ESRF	**Experiment title: High energy X-ray diffraction study of reversible structure on doped-$LaCoO_3$ perovskite: a dynamic approach**	**Experiment number**: MA-3625
Beamline: ID15A	**Date of experiment**: from: 13.9.2017 to: 19.9.2017	**Date of report**:
Shifts: 18	**Local contact(s)**: Stefano Checchia	*Received at ESRF:*

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Report:

This experiment was devoted to the study of the reversible structural properties of selected perovskite-type oxides to redox pulsing as a function of temperature. This behaviour is closely related to catalytic properties. Four samples were fully characterized in this respect using high energy X-ray diffraction at beamline ID15A: $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$, $La_{0.5}Sr_{0.5}CoO_3$ and $LaCo_{0.5}Fe_{0.5}O_3$ that are used as potential automotive exhaust catalysts. The setup of the equipment at the beamline required 2 shifts, especially because of calibration of gas mass flow meters with the requested gases and of mounting of the ESRF capillary setup as sample environment. Quartz capillaries of 2 mm diameter (0.01 mm wall thickness) were used, which are relatively easy to fill, achieve high gas flows (here 50 ml/min) and, especially, allow insertion of a 0.5 mm thermocouple at the sample position. However, perovskite-type oxides are materials of low surface area and low porosity. Three shifts were lost in the attempt to try and measure these samples: the major issue was that in some cases the sample bed within the capillary was too compact and sieving did not help. An experiment consisted in heating the sample to the desired temperature (200, 225, 250, 275, 300, 350, 400, 450 and 500°C) in 5 vol% O_2/He followed by repeated and alternate pulses of 5 vol% CO/He, 1 vol% Ar and 5 vol% O_2/He (30 s each). The same experiments were performed with 5 vol% H_2/He as reducing agent. Additional measurements were performed a) with different O_2 concentrations in order to estimate energy barrier of oxidation of the perovskite, and b) at 650°C to observe a situation where the perovskite-type structure does not recover easily. Above 300°C, the measurements at selected temperatures were intervalled by heating to 600°C in 5 vol% O_2/He in order to ensure restauration of the original structure, which was confirmed by XRD. Time-resolved HEXRD was collected at 79.5 keV at 0.5 s/pattern resolution using the Pilatus detector positioned 800 mm from the sample. One sample required ca. 3 shifts to complete the full sequence of temperature dependent experiments.

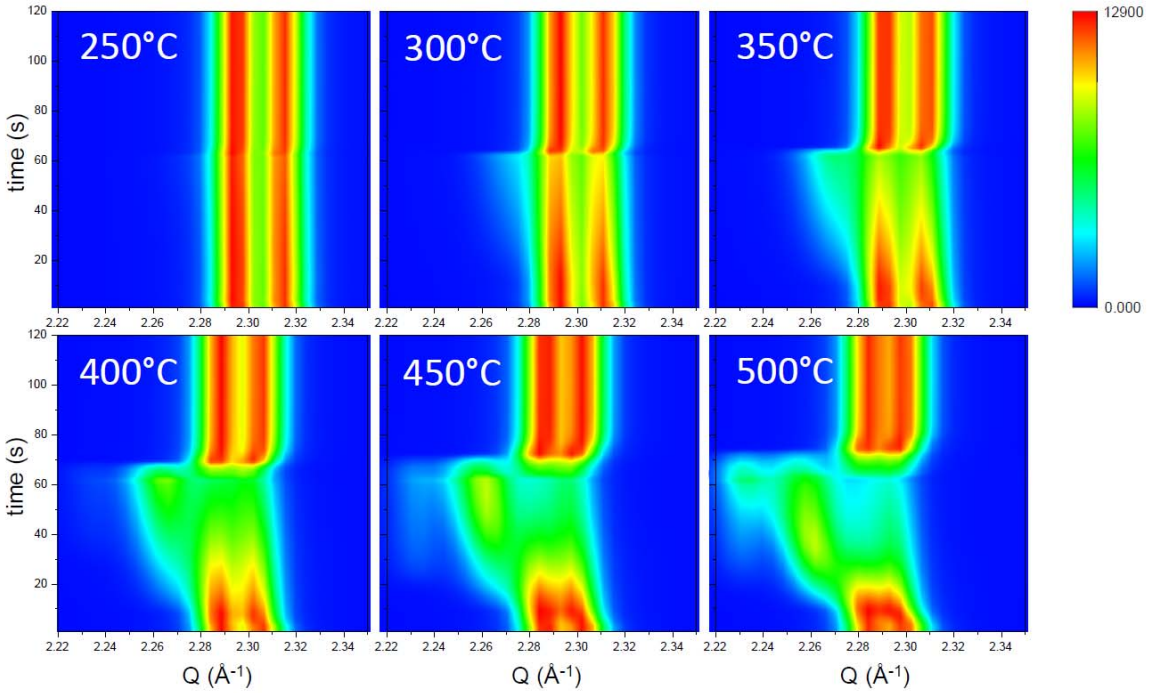

Figure 1: Time-resolved HE-XRD data (0.5s/pattern) during CO vs O_2 modulation at different temperatures.

The data quality was excellent as demonstrated in Figure 1, which displays 2D plots of the CO-O_2 pulse experiments on $LaCoO_3$ around the main doublet of the rhombohedral structure ((110) and (104) reflections). These experiments allowed to identify two regimes of temperatures where different extents of structural changes occur. Below 300°C, CO extracts oxygen atoms from the surface of the material. While no evident Q changes can be observed, the behaviour of the reflections treated according to phase sensitive detection (PSD) [1] suggests reversible expansion/contraction of the lattice upon removal of oxygen by CO. Above 300°C, oxygen removal increasingly generates new reflections at lower angles belonging to the $La_3Co_3O_8$ brownmillerite structure, an oxygen deficient perovskite-related oxide. At 500°C, it is clear that the rhombohedral structure of $LaCoO_3$ was completely lost in the CO pulse for ca. 2-3 s, however it was restored in the O_2 pulse. The appearance of the reflection at ca. 2.23 Å reveled the formation of the $La_2Co_2O_5$ phase, also an oxygen deficient perovskite-related structure. Despite these experiments, which removed the perovskite-type structure shortly, XRD data taken at every temperature before and after the pulse sequences indicate that the material did not lose substantial crystallinity.

Substitution of La by 20% Sr (not shown) exhibited lower reducibility at low temperature and practically started to show the changes of Figure 1-350°C only above 400°C. $La_{0.5}Sr_{0.5}CoO_3$ exhibited less reduction propensity than $LaCoO_3$ at equal temperature suggesting that reducibility is not linear with Sr substitution. Differences were observed in the reducibility order between CO and H_2. Partial substitution of Co in $LaCoO_3$ by Fe did not increase reducibility at low temperature.

All these measurements are of interest for the use of these materials as three-way catalysts of gasoline vehicles. An improved understanding of the structural behaviour of the materials under the conditions under which they operate in reality is useful to develop active and stable catalysts with new proeprties (absence of precious metals, low temperature activity). Similar studies should be performed on similar compositions and after addition to these samples of transition metals, e.g. copper that are active for relevant reactions such as NO reduction.

We would like to thank Dr. Checchia and all the team of beamline ID15A for their continuous support during beamtime and the friendly atmosphere.

[1] D. Ferri, M.A. Newton, M. Di Michiel, G.L. Chiarello, S. Yoon, Y. Lu, J. Andrieux, *Angew. Chemie Int. Ed.* **53** (2014) 8890.