In-situ X-Ray Diffraction revealing the reaction mechanism of ultrafast Transient Liquid Assisted Growth of superconducting thin films

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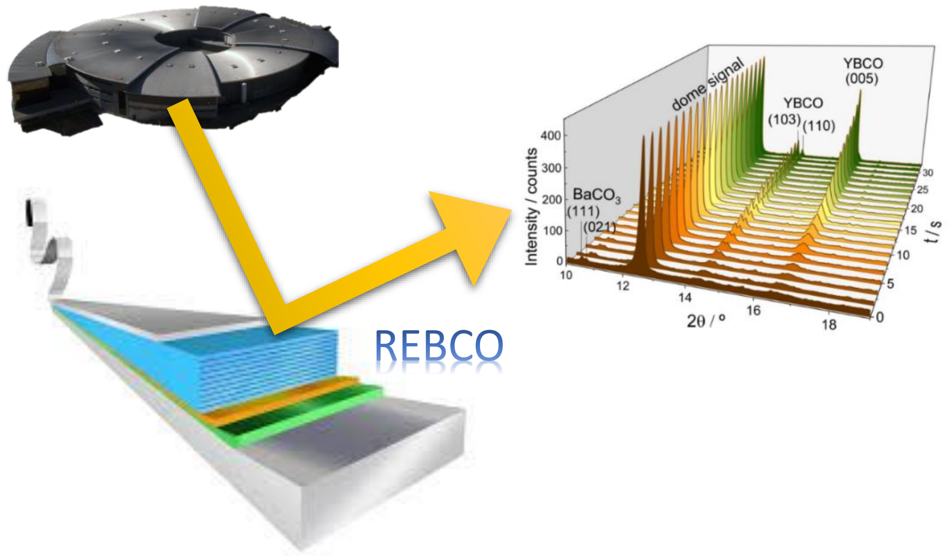
ALBA Synchrotron[3], Cerdanyola del Valles, Spain
SOLEIL Synchrotron[4], Saint Aubin, France



XI AUSE Conference
VI ALBA Users Meeting
Oviedo
2 – 6 September 2024

ICMAB EXCELENCIA SEVERO OCHOA · CSIC

Who are we and what do we do?

An interdisciplinary group of physicists, chemists, materials scientists and engineers committed to enable High Temperature Superconducting materials in our society.

Investigating fundamental understanding on Materials & Science of Superconductors to process scalability and integration in devices.

suman
SUPERCONDUCTING MATERIALS AND FUNCTIONAL NANOENGINEERED STRUCTURES

Prof. Rosa Palacin, ICMAB
BATTERIES + SUPERCONDUCTORS

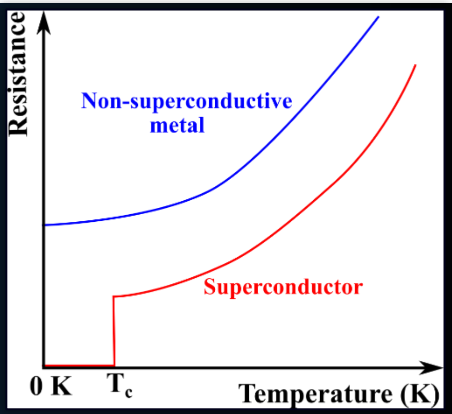
NET-ZERO INDUSTRY ACT
by European Commission
"Net-zero" CO_2 emissions by 2050

Why do we do what we do?

Functional materials for energy applications

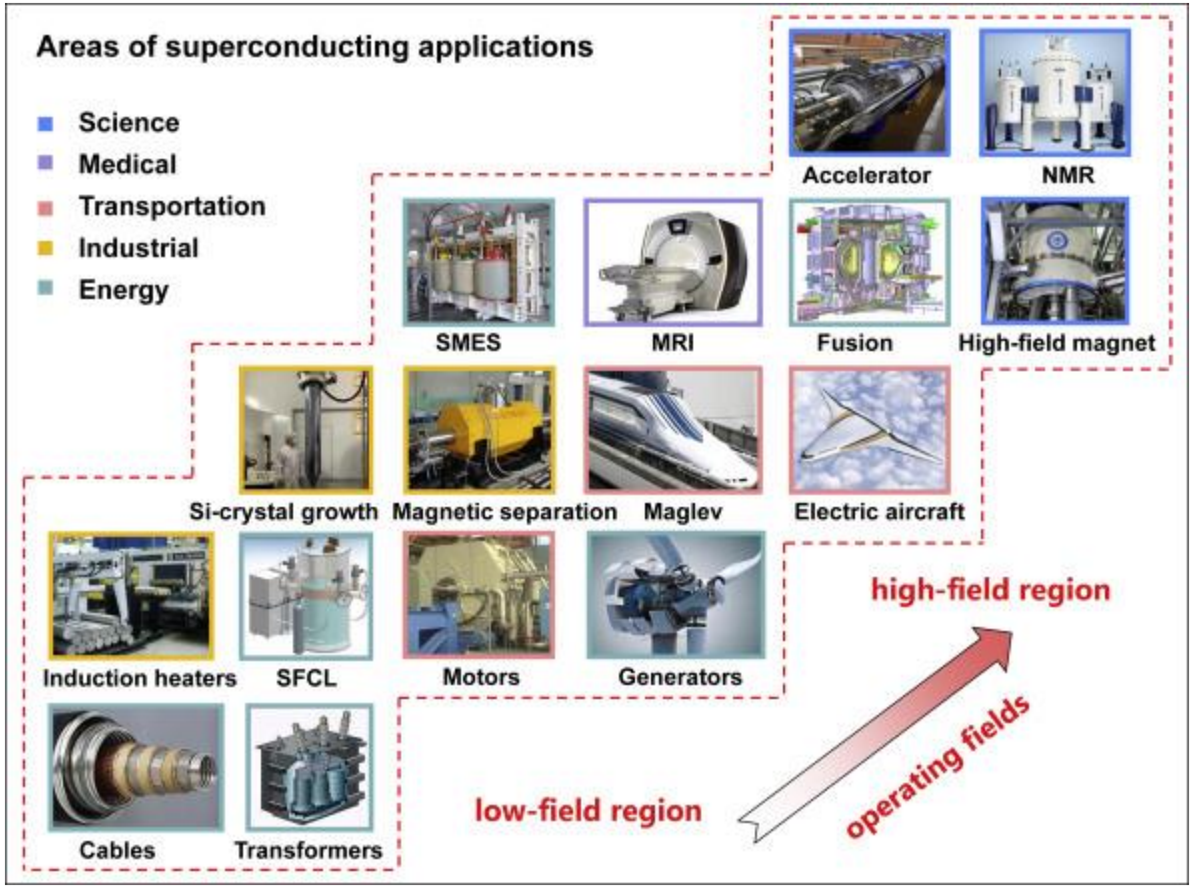
Superconducting Materials

- Lossless electrical transport
- Efficient energy transportation
- Enhance resilience of power grids
- New possibilities at high magnetic fields



[https://commission.europa.eu/strategy-and-policy/priorities-2019-2024/european-green-deal/green-deal-industrial-plan/net-zero-industry-act_en]

The power of High Temperature Superconductors

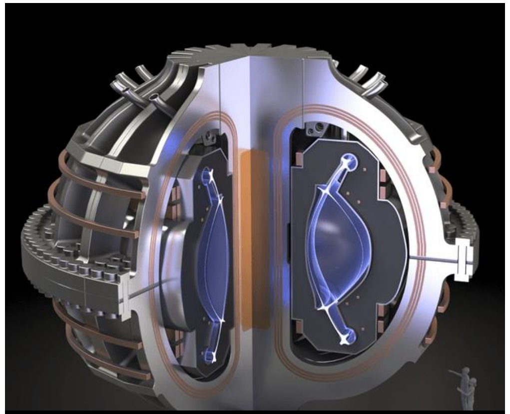


iScience 2021, Volume 24, Issue 6, 102541, *https://doi.org/10.1016/j.isci.2021.102541*

Off-shore plants of > 10 MW wind generators

Electric aircraft at NASA

Next generation High Energy Colliders

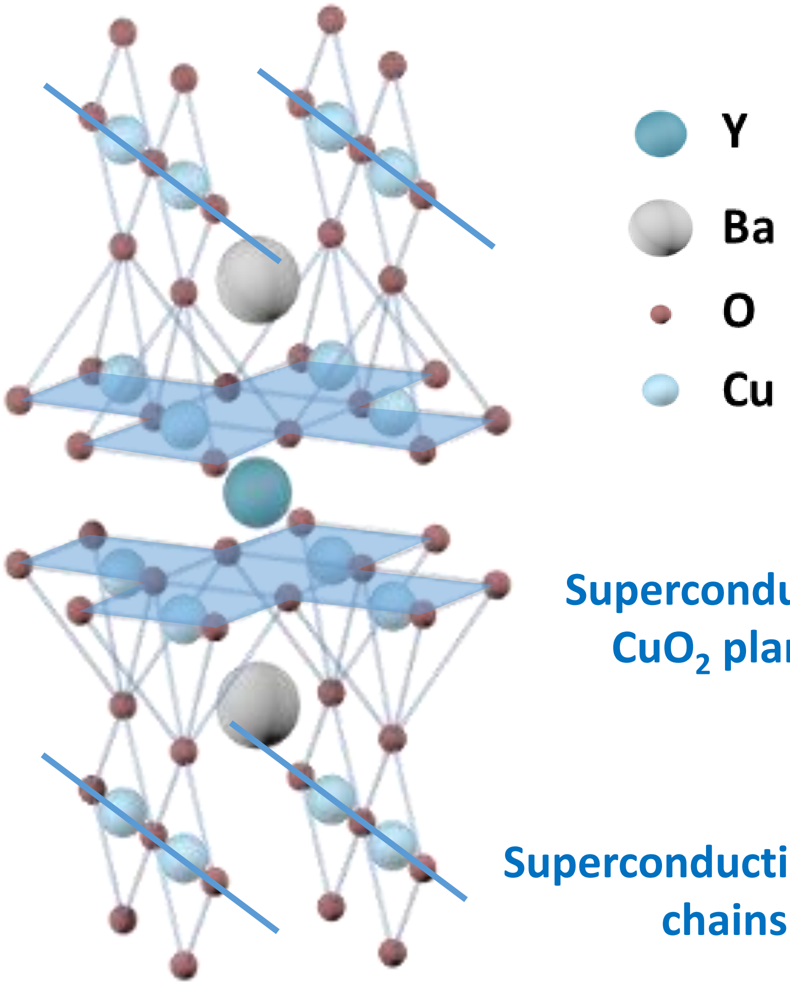


Commonwealth Fussion systems- MIT

Path to limitless, clean, fusion energy

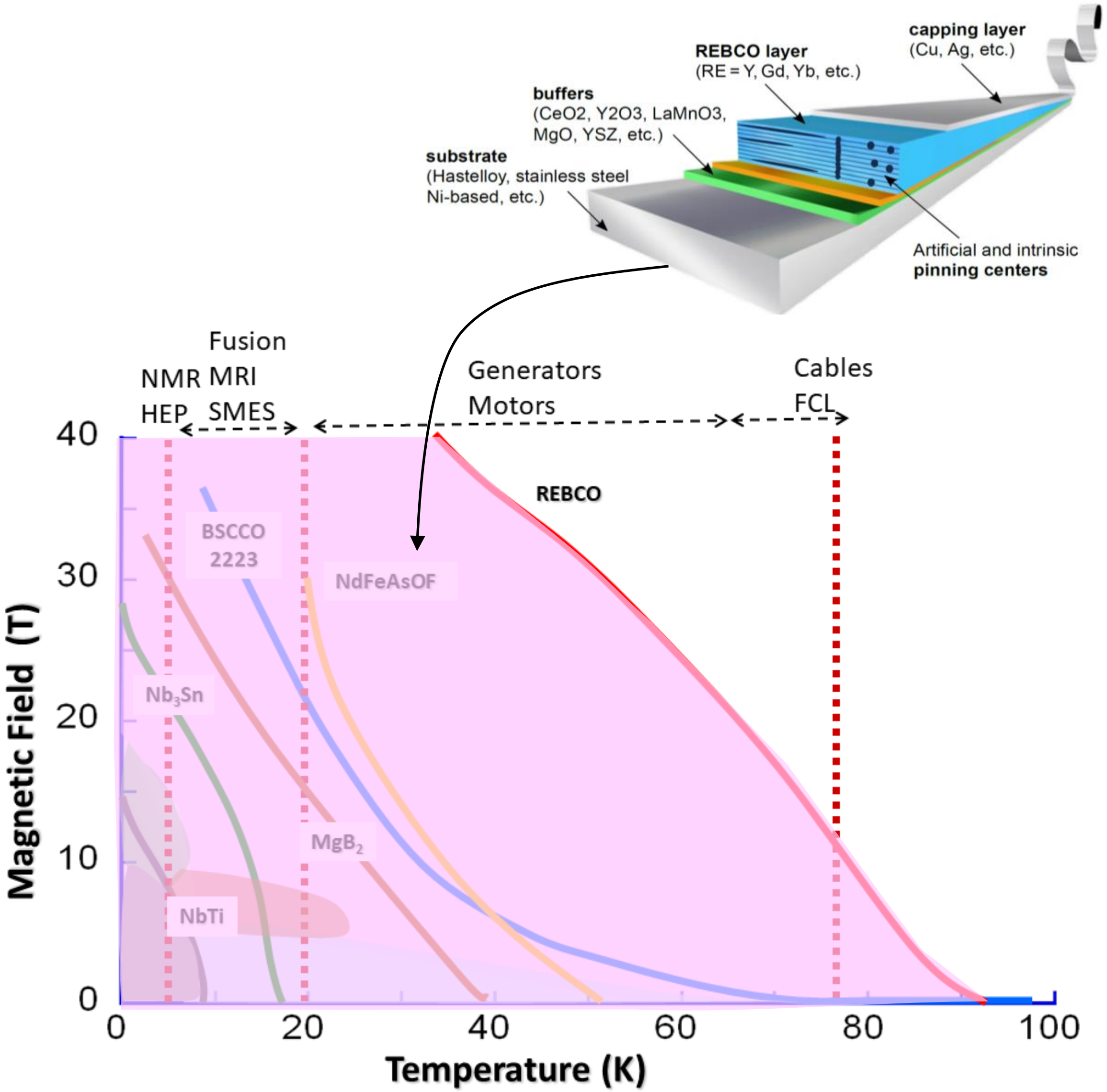
REBCO = The highest field and highest temperature superconductor

$REBa_2Cu_3O_{7-x}$, RE= Y, Rare Earth



Superconducting CuO_2 planes

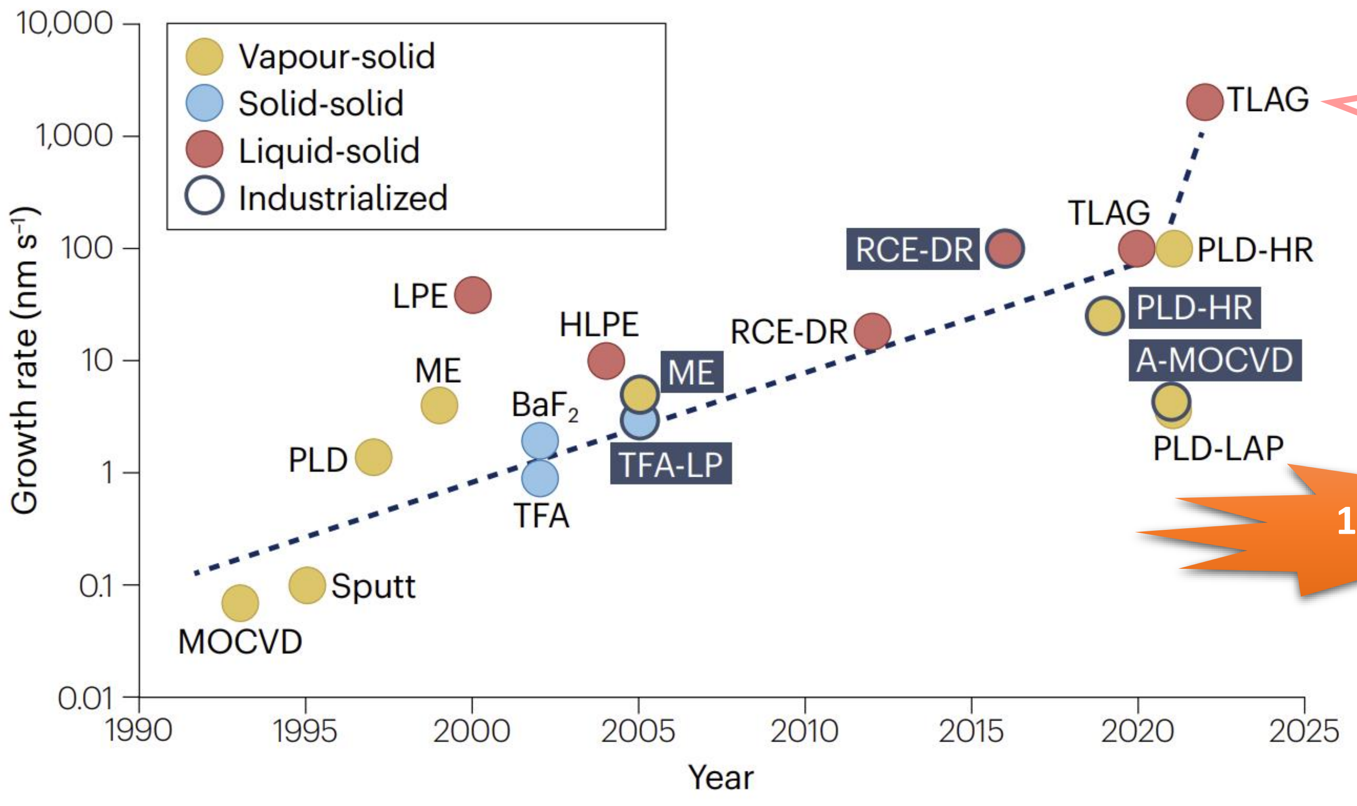
Superconducting Cu-O chains



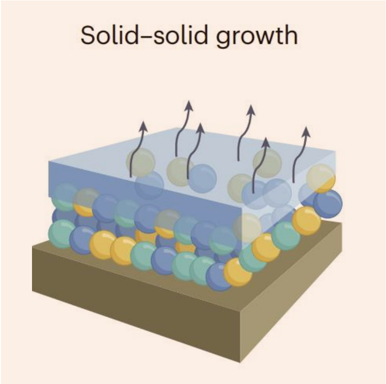
Reaching high Growth Rates: A path towards cost reduction

$$\downarrow \frac{Cost}{Perfomance} = \frac{total\ cost\ per\ year}{\color{red}{G}\ x\ L\ x\ W\ x\ (I_{c-w}/d)} = \frac{€}{kA\ x\ m}$$

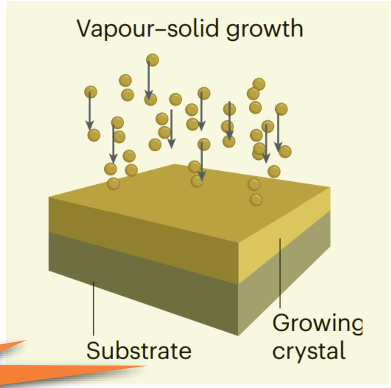
***G*= growth rate**
W= tape width
L= tape length
d=tape thickness



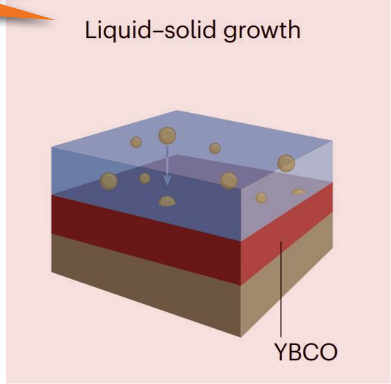
10-20 x $G_{industry}$



G= 0.5-5 nm/s



G= 0.5-25 nm/s



G=10-1000 nm/s

T. Puig et al, Nature Review Physics (2023, doi.org/10.1038/s42254-023-00663-3)

Transient Liquid Assisted Growth of REBCO films

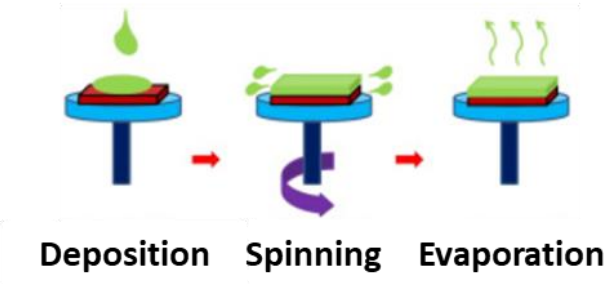
High-throughput, scalable and low cost production of Coated Conductors

$$(M\text{-}Prop) \longrightarrow \mathbf{BaCO_{3(s)} + CuO_{(s)}} + Y_2O_{3(s)} \longrightarrow \mathbf{(Ba - Cu^{I/II}\text{-}O)_{(l)} + Y_2O_{3(s)}} \longrightarrow YBa_2Cu_3O_{7-\delta}$$

Metal-organic inks

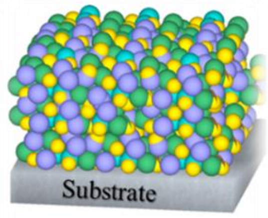
Deposition on substrate

Spin coating



Chemical solution deposition

Low Temperature pyrolysis



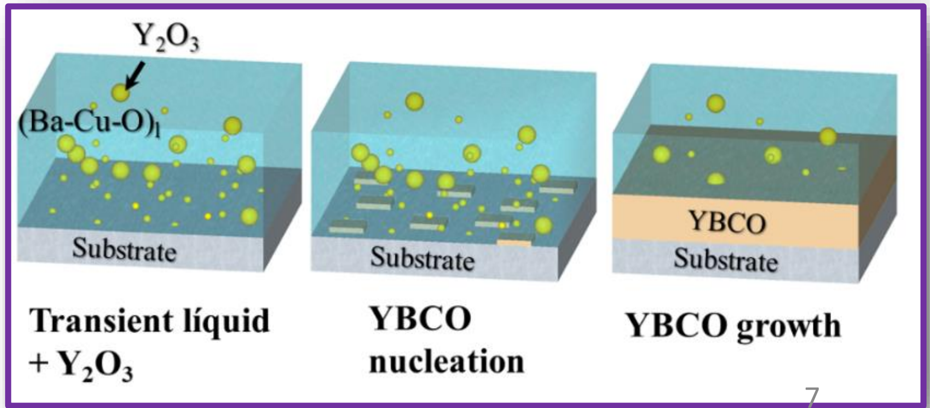
TLAG process

Ultrafast kinetic growth

High temperature crystallization

Experiment conditions:

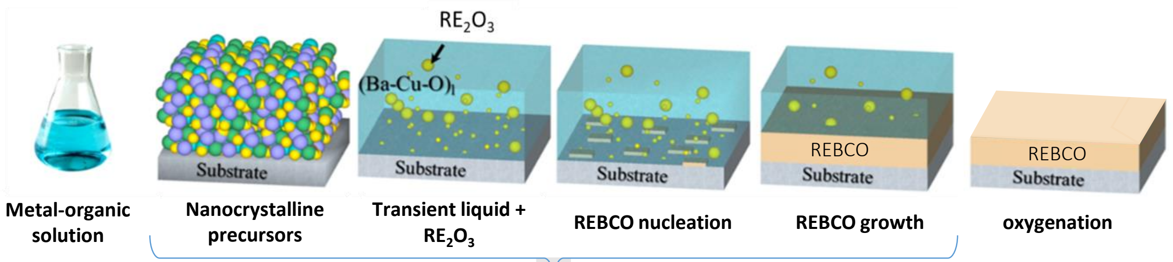
P_T, P_{O2}, Temperature, heating and presure ramp, gas velocity,...

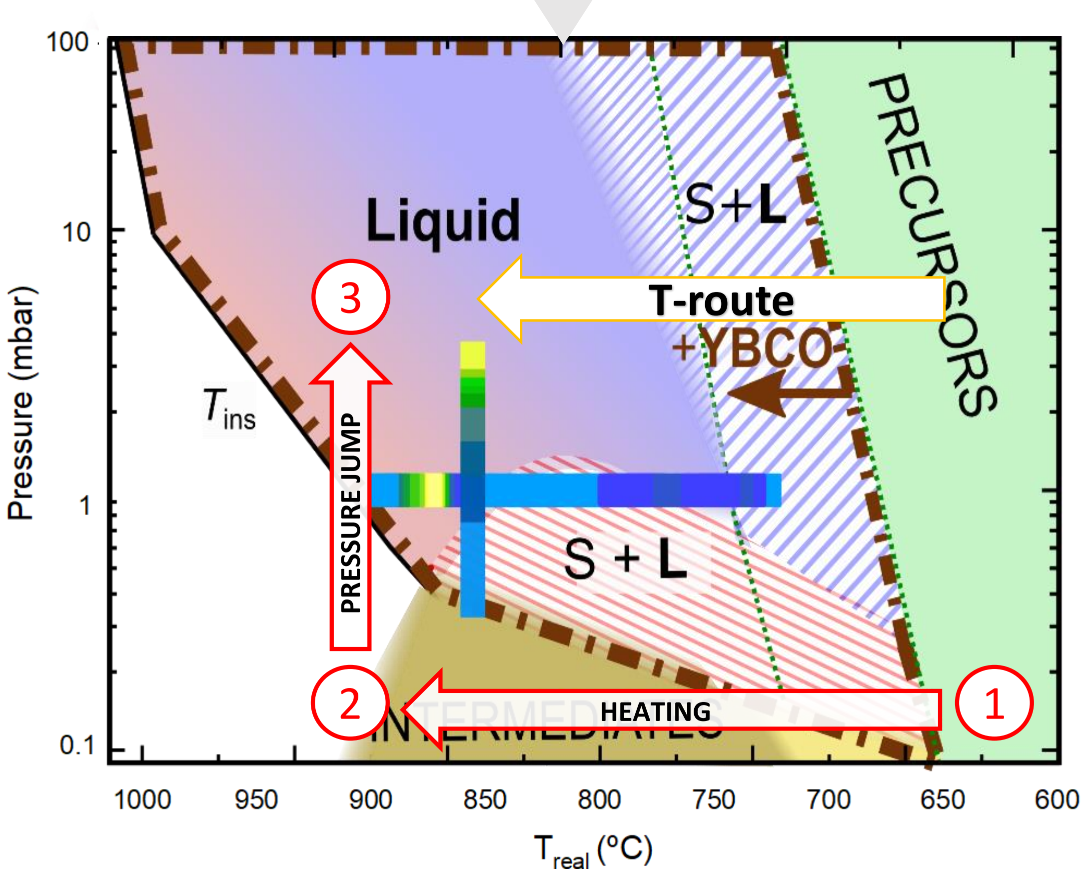


Need of advanced characterization for process understanding and optimization by in-situ growth at light sources:

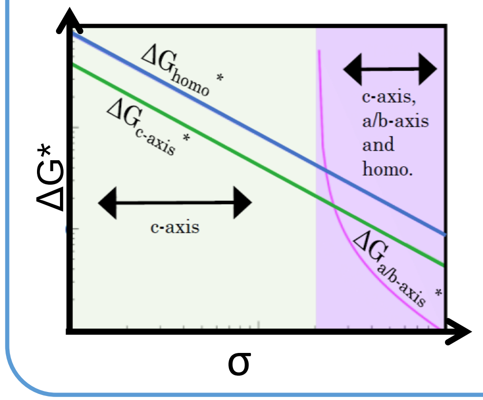
- X-ray diffraction (phase transformations and orientation)

TLAG growth control and characterization





Control of TLAG process: supersaturation σ



σ ↑ ⇒ growth rate ↑

σ ↑ ⇒ epitaxy ↓

Compromise between high growth rates and epitaxy

① Nanocrystalline precursors: $BaCO_{3(s)} + CuO_{(s)} + Y_2O_{3(s)}$

① HEATING ⇒ ② Intermediate reactions

② PRESSURE JUMP ⇒ ③ Transient liquid formation: $(Ba - Cu^{I/II} - O)_{(l)} + Y_2O_{3(s)}$

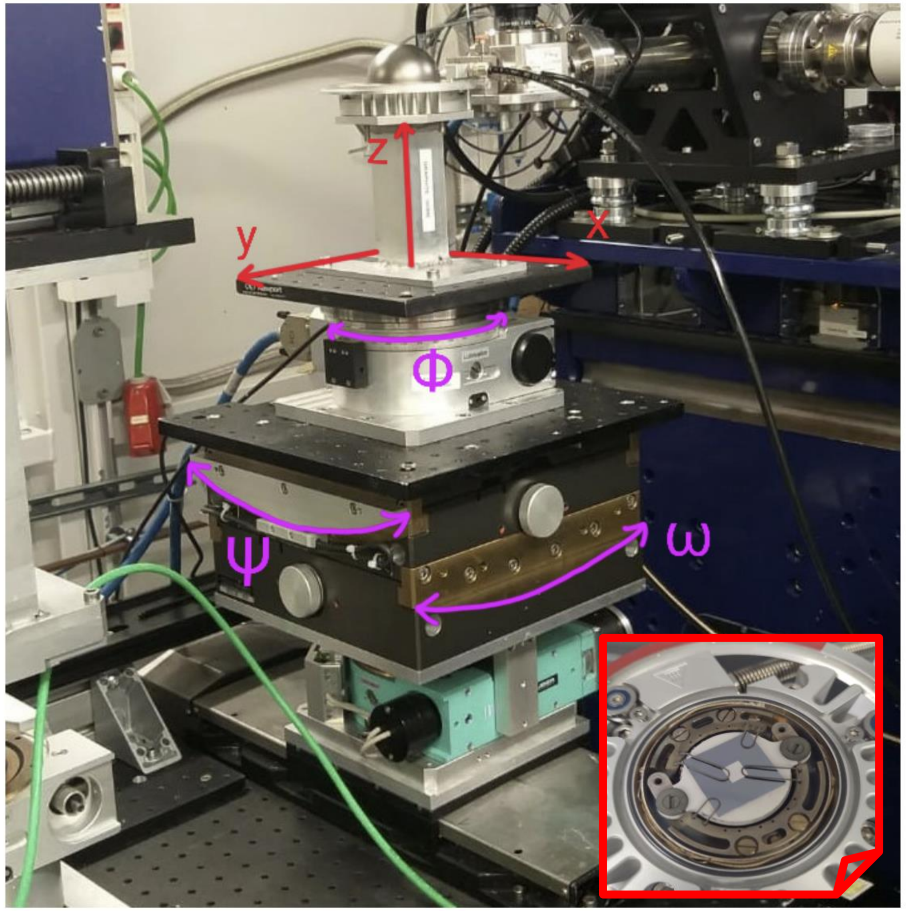
③ REBCO growth: $YBa_2Cu_3O_{7-\delta}$

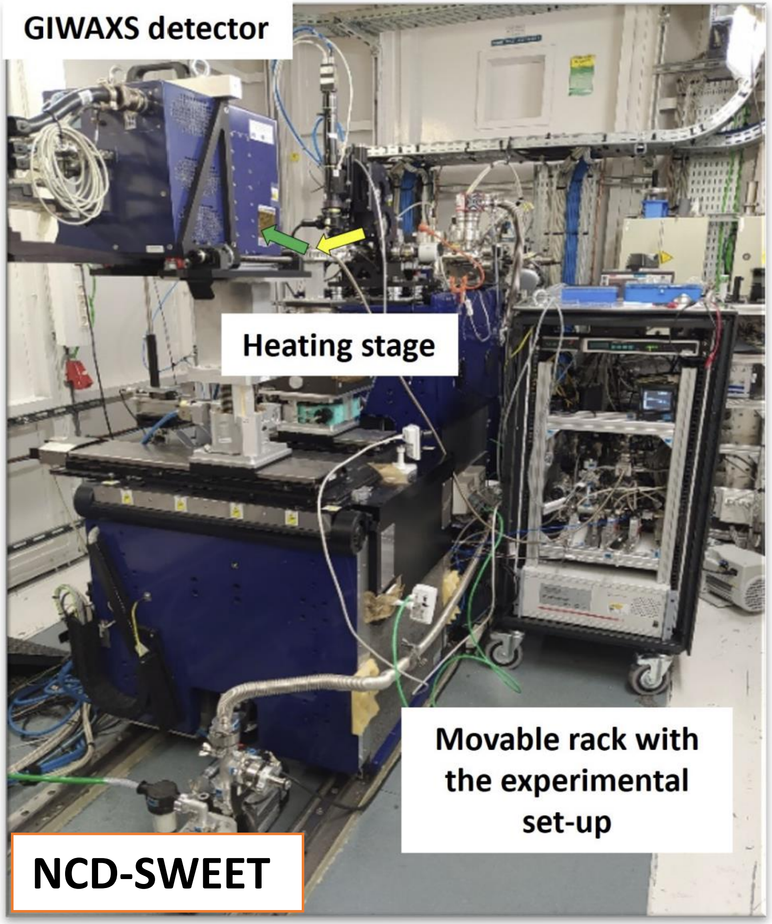
ALBA

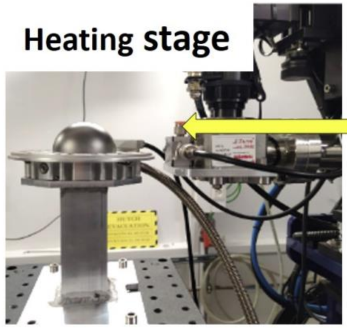
In-situ XRD at ALBA Synchrotron enables studying intermediate phase evolution and TLAG non-equilibrium growth mechanism

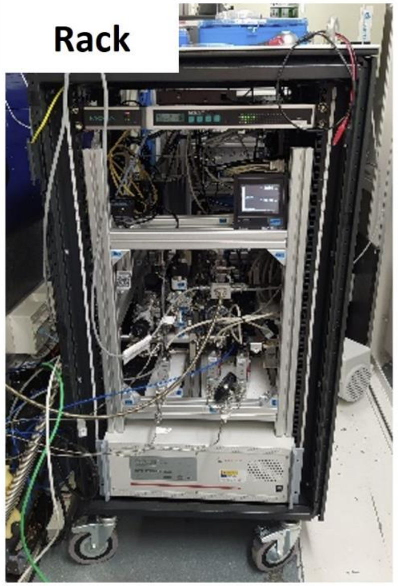
L. Soler et al, Nat. Commun. (2020); S. Rasi et al, J. Phys Chem C (2020); S. Rasi et al, Adv. Sci. (2022)

Enabling *in-situ* XRD characterization of TLAG at ALBA









- Rayonix 2D (GI)WAXS CCD detector (1920 x 5760 pixels)
- Pixel size: 44.27 x 44.27 µm
- Tunable Sample ↔ Detector distance (<300 mm)
- Down to 100 ms per XRD frame

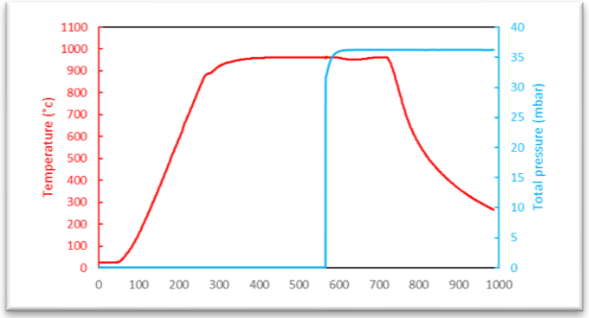
G of up to 2000 nm/s*

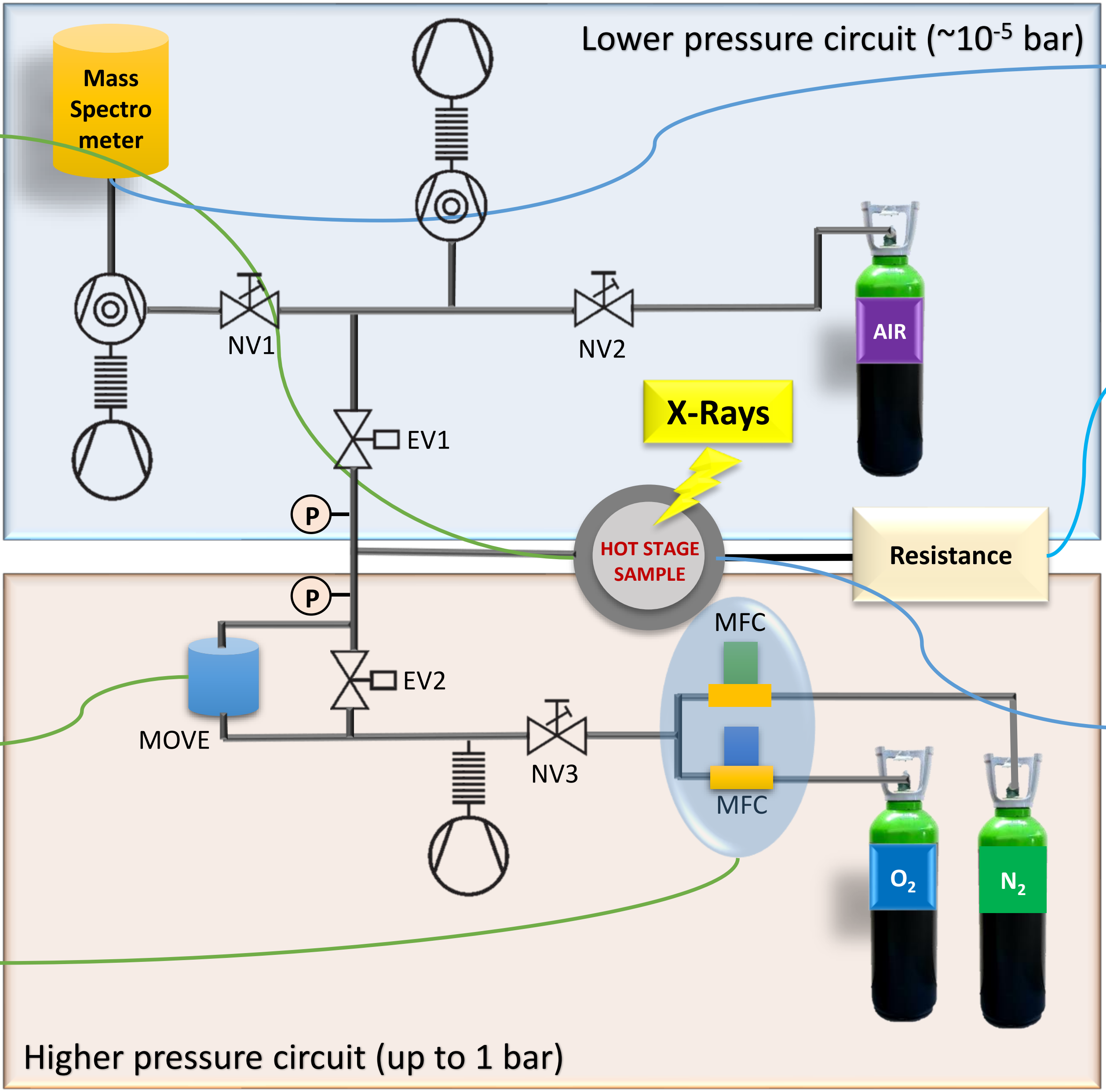
*t =400 nm

18 keV	YBCO (005)	YBCO (103)	$BaCuO_2$	$BaCO_3$	Y_2O_3	CuO
2θ positions [º]	16,99	14,50	12,97/12,61/13,32	10,6/11,9	12,9	15,7/17,08

In-situ TLAG-XRD-R-MS

- ✓ Temperature of the reaction (up to 1000° C)
- ✓ Heating rate (up to 300° C/min)
- ✓ T change at the pressure jump (calibration of the PID)

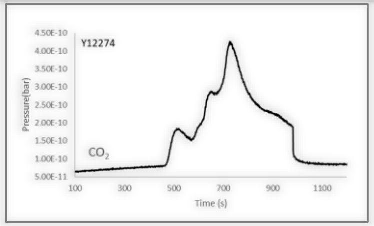




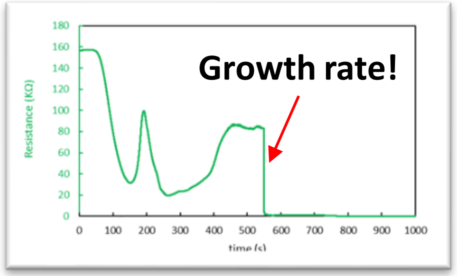
- ✓ Velocity of the pressure jump (0.4 s - minutes)

- ✓ Total pressure (up to 1 bar)
- ✓ Oxygen partial pressure (1 - 15 mbar)
- ✓ Flow rate (300 - 1000 ml/min)

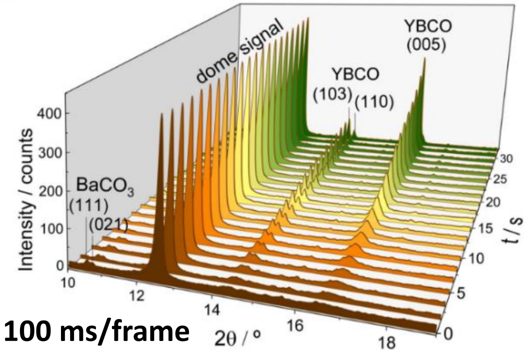
- ✓ Volatile products of reaction: $BaCO_3$ decomposition



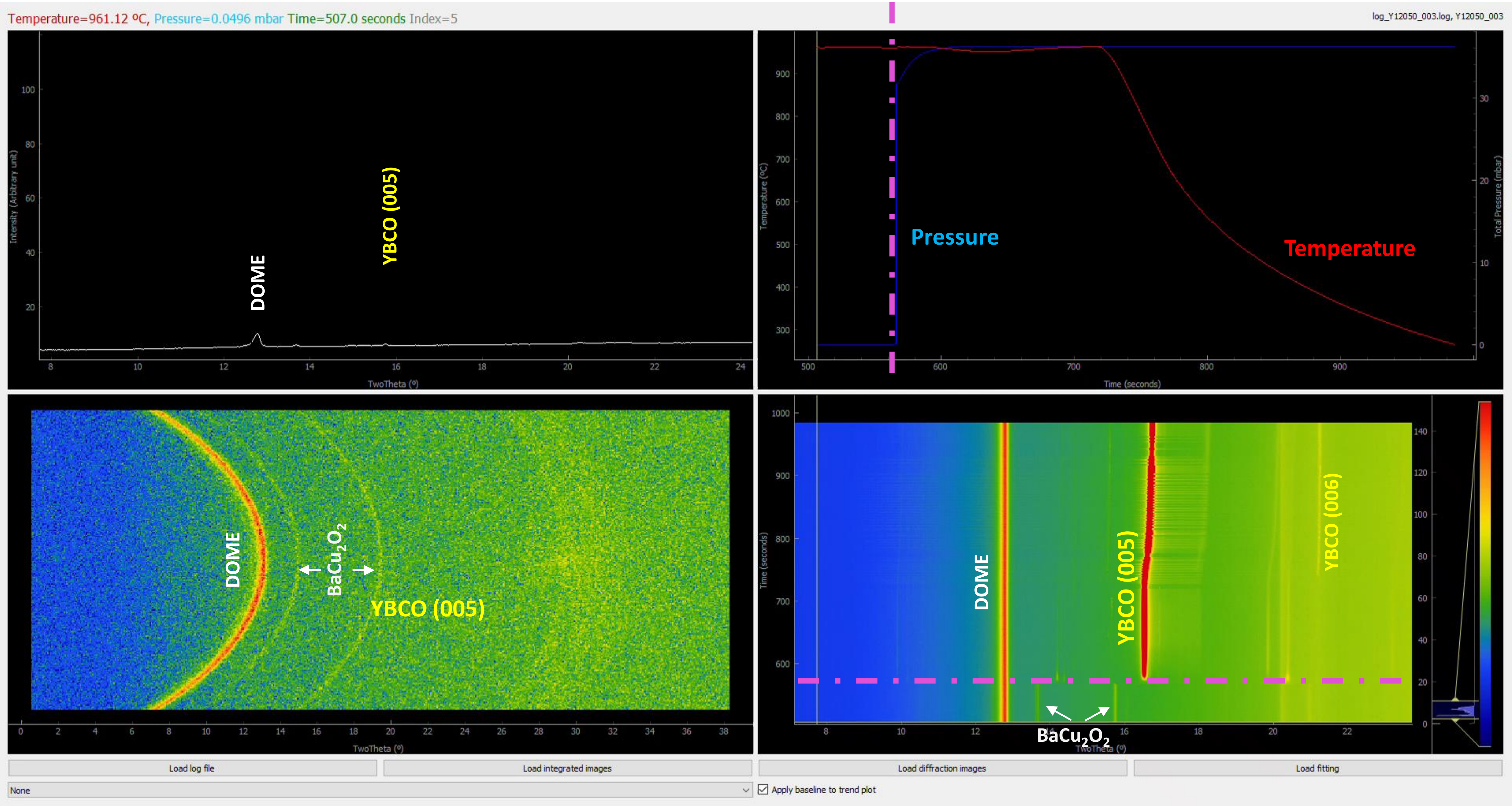
- ✓ Resistance of the film (insulator to metallic transition)



- ✓ X-Ray Diffraction

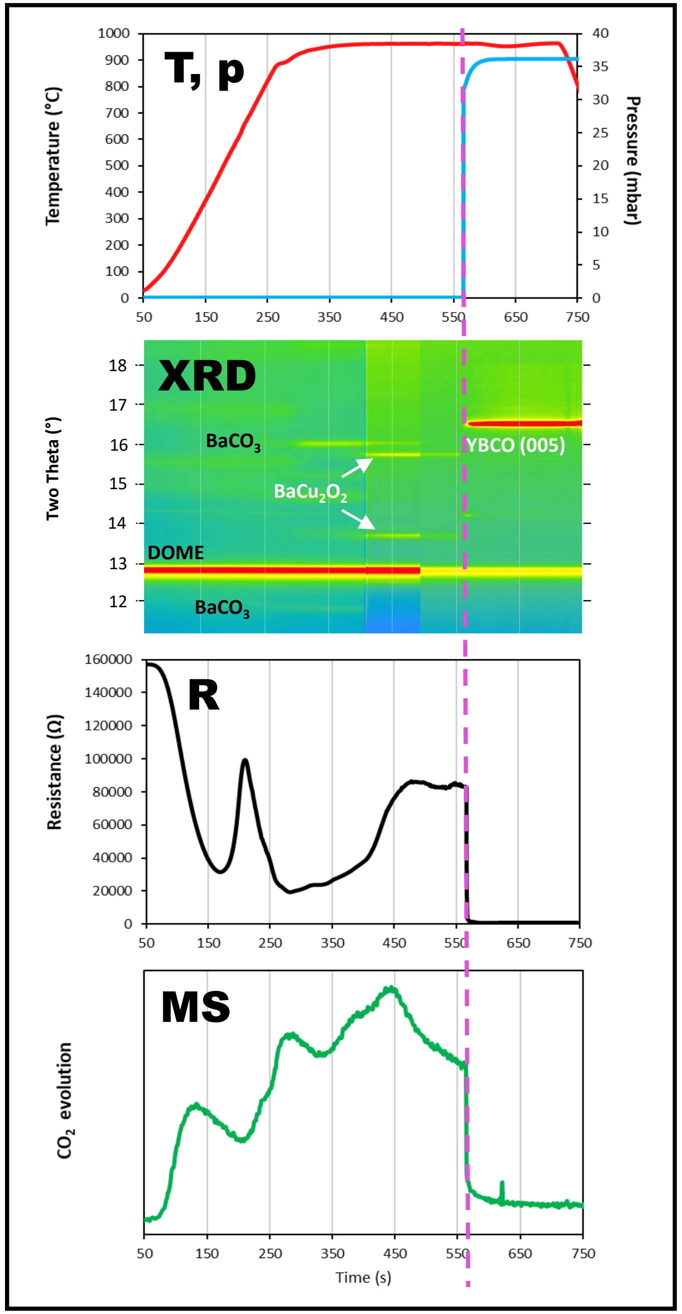


In-situ TLAG-XRD



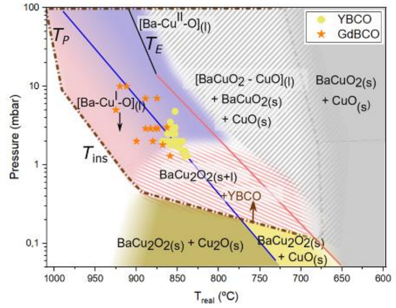
TLAG visualizer developed by Jordi Aguilar (now part of the ALBA Controls)

In-situ TLAG-XRD-R-MS

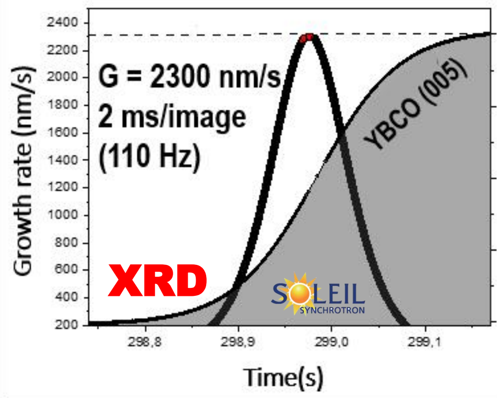


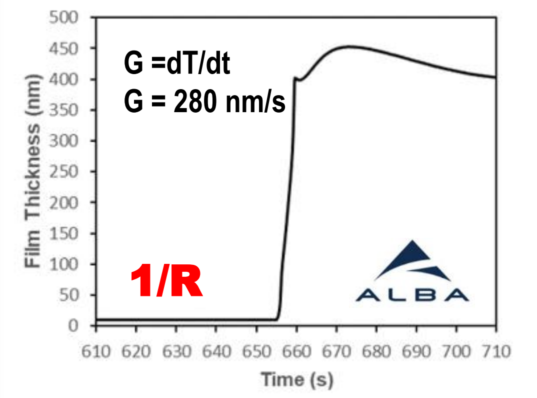
✓ **Time-correlated data**

For every XRD point: T, p, R and MS are collected



✓ **Growth rate calculation: two methods**

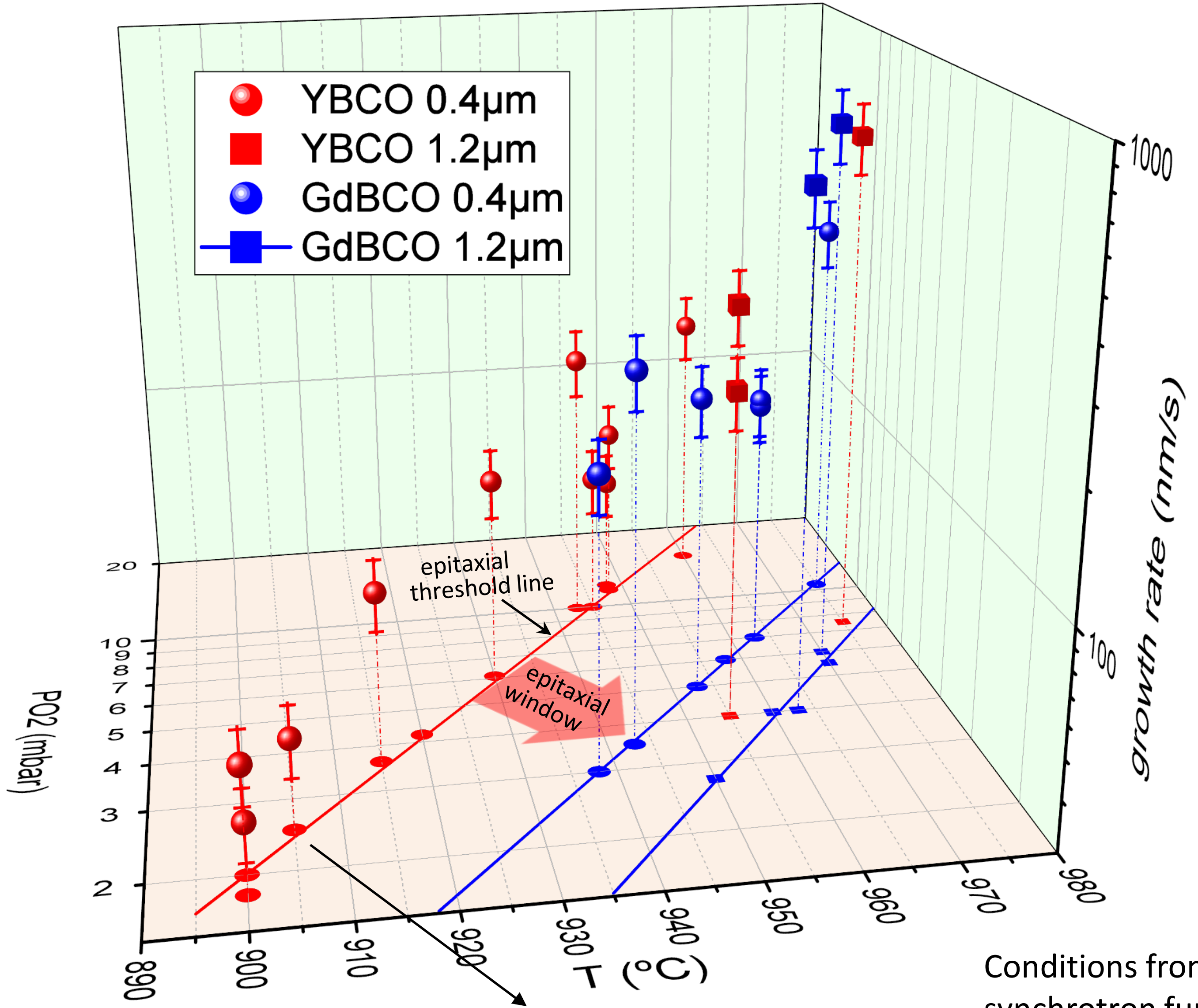




✓ **The BaCO$_3$ decomposition: crucial step**

$$BaCO_{3(s)} + CuO_{(s)} \xrightarrow{\uparrow CO_2} (Ba - Cu^{I/II}\text{-}O)_{(l)}$$

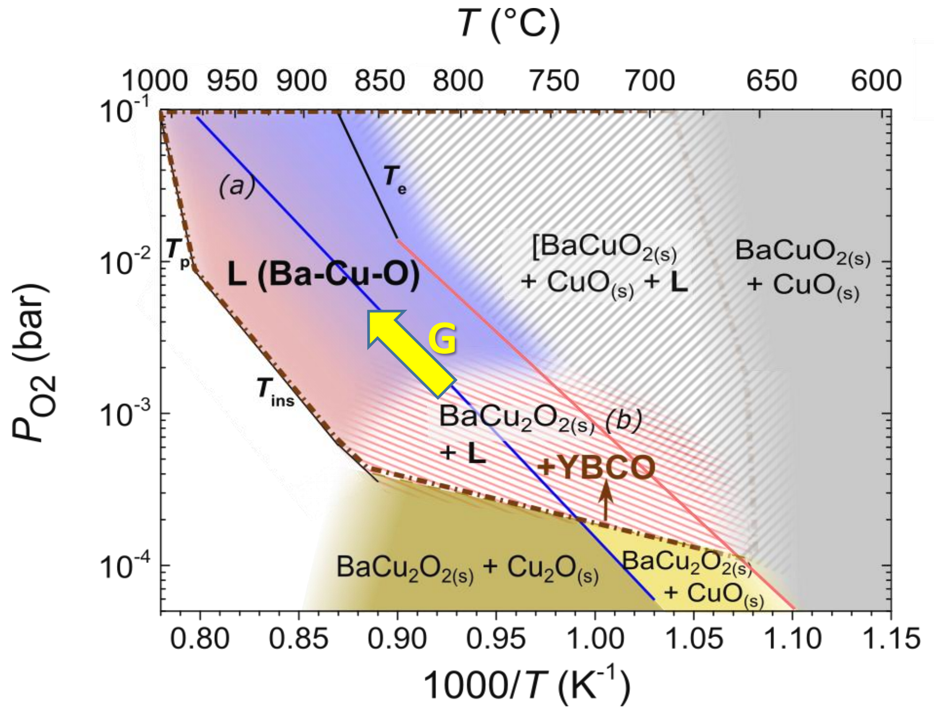
Growth rate dependence on TLAG growth conditions



$LnP_{O2} = m \cdot T - n$

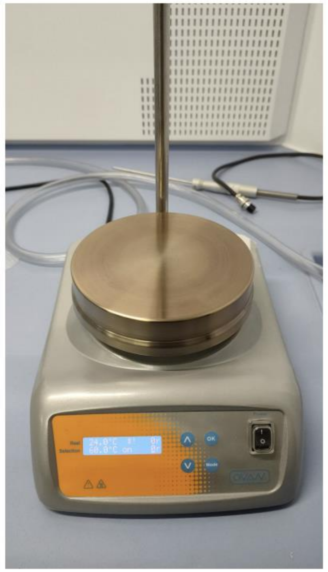
Conditions from ALBA synchrotron furnace

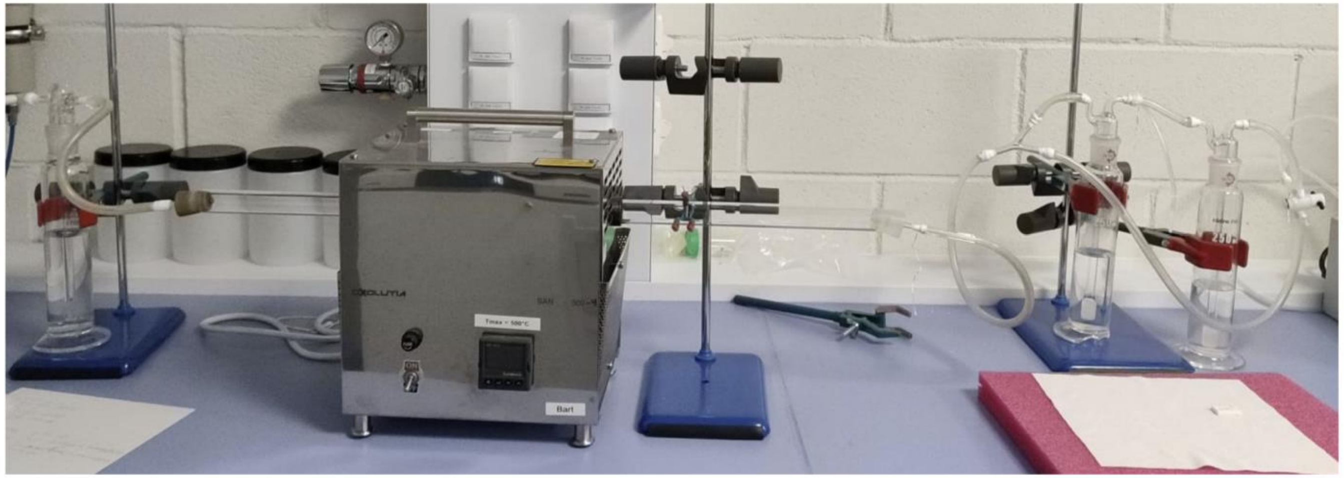
Growth rate, G, ↑ if P_{O2} (and T) ↑



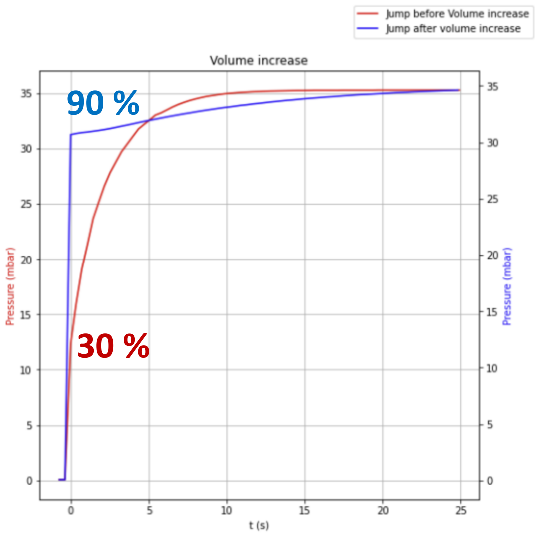
Sample preparation and test laboratory at ALBA (Battery Lab)

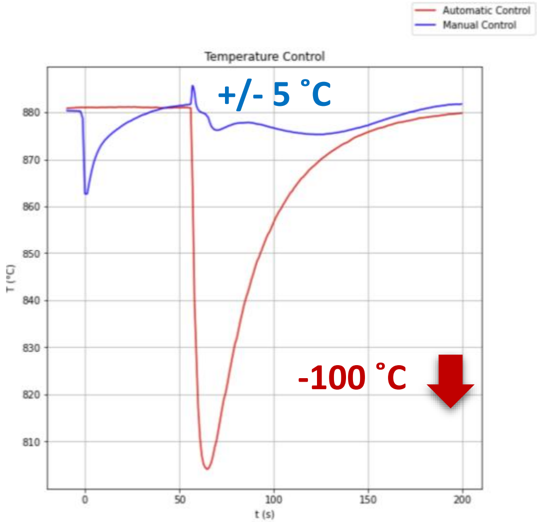
Deposition, pyrolysis and growth



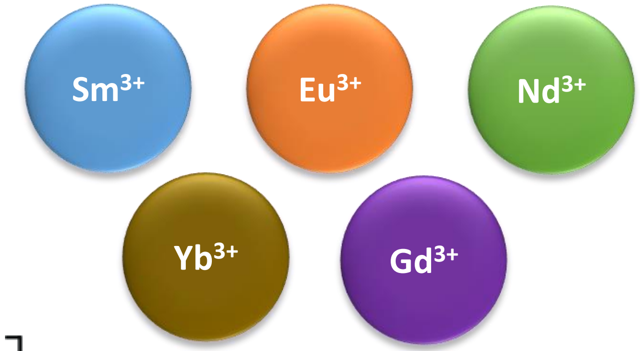


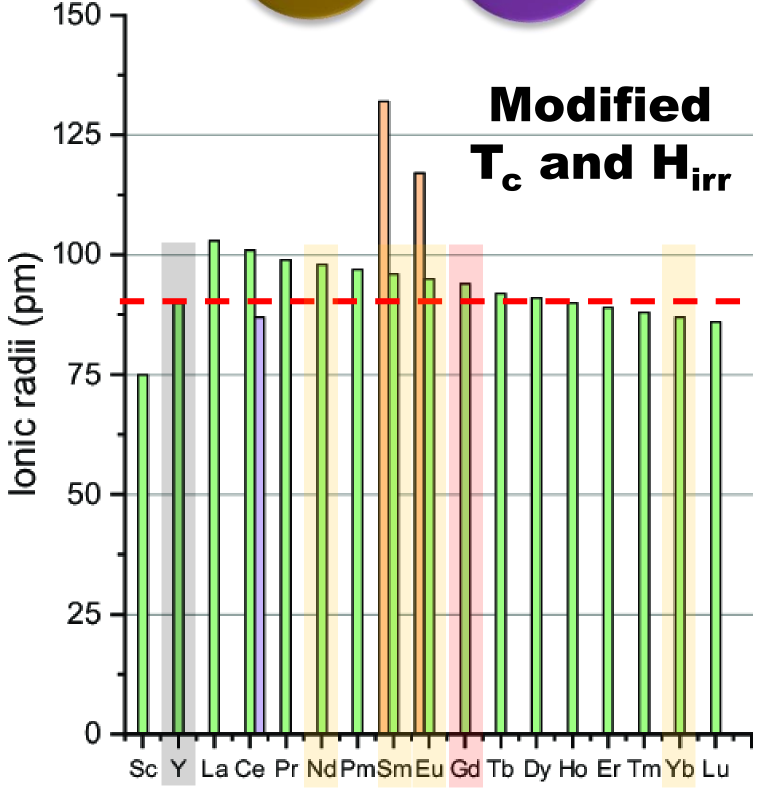
Pre-beamtime calibrations and tests





Effect of the Rare Earth on TLAG



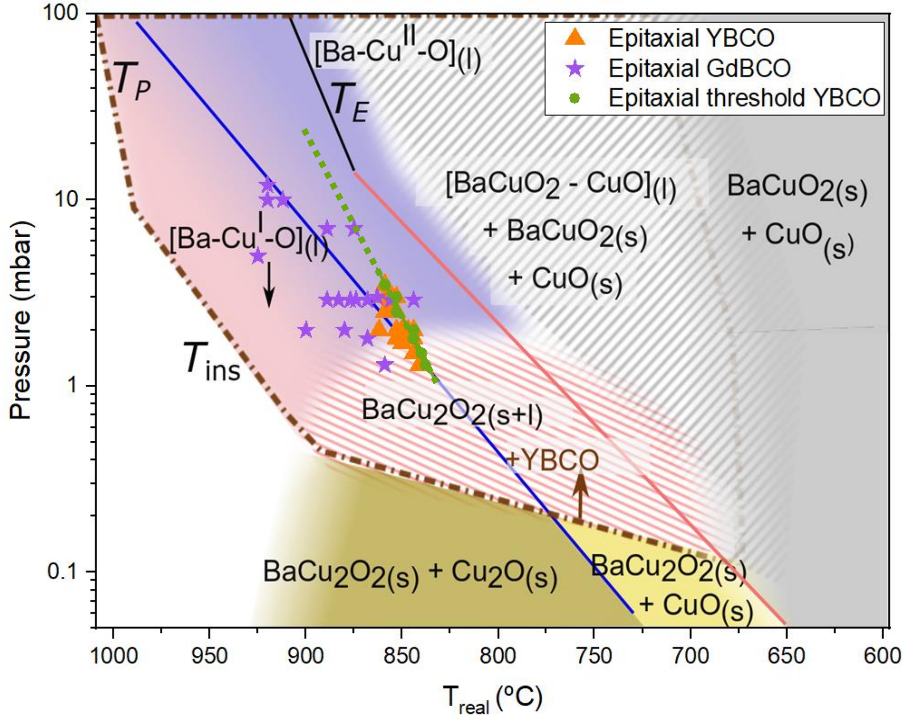


Modified T_c and H_{irr}

In TLAG the RE modifies:

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

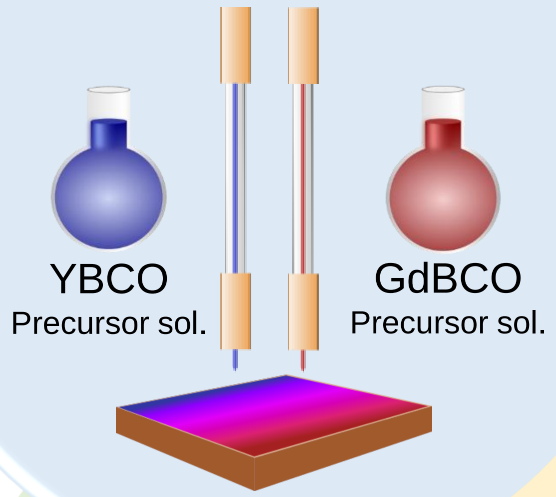
**Conditions from ICMAB furnance*



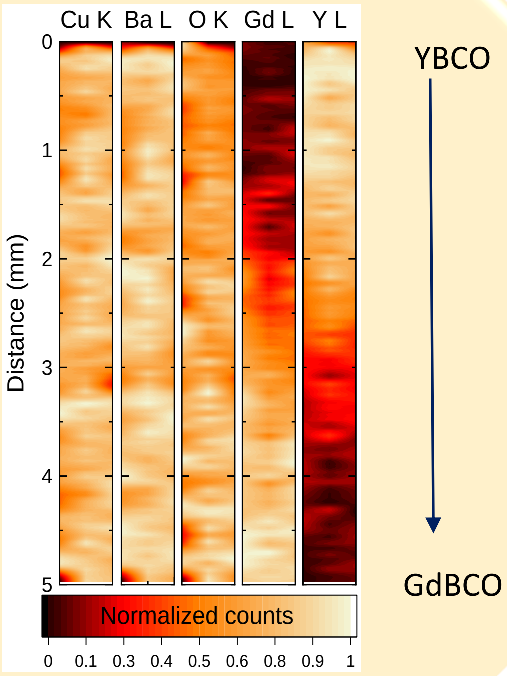
Wide range of conditions of p_{O2} and temperature has been demonstrated for the c-axis YBCO and GdBCO TLAG growth

Fast screening approach with mixed REBCO

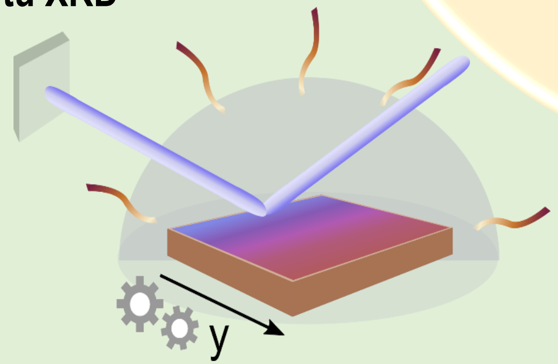
Combinatorial Ink Jet Printing



EDX analysis

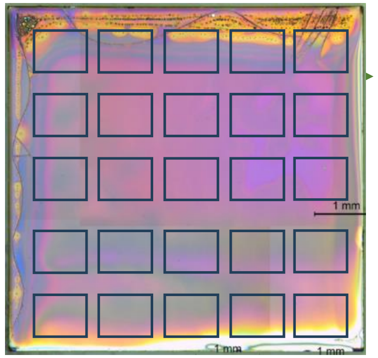


In-situ XRD

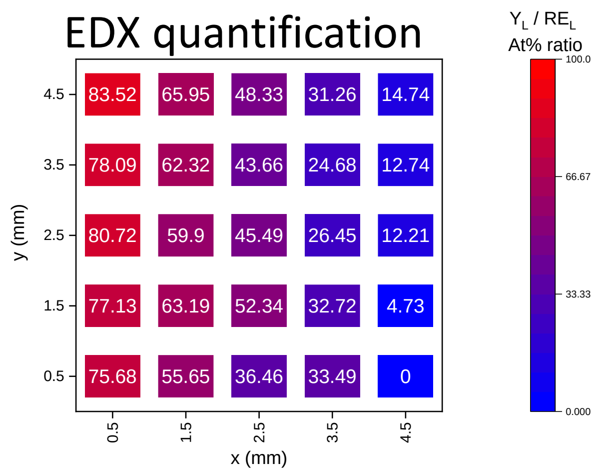


Data segmented by positions for analysis

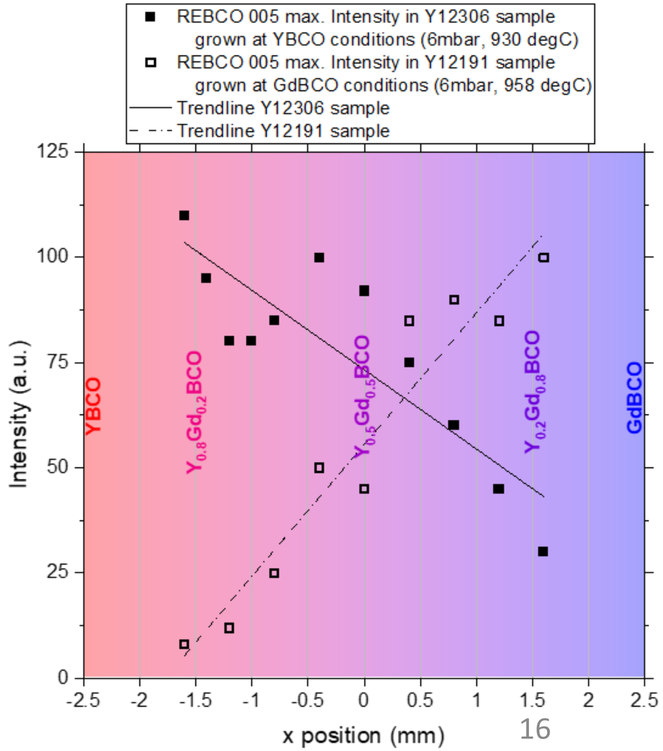
Optical Image



EDX quantification



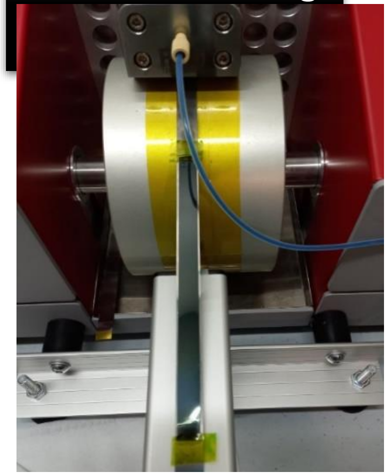
ALBA

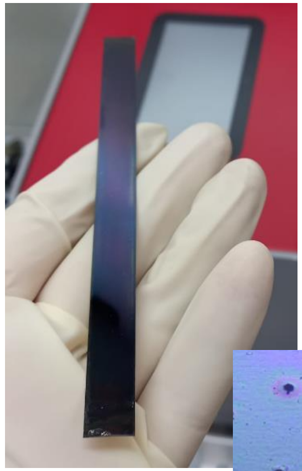


Fast screening across varying compositions

Towards industrialization of TLAG

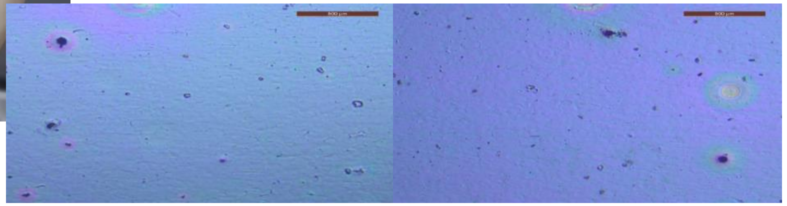
Slot-die coating





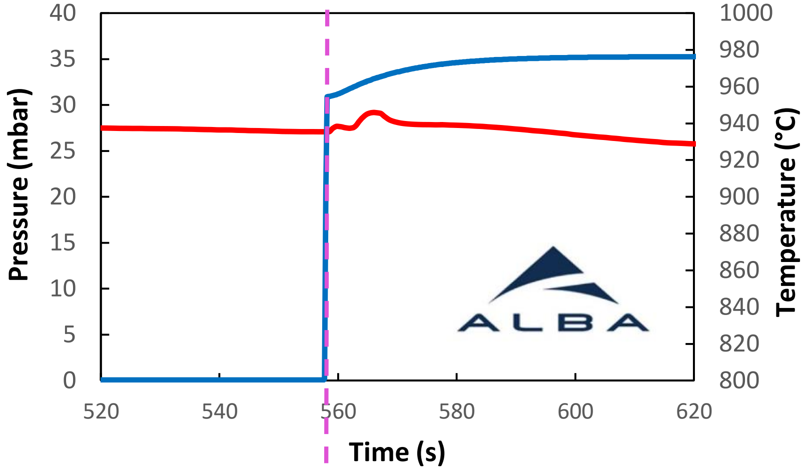
15 cm, pyrolyzed film (6 layers, ~3 μm)

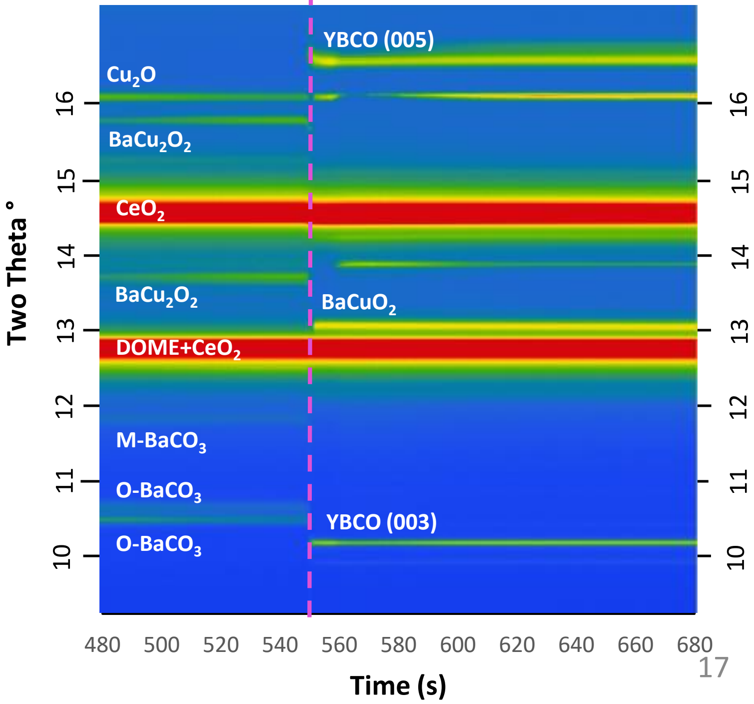
Homogeneous depositions and pyrolysis are reached



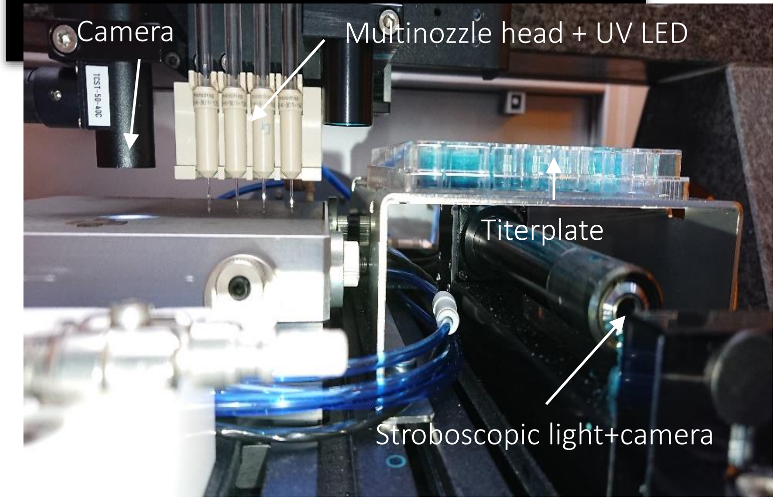
Piece of 6.5 cm pyrolyzed tape with 6 layers

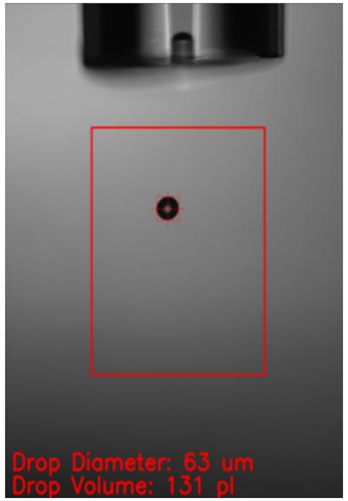
In-situ TLAG-XRD





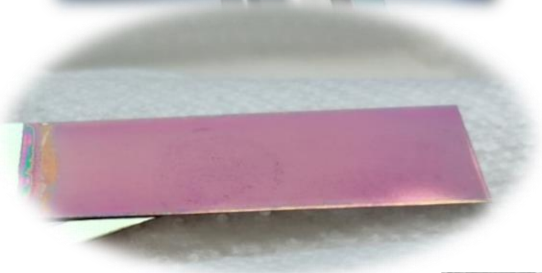
Ink Jet Printing deposition



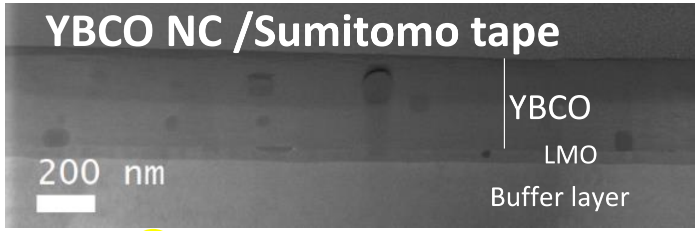


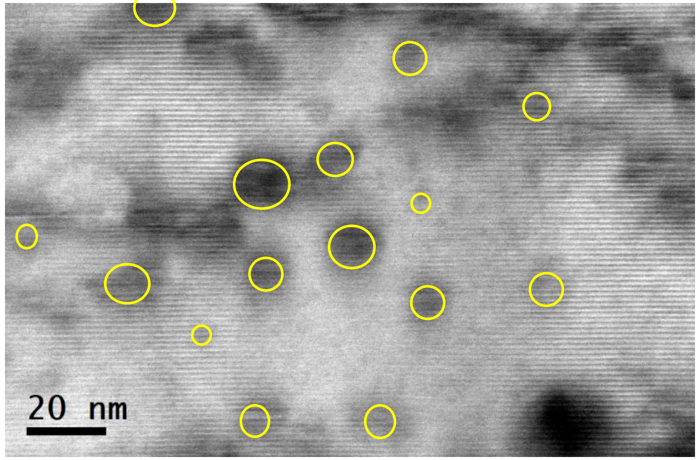
1.7 μm pyrolyzed film (1 layer)

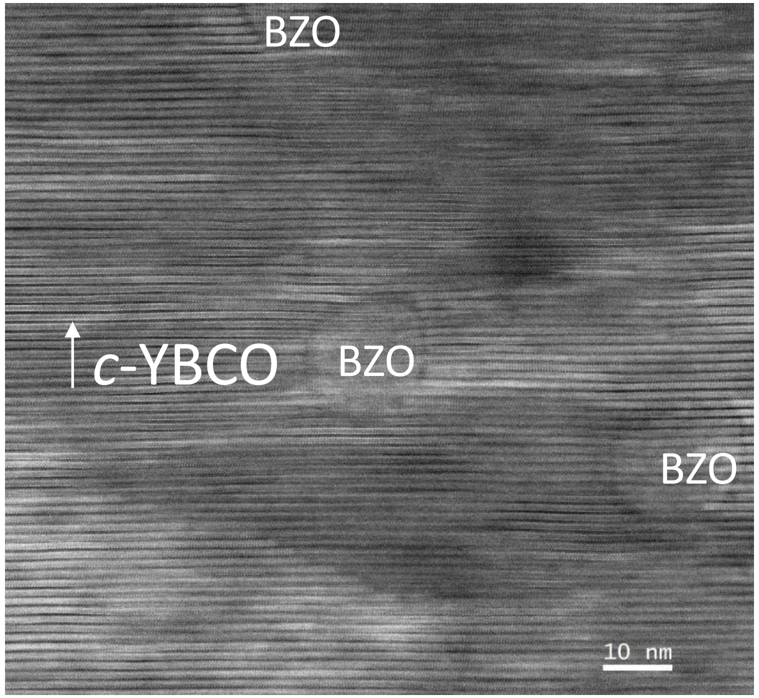
TLAG Coated conductors

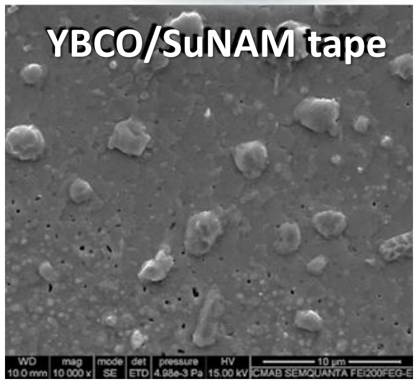


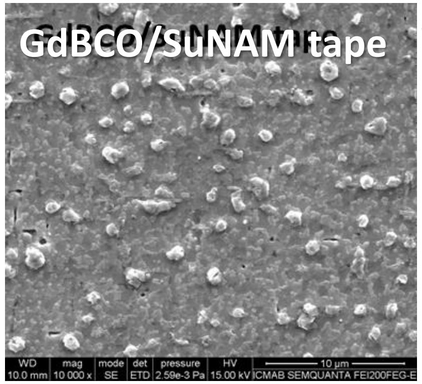
Slot die
now with 40 mm-width printhead capabilities

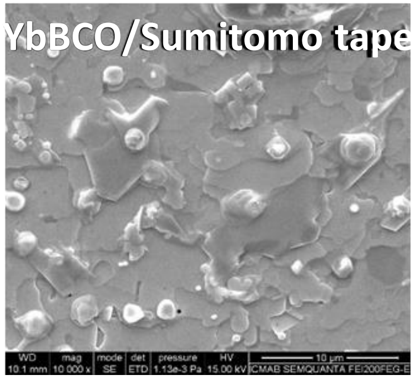












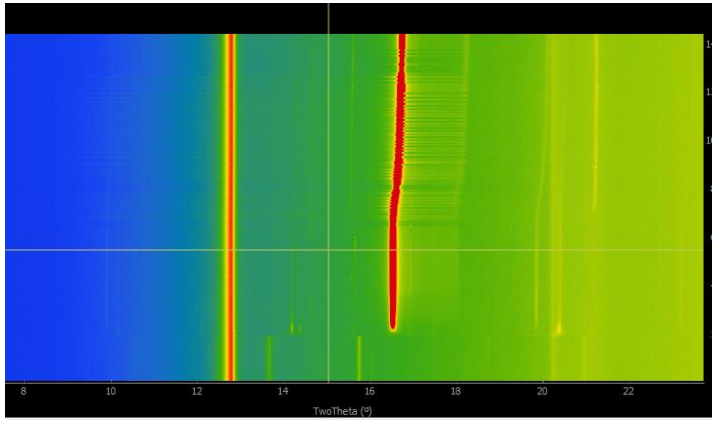
Microstructure is reproduced in 250-750 nm CC
High superconducting properties: **J_c(77K) =1.7-2 MA/cm^2**

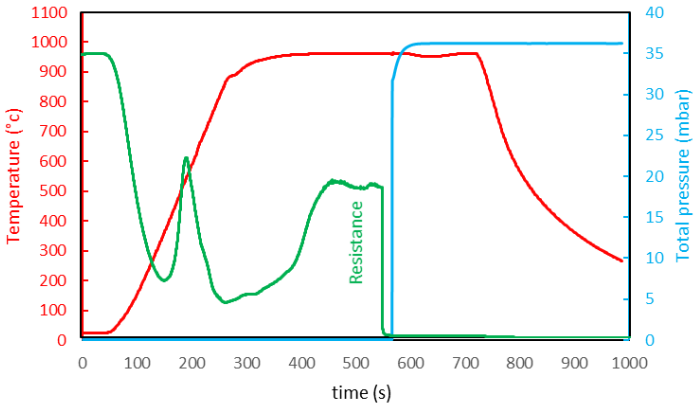
FUTURE

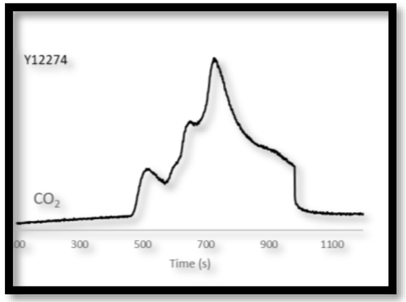
Correlative characterization

In-situ TLAG-X-RAY DIFFRACTION

NCD-SWEET beamline







- ✓ Crystalline phases
- Precursors
- Intermediates
- grown REBCO

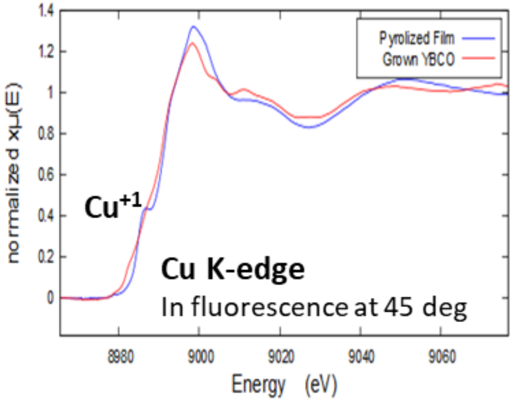
- ✓ $BaCO_3$
- Structure
- Decomposition

- ✓ Growth rate (XRD, R)
- ✓ No liquid information!

In-situ TLAG-X-RAY ABSORPTION

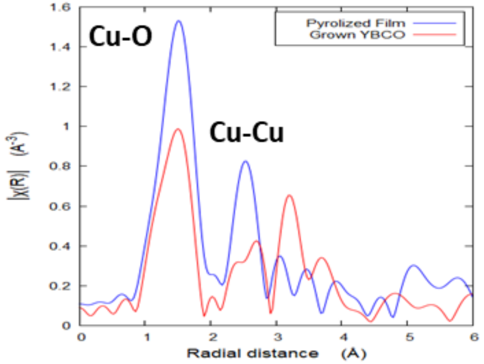
XANES

local electronic structure



EXAFS

first-order atomic pair correlation



CLAESS beamline

- ✓ Amorphous Transient Liquid
- Cu valence state

- ✓ Different liquid composition
- effect on the Cu valence

Summary

***In-situ* X-Ray Diffraction:**

- Essential to reveal the mechanisms of the TLAG growth of REBCO films
- Build non-equilibrium kinetic phase diagrams
- Correlation between precursors, intermediates, and final films with T, p, mass spectrometry and resistance

TLAG :

- non-equilibrium process kinetically controlled by supersaturation of the rare earth in the liquid
- ultrafast growth rates
- high performance films
- relatively low cost to performance ratio method
- may revolutionize the industrial applications of REBCO

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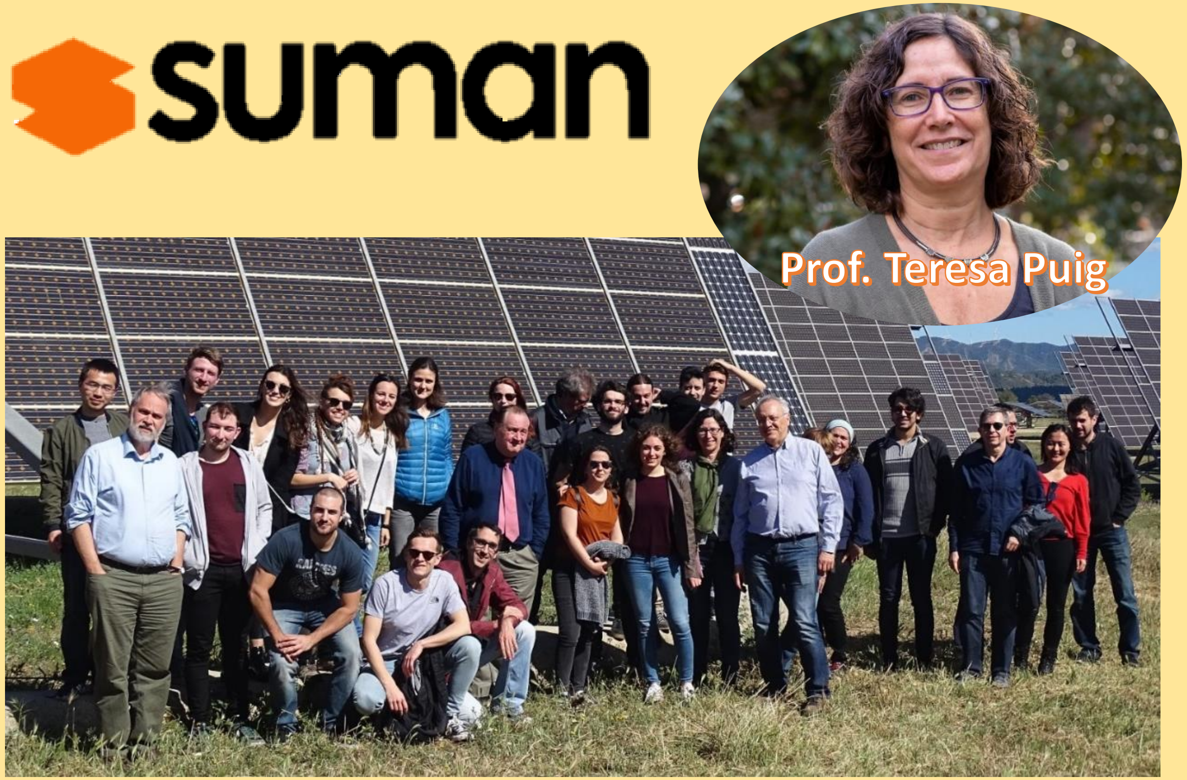
ALBA Safety Department

SOLEIL SYNCHROTRON

Cristian Mocuta – DiffAbs

suman



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