# DEFECTS IN LAYERED-STRUCTURE MIXED IONIC-ELECTRONIC $GdBaCo_2O_{5+\delta}$ AND $La_2NiO_{4+\delta}$: ROLE IN CHARGE TRANSPORT

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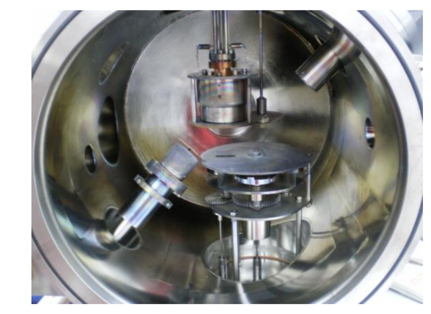
## INTRODUCTION

**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 oxide ionic conductivities, as well as fast surface oxygen exchange kinetics. Recent studies on the **$GdBaCo_2O_{5+\delta}$ (GBCO)** double-perovskite and the **$La_2NiO_{4+\delta}$ (LNO)** have shown interesting mixed ionic and electronic transport properties[1-6]. 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 epitaxial films offer an ideal geometry to access to 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)*-orientated $SrTiO_3$ (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 (point or planar) may lead to a variation of the oxygen content (δ) 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, $pO_2$). Domain orientation as well as the presence of defects are expected to have significant influence in conductivity as observed through the mixed ionic-electronic transport properties.

**Experimental setup**



**PLD chamber**

KrF excimer laser
λ = 248 nm (UV)

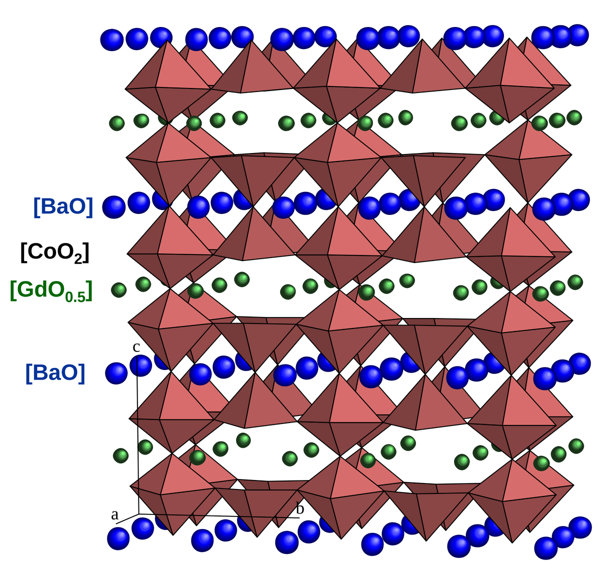
**PLD TECHNIQUE**

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 **condensate onto a substrate** a few centimeters from the target where the thin film growth takes place.

## STRUCTURE - CHARACTERISATION BY XRD

### $GdBaCo_2O_{5+\delta}$

**STRUCTURE**



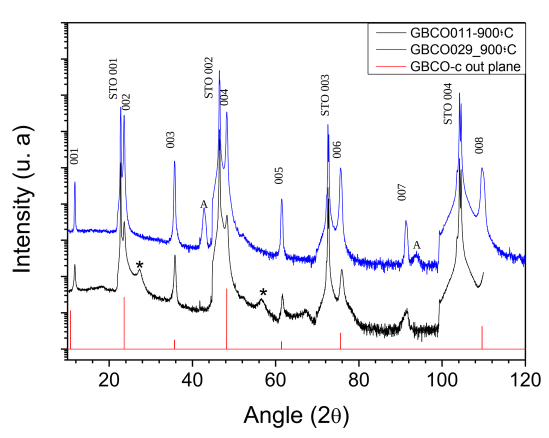

*Double perovskite Pmmm*
*a = 3.862Å*
*b/2 = 3.934Å*
*c/2 = 3.786Å [7]*

The gadolinium and barium ions are not randomly distributed into the structure, but ordered occupying alternate *(0 0 1)* layers. The oxygen vacancies are mainly located in the rare earth planes $[GdO]_\delta$ forming channels along the a-axis.

**DEPOSITION CONDITIONS**

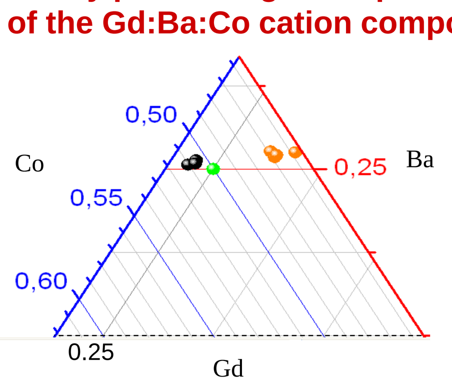
- Home-made targets of GBCO (one stoichiometric and other with excess cobalt)
- *(100)*-orientated STO, a= 3.905 Å
- Variation of the deposition temperature (800 – 900 ºC)

**X-RAY DIFFRACTION**



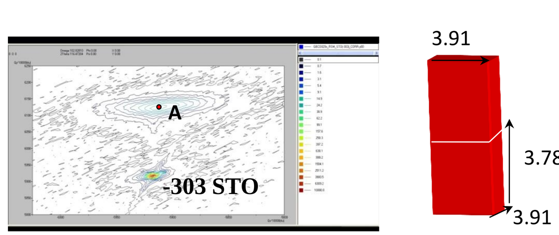

- Clear superstructure peaks *00l*, *l* = odd associated to the Gd/Ba order of the double perovskite
- **Stoichiometric target → *c*** in plane for low temperatures (800 ºC) and ***c*** out of plane for high temperatures (900 ºC). Reflections marked with * are related to the presence of planar defects
- **Co-excess target → c** out of plane for all temperatures. The superstructure peaks are more intense and more defined

**Ternary phase diagram representation of the Gd:Ba:Co cation composition**



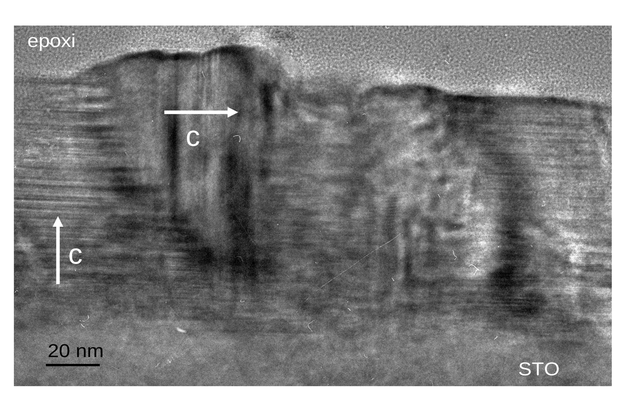

Layers deposited with the stoichiometric target show Co-depletion while films deposited with Co-excess target have a stoichiometry closest to the ideal composition (1:1:2)

**RECIPROCAL SPACE MAPPING**




**HRTEM MICROSTRUCTURE**

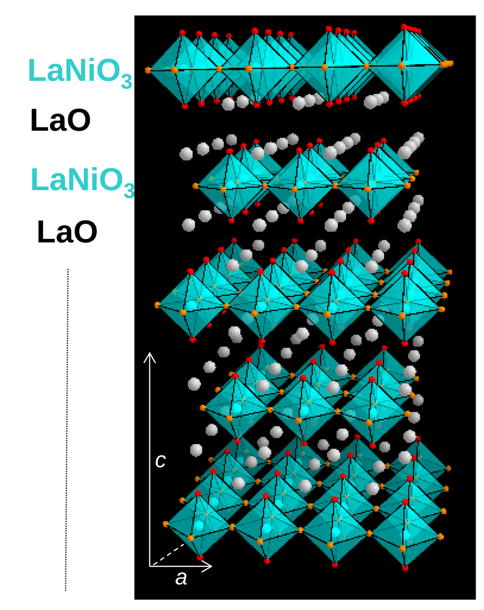
Planar defects are observed in $c_\perp$ and $c_{//}$ domains




High density of planar defects (Gd double planes) induced by Gd excess (Co deficit) for films deposited from stoichiometric target.

### $La_2NiO_{4+\delta}$

**STRUCTURE**




*Tetragonal I/4mmm*
*a= 3.861Å, c= 12.684Å*

**First member of the Ruddlesden-Popper family ($La_{n+1}Ni_nO_{3n+1}$)**

→ p-type electronic conductivity confined in the perovskite layers
→ Interstitially-driven ionic conductivity in the LaO layers [8-10]

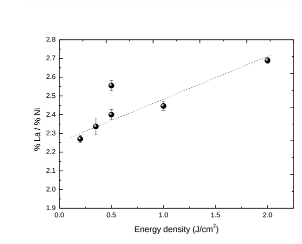
When n ↗ the $Ni^{3+}$ content ↗and consequently $\sigma_{el}$ ↗
$LaNiO_3$ (n → ∞) has a metallic behaviour.

**DEPOSITION CONDITIONS - STOICHIOMETRY**

- Home-made stoichiometric target of $La_2NiO_{4+\delta}$
- *(100)*-orientated STO, a= 3.905 Å

- La/Ni ratios were determined by microprobe wavelength dispersive X -Ray Spectroscopy
- **1.99<La/Ni<2.80** for all samples, indicating an **excess of La** for most of them.

Influence of laser fluence

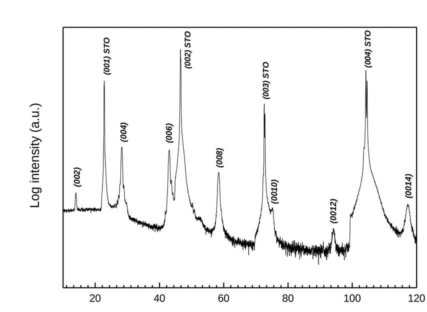


→ A **low laser fluence** favours a good stoichiometry transfer
→ A **low $pO_2$** (18-30mTorr) **or** a **high target-substrate distance** (70mm) permit to reach the expected stoichiometry

**Combination of $pO_2$-distance determines the position of the substrate into the plume that appears to be the most important parameter**

→ Optimum deposition temperature: **750°C**

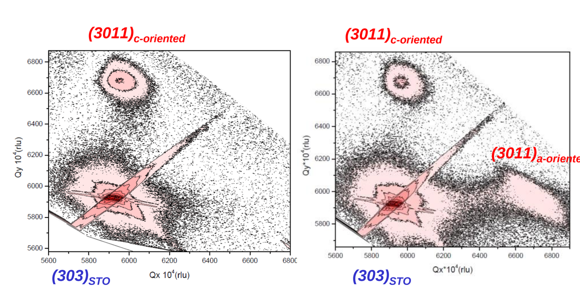
**X-RAY DIFFRACTION**



Highly **c-oriented** samples

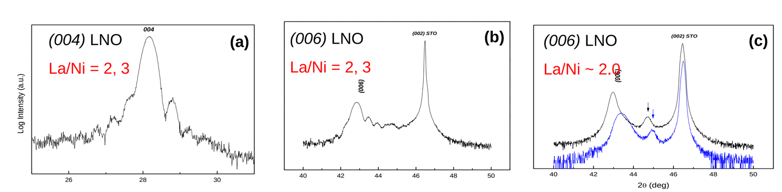
In some samples, presence of a little amount of oriented $La_2O_3$

**RECIPROCAL SPACE MAPPING**



Appearance of the a-orientation for compound with bad stoichiometry and with a thickness>45nm.

**HIGH RESOLUTION XRD**




- (a), (b): very good crystalline quality (Kiessig fringes)
- (c): worse crystallinity and appearance of a peak between the $(002)_{STO}$ and $(006)_{LNO}$ (Strain? additional perovskite planes?)

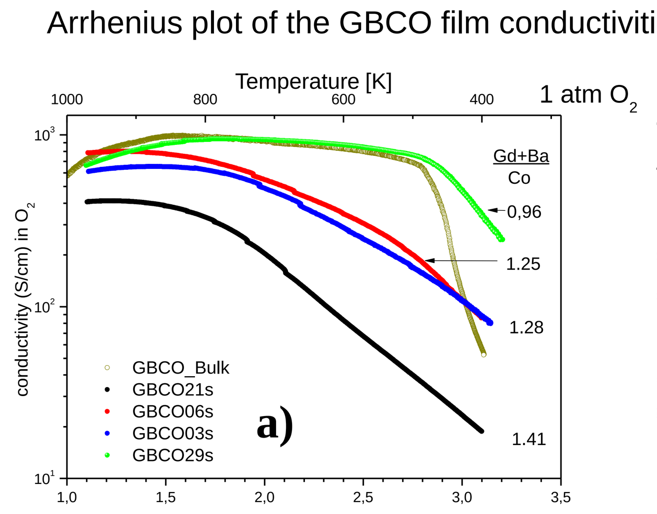
➡ **La-excess stabilises a high crystalline LNO phase**
↳ Lower La-excess: presence of $La_3Ni_2O_7$ planes ?

Hypothesis: **La-deficient LNO + $La_2O_3$** (La/Ni≈2.0) ⟶ **LNO + $La_2O_3$** (La/Ni≥2.2)

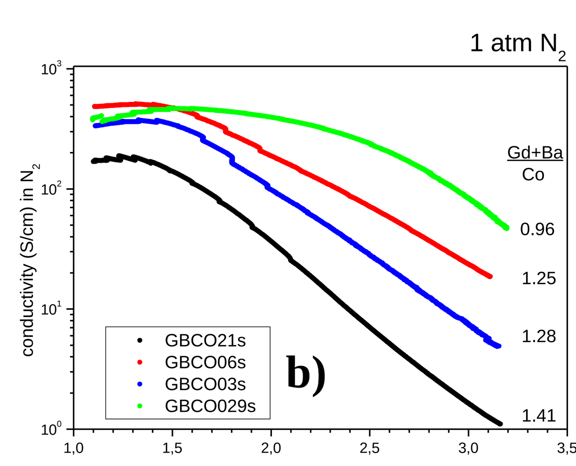
## TRANSPORT PROPERTIES

### $GdBaCo_2O_{5+\delta}$

Arrhenius plot of the GBCO film conductivities dependence with temperature, measured under 1 atm $O_2$ (*a*) and 1 atm $N_2$ (*b*).

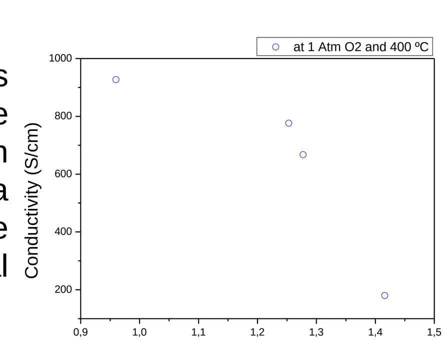


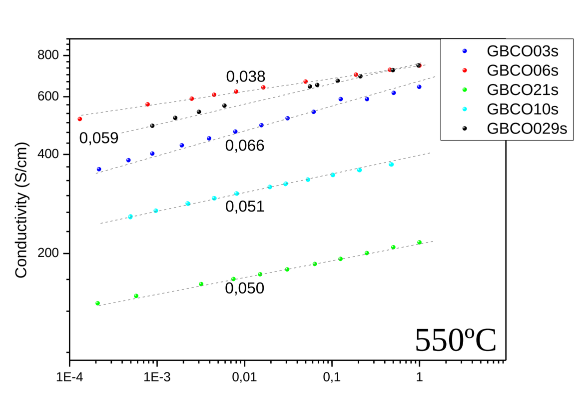

The conductivities of the films seem to increase as their average ([Gd]+[Ba])/[Co] composition ratio gets closer to the stoichiometric value of 1, reaching values near to the bulk (1000 S/cm). At the same time their activation energies increase from 0.09 to 0.18 eV for the films with ([Gd]b[Ba])/[Co]= 1.20-1.41.




Correlation between film stoichiometry deviation ((Gd+Ba)/Co ratio) and conductivity reduction [11].

The presence of defects associated with the ([Gd]+[Ba])/[Co] composition ratio deviation, induces a large decrease in the conductivity of the material at a local scale.



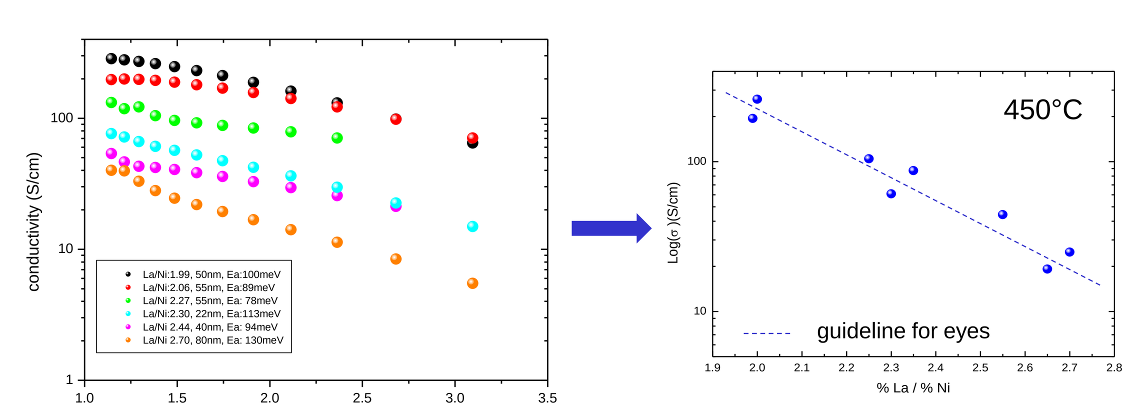




$pO_2$ dependence of the conductivity of the films measured at a constant temperature of 535 ºC. The important deviation from the ¼ classical power dependence is an indication of the complexity of the redox reactions in GBCO.

### $La_2NiO_{4+\delta}$

**IN-PLANE AC IMPEDANCE MEASUREMENTS**

- Pt electrodes deposited by PLD
- measured under synthetic air



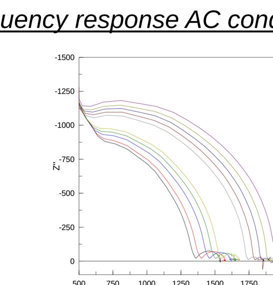

- More stoichiometric ⟶ more conducting
- For the best samples, higher values than bulk (90S/cm at 400°C) but a little bit lower than LNO thin films grown by MO-CVD (300S/cm for a 50nm-thin film) [12].
- Activation energies span from 78meV to 130meV that is in accordance with other authors [12].
- Linear dependence of Log(σ) as a function of the composition (La/Ni ratio)

The presence of $La_2O_3$ secondary phase seems to have a strong effect in electronic AC conductivity even in the cases in which the compound present a very good crystallinity.

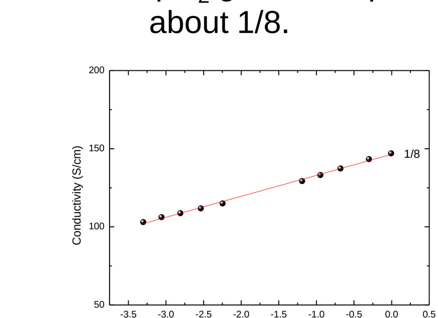
**CONDUCTIVITY - $pO_2$**

preliminary result

*Frequency response AC conductivity*



The evolution of the conductivity as a function of $pO_2$ gives a slope of about 1/8.




## CONCLUSION

**Conclusions**

- c-oriented epitaxial thin films of GBCO and LNO were successfully grown by PLD.
- The PLD method is often believed to transfer the exact stoichiometry from the target to the substrate. However, here we highlight that direct transfer is not so obvious and depend on deposition conditions. This deviation may be much stronger if we deal with volatile chemical species (as it is the case of Co in this work).
- As we saw, in particular with GBCO, the orientation of the material depends on substrate matching, but also might depend on composition. Little changes in the relative cations ratio may have a strong influence on film growth.
- Slight deviation from the expected stoichiometry may have dramatic effects on the electrical properties as it changes the electronic defects equilibrium. This influence can be much stronger if it involves transition metals (cobalt, nickel, iron...)
- Obtaining a very good crystalline compound is not a sufficient condition to get optimum electrical responses: the film microstructure has to be checked in order to detect planar defects (i.e. additional perovskite layer in LNO or cations ordering defects in GBCO) and eventually the presence of secondary phase at the local scale. As shown, both these types of defects have a high impact on transport properties.

***In progress and future works***

- 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 Profile (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.

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