ESRF	**Experiment title:** Performance of silver exsolved nanoparticles material Ag-$La_{0.80}Sr_{0.15}FeO_{3-d}$ for hydrogen production by thermal water splitting at moderate temperature.	**Experiment number**: IH-MA-324 and A25-2-1044
Beamline: BM25 Spline	**Date of experiment**: from: 17/01/23 to: 23/01/23	**Date of report**: 13/02/23
Shifts: 12	**Local contact(s)**: Juan Rubio	*Received at ESRF:*

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Report: The aim of the experiment was twofold. (1) Through the recording of XRD and XAS data, we studied the strtuctural and electronic changes asociated to the exsolution of silver nanoparticles; indeed, when Ag-doped $\mathbf{La_{0.80}Sr_{0.15}Ag_{0.05}FeO_{3-d}}$ is heated in mild conditions silvere is exsolved and the perovskite matrix experiences a sieres of changes worth to be studied. (2) Once Ag is exsolved, the $\mathbf{La_{0.80}Sr_{0.15}FeO_{3-d}}$ matrix is decorated with mental naomparicles. This materials is stable for alarge number of WS cycles; so structural and XAS study in WS operando conditions with the aim of determining in what extend the $\mathbf{Ag\text{-}La_{0.80}Sr_{0.15}FeO_{3-d}}$ material is as stable, reversible and durable for WS application. The variation of iron and silver oxidation states, the structural evolution and the eventual growth of silver NPs were intended to be studied.

As a reference three samples prepared ex-situ were studied by XRD and XAS at RT: $La_{0.85}Sr_{0.15}FeO_{3-d}$ (LSFO), $La_{0.80}Sr_{0.15}Ag_{0.05}FeO_{3-d}$ (LSAFO) and Ag-$La_{0.80}Sr_{0.15}FeO_{3-d}$ (Ag@LSFO). Figure 1a shows the XRD patterns of the three samples, no clear differences are observed, most likely due to low level of silver content, and to the nano size of the silver exsolved particles. More information is provided by the XAS spectra collected in the Fe-Kedge (Fig. 1b), and the Ag-Kedge (Fig. 1c). In the pristine materials iron is in oxidation state slightly higher than three; on heating around 200ºC the oxidation state increases most likely due to the exsolution of silver without loss of oxygen ions. Further heating induces reduction of iron most likely due to oxygen release and creation of oxygen vacancies. On its hand, silver is as Ag+ in the parent oxide, being exsolved as metallic nanoparticles.

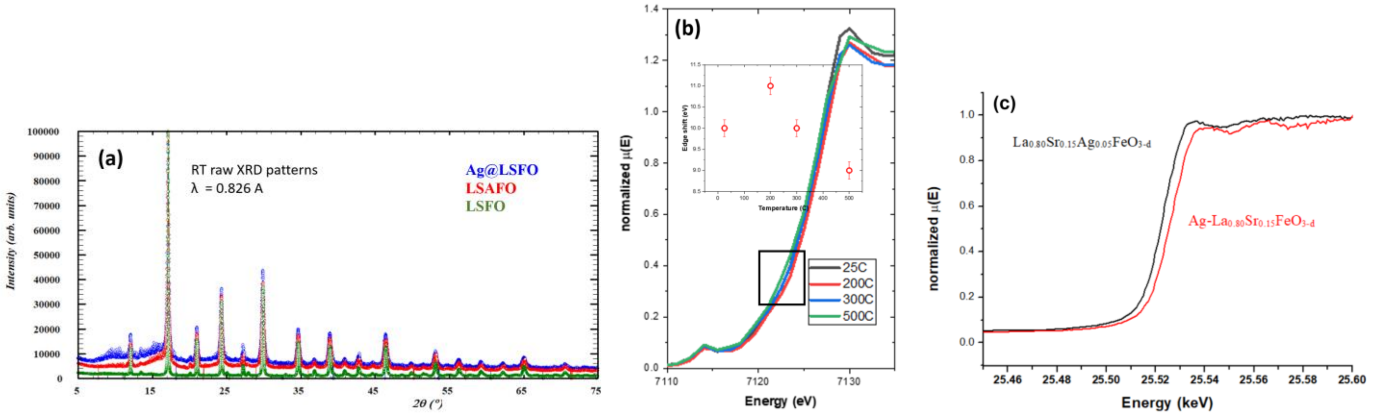

Figure 1. (a) SXRD patterns of the samples. **(b)** XAS spectra in the Fe-Kedge as a function o temprature. **(c)** RT XAS spectra in the Ag-Kedge before and after exsolution.

To study the exsolution process XRD patterns and XAS spectra (in the Fe-edge) were recorded on LSAFO at different temperatures from RT to 500 C in air. From XAS it is evident that exsolution occurs around 200ºC with oxidation of iron, which implies that oxygen is not released from the perovskite matrix, according to the processes described in Eq. (1). On heating further, iron is reduced, this being associated with oxygen loss according to Eq.(2). Due to experimental limitations (some beam shutdowns occur during the experiments days, and the change from Fe-Kedge to Ag-Kedge is a relatively time-consuming process) we decided to limit the XAS experiments to iron.

$$La_{0.80}Sr_{0.15}Ag_{0.05}FeO_{3-d} \rightarrow 0.05\ Ag + La_{0.80}Sr_{0.15}(Fe^{x}_{Fe})_{0.95}(Fe^{\bullet}_{Fe})_{0.05}O_{3-d} \qquad \text{Eq. (1)}$$

$$La_{0.80}Sr_{0.15}(Fe^{x}_{Fe})_{0.95}(Fe^{\bullet}_{Fe})_{0.05}O_{3-d} \rightarrow La_{0.80}Sr_{0.15}(Fe^{x}_{Fe})_{0.95+2y}(Fe^{\bullet}_{Fe})_{0.05-2y}O_{3-d-y} + y/2\ O_2 \qquad \text{Eq. (2)}$$

Finally, we performed some WS cycles, recording only XRD data (due to experimental limitations). **Figure 2** shows the pattern evolution upon cycling at 800° C. Once reduced in N_2, when a water-saturated stream is feed to the reaction chamber the unit cell of $La_{0.80}Sr_{0.15}FeO_{3-d}$ (matrix of the Ag@LSFO sample) contracts; conversely, in the second step when pure N_2 stream is applied, LSFO expands, most likely due to the reduction of iron cations.

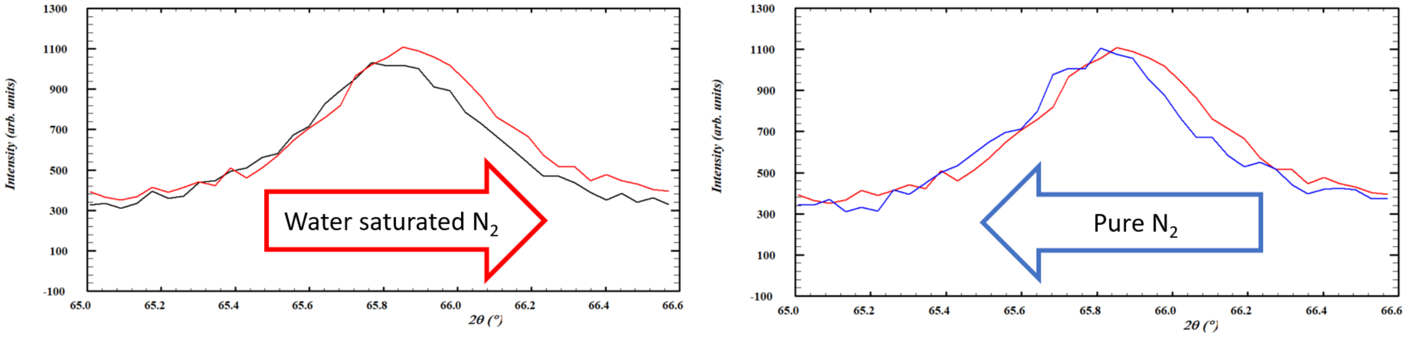

Figure 2. Displacement of the (040) peak upon cycling in pure N_2 (reduction stage, left panel) and water saturated-N_2 streams (reoxidation stage, right panel).