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Opportunities of solution grown YBCO coated conductors. Let's push them further

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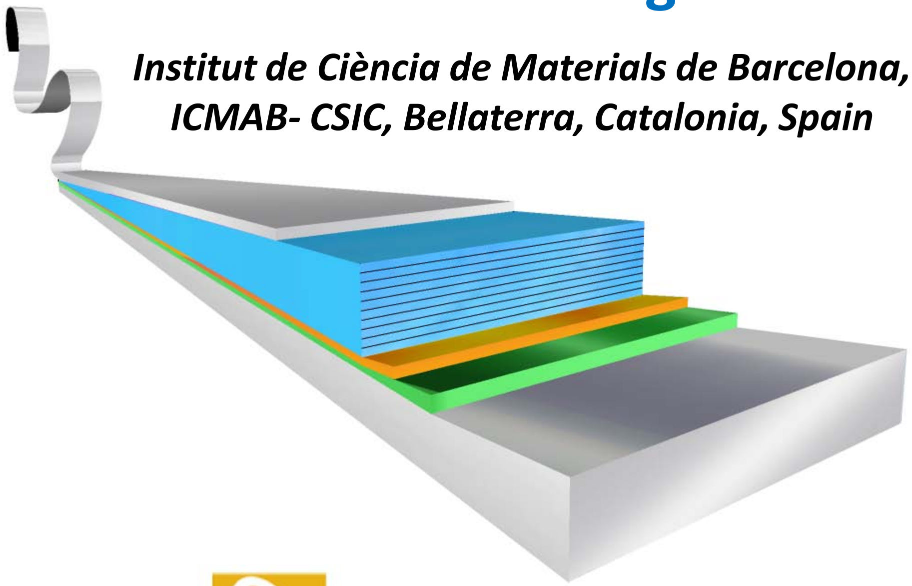

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nanoSELECT

Solution based *(CSD) Coated Conductors*

A versatile, scalable and low cost methodology for growth of nanostructured epitaxial coated conductor

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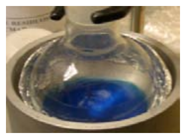
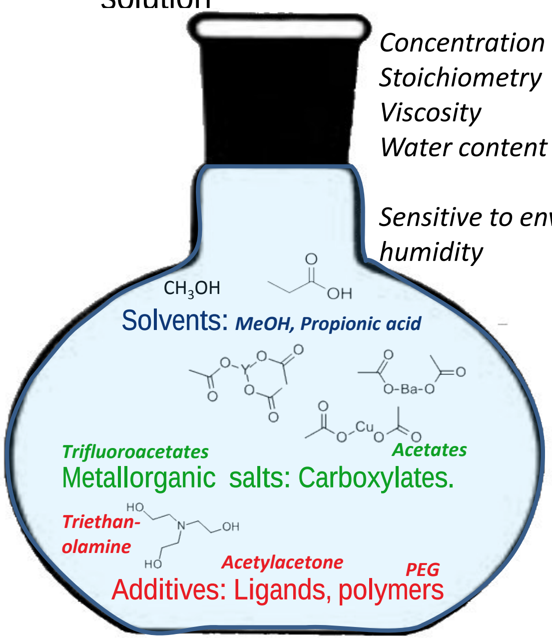
1. Precursor solution synthesis

metal-organic precursor solution





Concentration
Stoichiometry
Viscosity
Water content

Sensitive to enviromental humidity

- ✓ **Many different formulations**
- ✓ **Most keep some fluorinated metallorganic precursor to ensure a BaF_2 growth route**
- ✓ **Solvents are poorly discussed though water should be avoided**
- ✓ **Additives are key players for modulating solution rheology and properties**
- ✓ **Stability, scalability of the solution are key factors**

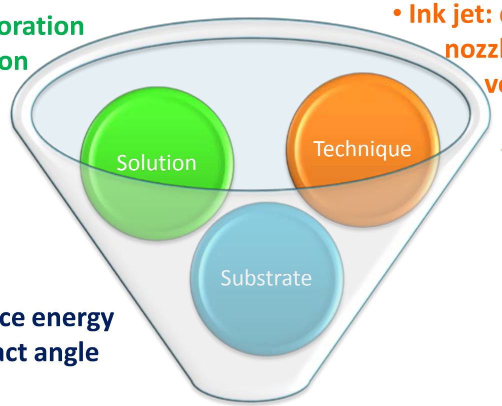
X. Obradors, T. Puig et al., SUST (2012)

Solution based *Coated Conductor*

2. Solution deposition

➡ Ink-jet printing, Dip coating, Slot coating, ...

- Solvent evaporation
- Surface tension
- Viscosity
- Density
- Stability



- Ink jet: driving waveform, nozzle diameter, drop volume, drop pitch
- Dip coating: withdrawn speed, vessel volume
- ....

- surface energy
- contact angle

Scalability
multinozzle
closed cartrige
high thickness
patterning

✓ **Many different deposition techniques**

✓ **Most need to cope with liquid properties and rheology need to be adapted**

✓ **Solvents are key players in the immediacy drying process**

✓ **Additives will help in rheology adaptation. Many possibilities and poor knowledge is yet achieved**

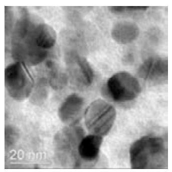
M. Vilardell et al, thin solid films (2013)

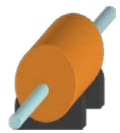
X. Obradors, T. Puig et al, SUST (2012)

Solution based *Coated Conductor*

3. Pyrolysis treatment

- Removal of organic precursors





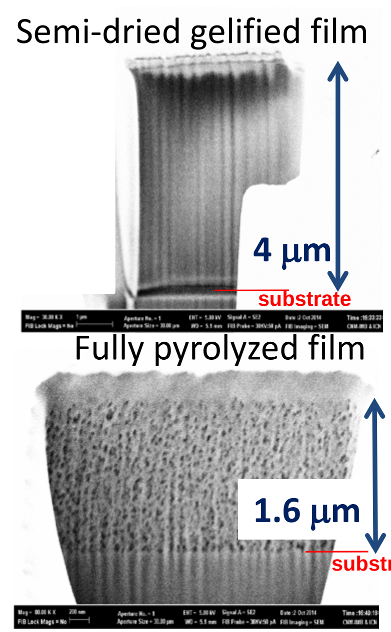
T_g= 300 - 500°C

$$Cu(TFA)_2 + 2Ba(TFA)_2 + 3Y(TFA)_3 + H_2O + O_2 \longrightarrow CuO + Ba_{1-x}Y_xF_{2-y}O_y + Y_2O_3 + \text{volatile products}$$

with many process parameters: T_g, r, P_{H_2O}, P_{O_2}, P_t, v_g, ...

Control of thermodynamic and kinetic parameters

- ✓ **Pyrolysis is not only thermal decomposition of the organics**
- ✓ **The layer strongly shrinkages, being this, one of the most crucial steps since large stresses need to be relieved**
- ✓ **All this process depends on solution formulation**
- ✓ **Additives will help in rheology adaptation. Many possibilities and poor knowledge is yet achieved**

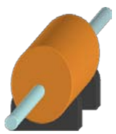


X. Obradors, T. Puig et al., SUST (2012)

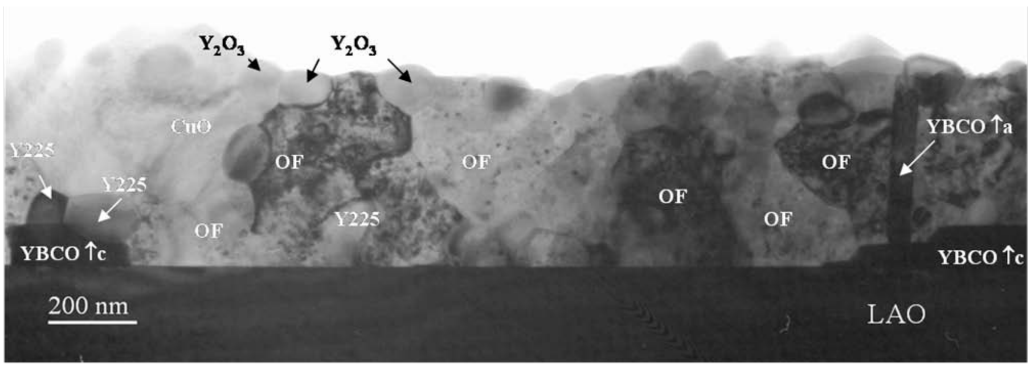
Solution based *Coated Conductor*

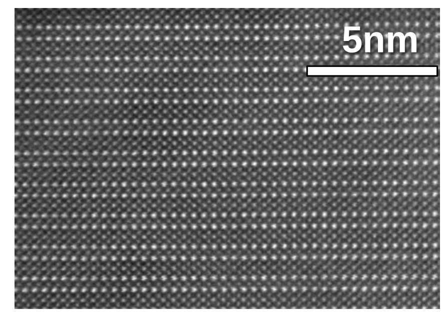
4. YBCO crystallization process

- Ex-situ crystallization: $Ba(O_xF_y)_2 + 3/2\ CuO + 1/4 Y_2O_3 + yH_2O\ (g) \rightarrow 1/2\ YBa_2Cu_3O_{6.5} + 2yHF\ (g)$



$T_g = 750 - 810^oC$ *with many process parameters :* $T_g, r, P_{H_2O}, P_{O_2}, P_t, v_g, \ldots$





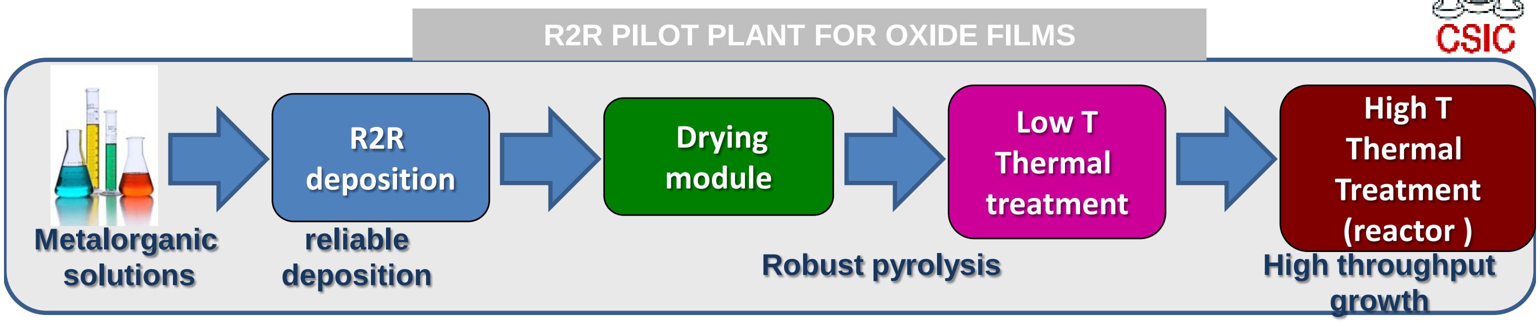
Complex phase transformation and nucleation

- ✓ **Growth of CSD YBCO implies complicated gas-solid phase transformations**
- ✓ **Nucleation easily occurs but fine tuning is complex**
- ✓ **Growth conditions need to be adapted for each buffer and thickness**
- ✓ **Growth rate is rather low and poorly controlled**

J.Gázquez et al., Chem Mat 18 (2006)

X. Obradors, T. Puig et al., SUST (2012)

For CSD being marketable



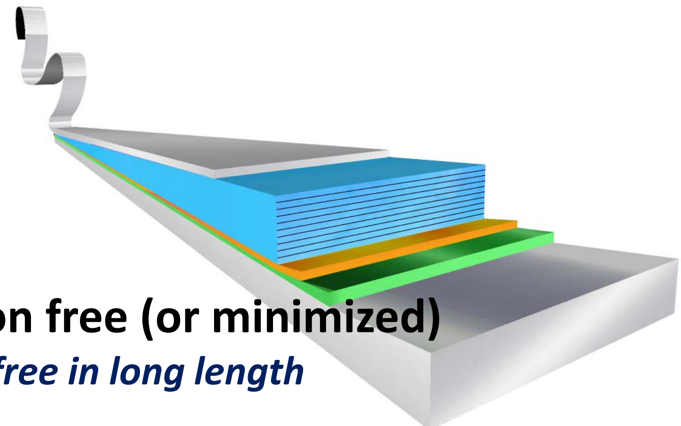
Low cost is compulsory, reliability is mandatory and high performance is advisory

Record values: 790 A/cm-w at 77 K (short samples) at ISTERA

Standard values: > 200 A/cm-w at 77 K (long length) at AMSC, Showa, D-nano

CSD is a powerful approach full of opportunities for cost-effective coated conductors with outstanding performances

What's needed to go beyond state of the art in solution based *CC*



1. **Thick layers with multi-deposition free (or minimized)**
Thick pyrolysis need to be robust and crack free in long length
Specific formulated solutions are required

2. **Higher throughput growth process**
High throughput requires high growth rates

3. **All-CSD coated conductor (low cost)**
CSD buffer compatibility should not be an issue

4. **Outstanding nanocomposite performance**
Artificial pinning centres need to be easily implemented for long length

… as most imperative issues and they are all beyond any CSD present knowledge

IEEE/CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), April 2015.
Plenary Presentation given at CCA 2014, Jeju Island, Korea, Nov. 30 - Dec. 03, 2014.

1.- Thick layers with multi-deposition free (or minimized)

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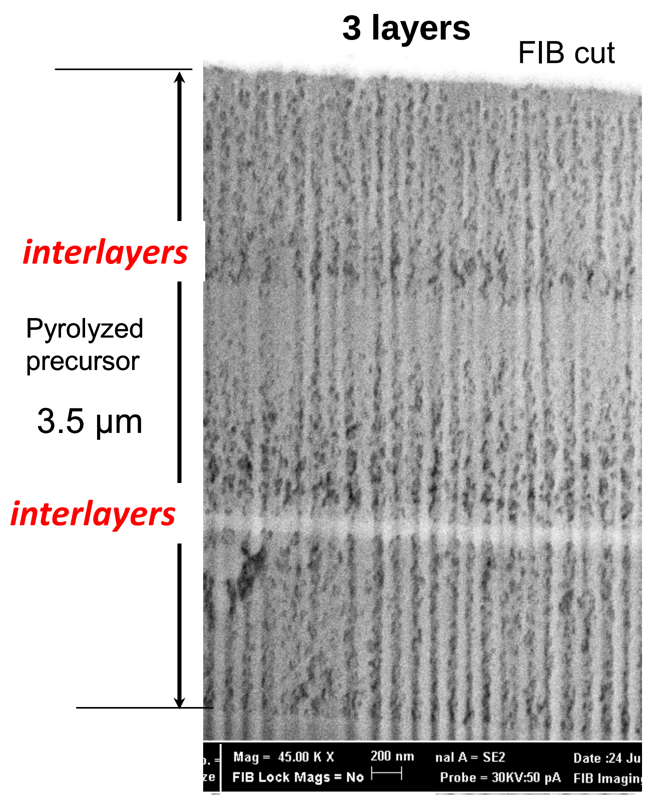
AIM: YBCO layers need to be beyond 3-5 μm

State of the art :

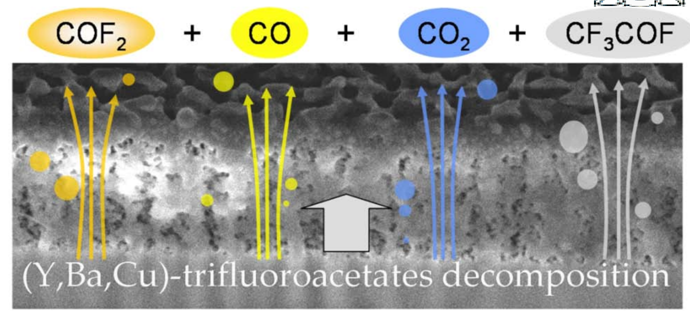
1. Deposition / pyrolysis multi – runs
   6 x 0.5 μm for 3 μm layers at ISTERA
2. Single Deposition / pyrolysis
   ~0.8 - 1μm at AMSC



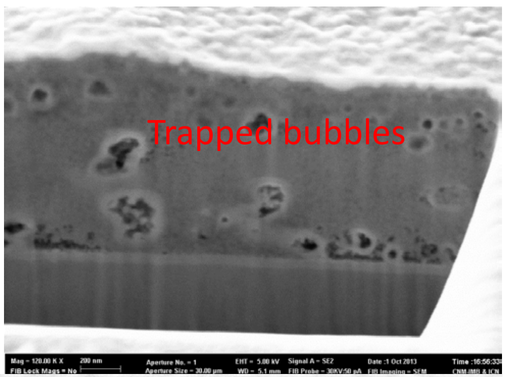
Key factors:

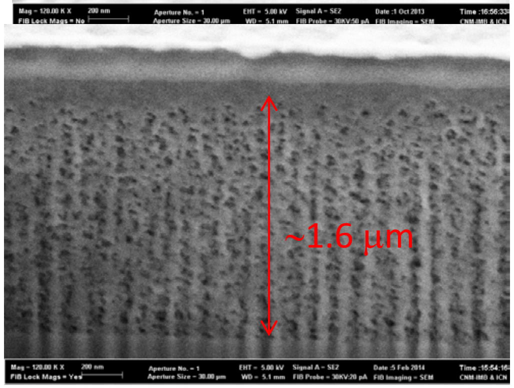
- Knowledge on thermo- viscoelastic properties of the gelified film is mandatory
- Role of solution formulation in the drying and shrinkage processes is needed
- Control of liquid movements beyond 1 μm thick layers is requested to increase homogeneity

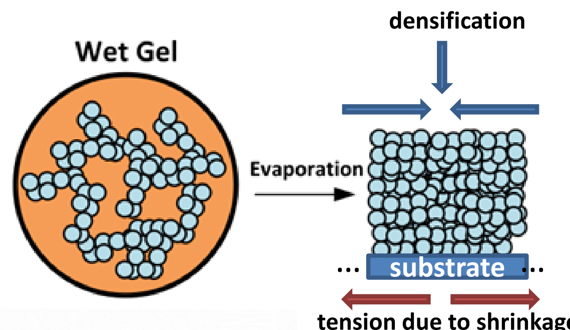
➢The shrinkage problem during pyrolysis

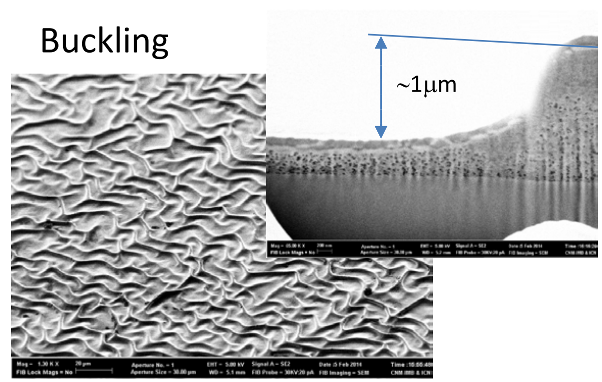


A thick pyrolysis should still ensure a crack-free layer with a homogenous release of gasses and reproducibility

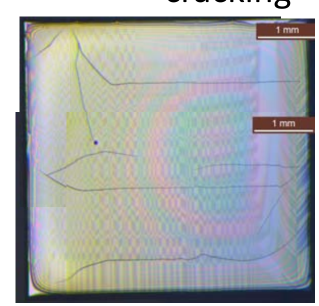




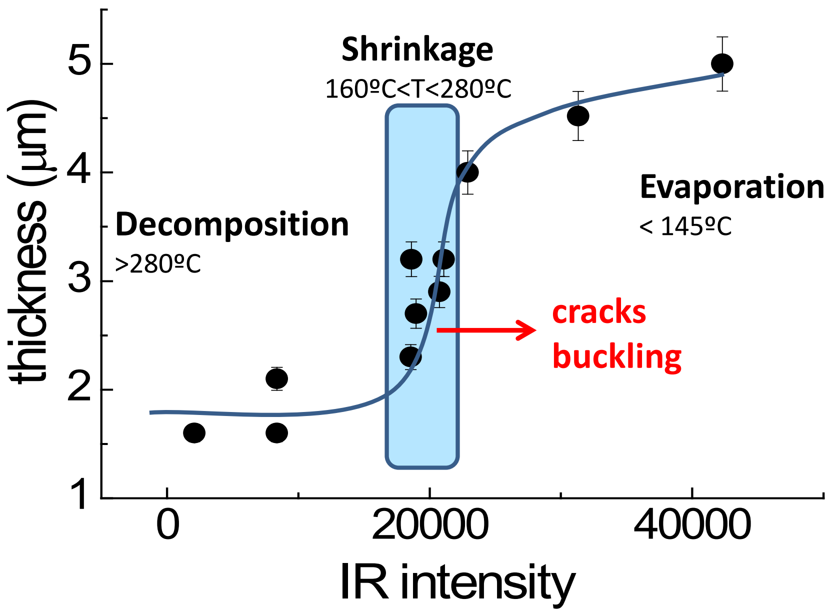


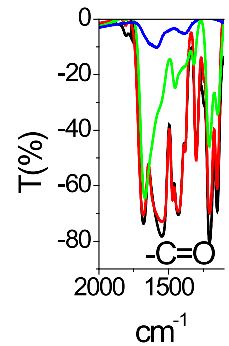


cracking



➢The shrinkage problem during pyrolysis





Shrinkage occurs earlier than decomposition

Each solution formulation is a different case

How can we control shrinkage during cure process ? What additives could help in keeping and unbreakable skeleton ?

2.- Higher throughput growth process

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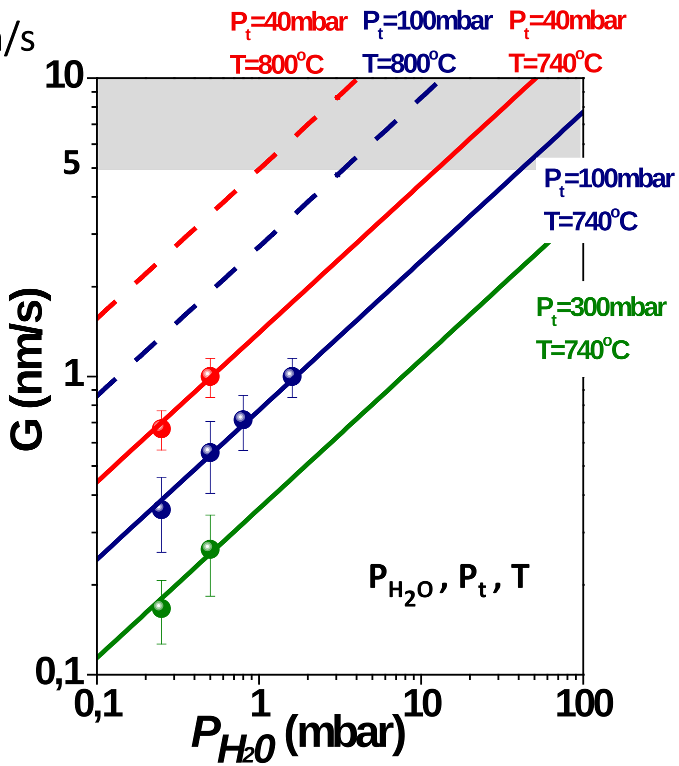
AIM: YBCO growth rate need to be 5-10 nm/s

State of the art :

Most CSD processes have growth rates of 1 nm/s



Key factors:

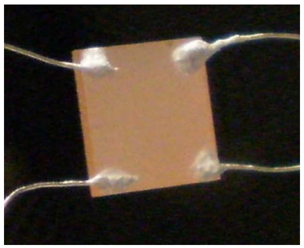
- Further knowledge on processing parameters increasing growth rate is needed (P_{H_2O}, P_t, T)
- YBCO nucleation is compromised at high growth rates

Solid-gas diffusion plus reaction kinetics model

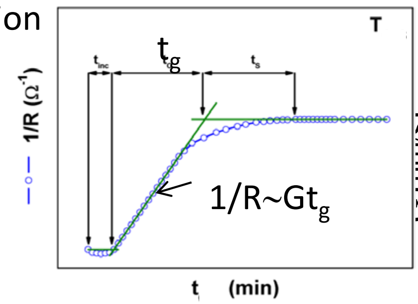
$$G(T) \approx C'' \left[\frac{P_{H_2O}^{1/2}}{(\alpha+\beta P_t+\gamma P_t/F)}\right] exp - (\Delta H^{\Theta}/RT)$$

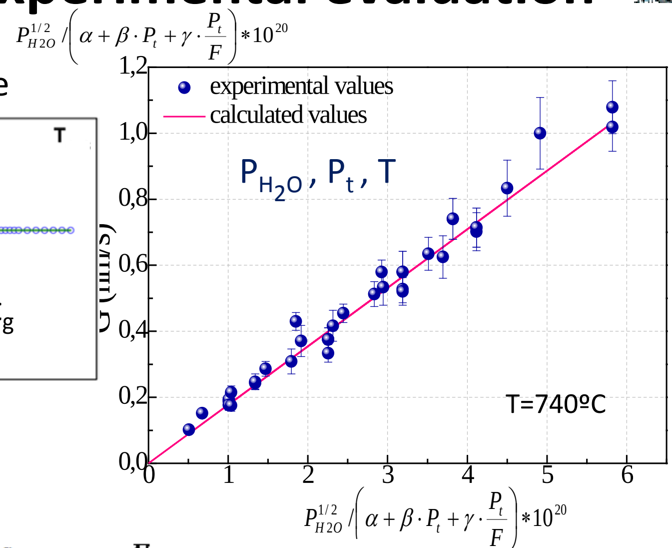
C. Sanchez et al., SUST (2014)

CSD YBCO growth rate, G, experimental evaluation

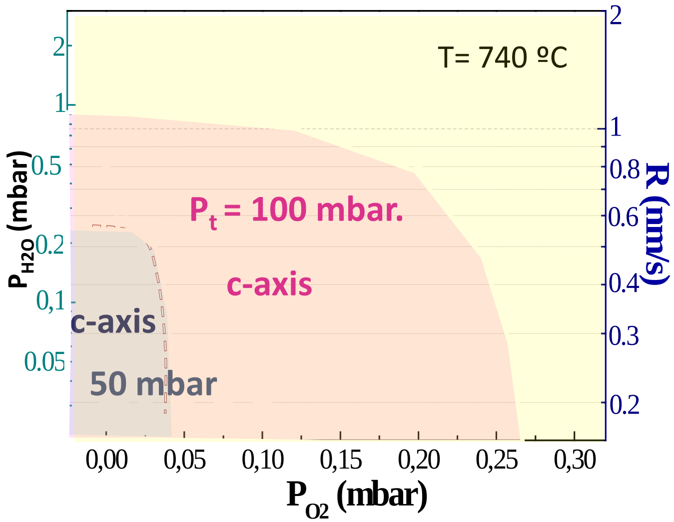


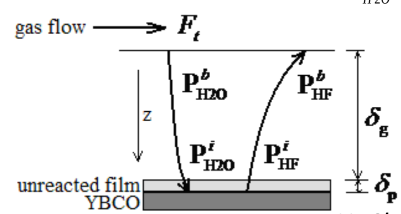
In-stiu resisitivity growth rate evaluation





Strong microstructural changes appear by decreasing P_t



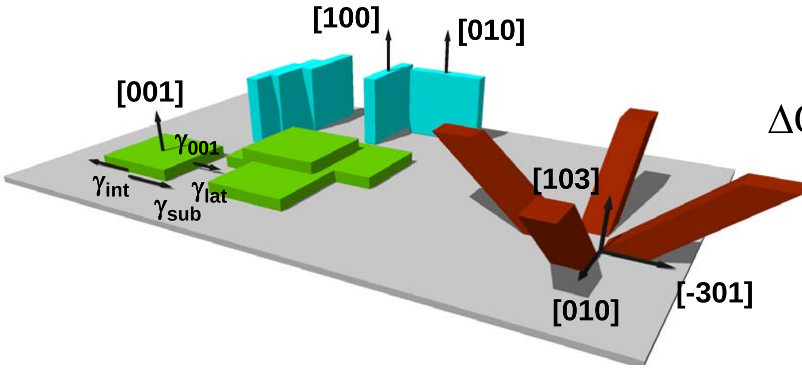


Solid-gas diffusion-reaction model

H. Chen et al., SUST 23 (2010)
X.Obradors et al., SUST 25 (2012)

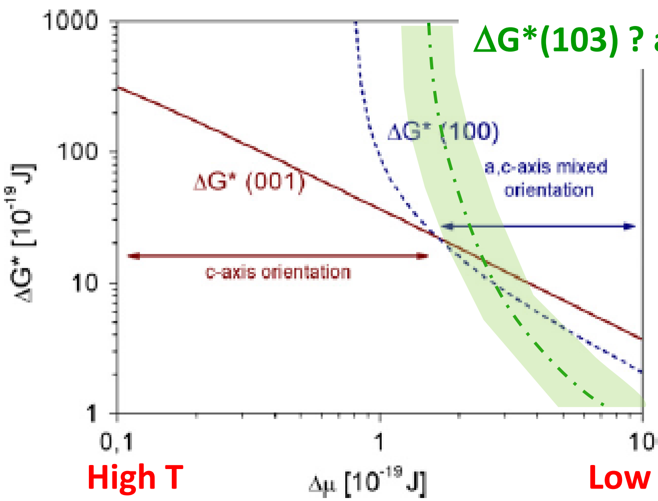
Main difficulty is to reach G> 1nm/s with full c-axis epitaxial orientation. Nucleation needs to be addressed in the gas-solid nucleation

➢ The multi-nuclei of CSD YBCO Volmer-Weber nucleation



$$\Delta G^* = \frac{\pi (h\gamma_{lat})^2}{-\left(\frac{h}{v}\right)\Delta\mu - (\gamma_{up} + \gamma_{int} - \gamma_{sub})}$$

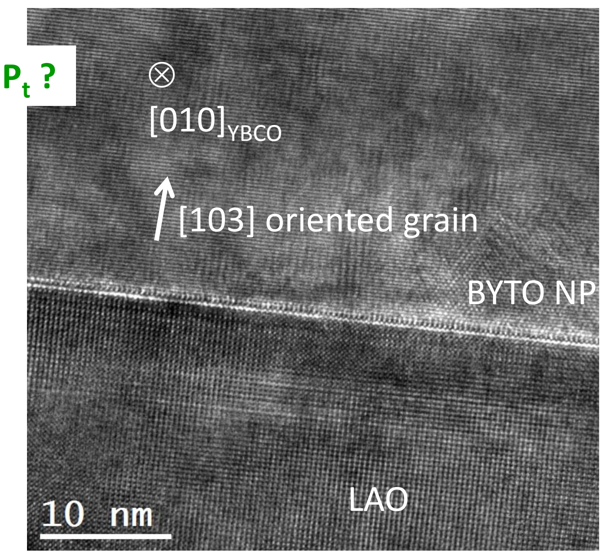
Δ G *: energy barrier to form an stable nuclei , γ_i: surface free energy/area



ΔG*(103) ? and at low P_t ?

High T   Low T

Y. Ichino et al., IEEE Trans. Applied Supercond. 13, 2735(2003)



How fast can a gas / solid reaction be while keeping epitaxial growth ?
How can we control nucleation to avoid (103) nuclei ?

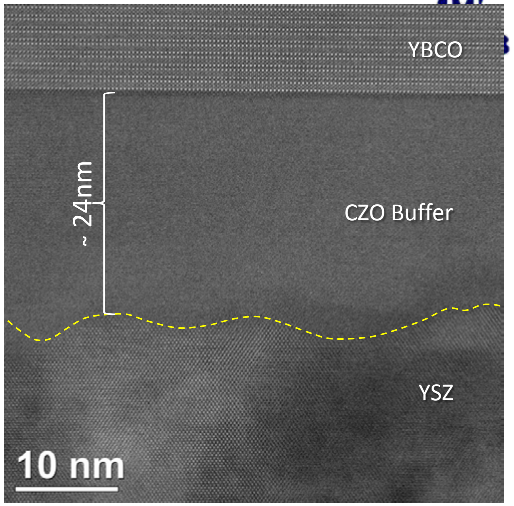
3.- All-CSD coated conductor

AIM: YBCO layer on a CSD buffer

State of the art :

1. Mostly vacuum buffer layers are employed
2. Few cases stay with a CSD buffer

CSD buffers : a CeO_2-based cap layers is common

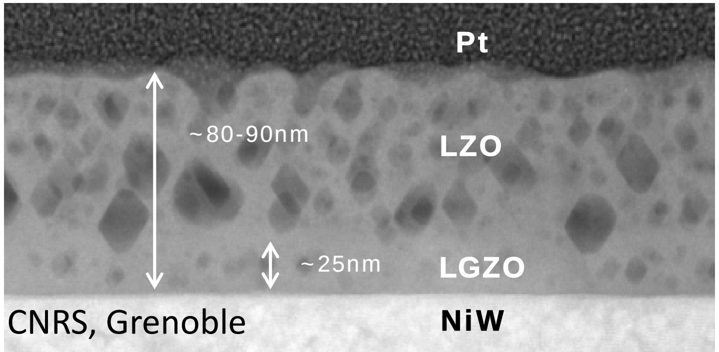


E. Bartolomé et al, SUST (2013)

Key factors:

- YBCO nucleation density strongly depends on the characteristics of the buffer surface

- CSD-YBCO growth on CSD-buffer require robust, dense and flat buffers usually implying too long thermal processes



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CSD YBCO epitaxy on CeO_2-based buffer

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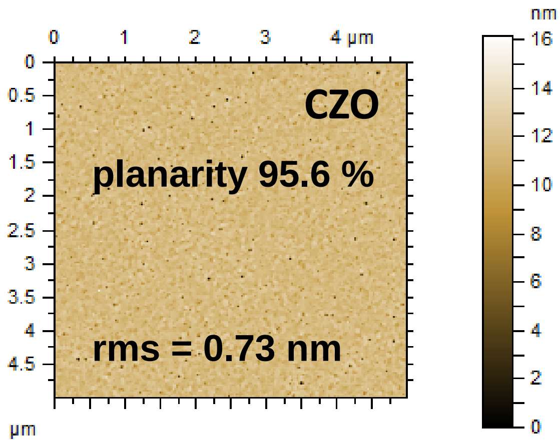
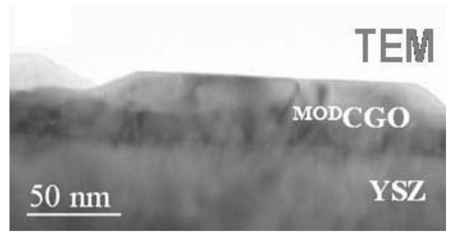
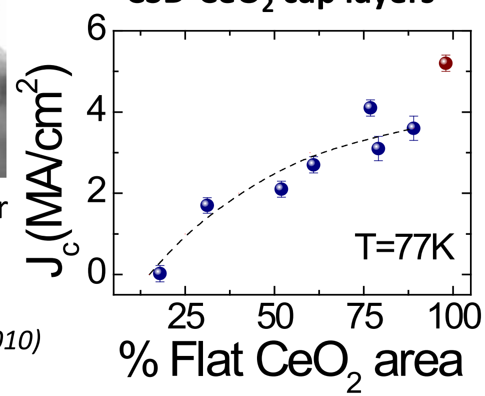


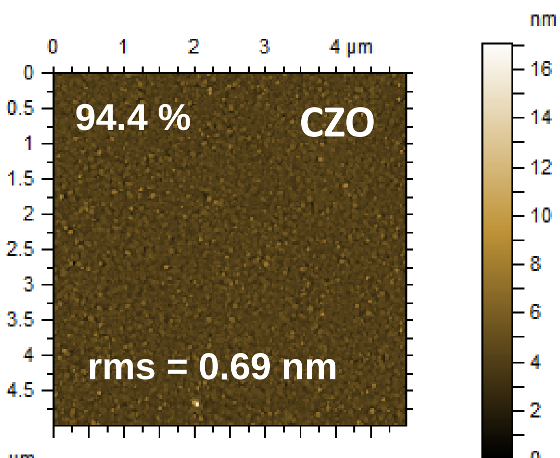


Surface planarity is essential for high quality heterostructures

M. Coll et al., JMR (2010)

High J_c TFAYBCO on CSD-CeO_2 cap layers





- **Shorter processing times (1:8)**
- **Air atmosphere in IBAD substrates**

- **it involves higher surface reactivity with YBCO growth**
- **c-axis nucleation is compromised**

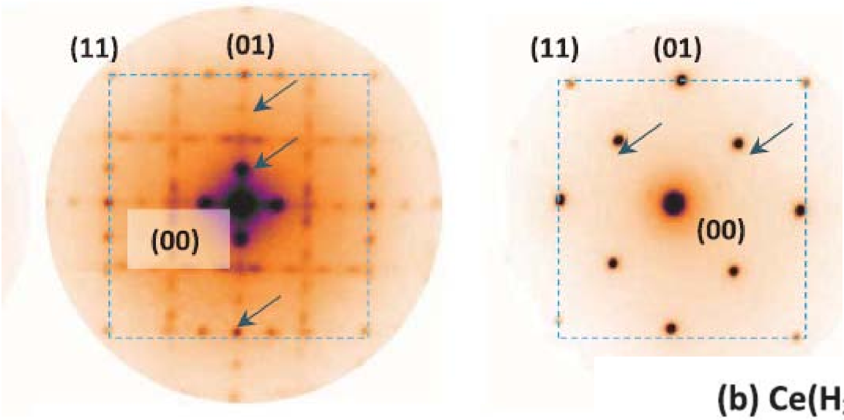
New growth processing conditions
PO_2, T, P_{H_2O}, …

CeO_2 surface reconstructions and YBCO nucleation density

PLD CeO_2

V. F. Solovyov et al., Scientific Reports 2014

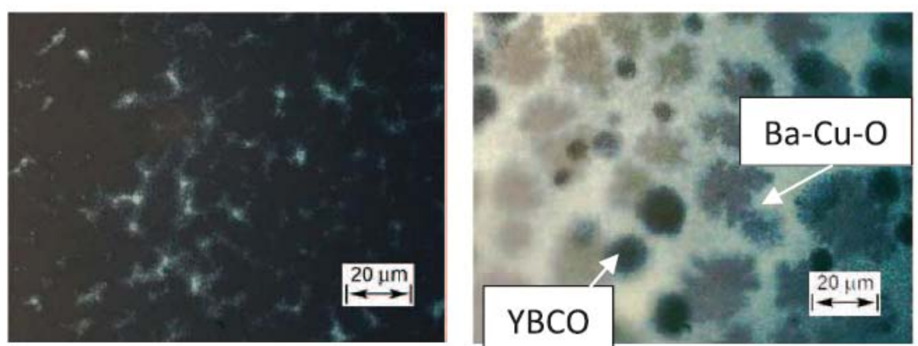
(b) $Ce(H_2O)$ (c) $Ce(O_2)$



CeO_2 surface activity can be modified by post-annealings

LEED diffraction patterns of (001) CeO_2 surface reconstructions upon different atmospheres due to surface oxygen ordering

(b) $Ce(H_2O)$ (c) $Ce(O_2)$



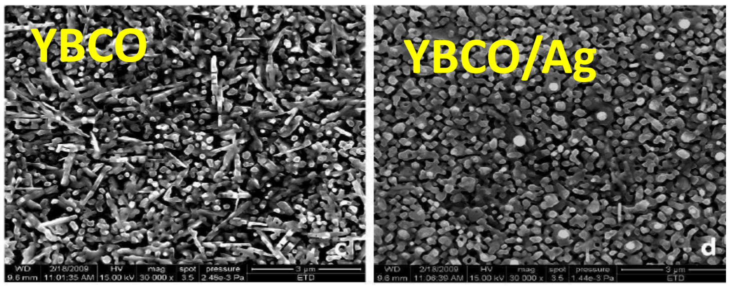
YBCO nucleation density depends on surface reconstruction (different surface activity)

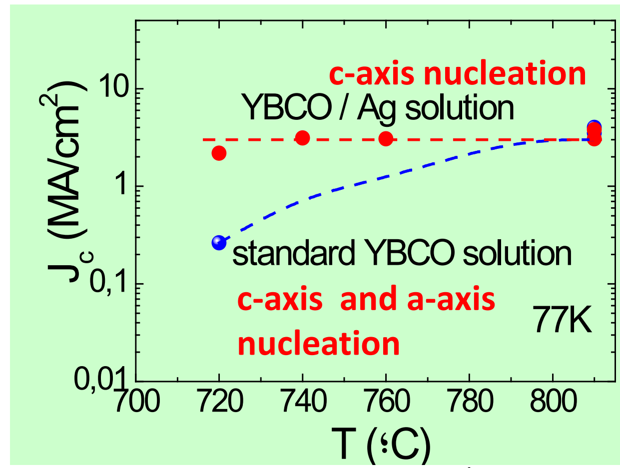
3 x J_c higher in $Ce(H_2O)$

YBCO nucleation is still poorly understood

➢The Ag case : the catalitic effect of Ag on YBCO nucleation

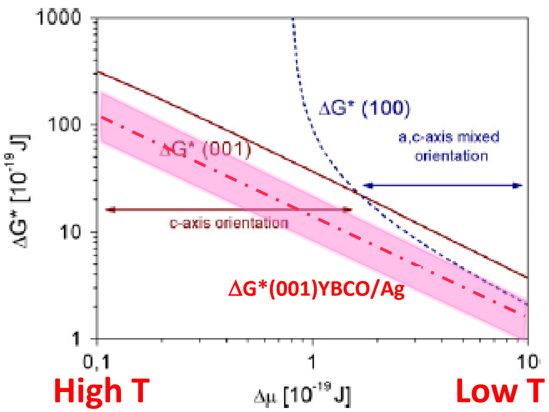
T= 720ºC on LAO substrates



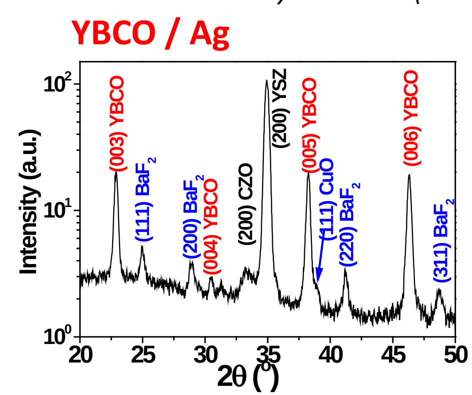


Physica C 482 (2012)

Ag may reduce supersaturation and enhance c-axis nucleation



c-axis nucleation and no reactivity achieved at 720ºC on CZO highly active surfaces



Understanding YBCO nucleation is becoming a critical issue

4.- Outstanding nanocomposite performance

AIM: High J_c(H) YBCO nanocomposites (3-5 μm thick)

State of the art :

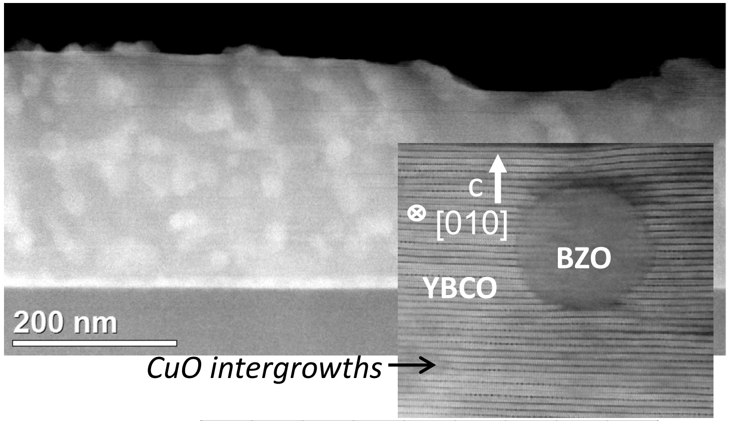
CSD nancomposites by addition of a metallogranic salt is a standarized process

Reached values: 50 A/cm-w @ 77K, 3 T (ISTERA)

J_c= 0.2 MA/cm^2 @ 77K, 3 T (ISTERA, ICMAB)

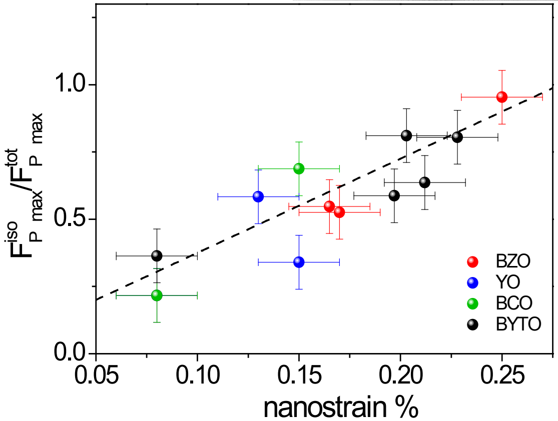
Goals: 500 A @ 65K, 3T

1000 A@ 40 K, 10 T



Key factors:

- It relies on spontaneous segregation of nano-second phases. It is hard to tune
- CuO intergrowth (Stacking Faults) are key players. Control on density and morphology of SF is needed
- Local lattice strains physically modulate the superconducting properties
- A method able to separate YBCO solution from nanoparticles formation should provide better tuning



J. Gutiérrez, et al., Nat. Mat. (2007), A. Llordés et al. , Nat. Mat. (2012)

New vortex pinning mechanism in CSD YBCO nanocomposites : *Nanostrain leads to unpaired regions*

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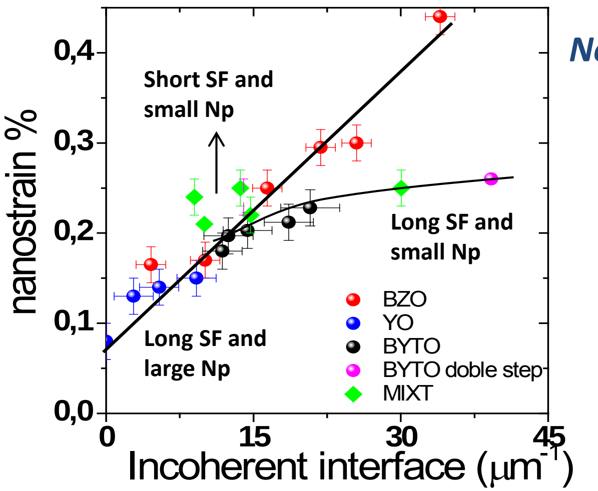
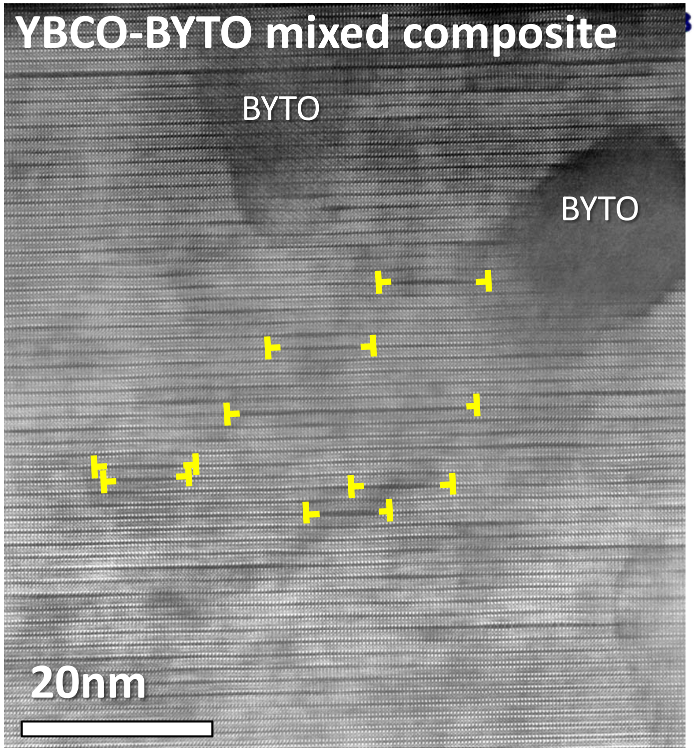
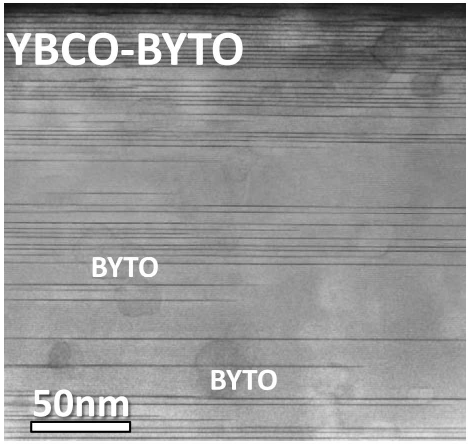
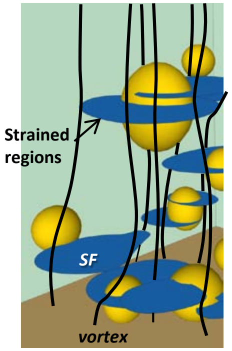


Not only incoherent interface matters

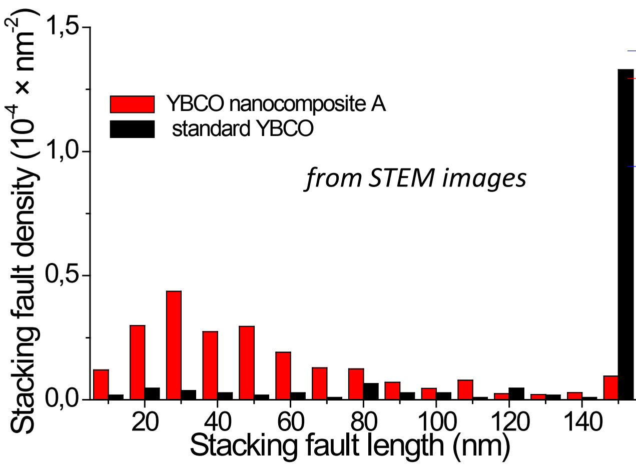


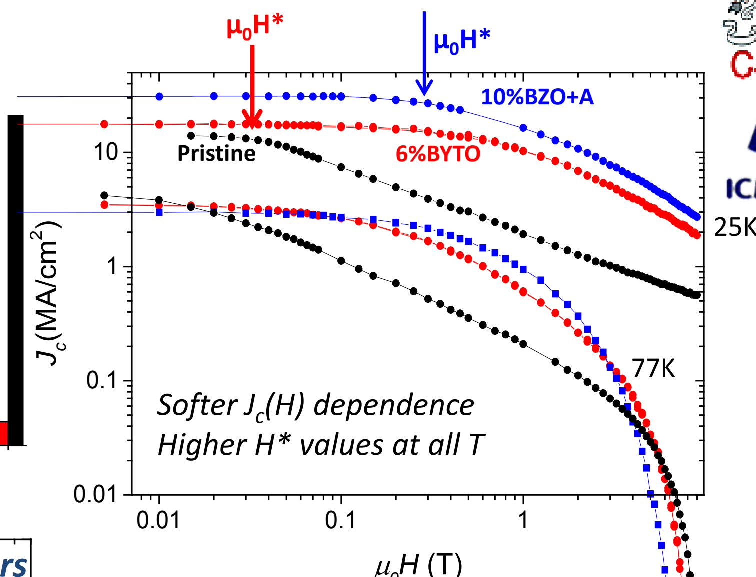


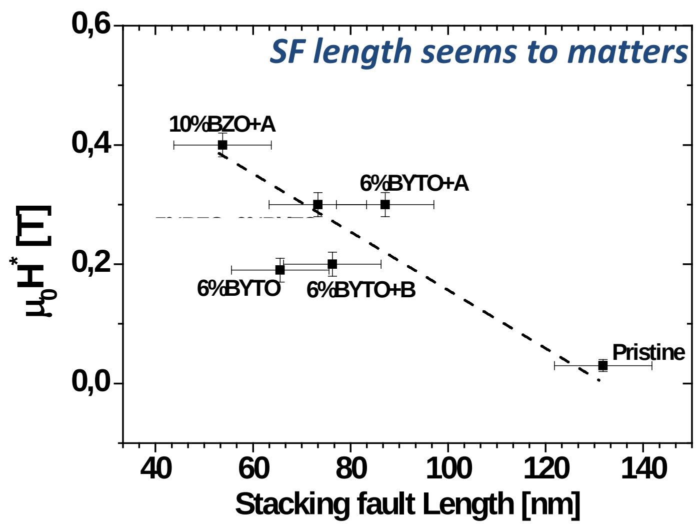


J. Gutiérrez, et al., Nat. Mat. (2007)
A. Llordés et al. , Nat. Mat. (2012)
M. Coll et al., SUST 26 (2013); SUST (2014)

The SF, what characteristics do really matter for vortex pinning ?







Ideal scenario for isotropic pinning:
Short SF and small Np

SF are key players to generate nanostrain, but how should we tune them ?

The challenges in YBCO nanocomposites from colloidal solution of preformed oxide nanoparticles

… a smart process though complex and still in its infancy

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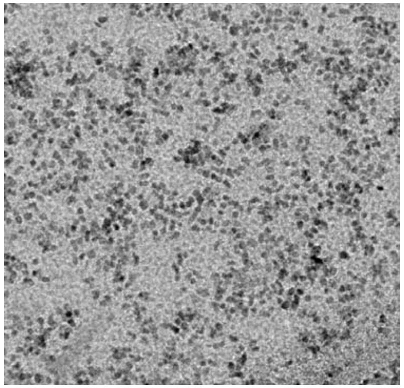
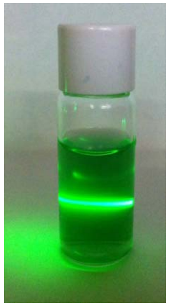
1. Oxide nanoparticles are scarcely **stable in alcoholic and ionic environment** of YBCO precursor solution **at high concentrations**

E. Solano et al., J Nanopart Res (2012) 14:1034

State of the art at EUROTAPES:

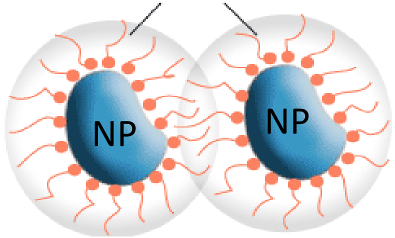


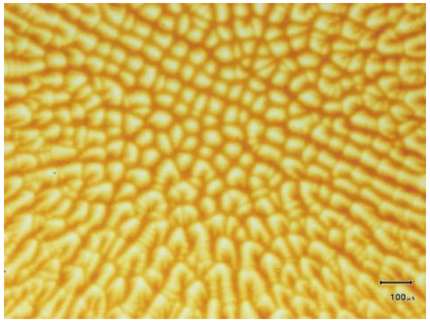
CeO_2 (2 ±0.4 nm)/YBCO-TFA

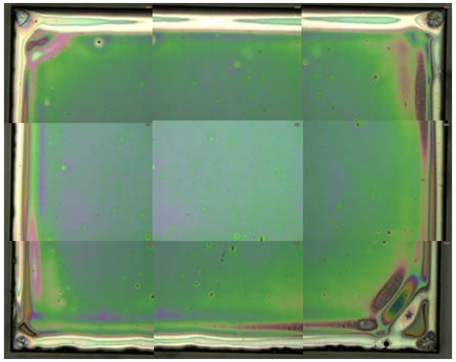


YBCO-TFA+ZrO_2 Np (8 nm)

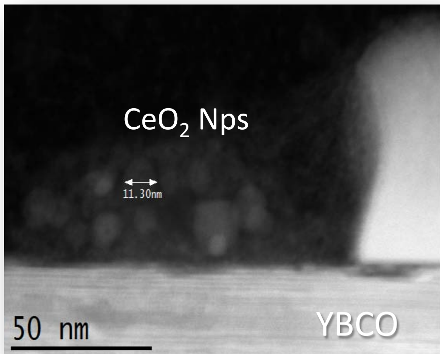
2. Too high concentrations of Np **stabilizing agents** may **induce inhomogeneous pyrolysis**



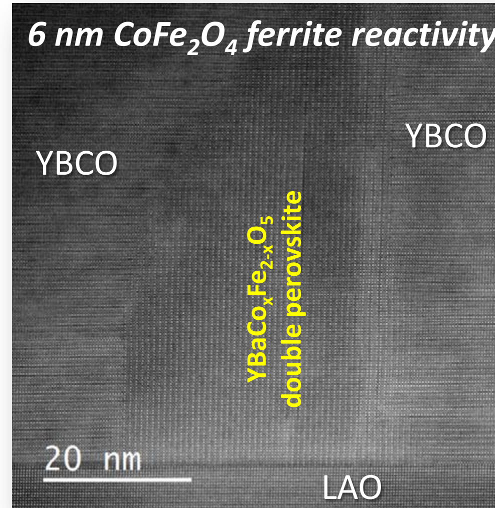




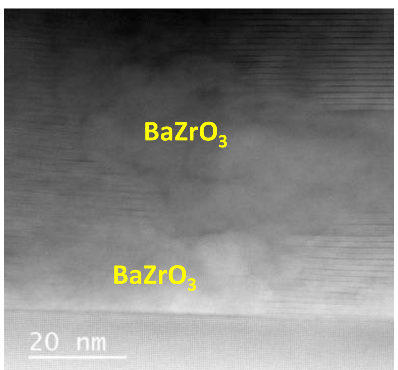
3. Growth of **colloidal solutions** tend to **hamper nanocomposites of small Np sizes**

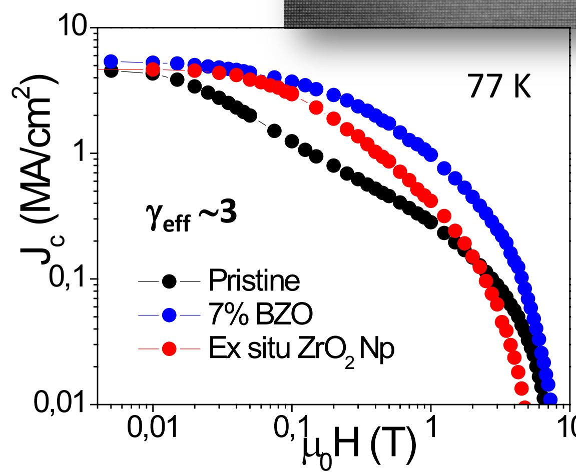


2 nm CeO_2 pushing effect



8 nm ZrO_2 Np: Coarsening





What is the best second phase composition ? How can we keep size, shape, distribution of preformed nanoparticles during YBCO growth ?

Conclusions

- CSD YBCO is a reality for cost-effective coated conductors with outstanding performances

- Strategic knowledge for being more marketable:
  - Thermo-viscoelastic properties of the gelified film for much thicker homogeneous pyrolyzed films
  - YBCO c-axis nucleation mechanisms for fast growth processes
  - Understanding buffer surface activity for c-axis nucleation on minimized reactivity conditions
  - key microstructure control of nanostrain in nanocomposites

Acknowledgements

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Keep going and let's make it possible !