Mesure de la stoechiométrie en oxygène dans des films de perovskites: étude de $LaNiO_3$

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Oxygen vacancies in Versailles

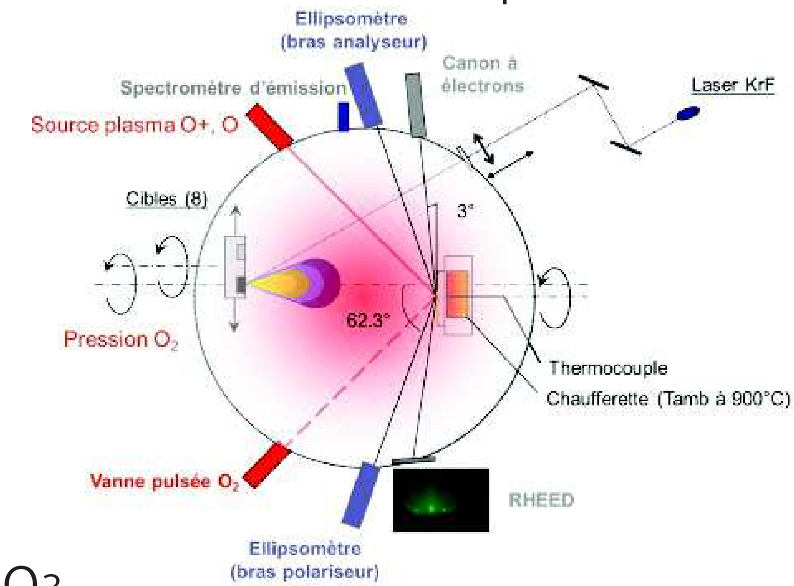
Control of physical properties by oxygen stoichiometry
Fonctional Oxides group (FOx) – Y. Dumont

Tuning magnetic properties and magnetic order and valence states in corundum $(Fe,Ti)_2O_3$ magnetic oxide semiconductor system :
L. Bocher et al., Phys. Rev. Lett. 111, 167202 (2013)

Control of type conductivity in the $FeTiO_{3-x}$ magnetic oxide semiconductor :
Chikoidze, E., et al. Appl. Phys. Lett. 102, 122112 (2013)

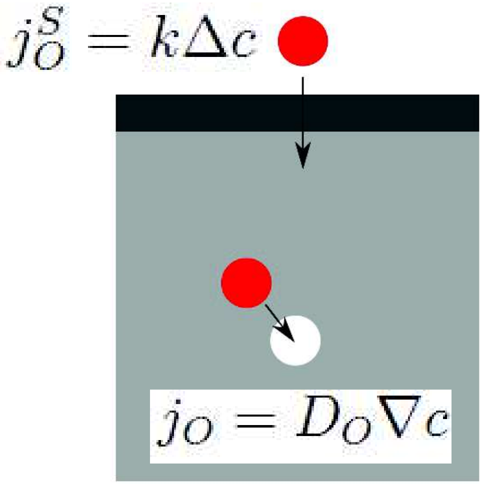
Reversible control of metal/insulator transition in $LaNiO_3$ strongly correlated electronic oxide :
B. Berini et al. Phys. Rev. B 76, (2007), 205417
B. Berini et al.J. Appl. Phys. 104, 103539, (2008)
B. Berini et al. Phase Transitions 84, 501 (2011)

Pulsed laser deposition



Oxygen vacancies in oxides

The concentration of oxygen vacancies (OV) is determined by 2 mechanisms:



1° Surface exchange

$$k = K^S e^{-E_a/k_B T}$$

2° Bulk diffusion

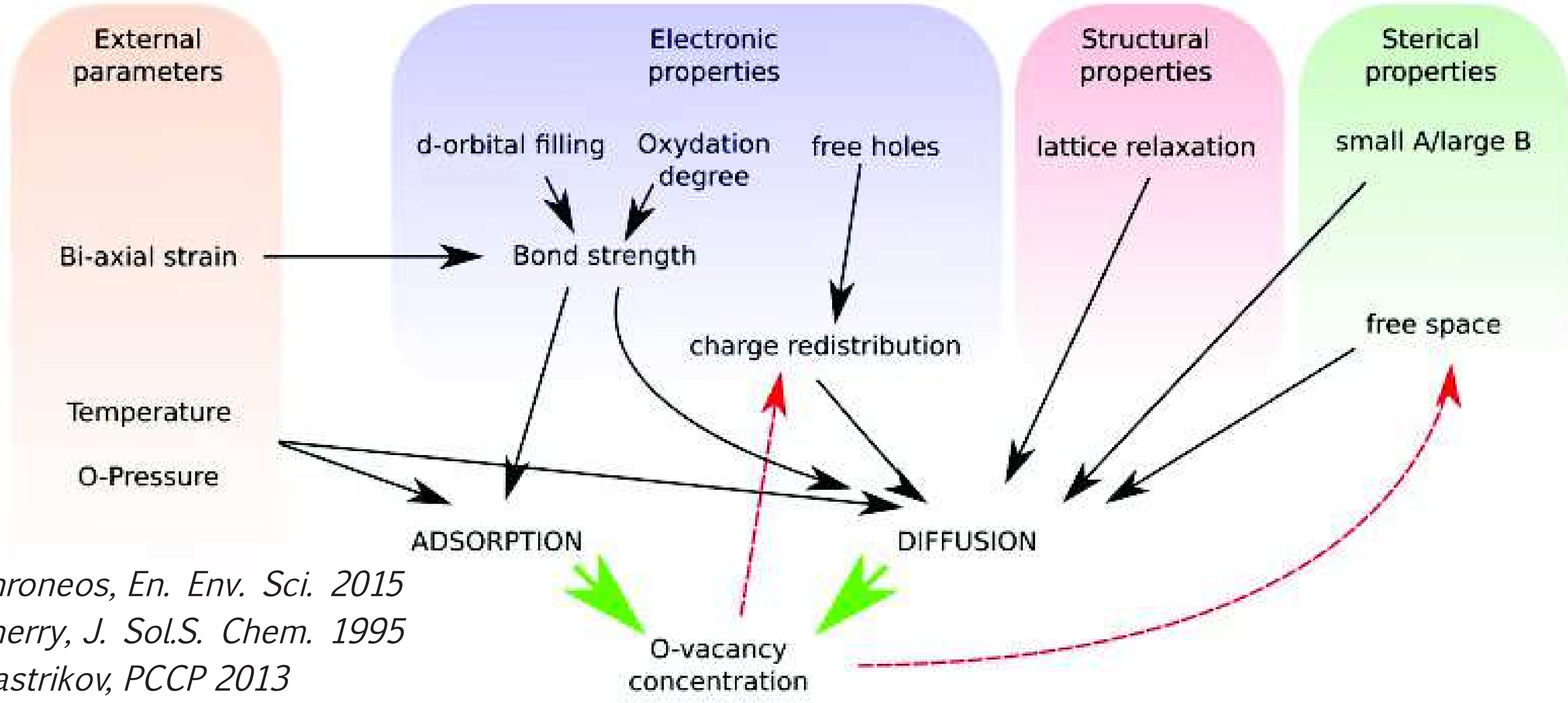
$$D_O = D_{V_{\ddot{O}}}[V_{\ddot{O}}] = K\left(e^{-\Delta H_{\mathrm{mig},V_{\ddot{O}}}/k_B T} \cdot e^{-\Delta H_{\mathrm{form},V_{\ddot{O}}}/kT}\right)$$

Strong dependence of *k* and *Do* on cation chemistry, surface orbital occupancy, carrier density and type, defects, substrate strain, …

[Vö] is very difficult to predict

Oxygen vacancies in oxides

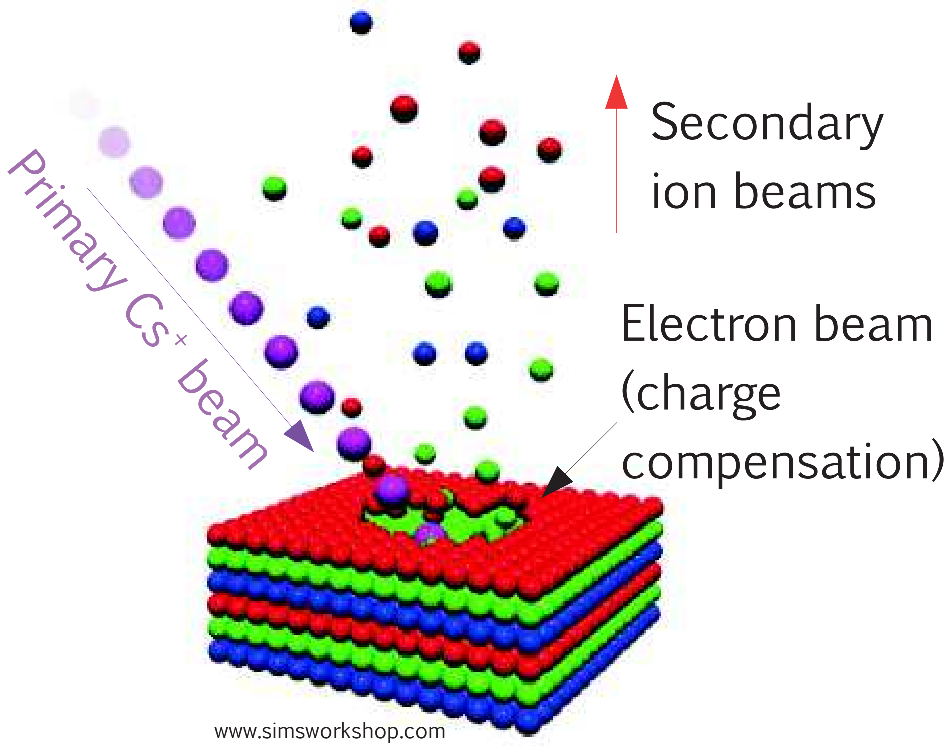
Interdependence of parameters of [Vö]



Chroneos, En. Env. Sci. 2015
Cherry, J. Sol.S. Chem. 1995
Mastrikov, PCCP 2013
Guo, Catalysts 2015
Muñoz-Garcia, Acc. Chem. Res. 2014
Mayeshiba, PCCP 2015

For given conditions, experiments are needed

Secondary ion mass spectroscopy



High relative mass accuracy: $m/\Delta m = 10^4$
Detection limits: 10^{14} at/cm^3
Depth resolution: ~3 nm + surf. roughness
Probed area: 150 x 150 µm²

Secondary ion intensity:

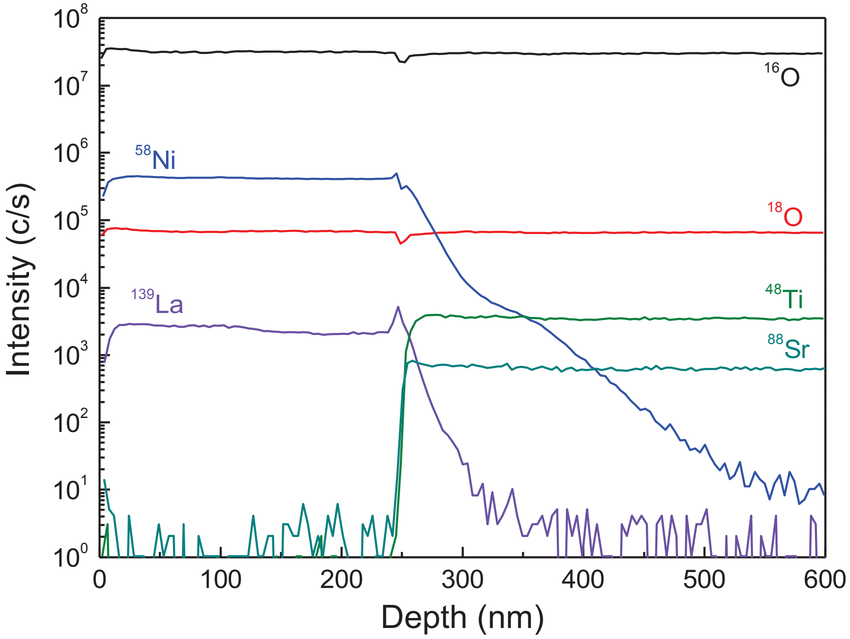
$$I = i_P \cdot \tau^{\pm} \cdot s \cdot \mathrm{T}$$

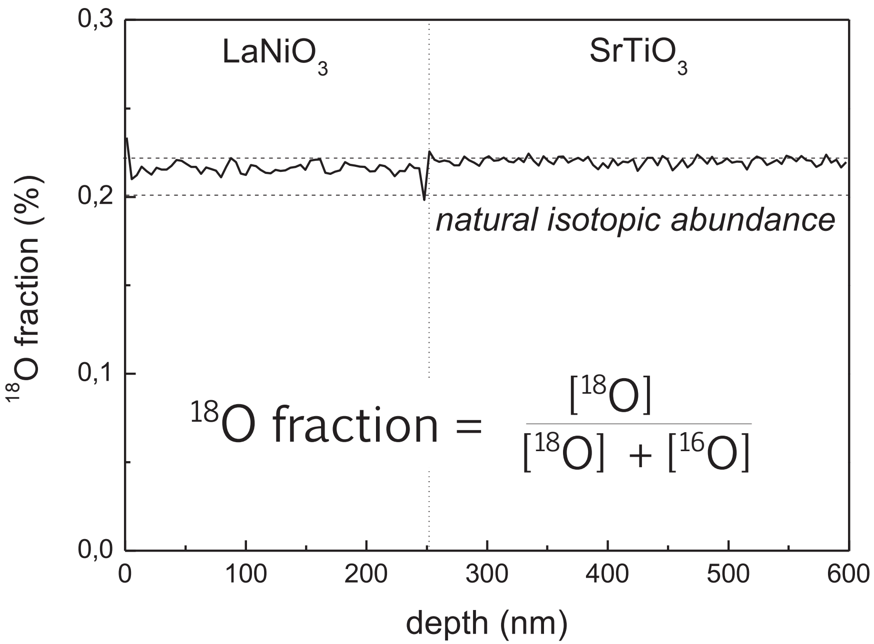
Primary current (Cs^+)
Ionisation rate (element dependent)
Sputtering rate (matrix dependent)
Transmission to detector

➡ **Relative technique: a reference is needed**

Reference sample

High-PO2 grown thick film of LaNiO3
Commercial SrTiO3 substrate
→ "Stoichiometric" references





$$^{18}O \text{ fraction} = \frac{[^{18}O]}{[^{18}O] + [^{16}O]}$$

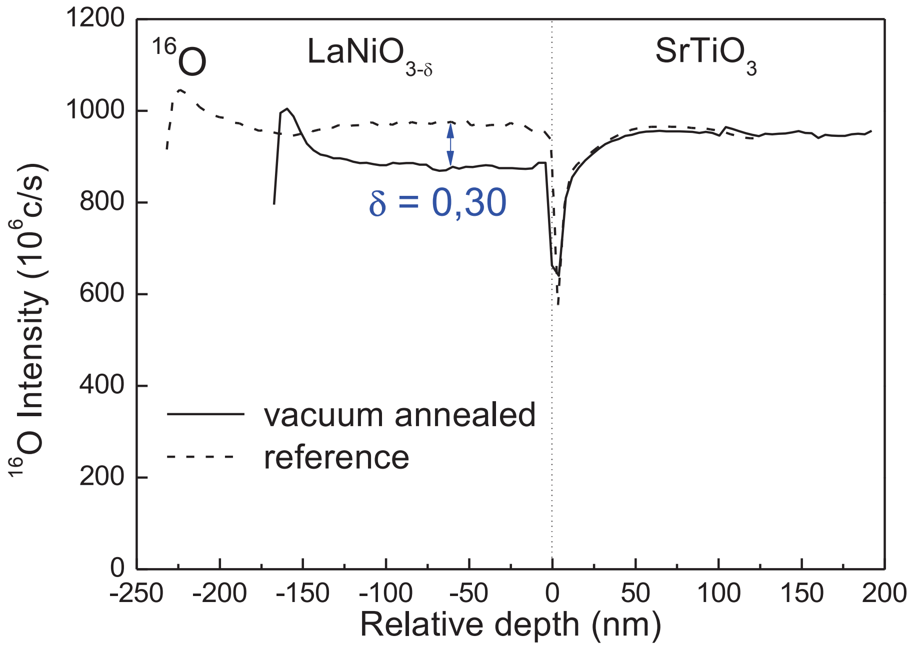
State of the art isotopic fraction accuracy

Method accuracy = stoichiometry of the reference material

Stoichiometry analysis

(i) Vacuum annealing: T = 350 °C, P = 10^{-7} mbar, 3 h (vacancy creation)

^{16}O profile



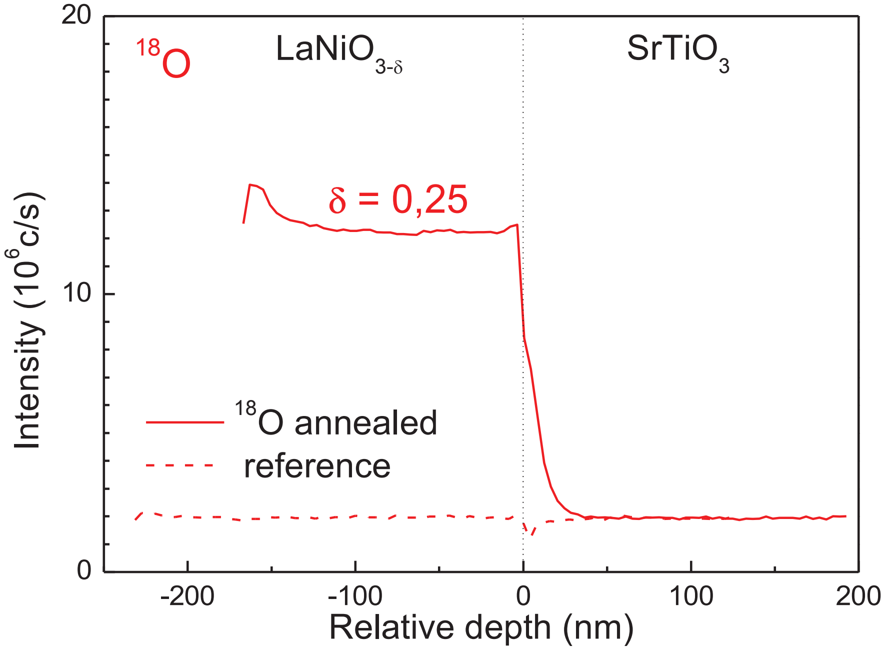
Formation of vacancies

$\delta = 0.30 \pm 0.05$

Stoichiometry analysis

(ii) Tracer incorporation: T = 300 °C, $P_{^{18}O_2}$ = 0,2 mbar, 30 min (reoxygenation)

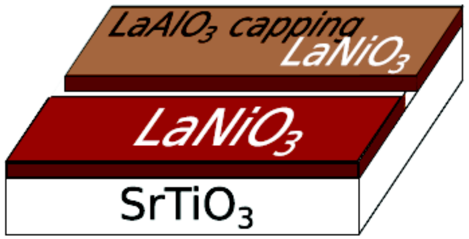
^{18}O profile



Incorporation of ^{18}O

→ $\delta = 0.25 \pm 0.05$

Oxygen filtering

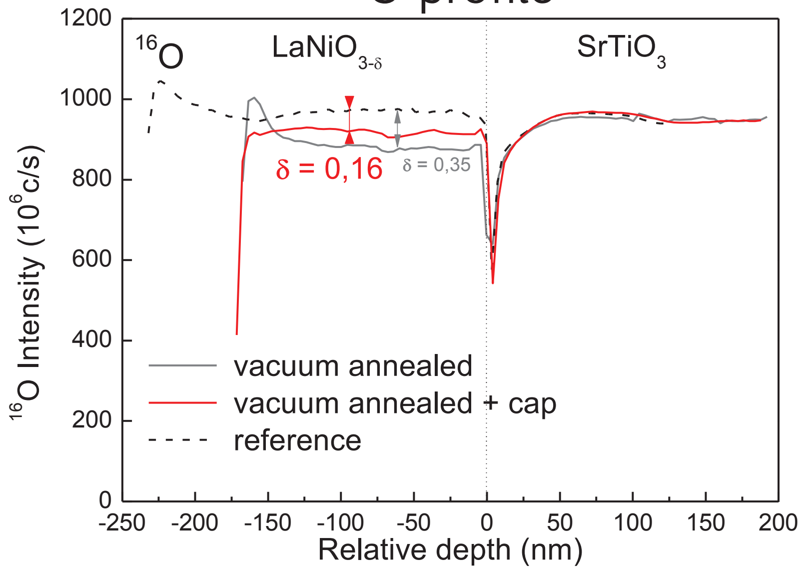


10 nm-thick $LaAlO_3$ capping layer

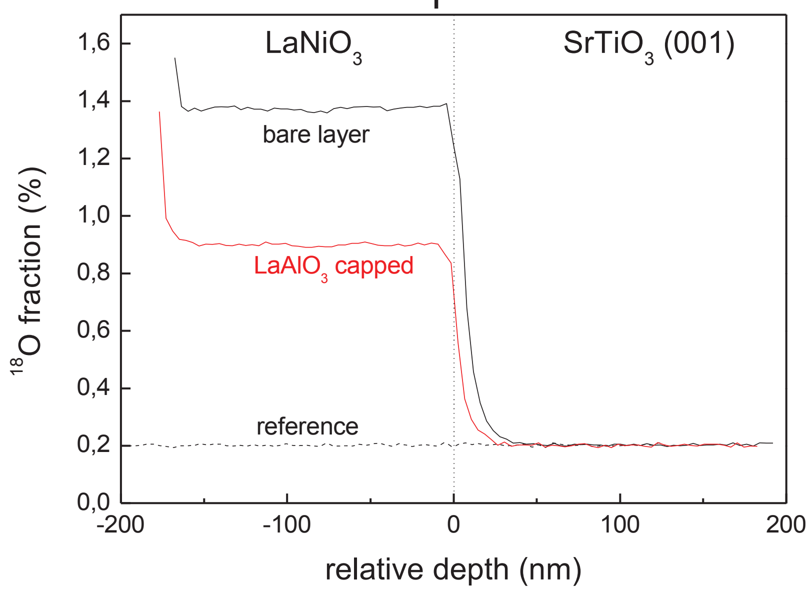
$E_a(LaNiO_3)$ = 0.65 – 0.80 eV; $E_a(LaAlO_3)$ = 1.88 eV

Same annealing conditions for capped and bare films

^{16}O profile



^{18}O profile



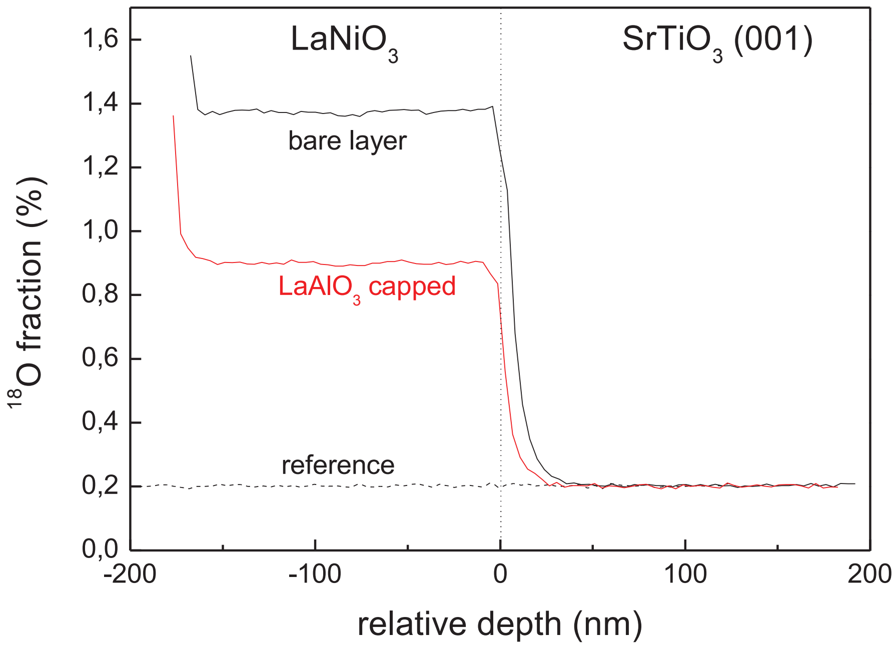
$LaAlO_3$ layer inhibits oxygen surface exchange

Possibility to quantify the O transmission through capping layer

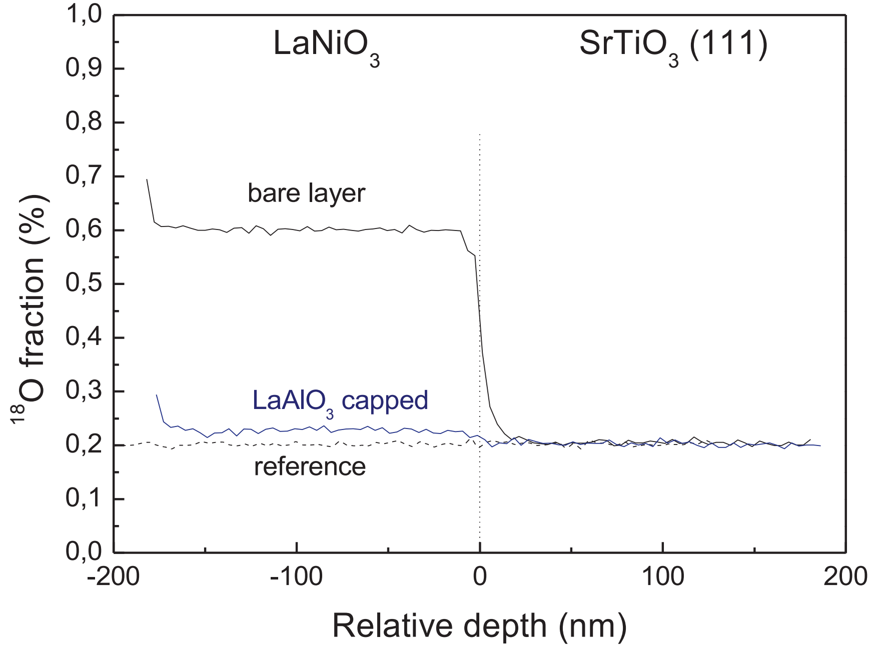
Surface effect

Diffusion is isotropic so substrate orientation affects surface reactivity only

(001) oriented surface



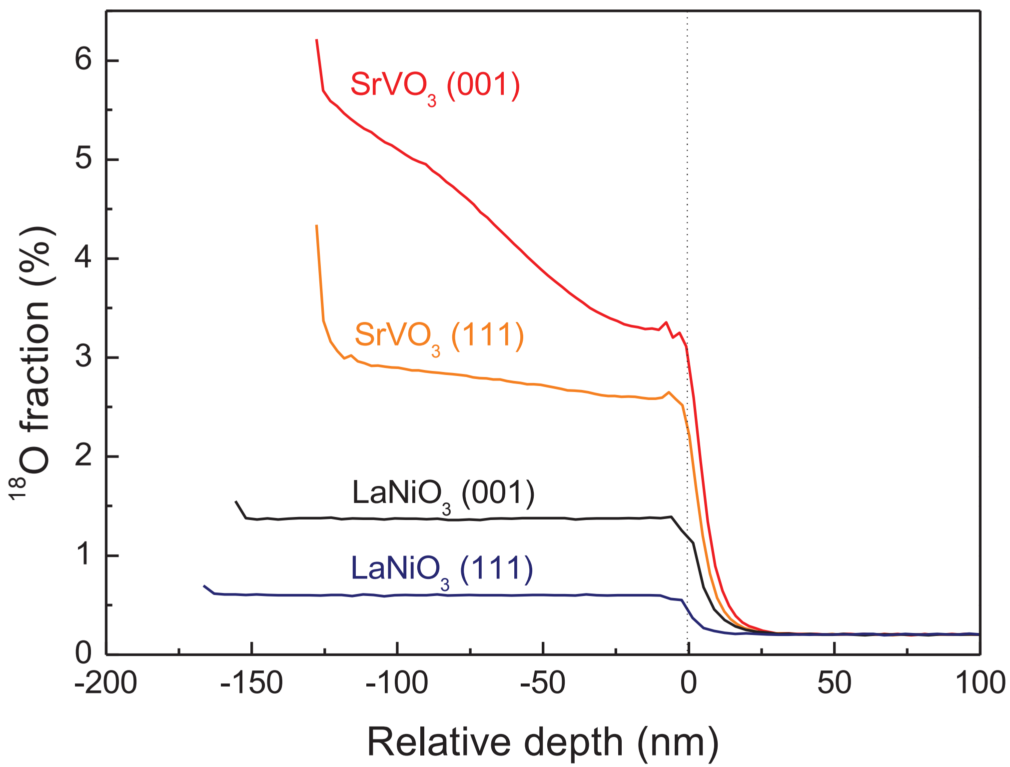
(111) oriented surface



(111) surfaces appear less reactive than (001) ones

Further investigations of surface state are required

Comparison with $SrVO_3$



<u>Concentration profile:</u>

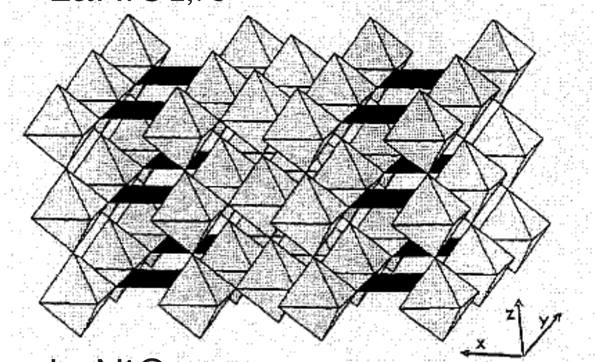
Smaller diffusion coefficient in SVO (frozen gradient)

<u>Incorporation amount:</u>

Higher surface oxygen reactivity

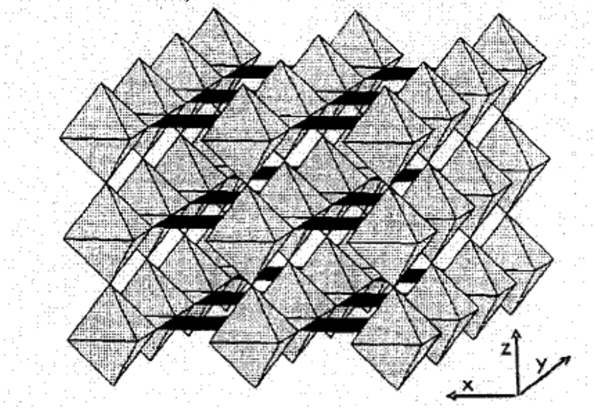
$LaNiO_3$: Vacancy ordering (in bulk)

$LaNiO_{2,75}$



Triclinic distorted $LaNiO_3$
1 NiO_4 square plane for
3 octahedra layers
Insulator

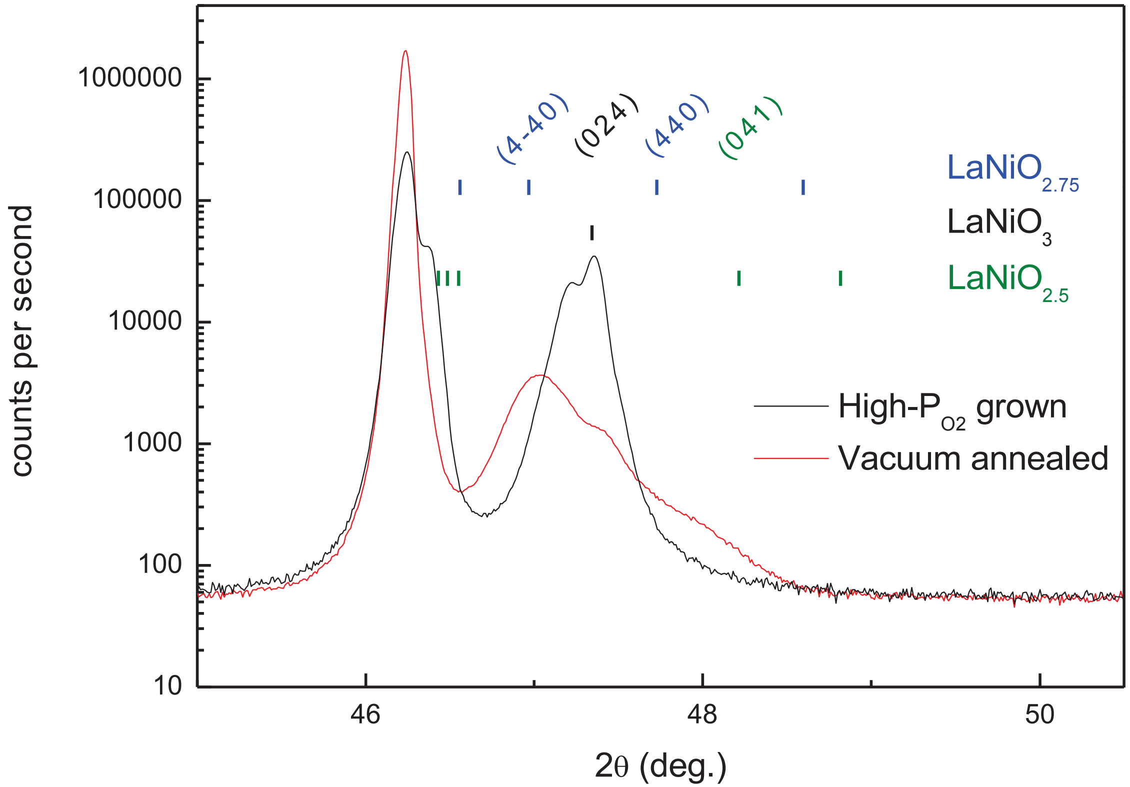
$LaNiO_{2,5}$



Monoclinic distorted $LaNiO_3$
1 NiO_4 square plane for
1 octahedra layer
Insulator

Sanchez et al., PRB ***54*** *(1996)*

$LaNiO_3$: Vacancy ordering (in films)



<u>High-P_{O2} grown film ($\delta \approx 0$)</u>

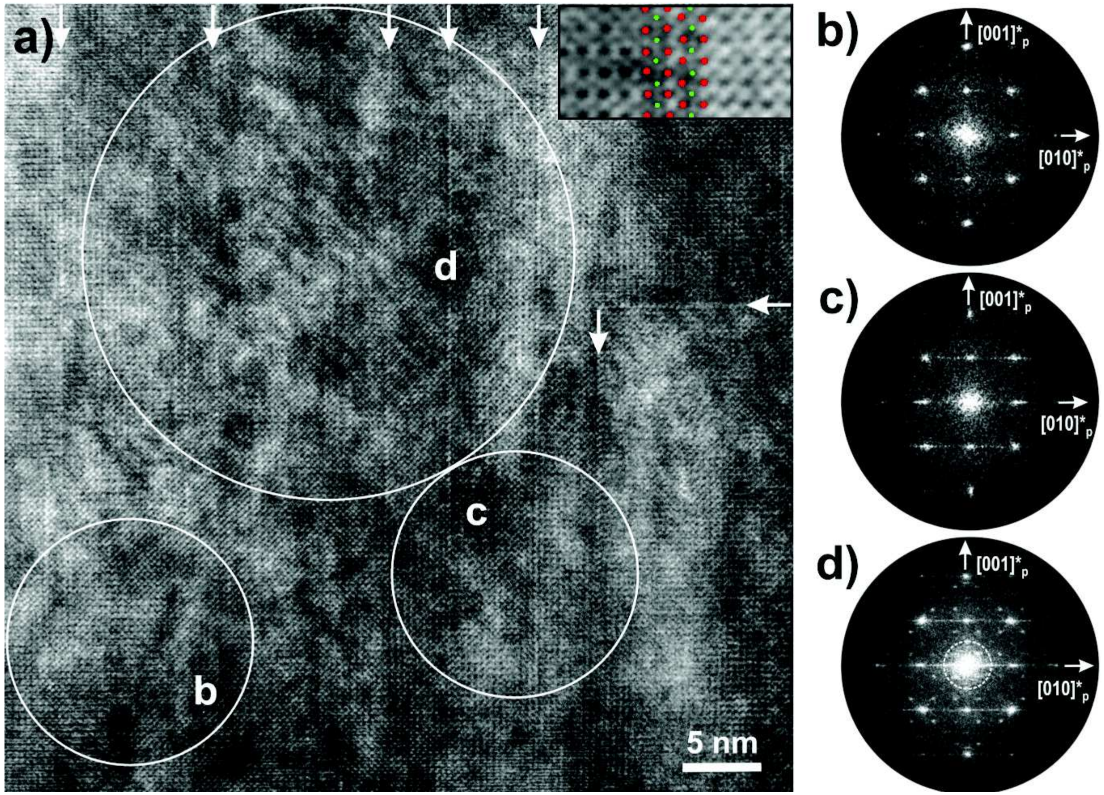
- $LaNiO_3$ matrix includes some $LaNiO_{2.75}$ domains
- $LaNiO_3$ grain size ≈ 50 nm

<u>Vacuum annealed films ($\delta \approx 0.25 \pm 0.05$)</u>

- Off-stoichiometry phases
- Coexistence of $LaNiO_3$ and $LaNiO_{2.75}$
- Possible presence of $LaNiO_{2.5}$
- $LaNiO_{2.75}$ grain size ≈ 20 nm

LaNiO3: Vacancy ordering (in films)

Vacuum annealed sample TEM cross-section



Collab. Ph. Boullay, CRISMAT (Caen)

Cationic lattice is stable upon annealing

Crystallite sizes of 20-50 nm

➡ **Geometry change** of the conducting medium

Coherent with the ρ increase by a factor 10 while carrier density remains constant ($2\ 10^{22}\ cm^{-3}$ ~ 1 carrier/Ni site)

Conclusions & perspectives

- Direct measurement of O-stoichiometry in film

- δ resolution $\approx$ 0.05 very promising

- Estimation of the annealing yields

- Evidence of surface effects

- $LaNiO_3$ case: vacancies distribution helps to refine physical properties interpretations

- High temperature electrical measurements

- Growth of ultra-thin films and (111) bilayers