Experimental report

06/06/2016

Proposal:	**5-21-1092**	**Council:**	10/2014
Title:	"In-situ" NPD study of the topotactic oxidation-reduction between SrMoO3-doped perovskite SOFC anode materials and SrMoO4 scheelites.		
Research area:	Materials		

This proposal is a new proposal

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Samples:	SrMo1-xMxo3 (M= Fe, Cr, Al, Ga) SrMo1-xMxo4 (M= Fe, Cr, Al, Ga)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	10/07/2015	13/07/2015

Abstract:

SrMo1-xMxO3-d (M= Fe and Cr; x= 0.1 and 0.2 and M=Ga, Al; x=0.1) perovskite phases perform successfully as anodes for solid-oxide fuel cells (SOFC), presenting a mixed electronic and ionic conductivity, and advantageously replacing the conventional cermets for intermediate-temperature-SOFCs. These perovskites are stable in reducing conditions (H2 atmosphere), as required for anode materials; however the annealing of the perovskite oxides in air leads, reversibly, to scheelite-like oxides. The reversibility of the scheelite (oxidized) and perovskite (reduced) oxides is an essential requisite for the cycling and performance of the fuel cells. We aim to understand the oxidation and reduction processes from perovskite to scheelite and vice versa: may they be considered as topotactic? We propose to examine these transformations by heating in air the perovskites at increasing temperatures across the oxidation reaction, as well as to investigate in-situ the reduction of the scheelite, across the phase transition temperature. We expect to obtain accurate information on the rearrangement of both crystal structures upon oxidation-reduction, for the four mentioned families of materials.

Recently, we have prepared and characterized new $SrMo_{1-x}M_xO_{3-\delta}$ (M= Fe and Cr; x= 0.1 and 0.2 [1-3] and M=Ga, Mg; x=0.1) perovskite phases that have been described to perform successfully as anodes for solid-oxide fuel cells (SOFC). These perovskites present a mixed electronic and ionic conductivity based, on the one hand, on the metallic conductivity of the pristine $SrMoO_3$ oxide, combined with the effect of doping with trivalent elements (M= Fe, Cr, Ga, Mg) at the Mo^{4+} positions, which gives rise to the presence of oxygen vacancies at the working temperatures of SOFC (700-850ºC).

These perovskite phases are stable in reducing conditions (H_2 atmosphere), as required for anode materials; however the annealing of the perovskite oxides in air leads, reversibly, to scheelite-like oxides. The reversibility of the scheelite (oxidized) and perovskite (reduced) oxides is an essential requisite for the cycling and performance of the fuel cells. Thermal analysis TG curves clearly display the stability of the doped Mo perovskites and their reversibility. Heating the “reduced” perovskite phases $SrMo_{1-x}M_xO_{3-\delta}$ (M= Fe; x= 0, 0.1 and 0.2) in oxygen atmosphere leads to the oxidation of these materials to give the mentioned $SrMo_{1-x}M_xO_{4-\delta}$ scheelite structures. Fig. 1 shows the thermal analysis curve obtained in O_2, involving the incorporation of oxygen atoms in the 300-500 ºC temperature range for the Fe-doped sample. Therefore, we have described the stabilization of four new families of oxygen-deficient scheelite oxides with formula $SrMo_{1-x}M_xO_{4-\delta}$ (M= Fe and Cr; x= 0.1 and 0.2 and M= Ga, Mg; x=0.1) resulting from the oxidation of the corresponding perovskite oxides.

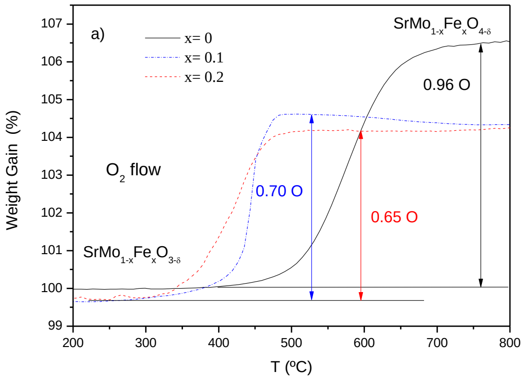

Fig. 1. TG curve illustrating the oxidation of Perovskite Sr(Mo,Fe)O_3 to Scheelite Sr(Mo,Fe)O_4

In this experiment we have measured the *in-situ* structural evolution of the samples to unveil the perovskite-sheelite transformation, by heating in air (within quartz containers allowing the oxygen exchange with air atmosphere) at increasing temperatures across the oxidation reaction of the perovskite, in order to complete our knowledge of the oxidation processes from perovskite to scheelite.

Neutron powder diffraction (NPD) data were collected in the diffractometer D2B. The high intensity mode ($\Delta d/d \approx 5 \cdot 10^{-4}$) was selected, with a neutron wavelength λ= 1.594 Å within the angular 2θ range from 8° to 150°. About 2 g of the sample was contained in a quartz tube open to the ambient atmosphere, placed in the isothermal zone of a furnace with a vanadium resistor operating under vacuum ($P_{O2} \approx 10^{-6}$ Torr). The measurements were carried out in air at 25, 200, 400, 600 and 800ºC. The collection time was of 3 h per pattern.

The $SrMo_{0.9}Mg_{0.1}O_{3-\delta}$ perovskite can be Rietveld-refined in the cubic *Pm-3m* space group at room temperature (Fig.3.). The inset on Fig. 3 shows the structure of the cubic perovskite.

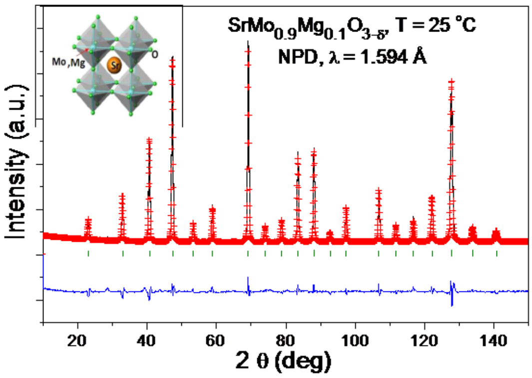

Fig. 3. NPD profile for $SrMo_{0.9}Mg_{0.1}O_{3-\delta}$ at 25 °C in air, refined in the cubic *Pm-3m* space group. The inset shows the crystal structure of the sample.

After heating in air at 400 °C the starting perovskite phase, a mixture of perovskite (*Pm-3m*) and schelite (*I4₁/a*) phases is observed. Fig. 4 shows the Rietveld plot including the *Pm-3m* and *I4₁/a* structures of this mixture, above the transition temperature between the two phases.

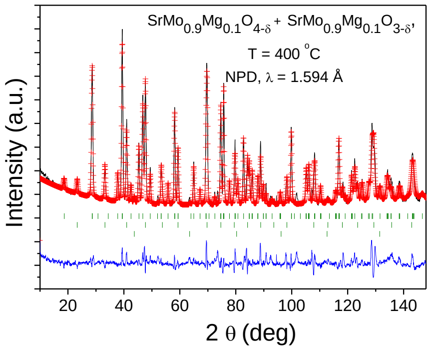

Fig. 4. NPD profiles for $SrMo_{0.9}Mg_{0.1}O_{4-\delta}$ scheelite and $SrMo_{0.9}Mg_{0.1}O_{3-\delta}$ perovskite at 400 °C.

After completing the thermal treatment and cooling down the samples, a complete scheelite phase is formed for $SrMo_{0.9}Fe_{0.1}O_{4-\delta}$ and $SrMo_{0.8}Cr_{0.2}O_{4-\delta}$ as shown in Fig. 5.

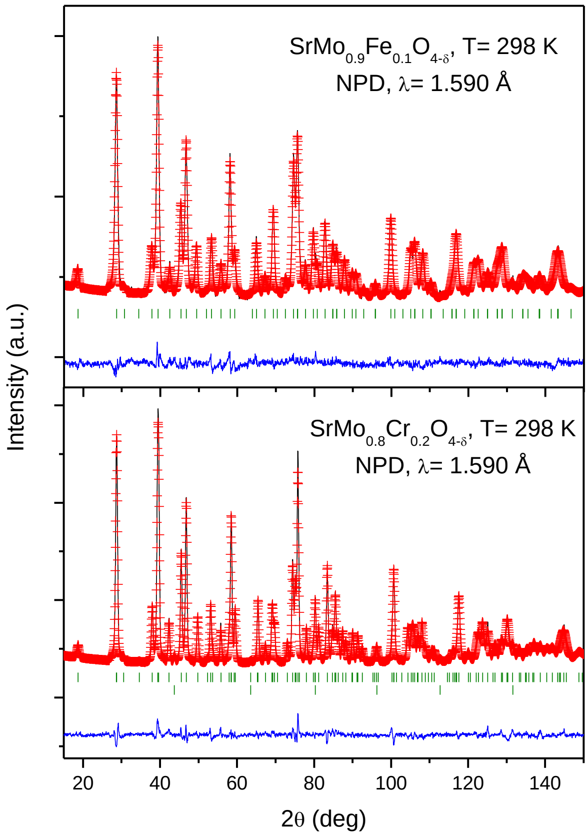

Fig. 5. Rietveld fits of the scheelite phases with M= Fe, Cr from NPD data at room temperature after the thermal treatment and cooling the samples.

[1] R. Martínez-Coronado, J.A. Alonso, A. Aguadero, M.T. Fernandez-Diaz. *Journal of Power Sources.* 2012 **208** 153-158.

[2] R. Martínez-Coronado, A. Aguadero, J.A. Alonso, M.T. Fernández-Díaz. *Materials Research Bulletin*. 2012 **47** 2148-2153.

[3] R. Martinez-Coronado, J.A. Alonso, A. Aguadero, M.T. Fernandez-Diaz. *International Journal of Hydrogen Energy*. 2014 **39** 4067-4073.