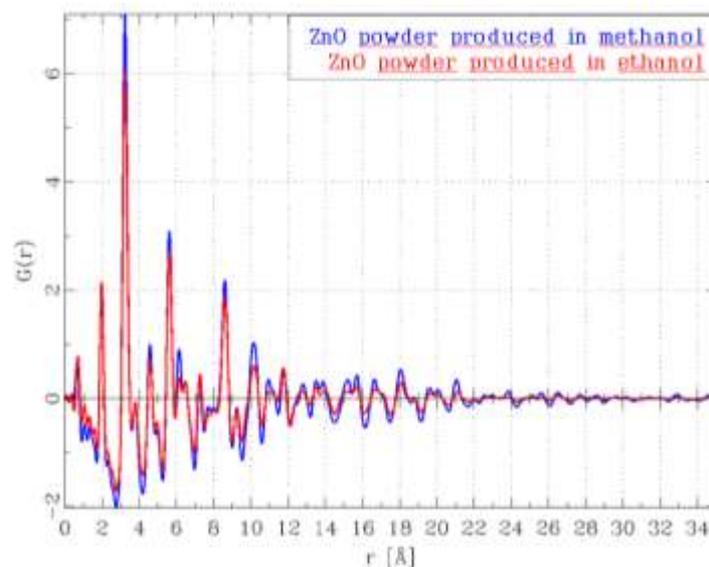


Fig. 1: Comparison of PDFs of wurztitic ZnO nanoparticles produced in methanol (blue) and ethanol (red)

This coincidence of the synthesis products within ethanol and methanol led us to the assumption that the synthesis should be comparable throughout the entire synthesis procedure. Hence, we decided to study the nucleation of the ZnO nanoparticles in methanol instead of ethanol due to the above mentioned advantages. However, when we evaluated the in-situ data back home, we realized that the course of the reaction strongly differs in ethanol and methanol. In ethanol, the synthesis goes along tetrahedral building units, which over time form nanoparticles of increasing size. In methanol, though, the solution features brucite, i.e. octahedrally, structured particles upon the addition of the base TMAH instead of the tetrahedral wurtzite structure of bulk ZnO. Fig. 2 shows a comparison of a fit of wurtzite ZnO and brucite ZnO particles to the same in-situ data set at a reaction time of 100 min after base addition. It is obvious, that brucite fits way better, in particular for larger distances, where the wurtzite fit fails entirely. This result astonished us and we concluded that during the production of powders the transformation of the brucite structure to the tetrahedral structure has to occur somewhere in between. The additional steps in the powder production are a precipitation of the particles with a hexane-acetone mixture, a centrifugation step as well as subsequent drying of the formed gels overnight in an exsiccator. Therefore, we conclude that one of those three steps initiates the structural rearrangement from brucite to wurtzite structure particles, since the powders do not show octahedral zinc hydroxide like platelets at all. We are currently running further in-house research to detect the determining reaction step.

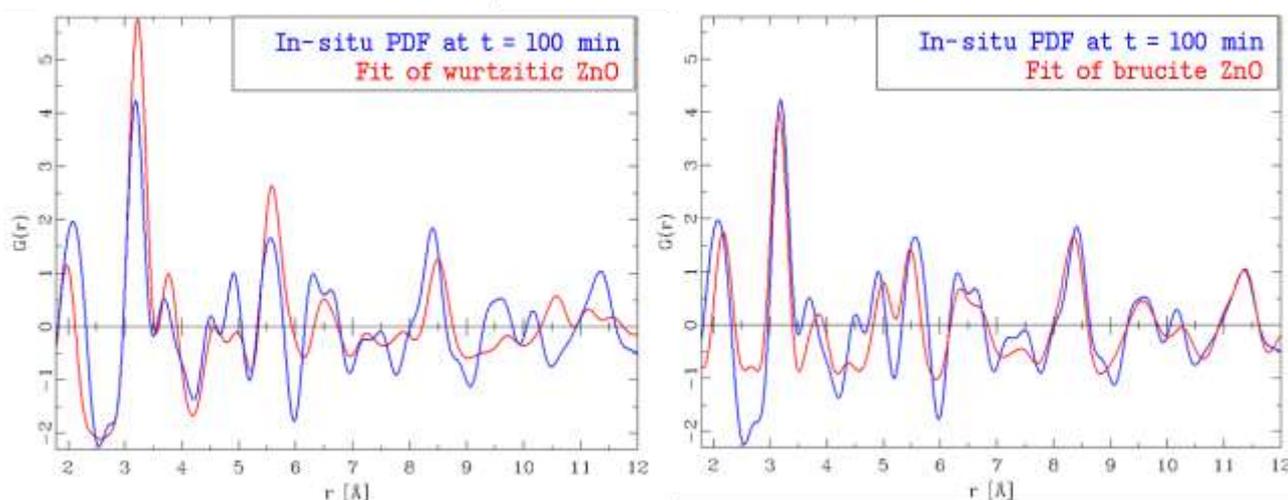


Fig. 2: Comparison of fits of wurtzite and brucite ZnO particles to the same insitu data in methanol