

# Experimental report

06/03/2024

**Proposal:** 5-24-707

**Council:** 4/2023

**Title:** "In-situ" evolution of the crystal structure of the  $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Co}_{1-x}\text{M}_x\text{O}_{3-d}$  and  $\text{SrCo}_{1-x-y}\text{Fe}_x\text{MyO}_{3-d}$  (M= Ti, Ir) SOFC cathodes.

**Research area:** Materials

This proposal is a resubmission of 5-24-695

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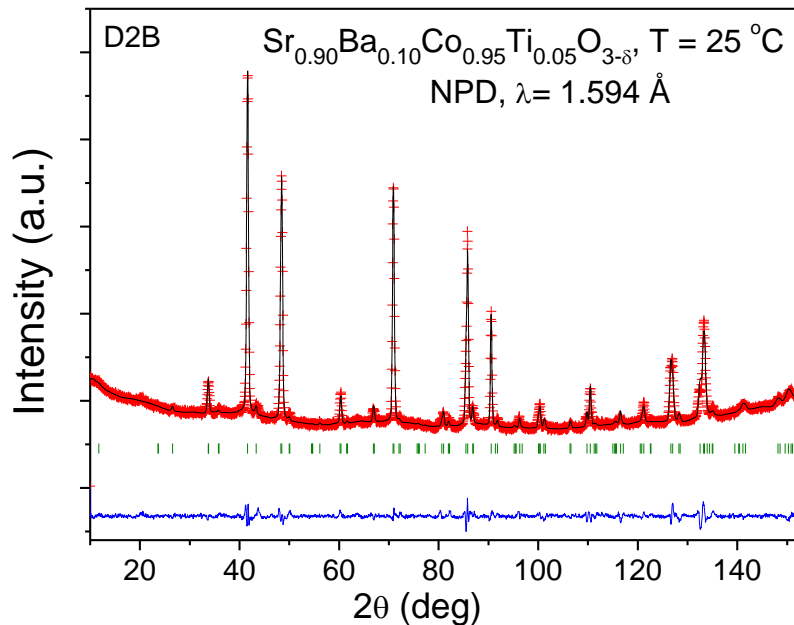
**Samples:**  $\text{SrCo}_{1-x-y}\text{Fe}_x\text{MyO}_{3-d}$   
 $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Co}_{1-x}\text{M}_x\text{O}_{3-d}$   
 $\text{SrCo}_{0.89}\text{Zr}_{0.11}\text{O}_3$

Instrument	Requested days	Allocated days	From	To
D2B	2	2	31/10/2023	03/11/2023

## Abstract:

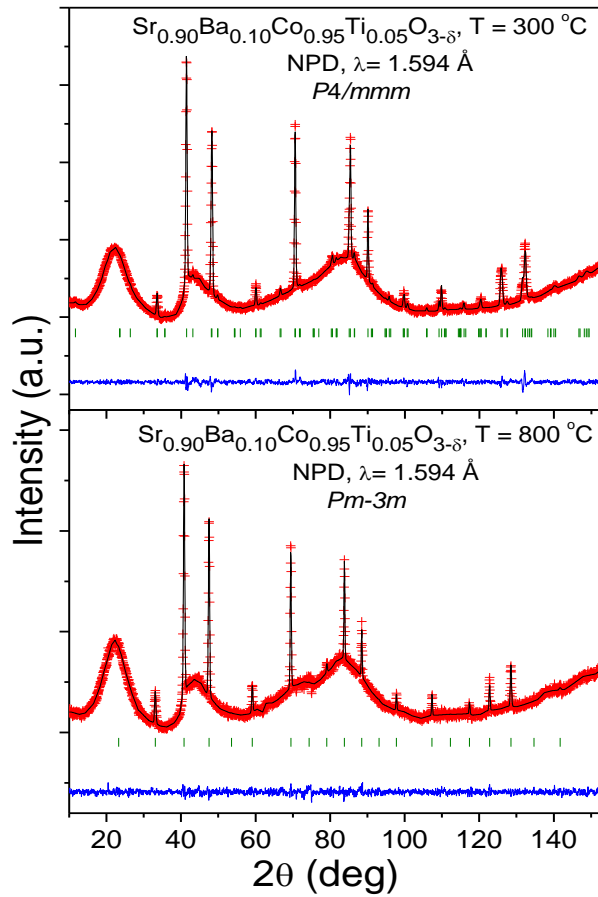
The novel perovskites  $\text{Sr}_{0.9}\text{Ba}_{0.1}\text{Co}_{1-x}\text{M}_x\text{O}_{3-d}$  and  $\text{SrCo}_{1-x-y}\text{Fe}_x\text{MyO}_{3-d}$  (M= Ti, Ir) have been evaluated as superior cathodes for solid-oxide fuel cells (SOFC); tests in single fuel cells yield output powers higher than 700 mW/cm<sup>2</sup> at 850 °C with H<sub>2</sub> as a fuel. In this experiment we aim at unravelling the oxide-ion diffusion path of this family of MIEC (mixed ionic-electronic conductor) oxides. We plan to study the thermal evolution of the crystal structure in order to get information about the actual crystal symmetry, the thermal displacements and oxygen contents, as well as the order-disorder of the oxygen vacancies and their evolution at the actual working conditions in a SOFC cell, in air at temperatures between RT and 900 °C.

The stabilization of a 3D perovskite-like framework in the  $\text{SrCoO}_{3-\delta}$  system has been a widely used strategy in order to obtain an adequate mixed ionic-electronic conductor to be used as cathode in intermediate temperature solid oxide fuel cells. For this purpose, several chemical substitutions have been performed in either the Sr (Ba, La, Sm) [1] or in the Co (Sc, Ni, etc) [2,3] positions or in both. In this work we have stabilized a perovskite phase by doping the  $\text{SrCoO}_{3-\delta}$  system with Ba and Ti contents in  $\text{Sr}_{0.90}\text{Ba}_{0.10}\text{Co}_{0.95}\text{Ti}_{0.05}\text{O}_{3-\delta}$ . The stabilization of a tetragonal  $P4/mmm$  structure has been obtained at 25 °C. Fig.1 illustrates the goodness of the fit for the NPD pattern for  $\text{Sr}_{0.90}\text{Ba}_{0.10}\text{Co}_{0.95}\text{Ti}_{0.05}\text{O}_{3-\delta}$  compound at 25 °C measured at the D2B diffractometer of the ILL (Grenoble, France).



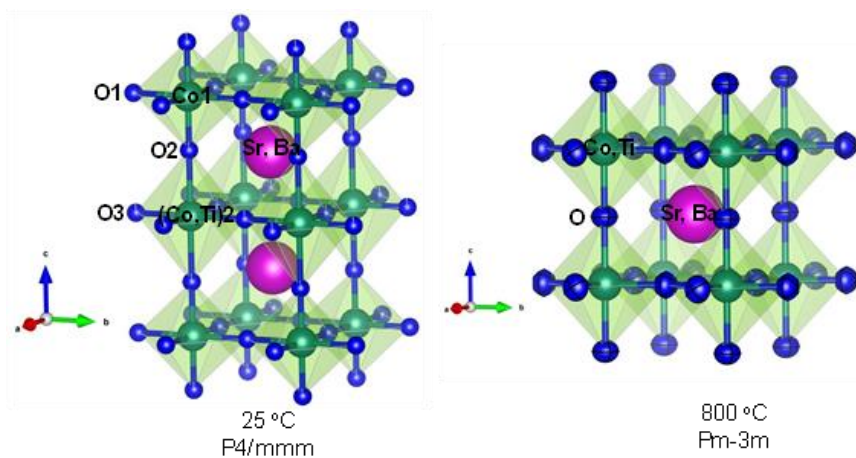
**Fig. 1.** Observed (red line), calculated (black line) and difference (bottom line) NPD Rietveld profile for  $\text{Sr}_{0.90}\text{Ba}_{0.10}\text{Co}_{0.95}\text{Ti}_{0.05}\text{O}_{3-\delta}$  at 25 °C.

Besides, in this experiment we have measured the in-situ structural evolution of the sample in the usual working conditions of a cathode in a SOFC (in air from 300 °C to 800 °C). Neutron powder diffraction (NPD) data were collected in the diffractometer D2B. A neutron wavelength of  $\lambda = 1.594 \text{ \AA}$  was selected within the angular  $2\theta$  range from  $10^\circ$  to  $155^\circ$ . 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. The measurements were carried out in air at 300, 600 and 800 °C. The collection time was of 3 h per pattern. The irregular background coming from the quartz container was interpolated from points devoid of reflections.



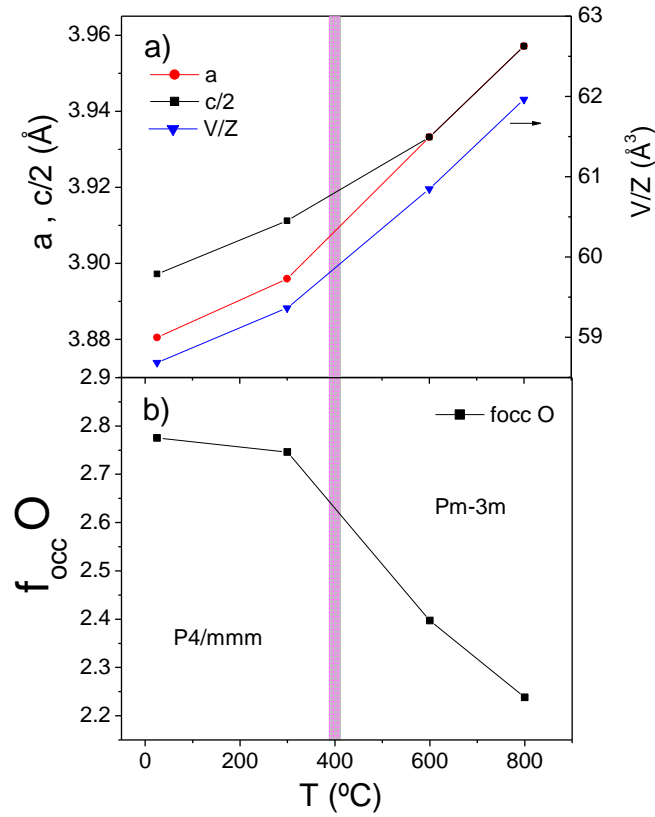
**Fig. 2.** Observed (red line), calculated (black line) and difference (at the bottom) NPD profiles for  $Sr_{0.90}Ba_{0.10}Co_{0.95}Ti_{0.05}O_{3-\delta}$  at 300 and 800 °C. The vertical markers correspond to the allowed Bragg reflections.

The crystal structure can be Rietveld-refined in the tetragonal  $P4/mmm$  space group till 300 °C (Fig. 2). At this temperature a tetragonal ( $P4/mmm$ ) to cubic ( $Pm-3m$ ) phase transition takes place.



**Fig. 3.** Crystal structures of the tetragonal and cubic phases.

Fig. 3 shows the crystal structures of the tetragonal and cubic phases. The thermal evolution of the lattice parameters and the oxygen content can be seen in Fig. 4a. The tetragonal superstructure is due to the long-distance ordering of the vacancies along the c-axis. The occupancy factors of O atoms strongly decrease (Fig. 4b) as temperature increases, which favours the oxygen ion mobility, as required in SOFC cathodes.



**Fig. 4.** Evolution depending on the temperature of (a) the unit-cell parameters (left axis) and volume (right axis) and (b) oxygen vacancies (left axis) and Biso (right axis). The inset shows the cubic perovskite structure obtained at 800  $^{\circ}\text{C}$ .

## References

- [1] T. Nagai, W. Ito, TR. Sakon, Solid State Ionics 177 (2007) 3433.
- [2] Z. Q. Deng, W. Liu, C. S. Chen, H. Lu, W. S. Yang, Solid State Ionics 170 (2004) 187.
- [3] P. Zeng, R. Ranj, Z. Chen, W. Zhou, H. Gu, Z. Shao, S. Liu, J. Alloys and Comp., 455 (2008) 465-470.