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Transient Liquid Assisted Growth (TLAG), a method for increasing coated conductors throughput and meeting future

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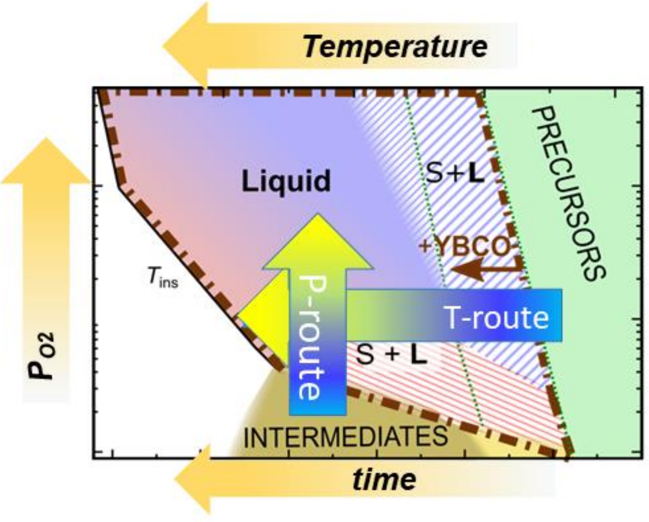
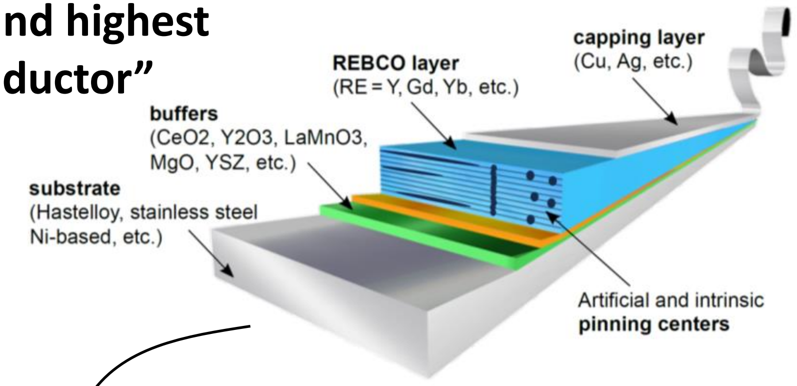
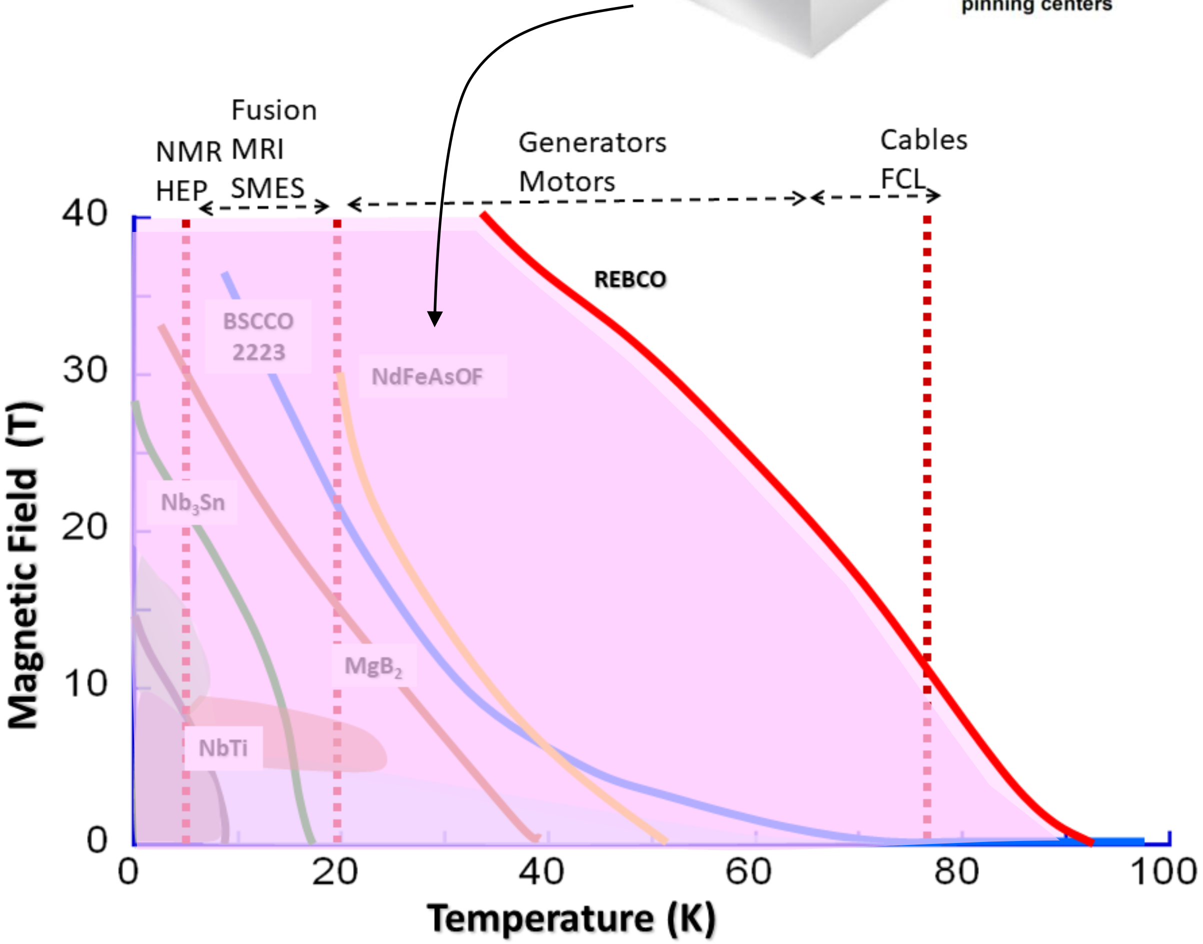


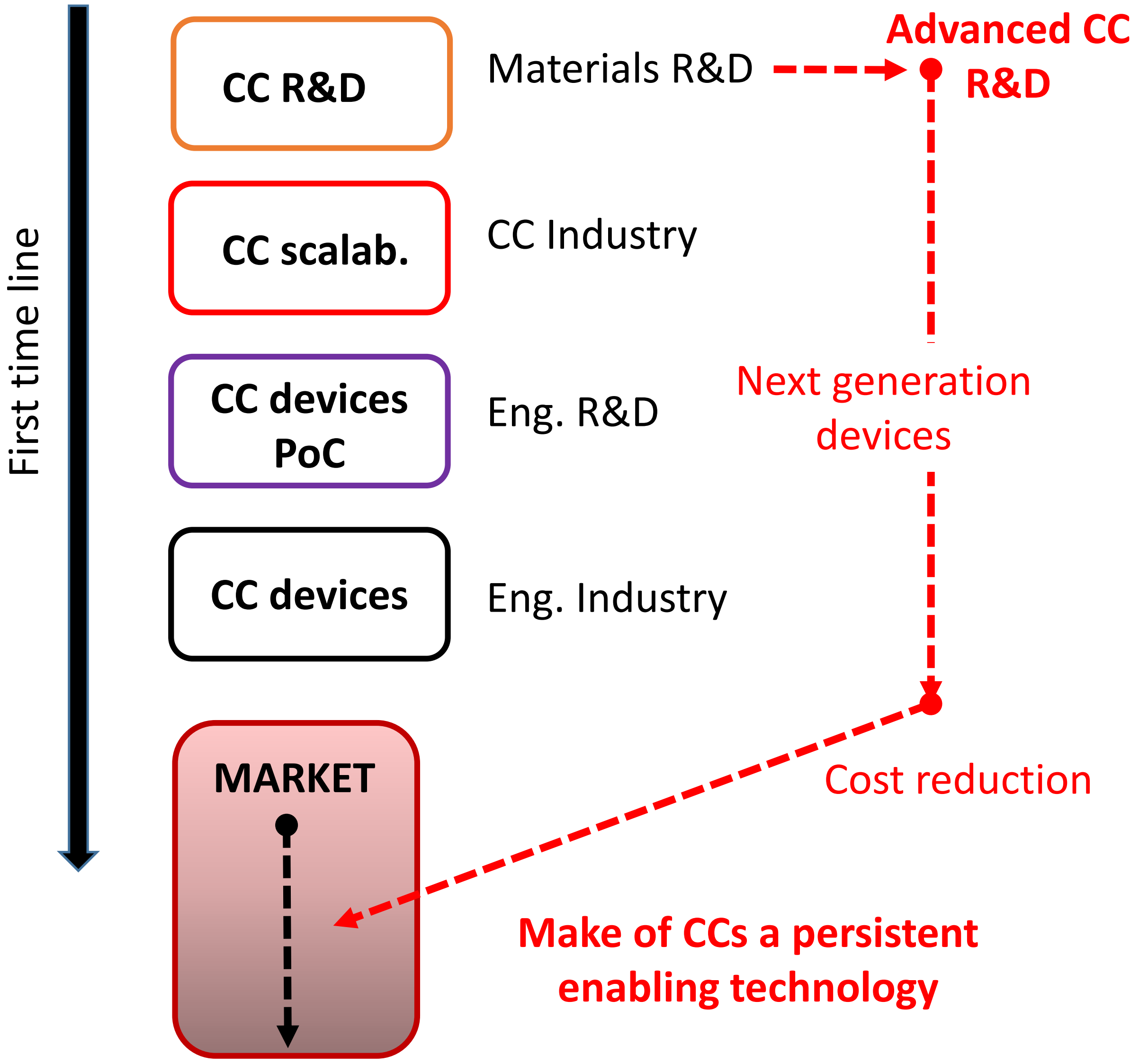
Work is supported by

REBCO COATED CONDUCTORS

“The highest Field and highest Temperature conductor”







CC R&D — Materials R&D

CC scalab. — CC Industry

CC devices PoC — Eng. R&D

CC devices — Eng. Industry

MARKET

Advanced CC R&D

Next generation devices

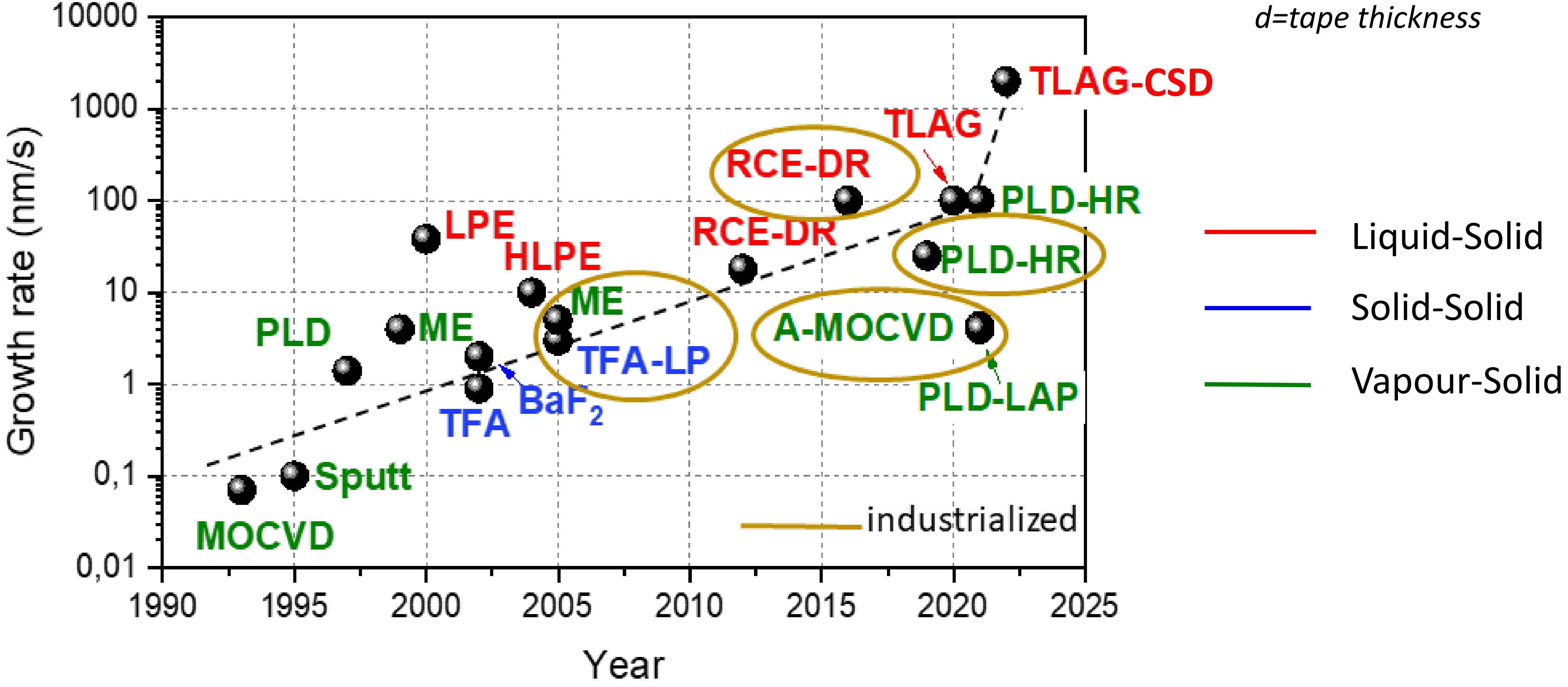
Cost reduction

Make of CCs a persistent enabling technology

Reaching high Growth Rate: A path towards cost reduction

Figure of merit: $\frac{Cost}{Perfomance} = \frac{total\ cost\ per\ year}{\mathbf{G}\ x\ L\ x\ W\ x\ (I_{c-w}/d)} = \frac{€}{kA\ x\ m}$

G= growth rate
W= tape width
L= tape length
d=tape thickness

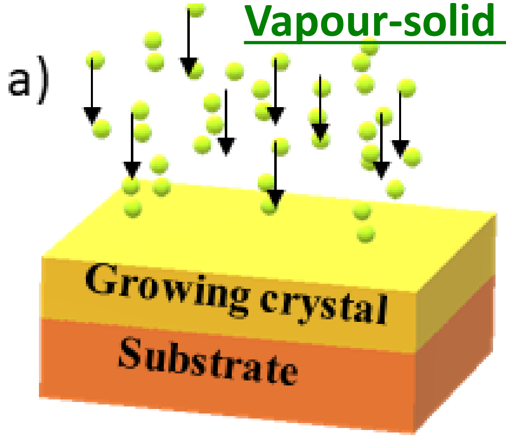


T. Puig et al, Nat Rev Phys (2023, doi.org/10.1038/s42254-023-00663-3)

REBCO growth processing

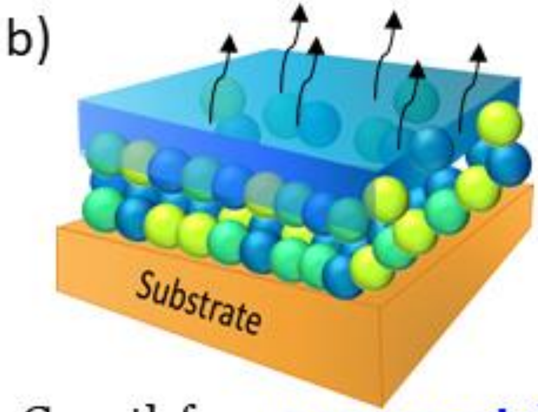
Supersaturation, σ, is the driving force for crystallization: **σ ∝ G** (growth rate)

Vapour-solid transformation



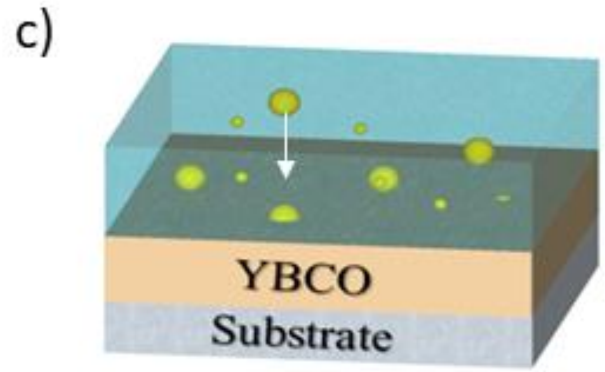
Growth from **vapour phase**
PLD, MOCVD, ME, MBE, Sputt

solid-solid gas mediated



Growth from **nanocrystalline solids**
TFA,**-MOD, BaF$_2$**

Liquid-solid



Growth from **liquid phase**
TLAG-CSD, RCE-DR, HLPE **, VLS**

$\sigma = (P_{ad} - P_{ad,e}) / P_{ad,e}$ Deposition rate
High vacuum environ.

$\sigma = f\,(\ln (P_{HF}^2 / P_{H_2O})$

$\sigma = (C_\delta - C_e) / C_e$ RE solubility,
Ba-Cu-O liquid

$P_{ad,e}$ = ad-atoms equilibrium pressure at surface growth front
P_{ad} = ad-atoms pressure at surface growth front

P_{HF} = HF partial pressure
P_{H2O} = water partial pressure

C_e = RE equilibrium concentration in the liquid
C_δ = RE actual concentration

Growth rate: G= 0.5-25 nm/s

G= 0.5-5 nm/s

G=10-1000 nm/s

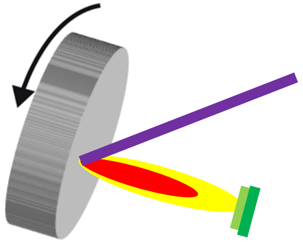
T. Puig et al, Nat Rev Phys (2023, doi.org/10.1038/s42254-023-00663-3), J. Driscoll et al, Nat Rev Mat (2021)

Transient Liquid Assisted Growth (TLAG)

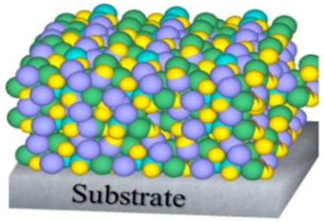
A new high throughput non-equilibrium kinetically controlled growth process

CSD

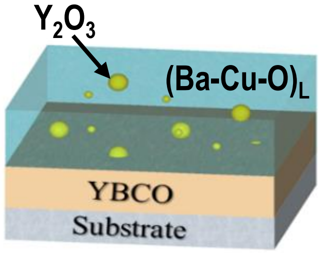
L. Saltarelli et al, ACS Appl. Mat. & Interf. (2022)
Patent EP22382741



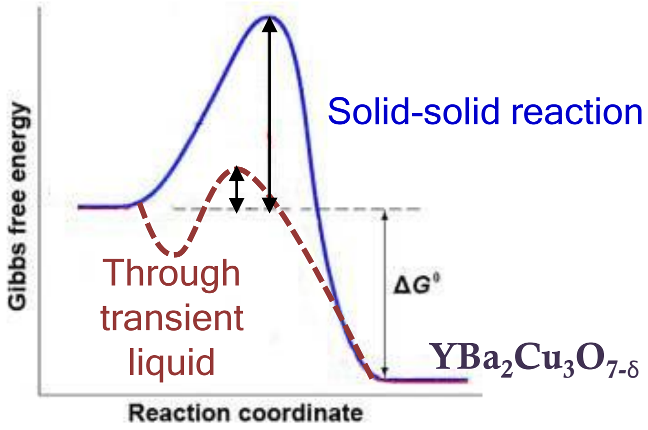
Low Temp PLD
A. Quetalto et al, SUST (2023)



Nanocrystalline precursors



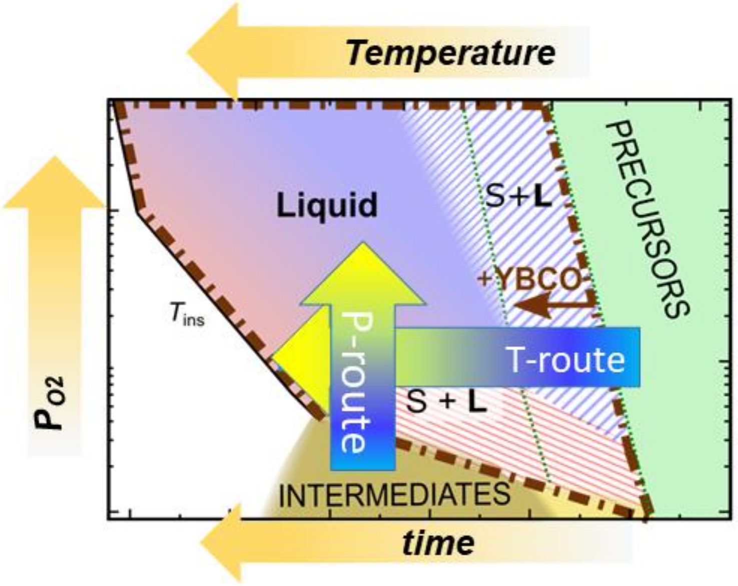
YBCO growth



CSD: $BaCO_{3(s)} + CuO_{(s)} + Y_2O_{3(s)}$
(mostly studied)

PLD: $(Ba\text{-}Cu^{I/II}\text{-}O)_s + Cu_2O_{(s)} + Y_2O_{3(s)}$

$$\rightarrow (Ba - Cu^{I/II}\text{-}O)_{(l)} + Y_2O_{3(s)} \rightarrow YBa_2Cu_3O_{7-\delta}$$



- **High throughput**
- **High growth rate** (2300 nm/s demostrated)
- **High performance** (2-5 MA/cm^2 at 77K)
- **Uses simple reactor**
- **Large area processing**
- **Low cost/performance ratio**

100 nm/s by **ultrafast-PLD** EuBCO/BHO
(transient liquid growth at high T PLD)

Y. Wu, Materials & Design 224 (2022)

L. Soler et al., Nat Comm (2020), S. Rasi, et al, Advance Science (2022)

WHAT DOES CONTROL TLAG ?

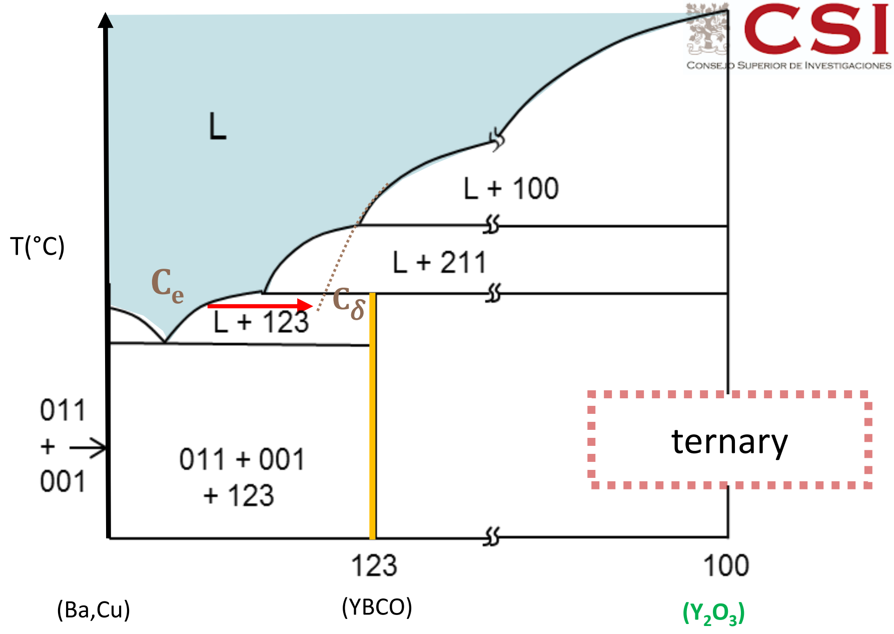
- **Supersaturation** $\sigma = (C_\delta - C_e) / C_e$
  C_e: RE equilibrium concentration
  - RE solubility (RE= Y, Gd, Sm, Yb, …)
  - Ba/Cu Liquid composition

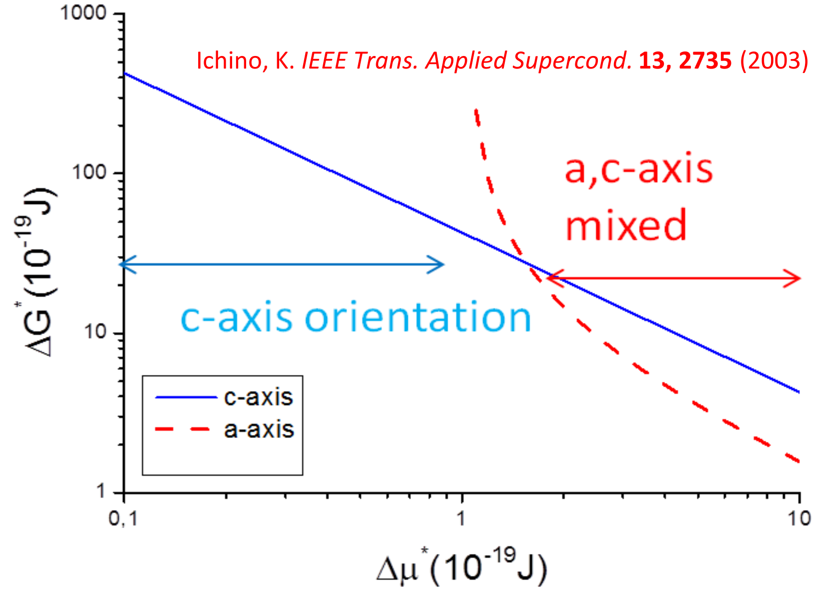
- Thermodynamic parameters: T, P_{O2}
- Kinetic parameters: heating ramp, pressure jump, gas velocity, P_{total}

- **C-axis growth** is controlled by supersaturation:

$$\boxed{\Delta\mu = kTln\frac{C_\delta}{C_e} = kTln(\sigma + 1)}$$

- TLAG is a non-equilibium process of **high supersaturation** and **ultrahigh growth rate**
  - high density of pinning defects is generated
  - pre-formed nanoparticles can be embeded



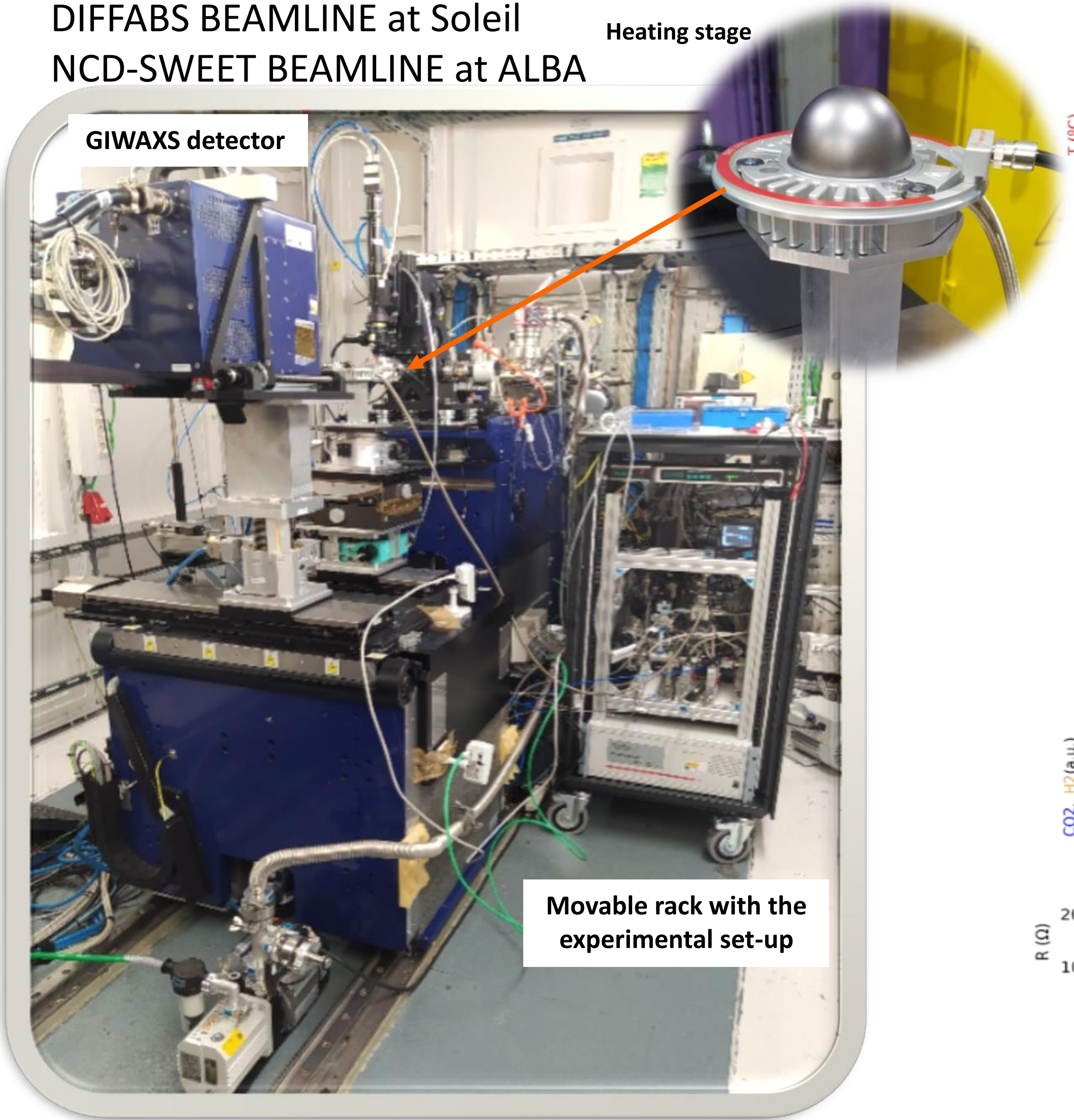


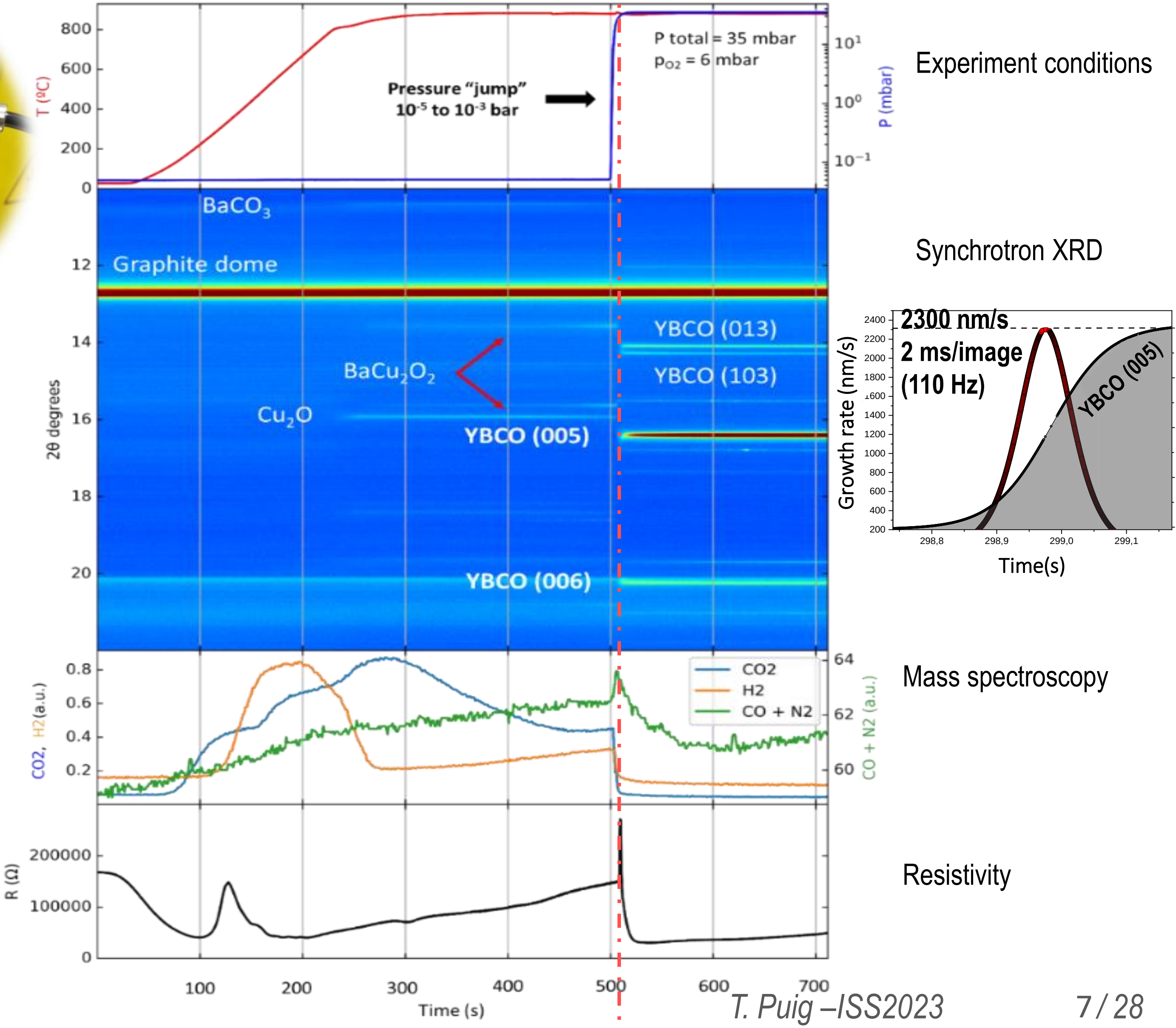
Ichino, K. *IEEE Trans. Applied Supercond.* **13, 2735** (2003)

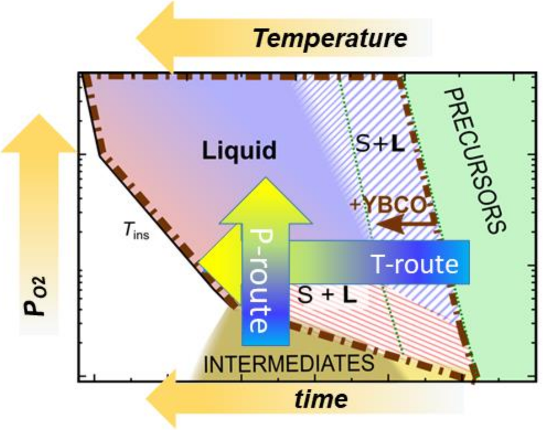
T. Puig et al, Nat Rev Phys (2023, doi.org/10.1038/s42254-023-00663-3)

Synchrotron installation

DIFFABS BEAMLINE at Soleil
NCD-SWEET BEAMLINE at ALBA







TLAG T-route

synchrotron
in-situ XRD

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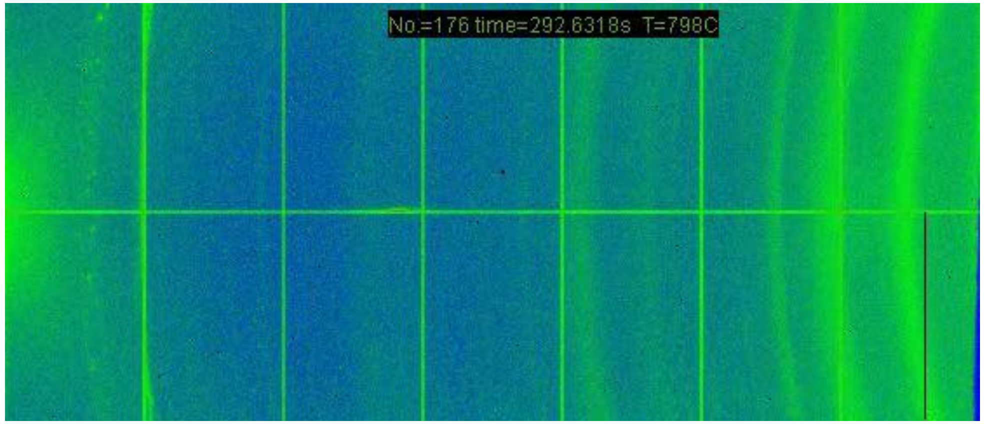
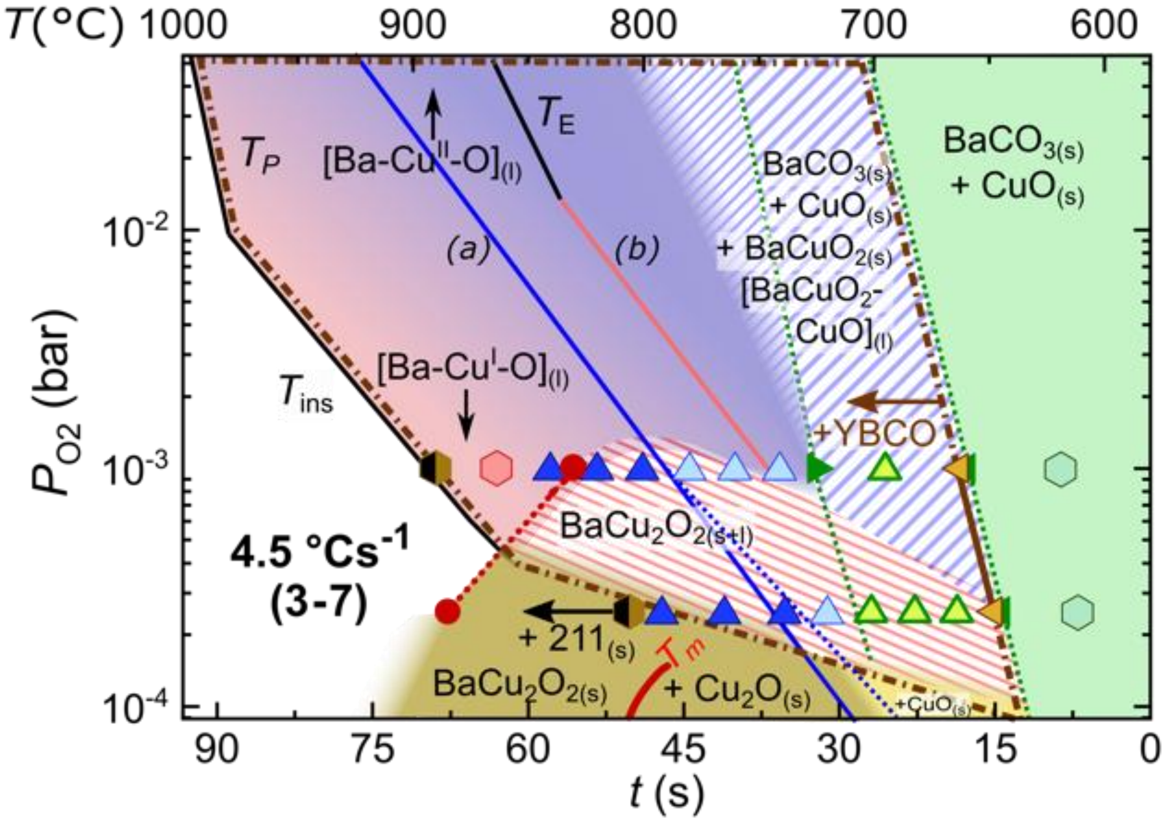
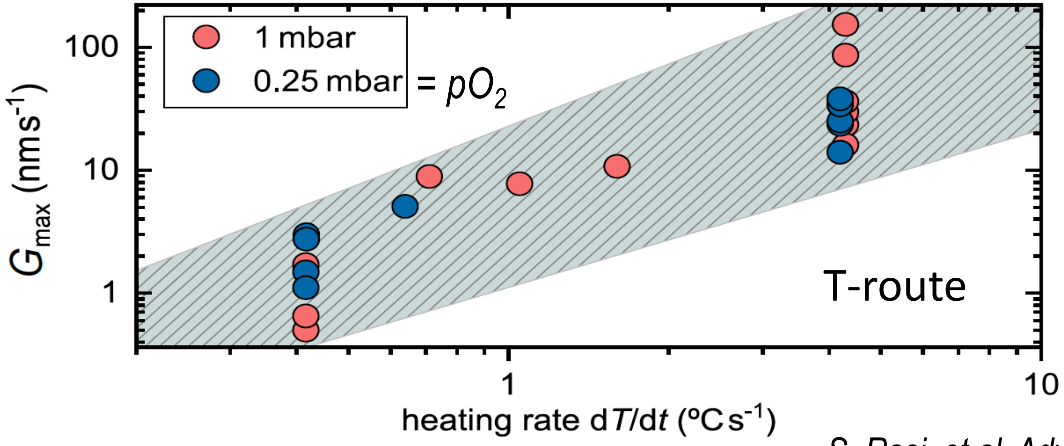
Kinetic process strongly differing from equilibrium reported phases



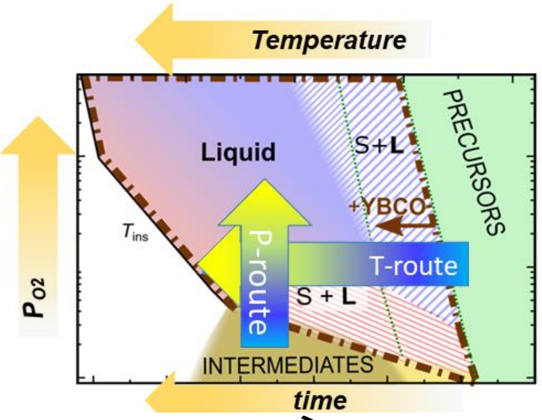




△ YBCO + $BaCO_{3(s)}$ + $CuO_{(s)}$
△ YBCO + $BaCuO_{2(s)}$ + $CuO_{(s)}$
△ YBCO + $CuO_{(s)}$
▲ YBCO + $Cu_2O_{(s)}$
⬡ YBCO
⬢ YBCO decomp.

T_E — $BaCuO_{2(s)}$+$CuO_{(s)}$ → $[BaCuO_2+CuO]_{(l)}$
T_m — $BaCu_2O_{2(s}$→ $[BaCu_2O_2]_{(l)}$
(a) — $CuO_{(s)}$ → $Cu_2O_{(s)}$
(b) — $BaCuO_{2(s)}$ → $BaCu_2O_{2(s)}$

S. Rasi, et al, Advance Science (2022)



TLAG T-route

Kinetic process strongly differing from equilibrium reported phases

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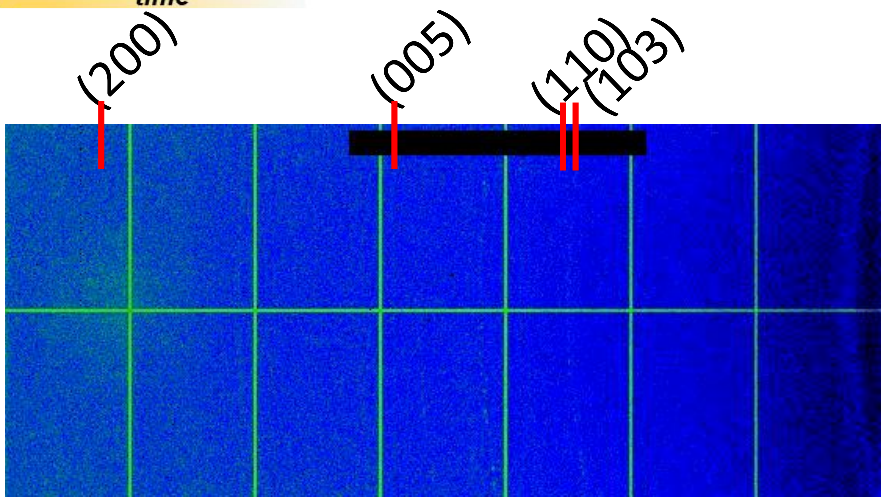
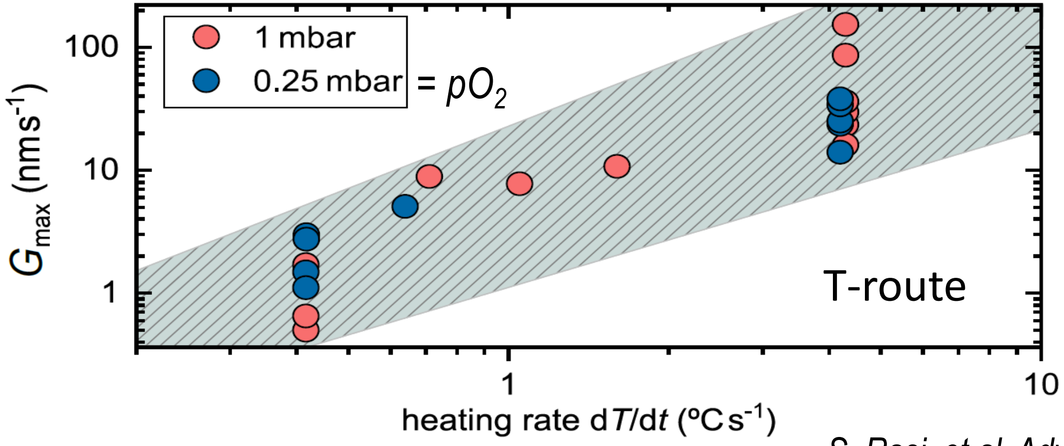
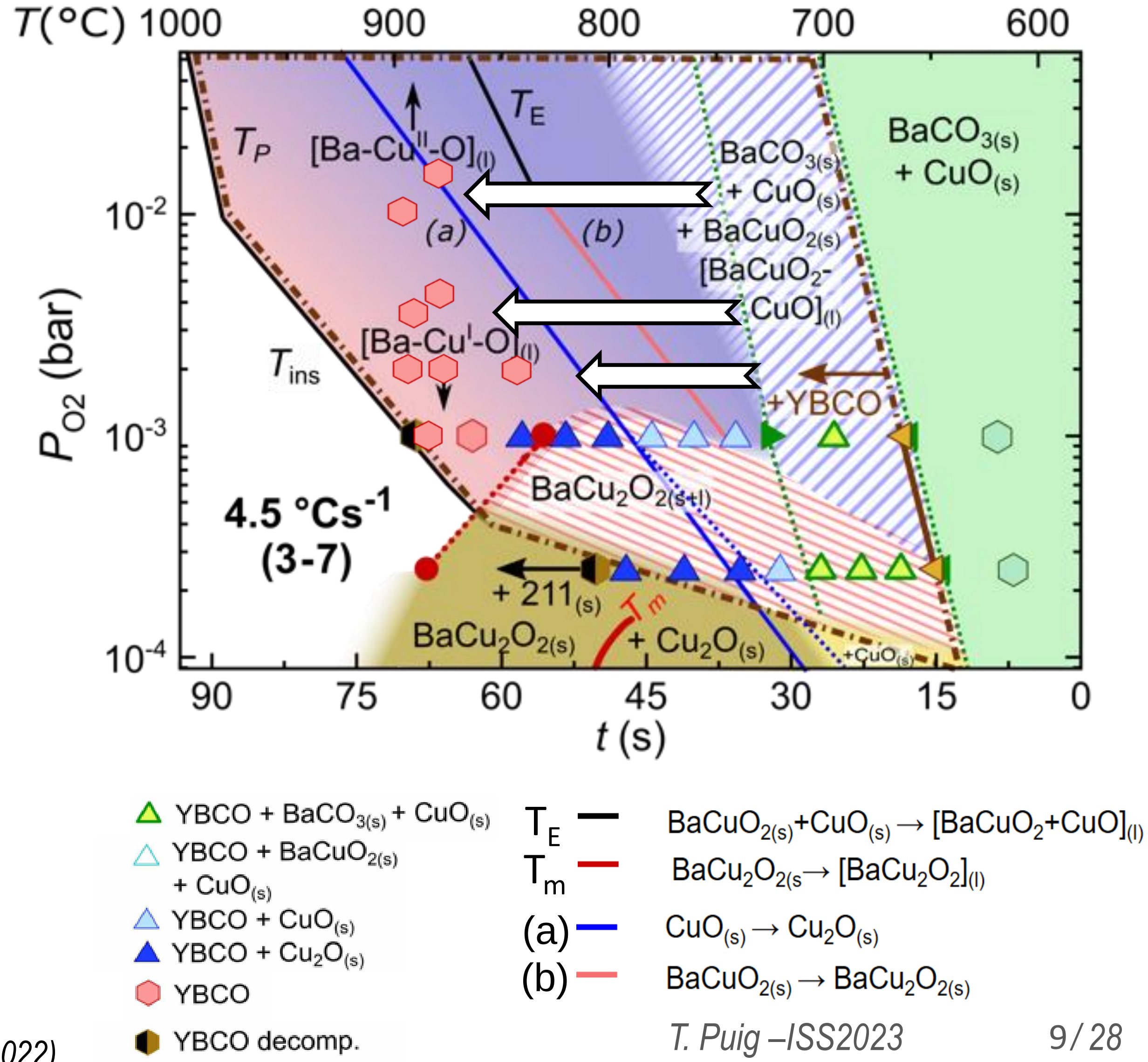




S. Rasi, et al, Advance Science (2022)



TLAG P-route

synchrotron
in-situ XRD

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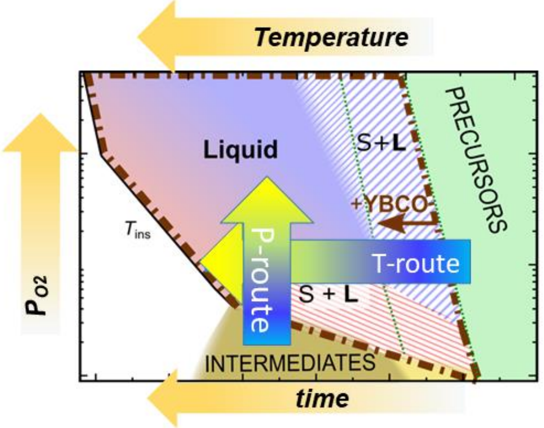
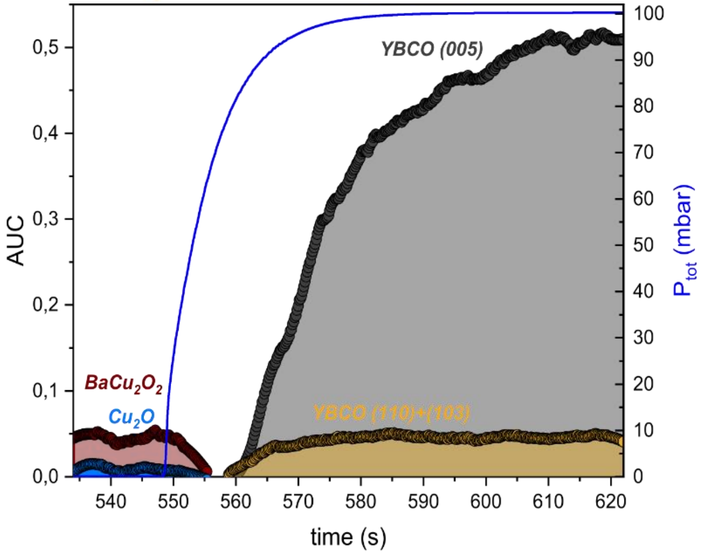
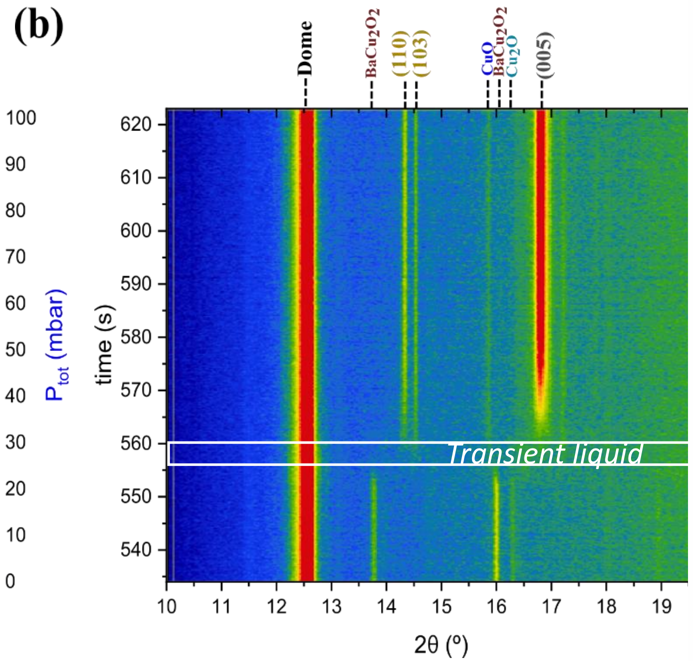
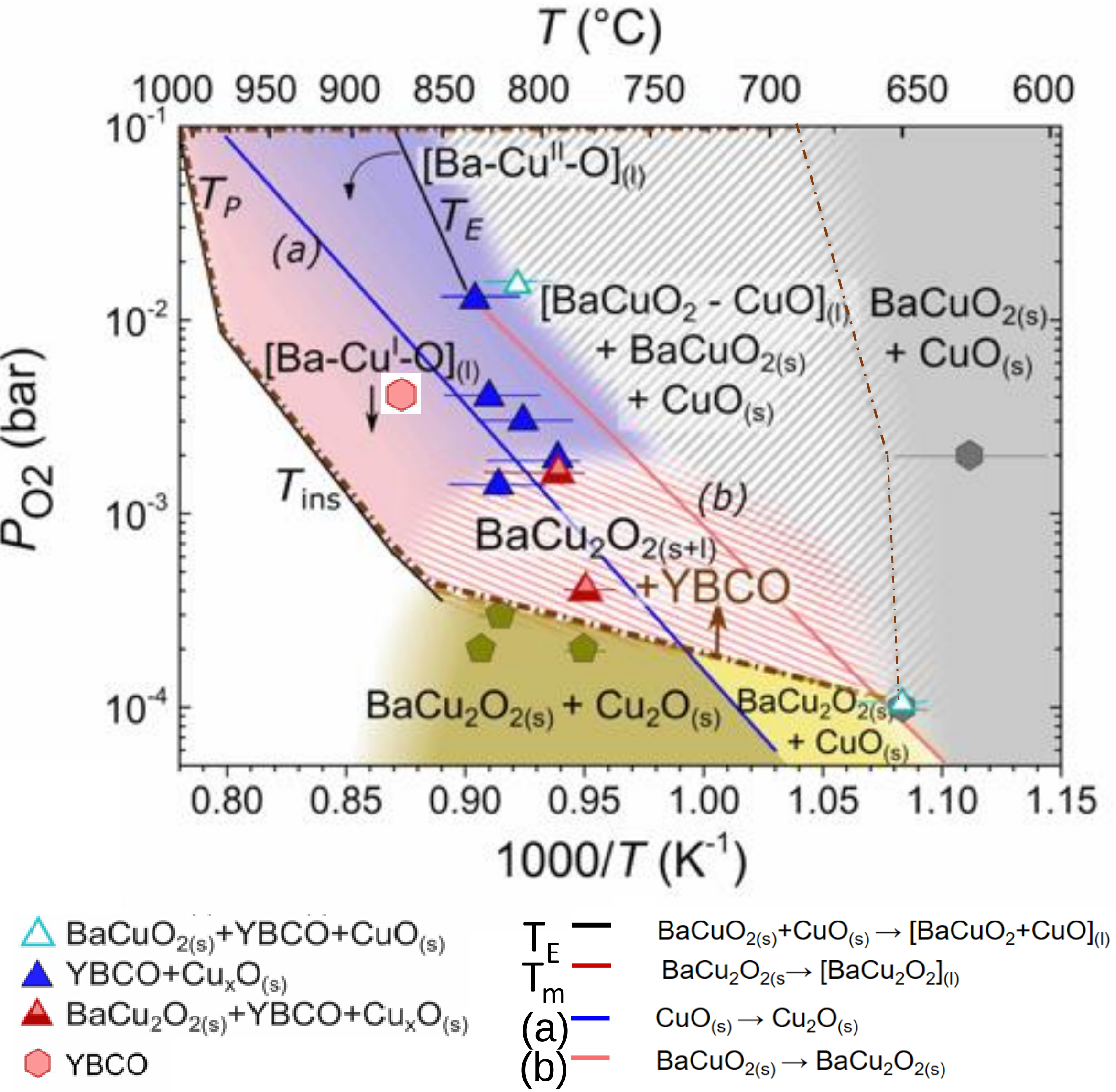
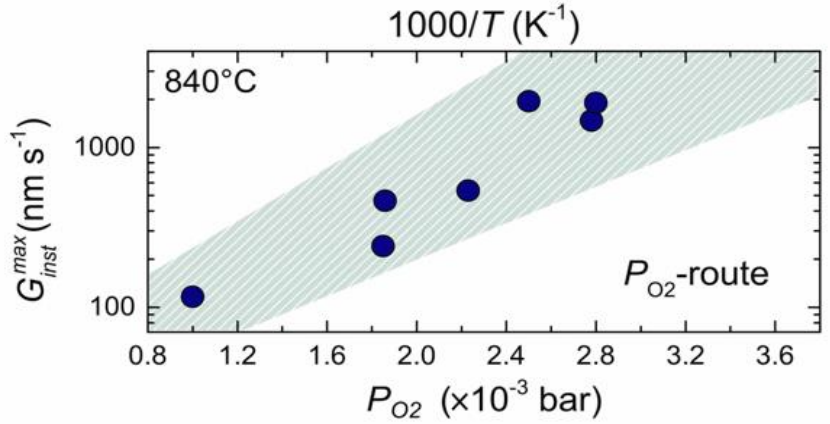
Kinetic process decoupling $BaCO_3$ reaction from YBCO formation





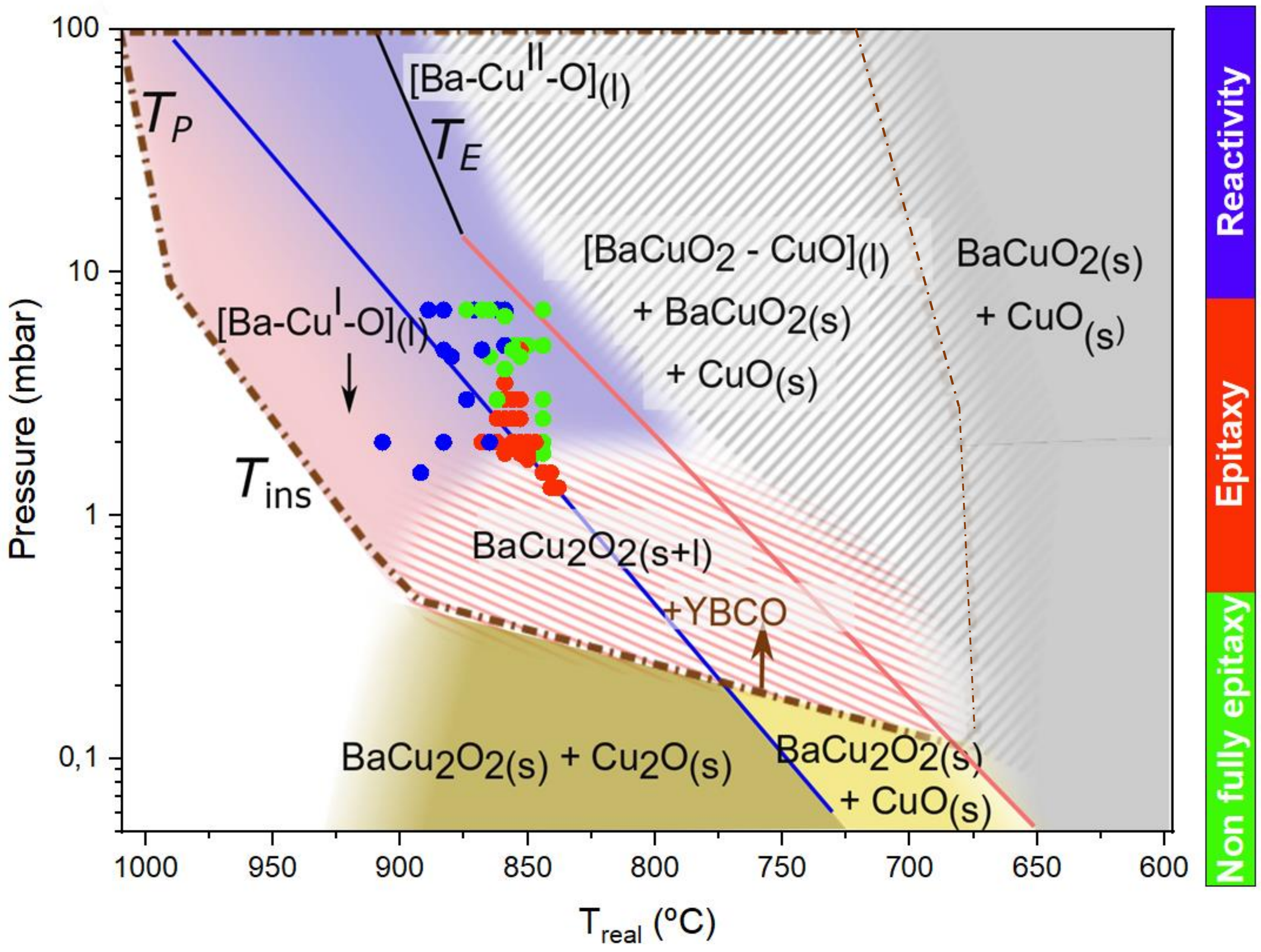


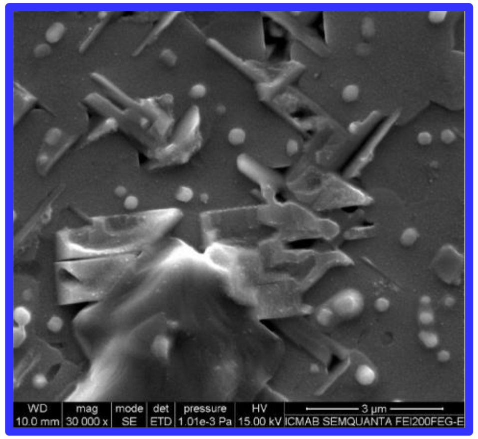


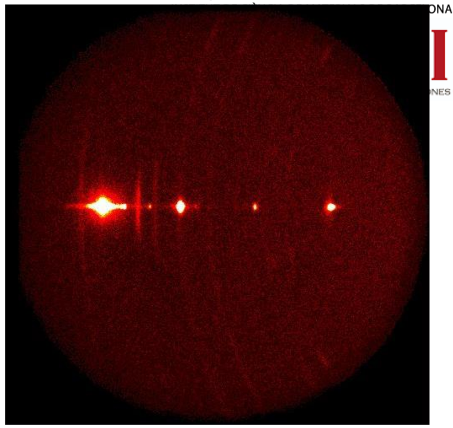


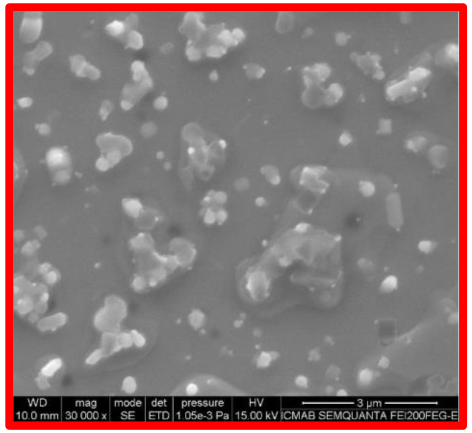
S. Rasi, et al, Advance Science (2022)

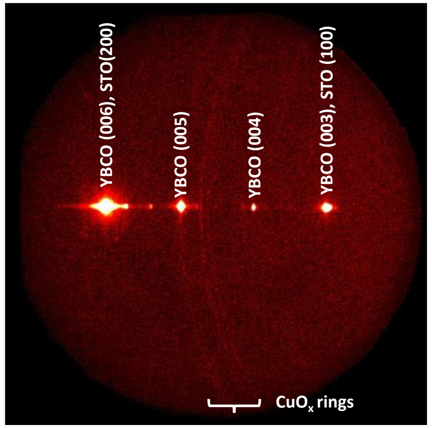
YBCO P-route epitaxial windows on STO

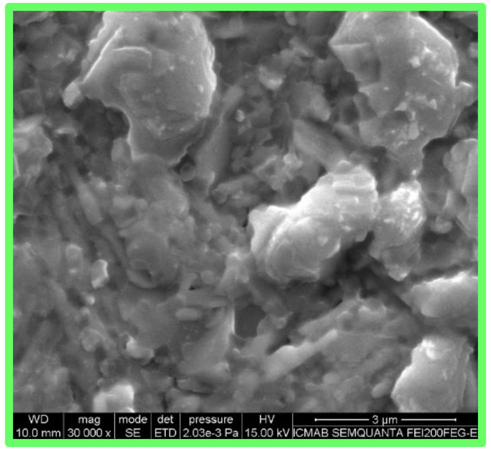


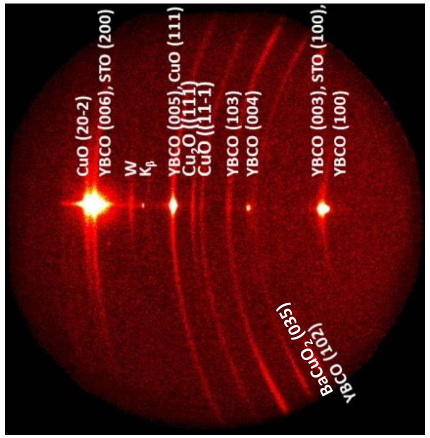






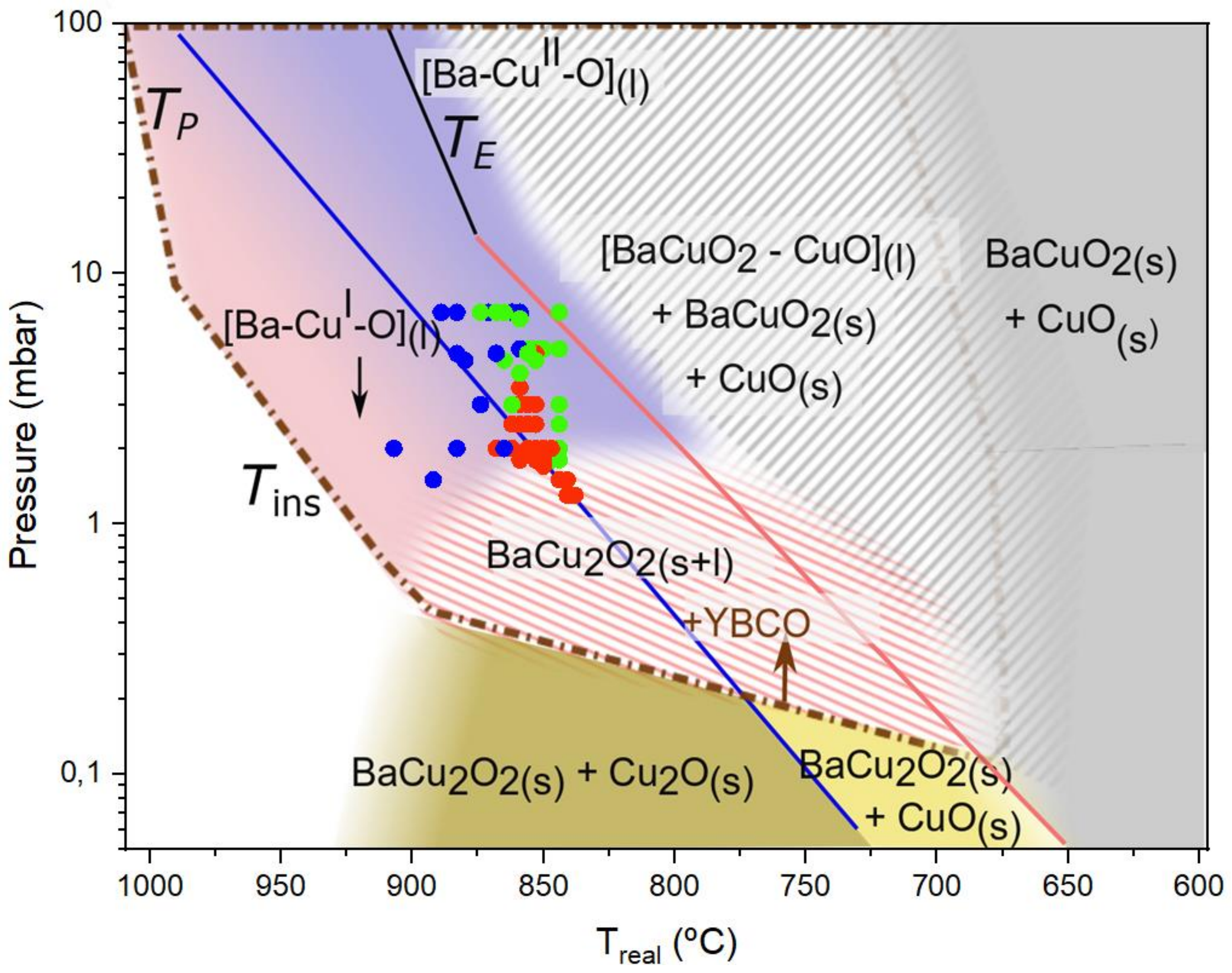




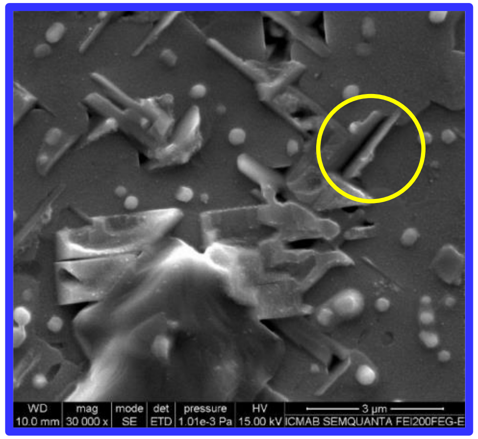


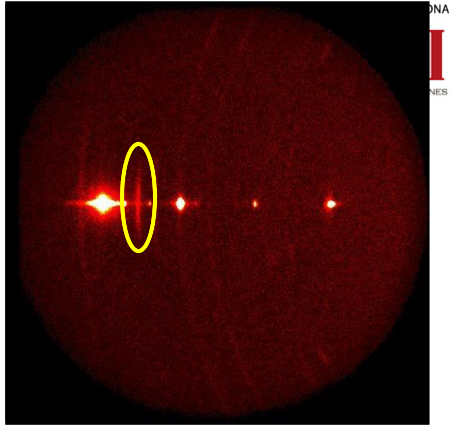
CuO segreation at tthe sufrace depends on the liquid composition chosen

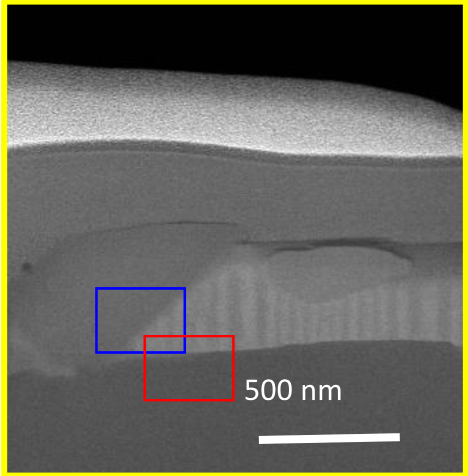
YBCO P-route epitaxial windows on STO

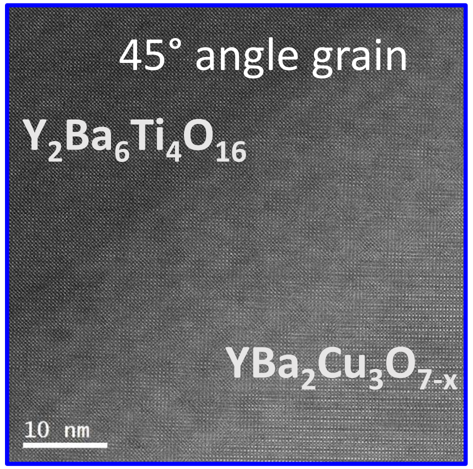


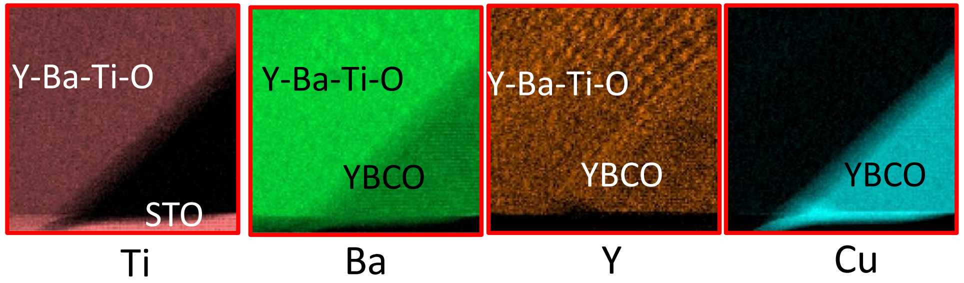
Reactivity





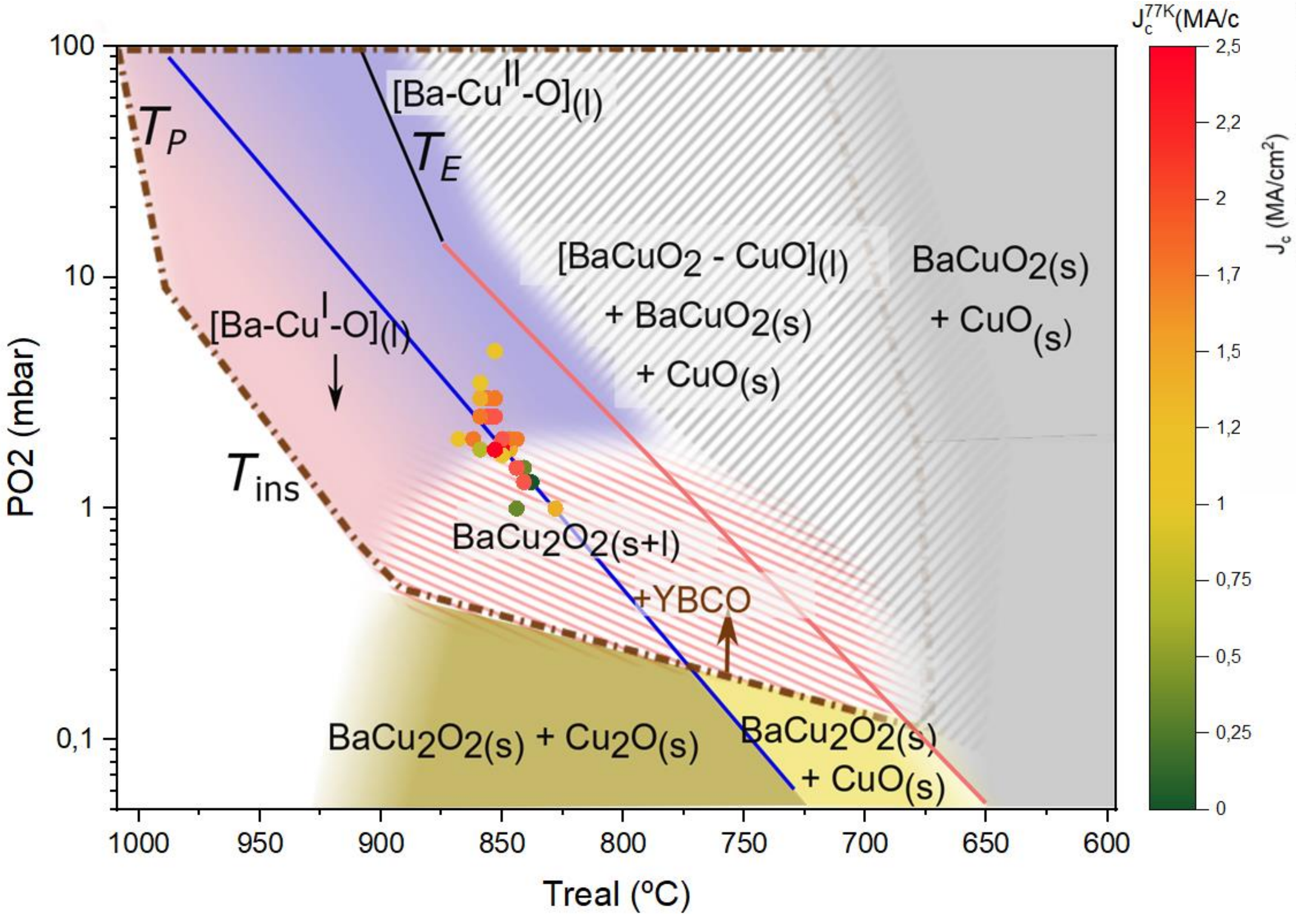




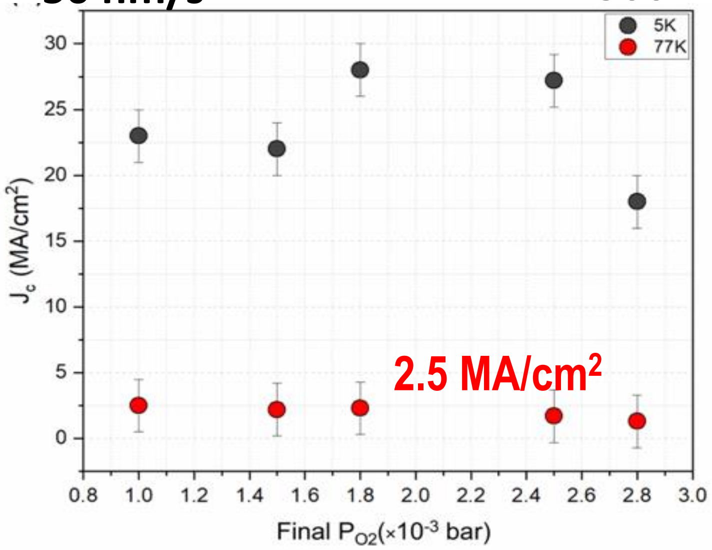


Liquid corrosion needs to be considered and minimized (buffer layers, RE, process conditions)

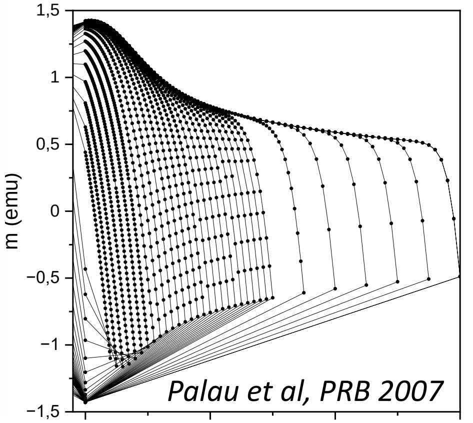
Critical currents at different growth conditions



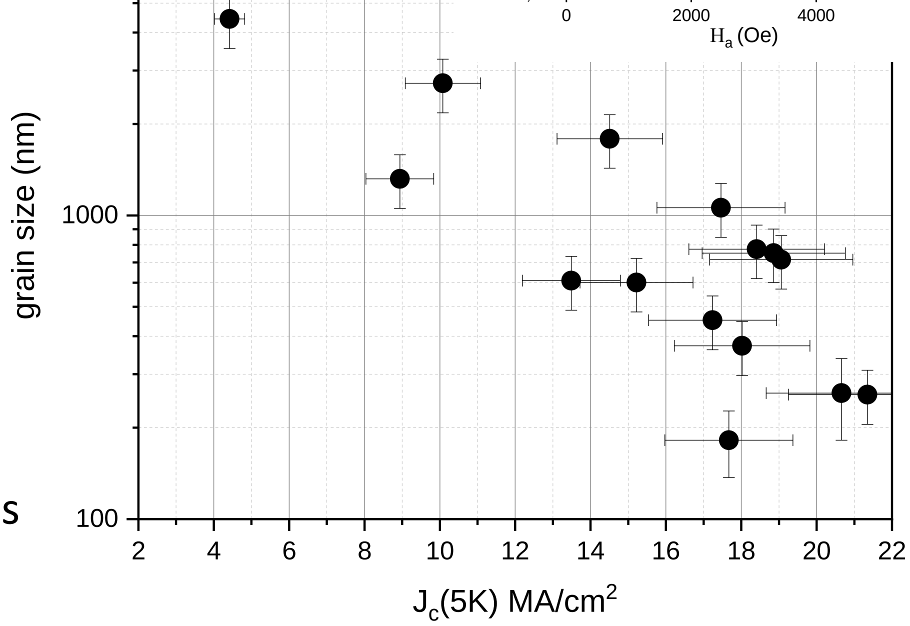
50 nm/s → 1500 nm/s



2.5 MA/cm^2



Palau et al, PRB 2007

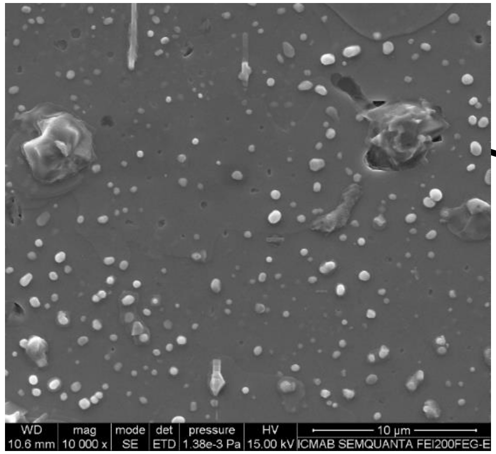


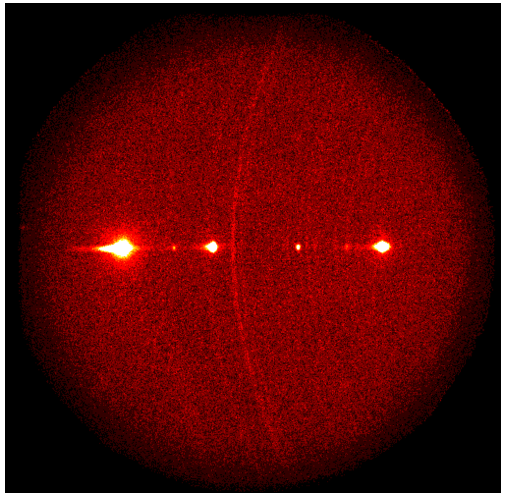
High nucleation densities (small grain sizes) favor high critical currents

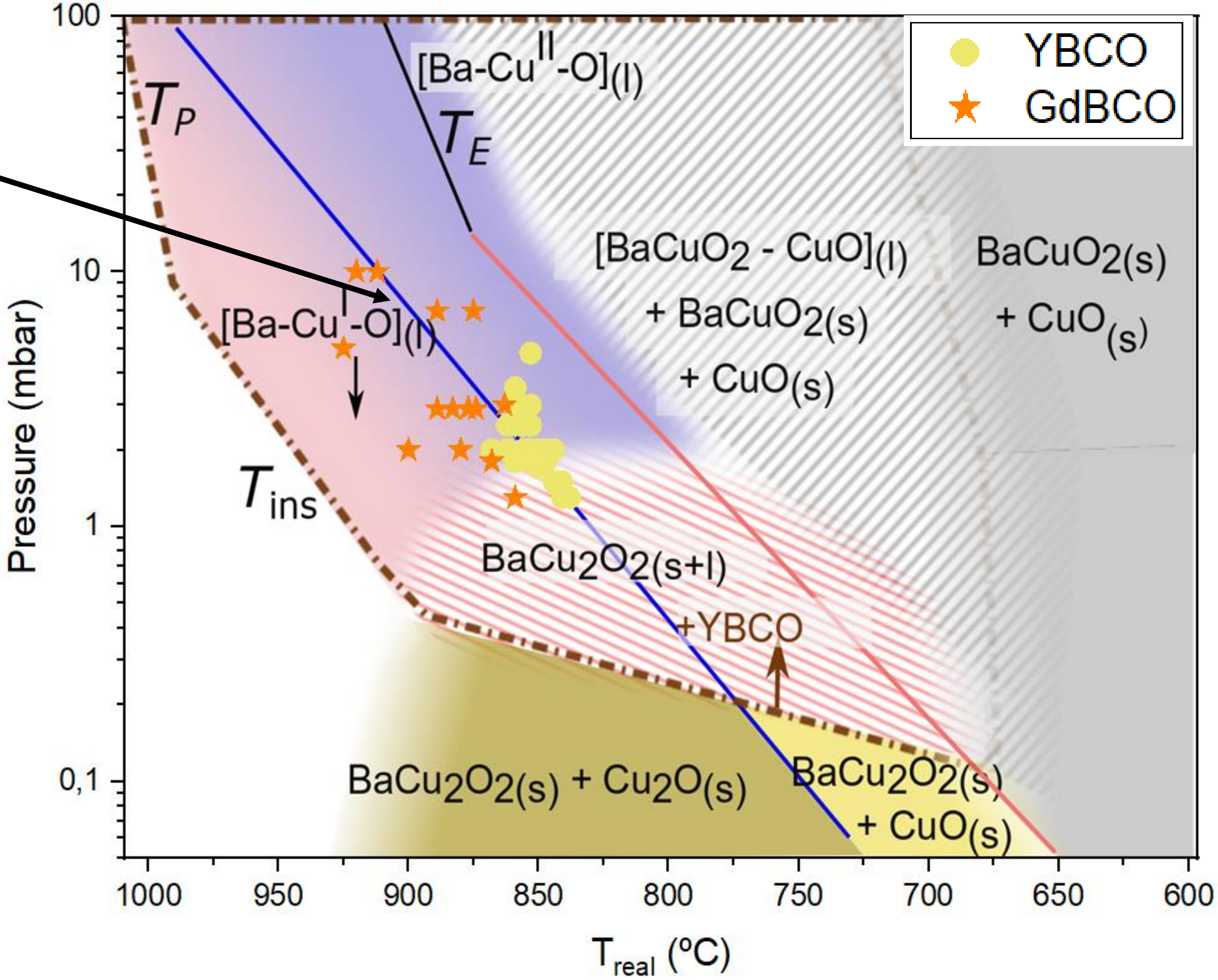
In agreement with BaF$_2$ methods (*Solovyov et al, SUST, 2008)*

S. Rasi, et al, Advance Science (2022)

GdBCO vs YBCO c-axis window on STO substrates in P-route







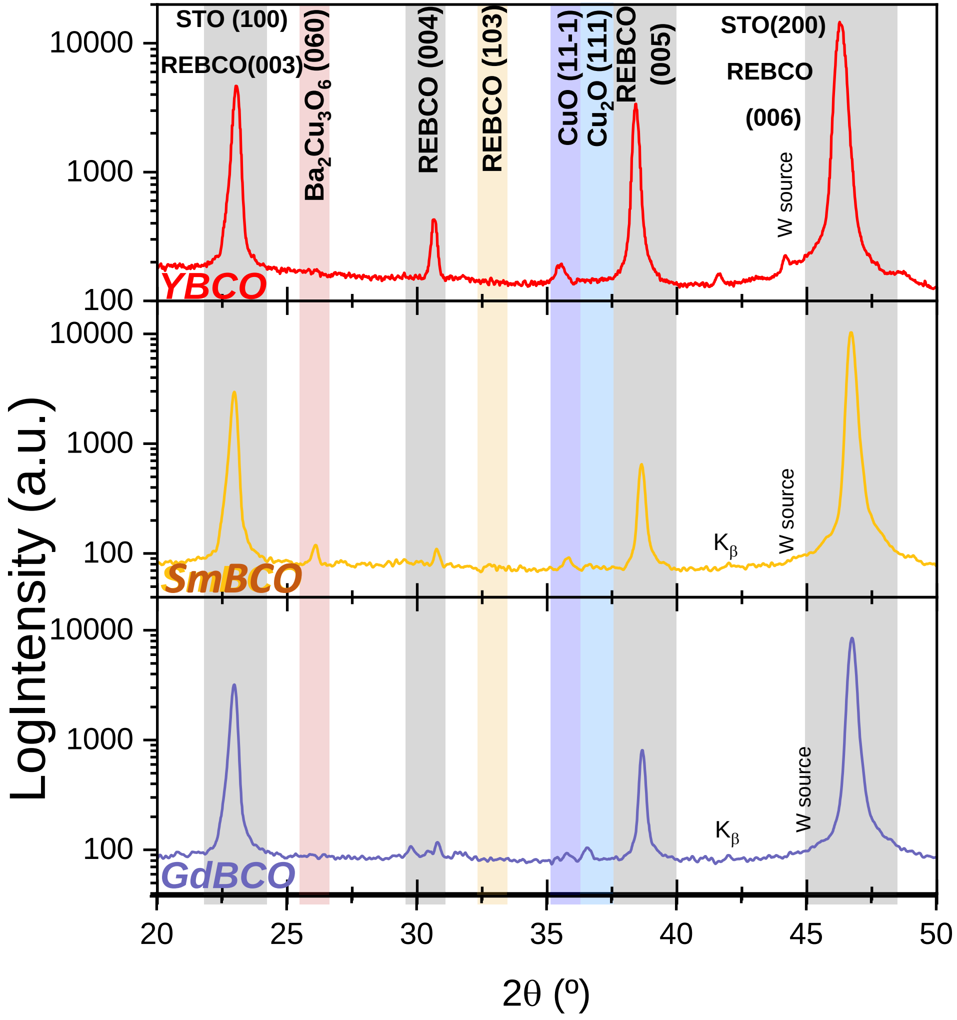
The RE modifies:

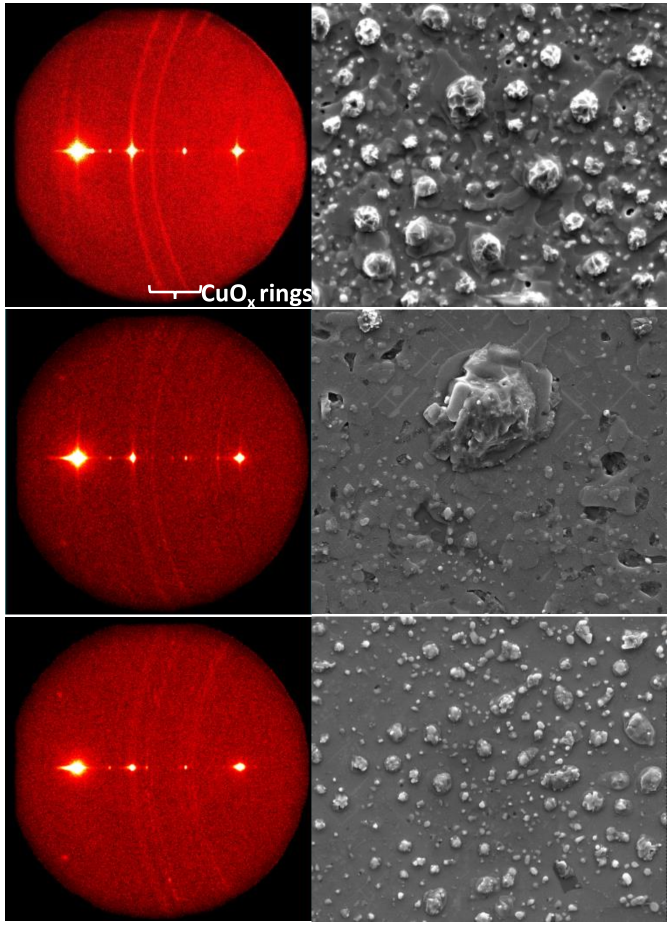
- Epitaxial windows
- Supersaturation value
- Solubility in the liquid
- Nucleation density
- Growth rate

GdBCO c-axis window is larger than YBCO. It also avoids reactivity with the STO substrate
This suggests a larger nucleation rate for GdBCO

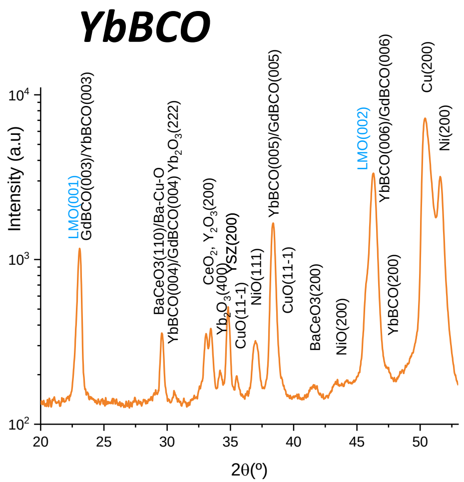
REBCO films with RE = Y, Gd, Sm, Yb

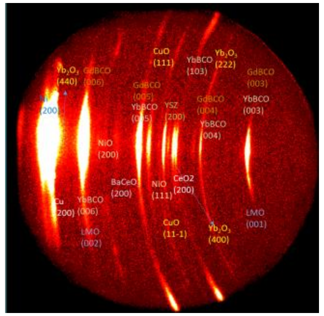
P-route examples on STO

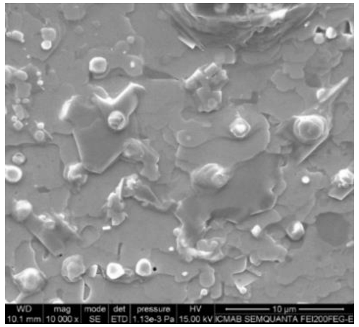




T-route example on CC



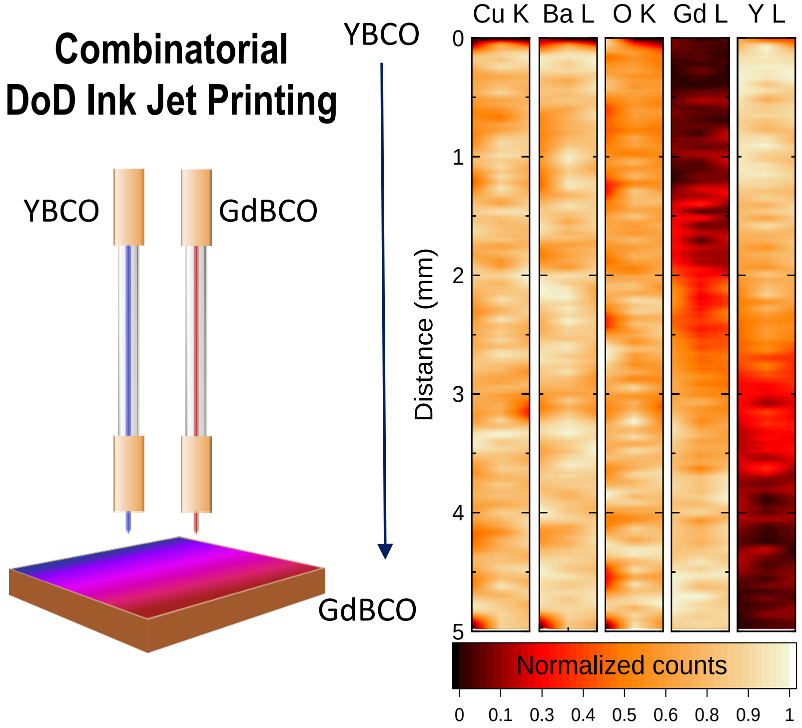


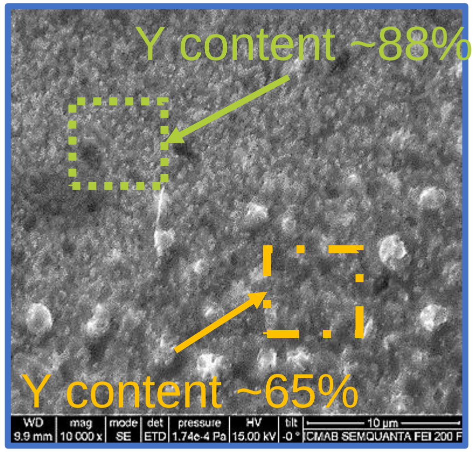


TLAG is compatible with REBCO film growth with different RE

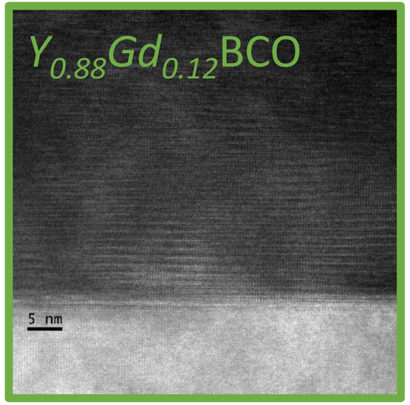
High Throughput Experimentation using Compositional Gradients enabling ML aproaches

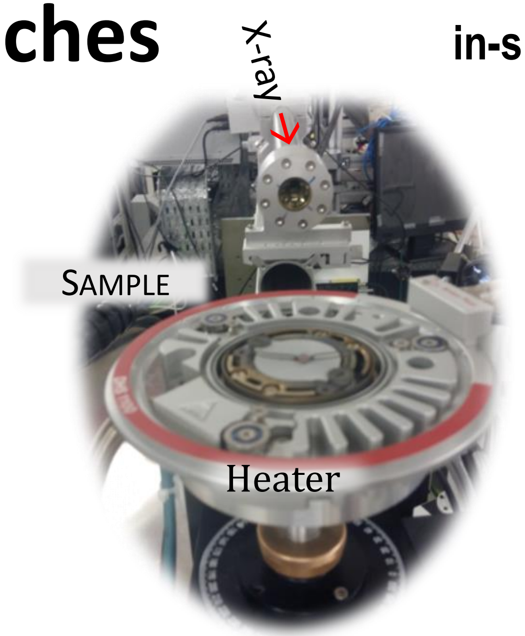
Combinatorial DoD Ink Jet Printing



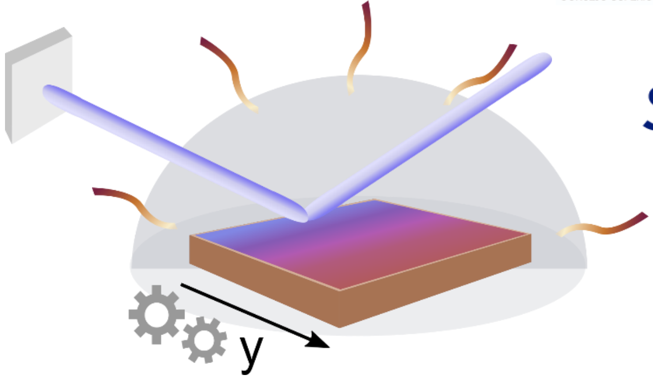


FIB cut

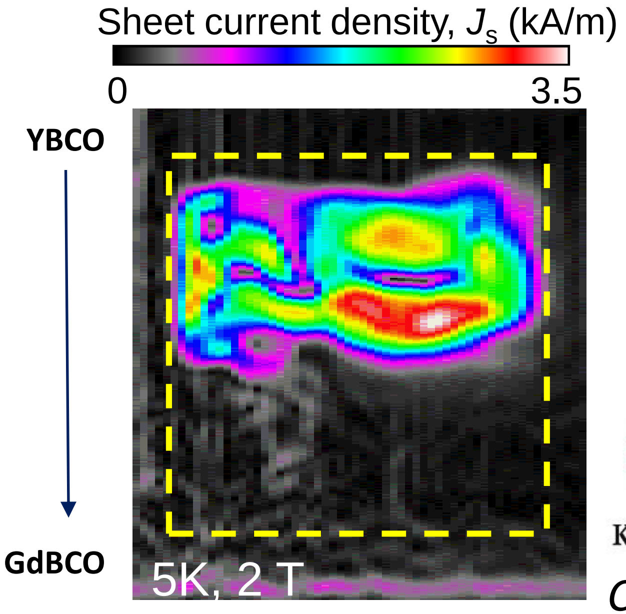


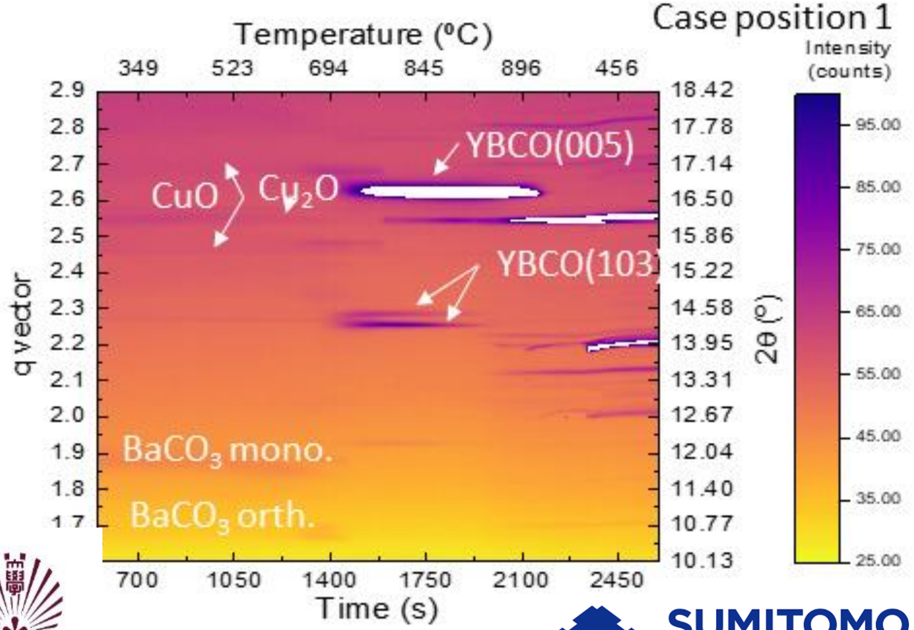


in-situ synchrotron XRD



Data is segmented by positions for analysis

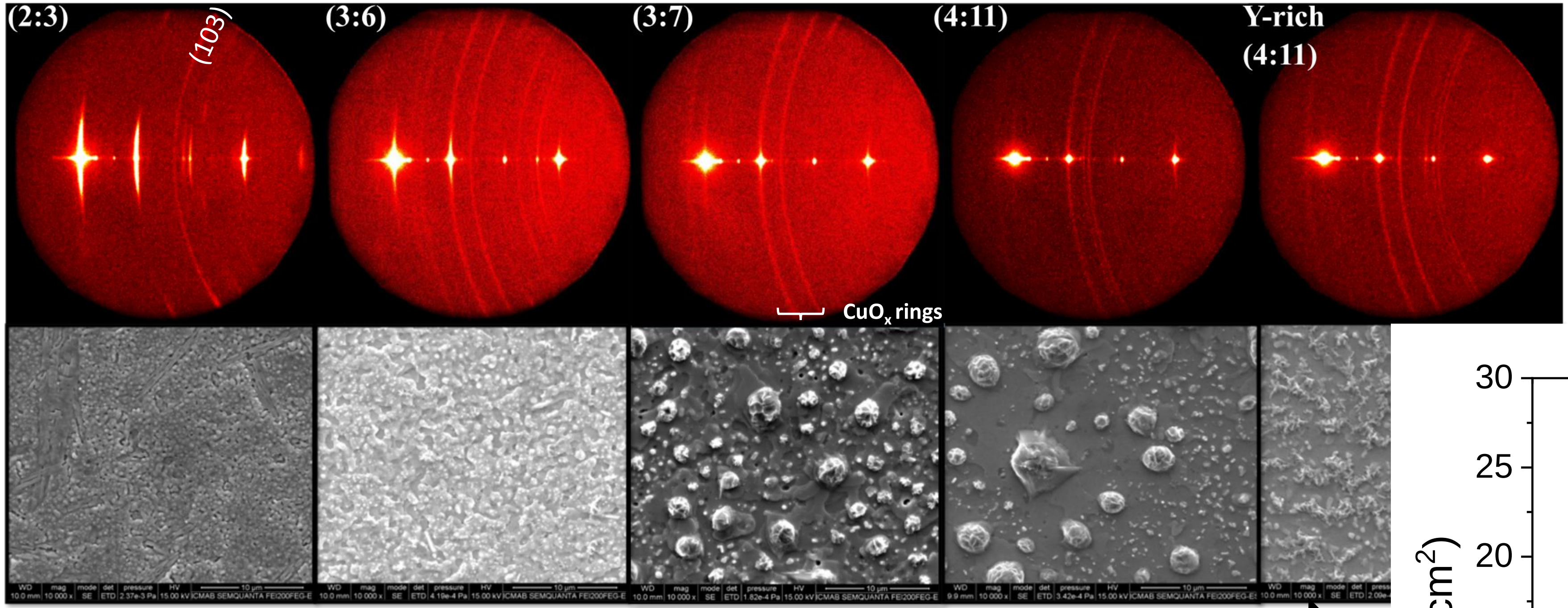




Collab. T. Kiss

Ba:Cu liquid composition, a way to control the supersaturation

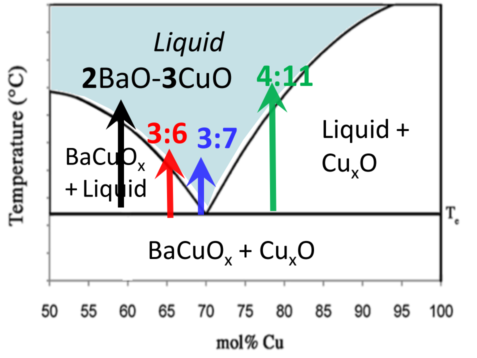
ICMAB
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA
EXCELENCIA SEVERO OCHOA
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

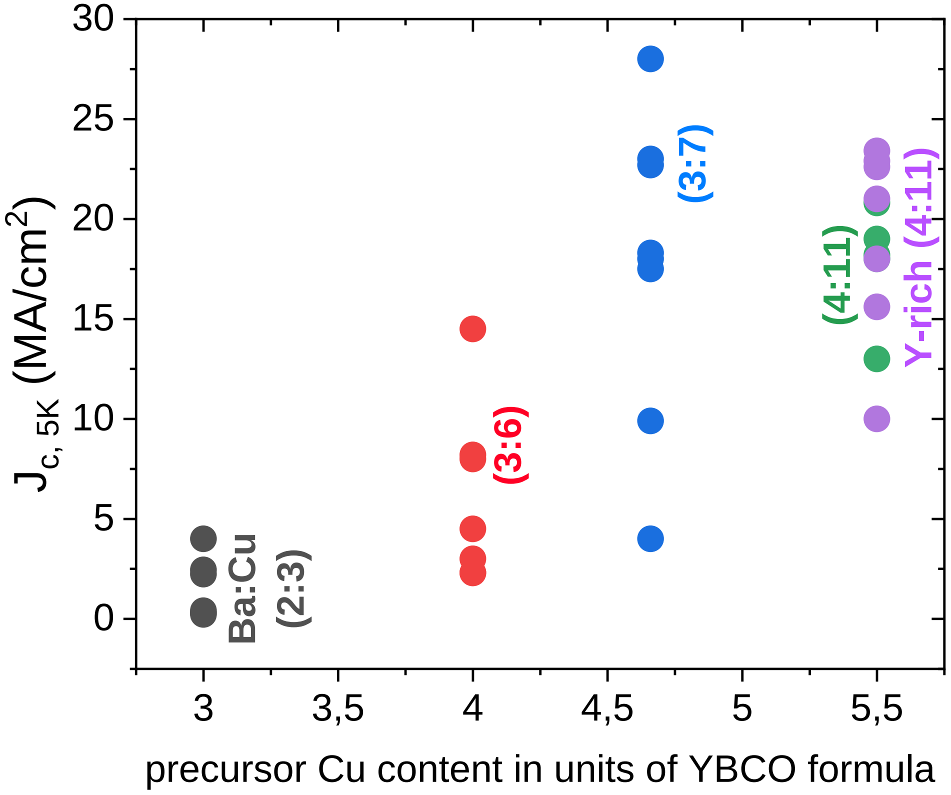


-Cu Supersaturation decreases +Cu

but Cu in excess needs to be expelled to the film surface

Experiments for YBCO composition





The (Ba:Cu) liquid composition:

Determines the supersaturation

c-axis growth

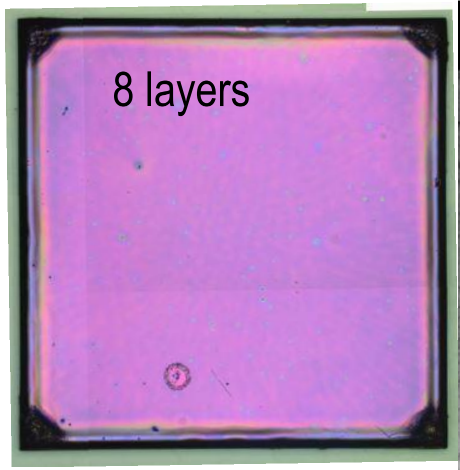
Nucleation density

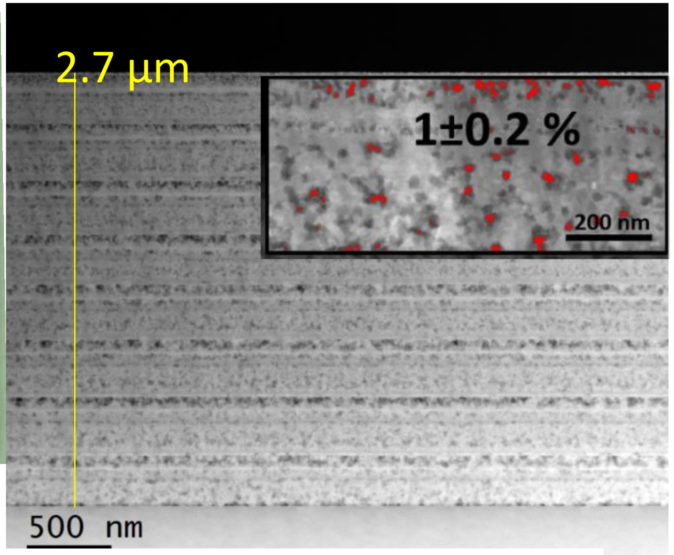
Growth rate

J_c at self-field

(3:7) is a good compromise
(our mostly chosen composition)

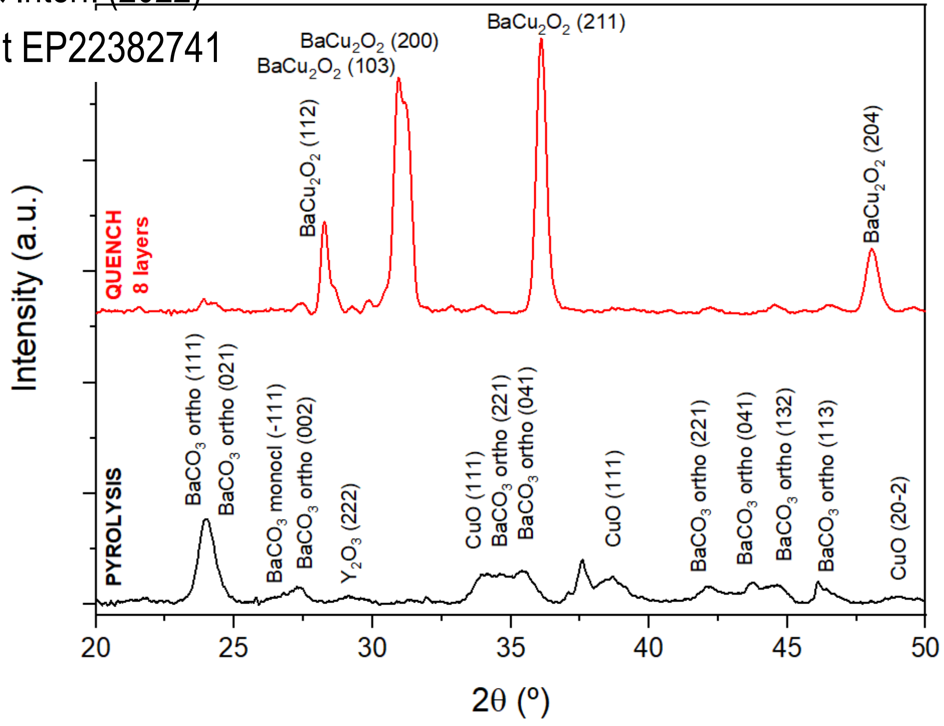
The thickness challenge

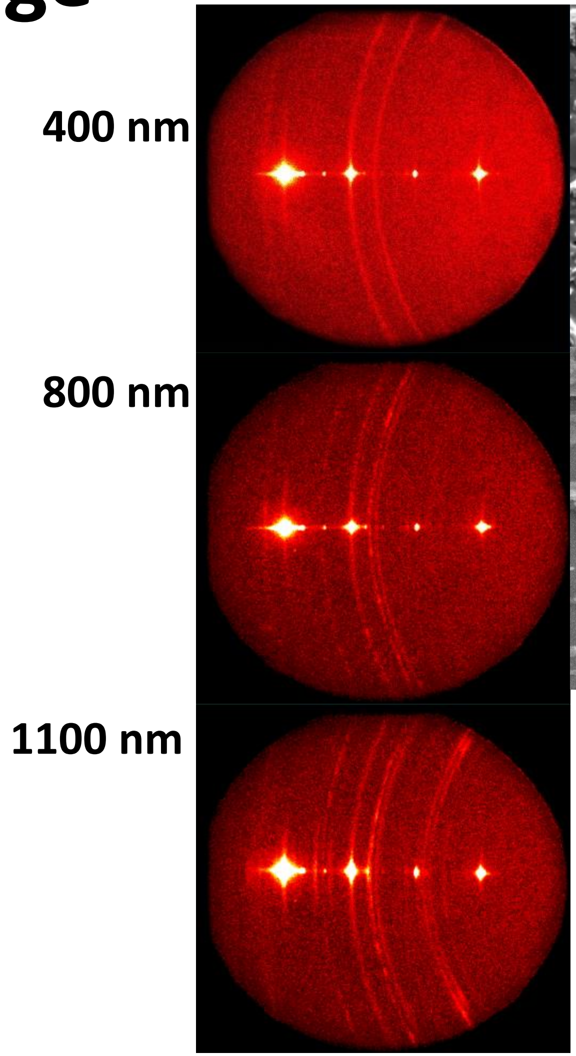


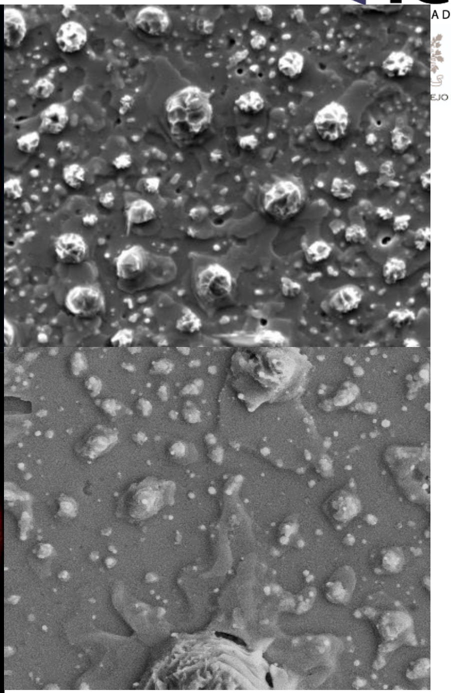


L. Saltarelli et al, ACS Appl. Mat. & Interf. (2022)

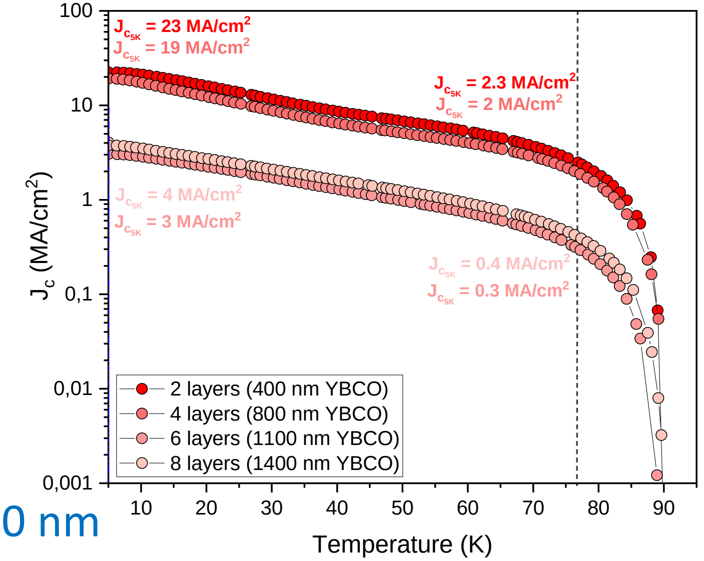
Patent EP22382741







Case YBCO



$BaCO_3$ is not an issue even at 2.7 µm

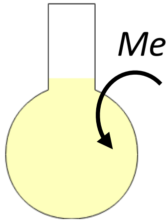
TLAG growth now optimized up to 800 nm

Interesting to test for other REBCO

TLAG nanocomposites with Multifunctional Colloidal Inks

Hybrid Hydrolitic-Solvothermal Synthesis (H2S2) of Nanoparticles

1.Hydrolitic (sol-gel) step: nucleation



Metal precursor, stabilizer, solvent

Hydrolysis and Polimerization

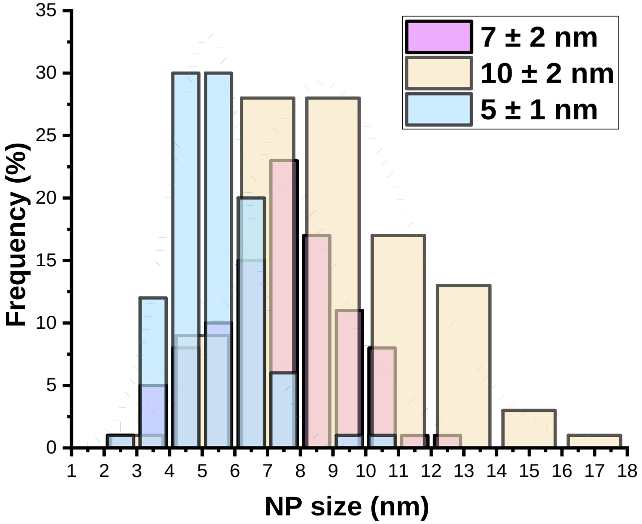
2. Solvothermal step: crystallization

Thermal activation

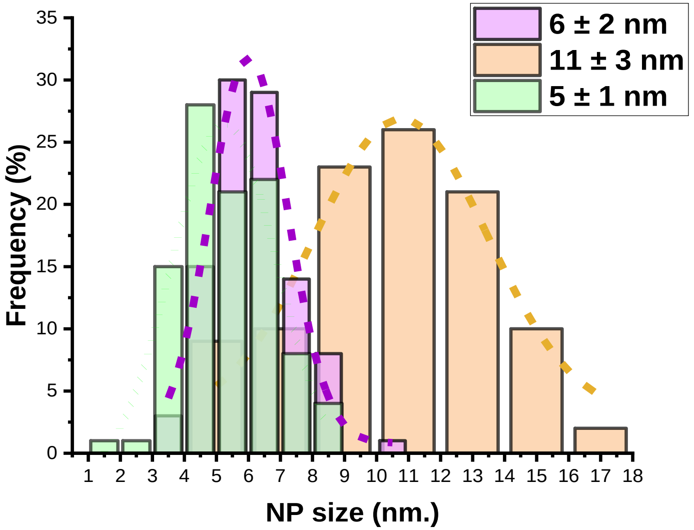
Autoclave

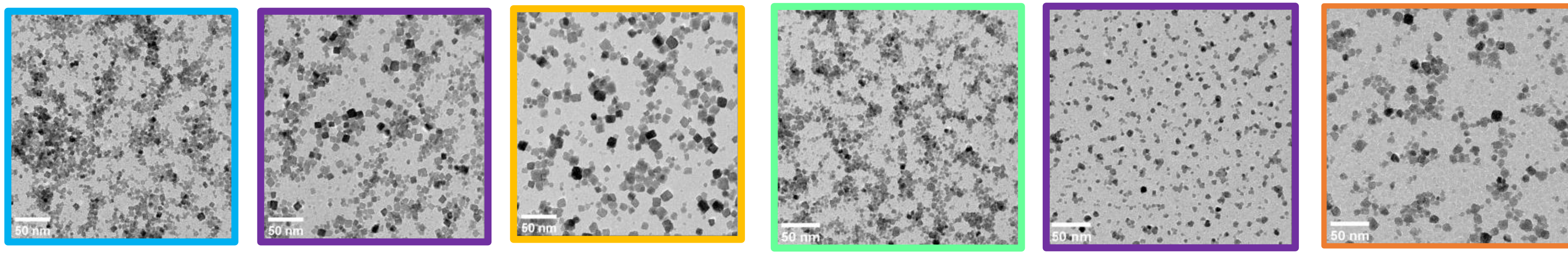
Scaled in MW

$BaZrO_3$ NP



$BaHfO_3$ NP





3. Stabilization in the REBCO precursor solution

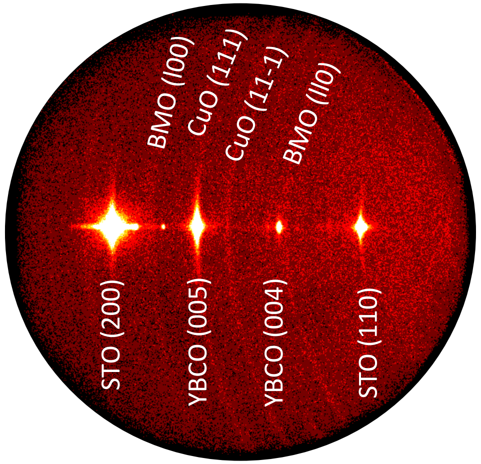
Multifunctional coloidal ink

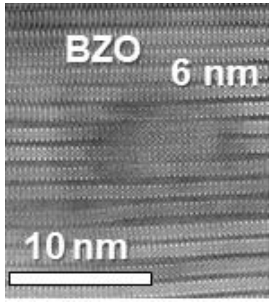
(Patent EP22382741)

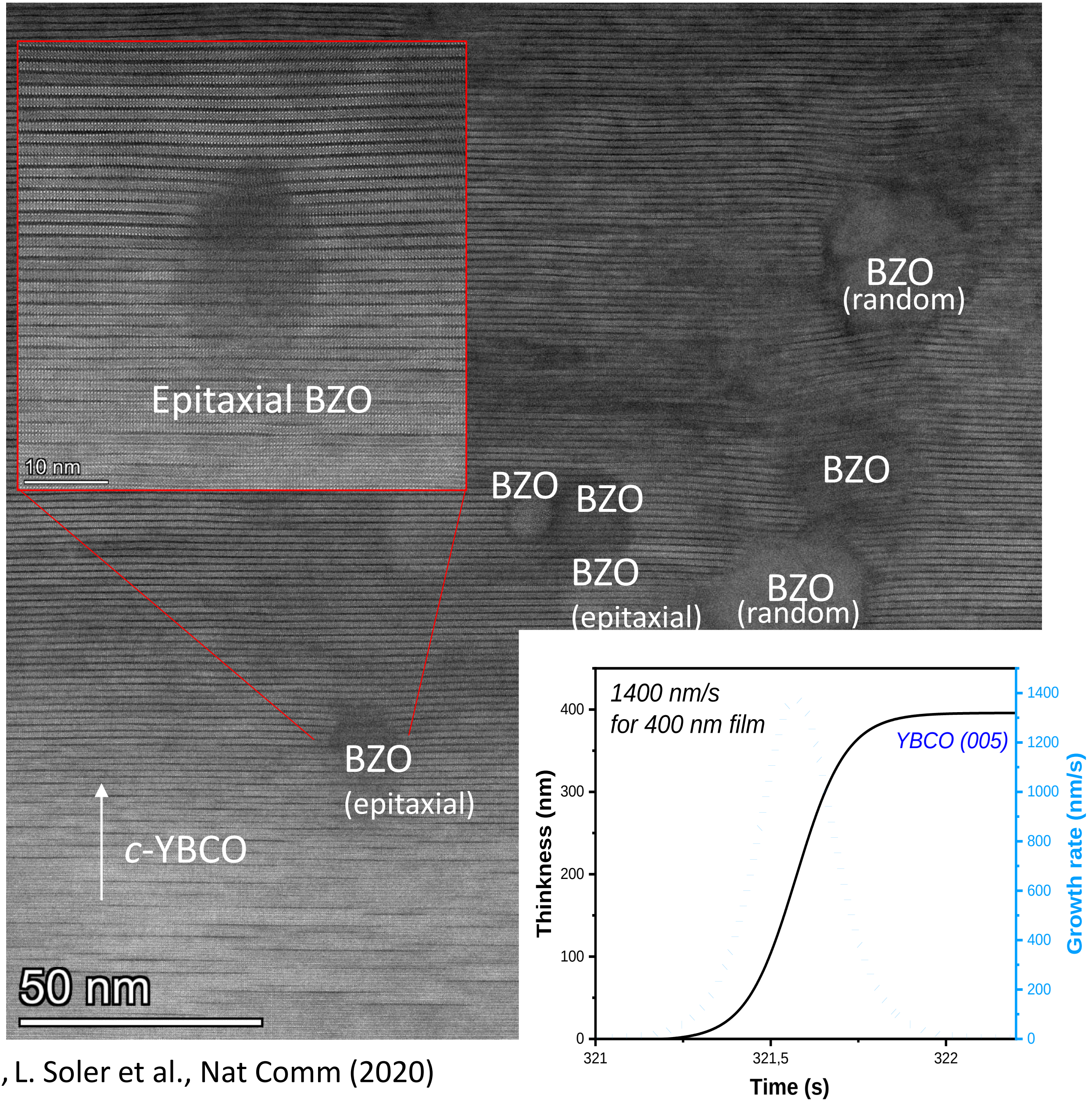
Small crystalline NP with narrow size distribution at high concentrations (> 100 mM)
Stable in REBCO precursor solution for more than 3 months and scalable

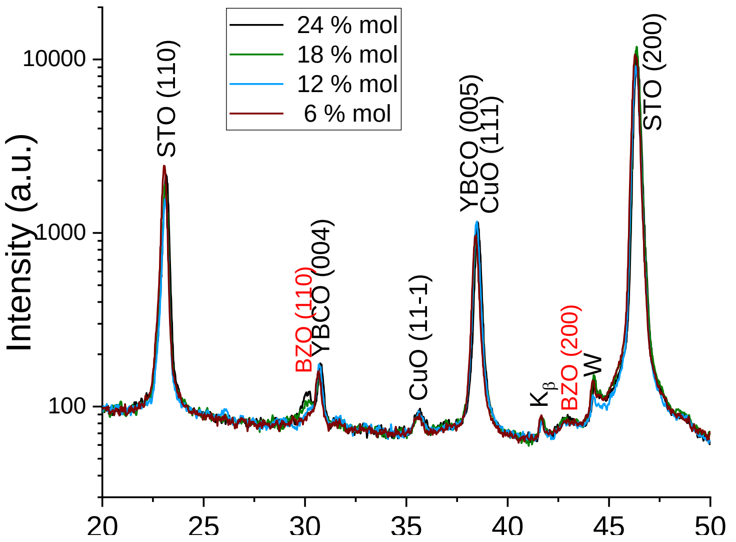
N. Chamorro et al, RSC Adv. (2020)

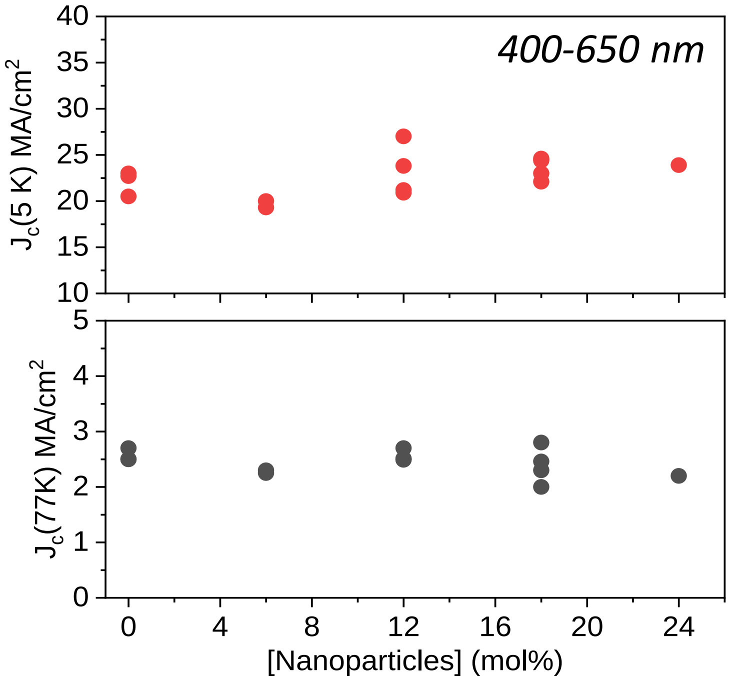
YBCO TLAG-CSD NANOCOMPOSITE FILMS











Small NP are epitaxial (capability to rotate)

Larger Np are randomly oriented

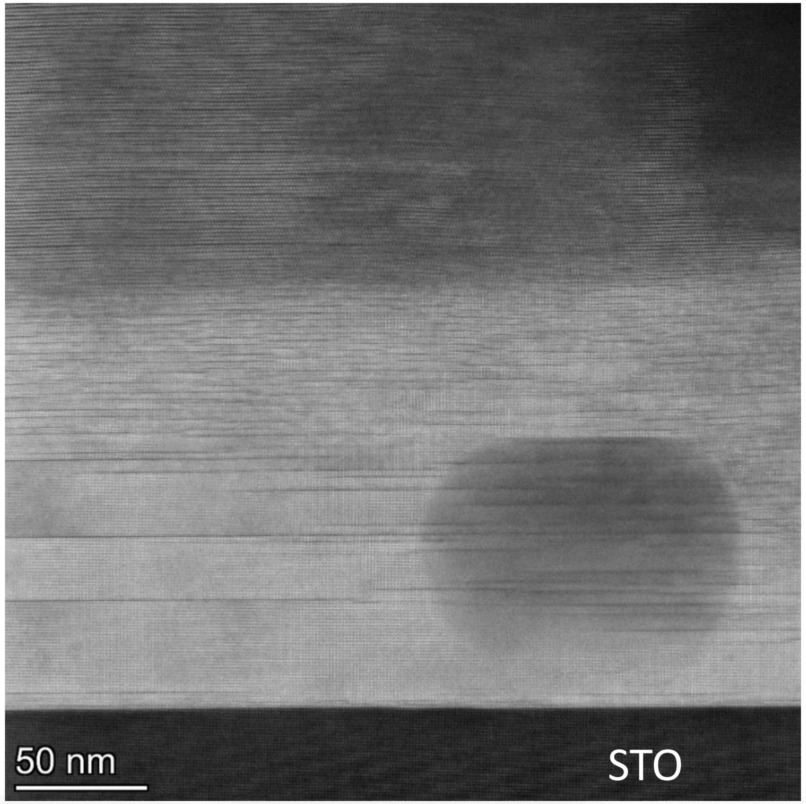
T. Puig et al, Nat Rev Phys (2023), L. Soler et al., Nat Comm (2020)

Microstructure of TLAG pristine films at high growth rates

Main defects:

-SF
-partial disloc.
-strain
-TB
-oxygen and cluster vacancies

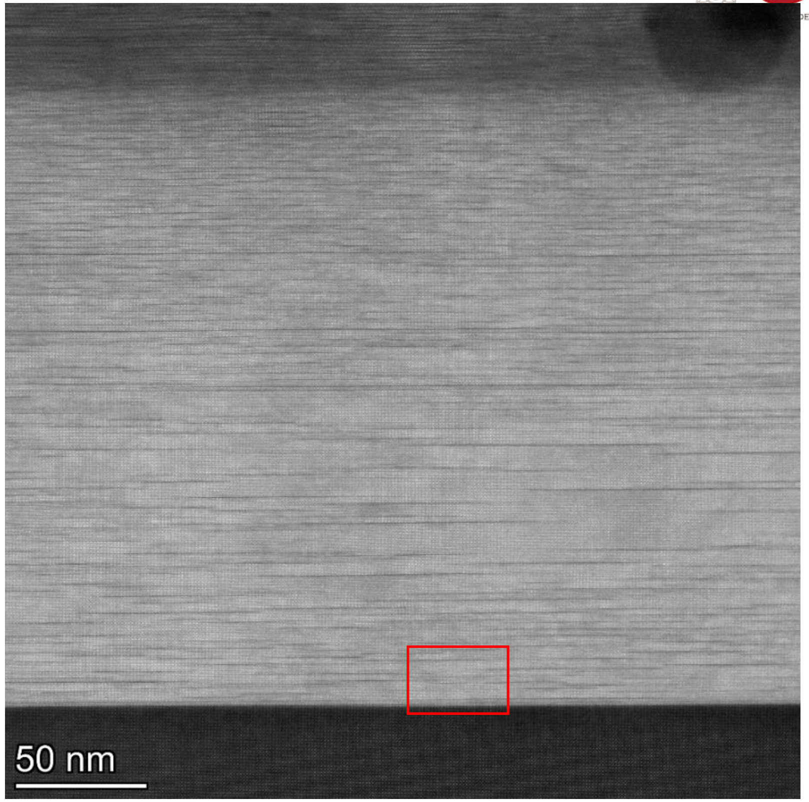
STEM-HAADF



High density of **long** intergrowths (SF)

High density of **short** SFs

Low density of **long** SFs



High density of **long** SFs

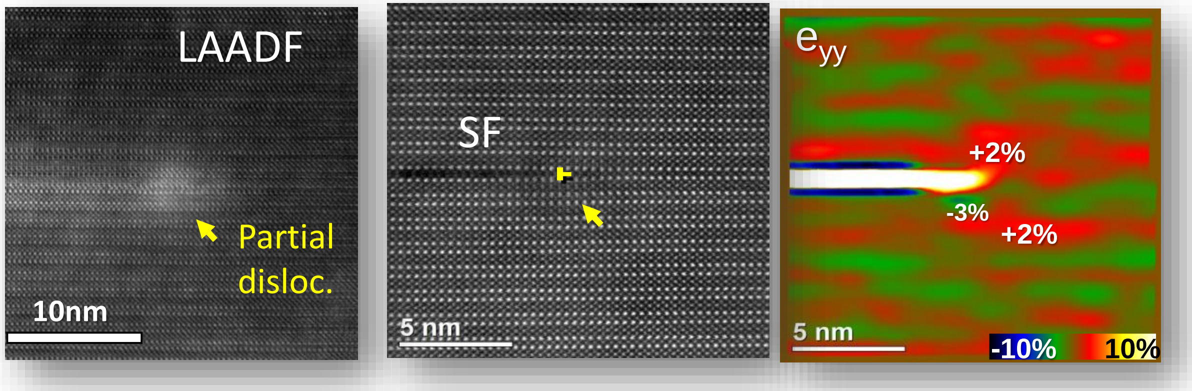
High density of **short** SFs

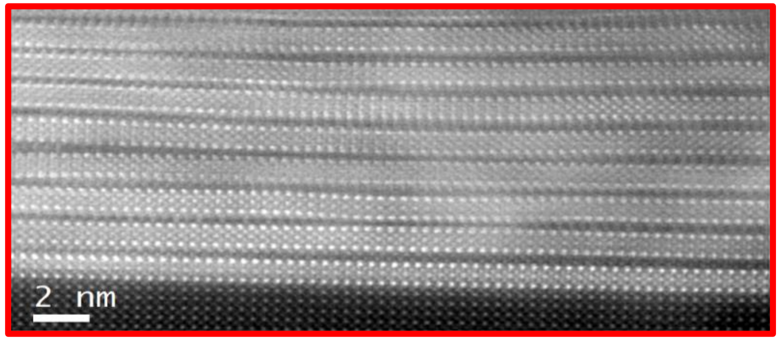
Medium density of **long** SFs

High density of **short** SFs

Strain accumulated at the partial dislocation sorrounding the SF (**NANOSTRAIN**)

Also measured by XRD (Williamson-Hall)





T. Puig et al, Nat Rev Phys (2023), L. Soler et al., Nat Comm (2020), A. Llordes et al, Nat Mat (2012)

Microstructure of TLAG nanocomposite films

Main defects:
- SF
- partial disloc.
- strain
- TB
- oxygen and cluster vacancies
- NP

STEM-HAADF

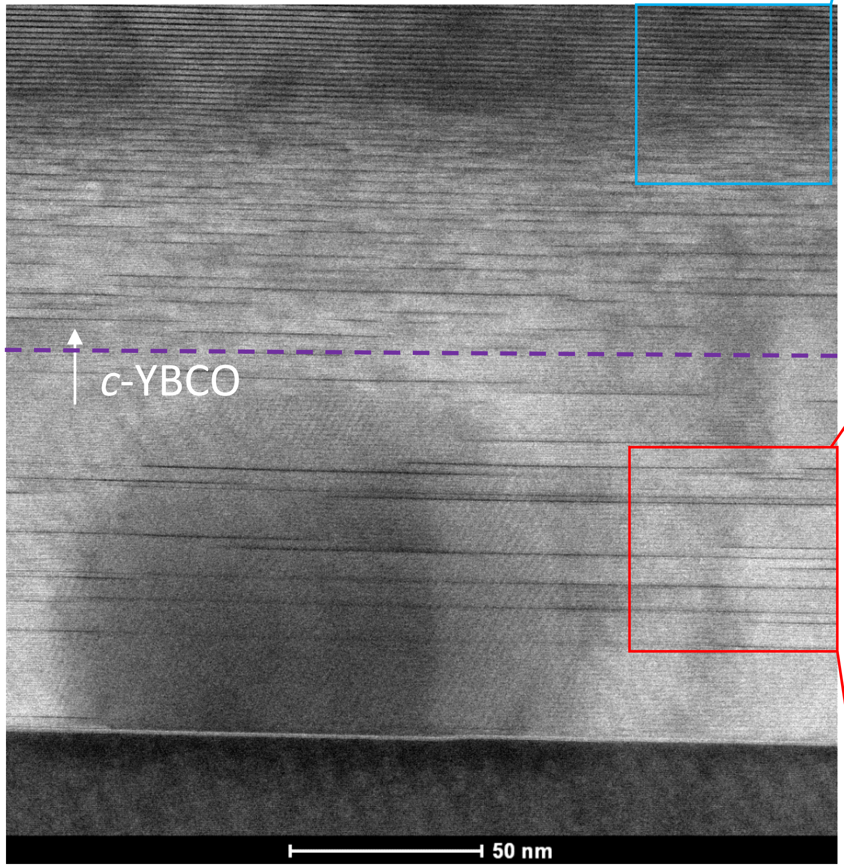
High density of **long** SFs

High density of **short** SFs

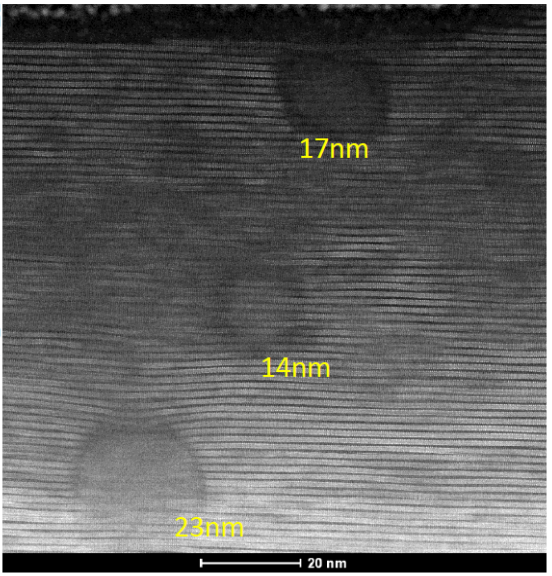
nanocomposite

pristine

Medium density of **long** SFs

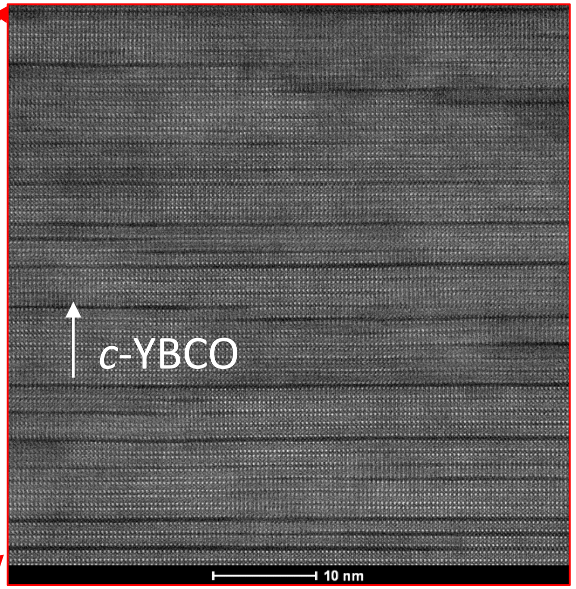


BZO NPs in YBCO *550 nm films*

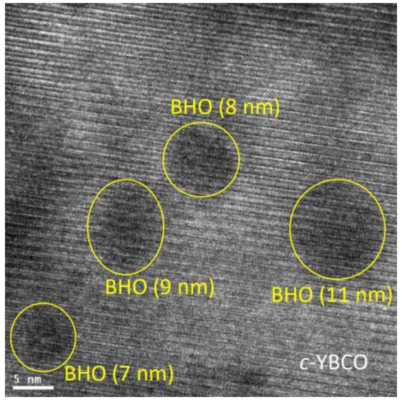


(14 nm BZO is epitaxial)

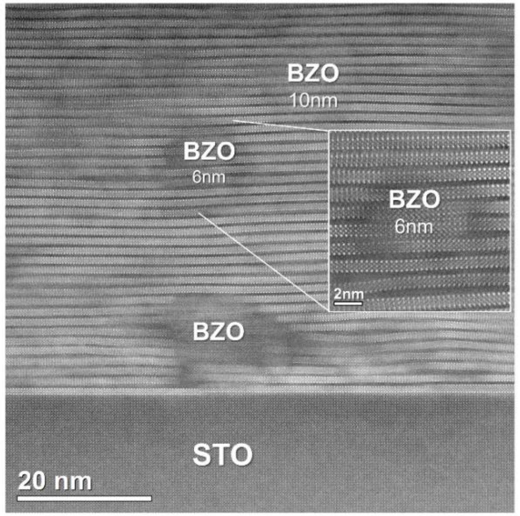
(23 nm is random)



BHO NPs in YBCO

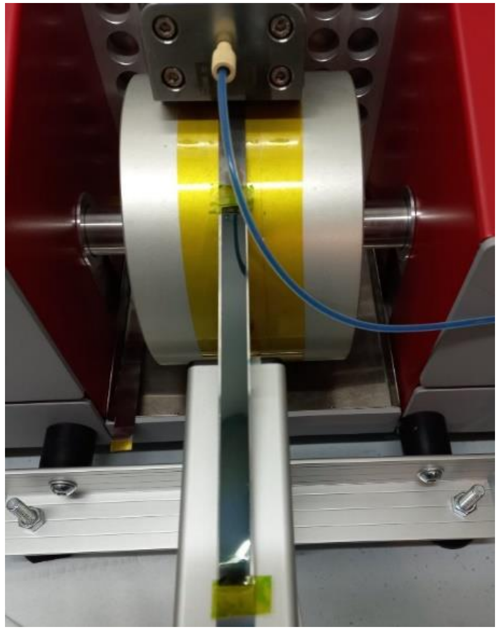


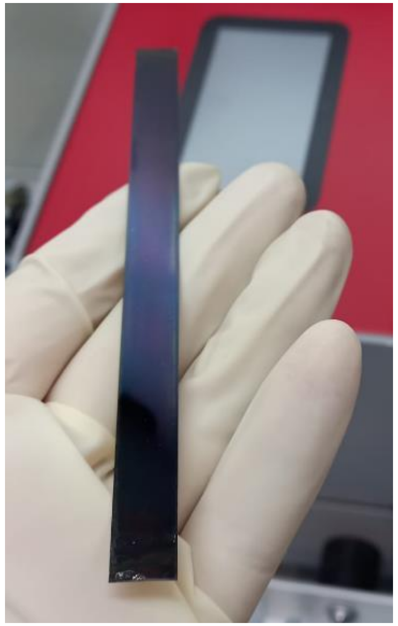
BZO NPs in YBCO

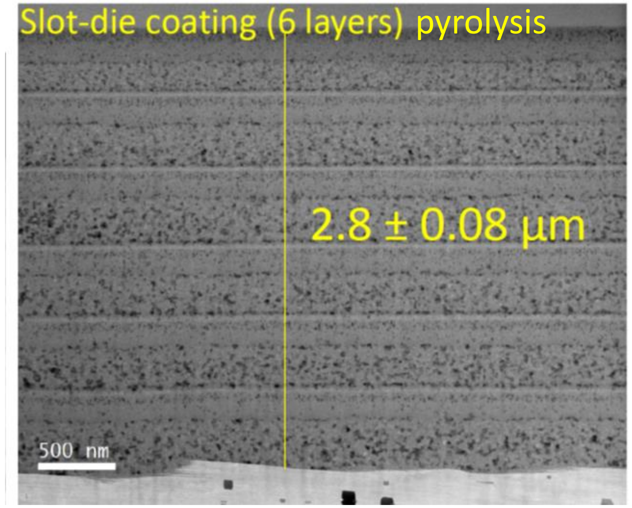


T. Puig et al, Nat Rev Phys (2023), L. Soler et al., Nat Comm (2020)

YBCO TLAG-CSD NANOCOMPOSITE CCs

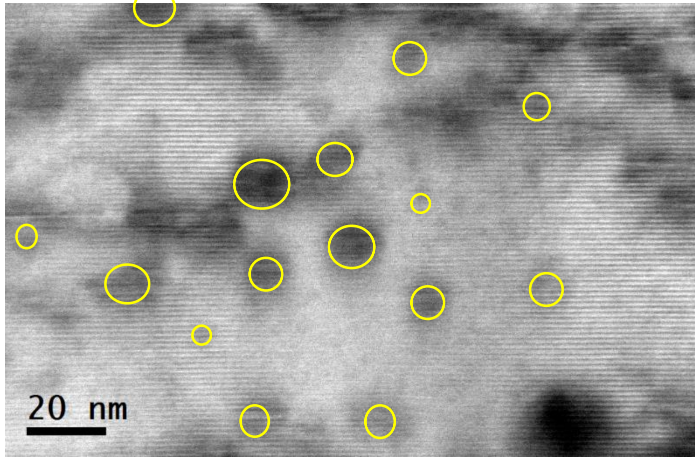


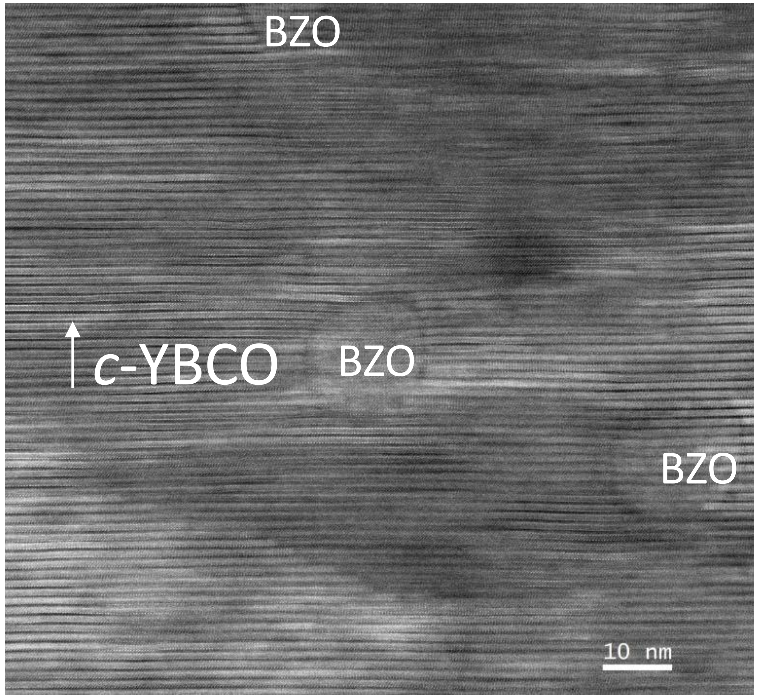




Buffer layers

Extended to technical substrates in collaboration with SUMITOMO ELECTRIC



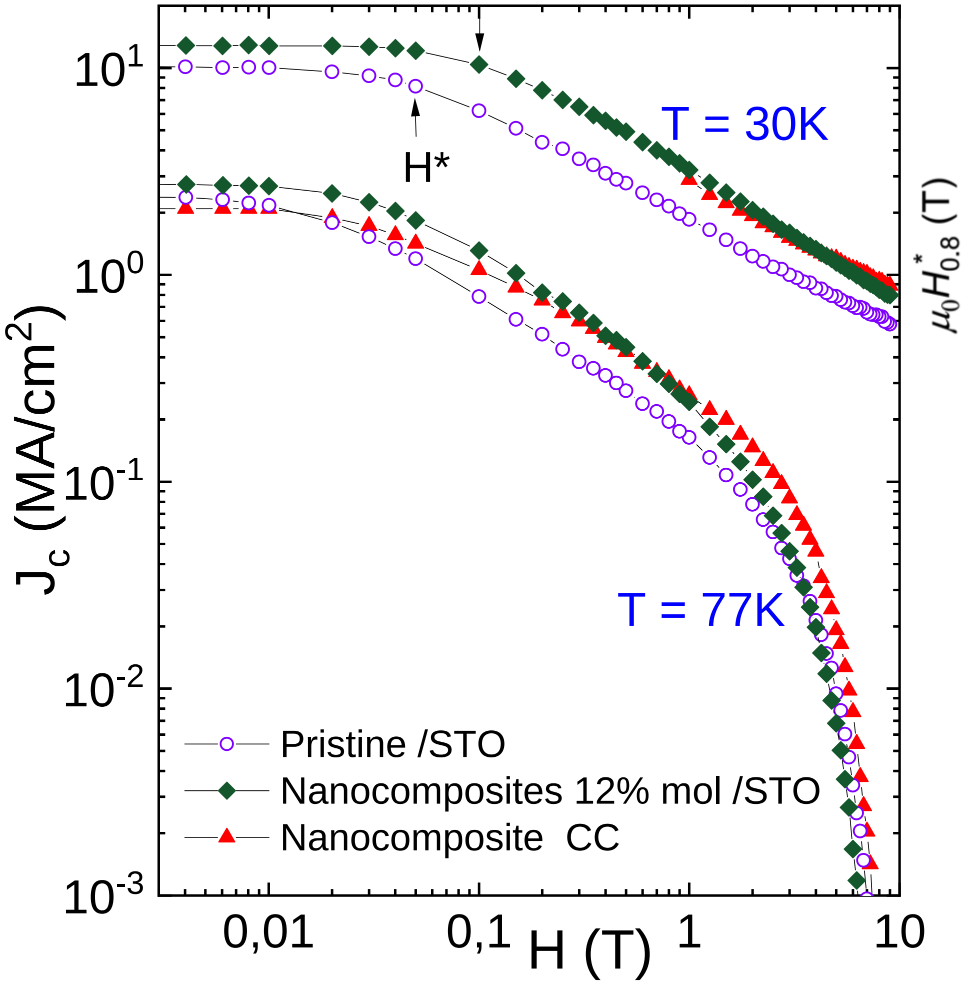


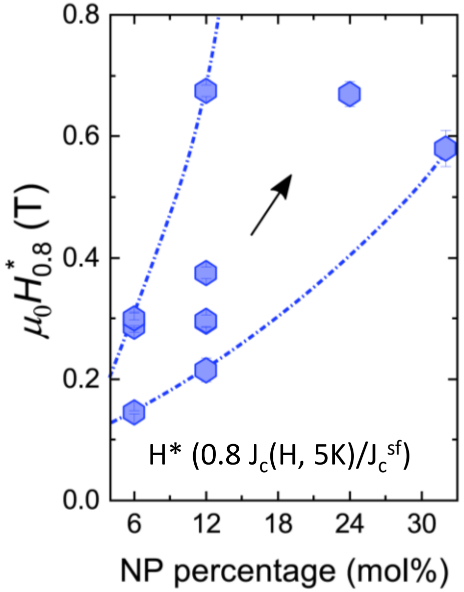
J_c(5K)= 24 MA/cm^2, J_c(77K)=2 MA/cm^2 (450 nm)
$I_{c,}$(77K) = 130 A/cm-w (750nm)
High density of defects is present as well as embeded nanoparticles

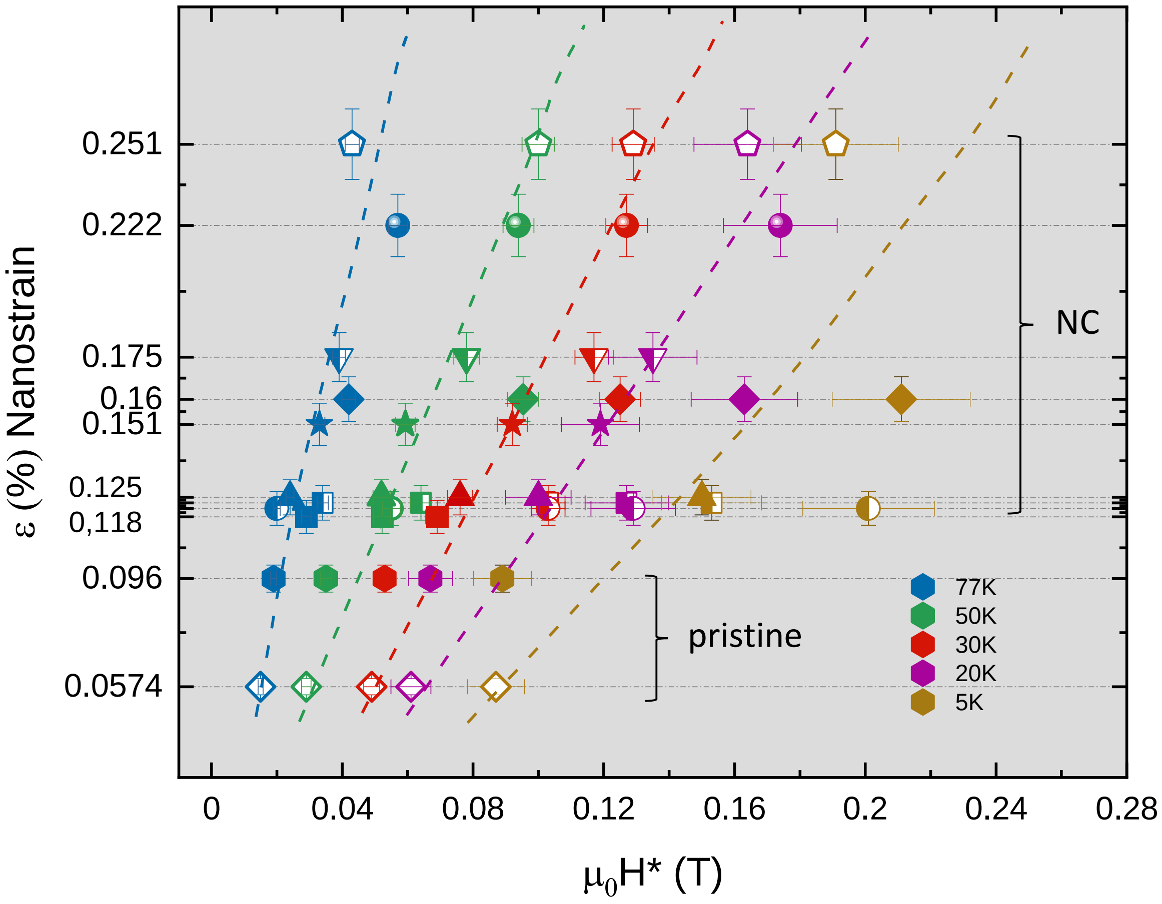
YBCO TLAG-PLD was extended to technical substrates in collaboration with SuNAM

A. Quetalto et al, SUST (2023)

Vortex pinning consequences at high growth rate: TLAG-CSD





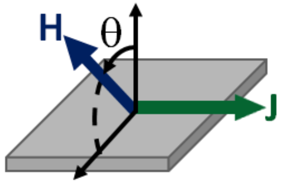


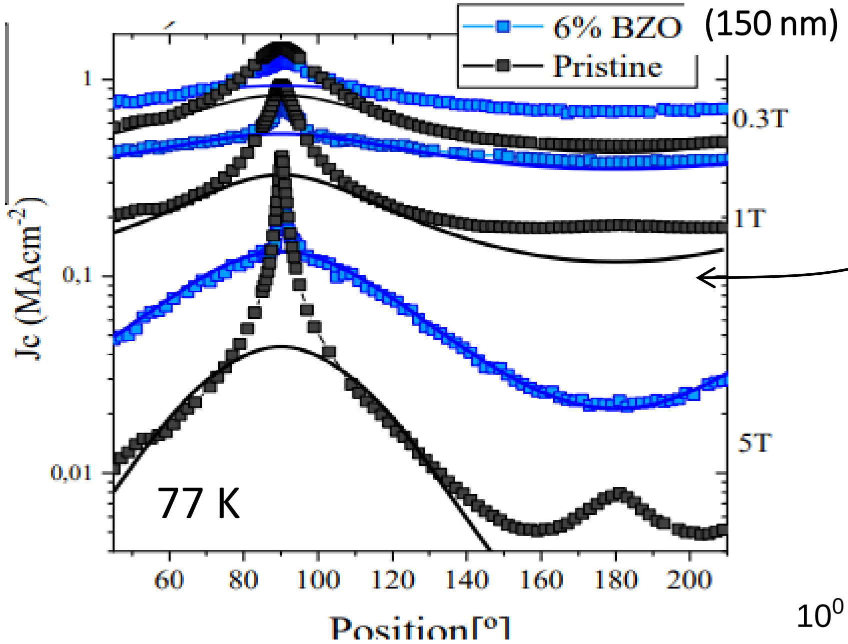
H*: single vortex regime (*measure of the density of pinning centers)*

Strong correlation between **Nanostrain, nanoparticles and H*** for many samples (pristine, nanocomposites (6- 18%) and several thickness)

T. Puig et al, Nat Rev Phys (2023 , doi.org/10.1038/s42254-023-00663-3) , L. Soler et al Nat Comm (2020)

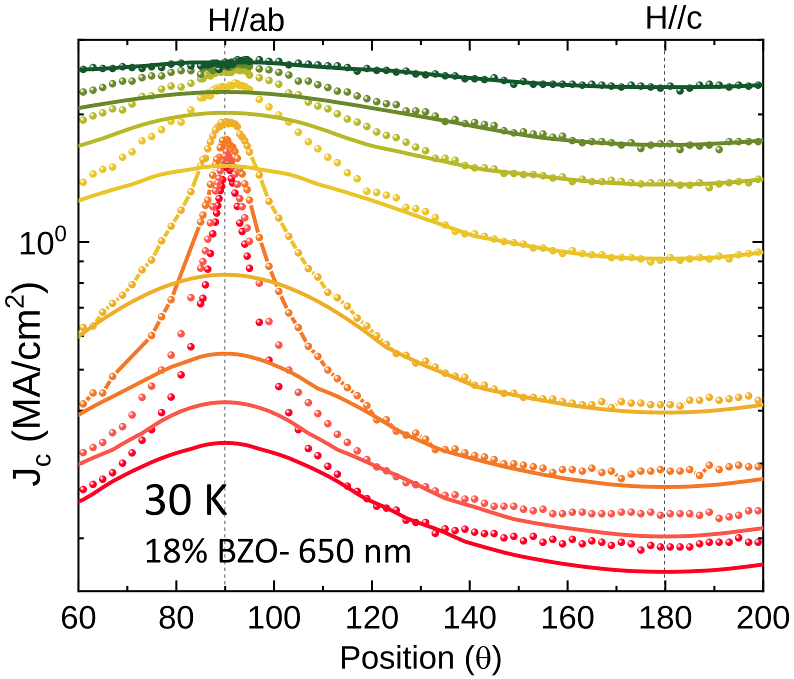
Angular dependence of transport currents

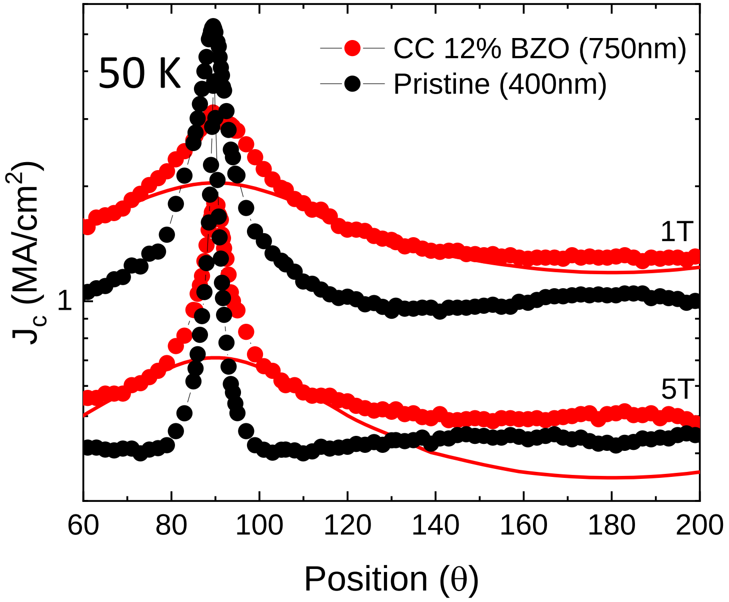


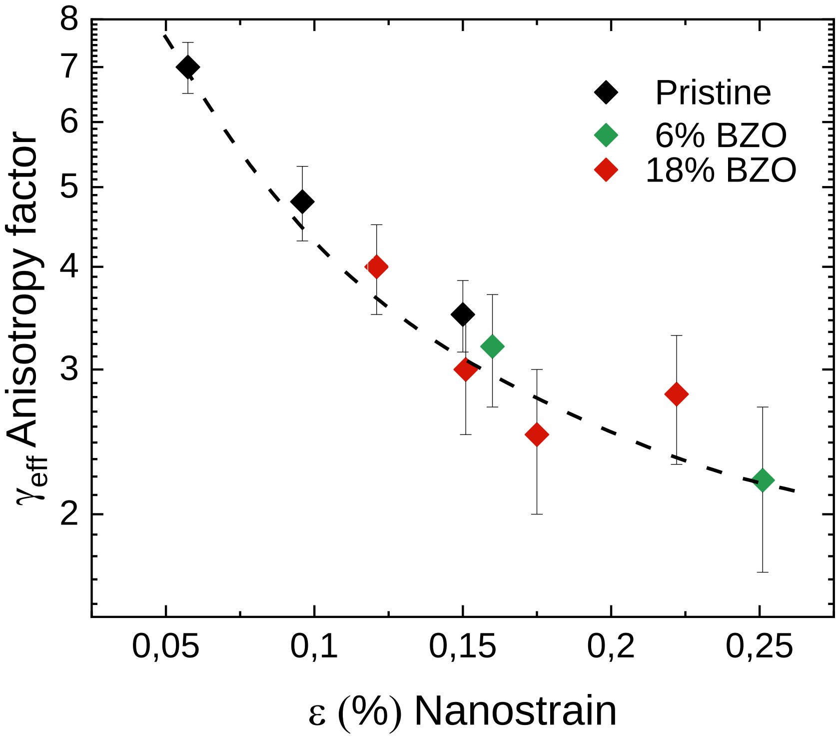


Blatter scalling approach

$$J_c^{iso}=J_c^{H//c}(\sin^2\theta/\gamma_{eff}^2+\cos^2\theta)$$



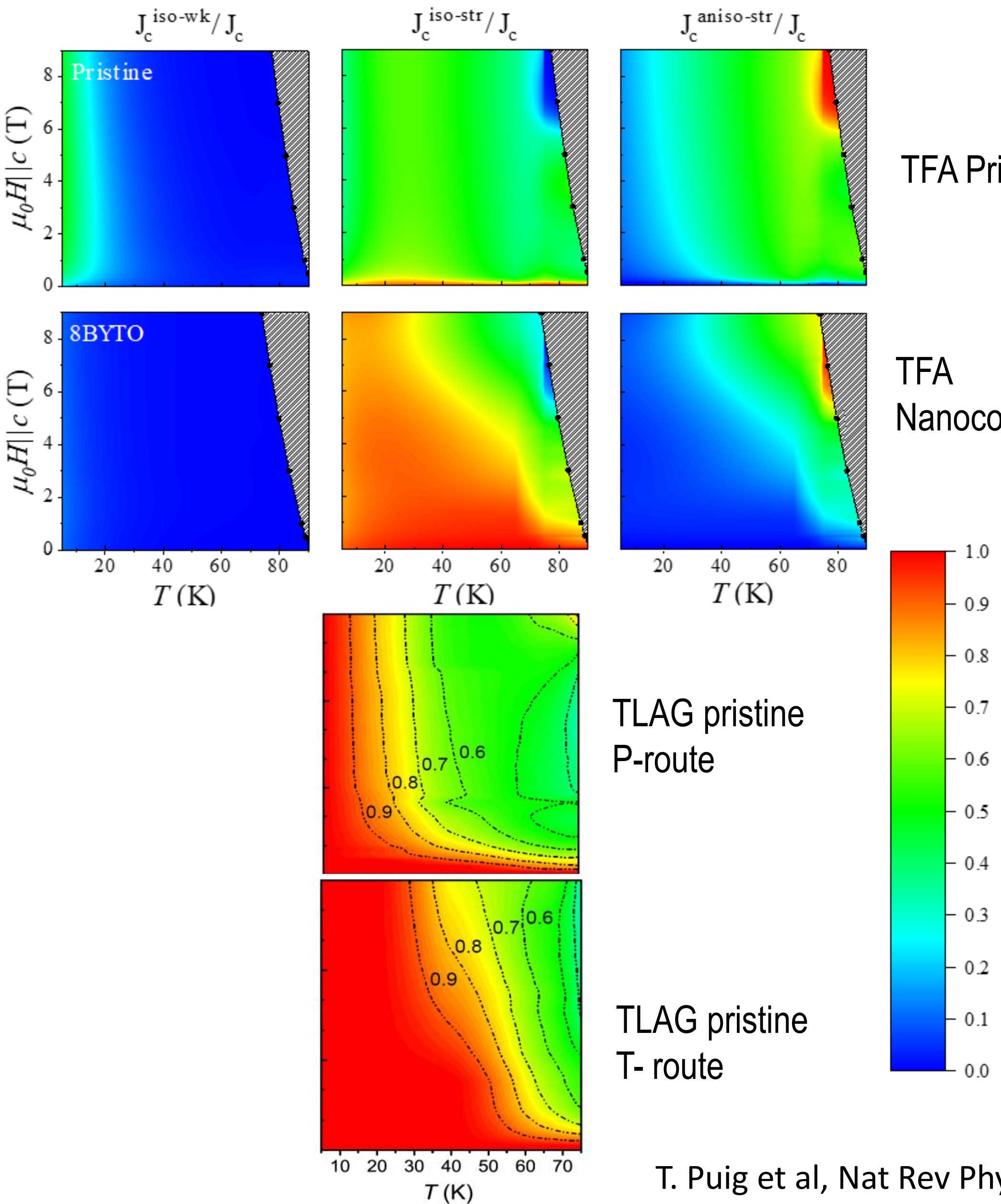




Strong correlation between **effective anisotropy** and **Nanostrain**

PINNING MODEL

$$J_c(T,H,\theta) = J_c^{iso\text{-}wk}(T,H,\theta)+J_c^{iso\text{-}str}(T,H,\theta)+J_c^{aniso\text{-}str}(T,H,\theta)$$



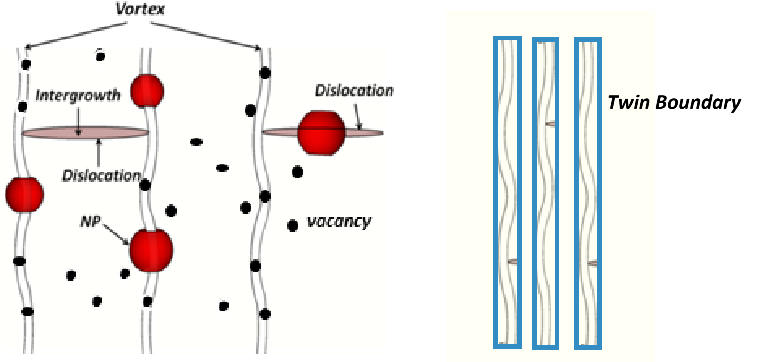
TFA Pristine

TFA Nanocomposites

TLAG pristine P-route

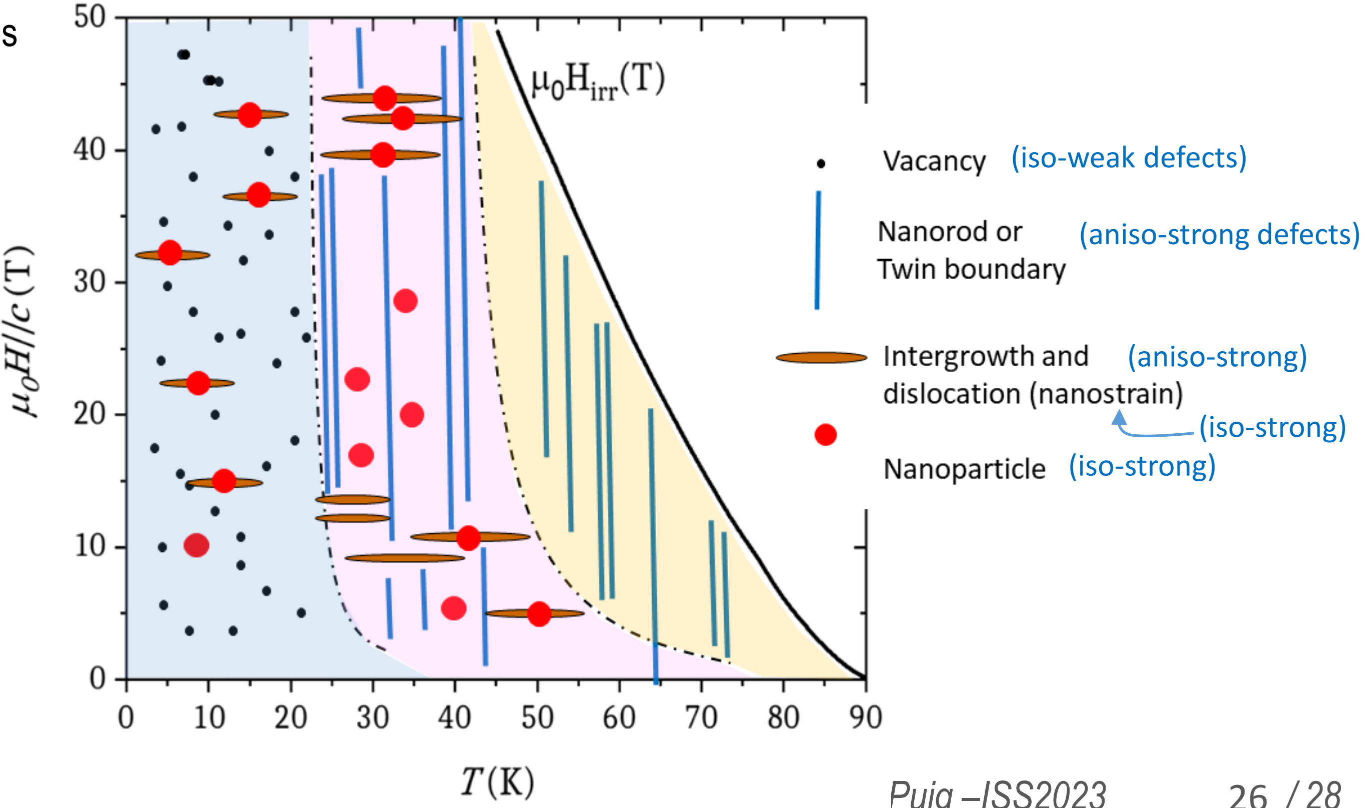
TLAG pristine T- route

Effective pinning landscape



at low temperature

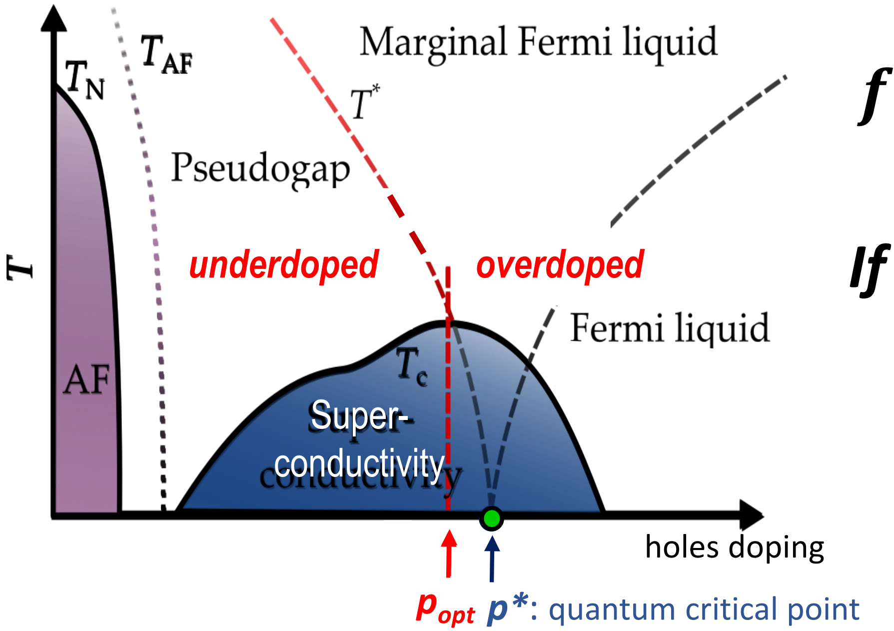
at high temperature



T. Puig et al, Nat Rev Phys (2023), F. Valles et al, Comm Mat 3(2022)

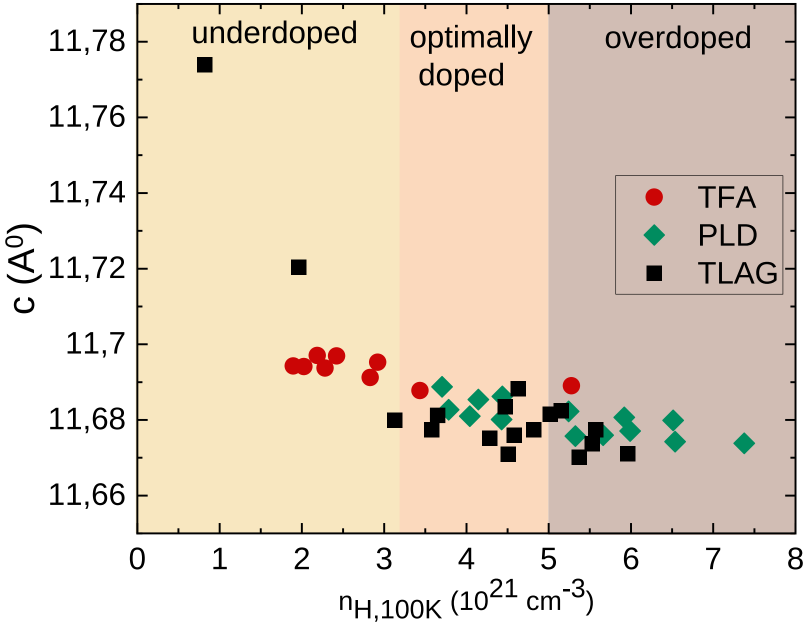
IEEE-CSC, ESAS and CSSJ SUPERCONDUCTIVITY NEWS FORUM (global edition), Issue No. 56, March, 2024. Invited presentation given at ISS 2023, Nov. 2023, Wellington, New Zealand

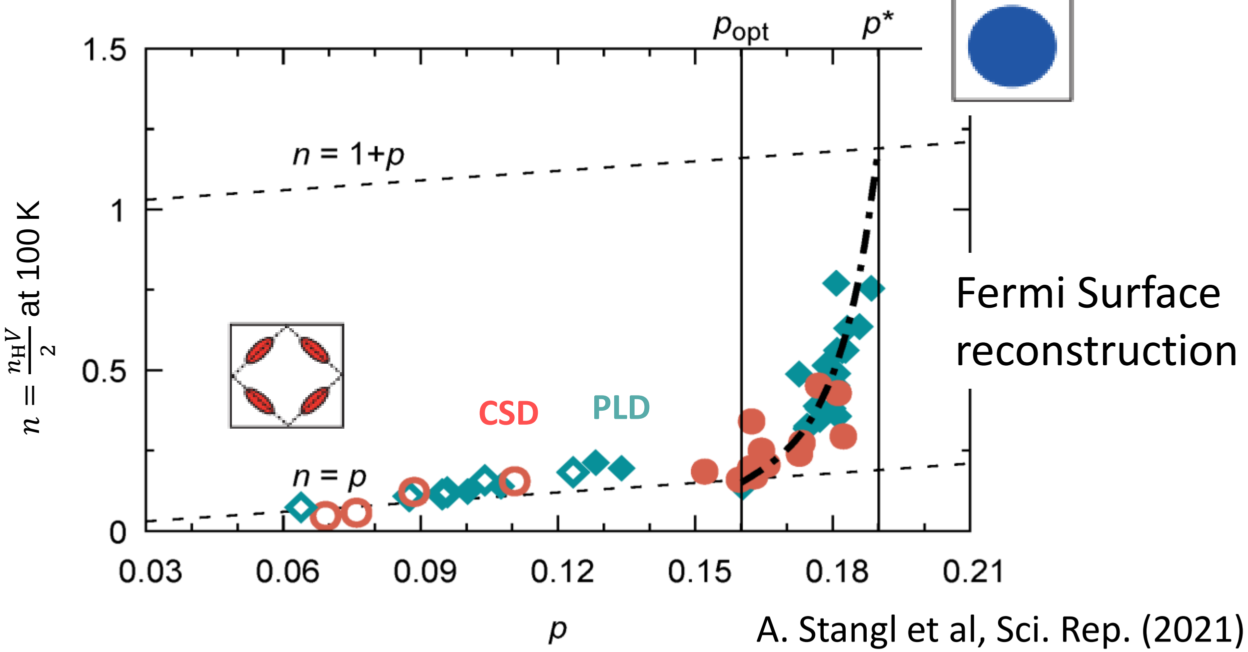
The Overdoped state



$$f_p \propto E_c \propto n_H$$

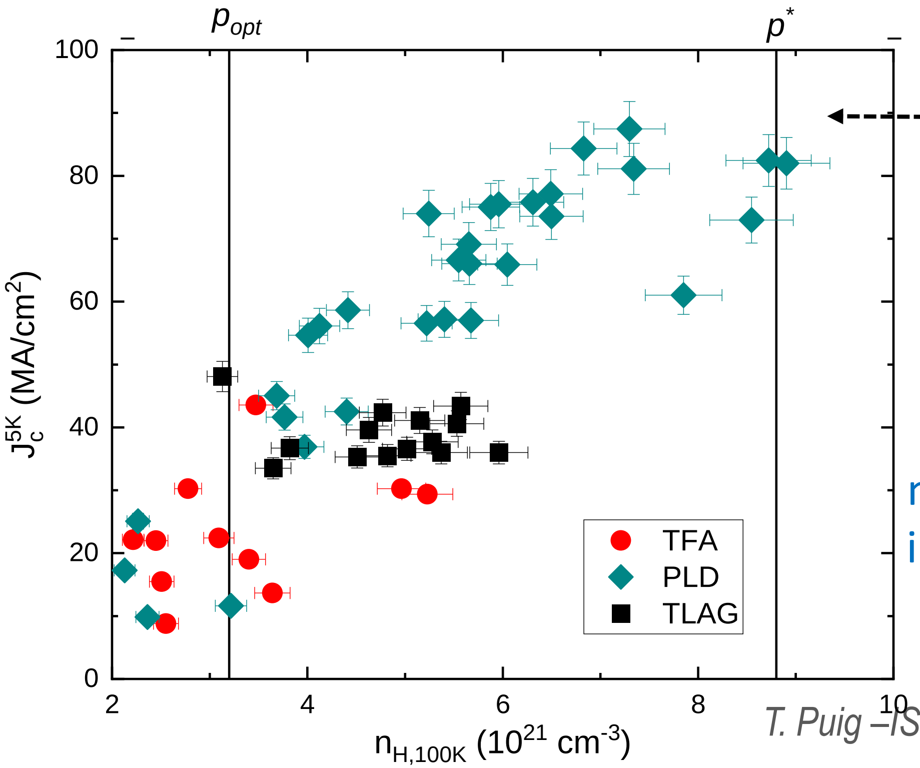
$$\text{If } n_H \uparrow \rightarrow J_c \uparrow$$





Fermi Surface reconstruction

A. Stangl et al, Sci. Rep. (2021)



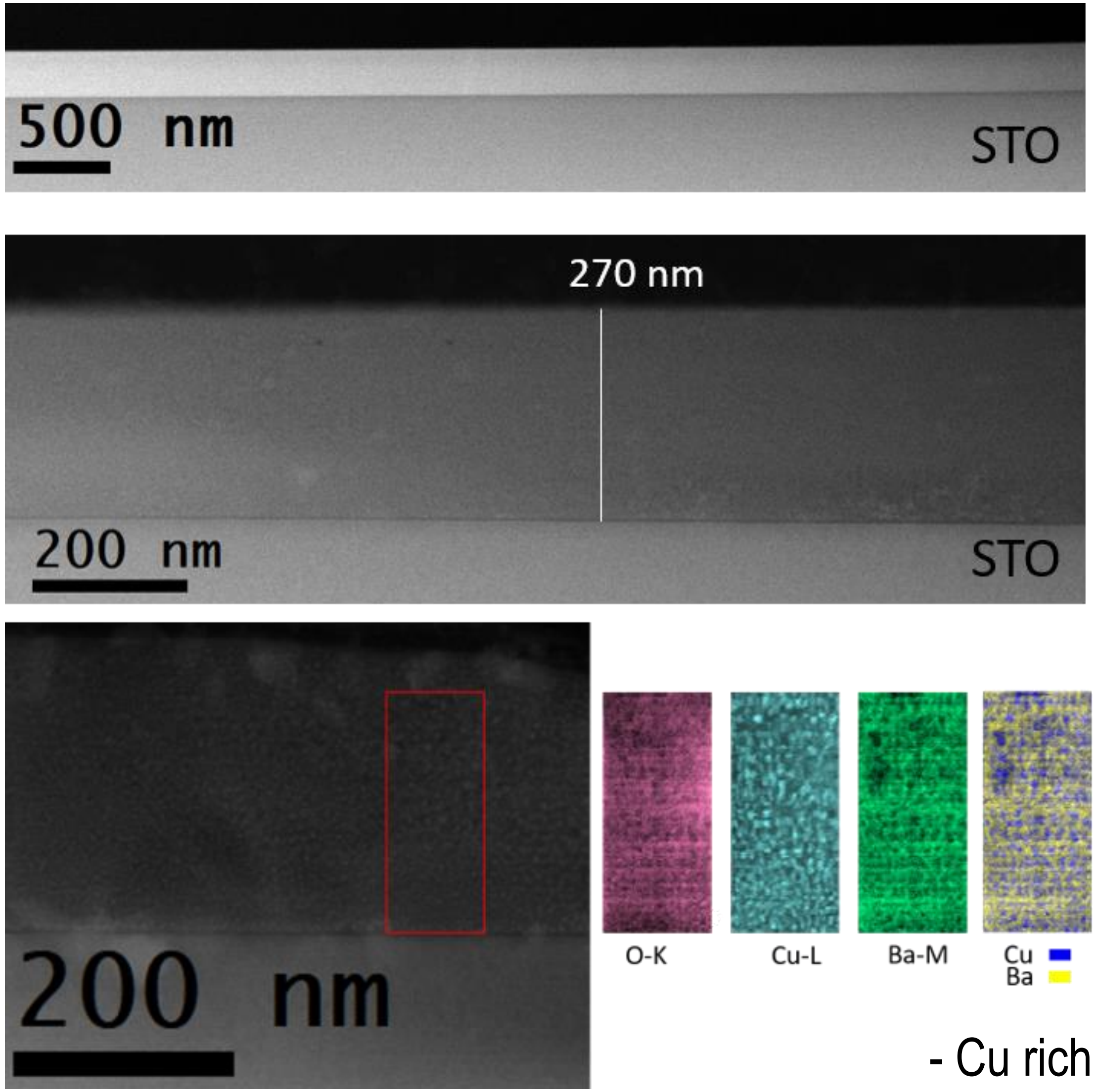
$$J_c(p^*) \approx \frac{1}{5} J_d(p^*)$$

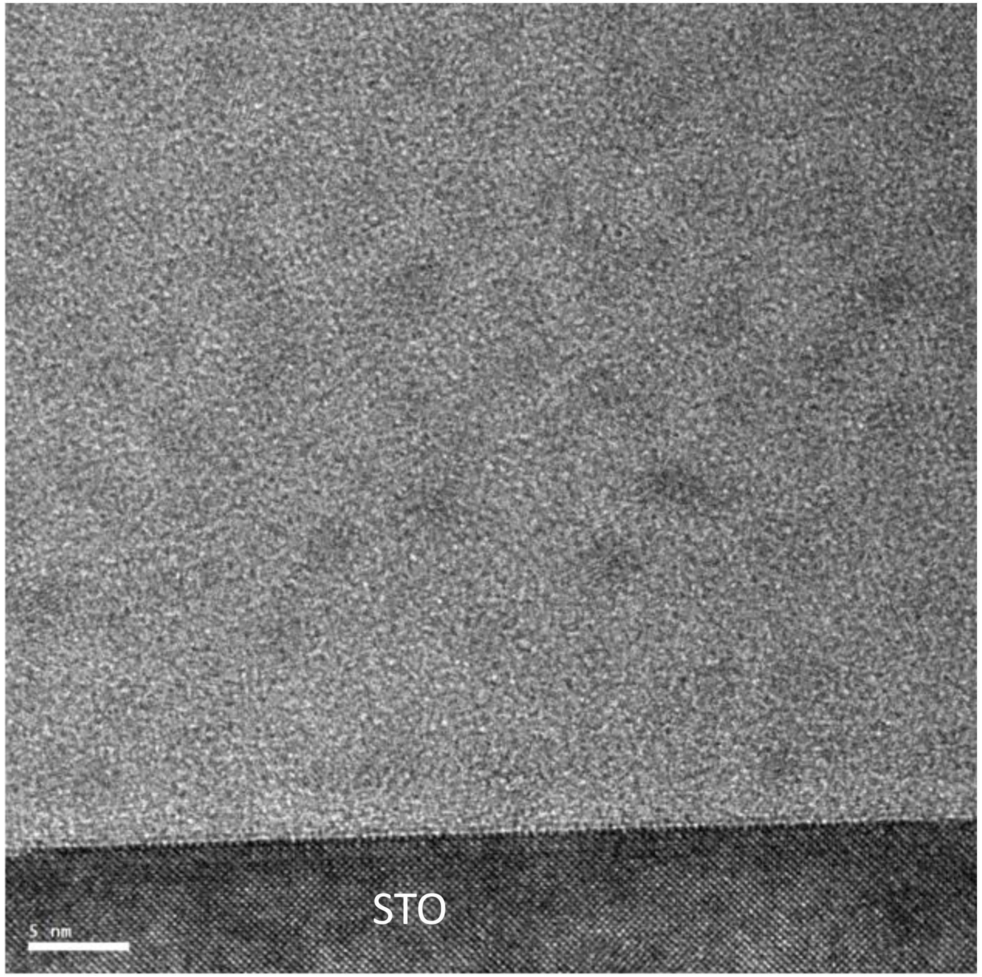
Interested in combining high throughput and nanocomposite CC in overdoped state

CONCLUSIONS

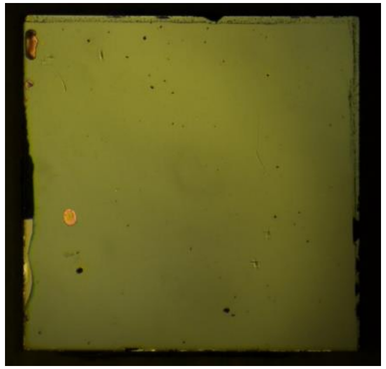
- **TLAG can contribute to make CCs a persistent enabling technology**
- Many opportunities/ challenges are being demonstrated
  - High throughput (high growth rate)
  - RE selection
  - High thickness
  - Nanocomposites
  - Coated Conductors
  - Rich vortex pinning
  - High performance
  - Overdoping
- Fast screening methodologies and machine learning should foster the High Throughput Experimentation required for its optimization
- **TLAG is an opportunity worth pursuing and expanding**

2. OXIDES PRECURSORS DEPOSITED BY PLD





200 ºC

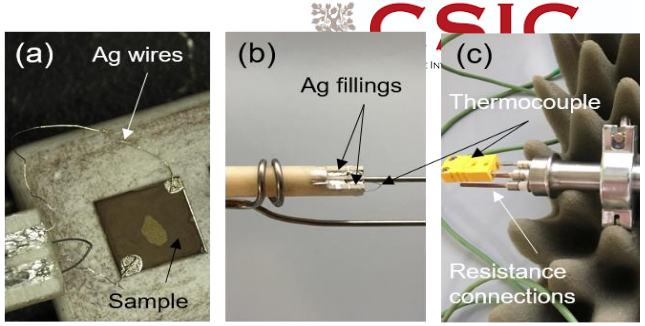


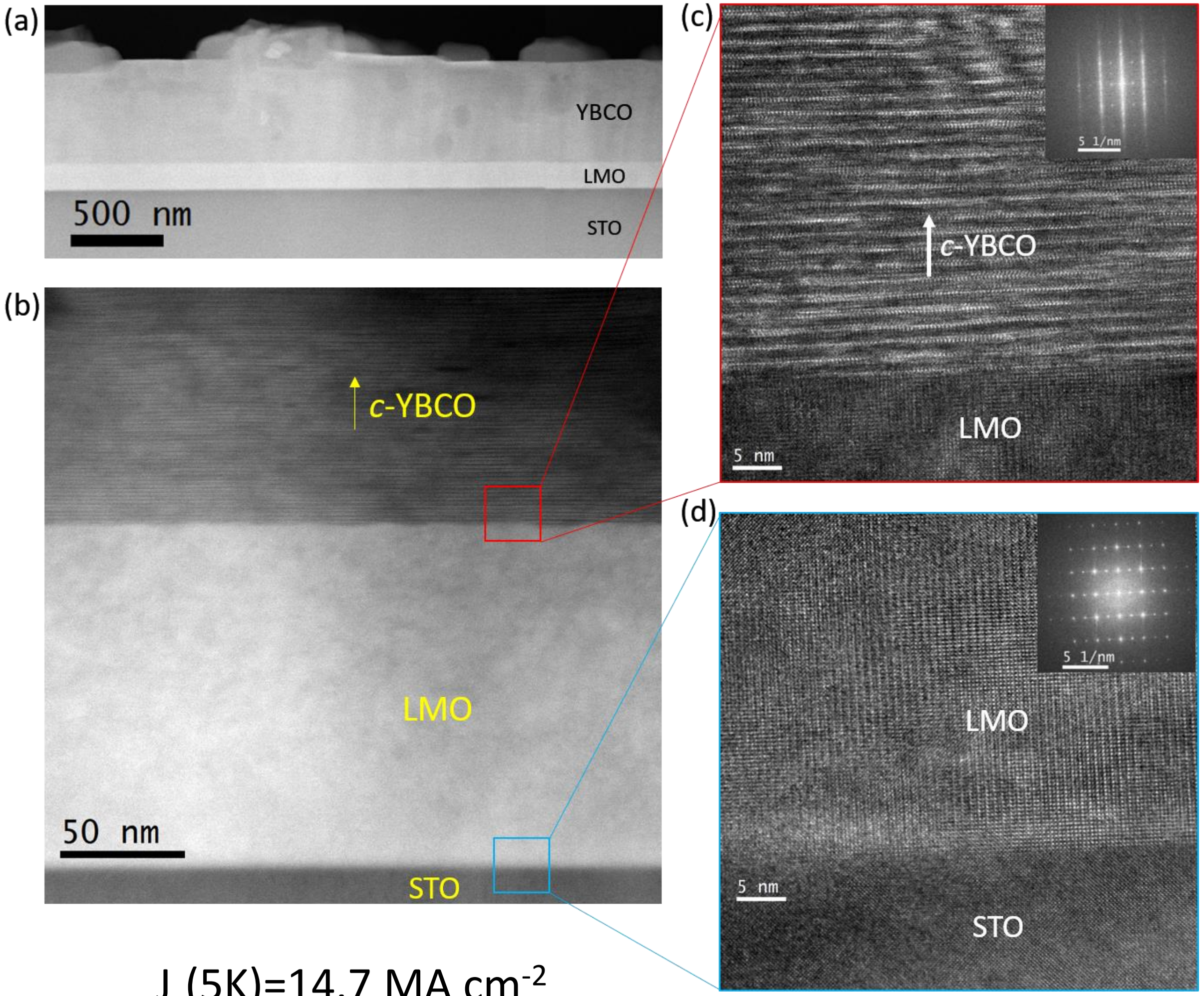
OM image

- Cu rich YBCO target
- Low temperature deposition (200-400ºC)
- Amorphous and homogeneous PLD precursors

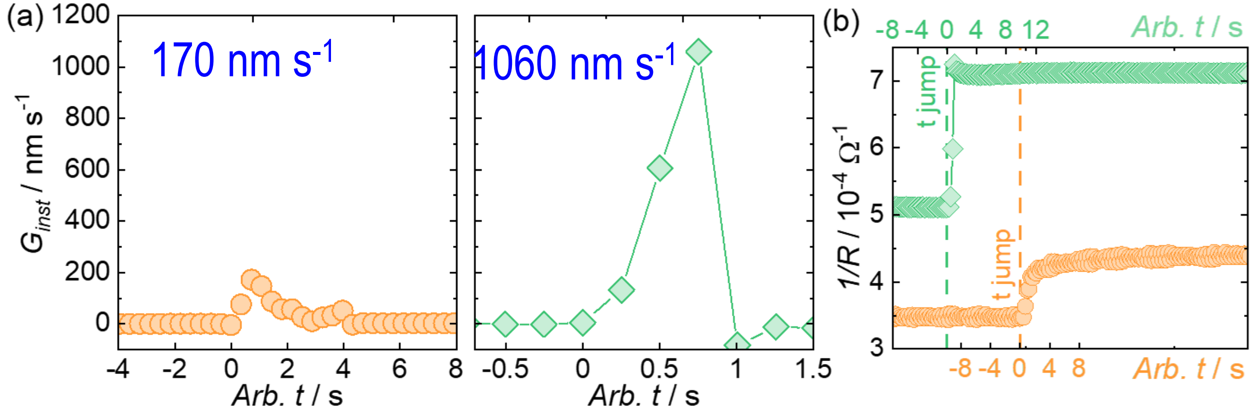
A. Quetalto et al, SUST (2023)

ULTRAFAST TLAG-PLD GROWTH





High defect density



Ultrafast growth rate ~1000 nm/s

J_c(5K)=14.7 MA cm^{-2}

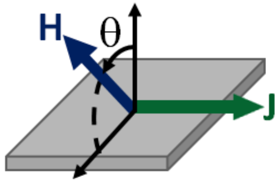
Jc(77K)= 1.7 MA cm^{-2}

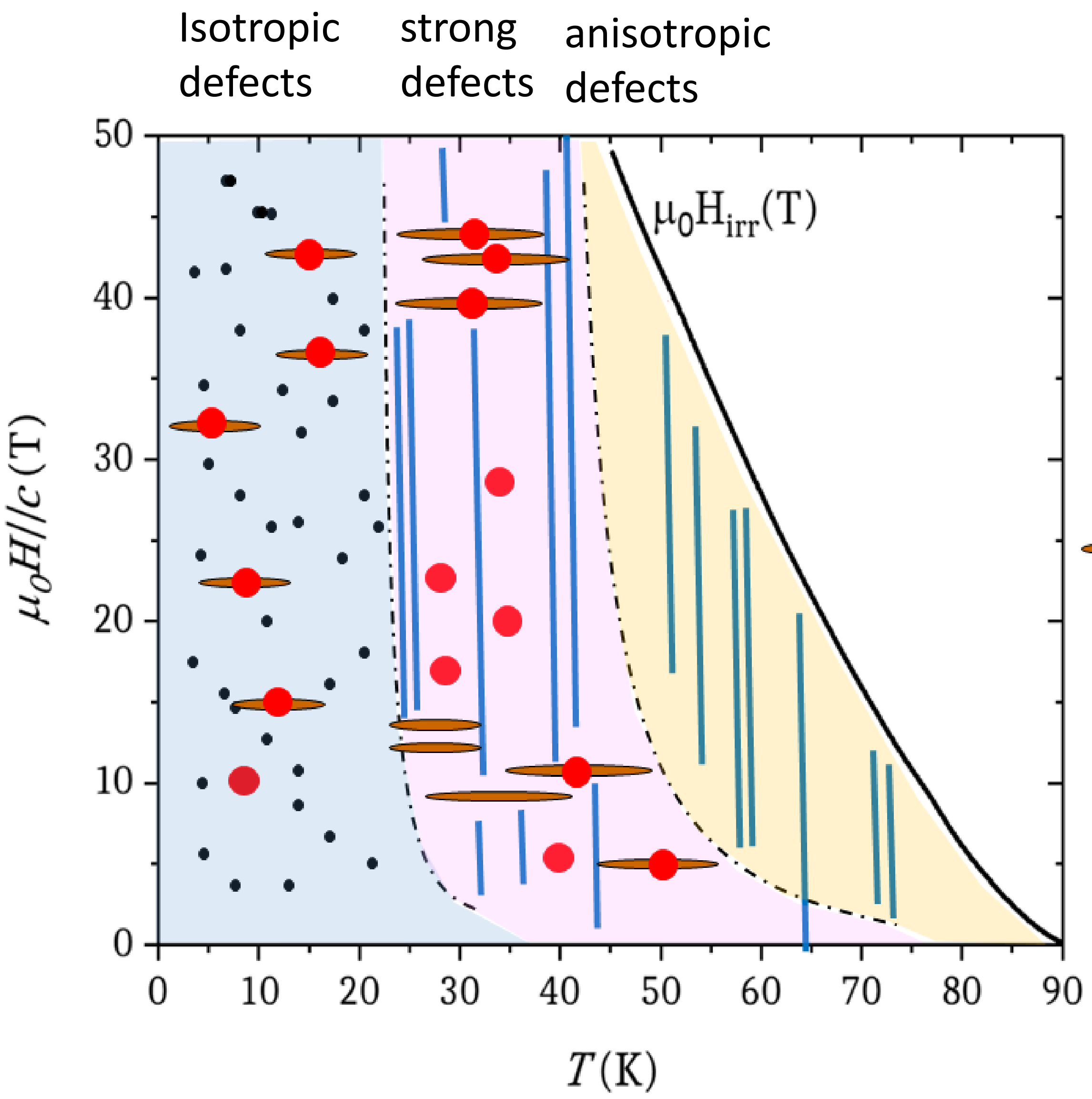
Extended to technical substrates in collaboration with SuNAM

A. Quetalto et al, SUST (2023)

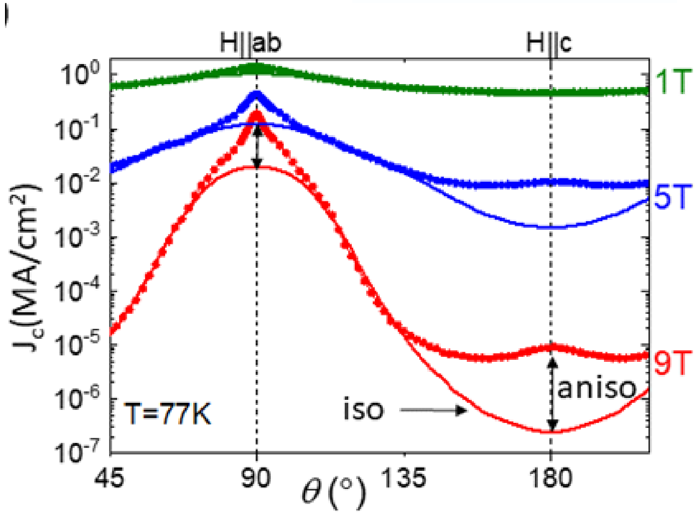
The complex magnetic phase diagram of nanocomposites: correlation with microstructure

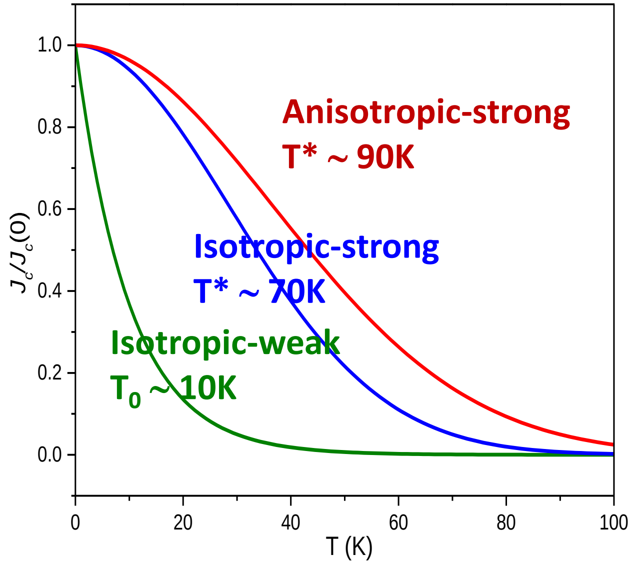
ICMAB
INSTITUT DE CIÈNCIA DE MATERIALS DE BARCELONA
EXCELENCIA SEVERO OCHOA





- ● Vacancy (iso-weak)
- Nanorod or Twin boundary (aniso-str)
- Intergrowth and dislocation (nanostrain) (aniso-str / iso-str)
- ● Nanoparticle (iso-str)





We need a simple route to classify APC for different processing methodologies

T. Puig et al, Nat Rev Phys (2023, doi.org/10.1038/s42254-023-00663-3)