X-ray photoelectron study on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ before and after thermal treatment and permeation test

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"Borsa giovani" tematiche materiali avanzati per applicazioni strutturali
in collaboration with R.S.E.

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Oxygen production

Usage

- oxyfuel combustion process (metal, glass production)
- gasification
- medical application

Production methods

- cryogenic distillation
  - large scale plant
  - high investment
  - high energy consumption
- pressure swing adsorption (PSA)
  - low investment
  - low energy consumption
  - slow cycle speed (regeneration process)
- membrane separation
  - low energy consumption
  - no loss in selectivity efficiency
  - issue in structural and chemical stability (change in mechanical proprieties)

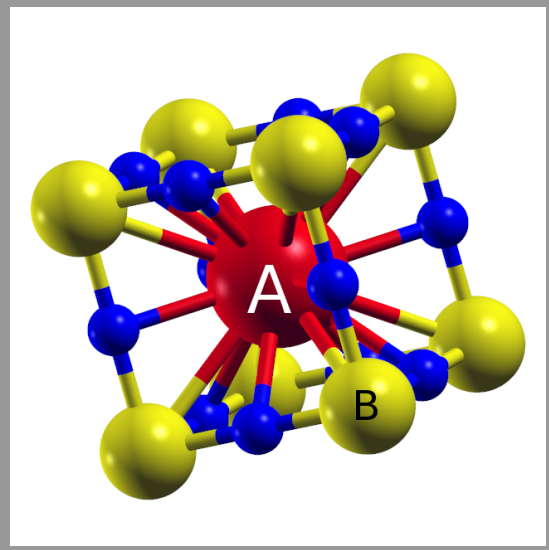
Perovskite

- A B O_3
  - Goldshmidt's tolerance factor :

    $t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_0)}$,

    $t > 1$ hexagonal
    $0.9 \leq t \leq 1$ cubic
    $0.71 \leq t \leq 0.9$ rhombohedral
    $t < 0.71$ different structures

    $R =$ ionic radius



  - different valence in cations

- very flexible material in properties

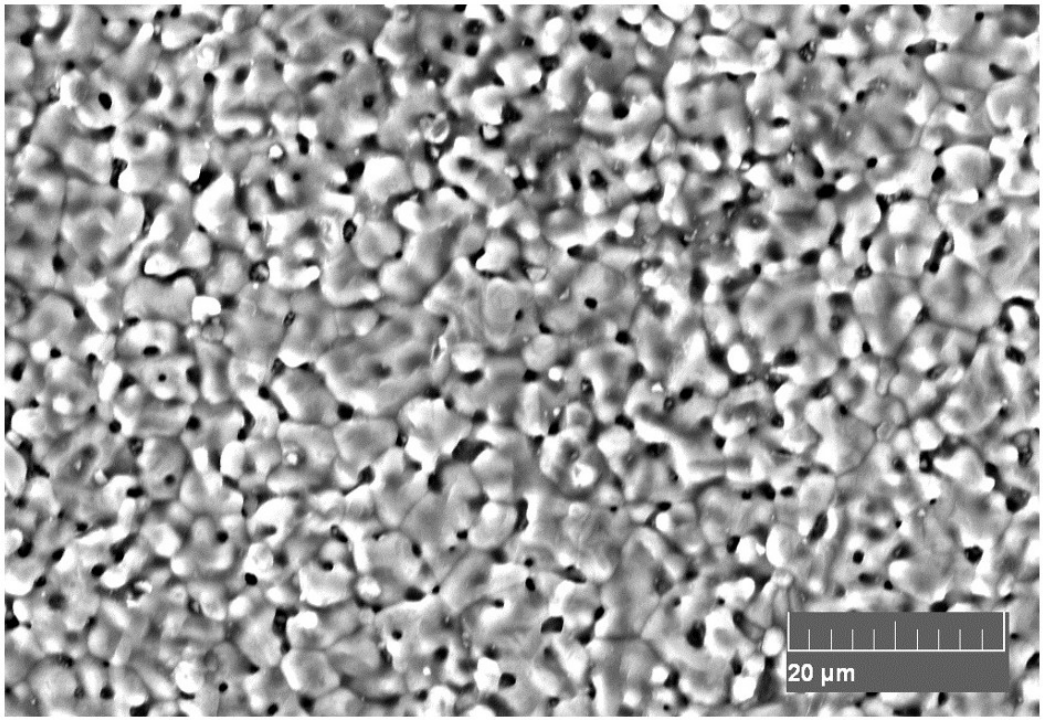
Perovskite in oxygen separation

- cubic or hexagonal structure
- oxygen vacancies A B $O_{3-\delta}$
- Sr (CoFe) $O_{3-\delta}$
- structural instability
- $Ba_{0.5}Sr_{0.5}$ $Co_{0.8}Fe_{0.2}$ $O_{3-\delta}$ (BSCF)
  $La_{0.6}Sr_{0.4}$ $Co_{0.2}Fe_{0.8}$ $O_{3-\delta}$ (LSCF)

The samples

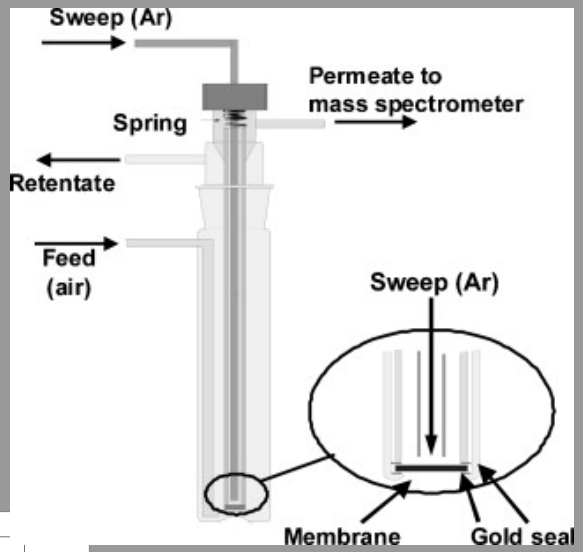
powder sintering at high temperature (Forschung-Zentrum Jülich)

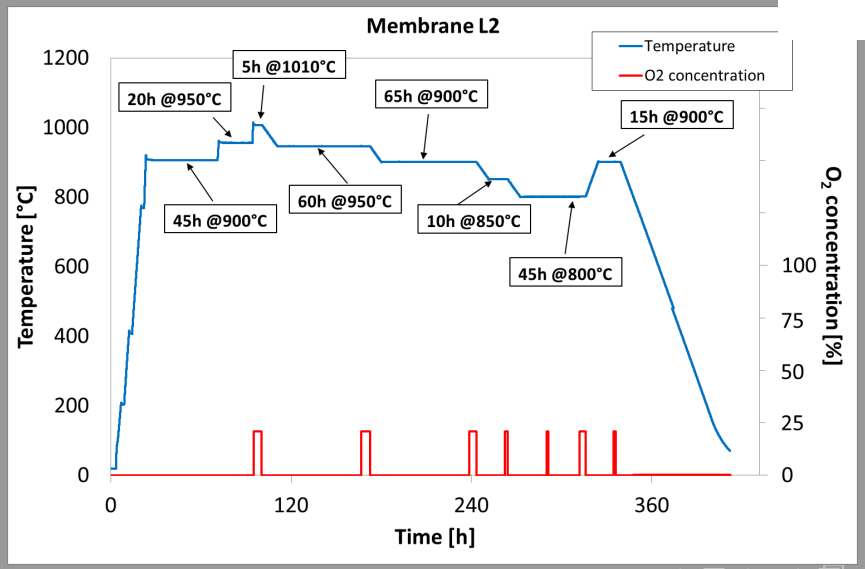
BSCF



Experimental condition

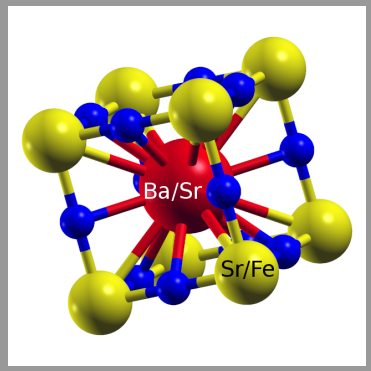
- annealing
  - phase transition Vs temperature (XRD)
  - thermal stress 780 °C for 1300 hr
- permeation
  - 750-1010 °C
  - feed gas O_2/N_2 250 Ncm^3/min
  - sweep gas He 50 Ncm^3/min

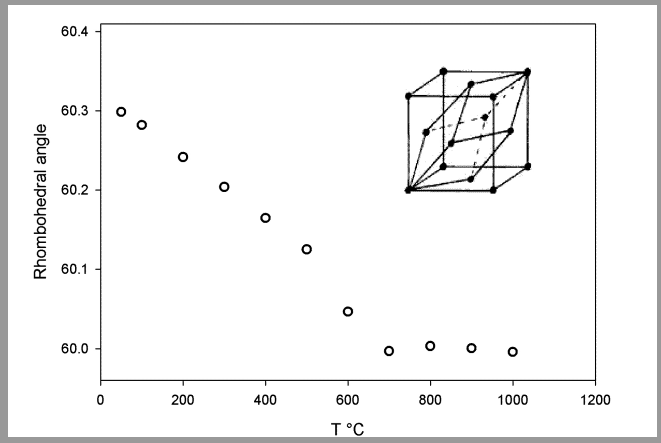




Crystal structure

- room temperature
  - BSCF cubic
  - LSCF rombohedral
- high temperature (700-850 °C)
  - BSCF cubic → hexagonal
  - LSCF rombohedral → cubic

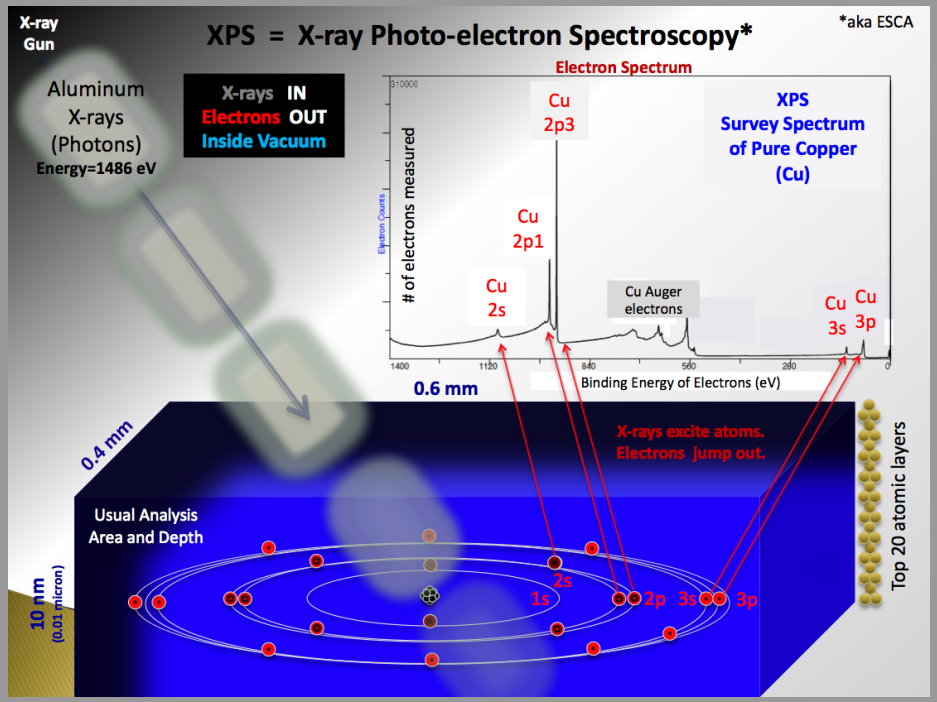




XPS

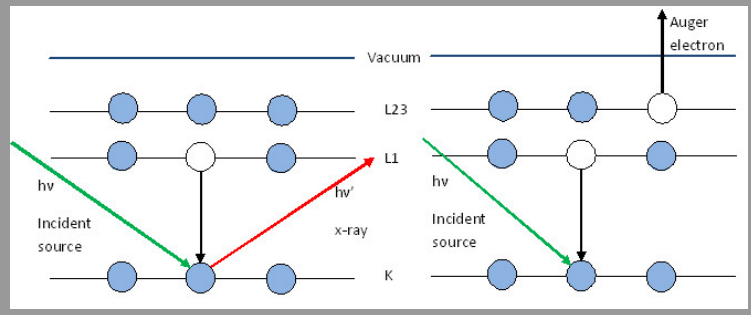
Specific fingerprint of elements

Photoelectrons

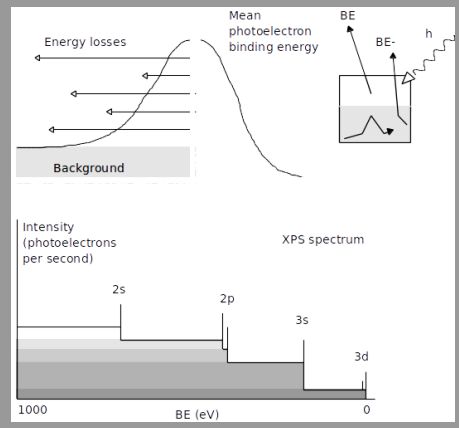


$$B.E. = h\nu - E_k - \phi_{work}$$

Auger electrons



Inelastic Background

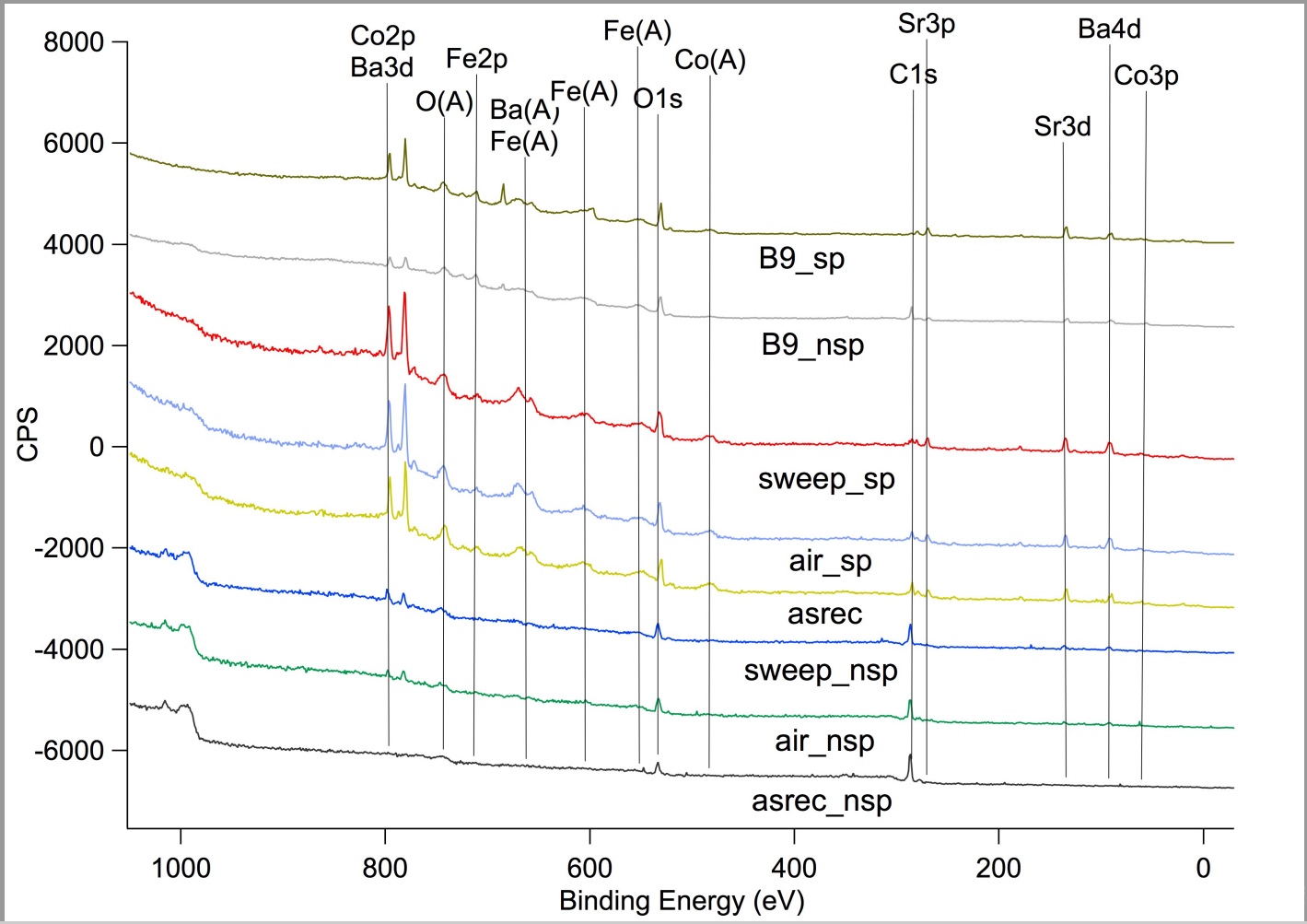


XPS setup

- Source
  - Mg X-Ray
  - energy $K_{\alpha 1,2}$ (2p$\rightarrow$ 1s) 1253.6 eV
  - width $\Delta E_s = 0.70$ eV
- Measurement chamber ($P < 10^{-8}$ mbar)
  - mean free path $\lambda \propto \frac{1}{n}$ (n= density of molecules)
  - avoid damage
  - minimize surface contamination
- Electron energy analyzer hemispherical
  - single channel
  - $\frac{\Delta E}{E_{pass}} = k$ where $\Delta E = resolution$

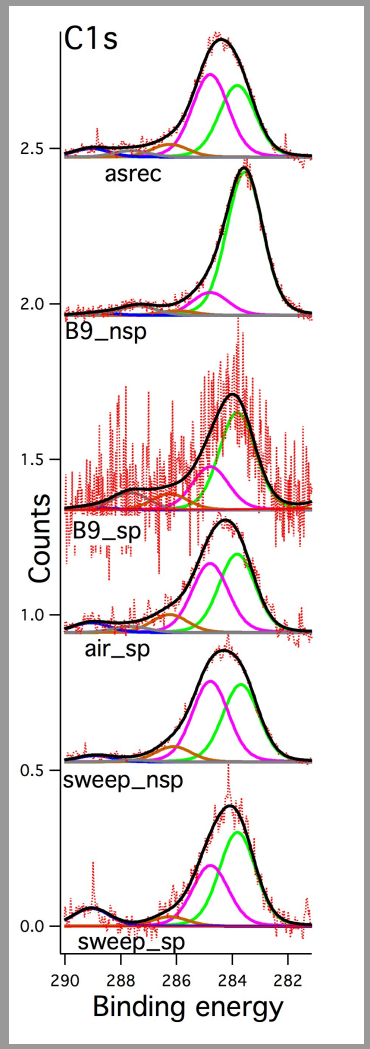
Wide spectra BSCF

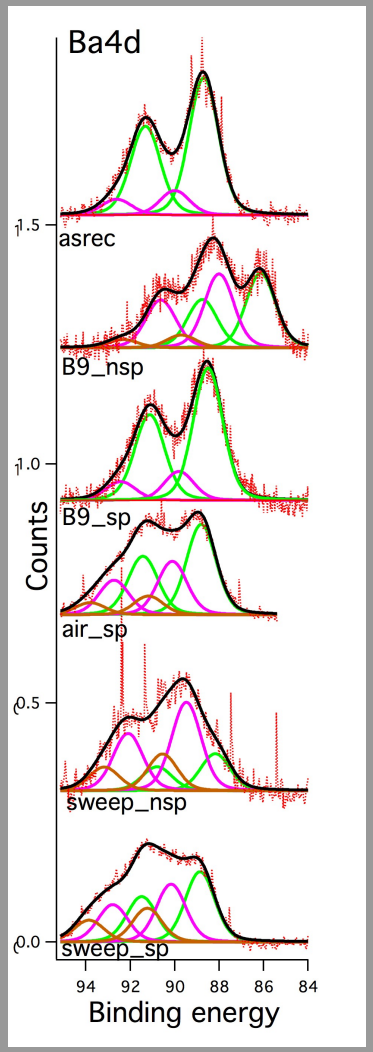
Pass energy $E_p = 100$ eV, energy step 1 eV

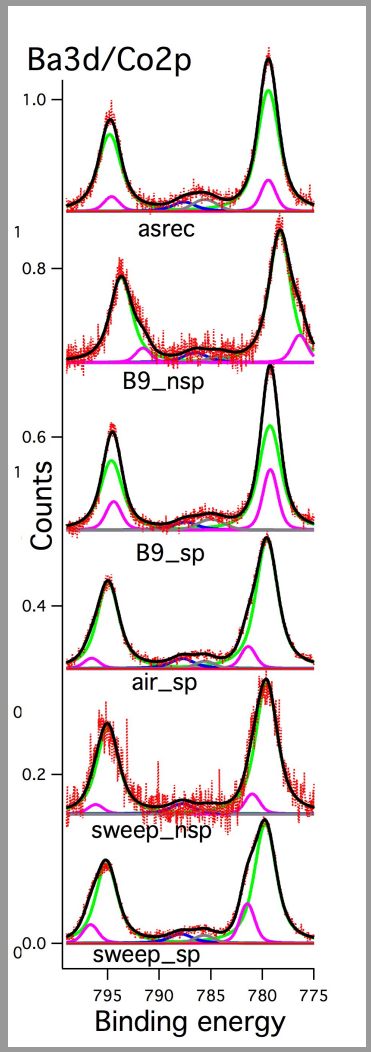


High resolution BSCF spectra

Pass energy 30 eV step energy 0.025 eV







Co(III)

Co(II)

Co(III)

Co(IIII)

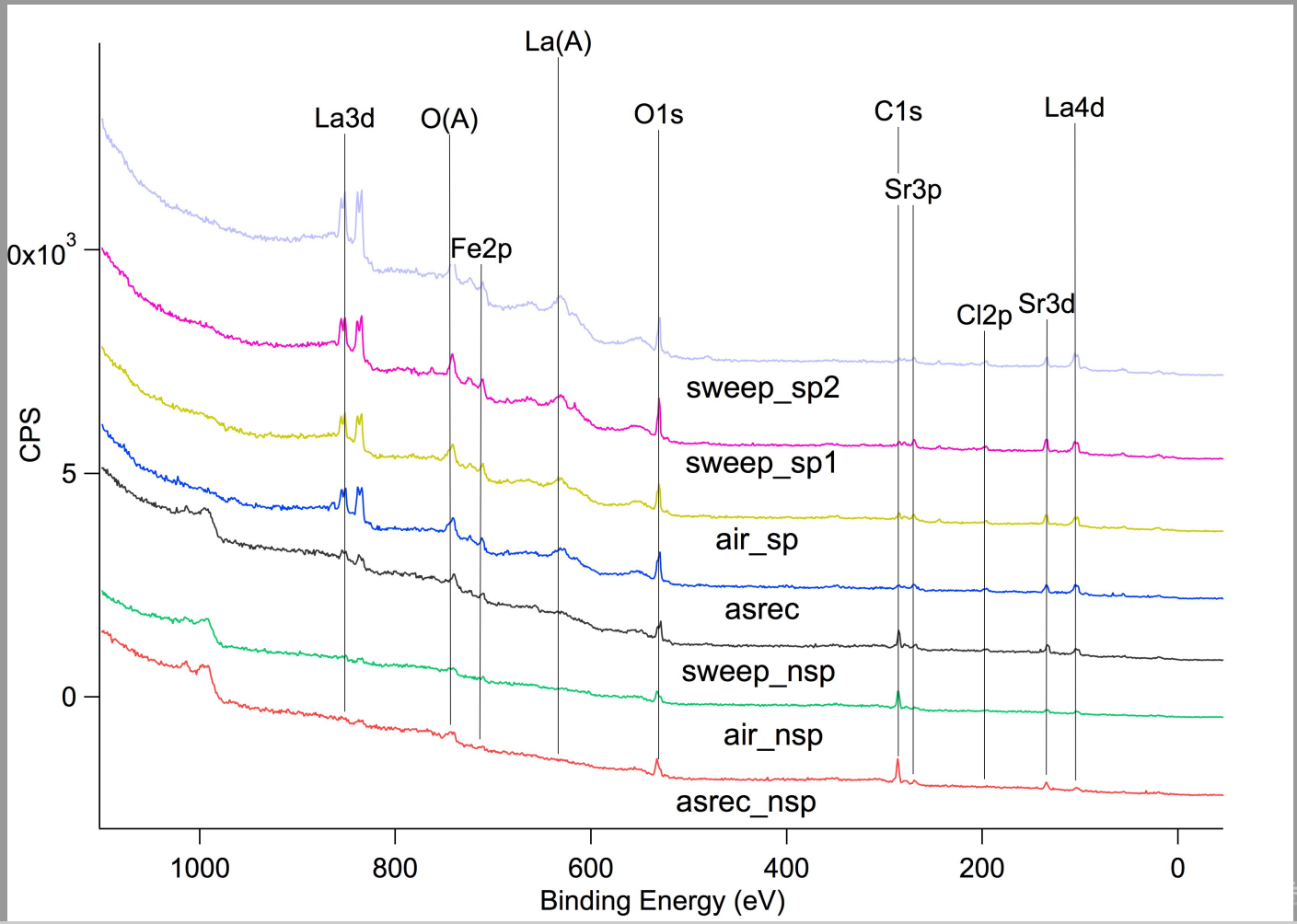
BSCF evolution

- As received
  - two chemical compounds compatible with Ba in BSCF and BaO
  - Co has a valence of 3+
- Annealed sample
  - $BaCO_3$ on surface
  - Co has a valence of 2+ on surface
- Feed exposed face (air) and sweep face
  - peaks compatible with Ba in BSCF, BaO and BaO_2
  - Co has a valence of 4+

The Co behavior confirms the XRD results

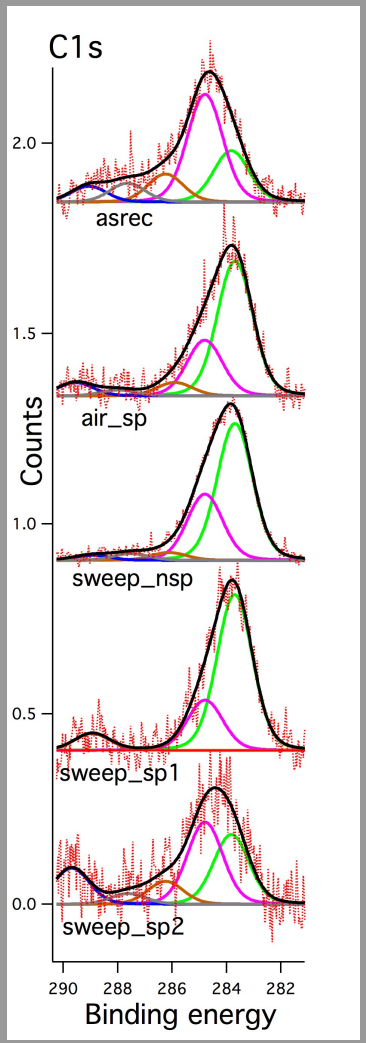
Wide spectra LSCF

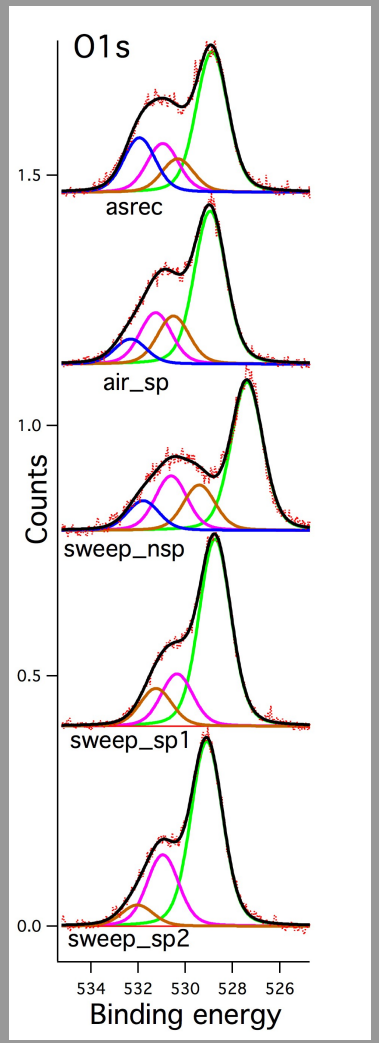
Pass energy $E_p = 100$ eV, step energy 1 eV

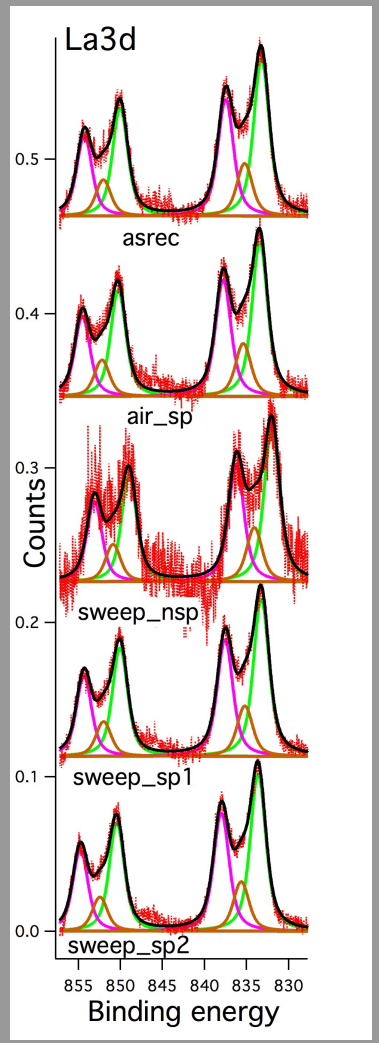


High resolution LSCF spectra

Pass energy 30 eV step energy 0.025 eV







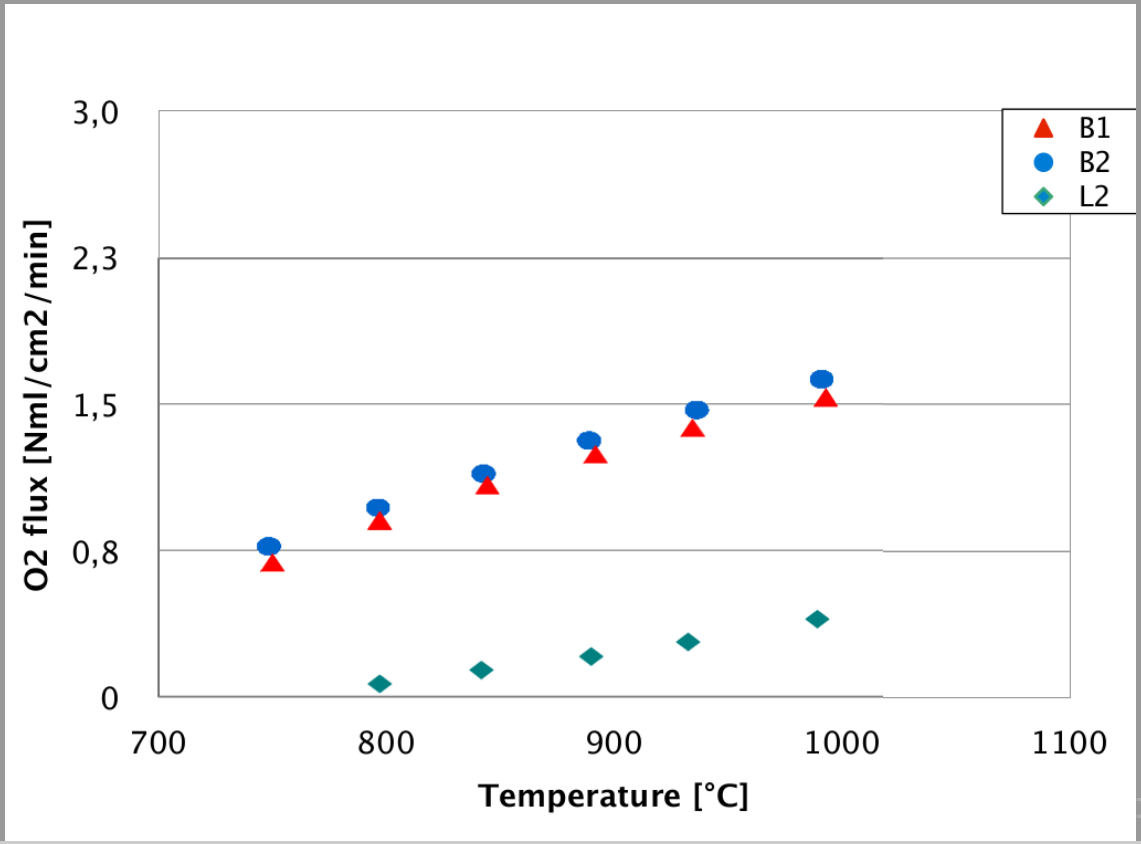
Observation on LSCF high resolution spectra

- O1s
  - peaks at about 529 eV are from oxygen in lattice
  - peaks in sweep face without sputtering at about 527.5 eV are from electron-rich oxygen in lattice
- La3d
  - main peak $3d^9 4f^0$
  - the other two peaks are multiplet splitting phenomena of state $3d^9 4f^1$ and hole in ligand site [1]
  - in all sample these peaks are very stable

[1] E.Talik et al.,MAT SCI ENG B-SOLID, 2014, 182, 74-80

Permeation results

- B1 120 h at 820 °C
- B2 215 h at 820 °C
- L2 215 h 820 °C



Conclusions

- BSCF
  - can work also a room temperature
  - better permeation than LSCF
  - more structural change in work condition
- LSCF
  - can work at temperature higher than 700 °C
  - less permeation than BSCF
  - more structural/electronic stability than BSCF

Thank you for

your attention

Spectral features

- Spin-orbit splitting
  - total angular momentum $j_{\pm} = l \pm 1/2$
  - degeneracy $2j_{\pm} + 1$
  - peaks area ratio $\frac{A_{j_-}}{A_{j_+}} = \frac{2j_- + 1}{2j_+ + 1}$
- Shake-up: the outgoing electron interacts with a valence electrons losing kinetic energy.
- Chemical shift is due to a change in core binding energy
  - electrostatic shielding of nuclear charge from all other electron
  - removal (increase B.E.) or addition (decrease B.E.) of electronic charge as a result of bonding
- Surface charging: an excess of positive charge shift BE to higher value

Quantification in XPS

$$n = \frac{I}{f\sigma\theta y\lambda AT}$$

$$n_x = \frac{I_x}{S_x}$$

S_x is the atomic sensitive factor

n= number of atom per cm^3
I= number of photoelectrons per second
f= X-ray flux photons/cm^2
σ= cross section
y= efficiency of photoelectron process
λ= inelastic mean free path
A= area of sample
T= detection frequency

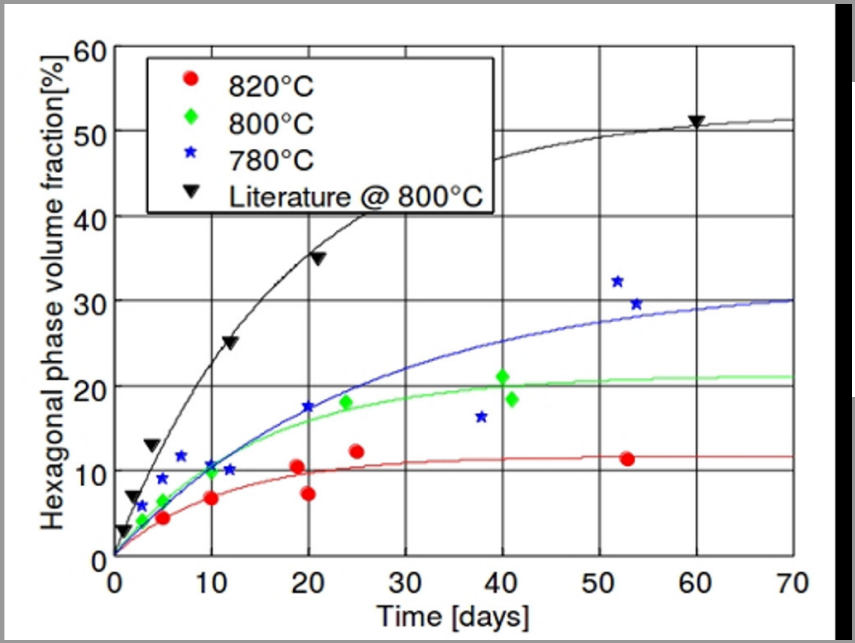
with these elements we can evaluate

- concentration of elements $C_x = \frac{\frac{I_x}{S_x}}{\sum_i \frac{I_i}{S_i}}$
- deconvolve overlapping signals

Crystal structure

Johnson-Mehl-Avrami

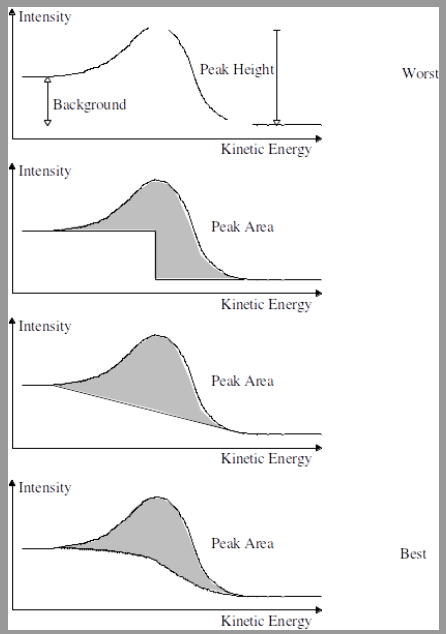
$\alpha_{hex}(t) = \alpha_{hex}(\infty)(1 - e^{-kt^n}),\ n = 1$



Aging temperature	$\alpha_{hex}(\infty)$	Characteristic time $\tau = \frac{1}{k}$ days
BSCF 780 °C	32.2%	26.3
BSCF 800 °C	21.2%	14.7
BSCF 820 °C	11.7%	11.5
BSCF 800 °C Literature	52.3%	17.8

Fitting high resolution spectra

Shirley background



peak shape Voigt that is a convolution of

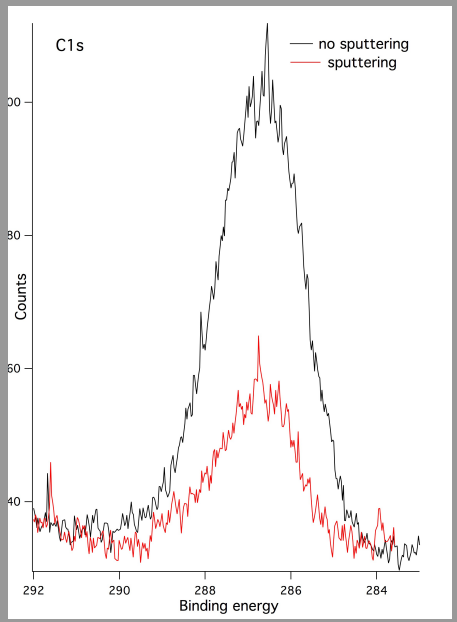
- Gaussian line shape
  - source width
  - analyzer resolution
- Lorentz line shape
  - hole life-time

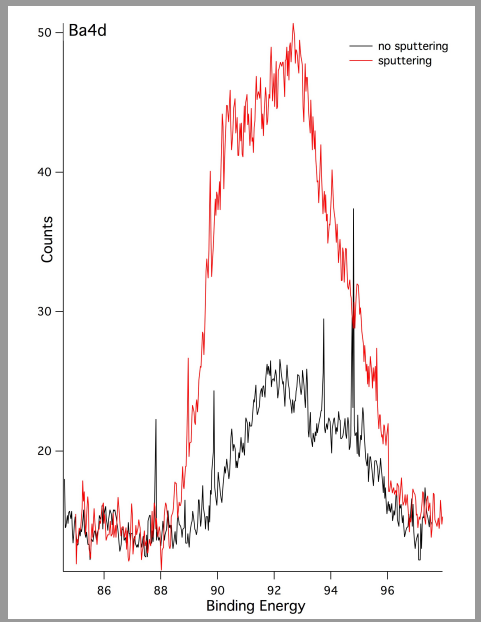
Our fit are obtained :

- background subtraction
- normalized area for each elements in each samples
- aligned C1s main peak at 284.8 eV

Sputtering

- reduce surface contamination
- Ar ions
- at the energy of 3.5 keV
- for 3 min





Measurement summary

Treatment	BSCF name	LSCF name
as received sample before sputtering	asrec_nsp	asrec_nsp
as received sample after sputtering	asrec	asrec
780 °C for 1300 hr before sputtering	B9_nsp	
780 °C for 1300 hr after sputtering	B9_sp	
permeated membrane sweep face before sputtering	sweep_nsp	sweep_nsp
permeated membrane sweep face after a first sputtering	sweep_sp	sweep_sp1
permeated membrane sweep face after a second sputtering		sweep_sp2
permeated membrane feed face before sputtering	air_nsp	air_nsp
permeated membrane feed face after sputtering	air_sp	air_sp

Properties

- catalytic property (oxidation-reduction process)
- high electronic/ionic conductivity (oxygen separation)
- superconductivity [2]
- colossal magneto-resistance [2]
- ferroelectricity [2]

[2] A. S. Bhalla, R. Y. Guo and R. Roy, Mater. Res. Innovations, 2000, 4, 3–26