

## Experiment 08-01-959, BM08

**Title:** Co-site during the formation of Co-based urchin-like hollow nanospheres

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**Experimental conditions:** XAS at Co K-edge during in-situ air annealing

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**Samples measured (substrate is silica):**

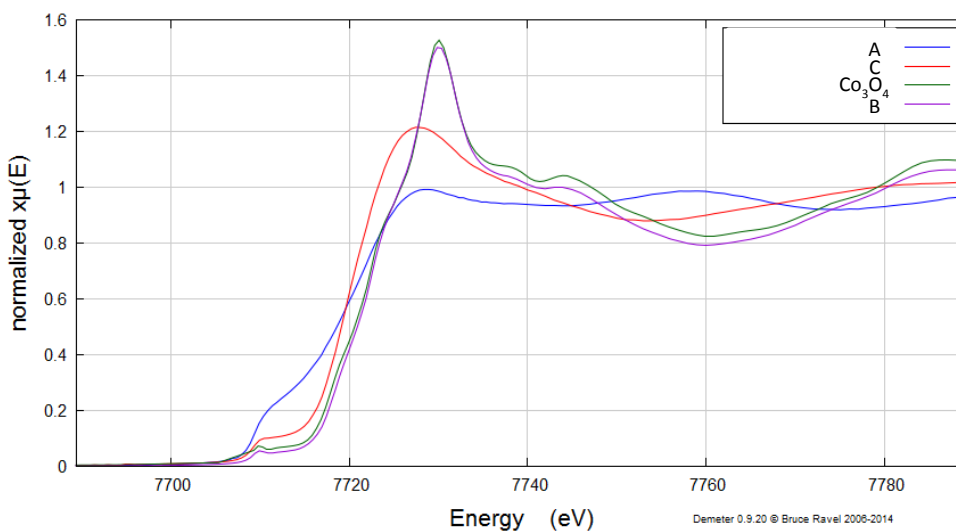
set A: Co deposition by plasma laser deposition (PLD)

set B: Co-O deposition by PLD

set C: Co-O-B deposition by PLD

set D: preformed nano-urchins structures by hydrothermal synthesis.

We have measured for all sets of samples XANES spectra during air annealing and full EXAFS spectra at specific annealing conditions. During air annealing the temperature was increased up to 490 °C. To test higher temperatures and oxygen rich atmosphere (larger air volume) we have also performed ex-situ annealing treatments in air. Some sets of samples during air annealing form urchins structures. The urchin formation was tested by scanning electron microscopy at ESRF. The experiment allowed to monitor the Co site during oxidation in general and urchin formation when it was the case. The experimental spectra from the samples were compared with those of Co-based compounds with defined oxidation state and site geometry. As an example, three XANES spectra from the PLD as-deposited samples (A, B, C) are shown below, indicating how the Co oxidation state depends on the deposition conditions.



In the following picture, an example of Fourier transform moduli of full EXAFS spectra for deposition 'C' after different air annealing processes (all ending with 1 h heating at T=500 C) is reported. Depending on the detail of

the air annealing ramps, the Co metallic fraction can be varied (signal in the region marked with the oval shape). This fraction is maybe correlated with the urchin formation. Nevertheless, the XAS spectra measured the average Co site in the samples, i.e., including both Co in the particles/urchins AND Co in the flat part of the deposited layer. Part of data have been published in the ref. above. To fully understand the mechanism of urchin formation, a new XAS experiment is needed to focus selectively on the Co site in the particles/urchins.

