Progress and Opportunities of the Transient Liquid Assisted Growth (TLAG) method

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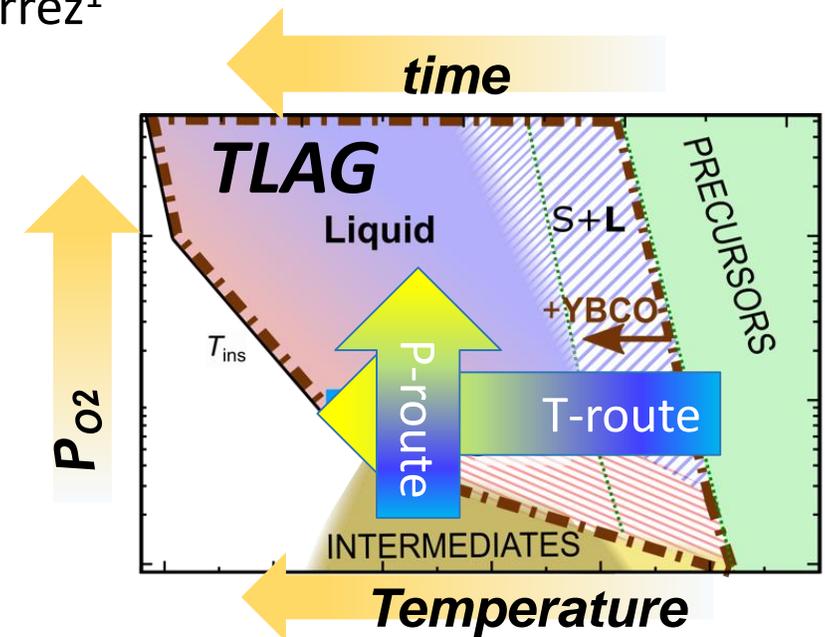
X. Obradors[1], R. Vlad[1], E. Pach[1,4], C. Pop[1], K. Gupta[1], C. Torres[1], O. Mola[1], A. Kethamkuzhi[1], E. Ghiara[1], V. Bertini[1], M. Voulhoux[1], D. Sanchez[2], S. Rasi[1], L. Salterilli[1], D. Garcia[1,3], S. Ricart[1], M. Tristany[1], R. Yanez[3], J. Farjas[2], E. Solano[4], L. Simonelli[4], J. Gutierrez[1]

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AIM: Design a robust, high throughput and flexible growth method for the manufacturing of CC at competitive cost/performance ratio

Opportunities of TLAG

-High growth rates > 1000 nm/s
-Compatible with low-cost chemical solution deposition (CSD) and others (i.e Low Temperature PLD deposition, LTPLD)
-Wide processing window
-Compatible with different Rare Earch (RE) and nanocomposite growth
-Well-suited for large area fabrication
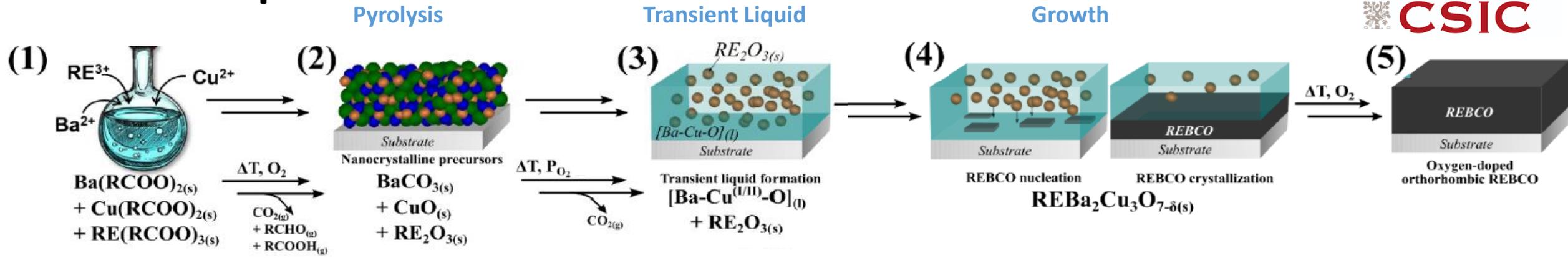-Easily scalable manufacturing equipment

Need of R&D in advanced CC materials

-Generate new ideas and understanding
-Develop breakthroughs that enable high-volume CC production at lower cost/performance
-Fast screening methodologies and AI approaches to guide predictions
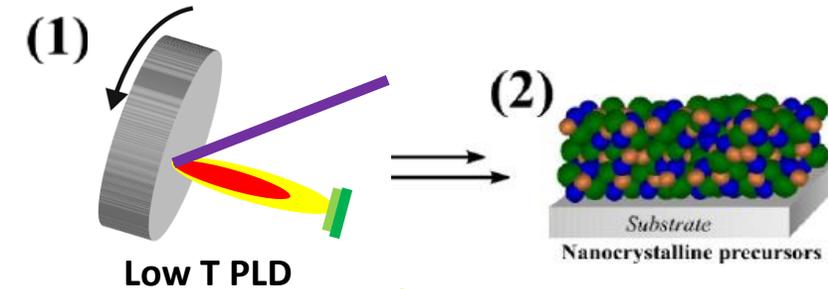-Contribute to making CC production a sustainable and transformative technology

Outline

-Progess in process understanding and processing windows
-Growth rates
-High Throughput Experimentation approach
-Vortex pinning and overdoping
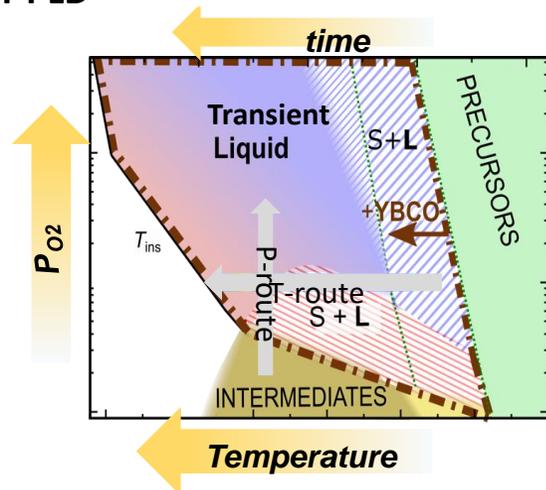-Towards large area Coated Conductors

❶ TLAG-CSD process

Pyrolysis — **Transient Liquid** — **Growth**

(1) RE^{3+}, Cu^{2+}, Ba^{2+}

$Ba(RCOO)_{2(s)}$
$+ Cu(RCOO)_{2(s)}$
$+ RE(RCOO)_{3(s)}$

$\xrightarrow{\Delta T, O_2}$ $CO_{2(g)}$ + $RCHO_{(g)}$ + $RCOOH_{(g)}$

(2) *Nanocrystalline precursors*
$BaCO_{3(s)}$
$+ CuO_{(s)}$
$+ RE_2O_{3(s)}$

$\xrightarrow{\Delta T, P_{O_2}}$ $CO_{2(g)}$

(3) $RE_2O_{3(s)}$ / $[Ba\text{-}Cu\text{-}O]_{(l)}$ / *Substrate*
Transient liquid formation
$[Ba\text{-}Cu^{(I/II)}\text{-}O]_{(l)}$
$+ RE_2O_{3(s)}$

(4) *Substrate* — **REBCO nucleation**; REBCO / *Substrate* — **REBCO crystallization**
$REBa_2Cu_3O_{7-\delta(s)}$

$\xrightarrow{\Delta T, O_2}$

(5) REBCO / *Substrate*
Oxygen-doped orthorhombic REBCO

TLAG-PLD process

(1) **Low T PLD**

(2) *Substrate* — *Nanocrystalline precursors*

Kinetically governed by RE liquid supersaturation $\sigma = (C_\delta - C_e) / C_e$

C_e: **thermody. param.** (T, P_{O_2}, Ba/Cu liq. composition, RE ion)
C_δ : **kinetic param.** (heating ramp, pressure ramp, …)

if $1/T$, P_{O_2}, Ba/Cu or r_{RE} ↑ → σ ↑

c-axis
dN/dt, nucleation rate
G, growth rate
A compromise is needed between ↑σ and epitaxy
σ

time · **Transient Liquid** · S+L · PRECURSORS · +YBCO · T_{ins} · P-route · T-route · S + L · INTERMEDIATES · P_{O_2} · **Temperature**

Fast advanced tools have been developed to understand the process

L. Soler et al., Nat Comm (2020), S. Rasi, et al, Advance Science (2022)
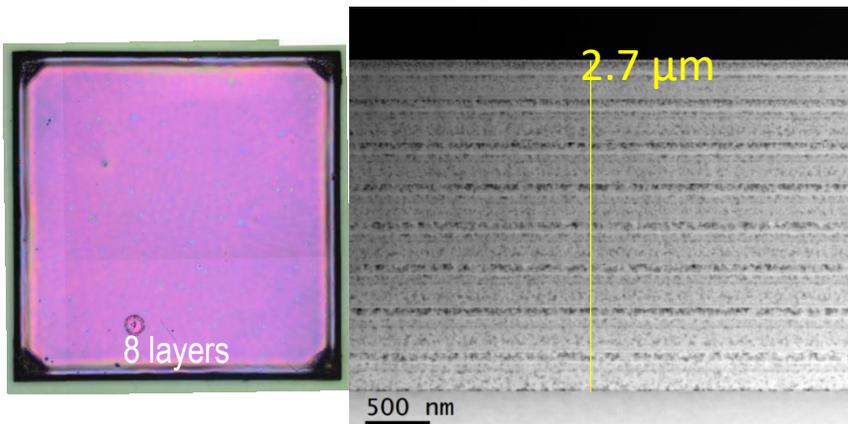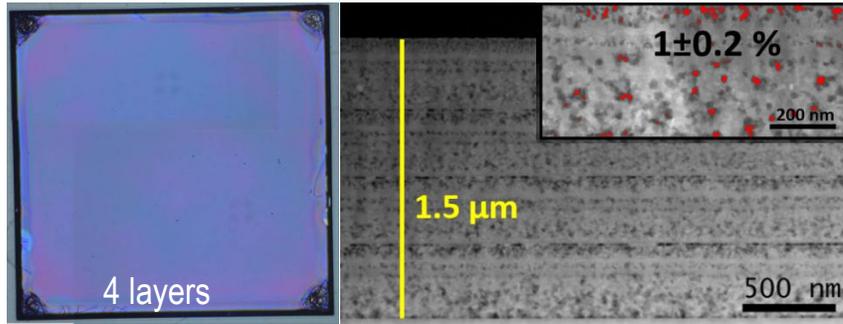A. Queralto et al, SUST (2023)

Inks, pyrolysis and multidepositions in TLAG-CSD

The increase in Cu content facilitates the decrease of supersaturation

Multifunctional ink
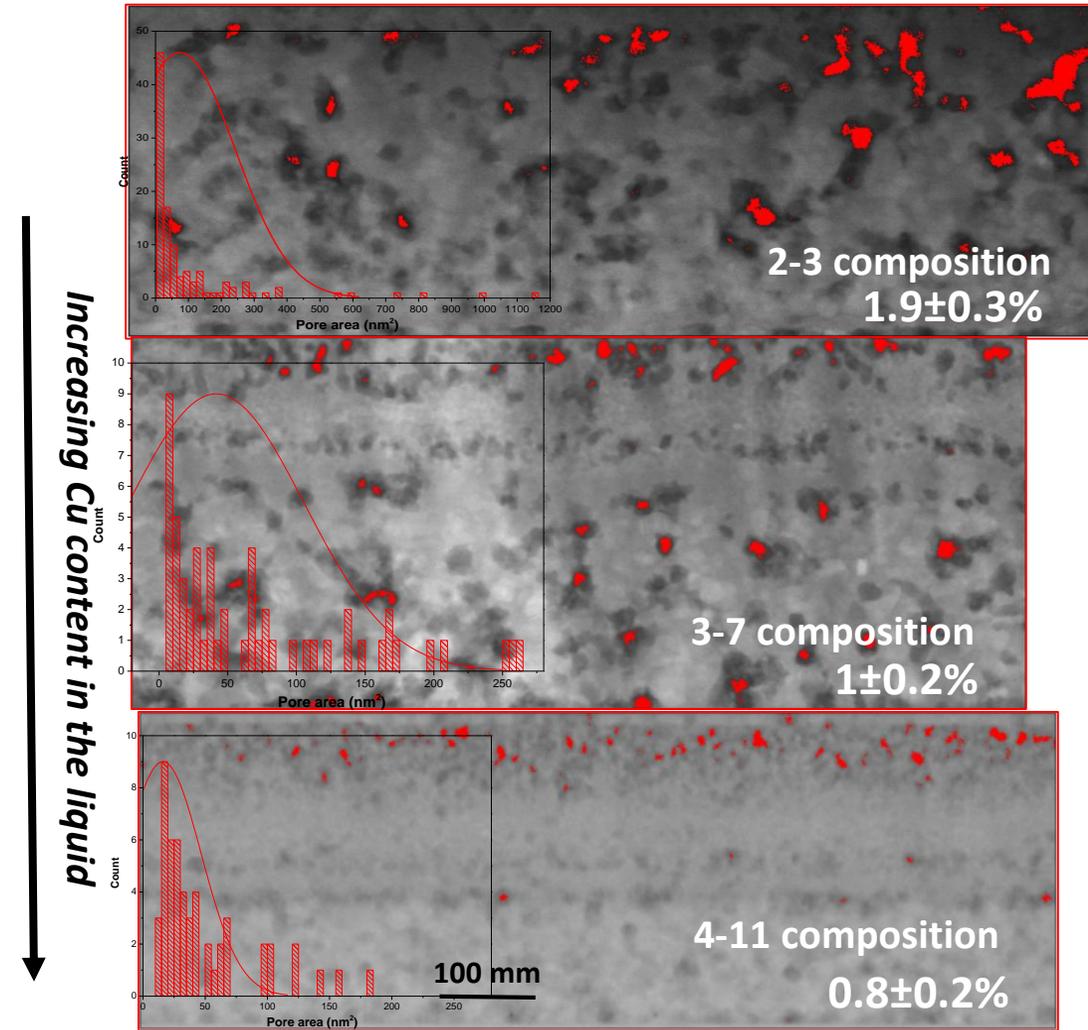Patent EP22382741

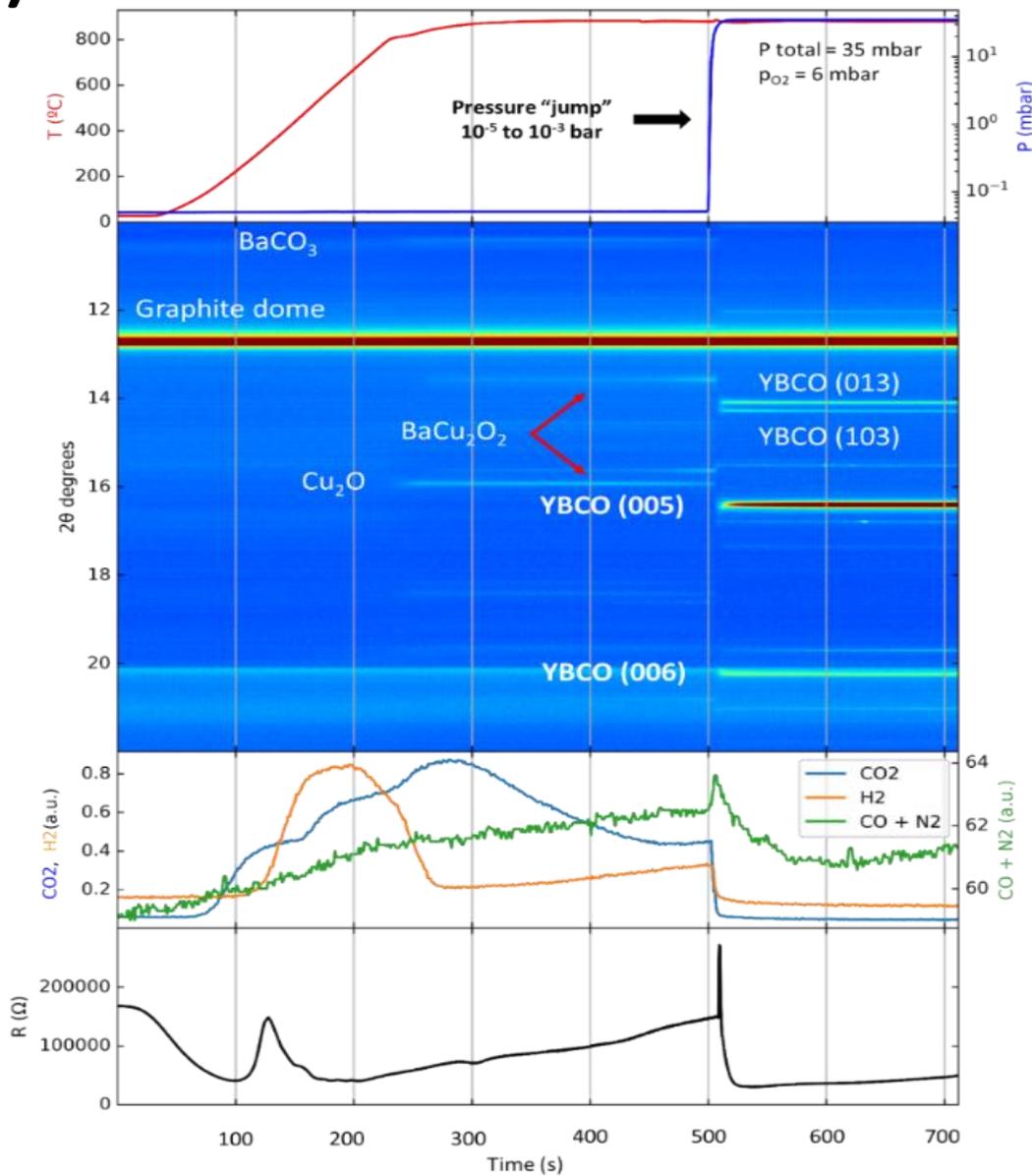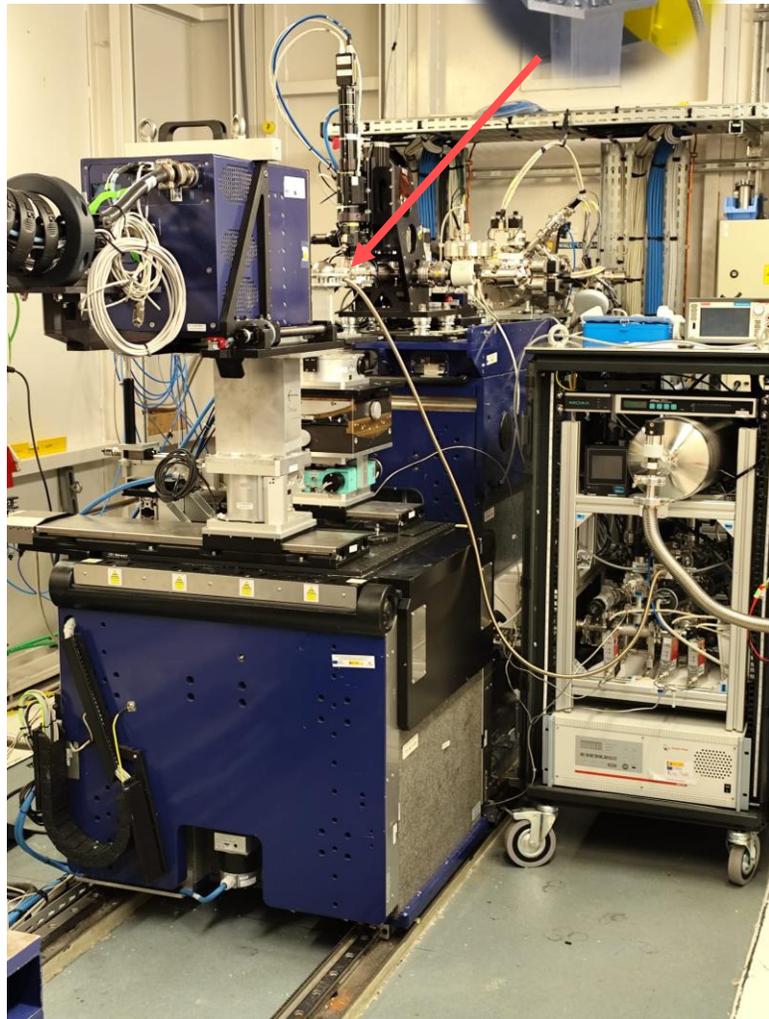Adapted to multideposition with
no loss in homogeneity

1 ± 0.2 %

200 nm

4 layers

1.5 µm

500 nm

Also demonstrates for
REBCO inks with RE= Y,
Er, Gd, Sm, Yb

2.7 µm

8 layers

500 nm

Increasing Cu content in the liquid

Count · Pore area (nm²)

2-3 composition
1.9±0.3%

3-7 composition
1±0.2%

100 mm

4-11 composition
0.8±0.2%

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

❷ Understanding TLAG growth mechanisms through in-situ 2D X-Ray Diffraction (XRD)

NCD-SWEET beamline

Experiment conditions

ETJL Joint laboratory

TLAG-LTPLD experiments March 2025

Synchrotron XRD

Mass spectroscopy

Resistivity

TLAG kinetic phase diagram from evolution of phases

BaCO₃ elimination and intermediate phases

REBCO growth

Epitaxial growth

Wide processing window further controlled by RE ion

Understanding TLAG growth mechanisms through in-situ X-Ray Absorption Spectroscopy (XAS)

CLAESS beamline

Identification of liquid characteristics in the processing window

By in-situ resistivity

YBCO

Epitaxial window

Growth rate, G, ↑ if P$_{O2}$ (and T) ↑

Grain size, a, ↓ if P$_{O2}$ (and T) ↑
(in agreement with ↑ nucleation density and ↑ supersaturation)

Going to high G is beneficial also for J$_c$

A. Palau et al, PRB (2007)
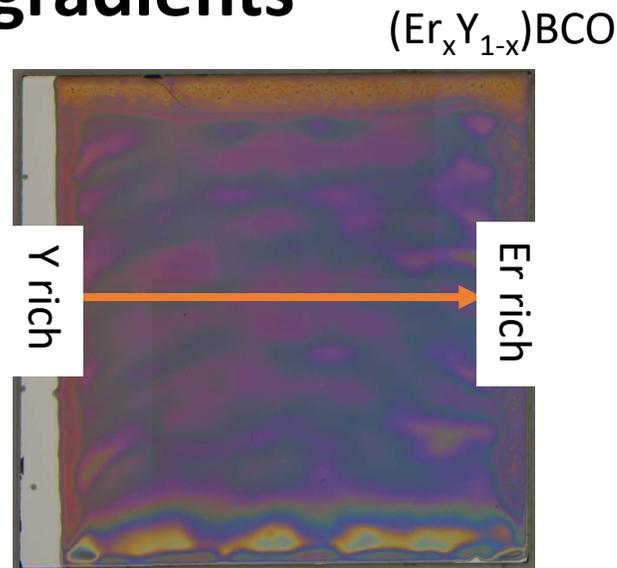
J$_c$ ↑ if grain size, a, ↓
(in agreement with other CSD methods)

High Throughput Experimentation using Combinatorial RE Compositional gradients

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Via inkjet printing

$(Er_xY_{1-x})BCO$

Y rich → Er rich

Collab. Z. Wu, T. Kiss
九州大学
KYUSHU UNIVERSITY

$(Gd_xY_{1-x})BCO$

Gd elemental map from XAS

EDX Automated measurement

100% Y
Y/RE

100% Er

Scanning Hall Probe Microscopy

(Gd/Y)BCO   (Er/Y)BCO
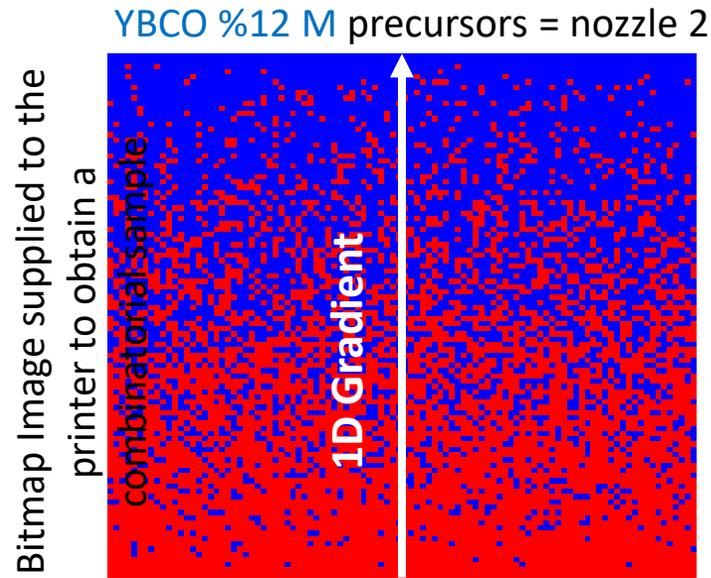
Reference YBCO

Towards Machine Learning strategies for J_c prediction

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High Throughput Experimentation using Combinatorial Compositional gradients: Nanocomposites (work in progress)

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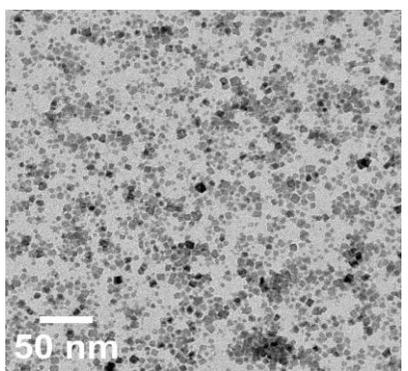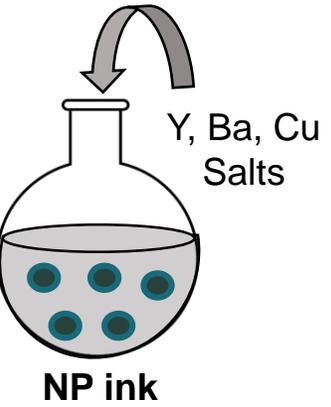EXCELENCIA SEVERO OCHOA
CSIC
CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
九州大学
KYUSHU UNIVERSITY

YBCO %12 M precursors = nozzle 2

Bitmap Image supplied to the printer to obtain a combinatorial sample

1D Gradient

YBCO precursors = nozzle 1

$BaMO_3$ (M= Zr, Hf)

Y, Ba, Cu Salts

NP ink

50 nm

Sheet current density, J_{s0} (kA/m)

0.0   201.4

12% M BZO

0% M BZO

Collab. Z. Wu, T. Kiss

Sheet current density, J_s (A/m)

$B^* =$ 0.60
0.34
0.29
0.30
0.11

11% BZO
7.5% BZO
6% BZO
3.5% BZO
1% BZO

5 K

10^5

10^4

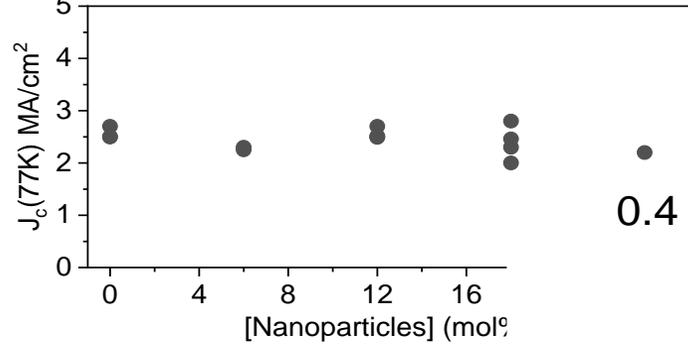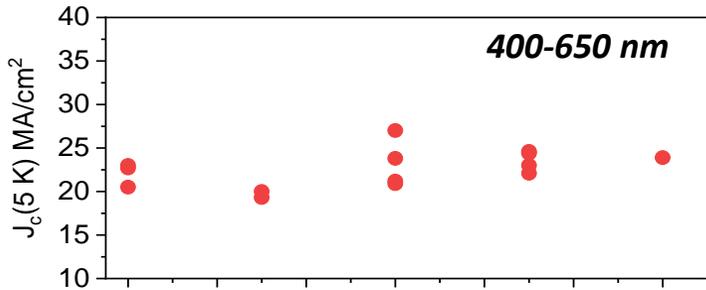Magnetic field, B (T)

0.001   0.01   0.1   1   10

Open opportunities towards gradients with different nanoparticles composition and size

$$J_s(B,x,y) = J_{s0}(x,y) * (1 + \frac{B}{B^*(x,y)})^a$$
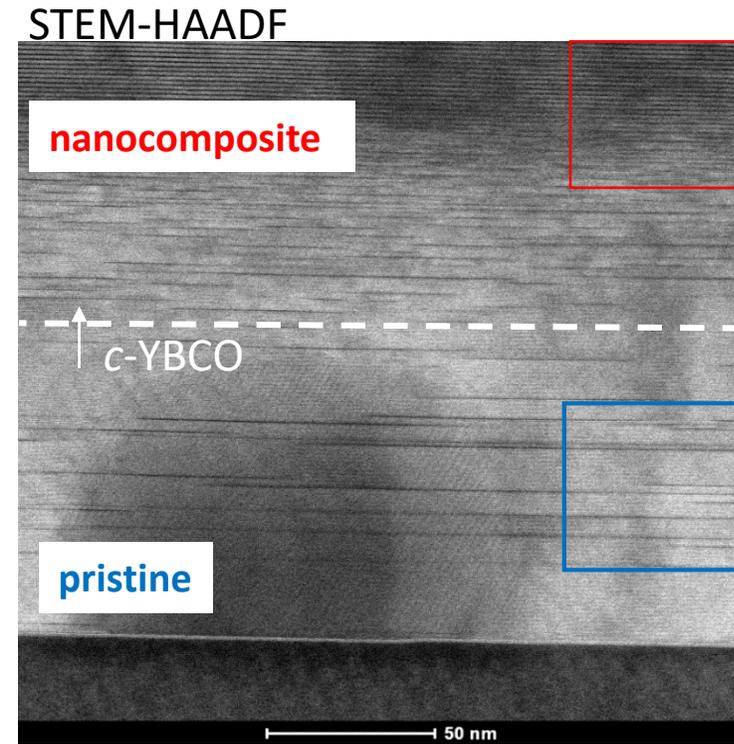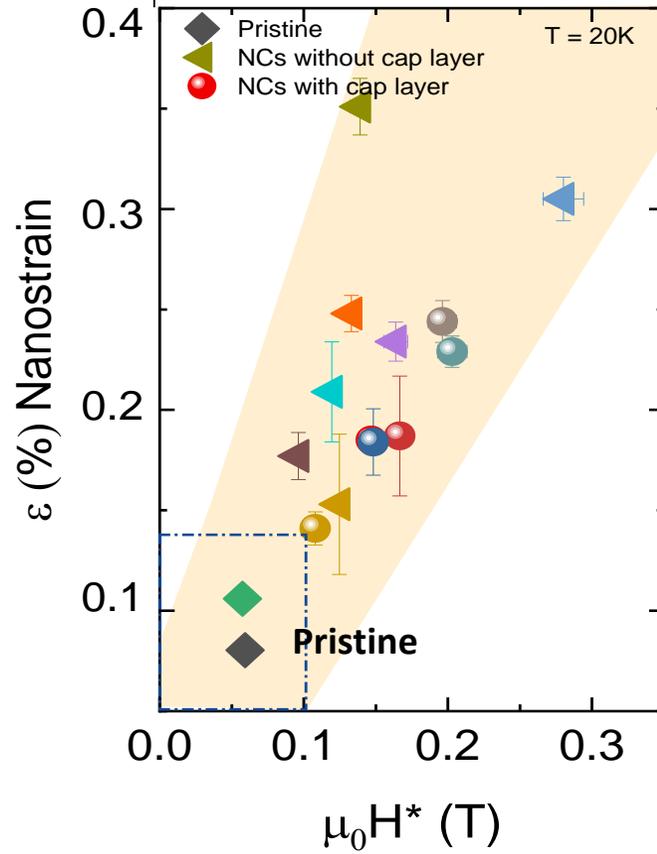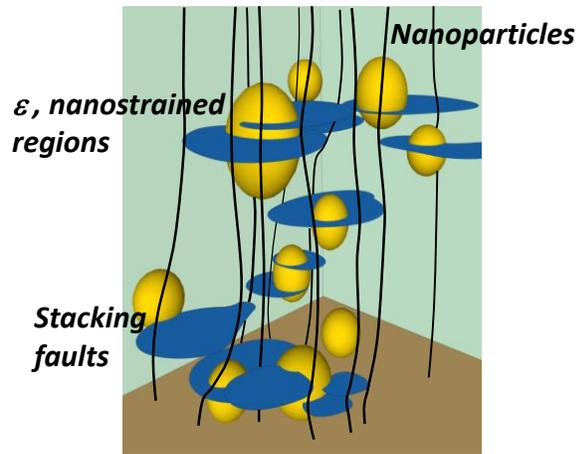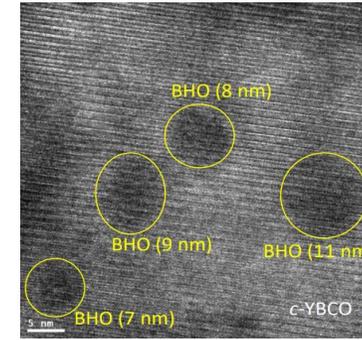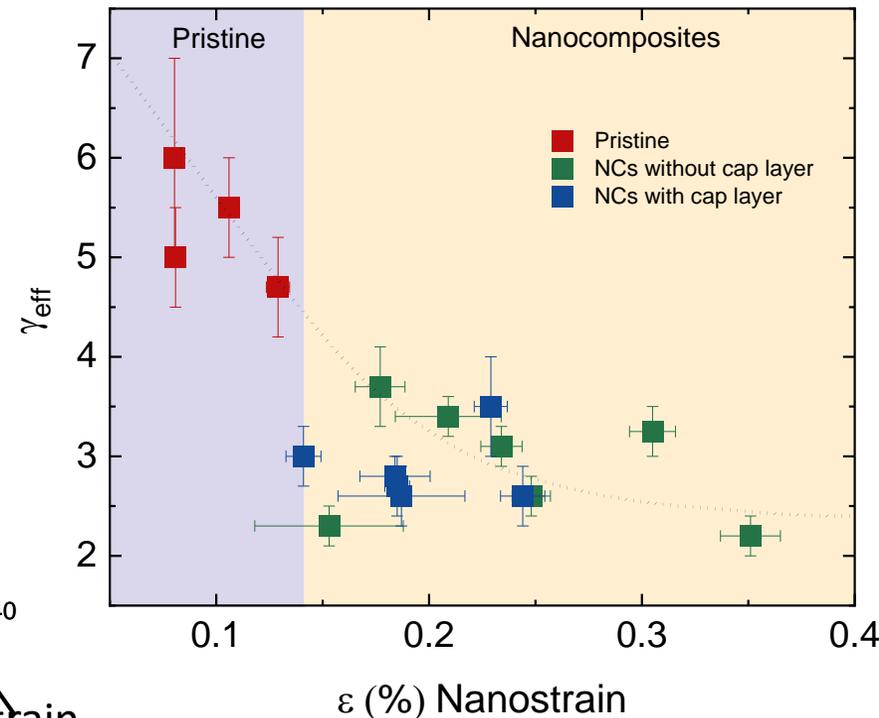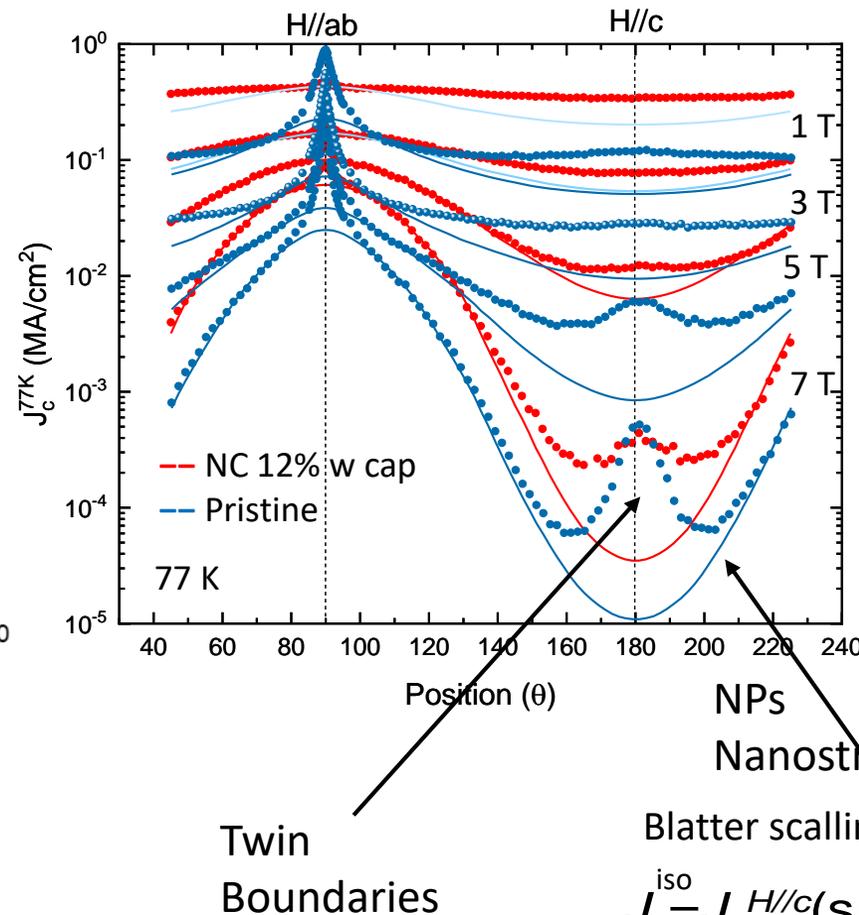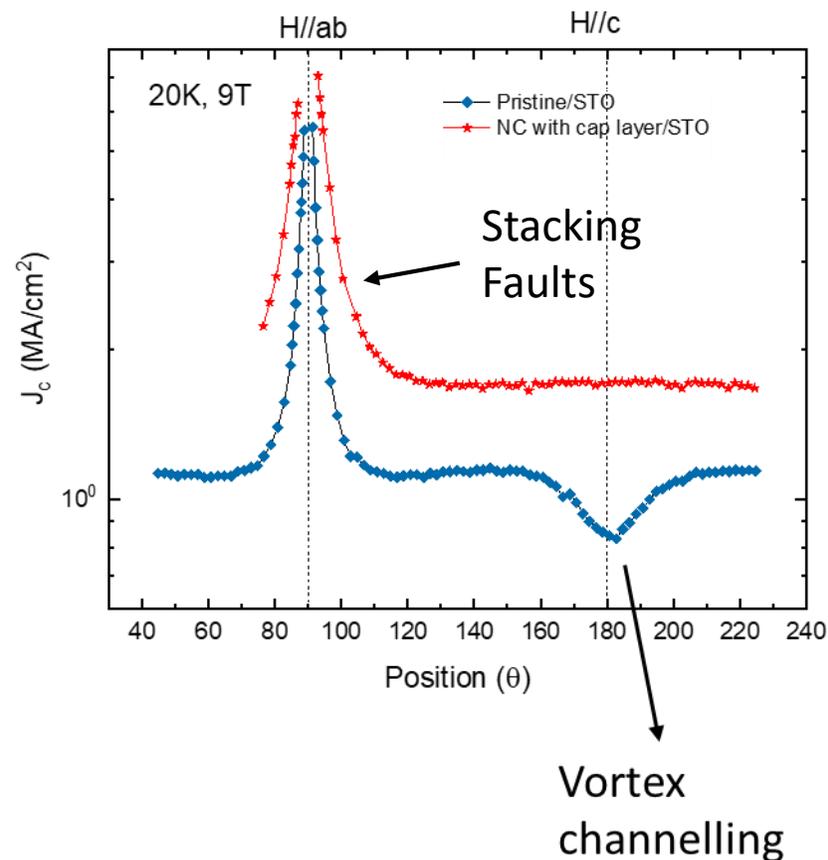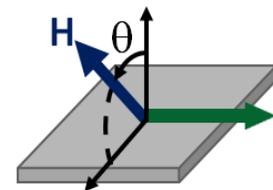
(Patent EP22382741)

❺ Vortex Physics in TLAG Nanocomposites

Tuning of vortex pinning by nanostrain and nanoparticles depend on process parameters
(i.e. supersaturation, growth rate)

400-650 nm

J_c(5 K) MA/cm²

J_c(77K) MA/cm²

[Nanoparticles] (mol%)

Pristine
NCs without cap layer
NCs with cap layer
T = 20K

ε (%) Nanostrain

Pristine

$\mu_0 H^*$ (T)

Nanoparticles

ε, nanostrained regions

Stacking faults

STEM-HAADF

BHO (8 nm)
BHO (9 nm)
BHO (11 nm)
BHO (7 nm)
c-YBCO

nanocomposite

17nm
14nm
23nm

c-YBCO

pristine

c-YBCO

T. Puig et al, Nat Rev Phys (2024)

Vortex Pinning anisotropy in TLAG films

Stacking Faults

Vortex channelling

Twin Boundaries

NPs Nanostrain

Blatter scalling approach

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

Nanocomposites decrease vortex dissipation and induce less anisotropy
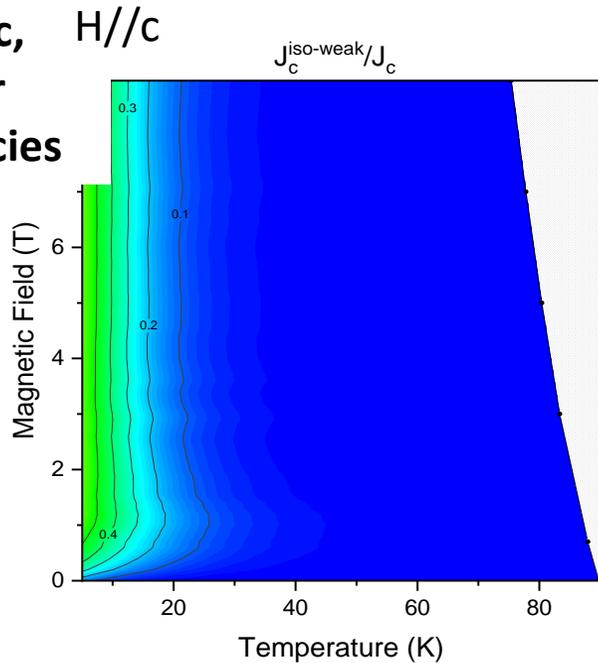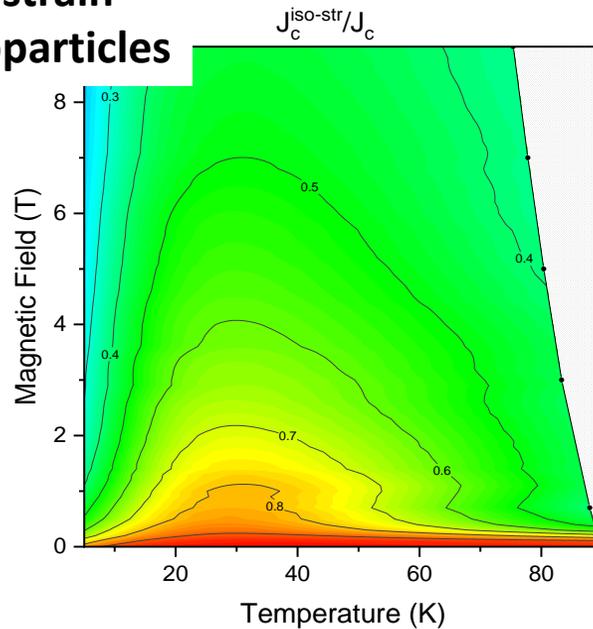**Vortex behaviour depends on T, H, θ and process parameters**

F. Valles et al, Comm Mat 3 (2022)

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TLAG Vortex Pinning diagrams

$$J_c(T) = J_c^{iso-wk}(T) + J_c^{iso-str}(T) + J_c^{aniso-str}(T)$$

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Atomic, cluster vacancies — H//c

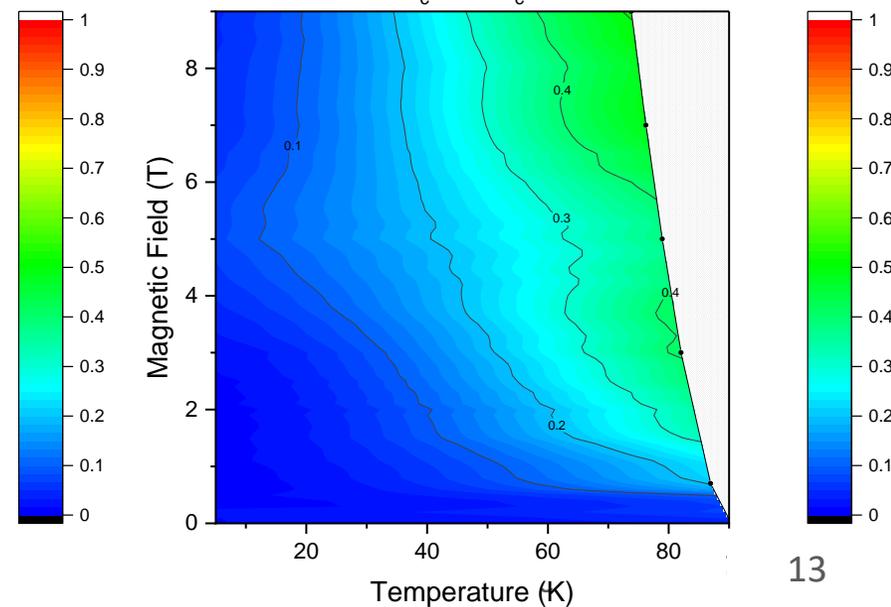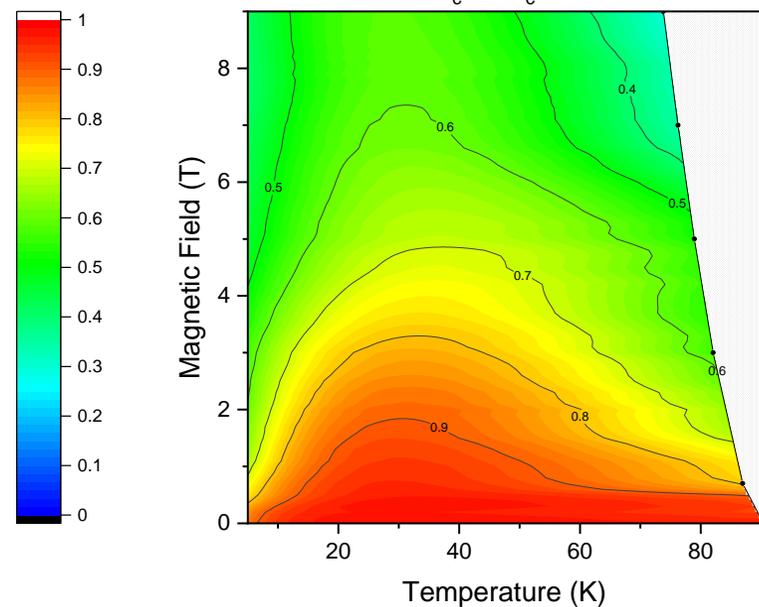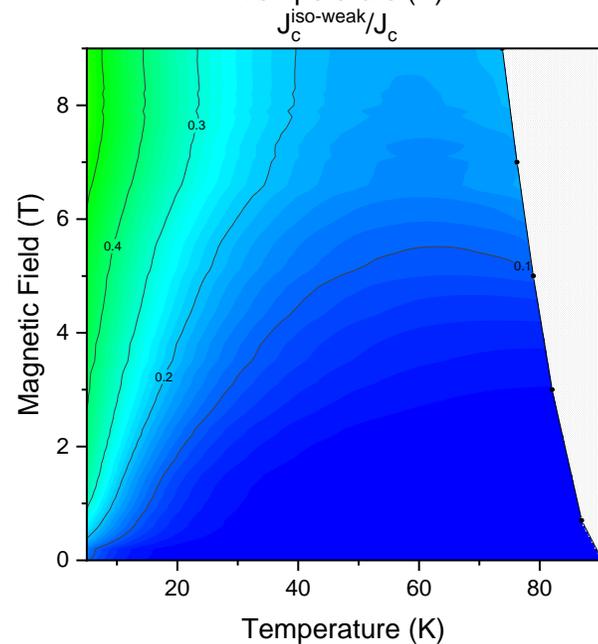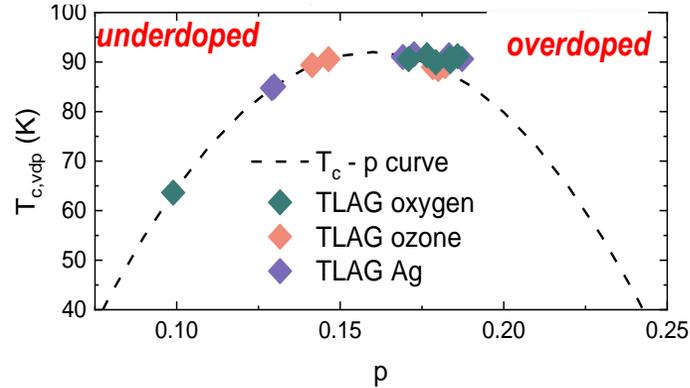**Nanostrain Nanoparticles**

Twin boundaries

Pristine

YBCO + 18% BZO
NC without cap layer

The overdoped state: Opportunity to increase pinning efficiency

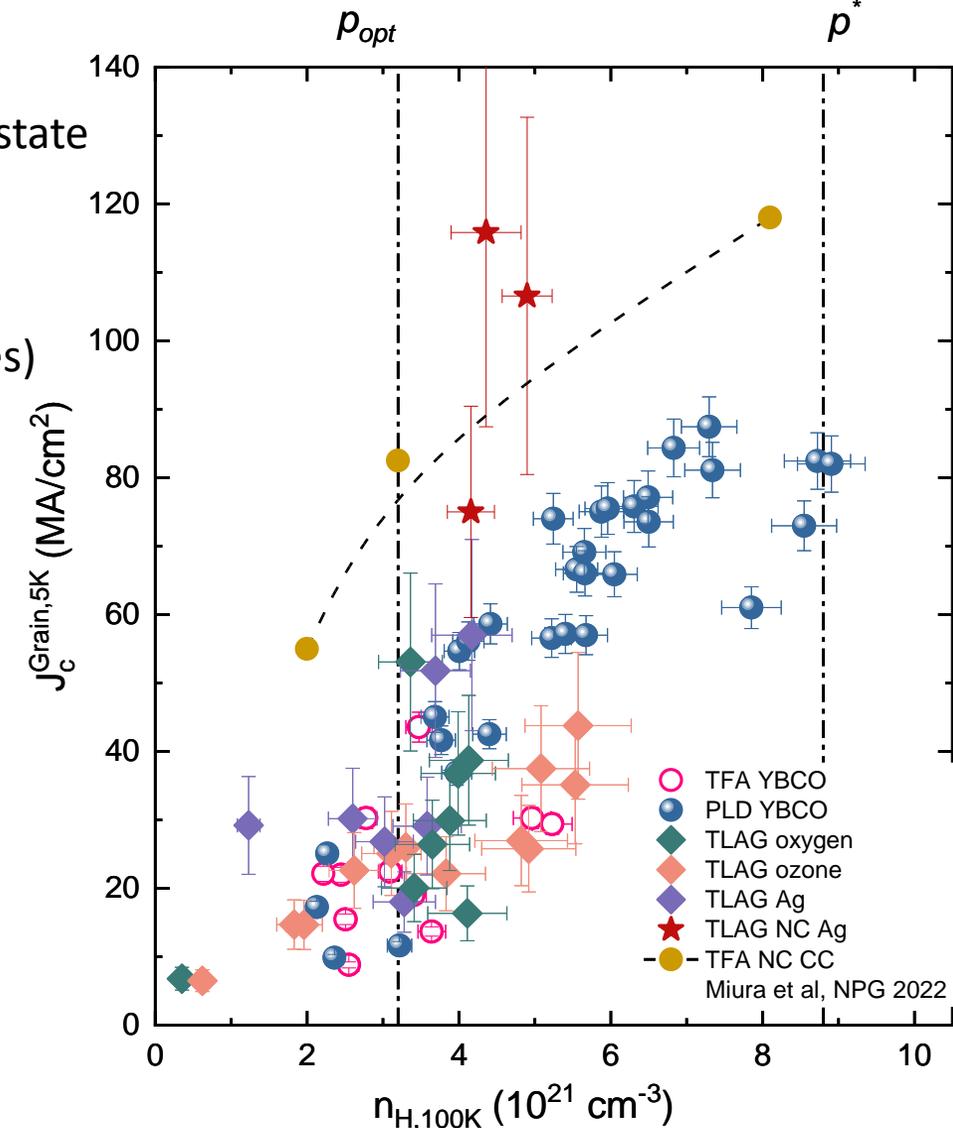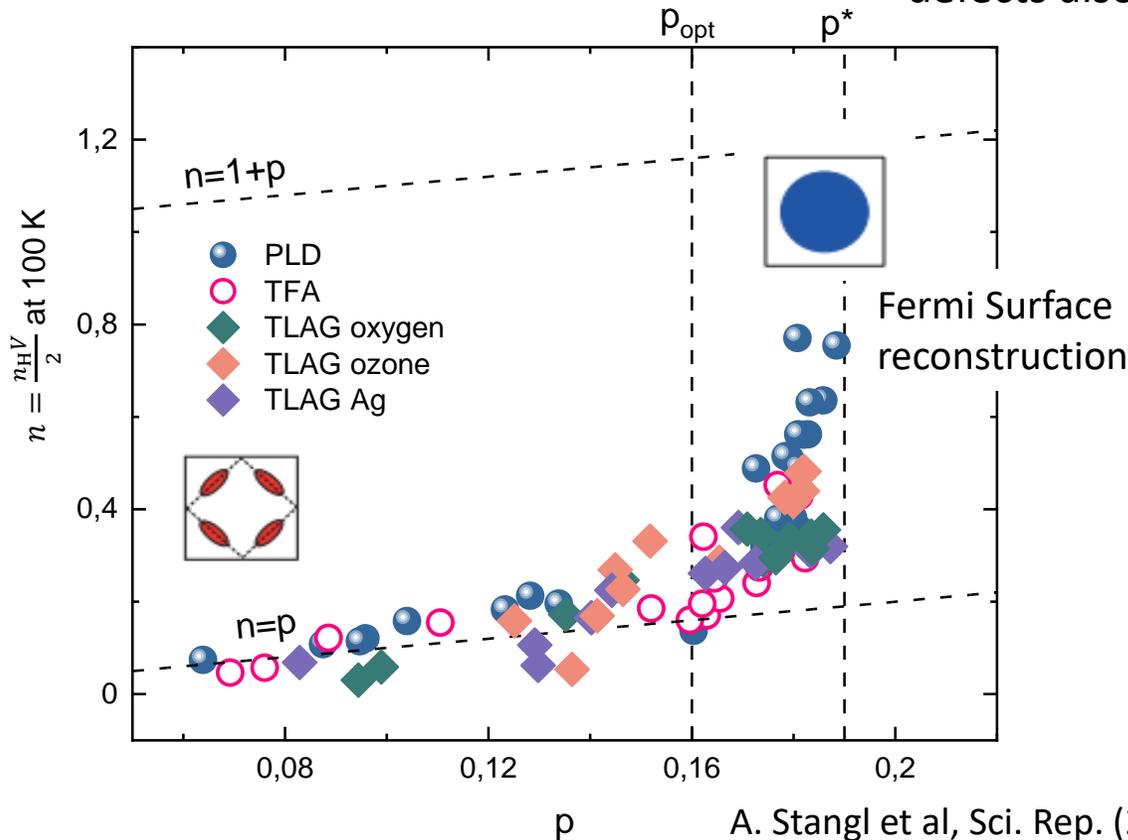**where charge carrier density and condensation energy increases**

$$n_H \propto E_c \propto f_p$$

Strong increase of J_c in overdoped state

$$\lambda\downarrow, \xi\downarrow \rightarrow E_c\uparrow$$

(Higher efficiency of pinning defects also for nanocomposites)
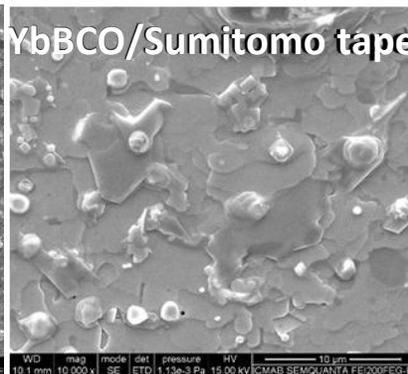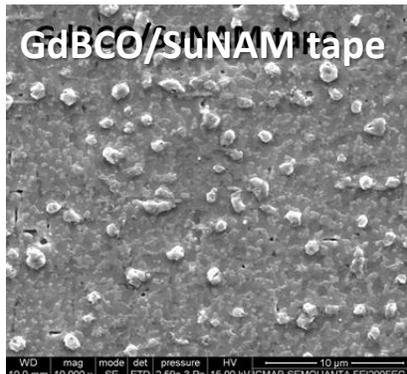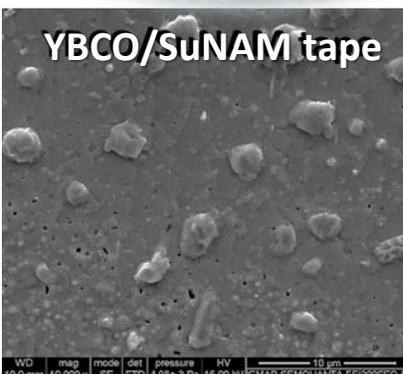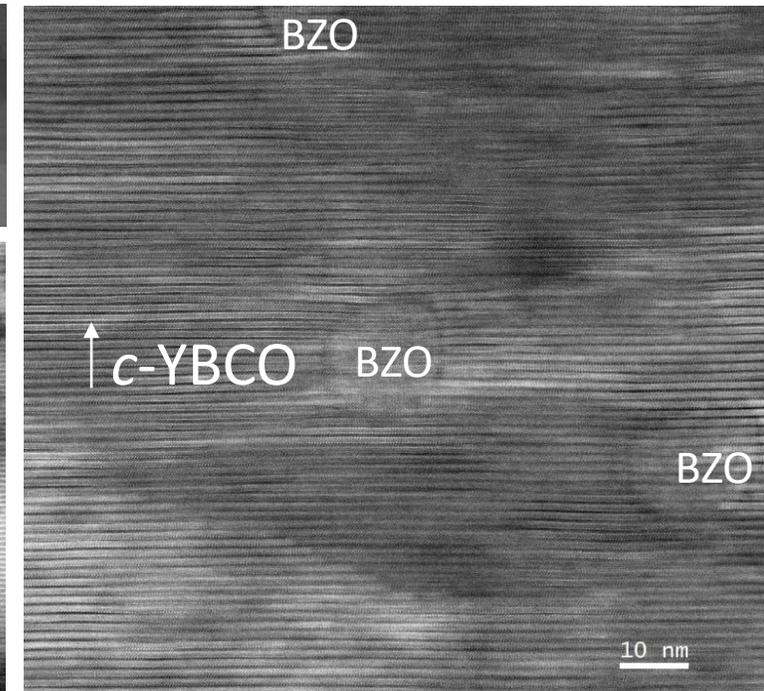
Study of different oxygenation methods

Fermi Surface reconstruction

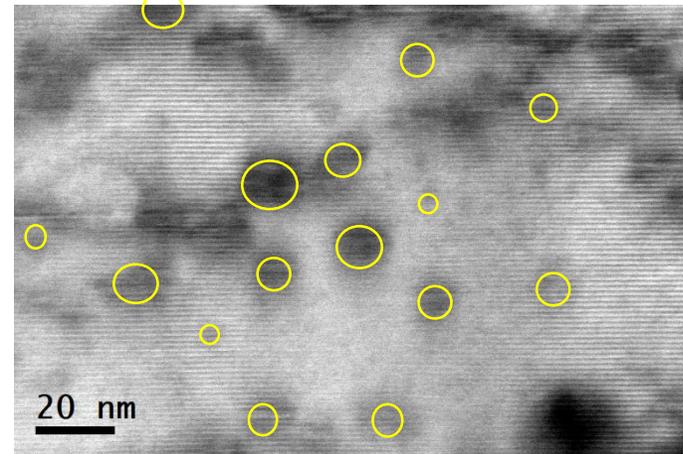A. Stangl et al, Sci. Rep. (2021), X. Obradors et al, Nature Mater. N&V (2024)

Towards wide area TLAG Coated Conductors

Colloidal Ink
scaled ~ liter

Slot die
now with 40 mm-width printhead capabilities

YBCO NC /Sumitomo tape

YBCO

LMO

Buffer layer

200 nm

20 nm

BZO

c-YBCO   BZO

BZO

10 nm

YBCO/SuNAM tape

GdBCO/SuNAM tape

YbBCO/Sumitomo tape

Microstructure is reproduced in 250-750 nm CC
High superconducting properties: J_c(77K) =1.7-2 MA/cm^2

Construction of a furnace for 40 mm-wide tape is on going

Conclusions and outlook

- TLAG is a high-throughput process, very versatile and with a large processing window that can support large volume CC fabrication while reducing cost/performance ratio

- In-situ Synchrotron techniques are ideal to underpin the TLAG mechanisms

- High Throughput Experimentation with combinatorial gradients and AI should accelerate the selection of compositions and conditions

- Vortex pinning in the overdoped state is the future to achieve higher efficiency due to the increase in condensation energy in a robust way

- TLAG should be a large area processing method that adapts to the needs of increased production as well as opens to new applications