



## 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://www.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.



	<b>Experiment title:</b> In-situ studies of Cu-V-O nanoparticle colloidal synthesis.	<b>Experiment number:</b> CH-5233
<b>Beamline:</b>	<b>Date of experiment:</b> from: 25.10.2017 to: 30.10.2017	<b>Date of report:</b> 16.02.2018
<b>Shifts:</b>	<b>Local contact(s):</b> Dr. Wouter Van Beek	<i>Received at ESRF:</i>

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**Report:**

The experimental campaign concerned in-situ studies of colloidal synthesis for the preparation of ligand-capped copper and copper-vanadates nanocrystals. Experiments were carried out using a custom made in-situ cell, which was built for the described experiments. This cell enables in-situ studies of reactions in a three-necked flask up to 300°C and at energies as low as 5 keV, which is necessary for following the vanadium K-edge XANES. The aim was to elucidate the influence of different solvents and precursors on the products, and to study the evolution of V and Cu containing compounds during the heating. The cell was assembled, and mounted on a x-y-z-tilt stage during the first hours of the beamtime.

The **first set of experiments** included the synthesis of Cu-V-O compounds. Four synthesis (A, B, C, D) with varying amounts of reactants were carried out to follow the changes in XANES of copper and vanadium at the K-edges. These reactants are oleic acid and oleylamine; their total amount was 2 mmol, 10 mmol, 20 mmol, 30 mmol in A, B, C and D respectively. The procedures were variations of a synthesis developed by our group that resulted in the formation of different phases and in different ratios, specifically small amounts of  $\beta$ -Cu<sub>2</sub>V<sub>2</sub>O<sub>7</sub>, together with V<sub>3</sub>O<sub>5</sub> and Cu, based on ex-situ XRD in our laboratory. The aim was to establish the mechanism of phase transitions and to elucidate the reaction path between the precursors to eliminate the bi-phasic products. The results from the V K-edge are presented in Figure 1 while the results for the Cu K-edge are only discussed. The heat treatment consisted in a ramp to 280°C during ~30min, followed by a 30min soaking. By comparing the obtained data with our own references and those found in literature, it was concluded that during the process the vanadium reduces from the initial 4+ in VO(acac)<sub>2</sub> to 3+/4+. This is accompanied by a change in the local symmetry around V atoms, as can be seen in the decrease of the pre-edge peak signal at around 5470 eV at 260°C. From the XRD patterns, the synthesis product was identified as V<sub>3</sub>O<sub>5</sub>. A slight difference was noted in the XANES spectra between the products of synthesis A or B, and C or D. Lower concentrations of oleic acid and oleylamine result in a slightly lower oxidation state of the product, and a decrease in the local symmetry judging by the intensity of the pre edge feature.

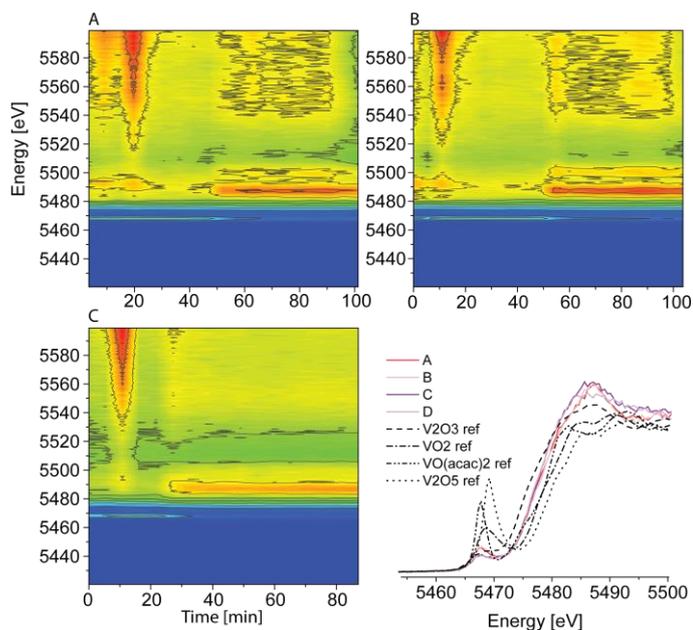


Figure 1: In-situ XANES at V K-edge during CVO synthesis A, B, and C. Bottom right corner: comparison of final spectra of the products.

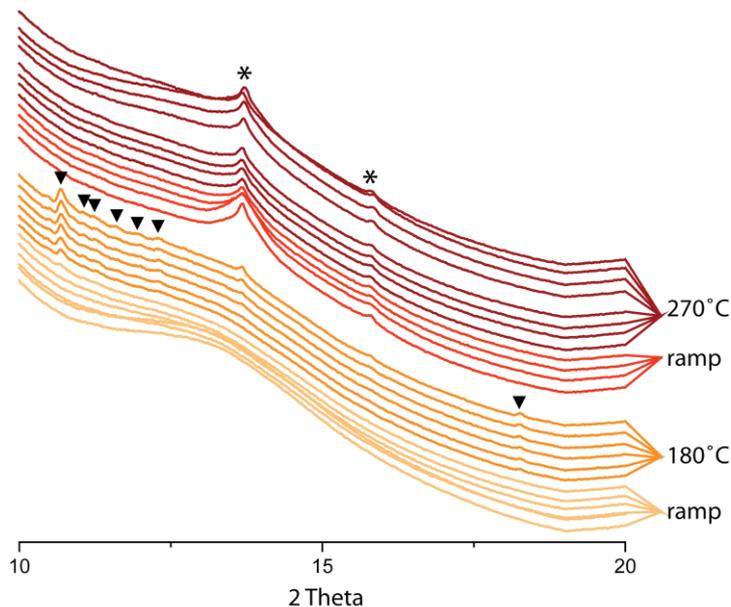


Figure 2: in-situ XRD of the Cu nanoparticle synthesis. Data was acquired with  $\lambda=0.505\text{\AA}$ .

In the case of Cu K-edge, at the same temperature of  $260^{\circ}\text{C}$  we observed a shift from the initial Cu  $1+$  in the copper precursor to Cu metal. The products are Cu nanocrystals, which can be concluded by comparing the Cu foil reference with the final XANES spectra during the reactions. The pre-peak feature is higher in intensity, and the oscillations are dampened, which has been often reported as the influence of the nano-size crystallites on the XANES. Hence, in each case the major products of the reactions were  $\text{V}_3\text{O}_5$  and Cu. The interesting observation from the XANES is that both reduction reactions,  $\text{VO}(\text{acac})_2 \rightarrow \text{V}_3\text{O}_5$  and  $\text{CuOAc} \rightarrow \text{Cu}$  occur simultaneously, which might mean one is involved in the other. We have performed two test reactions using the same process for the two precursors alone, to verify whether they interact. The products were analyzed by XRD at our laboratory. The XRD patterns indicate a distorted  $\text{V}_3\text{O}_5$  phase when the Cu precursor was absent. In the presence of the Cu precursor, the pattern is of much higher quality, and all reflections from  $\text{V}_3\text{O}_5$  are observed. We observe almost the same products when the Cu precursor is absent, as in the case of the synthesis with both precursors present. This means that little or no interaction between the two precursors is taking place. Moreover, we do not observe the formation of any intermediates during the heat treatment, which might prevent the formation of a ternary phase. This issue can be addressed by the hot-injection method, but in this case it appears the problem lies elsewhere. Most likely, the observed reactions proceed due to the presence of oleylamine, which acts as a reducing agent, while oleic acid acts as a capping agent. The presence of oleylamine stabilizes the vanadium and copper containing species at a lower oxidation state, and the capping agent prevents interactions between them. These findings hint at the possibility of a modified strategy to achieve phase pure Cu-V-O nanocrystals. We plan to change the ligands and try to use a more reactive vanadium precursor, in order to ease the accessibility of the two reactants, and direct the reaction towards a ternary phase formation.

In **the second set of experiments** we studied the nucleation process of Cu nanocrystals by coupling XRD and XAS at the Cu K-edge. The synthesis is well established in this case, hence we chose it as a model system to study the capabilities of the developed in-situ cell. Four experiments were carried out, where we followed the structural changes occurring during the transformation of CuOAc precursor into  $\sim 10$  nm ligand capped Cu nanoparticles. The thermal treatment consisted in a ramp to  $180^{\circ}\text{C}$  during 30-40min, a 30min plateau at  $180^{\circ}\text{C}$ , followed by another 10min ramp to  $270^{\circ}\text{C}$  and a 30min dwell time at this temperature. Peak shape examination hints at the presence of two major populations in terms of crystallite sizes. Rietveld analysis indicates a crystallite size of 6 and 18 nm. From the TEM image analysis we find a size distribution within these limits, with an average size of 10 nm. We observe no temporal evolution of the size of the Cu crystallites during the heat treatment. We propose that the set of reflections at  $180^{\circ}\text{C}$  comes from Cu nanoclusters which are an intermediate state during the nucleation. Dedicated experiments are planned to elucidate the mechanism of this non-classical nucleation.