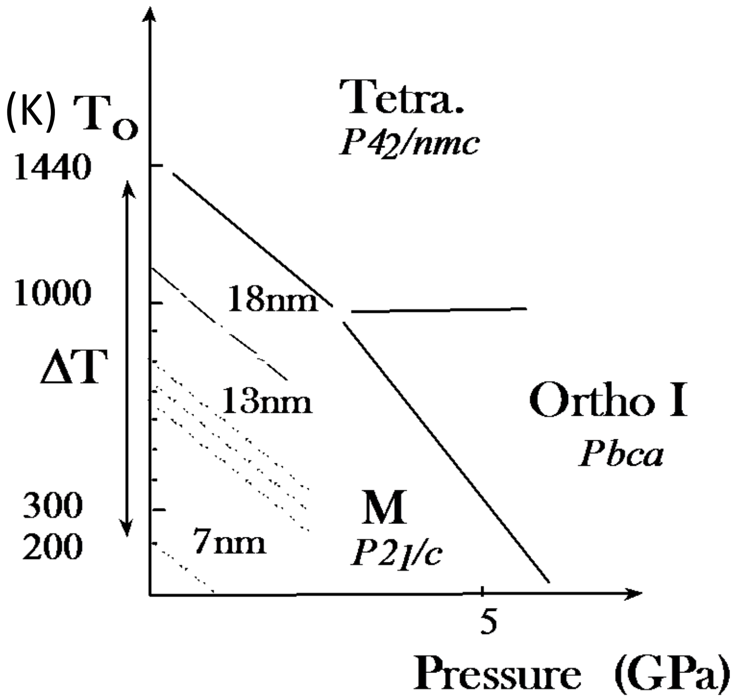
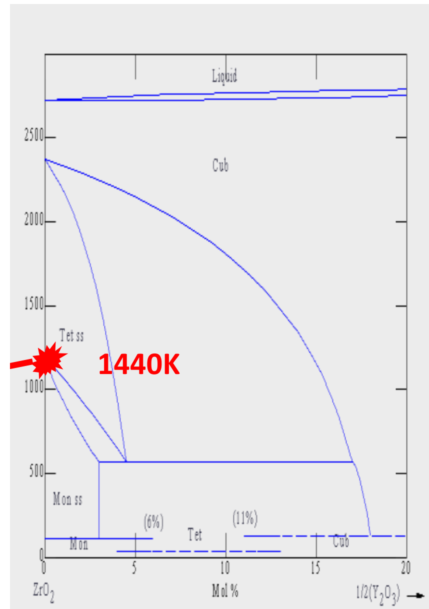
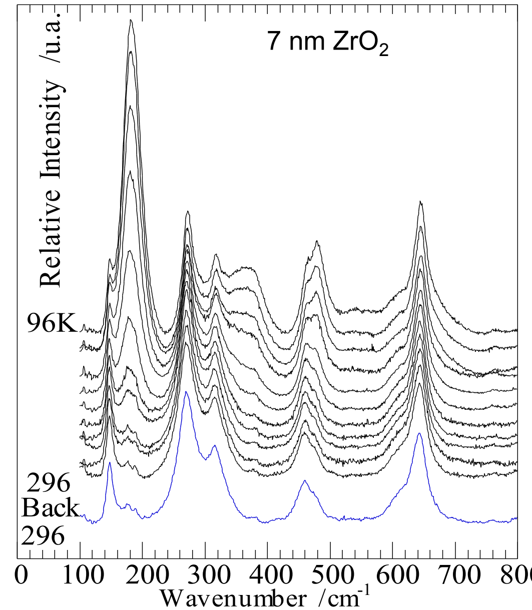
- **ZrO_2 - based powders**
  Phase transitions

T_{MT} bulk ≈ 1440K (µm)







Raman spectra of ZrO_2 from 96K to 300K

Phases diagram P-T of ZrO_2 versus crystallite size deduced from Raman P-T and XRD measurements

Effect of crystallite size = Effect of internal pressure + entropic contribution

STABLE TZP

E. Djurado, P. Bouvier, G. Lucazeau, *Journal of Solid State Chem.* 149 (2000) 399
P. Bouvier, E. Djurado, G. Lucazeau, T. le Bihan, *Phys. Rev. B* 62 (13) (2000) 8731
P. Bouvier, E. Djurado, C. Ritter, A. J. Dianoux and G. Lucazeau, *Int. J. of Inorg. Mat*. 3 [7] (2001) 647

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CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$)

SINTERING DIFFICULTIES

⬇

LOW FINAL DENSITY ~92% TD → T > 1500°C [1]

MICROSTRUCTURAL HETEROGENEITY [2]

Objectives

CONTROL POWDER MICROSTRUCTURE (USP)

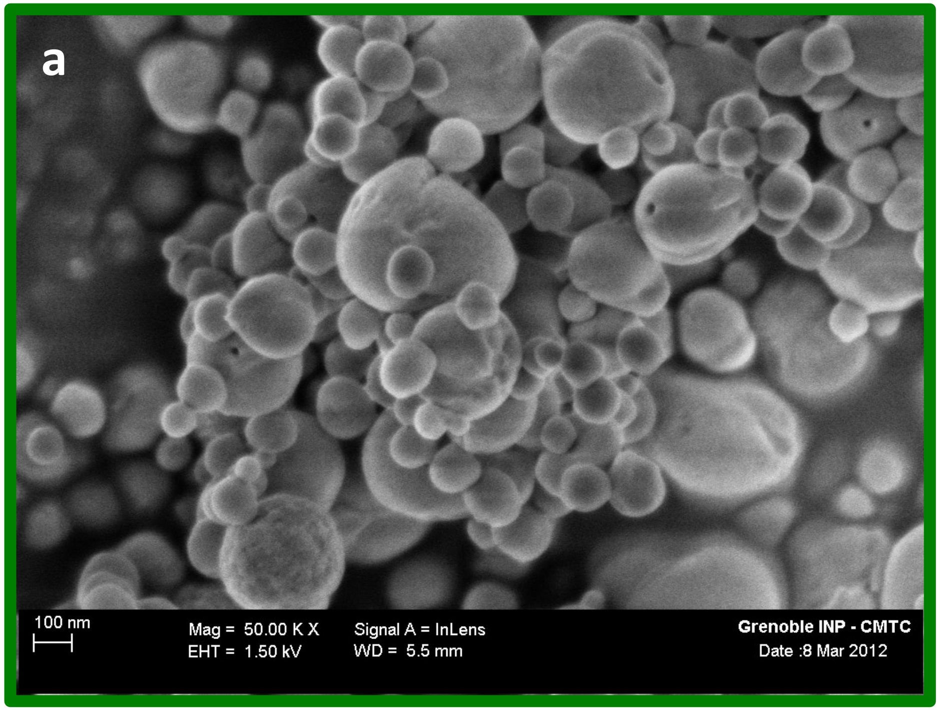
⬇

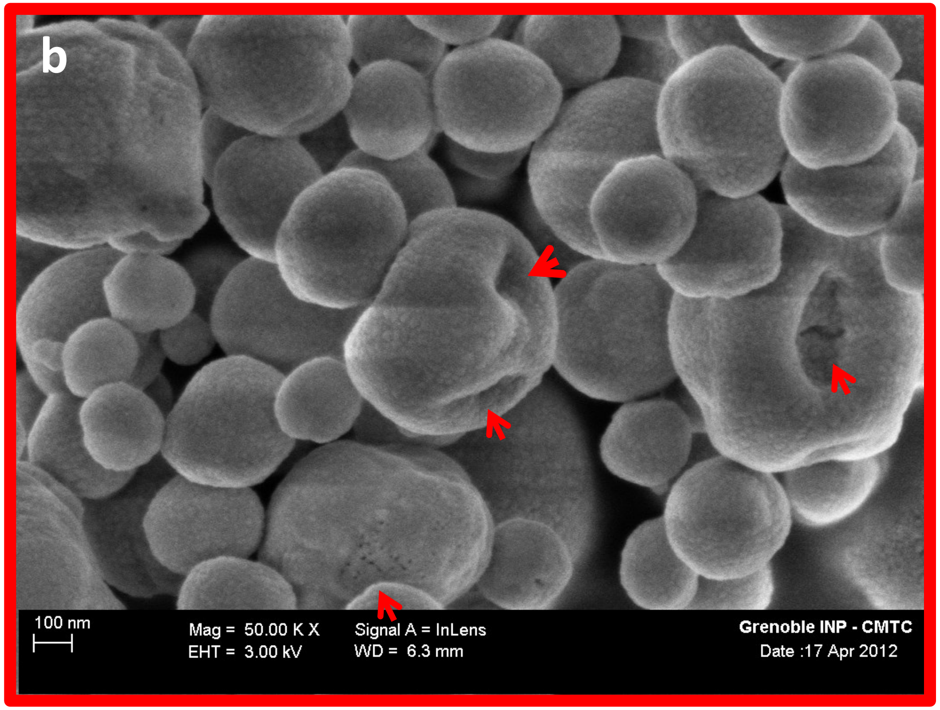
INCREASE DENSIFICATION

1. Ruiz-Trejo, E.; Benítez-Rico, A.; Gómez-Reynoso, S.; Angeles-Rosas, M. *Journal of The Electrochemical Society*, 2007, 154, A258-A262
2. Li, Z.; Mori, T.; Auchterlonie, G.J.; Zou, J.; Drennan, *Journal Materials Research Bulletin* 2012, 47, 763–767

CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$) - **Morphology**

T (°C)	f (kHz)	C ($mol.L^{-1}$)	Q ($L.min^{-1}$)	Morphology
400	2500	2.5×10^{-3}	3 / 6	Small and dense particles with ovoid shape (a)
1000	2500	2.5×10^{-2}	3 / 6	Porous and uneven particles (b)





Increase T (°C) → Grain growth is increased → Larger crystallization

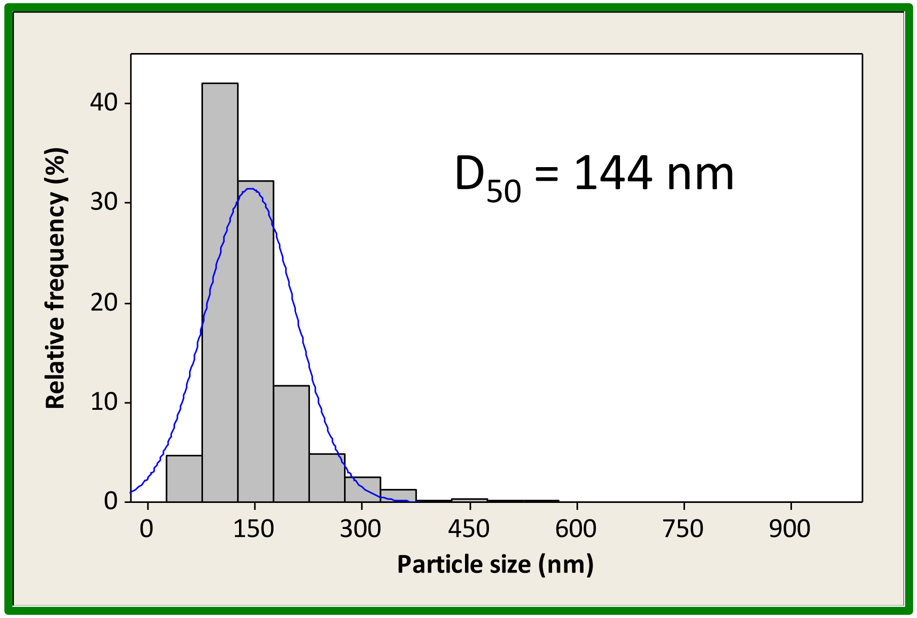
Increase C ($mol.l^{-1}$) → Density of matter is increased → Uneven particles

CGO Particle size and Particle size distribution

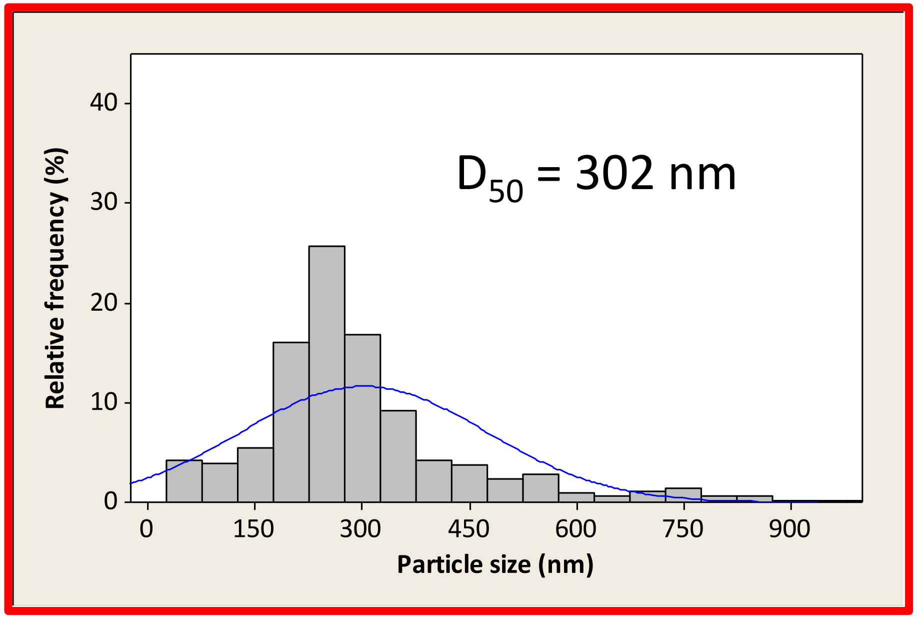
Analysis of SEM images by ImageJ software

C ($mol.L^{-1}$)	T (°C)	f (kHz)	D ($L.min^{-1}$)
2.5×10^{-3}	400	2500	6

C ($mol.L^{-1}$)	T (°C)	f (kHz)	D ($L.min^{-1}$)
2.5×10^{-2}	1000	2500	6



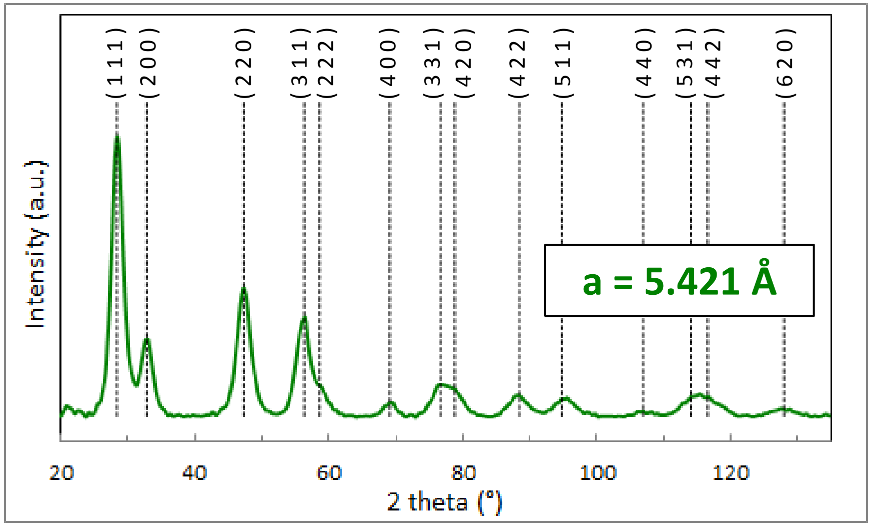
Narrow Distribution (CGO ND)

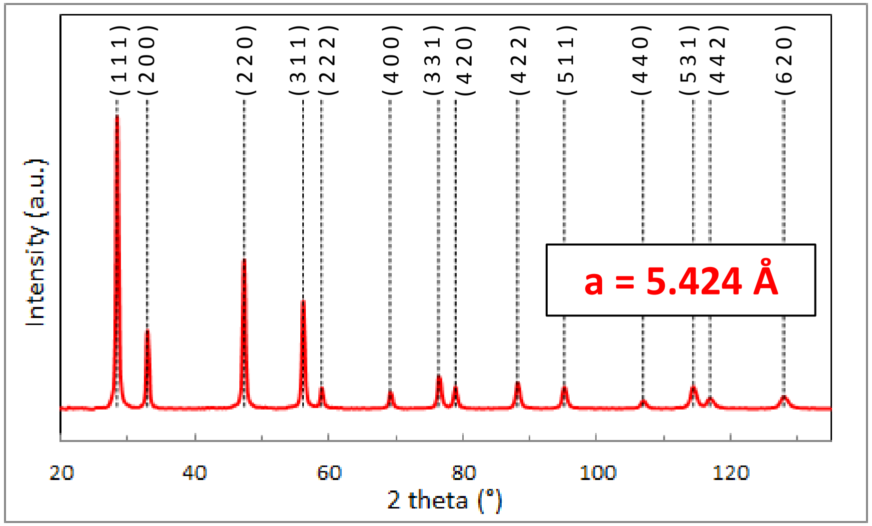


Large Distribution (CGO LD)

CGO Crystallite size

Cubic CGO single phase - fluorite - $Fm\bar{3}m$





PANalytical X'Pert Pro MPD diffractometer in the Bragg–Brentano geometry
20 - 135° in 2θ, step : 0.084°, step time : 360 s, with Cu radiation λ = 0.154056 Å

Structure profile refinement FullProf program

Scherrer equation

$$L = \frac{0.9\lambda}{\Delta\theta * \cos\theta_0} \quad with\ \Delta\theta = \sqrt{FWHM^2_{sample} - FWHM^2_{Si}}$$

CGO Narrow D

L = 3.7 nm ± 0.1 nm

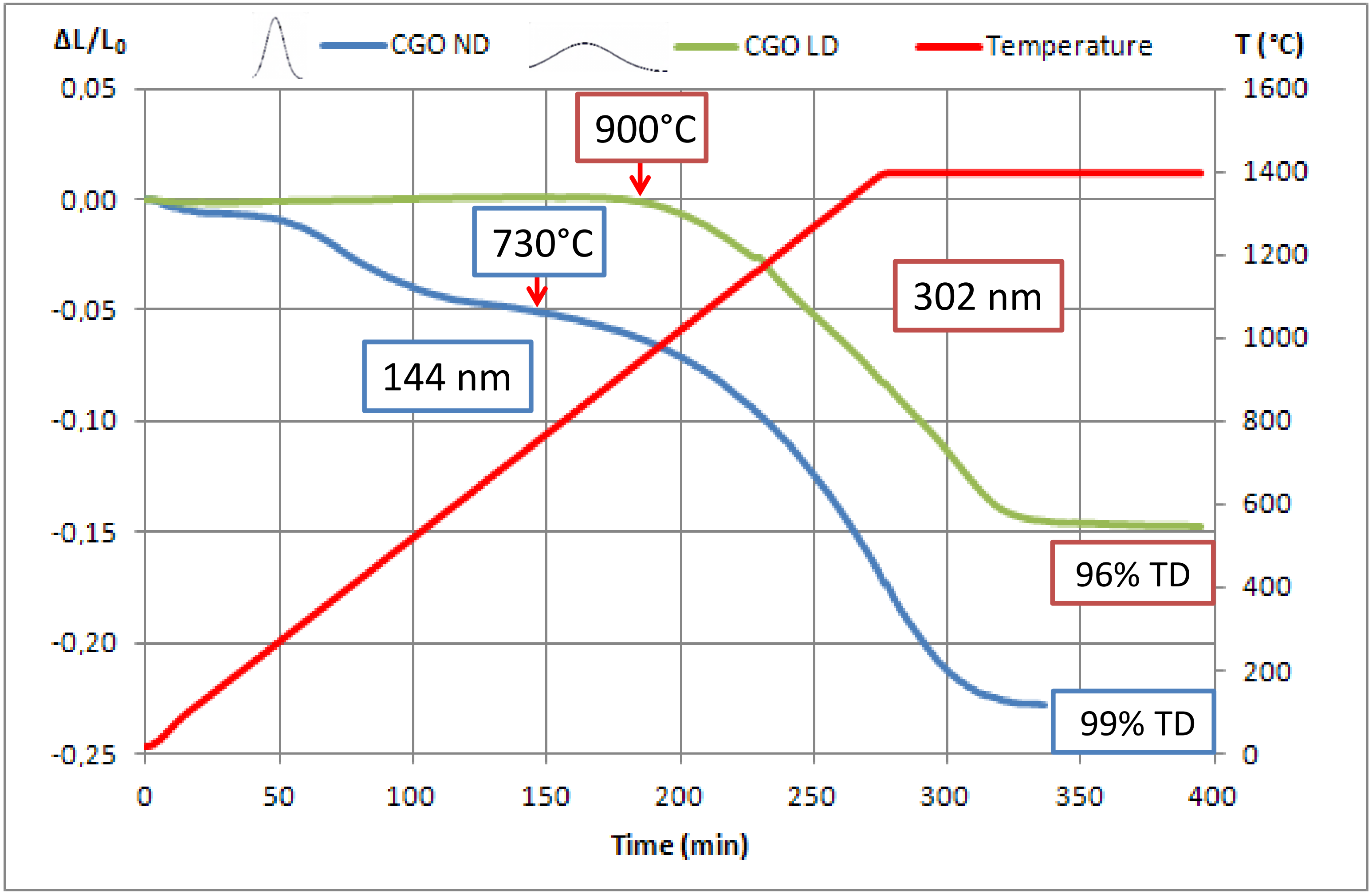
C ($mol.L^{-1}$)	T (°C)	f (kHz)	D ($L.min^{-1}$)
2.5×10^{-3}	400	2500	6

CGO Large D

L = 21.2 nm ± 0.1 nm

C ($mol.L^{-1}$)	T (°C)	f (kHz)	D ($L.min^{-1}$)
2.5×10^{-2}	1000	2500	6

CGO Sintering behavior



C. Goulart et E. Djurado, Journal of the European Ceramic Society 33 (2013) 769–778

Smaller particles and narrower distribution → better densification at lower temperatures

CGO DENSIFICATION is strongly dependent on CGO powders characteristics

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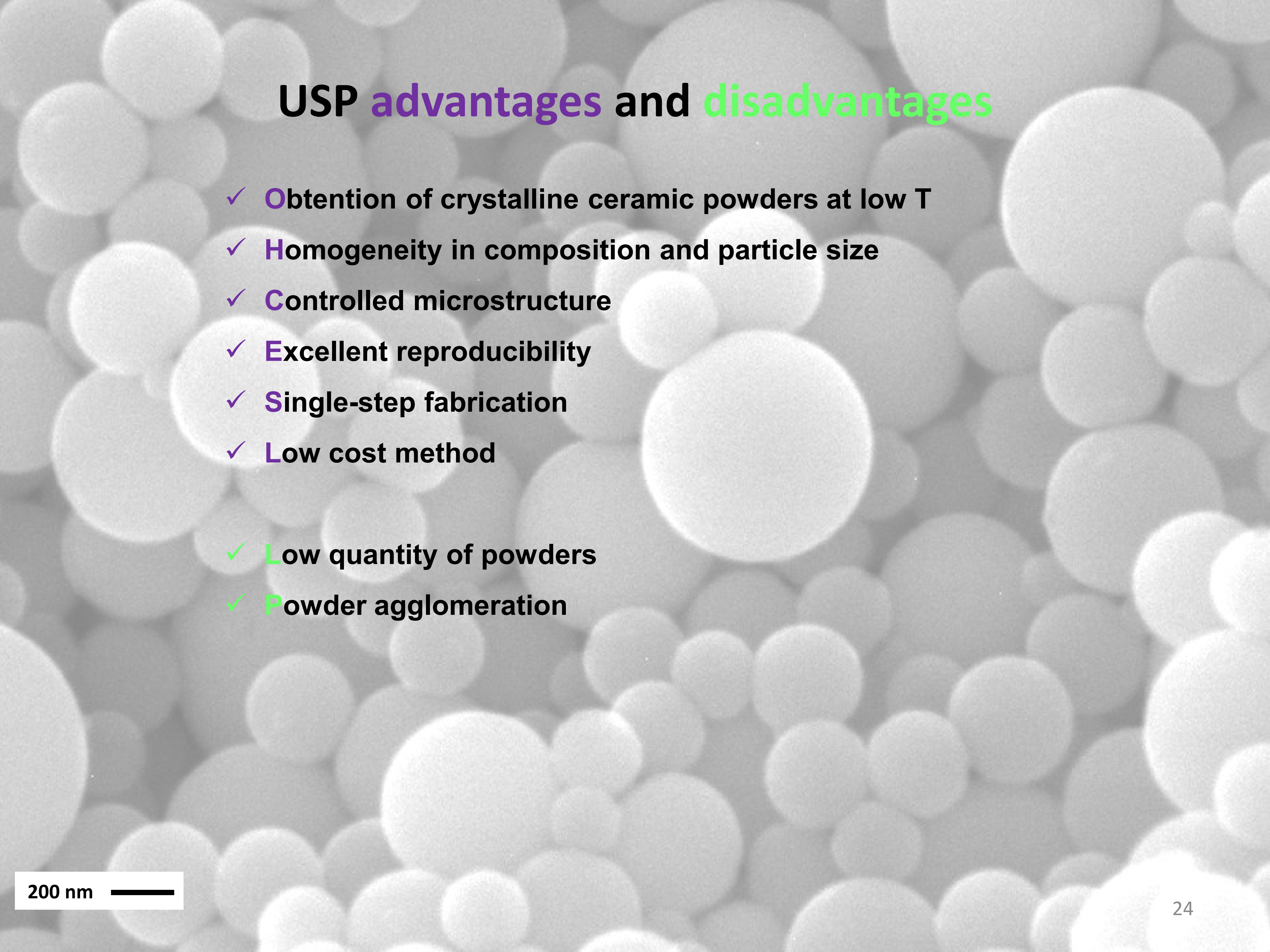
USP advantages and disadvantages

- ✓ Obtention of crystalline ceramic powders at low T
- ✓ Homogeneity in composition and particle size
- ✓ Controlled microstructure
- ✓ Excellent reproducibility
- ✓ Single-step fabrication
- ✓ Low cost method

- ✓ Low quantity of powders
- ✓ Powder agglomeration



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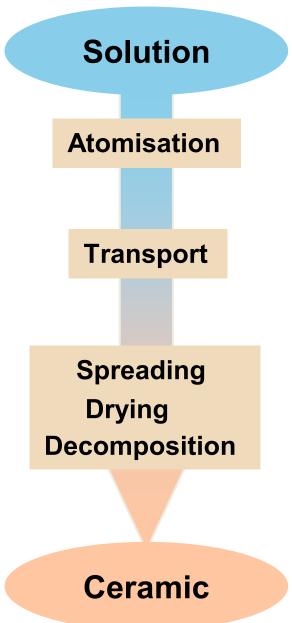
Electrostatic Spray Deposition (ESD): from solution to ceramic
to deposit nanostructured films



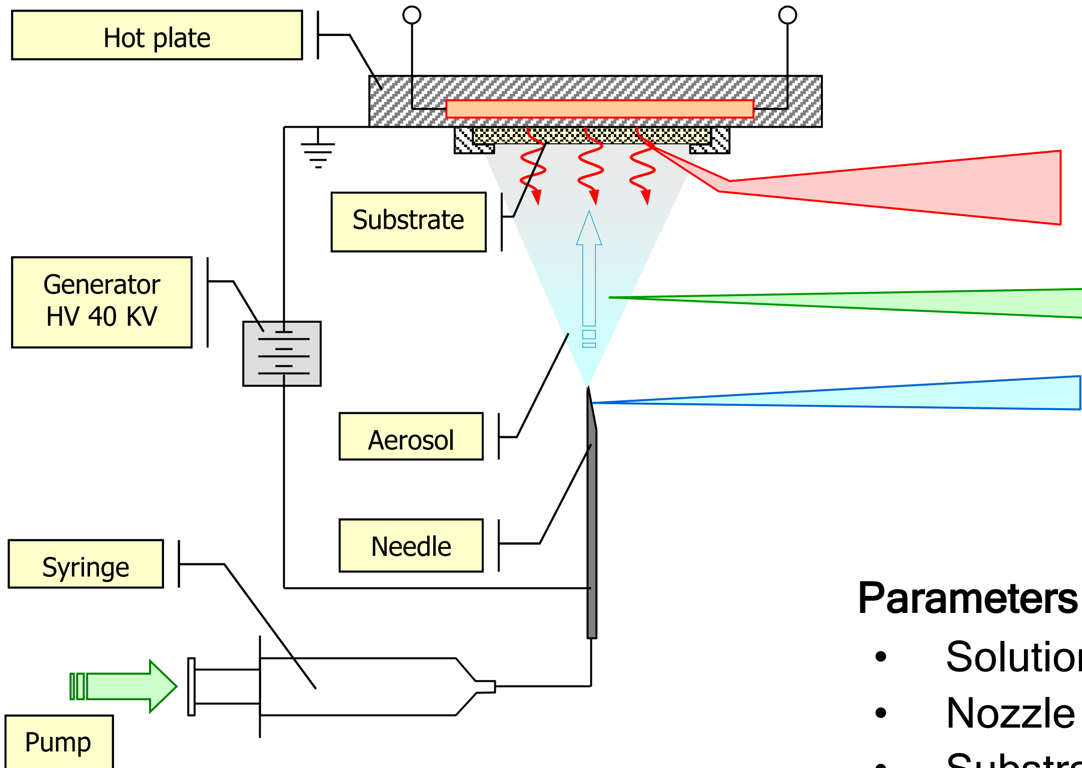
Spray pyrolysis process

- **atomisation** - by pneumatic pulverisation, ultrasound or by electrostatic
- **transport of the aerosol** - gas flow, electrical field.
- **evaporation of solvent, decomposition / sublimation, chemical reaction** - during transport or on the substrate
- **recristallisation.**

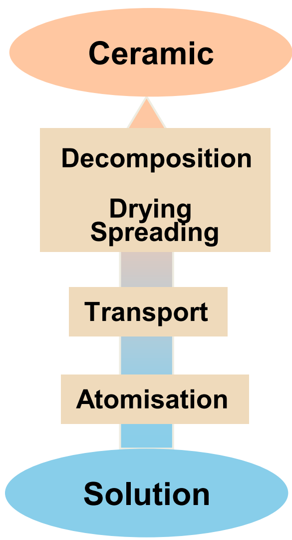
ESD : atomisation and displacement of the aerosol in the electric field applied between needle and substrate.

ESD PROCESS

Set-up



Principle



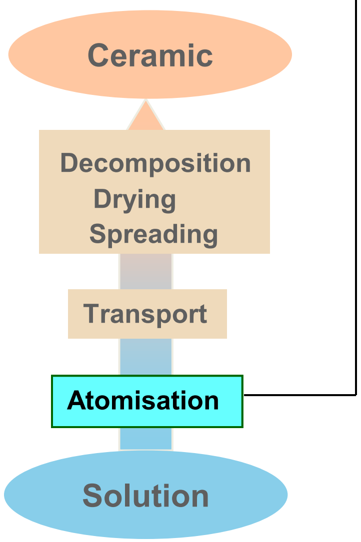
Vertical installation to avoid atypic droplets and solution running on the substrate

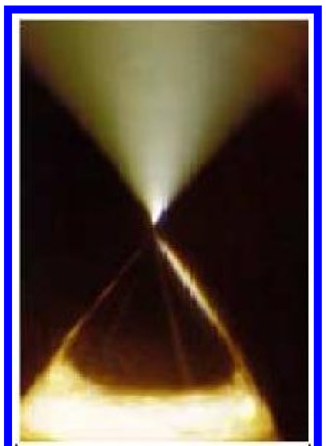
Parameters to control

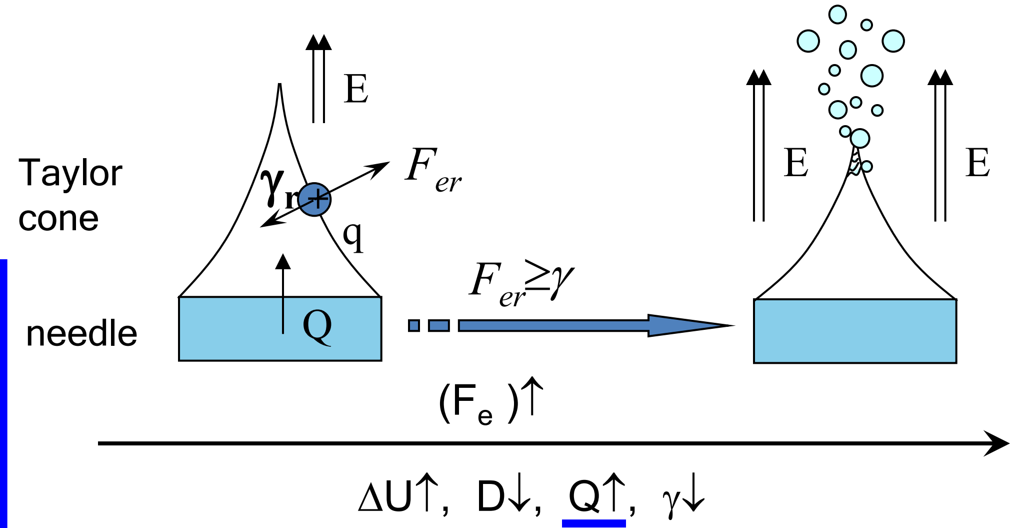
- Solution flow rate
- Nozzle to substrate distance
- Substrate temperature
- High DC voltage between needle and substrate
- Precursors solution (precursors, solvants and additives)

ESD Principle : **This process obeys to electrohydrodynamic atomisation laws of liquids to produce an aerosol from a liquid precursor in high voltage which is then directed to a heated substrate**

THE FIRST STEP OF THE ESD PROCESS: ATOMISATION



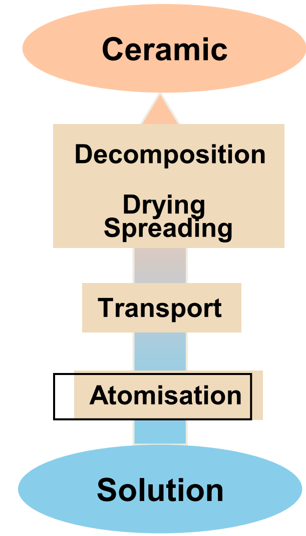


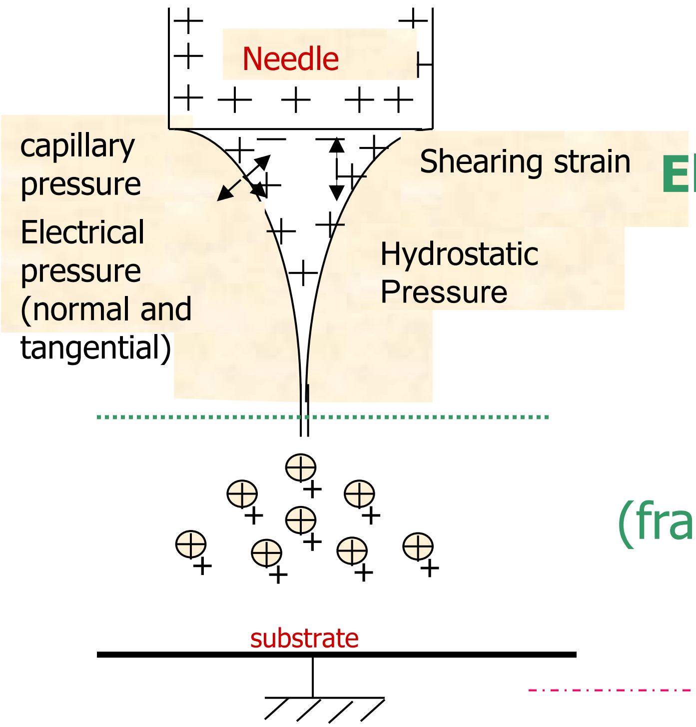


Fragmentation of the surface of a liquid in an electrical field, at the top of the needle

When a solution is constrained to pass through a thin metal needle connected to voltage, an electrostatic field is set up across the needle and the grounded plate acting on ions in the solution. In the case of a positive potential, positive ions move to the surface of the solution. The surface charge causes an outward electrostatic pressure on the solution which is opposite to the inward directed pressure from the surface tension. This leads to surface instabilities and distorsion into a stable conical shape (Taylor cone), as electrohydrodynamic mechanisms.

THE FIRST STEP OF THE ESD PROCESS : ATOMISATION





Electro – Hydrodynamic phenomena

(formation of a cone and liquid jet)

Hydrodynamic phenomena

(fragmentation of the liquid jet in droplets)

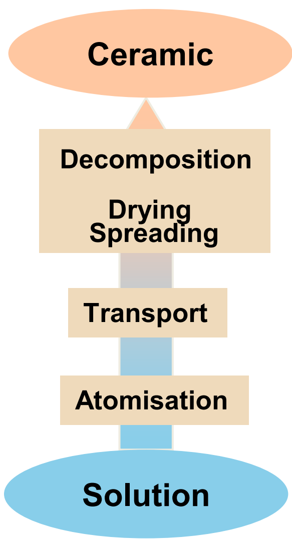
$$d_g = 3{,}78\,\pi^{-\frac{2}{3}}\,Q^{\frac{1}{2}}\left(\frac{\rho\varepsilon_0}{\gamma\lambda}\right)^{\frac{1}{6}} f_b \quad *$$

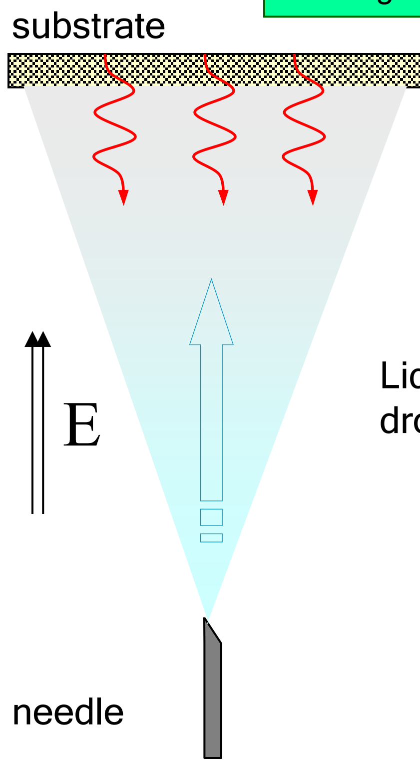
- λ conductivity (S/m)
- Q rate (m^3/s)
- γ surface tension (N/m)
- ρ volumic mass (kg/m^3)
- ε_0 vacuum electrical permittivity
- f_b adimensional radius of the break jet point

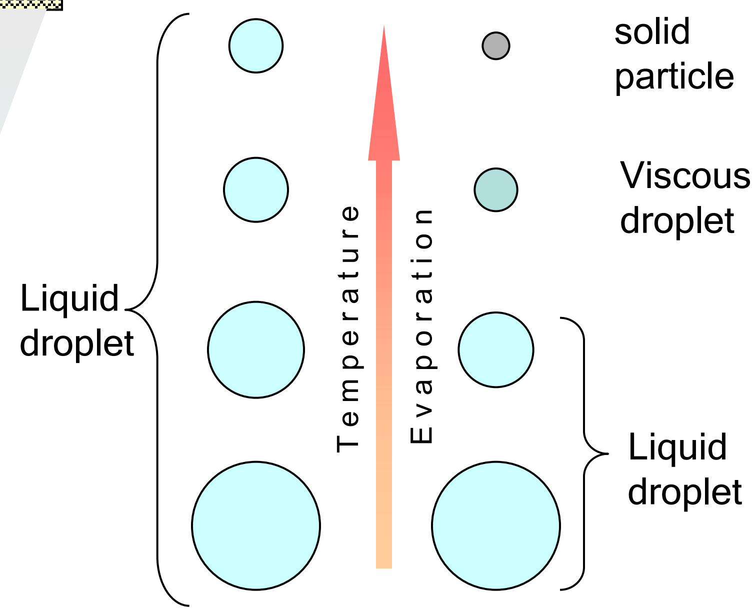
*Ganan-Calvo- Physical Review Letters 79 (2) 1997 pp. 217-220

THE SECOND STEP OF THE ESD PROCESS : AEROSOL TRANSPORT

An electrostatically produced charged droplet is attracted towards a grounded substrate by Coulombic forces
Heating step and solvent evaporation





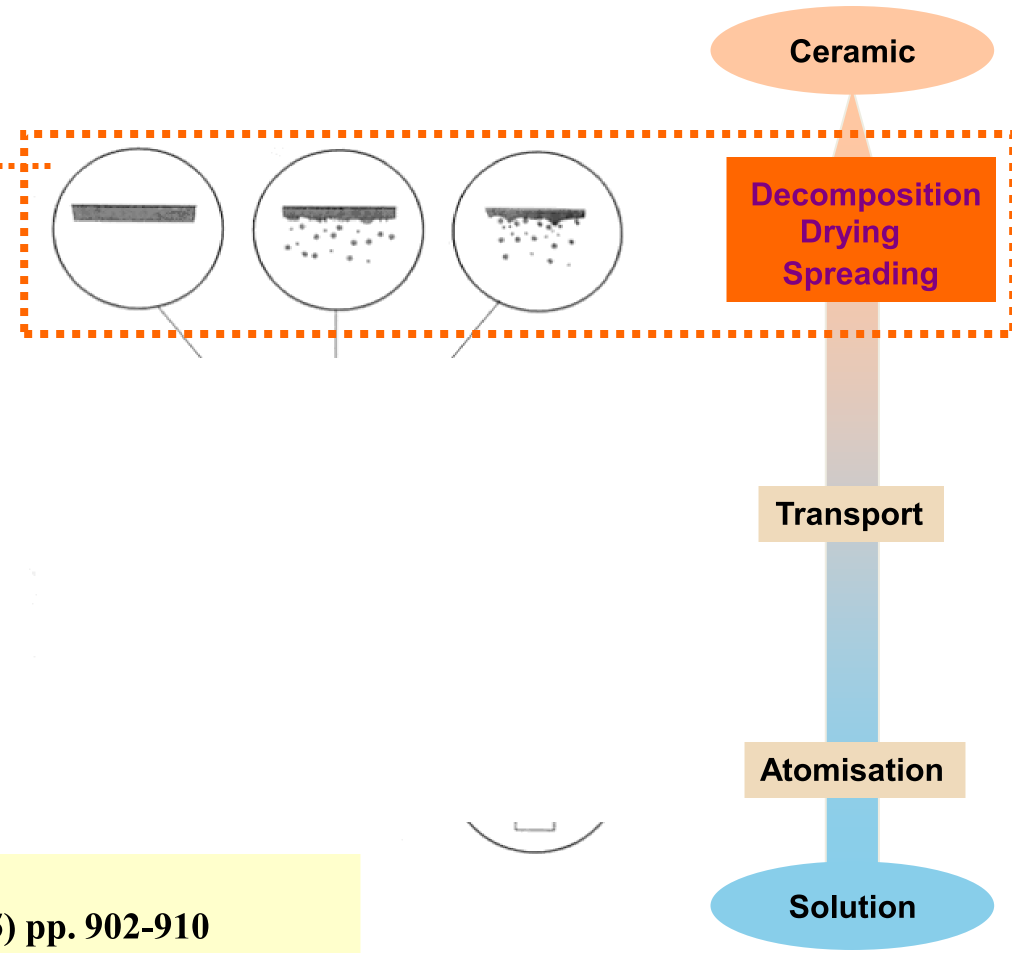


Solvent too volatile
or
temperature too high

In multi-jet mode, distribution of droplets size is large → droplets <u>and</u> particles

THE THIRD STEP OF THE ESD PROCESS :
SPREADING, DRYING, DROPLETS DECOMPOSITION

Two phenomena:



- Spreading and drying of droplets

Combined mechanism → dense (under)layer
spreading/evaporation/precipitation

- Film growth

Preferential landing → porous film

R. NEAGU et al., Chemistry of Materials, 17 [5] (2005) pp. 902-910

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Optimization study of the ESD process to coat thin dense zirconia-based films

Two directions :

- The influence of **process parameters**

R. NEAGU and al., Solid State Ionics 177 (2006) 1981-1984

- The influence of chemical **parameters**

- nature and concentration of precursors
- nature of solvents

$\longrightarrow \sigma, \gamma, T_{eb}$

R. NEAGU and al., Solid State Ionics 177 [17-18] (2006) 1451-1460.

Optimisation of the process parameters

- Study of the influence of process parameters
  - Substrate temperature
  - Nozzle to substrate distance
  - Solution flow rate

Experimental conditions to optimize :

- Substrate temperature: from 300° to 575°C
- Nozzle to substrate distance: from 27 to 57 mm.
- Solution flow rate: from 0.5 to 2.5 ml/h.
- Coating time : 1 h.