Influence of synthetic method on the properties of La$_{0.5}$Ba$_{0.5}$FeO$_3$ SOFC cathode

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[2] Pontificia Universidad Católica del Perú (PUCP), Dpto. Ciencias, Sección Químicas. Av. Universitaria 1801. Lima-32, Perú.

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Contents:

- **Introduction**

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  Perovskites

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  Glycine nitrate combustion process

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  Microstructure
  Bulk conductivity
  Thermal expansion coefficient
  Polarization resistance

- **Conclusions**
- **Acknowledgments**

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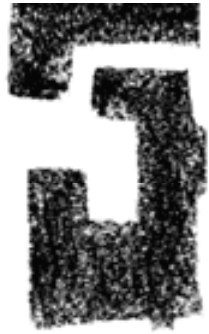
Perovskites $Ln_{1-x}M_xBO_3$
Ln = trivalent lanthanide
M = divalent alkaline-earth cations
B = transition metal
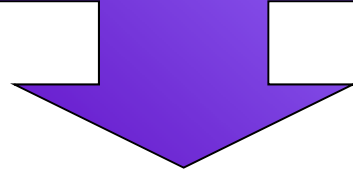
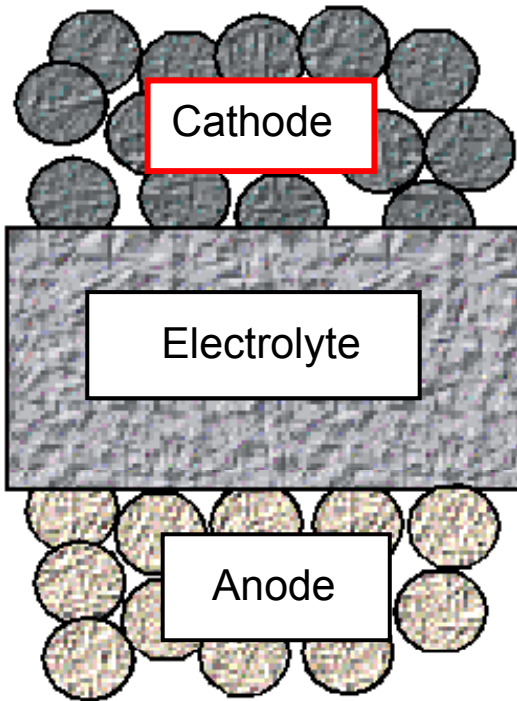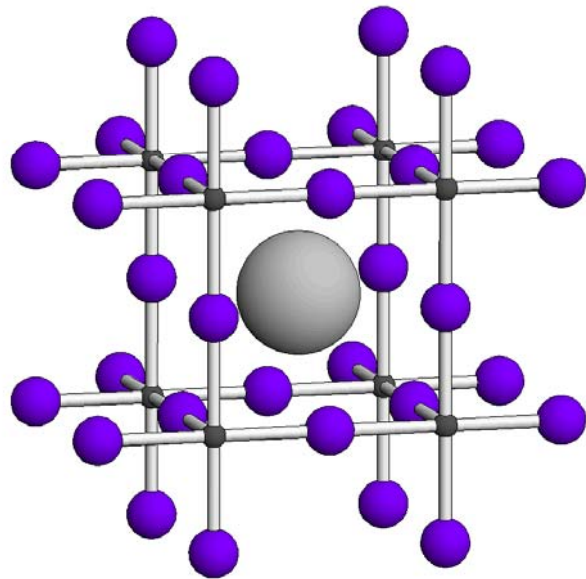| **Materiales**		**Electrical properties**	**Thermomechanical properties**	**Stability**
Perovskite ABO_3 with YSZ or SDC (samaria doped ceria) composite	Cathode	Conductivity $(\sigma_{el} + \sigma_{ion})$ Catalytic activity	Porosity Thermal expansion coefficient (TEC) Adhesion	Under reducing atmospheres
Yttria doped zirconia YSZ	Electrolyte	Ionic conductivity $(\sigma_{ion} \gg \sigma_{el})$	Gas-tigtness Mechanical stability	Under reducing and oxidizing atmospheres
Nickel-YSZ cermet	Anode	Catalytic activity Conductivity $(\sigma_{el} + \sigma_{ion})$	Adhesion Thermal expansion coefficient (TEC) Porosity	Under oxidizing atmospheres

Ivers-Tiffée, E.; Weber, A. y Herbstritt, D. J. Eur. Ceram. Soc., 21, 2001, 1805-1811.

ABO_3

○ A (Ln^{3+}, M^{2+})

● O

• B (Fe, Mn, Co)

Parameters that control the A position of the perovskite

Tolerance factor (Goldschmidt)
Define the stability of perovskites

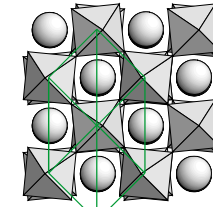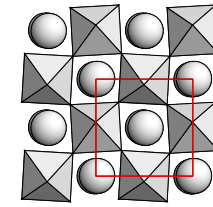$$t = \frac{(r_A + r_O)}{2^{½} \cdot (r_B + r_O)}$$

t = 1 **Ideal perovskite**

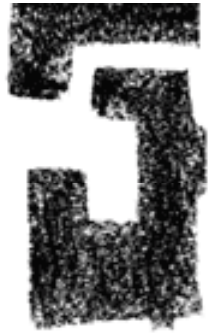t ≠ 1 **Non-ideal perovskite**

$Pm3m$ ($a^0b^0a^0$) $R\bar{3}c$ ($a^-a^-a^-$) $Pnma$ ($a^-b^+a^-$)
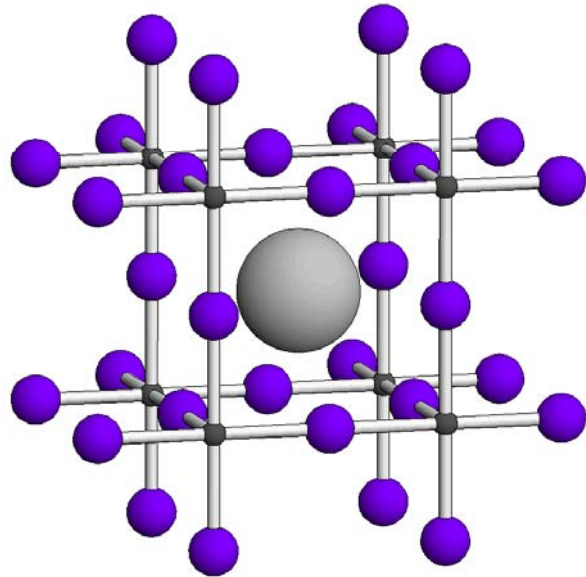
Perfect adjustment   Mismatch
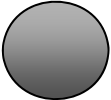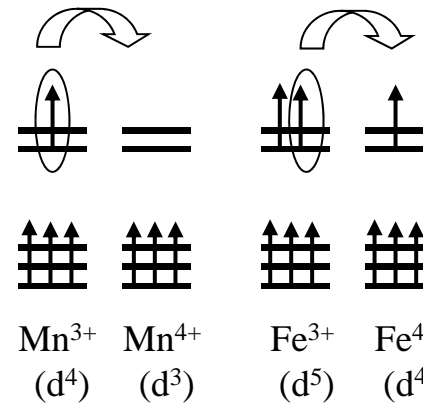between the sizes of the atoms that form
the structure

ABO_3

Parameters that control the A position of the perovskite

Tolerance factor (Goldschmidt)
Define the stability of perovskites

$$t = \frac{(r_A + r_O)}{2^{\frac{1}{2}} \cdot (r_B + r_O)}$$

$t = 1$ Ideal perovskite

$t \neq 1$ Non-ideal perovskite

Hole doping level x

$Ln^{3+}_{1-x}M^{2+}_{x}BO_3 \longrightarrow B^{3+} \quad B^{4+} \longrightarrow$ **Increase of t**

A (Ln^{3+}, M^{2+})

O

B (Fe, Mn, Co)

Mn^{3+} Mn^{4+} Fe^{3+} Fe^{4+}
(d^4) (d^3) (d^5) (d^4)

ABO_3
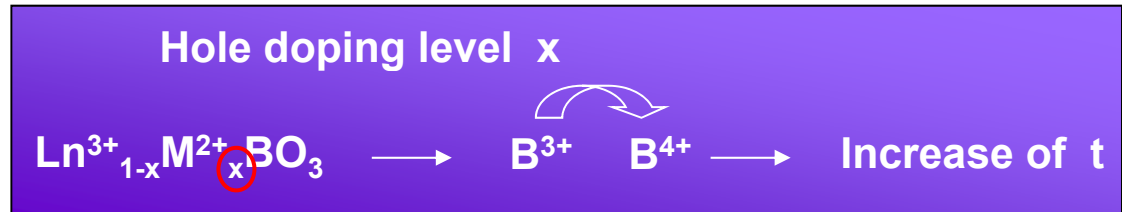
A (Ln^{3+}, M^{2+})

O

B (Fe, Mn, Co)

Parameters that control the A position of the perovskite

Tolerance factor (Goldschmidt)
Define the stability of perovskites

$$t = \frac{(r_A + r_O)}{2^{1/2} \cdot (r_B + r_O)}$$

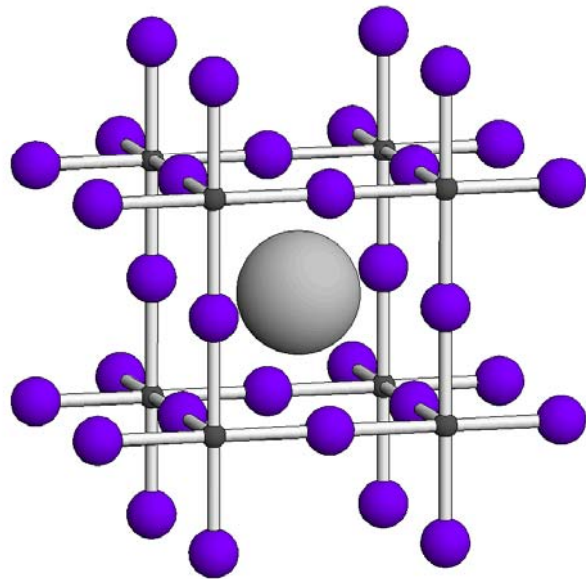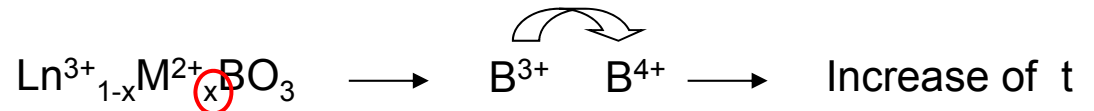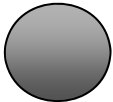$t = 1$ Ideal perovskite

$t \neq 1$ Non-ideal perovskite

Hole doping level x

$Ln^{3+}_{1-x} M^{2+}_x BO_3 \longrightarrow B^{3+} \quad B^{4+} \longrightarrow$ Increase of t

Mean ionic radious $<r_A>$

$<r_A> = \sum_i yi \cdot ri$

$<r_A>$ increases $\longrightarrow$ increase of t

Parameters that control the A position of the perovskite

Tolerance factor (Goldschmidt)
Define the stability of perovskites

ABO_3

A (Ln^{3+}, M^{2+})

O

B (Fe, Mn, Co)

$$t = \frac{(r_A + r_O)}{2^{1/2} \cdot (r_B + r_O)}$$

$t = 1$ Ideal perovskite

$t \neq 1$ Non-ideal perovskite

Hole doping level x

$$Ln^{3+}_{1-x}M^{2+}_{x}BO_3 \longrightarrow B^{3+} \quad B^{4+} \longrightarrow \text{Increase of } t$$

Mean ionic radious $\langle r_A \rangle$

$$\langle r_A \rangle = \sum_i y_i \cdot r_i$$

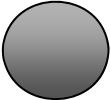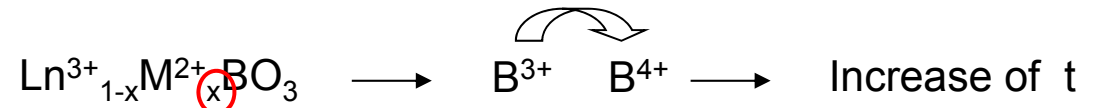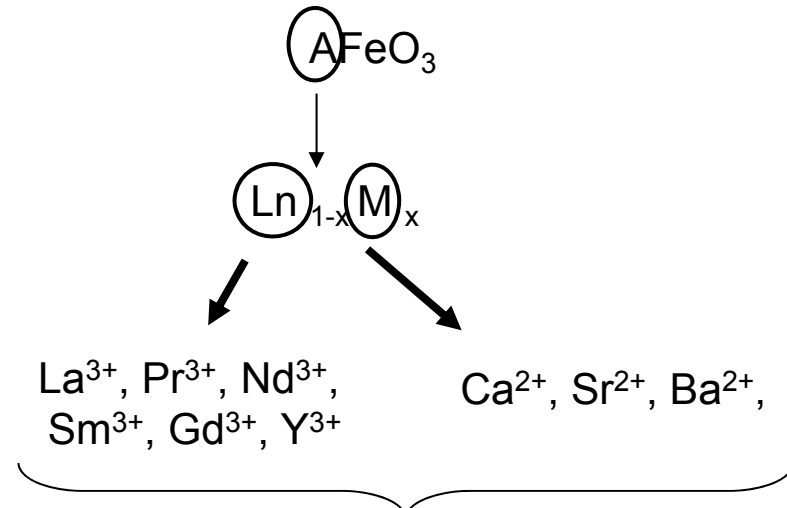$\langle r_A \rangle$ increases $\longrightarrow$ increase of t

A cation size disorder A $\sigma^2(r_A)$

$$\sigma^2 \langle r_A \rangle = \langle r^2_A \rangle - \langle r_A \rangle^2$$

Perovskites

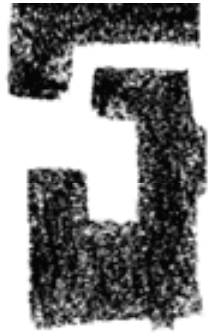$AFeO_3$

$(Ln)_{1-x}(M)_x$

La^{3+}, Pr^{3+}, Nd^{3+},
Sm^{3+}, Gd^{3+}, Y^{3+}

Ca^{2+}, Sr^{2+}, Ba^{2+},
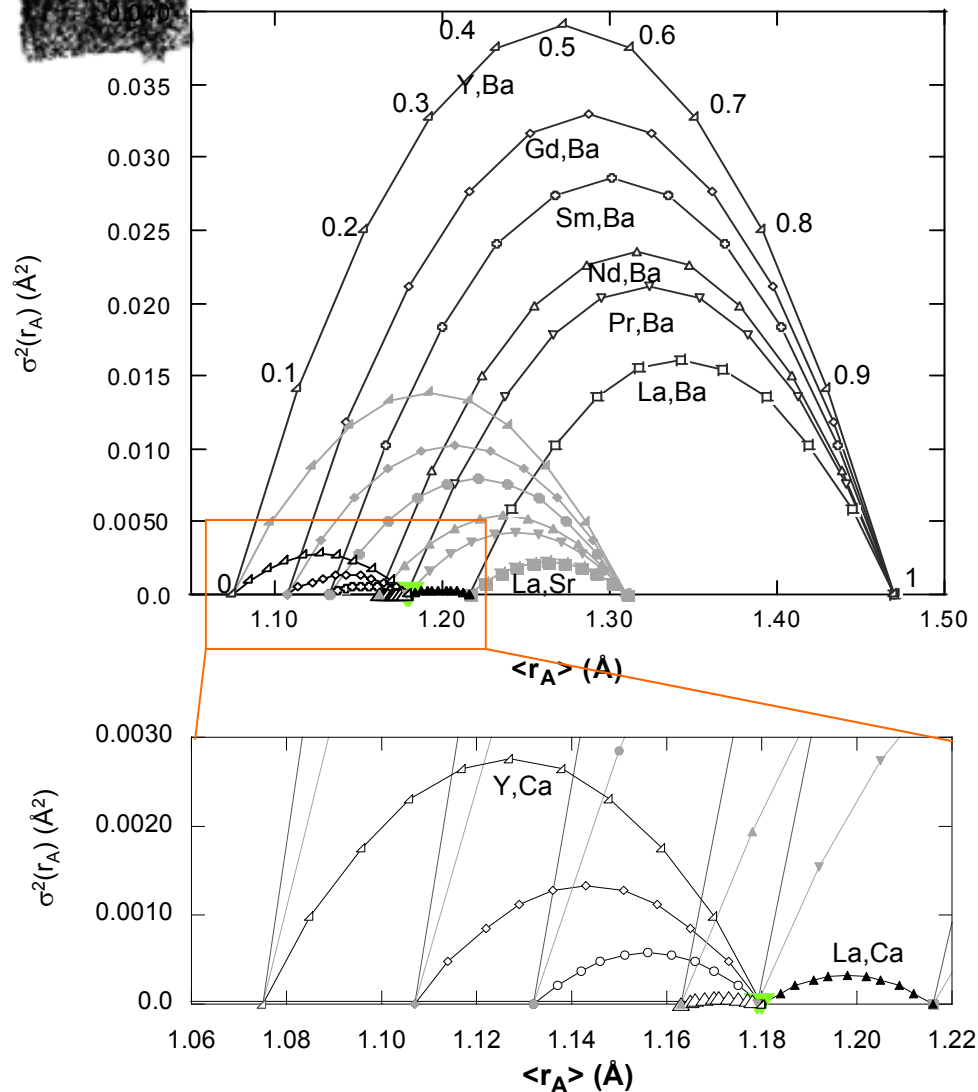
An extremely wide variety

of combinations of chemical elements

Stable phases

Interesting properties

Focus of research

In this research, a $La_{0.5}Ba_{0.5}FeO_3$ perovskite has been synthesized by these two different methods (<u>ceramic and glycine-nitrate routes</u>) in order to study the synthetic method influence on the properties of this compound as IT-SOFC cathode material.

This composition has been chosen due to its **intermediate hole doping level** (0.5) and **high average size of the A-site cations** ($<r_A>$ = 1.48 Å, where r_A are standard 12-coordinate ionic radii) that according with previous studies should show interesting properties for its use as **SOFC cathode**.

R.D. Shannon, Acta Cryst, 1976, *A32*, 751-767.

G. Ch. Kostogloudis, Ch. Ftikos, J. European Ceram. Soc., 19 (1999) 497-505.

K. Vidal, L.M. Rodríguez-Martínez, L. Ortega San-Martín, A. Martínez-Amesti, M.L. Nó, T. Rojo, A. Laresgoiti, M.I. Arriortua, J. Power Sources, 92 (2009) 175-179.

A. Ecija, K. Vidal, A. Larrañaga, A. Martínez-Amesti, L. Ortega-San-Martín, M. I. Arriortua, Solid State Ionics, 201(1) (2011) 35-41.

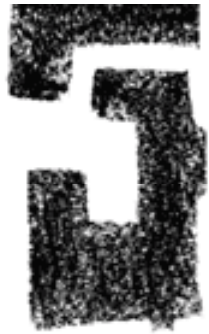L. Jia, X. Wang, W. Li, K. Li, B. Chi, J. Pu, L. Jian, S. Yuan, J. Power Sources, 253 (2014) 138-142.
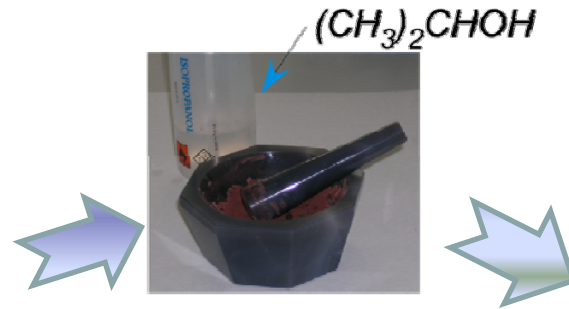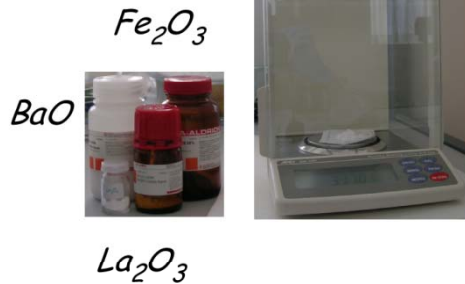
Contents:

Solid state reaction

Experimental preparation

Stoichiometric amounts of oxides of the corresponding elements were mixed in an agate mortar

Fe_2O_3

BaO

La_2O_3

$(CH_3)_2CHOH$

The powder was weighed and then manually grinded in an agate mortar with isopropanol for homogenization
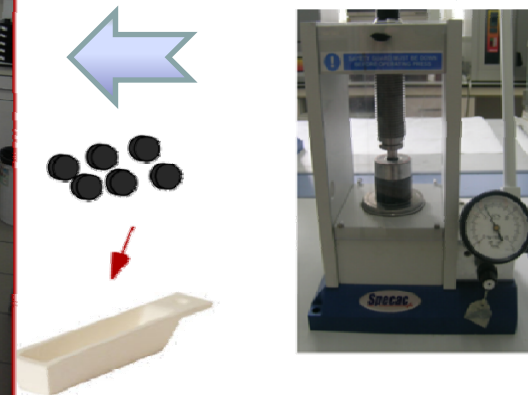
The mixture was calcined in air at 950ºC (2h)

CO_2

950 ºC
3 ºC/ min   2h   5 ºC/ min
25 ºC   25 ºC

The product obtained was ground, pelletized again, fired at 1350ºC for 60h and rapidly cooled to room temperature ("quenching")

"Quenching"

1350 ºC → 25 ºC
5 ºC/ min 60h
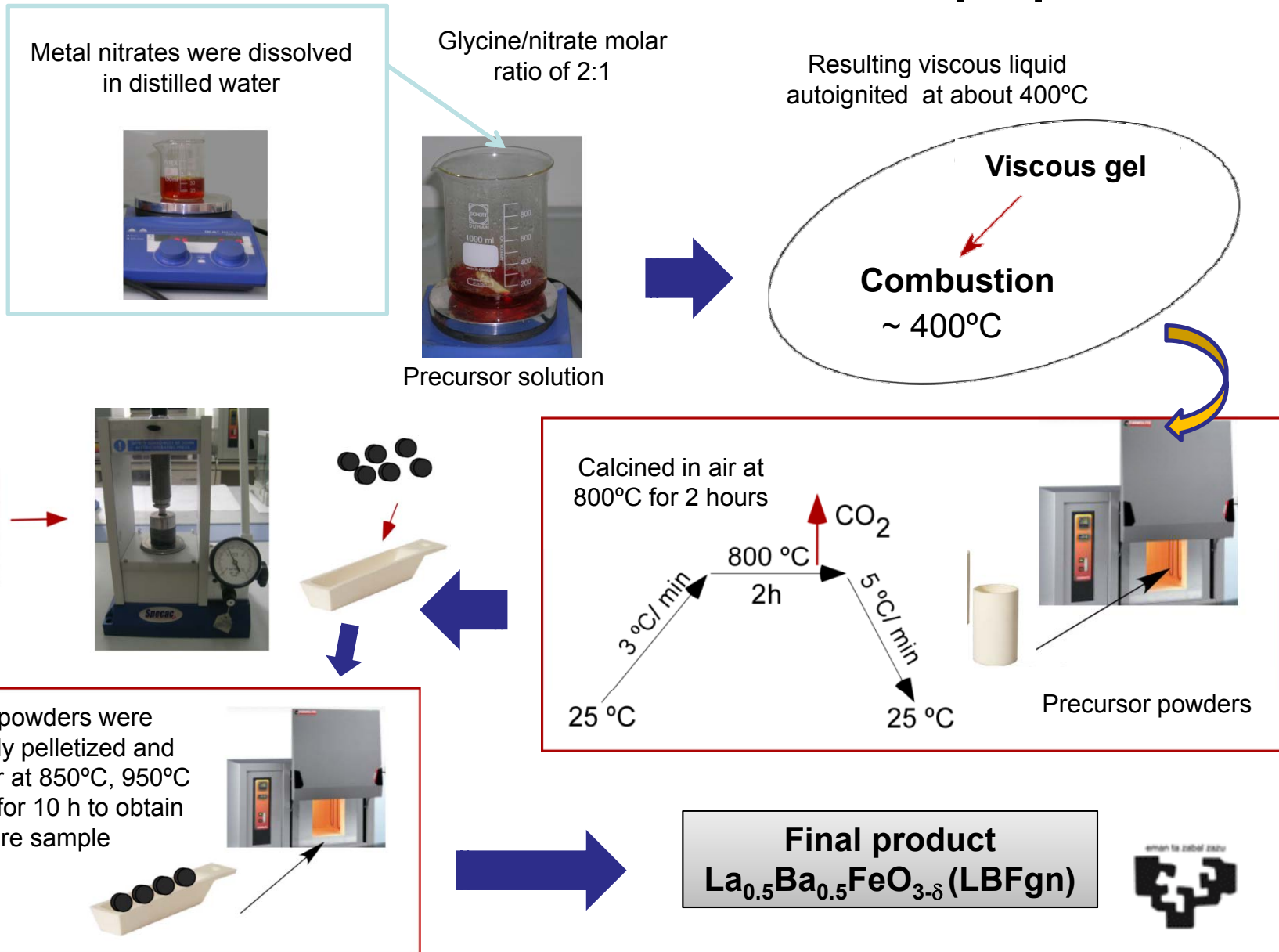25 ºC

Final product
$La_{0.5}Ba_{0.5}FeO_{3-\delta}$ (LBFss)

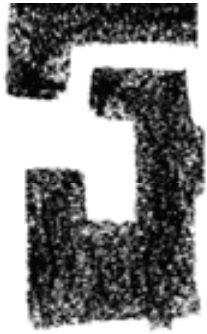# Glycine nitrate combustion process | Experimental preparation
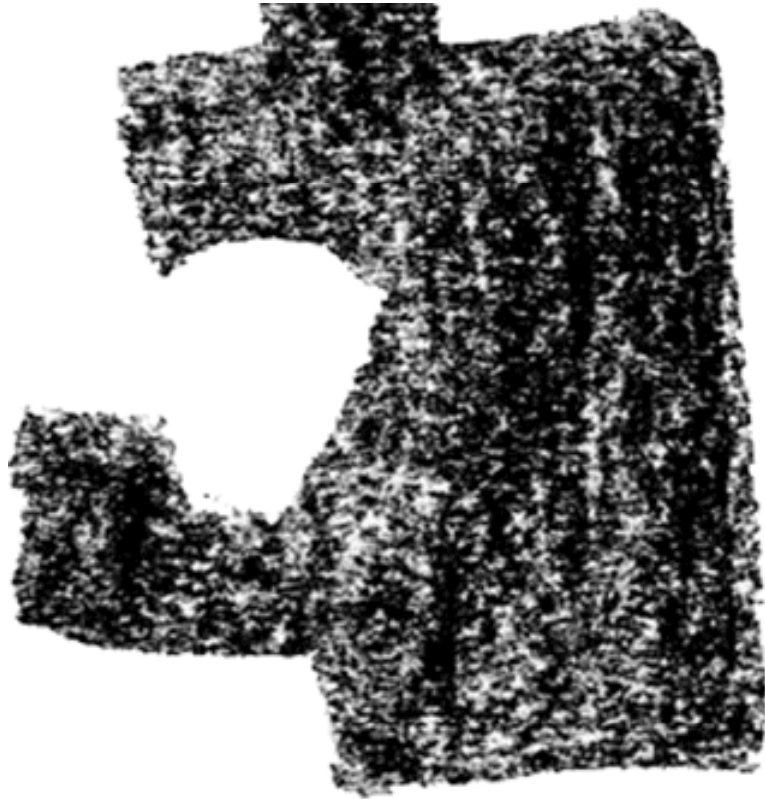
Metal nitrates were dissolved in distilled water

Glycine/nitrate molar ratio of 2:1

Resulting viscous liquid autoignited at about 400ºC

Viscous gel

Combustion
~ 400ºC

Precursor solution

Calcined in air at 800ºC for 2 hours

CO_2

800 ºC
2h

3 ºC/ min

5 ºC/ min

25 ºC

25 ºC

Precursor powders

Obtained powders were subsequently pelletized and calcined in air at 850ºC, 950ºC and 1050ºC for 10 h to obtain the pure sample

Final product
$La_{0.5}Ba_{0.5}FeO_{3-\delta}$ (LBFgn)

Contents:

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Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

Compound	Nominal composition	Experimental composition		
		La	Ba	Fe
LBFss	$La_{0.5}Ba_{0.5}FeO_3$	0.48(3)	0.52(2)	1.00(1)
LBFgn	$La_{0.5}Ba_{0.5}FeO_3$	0.49(2)	0.51(2)	1.00(1)

Results from chemical analyses show a good agreement between the analyzed chemical compositions of the prepared powders and the nominal compositions.
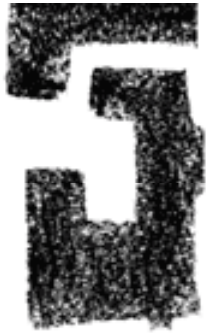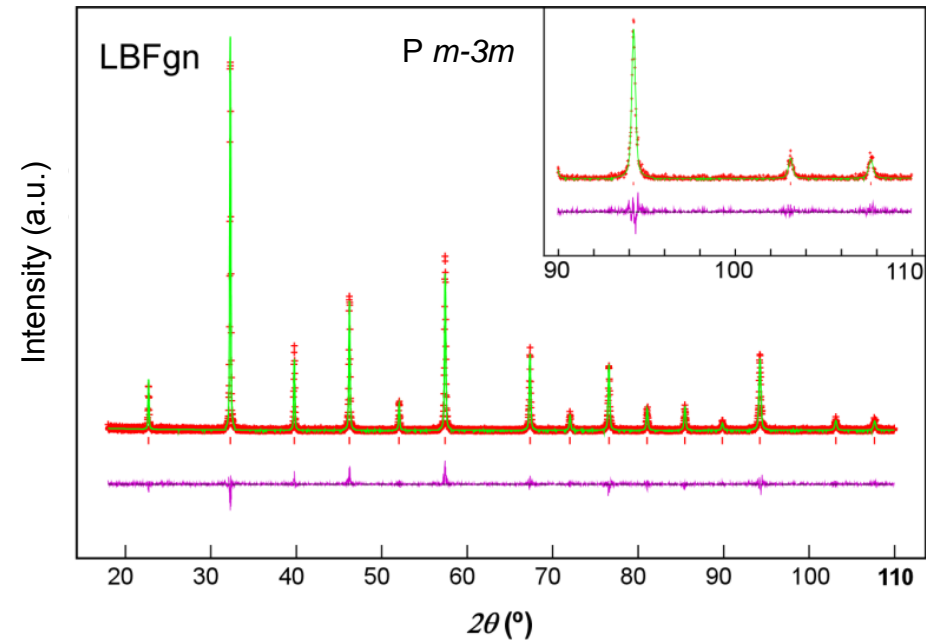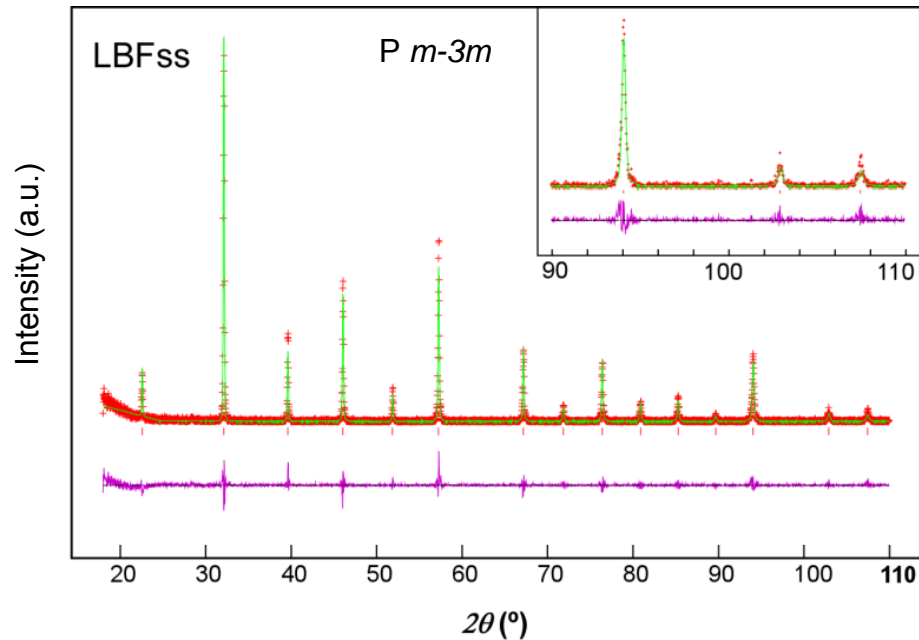
# Difracción de Rayos X (DRX) | Characterization

Rietveld method, program GSAS.

Results on the Rietveld analysis of these powder diffraction patterns show cubic symmetry (P *m-3m*) for the samples.

H. M. Rietveld, J. Appl. Crystallogr., 2 (1969) 65-71.

Larson A.C., Von Dreele R.B., "GSAS: General Structure Analysis System", LAUR, 86, 1994.
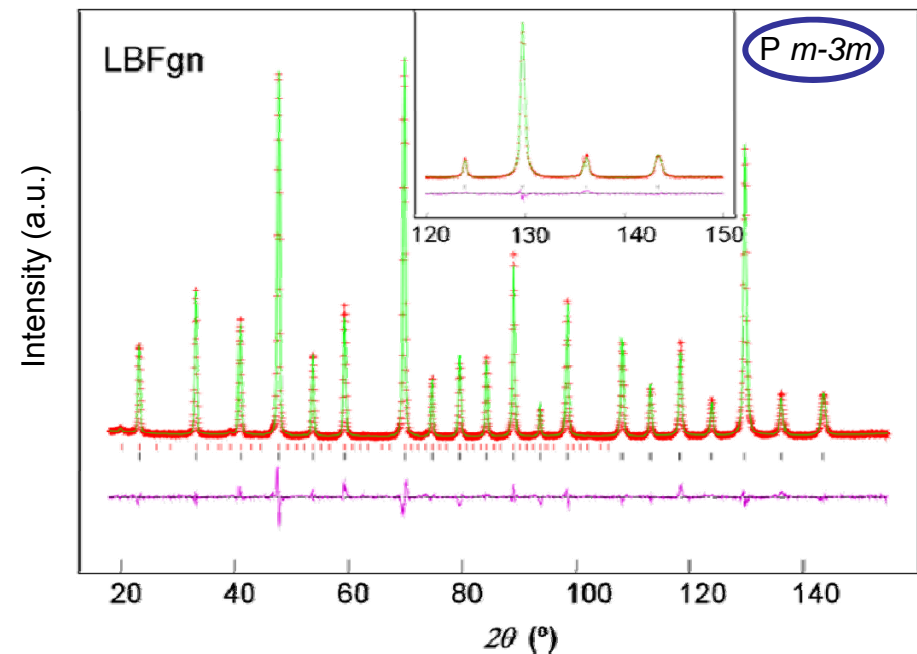
Rietveld method, program GSAS (considering a G-type magnetic structure).
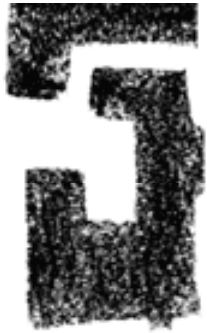
Neutron powder diffraction data collected with D2B diffractometer of the Institute Laue-Langevin.

Neutron diffraction measurements were performed in order to obtain information about the oxygen stoichiometry and to clarify the crystal structure of both phases. Structure refinements were carried out by fitting simultaneously the X-ray and neutron diffraction data.

H. M. Rietveld, J. Appl. Crystallogr., 2 (1969) 65-71.

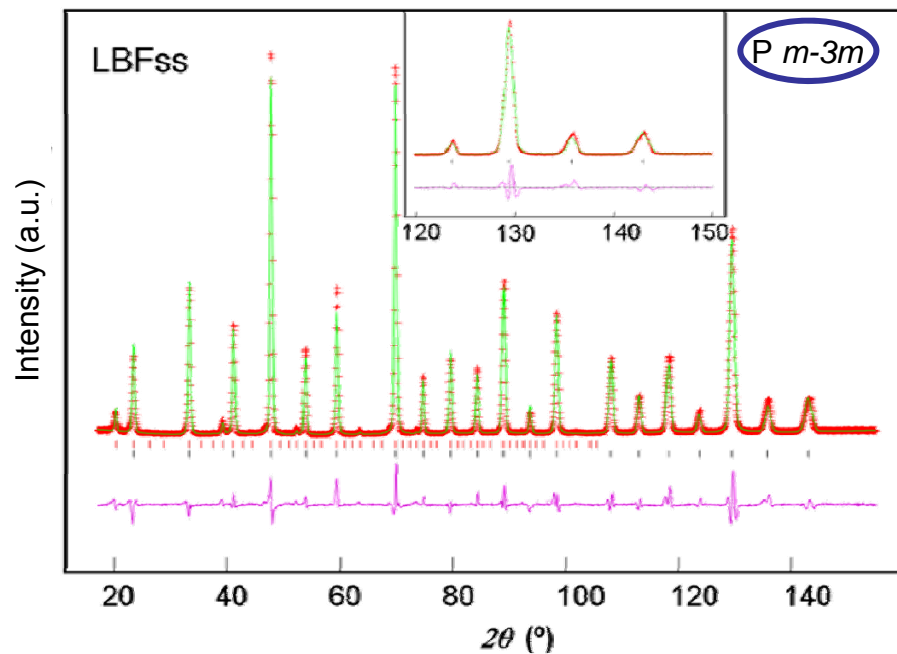Larson A.C., Von Dreele R.B., "GSAS: General Structure Analysis System", LAUR, 86, 1994.

Compound	a(Å)	V(Å^3)	$\rho_{teórica}$ (g/cm^3)	d<A-Fe> (Å)	d<A-O> (Å)	d(Fe-O) (x6) (Å)
LBFss	3.9392(3)	61.12(1)	6.536	3.4114(2)	2.7854(4)	1.9696(1)
LBFgn	3.9381(1)	61.07(1)	6.568	3.4105(1)	2.7847(1)	1.9690(1)

Compound	O occupancy	3-δ
LBFss	0.971(3)	2.91(1)
LBFgn	0.992(4)	2.98(1)

The main difference is observed in the oxygen stoichiometry. $\Rightarrow$ Differences in cooling rates.

Fast cooling of the powder sample leads to an increase of the mole ratio of Fe^{3+} and oxygen vacancies.

This is due to the time is not enough for all oxygen vacancies were filled and therefore, the iron cation was mostly kept in a lower valance state (Fe^{3+}).
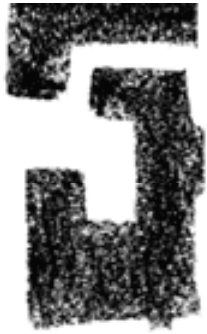
X.D. Zhou, Q. Cai, J. Yang, W.J. Yelon , W.J. James, H.U. Anderson, Solid State Ionics, 175 (2004) 83-86.

J.B. Yang, W.B. Yelan, W.J. James, Phys. rev. B, 66 (2002) 184415-1-184415-9.

K.S. Roh, K.H. Ryu, C.H. Yo, J. Mater. Sci., 30 (1995) 1245-1250.

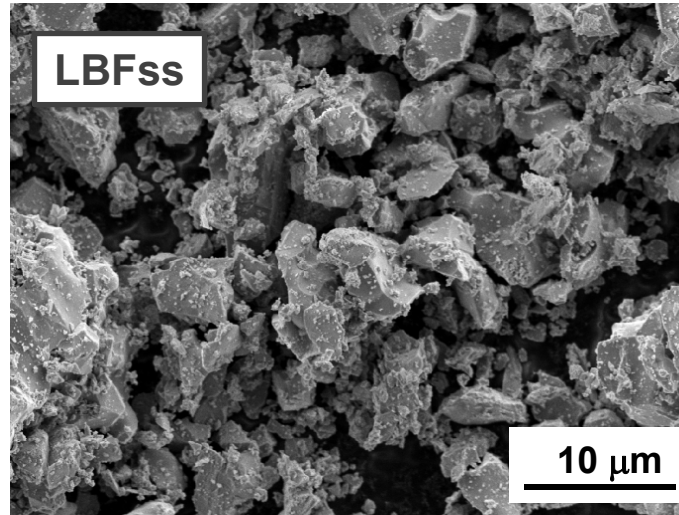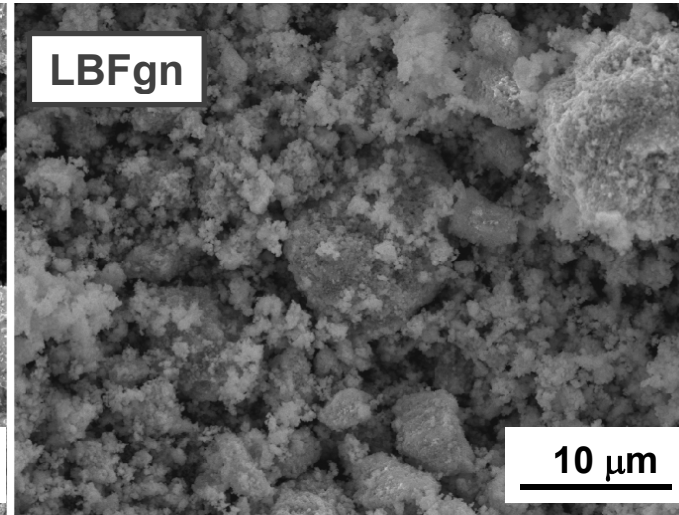L.Ge, Z. Zhu, Z. Shao, S. Wang, S. Liu, Ceram. Inter., 35 (2009) 3201-3206.

Scanning Electron Microscope (SEM).

• Microstructure with heterogeneous grain sizes (from ~ 0.5 to 4 μm) and shapes.

• Particles of grain sizes about 150 nm forming agglomerates.

The higher calcination temperature at which is formed and longer reaction time of the ceramic process can explain the bigger grain size .

M.E. Melo Jorge, A. Correia dos Santos, M.R. Nunes, Inter. J. Inorg. Mater., 3 (2001) 915-921.

S. Li , Z. Lu, X. Huang, B. Wei, W. Su, J. Physics. Chem. Solids, 68 (2007) 1707-1712.

A. Ecija, K. Vidal, A. Larrañaga, L. Ortega-San-Martín, M.I. Arriortua: "Synthetic Methods for Perovskite Materials. Structure and Morphology", Advances in Crystallization Processes, Dr. Yitzhak Mastai (Ed.), ISBN: 978-953-51-0581-7, 2012.
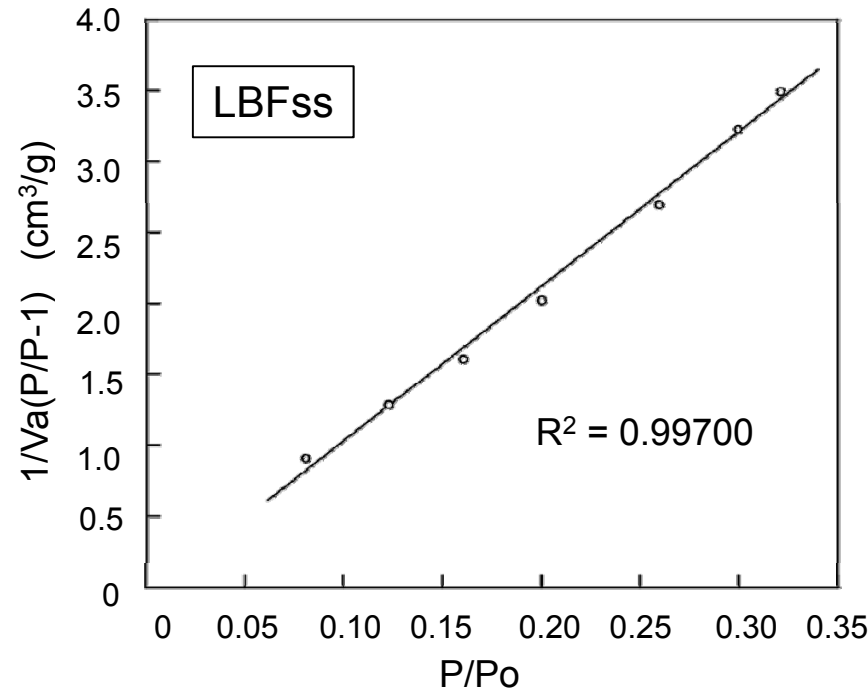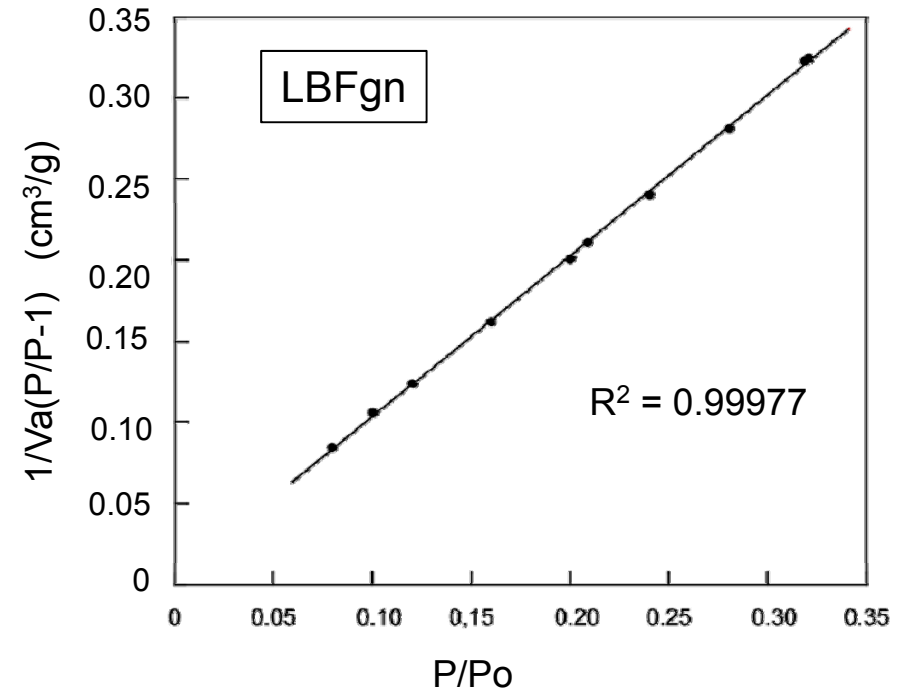
Brunauer-Emmett-Teller nitrogen adsorption (BET) method.

LBFss

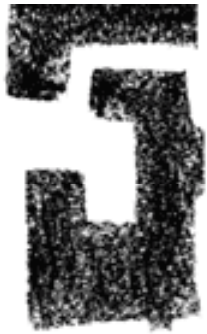$R^2 = 0.99700$

LBFgn

$R^2 = 0.99977$

S_{BET} LBFss : 0.44 $m^2 \cdot g^{-1}$

S_{BET} LBFgn: 4.26 $m^2 \cdot g^{-1}$

The glycine-nitrate method leads to powders with significant larger surface areas than the solid state reaction.

S. Brunauer, P.H. Emmet, E. Teller, J. Am. Chem. Soc., 60 (1938) 309-319.
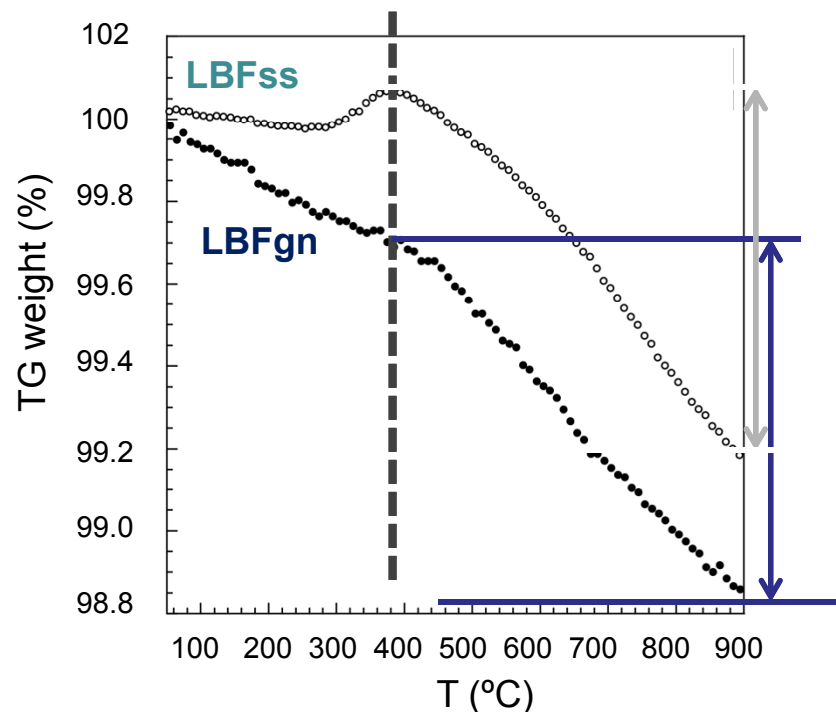
S. Nakayama , J. Mater. Sci., 36 (2001) 5643-5648.

The samples were heated up to 900ºC at 5ºC/min, under continuous flow of air.

Partial re-oxidation of Fe^{3+} to Fe^{4+} and the recovery of some of the oxygen content (~0.3%) that was lost during the quenching of the sample (265-400ºC).

Sample continues losing oxygen (~0.75 %) from ~ 600ºC.

Slight weight loss in air (~0.4%) from 25ºC to about 470ºC which is attributed to desorption of physically absorbed water and carbon dioxide.

The weight of the sample starts to decrease from 470ºC and continuously decreases (0.82%) up to 900ºC .

Therefore, despite the higher non-stoichimetry of LBFss at room temperature, both samples have similar oxygen content at high temperatures.
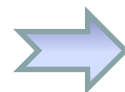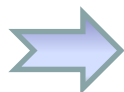
W. Zhu, Z. Lü, S. Li; B. Wei, J. Miao, X. Huang, K. Chen, N. Ai, W. Su, J. Alloys Compd., 465 (2008) 274-279.

X.D. Zhou, Q. Cai, J. Yang, W.B. Yelon, W.J. James, H.U. Anderson, Solid State Ionics, 175 (2004) 83-86.

Powders of the samples

Pressed into pellets

Sintered at 1350ºC

Diamond saw

2 cm

2 cm

6 cm

Rectangular bars

Electrical conductivity | Characterization

Four-point method   30-900ºC in air

SEM micrographs

The electrical conductivity measured by the four–point method increases with increasing temperature, goes through a broad maximum and then decreases ⟹ *hopping of p-type small polarons*.
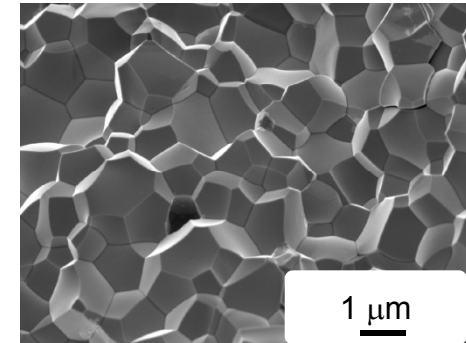
LBFgn sample presents higher values of electrical conductivity.

87%   LBFgn

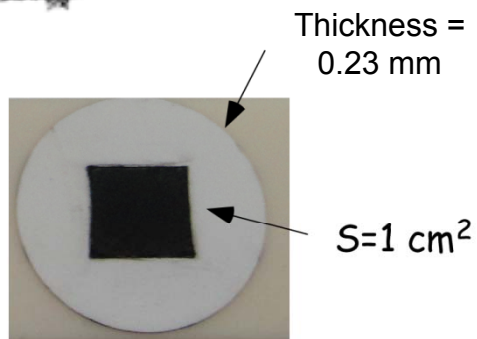83%   LBFss
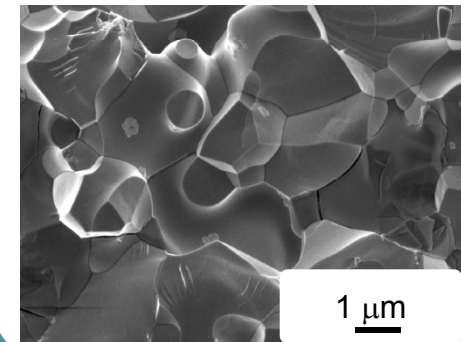
Electrochemical impedance spectroscopy (EIS) | Characterization
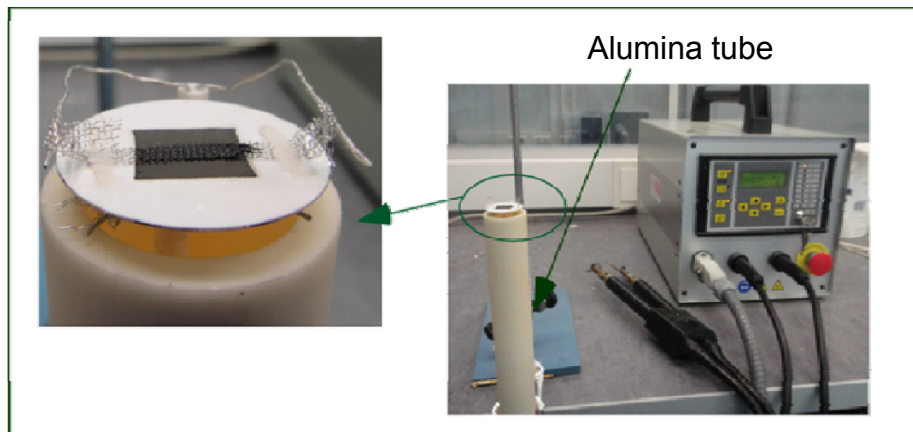

Thickness = 0.23 mm

S=1 cm²

The cathode layers were deposited onto both sides of the electrolyte, 8YSZ, by wet colloidal spraying.

1050 °C
2h
2 °C/ min
2 °C/ min
25 °C
25 °C

Cathode layers were sintered.

Alumina tube
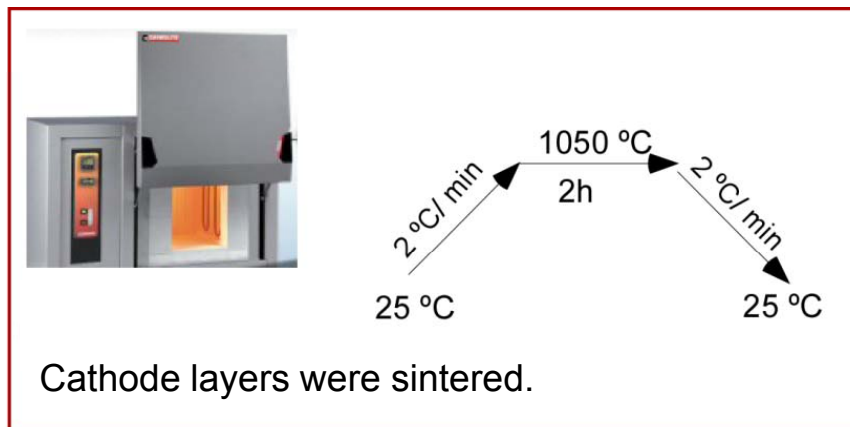
Impedance measurements of the symmetric cells were performed in air at 700 and 800°C.
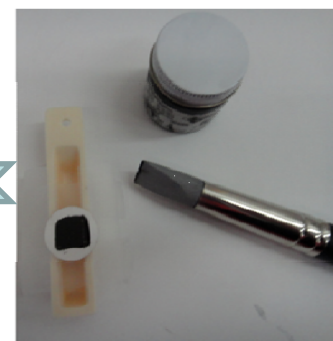
Impedance measurements of the cathode suspensions were performed on symmetrical cells, with AC signal amplitude of 10 mV over the frequency range of 10^6-0.01 Hz at 700 and 800ºC.
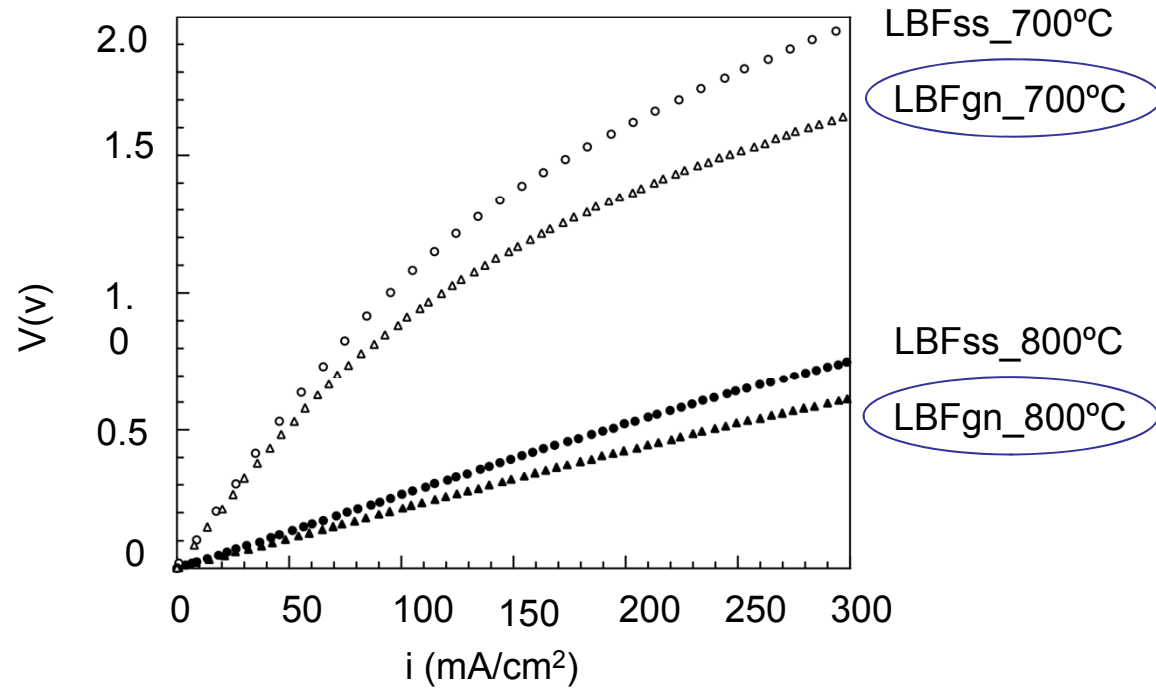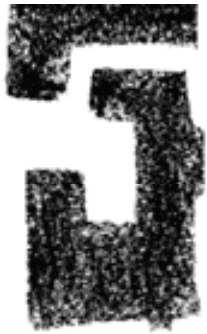
Electrochemical impedance spectroscopy (EIS) | Characterization

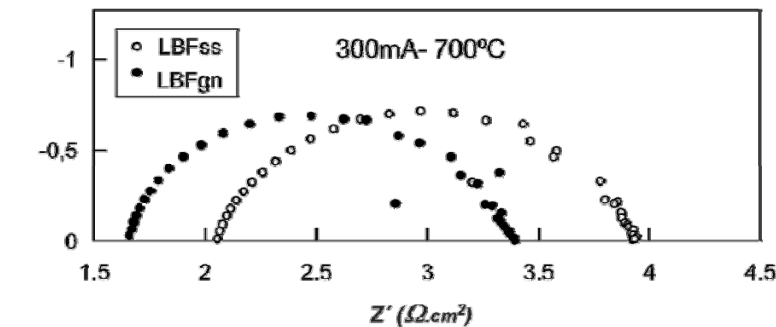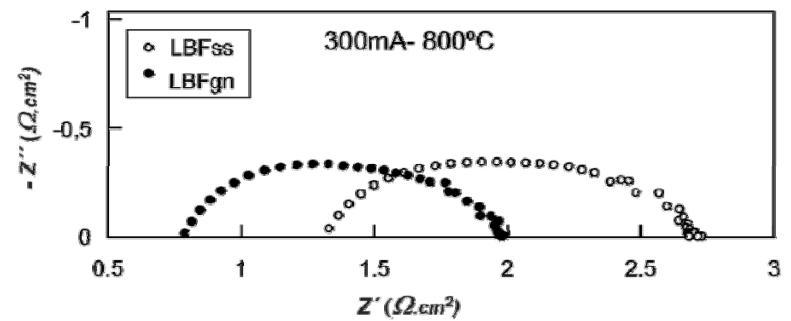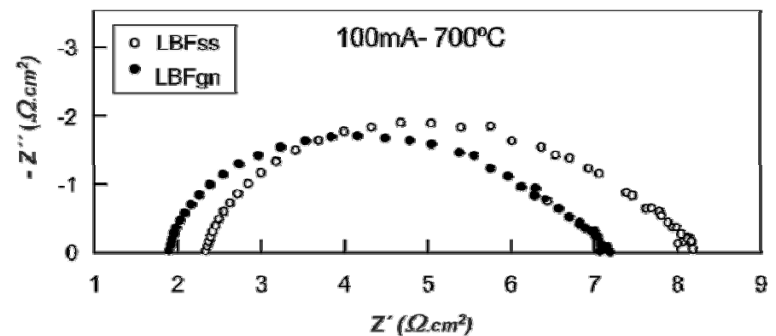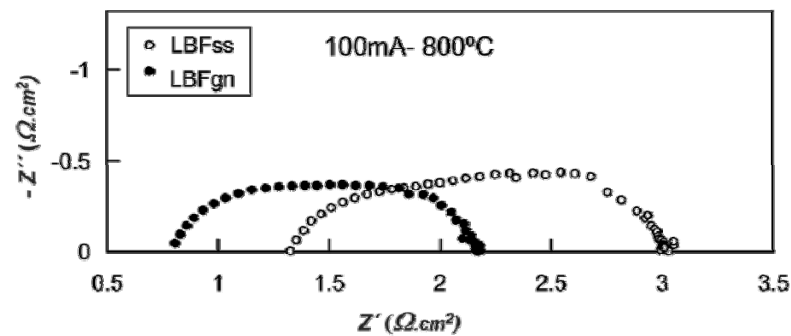Current–voltage (*IV*) curves at 700 and 800ºC.

Better performance for LBFgn

LBFss_700ºC
LBFgn_700ºC
LBFss_800ºC
LBFgn_800ºC

The impedance spectra of the two compounds obtained at OCP, 100 and 300 mA at 800 and 700ºC.
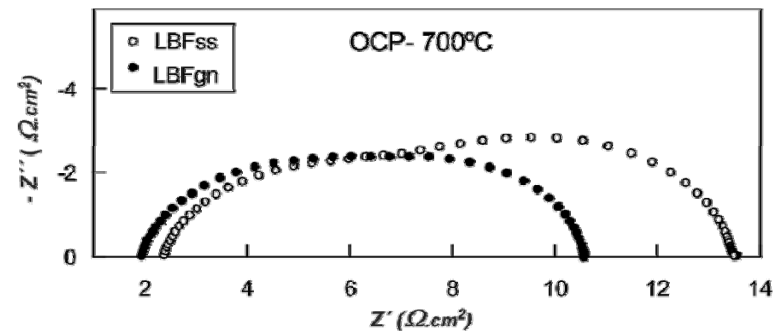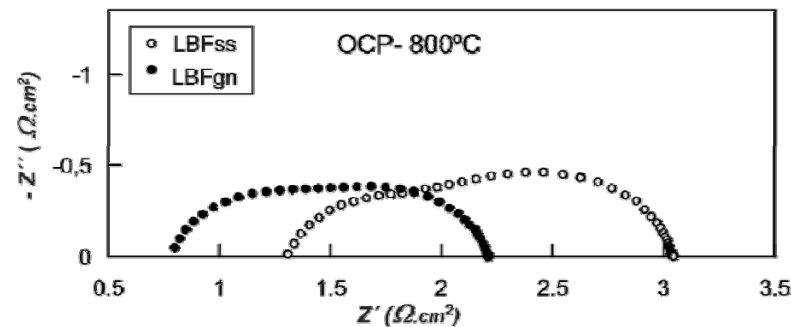
Sample	T(ºC)	$R_\Omega(\Omega.cm^2)$			$ASR(\Omega.cm^2)$			$R_p(\Omega.cm^2)$		
		OCP	100mA	300mA	OCP	100mA	300mA	OCP	100mA	300mA
LBFss	800	1.31	1.32	1.30	3.04	3.00	2.71	1.74	1.68	1.41
LBFgn	800	0.78	0.78	0.79	2.21	2.16	2.00	1.43	1.38	1.21
LBFss	700	2.35	2.33	2.04	13.58	8.09	3.93	11.16	5.75	1.89
LBFgn	700	1.93	1.88	1.65	10.52	7.16	3.37	8.59	5.28	1.72

The polarization resistance increases with decreasing the temperature due to lower mobility of the ions. Polarization resistance values are similar being slightly lower for the LFBgn sample.

Ohmic resistance values are lower in the case of the compound prepared by glycine-nitrate route.

F. Qiang, K. Sun, N. Zhang, S. Le, X. Zhu, J. Piao, J. Solid State Electrochem., 13 (2009) 455-467.
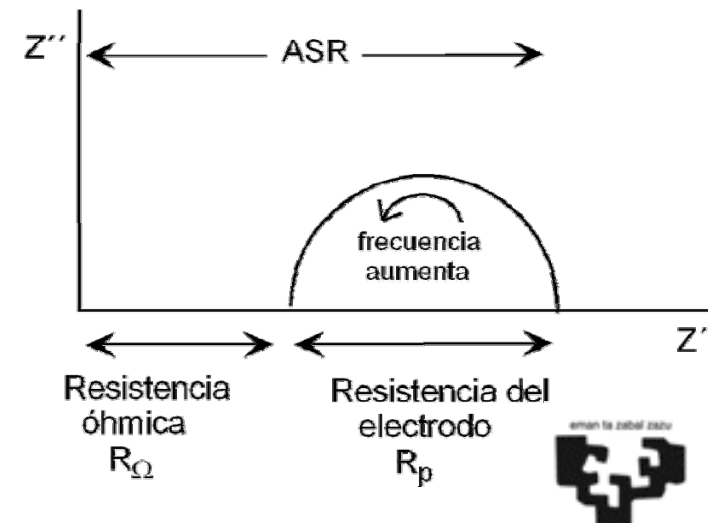
Scanning electron microscopy (SEM)

The higher value of ohmic resistance of the LBFss sample is attributed to a possible worse contact between the cathode and the electrolyte. This is maybe due to the bigger particle size of the LBFss powder.
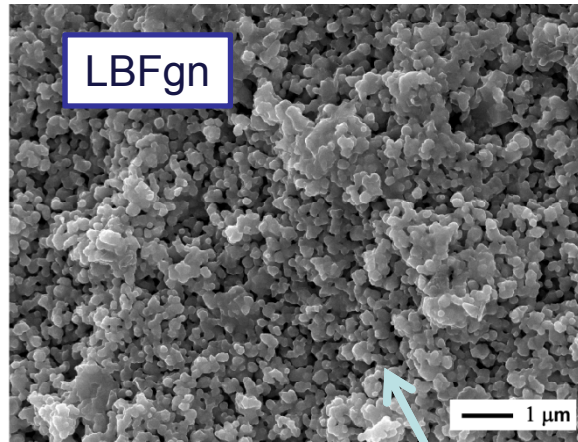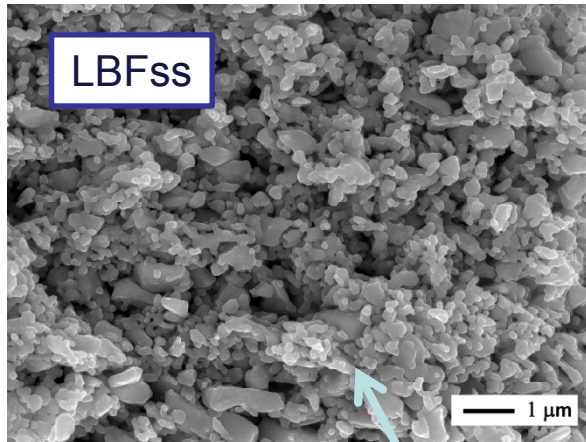
Cross-sectional microstructures

LBFss

LBFgn
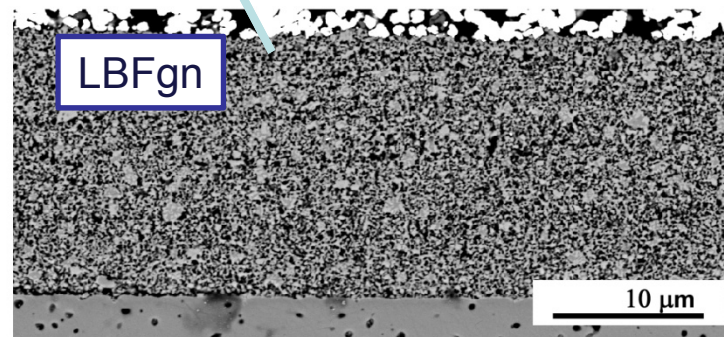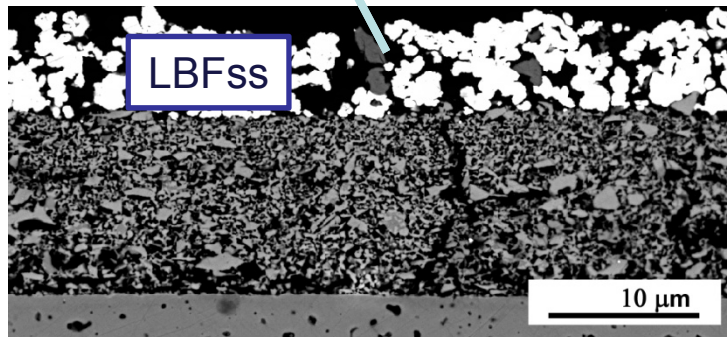
Pt

Cathode

Electrolyte

Contents:

- # Introduction

  Solid oxide fuel cells

  Perovskites

- # Experimental preparation

  Solid state reaction

  Glycine nitrate combustion process

- # Characterization

  Structure (X-ray and neutron diffraction)

  Microstructure

  Bulk conductivity

  Thermal expansion coefficient

  Polarization resistance

- # Conclusions

- # Acknowledgments

5
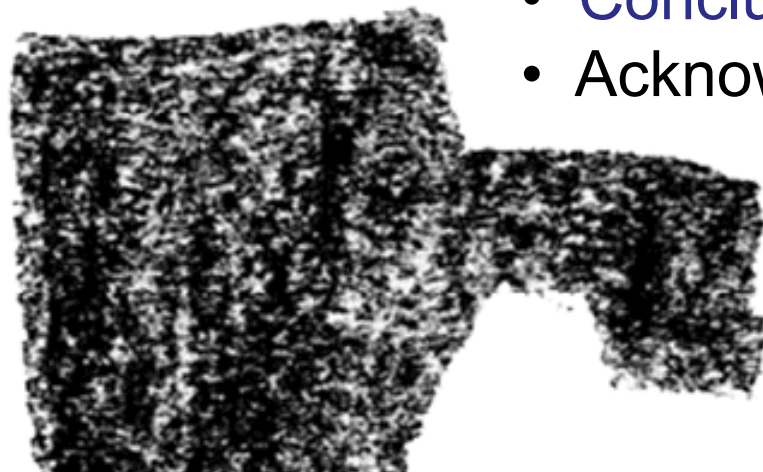
$La_{0.5}Ba_{0.5}FeO_3$ compound has been obtained by ceramic and glycine nitrate methods .

At room temperature, both compounds show cubic symmetry (S.G: *P m-3m*), being the oxygen vacancy content the main structural difference observed. However, at high temperature the oxygen content of the samples become similar.

The compound obtained by glycine-nitrate method presents the most suitable characteristics as cathode material: fine particle sizes, higher surface areas and the lower area specific resistance values at 700 and 800ºC.

Therefore, it can be concluded that the glycine-nitrate process is a more appropriate technique for preparing perovskite cathodes.
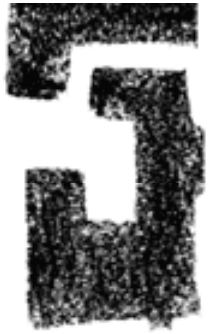
Acknowledgements

Thank you very much for your attention

eman ta zabal zazu

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