Experimental report

02/08/2022

Proposal:	**CRG-2658**	**Council:**	4/2019
Title:	Thermal evolution of phase composition and the structure of phases present in IT-SOFC samples of $TbBaCo_2O_{5+d}$ prepared by slow cooling in air		
Research area:			

This proposal is a new proposal

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Samples: $BaTbCo_2O_5$

Instrument	Requested days	Allocated days	From	To
D1B	5	2	11/09/2019	13/09/2019

Abstract:

Thermal evolution of phase composition and the structure of phases present in IT-SOFC samples of $TbBaCo_2O_{6-\delta}$ prepared by slow cooling in air

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The aim of the proposal CRG-2658 was to determine the evolution of the composition and the structure of each phase present in a sample of $TbBaCo_2O_{5-\delta}$ prepared by slow cooling in air as a function of temperature in air, with especial attention to IT-SOFC working conditions.

Previous studies on the sample using PXRD, SAED, HREM and TGA revealed that, contrary to what widely accepted, when $REBaCo_2O_{5+\delta}$ (RE = Gd and Tb) are prepared in air and slowly cooled from the reaction temperature a mixture of two phases is obtained. We determined that for our slow-cooled $TbBaCo_2O_{6-\delta}$ δ=0.60 and the sample consists of 44% pseudo-tetrahedral $TbBaCo_2O_{5.00(2)}$ (112-like phase) and 56% $TbBaCo_2O_{5.71(2)}$ (diagonal-like phase).

A detailed characterization of the sample as well as its thermal evolution is necessary to understand its performance as IT-SOFC cathode material.

We successfully recorded and analyzed several NPD patterns; the results are submitted to Chem. Mat. and a summary is presented below.

The oxygen content in the $TbBaCo_2O_{6-\delta}$, is dependent on the synthesis conditions and further thermal treatments. Common solid state preparation methods with relatively slow cooling rates lead to coexistence of phases with different oxygen content. Since the electrical and electrochemical properties of this type of layered perovskites are highly influenced by the anion vacancies concentration and their location in the structure, careful analysis of the formation conditions of stable phases is needed to optimize the properties of these materials for different applications.

The 122 and 112 phases are predominant, indicating that location and ordering of the anion vacancies in the $TbO_{1-\delta}$ planes stabilize the crystal structure (Fig. 1).

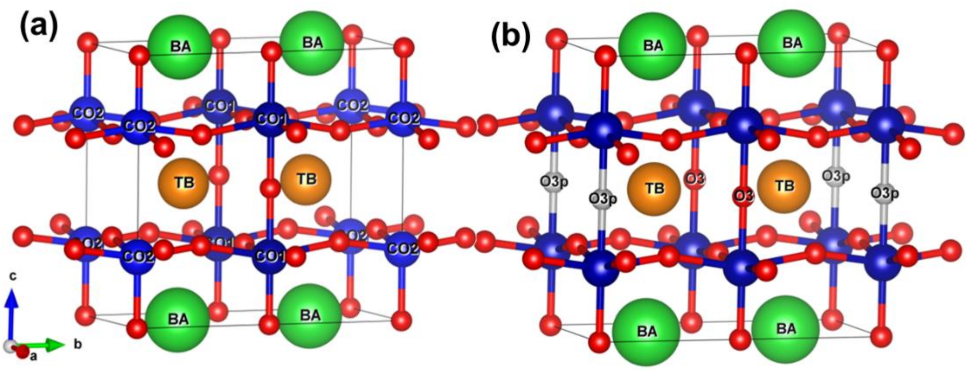

Figure 1. (a) Schematic representation of the structure of ordered 122-like phase: O3 positions are occupied and O3p positions are empty; (b) disordered 122-like structure: both O3 and O3p positions are occupied.

The evolution of the crystal structure of $TbBaCo_2O_{6-\delta}$ during thermal oxygen release on heating consists of modulation from the 122-phase to the 112-phase by creation of anion vacancies within the $TbO_{1-\delta}$ planes. These phases coexist up to 400 ºC (Fig. 2) whereas at higher temperature the sample consist of a single tetragonal phase with variable oxygen content depending on temperature (Fig. 3). Worth to note, at the SOFC operating temperatures (800 ºC) some extra oxygen remains in the $TbO_{1-\delta}$ planes.

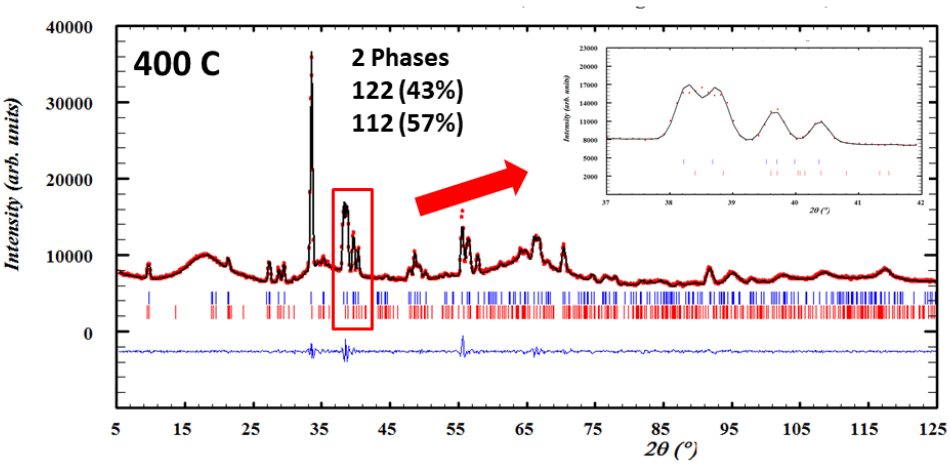

Figure 2. Experimental and calculated NPD patterns at 400 ºC, on heating in air, of 1C-TBCO sample. The red points represent the experimental pattern, the continuous black line the calculated using the refined structural model and the blue line is their difference. Vertical blue and red bars indicate the positions of nuclear Bragg peaks of the 112 and 122 phases respectively. In the inset shows a zoom of an especially relevant zone of the diffraction pattern.

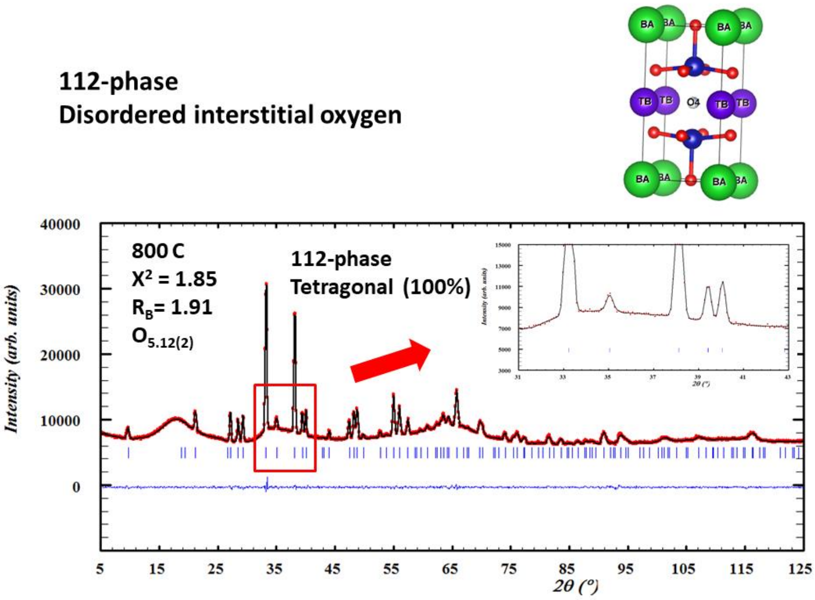

Figure 3. Experimental and calculated NPD patterns at 800 ºC, on heating in air, of 1C-TBCO sample. The red points represent the experimental pattern, the continuous black line the calculated using the refined structural model and the blue line is their difference. Vertical blue bars indicate the positions of nuclear Bragg peaks of the 112-phase. In the inset shows a zoom of an especially relevant zone of the diffraction pattern. A representation of the structure is also given, as well as the agreement factors of the fitting.

In a similar way, modulation from the 112-phase to the 122-phase takes place during thermal oxygen uptake on cooling by location of oxygens following an ordered pattern. Location of the anion vacancies within the $TbO_{1-\delta}$ planes even at the highest temperatures of the study support the 2D character of the high anion conduction of the $LnBaCo_2O_{6-\delta}$ oxides.