ESRF	**Experiment title:** Understanding the interconversion between iron oxide epitaxial thin films oxidation mechanism and H2O and CO2 catalytic splitting	**Experiment number**: A25-2-1050
Beamline:	**Date of experiment**: from: 06/02/23 to: 15/02/23	**Date of report**: 15/02/2023
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Report:

The aim of this proposal was to study the structural transition of FeO-Fe_3O_4-Fe_2O_3 in epitaxial thin films under different oxidation atmospheres (O_2, H_2O and CO_2) and temperatures (200-900ºC) by means of in-situ X-ray Diffraction to understand the interplay between lattice oxidation and catalytic response of iron oxide thin films, with the future goal of its application in the production of clean energy.

We analized the phase transformation of iron oxides as epitaxial thin films on $SrTiO_3$ substrates. We increased the temperature of the sample in a fixed partial pressure of the reduction atmosphere. We first demonstrated the cyclic reduction and oxidation process on iron oxide epitaxial thin films by annealing in UHV and O_2. Here, we studied the oxidation-reduction behaviour of the epitaxial thin films in UHV (10^{-10} mbar), O_2 and CO_2 atmospheres with low partial pressures in the range from10^{-8} to 10^{-4} mbar by in-situ XRD where we found an unexpected active participation of the substrate in the redox process (figure 1). When heating the sample above 800ºC, the substrate releases oxygen creating oxygen defects at the STO/layer interface. The released oxygen is taken by the thin film, preventing the oxide film to reduce. When the sample is cooled down, the substrate takes oxygen from the thin film in order to eliminate its oxygen defects, reducing the layer.

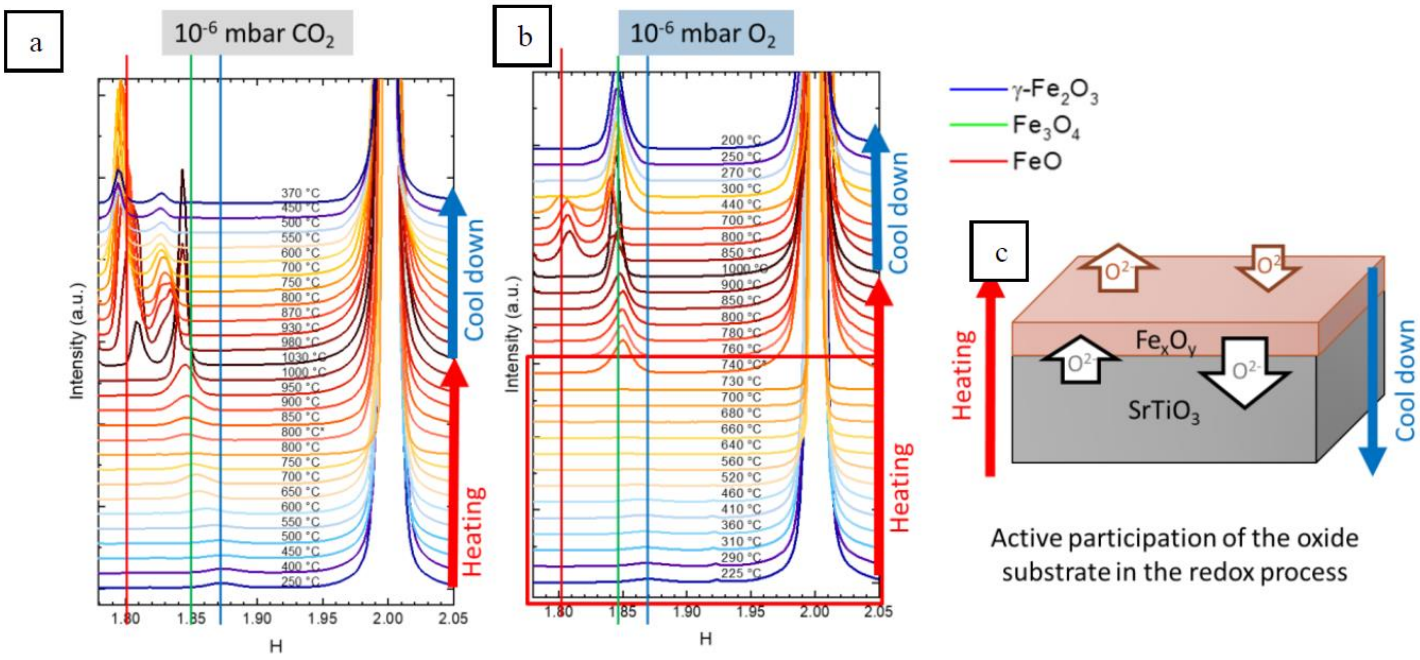

Figure 1. SXRD data showing the structural transition FeO-Fe_3O_4-Fe_2O_3. Annealing from RT to 1000°C and posterior cooldown of the sample under (a) 10^{-6} mbar of CO_2 and (b) 10^{-6} mbar of O_2. The red, green and blue lines represent the theoretical positions of the diffraction peaks depending on the formed oxide phase: FeO, Fe_3O_4 and γ-Fe_2O_3 respectively. (c) Schema of the participation of the substrate

We plan to extend the study to the mbar range. We foresee to use in-situ X-ray diffraction to characterize the structural transformation during the reduction-oxidation process FeO-Fe_3O_4-Fe_2O_3 on epitaxial thin films under O_2, CO_2, H_2O and N_2 atmospheres (mbar range) in the temperature range from 200 ºC to 900ºC. The aim of this experiment is to understand the oxidation mechanism of iron oxide epitaxial thin films that drives the catalytic splitting of CO_2 and H_2O.