Experimental report

20/07/2022

Proposal: 5-24-676 **Council:** 4/2021

Title: Crystallography and oxygen mobility in novel mixed-conducting perovskites for SOFC cathodes

Research area: Materials

This proposal is a new proposal

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Samples: BaFe0.75Ta0.25O3-¿
SrCo0.9Sc0.1O3-¿
BaFe0.875Re0.125O3-¿
Ba0.75Sr0.25Fe0.875Ga0.125O3-¿

Instrument	Requested days	Allocated days	From	To
D2B	3	3	27/08/2021	30/08/2021

Abstract:

Recently, a theoretical study has determined that new compositions with perovskite structure could be considered as potential cathodes with high oxygen activity for solid oxide fuel cells. In our work, we have synthesized four of these new phases: Ba0.75Sr0.25Fe0.875Ga0.125O3-¿, BaFe0.75Ta0.25O3-¿, BaFe0.875Re0.125O3-¿ and SrCo0.9Sc0.1O3-¿. Impedance spectroscopy measurements of the sintered pellets and the symmetrical cells reveal evidence of mixed ionic and electronic conduction in the proposed materials, showing a promising behaviour for application is SOFCs.

In this neutron thermodifraccion experiment, we would like to identify the connection between the electrical properties and the structural features of these compounds, such as the temperature dependence of the oxygen content, possible cation and/or oxygen vacancies ordering in the sample and the thermal parameters. We consider that 3 days of beamtime at D2B diffractometer are necessary to complete the study.

Recently, a theoretical study has determined that new compositions with perovskite structure could be considered as potential cathodes with high oxygen activity for solid oxide fuel cells [1]. In our work, we have synthesized four of these new phases: $Ba_{0.75}Sr_{0.25}Fe_{0.875}Ga_{0.125}O_{3-\delta}$, $BaFe_{0.75}Ta_{0.25}O_{3-\delta}$, $BaFe_{0.875}Re_{0.125}O_{3-\delta}$ and $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$. Impedance spectroscopy measurements of the sintered pellets and the symmetrical cells revealed evidence of mixed ionic and electronic conduction in the proposed materials, showing a promising behaviour for application is SOFCs. We aimed to study the correlations between the electrochemical/charge transport properties, and the structural properties determined from neutron powder diffraction data of these novel perovskite phases. In this neutron thermodifraccion experiment, we have measured the in-situ structural evolution of $Ba_{0.75}Sr_{0.25}Fe_{0.875}Ga_{0.125}O_{3-\delta}$, and $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ samples in the usual working conditions of a cathode in a SOFC (in air from 25 ºC to 800 ºC). 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 155°. 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, 300, 550 and 800 ^{o}C for $Ba_{0.75}Sr_{0.25}Fe_{0.875}Ga_{0.125}O_{3-\delta}$ and at 25, 200, 550 and 800 ^{o}C for $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$. The collection time was of 3 h per pattern. The irregular background coming from the quartz container was interpolated from points devoid of reflections.

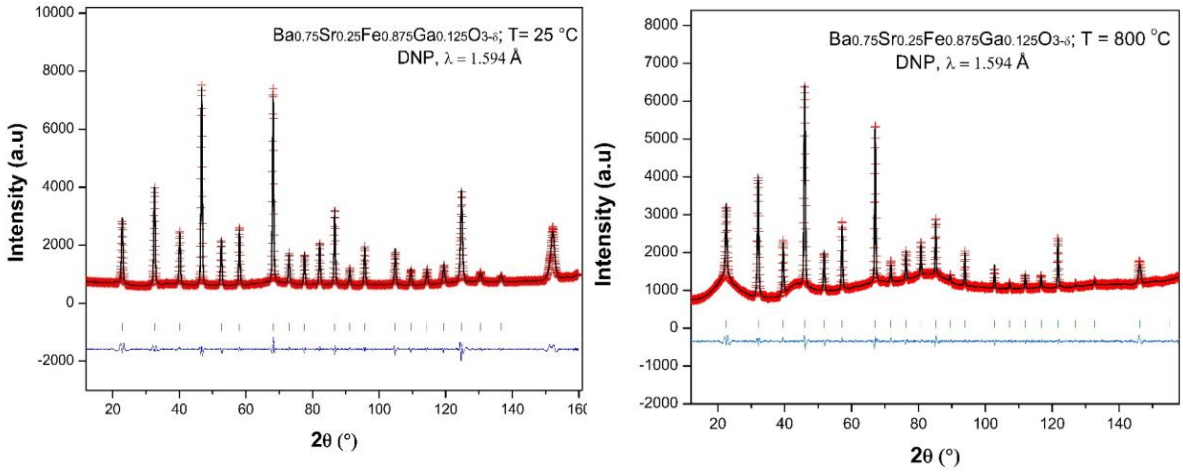

Figure 1. Observed (crosses), calculated (full black line) and difference (blue at the bottom) neutron powder diffraction (NPD) profile for $Ba_{0.75}Sr_{0.25}Fe_{0.875}Ga_{0.125}O_{3-\delta}$ at 25 °C and 800 °C. The irregular background above RT comes from the quartz container used for data collection, permitting the sample to be in contact with air at high temperatures.

$Ba_{0.75}Sr_{0.25}Fe_{0.875}Ga_{0.125}O_{3-\delta}$ was Rietveld-refined in the cubic Pm-3m space group at all temperatures (Fig. 1). The oxygen occupancy factor decreases with increasing temperature. A progressive increase in the oxygen vacancy content is essential to ensure ion conduction within the cathode. Fig, 2 shows the cubic structure, occupancy factors and thermal displacement factors of oxygen atoms (ellipsoids) at room temperature and at the operating temperature of a SOFC (800 °C). It is evident that, at the operating temperature of the SOFC, the thermal vibration of the oxygen atoms is greater than at room temperature. This is excellent for the conduction of oxygen ions.

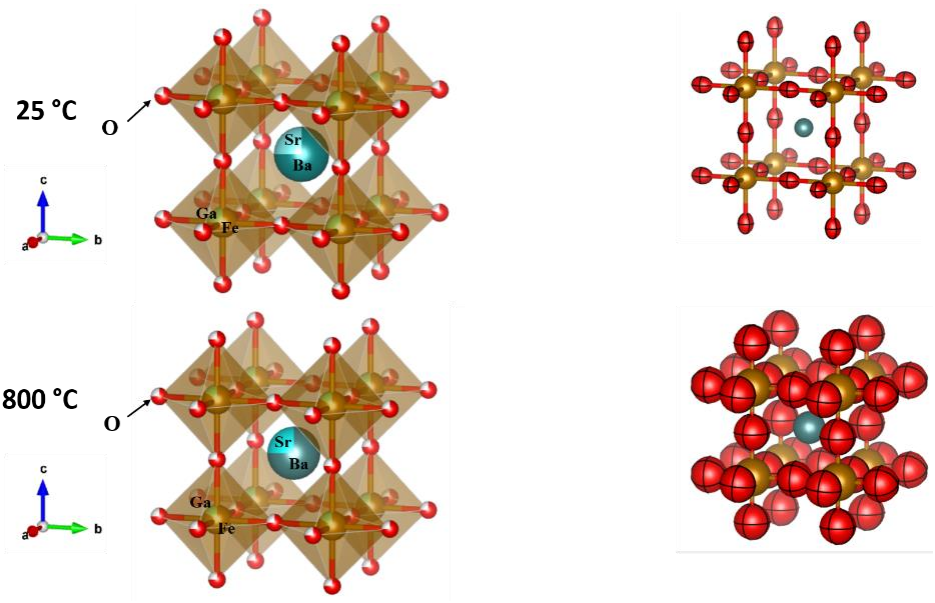

Fig. 2. Crystal structures of the cubic phases at RT and 800 ^{o}C.

$SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ was Rietveld-refined in the tetragonal *P4/mmm* space group till 200 ^{o}C (Fig. 3). Between 200 and 550 ^{o}C a tetragonal (*P4/mmm*) to cubic (*Pm-3m*) phase transition took place that remained at 800 ^{o}C (Fig.3). Fig. 4 shows the crystal structures of the tetragonal and cubic phases.

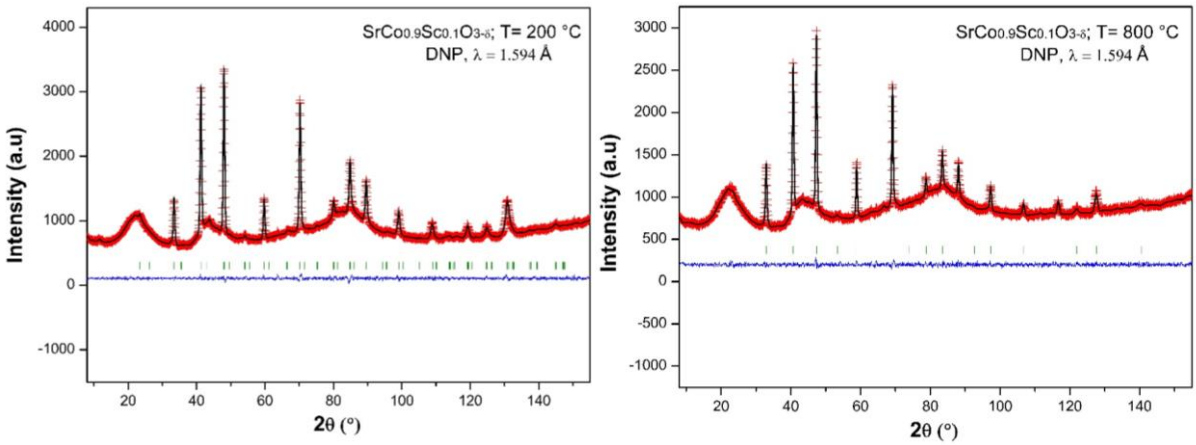

Figure 3. Observed (crosses), calculated (full black line) and difference (blue at the bottom) neutron powder diffraction (NPD) profile for $SrCo_{0.9}Sc_{0.1}O_{3-\delta}$ at 200 °C and 800 °C, refined in a tetragonal P4/mmm and cubic Pm-3m space groups, respectively.

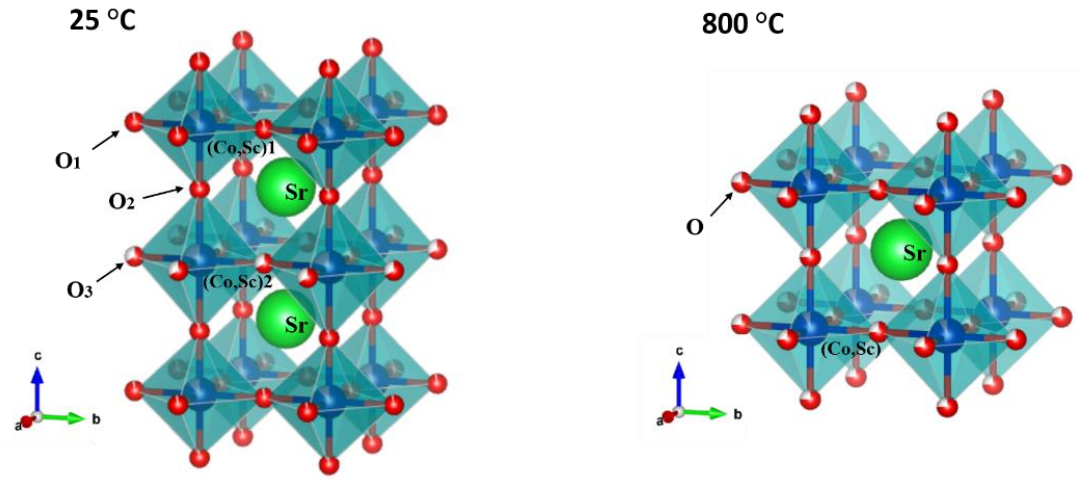

Figure. 4. Crystal structures of the tetragonal and cubic phases.

At the operating temperature of a SOFC (800 °C), an oxygen deficiency of δ = 0.704 was observed, which corresponds to a composition of $SrCo_{0.9}Sc_{0.1}O_{2.296}$.

[1] Jacobs, R. Advanced Energy Materials, 8(11) (2018) 1702708.