Evaluation of the Mass Transport Properties of $La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ nanostructures by Finite Element Method (FEM) Simulations

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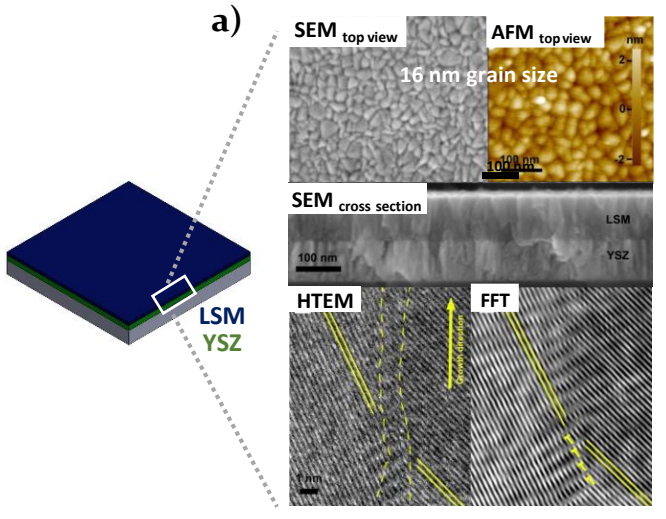
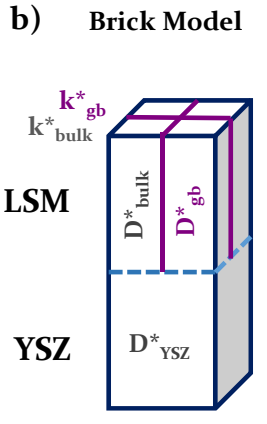
▪ NANOENGINEERING THIN FILMS: nanostructures with a high density of grain boundaries (GBs)

$La_{0.8}Sr_{0.2}MnO_{3\pm\delta}$ (LSM) dense film deposited by PLD on polycrystalline YSZ films

Microstructural Characterization

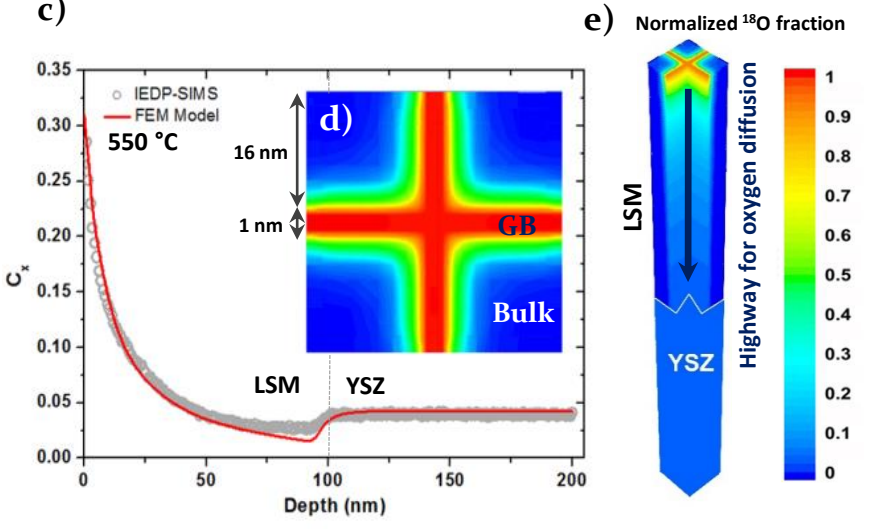


(a) The high density of vertically aligned GBs leads to a high concentration of strain-induced defects.



(b) Model proposed for the FEM simulations.

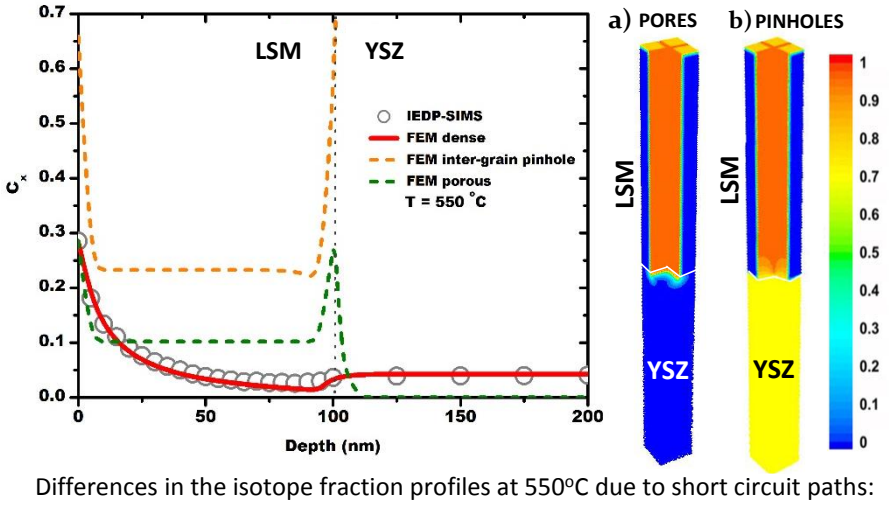
Mass transport properties by IEDP-SIMS and FEM simulations



(c) Normalized ^{18}O isotopic fraction and fitted solution by FEM at 550ºC.
(d) Top view and (e) cross section of the isotopic fraction map by FEM.

▪ EFFECT OF DEFECTS in diffusion profiles

Short circuit paths down nanopores or inter-grain pinholes



Differences in the isotope fraction profiles at 550ºC due to short circuit paths: (a) porosity in the place of GB and (b) 1x1nm² squared inter-grain pinholes inside GB. The presence of defects in the LSM dense thin films is discarded

▪ GEOMETRIC EFFECTS

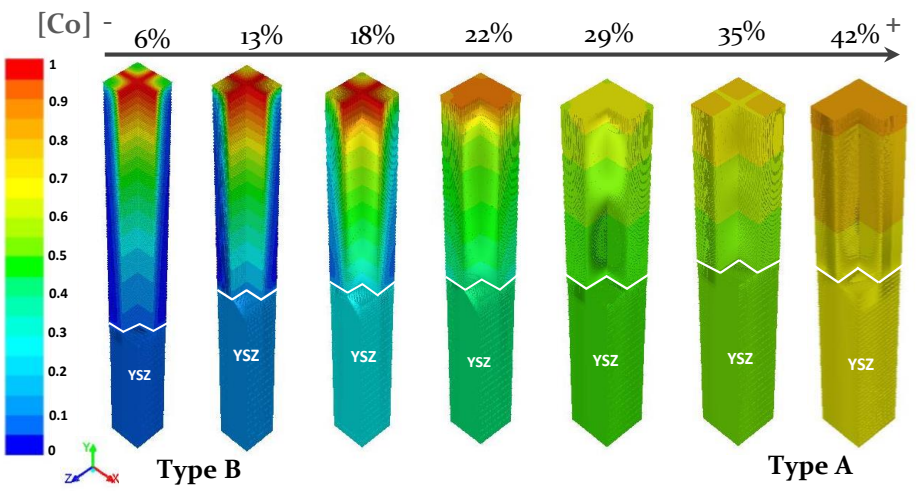
Variation of the grain size and the grain boundary width (according to the grain size study from the structural characterization)

	D^*_b ($cm^2 \cdot s^{-1}$)	D^*_{GB} ($cm^2 \cdot s^{-1}$)	k^*_{GB} ($cm \cdot s^{-1}$)
6% [Co] LSMC			
Grain width (nm) and 1 nm GB			
15	3.5×10^{-17}	3.9×10^{-12}	2.6×10^{-4}
21	7.0×10^{-17}	3.5×10^{-12}	2.0×10^{-4}
27	1.1×10^{-16}	3.2×10^{-12}	1.3×10^{-4}
GB width (nm) and 21 nm grain			
0.5	9.8×10^{-17}	4.3×10^{-12}	3.0×10^{-4}
1.5	5.8×10^{-17}	2.1×10^{-12}	1.9×10^{-4}
13% [Co] LSMC			
Grain width (nm) and 1 nm GB			
18	5.5×10^{-17}	2.9×10^{-12}	8.2×10^{-5}
25	9.8×10^{-17}	2.8×10^{-12}	8.0×10^{-5}
32	1.7×10^{-16}	2.6×10^{-12}	7.9×10^{-5}
GB width (nm) and 25 nm grain			
0.5	1.9×10^{-16}	2.7×10^{-12}	1.0×10^{-4}
1.5	8.0×10^{-17}	2.1×10^{-12}	7.9×10^{-5}

- ✓ The variation of the grain width mainly affects D^*_b and D^*_{GB}.
- ✓ The k^*_{GB} value is much less sensitive.
- ✓ Changes in the k^*_b value are insignificants.
- ✓ The effect of the grain boundary width modifies in the same order the k^*_{GB}, D^*_{GB} and D^*_b due to the decisive influence of GBs and their interaction with the bulk.

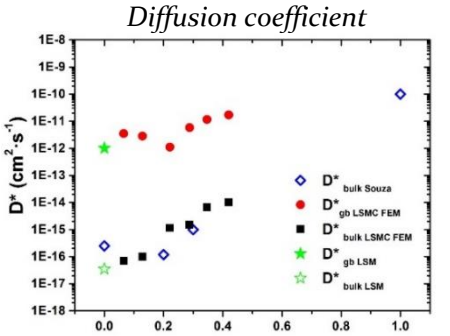
▪ DOPANT EFFECT : $La_{0.8}Sr_{0.2}Mn_{1-x}Co_xO_{3\pm\delta}$ (LSMC)

Isotopic fraction maps for LSMC/YSZ calculated by FEM

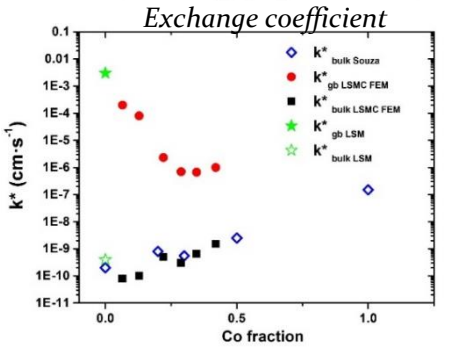


An increase in Co concentration leads to a change of the diffusion regime according to the Harrison's classification from the type B (D^*_b and D^*_{GB}) to the type A (effective diffusion coefficient D_{eff}).

Diffusion coefficient



Exchange coefficient



- ✓ Large increase in both D^*_b and D^*_{GB} for %Co > 20%, probably related to an increase of the $V_O^{\cdot\cdot}$
- ✓ The increase of $V_O^{\cdot\cdot}$ is similar in the grain and GBs.
- ✓ K^*_b increases with Co content, probably related to an increase of the $V_O^{\cdot\cdot}$ in the grain.
- ✓ k^*_{GB} decreases with %Co up to 22%. It might be due to a higher E_a for O_2 adsorption in LSMC compared to LSM.
- ✓ The O^{2-} incorporation probably is enhanced due to high density of GBs in the nanostructure.

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