

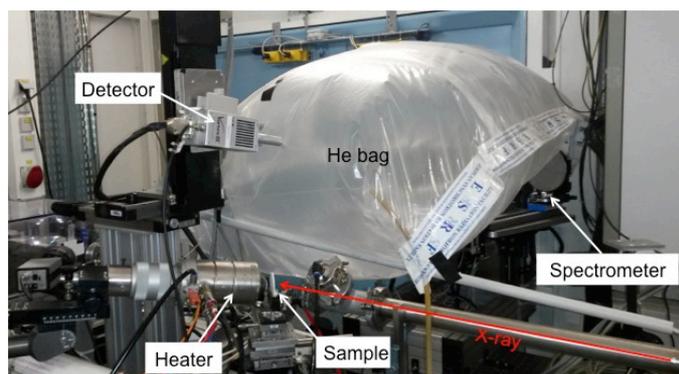


	<b>Experiment title:</b> In situ site-selective EXAFS investigation of the transformation of nanoconfined Co(II)Co(III) Prussian Blue Analog into oxide	<b>Experiment number:</b> 30-02 1065
<b>Beamline:</b> FAME	<b>Date of experiment:</b> from: 12/02/2014 to: 18/02/2014	<b>Date of report:</b> 15/04/2014
<b>Shifts:</b> 18	<b>Local contact(s):</b> Olivier PROUX	<i>Received at ESRF:</i>
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The goal of the proposed experiment was to directly probe the change in the electronic and local structure of the Co cations accompanying the formation of  $\text{Co}_3\text{O}_4$  from the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor during calcination by means of *in situ* Co K-edge site-selective X-ray Absorption Spectroscopy (XAS). Using the high-energy resolution spectrometer available on the FAME beamline, we planned to record the X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectra for the two types of Co cations ( $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ ) present in the PBA structure and hence understand the role of each cation on the calcination process. With such knowledge, the formation of the  $\text{Co}_3\text{O}_4$  oxide from the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor is expected to be completely understood, and hence the syntheses of confined mixed oxides better apprehended.

#### Results and the conclusions of the study

During this beamtime, we followed the *in situ* calcination of the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor into  $\text{Co}_3\text{O}_4$  oxide using site-selective XAS. The  $\text{K}\beta$  emission lines of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  references were first measured, along with the  $\text{K}\beta$  spectrum of the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor; this initial step enabled to (i) calibrate the spectrometer for the HERFD-XAS measurements and (ii) estimate the relative proportions of each oxidation state ( $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ ) in the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor. For each oxidation state, HERFD-XANES spectra were recorded at room-temperature and 5 temperatures up to  $400^\circ\text{C}$ , using the blowing heater from the Sample Environment Lab, which has been calibrated prior the calcination of the sample. The integration of the heater inside the spectrometer setup was realized with both the teams of the Sample Environment Lab and the FAME beamline (Fig. 1).

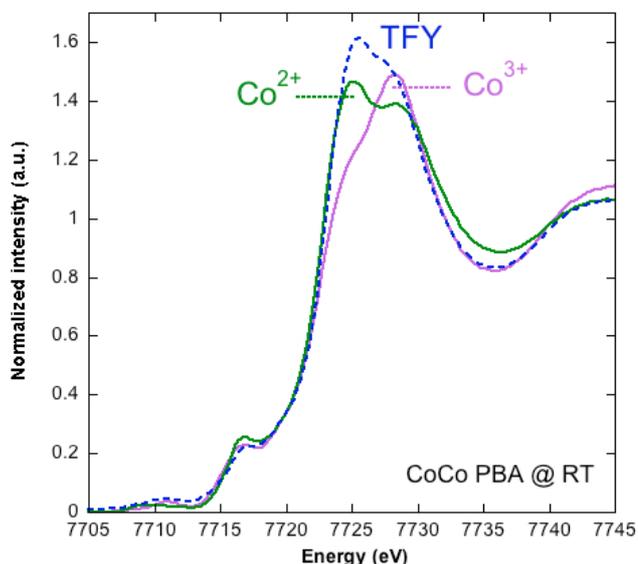


**Figure 1:** Experimental setup for *in situ* site-selective XAS

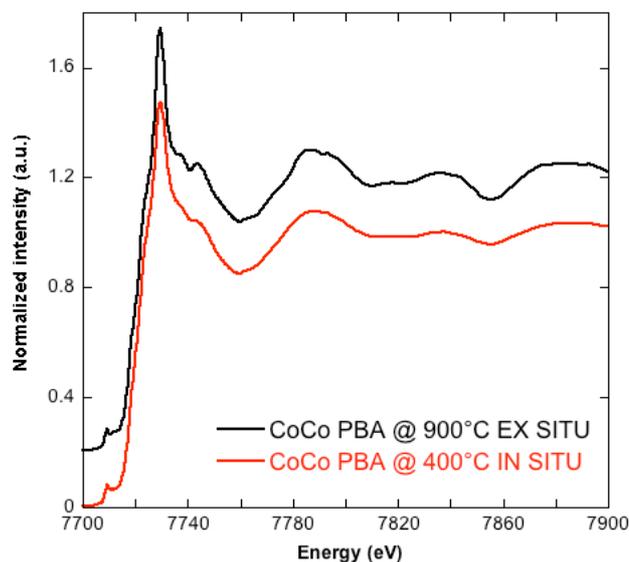
Thanks to the high resolution of the spectrometer available on FAME, the  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  contributions could be well separated and the spectra for each oxidation state were nicely resolved. The normalized spectra obtained at room temperature are presented in Fig. 2, along with the spectrum recorded in the TFY mode. It is very clear from this figure that the TFY mode cannot discriminate the contributions from each site. The spectra of each oxidation state show very different spectral features, both in the edge (Fig. 2) and the pre-edge, as well as in the EXAFS part. The changes for each site during the *in situ* calcination process could be well followed till the complete oxidation of the precursor into the  $\text{Co}_3\text{O}_4$  oxide. The TFY-XANES spectra of the *in situ* calcinated oxide and the *ex situ* one are compared in Fig. 3. The similarity between the two spectra clearly demonstrates that the *in situ* process was identical to those who happens during heating in the oven in the lab, and that the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor was entirely transformed into  $\text{Co}_3\text{O}_4$  oxide. The only difference lies in the apparent lower cristallinity of the *in situ* calcinated oxide, revealed by the smoother features. Tests have been performed on the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor confined in the mesoporous silica. Beam damages have been observed, and therefore this compound was not measured *in situ*.

The investigation of the use of PBA as precursor for oxide started with the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA and the corresponding  $\text{Co}_3\text{O}_4$  oxide as it is the simplest case. Indeed no phase demixion can occur during this calcination process since only one transition metal is present. Therefore, as the next step of this study, we also measured during this beamtime the HERFD-XANES spectra at the Co K-edge of the  $\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$  PBA precursor. The measurements were performed for the *ex situ* calcinated compound and during the *in situ* calcination using the heater; as for the  $\text{Co}^{\text{II}}\text{Co}^{\text{III}}$  PBA precursor, the spectra of the *in situ* and *ex situ* calcinated oxides are identical.

To conclude, we have succesfully followed by XAS the calcination of PBA leading to the formation of oxides. The stability of the FAME beamline and of the heating system from the Sample Environment Laboratory, associated with the high quality of the FAME spectrometer (using crystals from FAME and ID26), enabled to record very high quality data. Their interpretation, in particular from the EXAFS, will bring fundamental information on the formation of the  $\text{Co}_3\text{O}_4$  oxide from the  $\text{CoCo}$  PBA.



**Figure 2:** Co K-edge HERFD-XANES spectra of a  $\text{CoCoPBA}$  recorded at room temperature for the  $\text{K}\beta$  lines of  $\text{Co}^{2+}$  (green line) and  $\text{Co}^{3+}$  (dark line), along with the TFY XANES spectrum (blue line).



**Figure 3:** Co K-edge TFY XANES spectra recorded for the bulk  $\text{CoCo}$  PBA after *in situ* calcination at  $400^\circ\text{C}$  (red line), compared with a *ex situ* reference sample calcinated at  $900^\circ\text{C}$  (black line).

**Justification and comments about the use of beam time :** Three shifts were dedicated to the alignment of the beamline and of the 5 crystals of the spectrometer, the investigation of reference samples and the setup (including calibration) of the heating system. The 16 other shifts enabled to investigate the samples for the different calcination temperatures. Since the  $\text{CoCo}$  PBA confined in mesoporous silica presented radiation damages, we choose to investigate only the bulk compound, for both the  $\text{CoCo}$  and  $\text{CoFe}$  PBAs.