

Experimental report

04/12/2025

Proposal: 5-23-799

Council: 4/2023

Title: Structural and oxygen vacancies study of the $\text{La}_4\text{BaCu}_{5-x}\text{Ni}_x\text{O}_{13+\delta}$ perovskite at operation temperature for SOFC applications

Research area: Materials

This proposal is a new proposal

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Samples: $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$
 $\text{La}_4\text{BaCu}_3\text{Ni}_2\text{O}_{13+\delta}$

Instrument	Requested days	Allocated days	From	To
D1B	3	3	08/09/2023	11/09/2023

Abstract:

Among the multiple possibilities of doping the parent structure $\text{La}_4\text{BaCu}_5\text{O}_{13+\delta}$, we chose to introduce the Ni cation in the B site, in order to probe the properties of $\text{La}_4\text{BaCu}_{5-x}\text{Ni}_x\text{O}_{13+\delta}$ family as cathode in SOFC. We have synthesized $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ ($x=1$) and $\text{La}_4\text{BaCu}_3\text{Ni}_2\text{O}_{13+\delta}$ ($x=2$) compounds using the sol-gel method. A complete study of the crystalline structure would complete the scenario, because X-ray diffraction does not allow differentiating the two cations present in the B site. Anderson et al. reported the study of the crystal structure of $x=1$ sample, but $x=2$ sample has not been studied by Neutron diffraction in order to obtain a reliable model of the material structure. More importantly, there are no detailed reports in the literature for the behavior of oxygen vacancies when changing the oxygen partial pressure, correlating structural and functional properties. Detailed neutron diffraction experiments as a function of temperature and oxygen partial pressure will help us to understand the conductivity mechanisms of these compounds. These aspects are very important for a complete analysis of these novel materials for SOFC cathode applications.

Structural characterization and oxygen vacancies study of the perovskite $\text{La}_4\text{BaCu}_5-x\text{Ni}_x\text{O}_{13+\delta}$ ($x=1$ and 2) at operation temperature for applications in SOFC

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The DIB instrument at the ILL was used to investigate the evolution of the crystal structure of polycrystalline oxygen-deficient perovskite samples, $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ and $\text{La}_4\text{BaCu}_3\text{Ni}_2\text{O}_{13+\delta}$, under high temperature conditions. The experiments were performed under different atmospheres to monitor the oxygen content within the crystal structure and study the oxygen conductivity mechanism, aiming to explain the behaviour of these materials under solid oxide cell operation conditions.

The aim of these measurements was to provide insights into the oxygen exchange mechanism and the distribution of the oxygen vacancies in the perovskites $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ and $\text{La}_4\text{BaCu}_3\text{Ni}_2\text{O}_{13+\delta}$. Moreover, the study focused on evaluating the structural stability of these materials, which is crucial for understanding their performance as cathode under solid oxide cell operating conditions. The recorded diffraction data will allow us to carry out a detail Rietveld refinement to confirm the structure of the materials and asses their stability. The materials were refinement under the tetragonal space group P4/m.

The measurements of both materials demonstrated that, within the temperature range studied (RT-843 °C), they exhibit isostructural behavior with the previously reported $\text{La}_4\text{BaCu}_5\text{O}_{13+\delta}$ compound, without showing any phase transitions [1]. Moreover, the samples were tested under three different atmospheres (N_2 , air and Argon), and across the entire temperature range both materials remained stable, with no evidence of additional diffraction peaks. It is worth mentioning that some extra peaks observed in the patterns resulted from reactions between the materials and the quartz sample holder.

To study the oxygen content in the structure, the oxygen occupancy was fixed to 13 atoms during the Rietveld refinements, and the Fourier maps provided an initial hypothesis regarding the possible oxygen migration mechanisms under SOFC operating conditions.

This analysis was performed for the $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ compound, while the data for $\text{La}_4\text{BaCu}_3\text{Ni}_2\text{O}_{13+\delta}$ are still being processed. Although the current model offers a preliminary view of potential conduction mechanisms, it may contain inaccuracies. For this reason, electrochemical experiments and complementary techniques are currently being carried out to validate the results.

Figure 1 shows the Rietveld fit for $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ at 843 °C under air atmosphere, where the excluded region corresponds to a peak arising from the reaction with the sample holder. Figure 2 shows the evolution of the unit cell volume of $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ under the different atmospheres. Finally, figure 3 presents the Fourier map, where the residual electron density and possible conduction pathways can be observed.

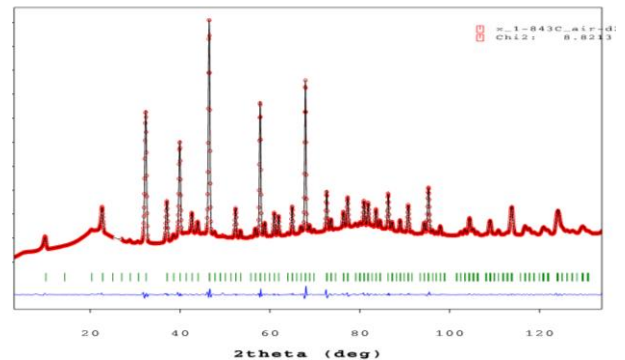


Figure 1: Fitting of the diffraction pattern of the sample $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ taken at 843 °C under air atmosphere

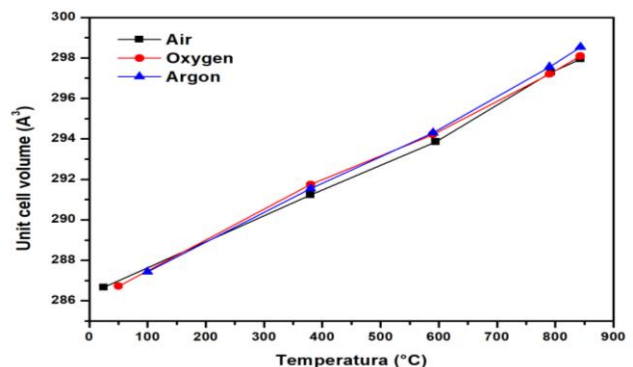


Figure 2: Experimentally determined cell parameters for $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ under different atmospheres.

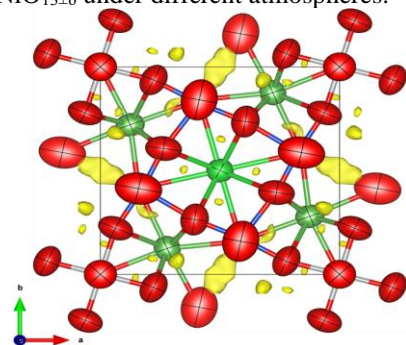


Figure 3: Fourier maps model for $\text{La}_4\text{BaCu}_4\text{NiO}_{13+\delta}$ at 843 °C under air atmosphere.

- [1] M. Macias, et. Al., Solid State Ionics, 2016, 228, 68-75