INTRODUCTION

Mixed ionic-electronic conductors (MIECs) are of great interest as potential cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) and oxygen gas separation membranes, because of their high electronic and ionic conductivities, as well as fast surface oxygen exchange kinetics. Recent studies on the GdBaCo$_2$O$_{5+δ}$ (GBCO) double-perovskite and the La$_2$NiO$_{4+δ}$ (LNO) have shown interesting mixed ionic and electronic transport properties\([1,2]\). Due to their layered structure they present high anisotropy in their charge transport (continuous paths of oxygen vacancies for GBCO and planes of interstitials positions for LNO). Therefore, thin films offer an ideal geometry to access the intrinsic transport properties of these materials.

Here, we present a study of both these materials. GBCO and LNO thin films were grown on (100)-oriented Si/STO (STO) substrates using the Pulsed Laser Deposition (PLD) technique. The control of the deposition of naturally-layered structures is one of the challenges when growing thin films. Indeed, in these compounds, deviation to the composition or presence of defects (spotty or planar) may lead to a variation of the electronic (e) and mixed-valence cations proportion and consequently to a variation of the related transport properties. The composition and microstructure of these materials were studied as a function of deposition conditions (temperature, laser fluence, target-substrate distance, $p$O$_2$). Deposition conditions as well as the presence of defects are expected to have significant influence in conductivity as observed through the mixed ionic-electronic transport properties.

PLD Technique

The principle of the PLD consists in focusing of a laser beam on a ceramic target of the desired compound. This leads to the vaporization (so-called ablation) of the material in a high-vacuum chamber and the generation of a plasma (plume) with highly-energetic species. The ablated material condensates on a substrate a few centimeters from the target where the thin film growth takes place.

TRANSPORT PROPERTIES

The conductivity of the films seems to increase as their average (GdBaCo)$_2$O$_5$ composition ratio gets closer to the stoichiometric value of 1, reaching values near to the bulk (1000 S/cm). At the same time their activation energies increase from 0.58 to 0.81 eV for the films with (GdBaCo)$_2$O$_5$: 1.20-1.41.

The presence of defects associated with the (GdBaCo)$_2$O$_5$ composition ratio deviation, induces a large decrease in the conductivity of the material at a local scale.

In-plane AC impedance measurements reveal that La$_2$NiO$_{4+δ}$ films exhibit a high conductivity, with a frequency independence of approximately 1.8.

The evolution of the conductivity as a function of $p$O$_2$ gives a slope of about 1.8.

In-plane AC IMPEDANCE MEASUREMENTS

- Pt electrodes deposited by PLD
- Measured under synthetic air

- More stoichiometric...more conducting
- For the best samples, higher values than bulk (905 S/cm at 400°C) but a little bit lower than LNO thin films grown by MO-CVD (900$/\mu$m for a 50nm-thin film)\[12\].
- Activation energies span from 78 mV to 130 mV that is in accordance with other authors\[15\].
- Linear dependence of Log($\sigma$) as a function of the composition (La/Ni ratio)

The presence of La$_2$O$_3$ secondary phase seems to have a strong effect in electronic AC conductivity, even in the cases in which the compound presents a very good crystallinity.

CONCLUSION

- Study of the effect of different film orientations on the electrical conductivity.
- Study of the oxygen surface exchange kinetics of both GBCO and LNO materials.
- Study of the variation of the oxygen diffusivity by Isotope Exchange Depth Profiling (IEDP).
- In-situ control of growth by Reflection High Energy Electron Diffraction (RHEED). A study is in progress in LNO films and is the next step for the growth control of GBCO films.
- Microstructure study of LNO films too in order to confirm our hypothesis.