



Can we reach fast growth methods for Coated Conductors at competitive costs ?

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T. Puig- EUCAS 2019

Acknowledgements



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H. Lee, M. Moon, *SuNAM Co, Gyeonggi-do, Korea*



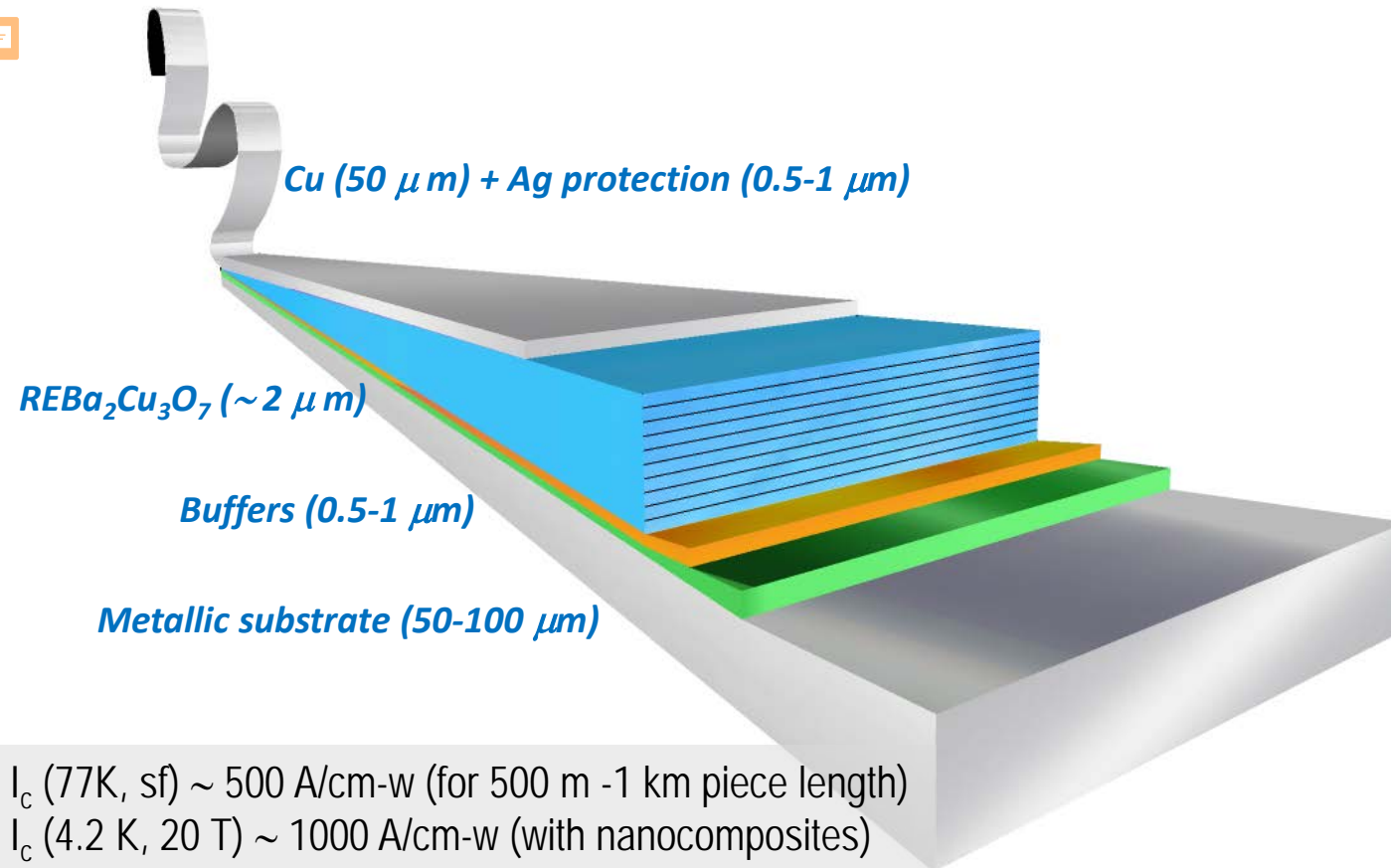
A. Usoskin, U. Betz, *Bruker HTS BmbH, Alzenau, Germany*



Y. Yamada, *Shanghai Superconductor Technology Co, Pudong Shanghai, P.R. China*



REBCO is the opportunity and the challenge at high magnetic fields



25-yr of Coated Conductor technology development



Pros:

- High T_c
- High H_{c2}
- High J_c
- High IL

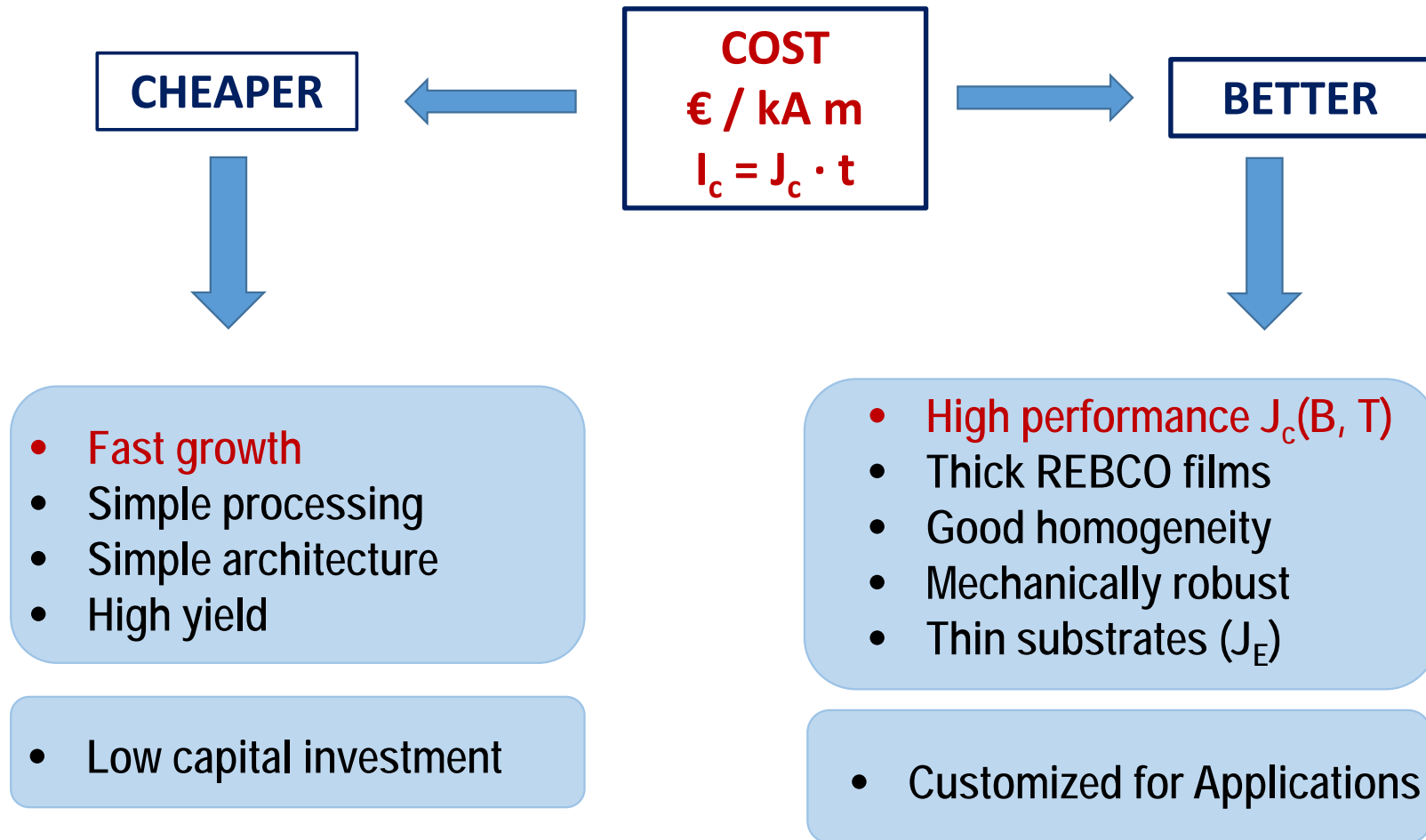
Cons:

- Grain boundaries
- Anisotropy
- Small coherence length (nanometric pinning centres)
- High thermal excitations
- Robustness
- Biaxial texture \Rightarrow high cost

Cost= €/ kA-m

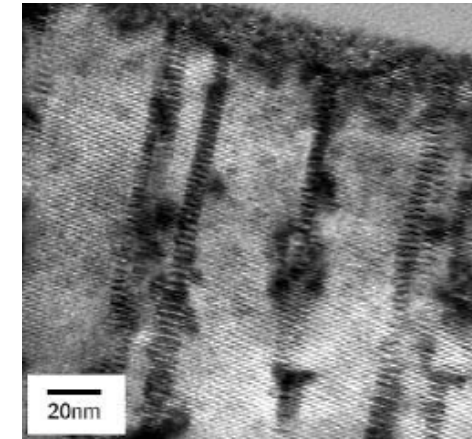
How to decrease cost of Coated Conductors

What would be an acceptable cost ?

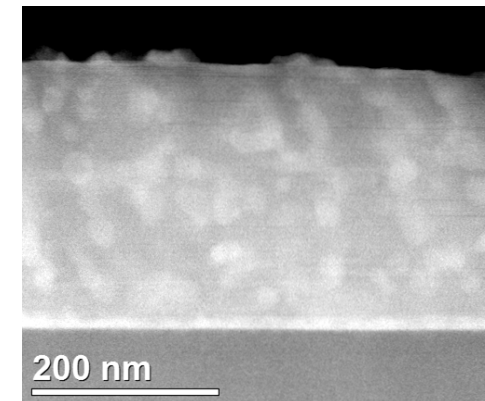


NANOCOMPOSITES

PLD (also for MOCVD)



CSD



S. Kang, *Science* 311 (2006), J. Guiterrez, *Nat Mat* 11 (2007)



Present state in Industrial Coated Conductor growth

	MOCVD	PLD	Evaporation	RCE-DR	TFA-CSD	TLAG-CSD
Nanocomposite growth feasibility	Green	Green	Red	Red	Green	Green
Throughput (m/h)	Orange	Green	Orange	Green	Orange	Green
Fabrication costs	Orange	Orange	Orange	Orange	Green	Green
Growth rate (nm/s)	Red	Orange	Red	Green	Red	Green

Transient Liquid Assisted Growth - CSD



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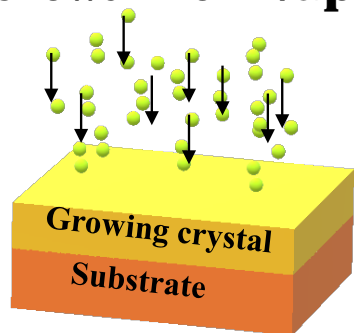
CSIC



MAB

Growth mechanisms for epitaxial REBCO films crystallization

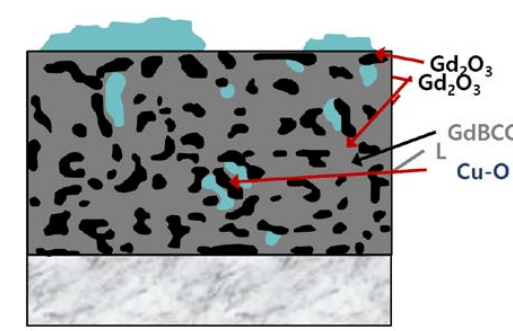
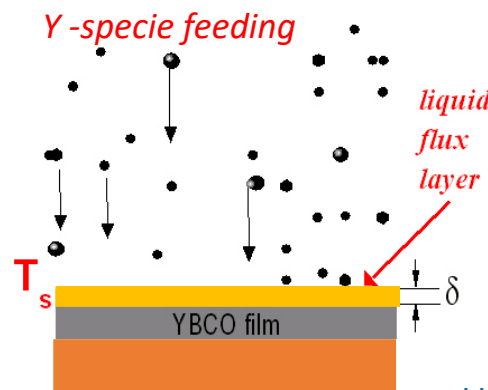
Growth from **vapour** phase



- PLD
- MOCVD
- Evaporation

PLD : 5-12 nm/s (Superox), 14 nm/s (SST)
 A-MOCVD: 3 nm/s (U. Houston), Evapor.: 4 nm/s (THEVA)

Growth from high temperature supersaturated **equilibrium liquids**

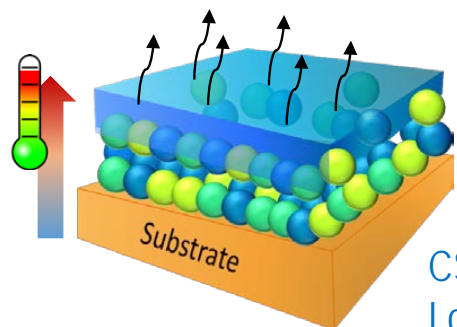


-RCE-DR (ex-situ)

- HLPE, VLS, TPE

HLPE: ~10 nm/s (UCAM)
 RCE-DR: 30-100 nm/s (SUNAM)

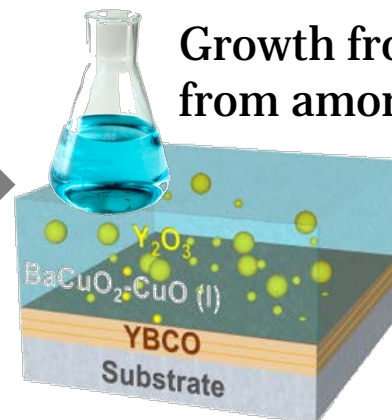
Growth from **amorphous precursor solids**



- CSD (ex-situ)

CSD : ~1 nm/s
 Low cost

Growth from **transient liquids** derived from amorphous precursor solids



- **TLAG-CSD (ICMAB)**

Growth rates from liquids : ~100 nm/s
 Scalable and low cost

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Fast growth processing of CC and its compatibility with high currents



Intrinsic factors: → **High growth rates**

- Growth mechanisms
- Materials growth rate (YBCO, GdBCO,..)

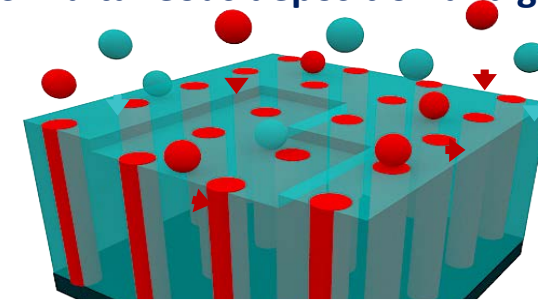
Extrinsic factors: → **High manufacturing rates**
for in-situ growth methods (PLD, MOCVD, evaporation)

- High deposition velocity
- High deposition area
- Multi-plume
- Multi-lane
- PLD high power and frequency laser,...
- Nanocomposites might be compromised

for ex-situ growth methods (RCE-DR, CSD, TLAG-CSD)

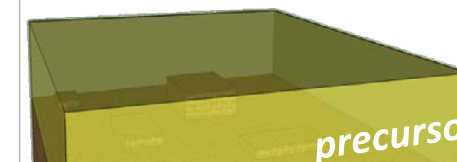
- Independent deposition and growth processes
- Multi-turn deposition
- Furnaces dimensions
- High deposition area
- Nanoparticles may not be compromised
- Some high growth rate processes are being used

In-situ growth methods
Simultaneous deposition and growth

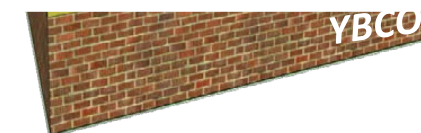


PLD@Bruker and PLD@SST

Ex-situ growth methods
Sequential deposition and growth



RCE-DR@SuNAM and TLAG@ICMAB





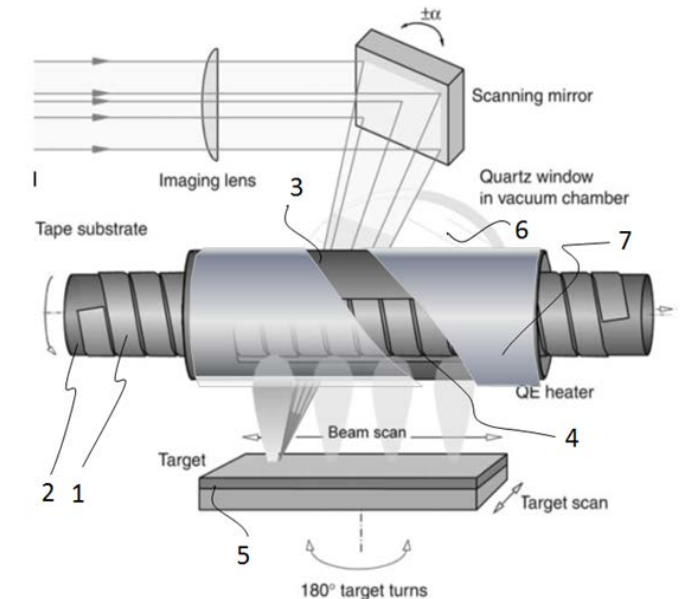
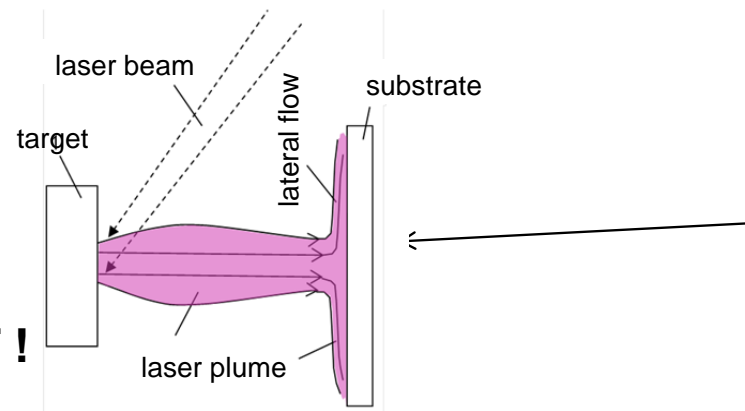
BRUKER HTS GmbH



- The processing speed of long length **DD YBCO films** by Pulsed Laser Deposition is performed in a **dynamic mode**. Main impact factors on the processing speed are:
 - Target properties
 - **Beam scan** parameters
 - **Substrate rotation** and movement
 - Process environment (T, p)
- The **deposition rate in the static mode exceeds 150 nm/s** at the maximum of the local film thickness distribution

Multi-plume, multi-turn, high power and high frequency laser

$I_c=1200 \text{ A/cm-w at } 4.2 \text{ K @ } 20 \text{ T} !$



Strategy for “fast growth” in PLD at SST

Multi-plume- Multi-lane PLD: typical growth rate in a mass-production is Average rate= 20nm/sec between 10-50nm/sec (tape speed 120m/hr)

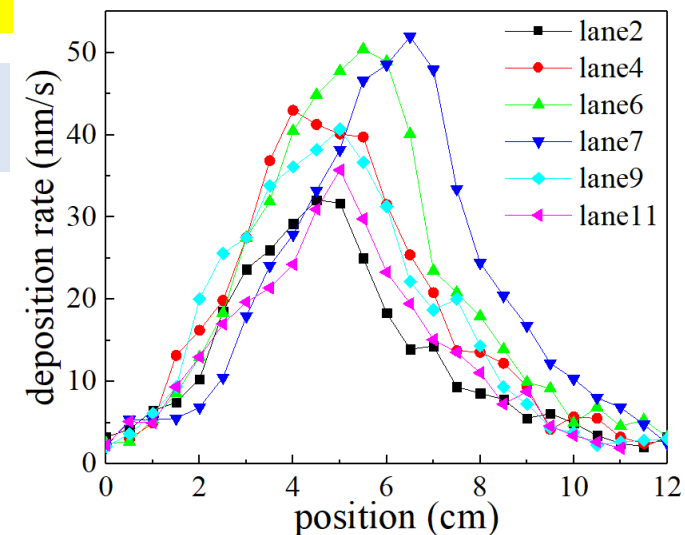
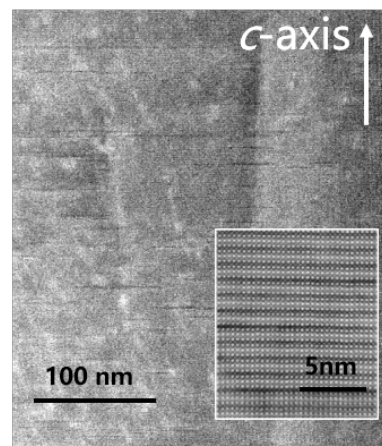
Need to balance between I_c and production speed

High deposition rate makes more stacking faults and high I_c at low temperatures. → favorable for realistic industry operation

High I_c with SF without columnar structure

$I_c=1200$ A/cm-w at 4.2 K @ 17 T !

Material: Y→Gd (production speed was doubled.)



Compromised between rate and area

Next strategy:

Material: Y→Gd, APC

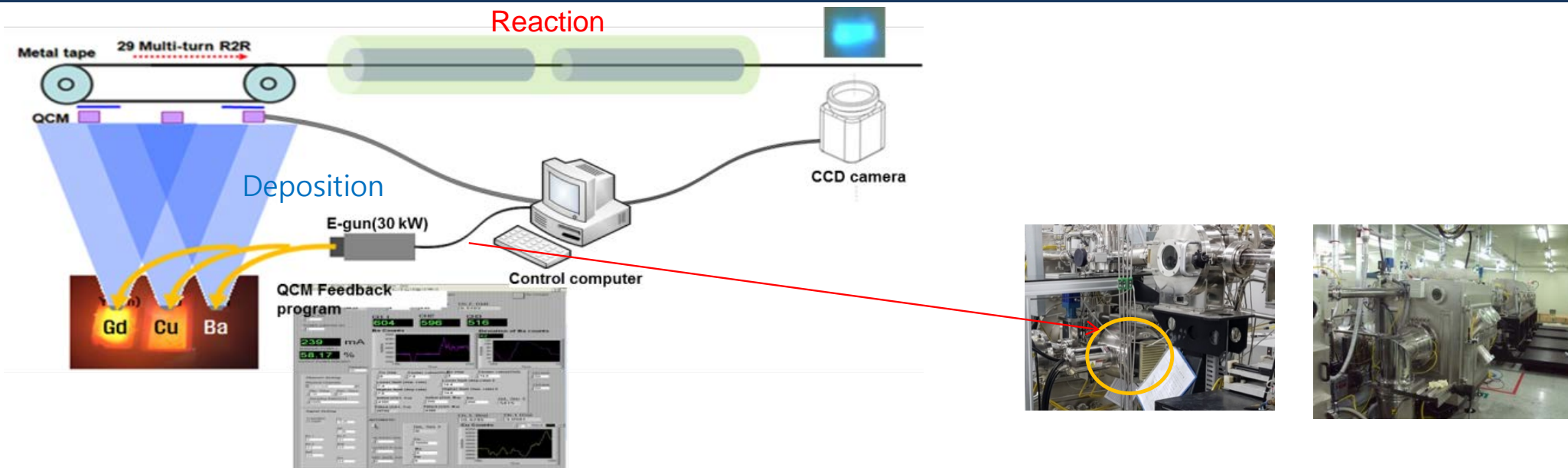


Re-survey for high rate, wide temp. range, PO2 (stability in production)



Next
MBCO+APC'

Introduction of RCE-DR process & system



- RCE-DR : Reactive Co-Evaporation by Deposition & Reaction (SuNAM, R2R)
- **High rate co-evaporation at low temperature & pressure** to the target thickness(> 1 μm) at once in deposition zone (6 ~ 10nm/s) – 120 m/h tape speed
- **Fast conversion(up to 100 nm/sec)** from **amorphous glassy phase to superconducting phase** at high temperature and oxygen pressure in reaction zone
- **Simple, high deposition rate & area, low system cost**
- **Easy to scale up :single path**
- Verified for Gd, Y, Sm,

$I_c=750 \text{ A/cm-w at } 77 \text{ K, sf !}$



	PLD	RCE-DR	TLAG-CSD
Growth rate (nm/s)	5-10 (16 for LA-PLD*)	~100	100
Deposition velocity	High power laser Multi Plum Multi-lane Drum	6-10 nm/s multiturn evaporation	Multi-lane pyrolysis & furnace length
Deposition area	High	High	High
Reel-to-reel adaptation	Achieved	Achieved	Easy
Tape speed	120 m/h (SST)	120 m/h Limited by deposition speed	60 m/h (pyrolysis) 700 m/h (growth)
Average manufacturing rate	150 nm/s (BRUKER) 20 nm/s (SST)		100 nm/s x number of parallel tapes



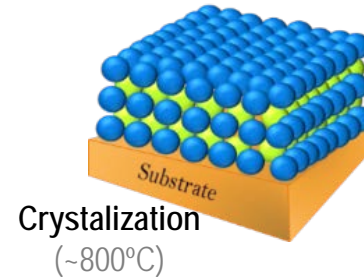
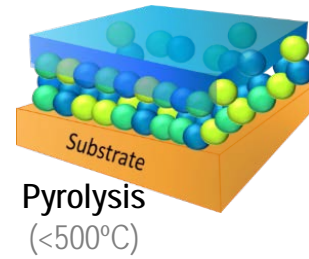
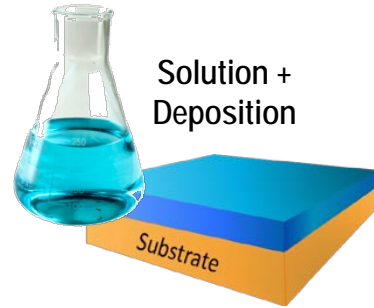
* Cambridge Liquid-assisted PLD variant

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YBCO-CSD Growth methods

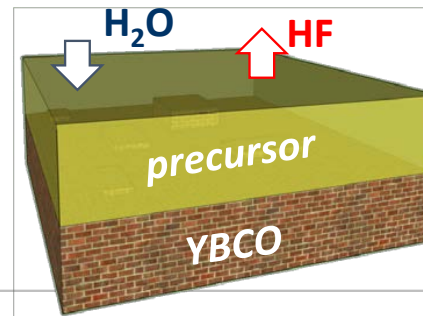
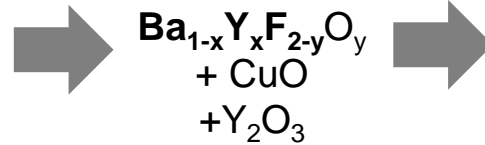


Decoupled processes



TFA- route

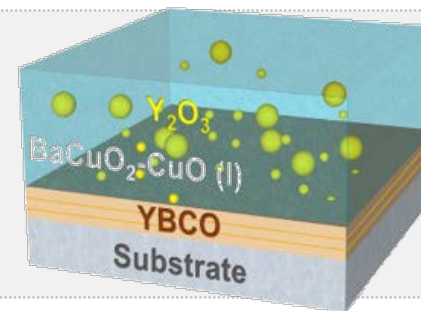
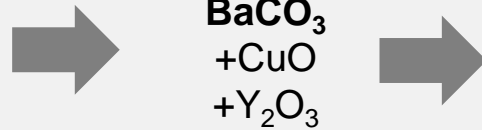
Trifluoroacetate based precursors



- ❖ Gas-solid conversion reaction
- ❖ Slow growth rates (~ 1 nm/s)
- ❖ Slow HF removal – complex reactor

TLAG- route

Fluorine Free based precursors



- ❖ Liquid-solid conversion reaction
- ❖ Fast growth rates-100 nm/s
- ❖ Dependent on BaCO_3 decomposition
- ❖ Simple reactor –environment friendly

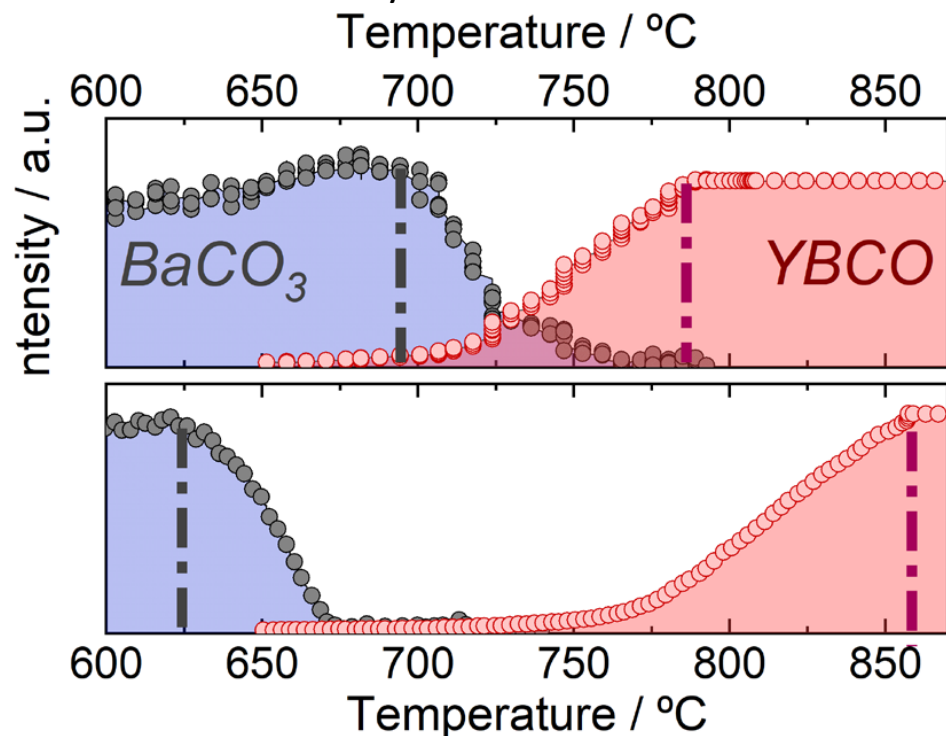
TLAG = Transient Liquid Assisted Growth

TLAG-CSD

BaCO₃ decomposition is not an issue

(T, P_{O₂}, P_{total}, heating ramp, composition...)

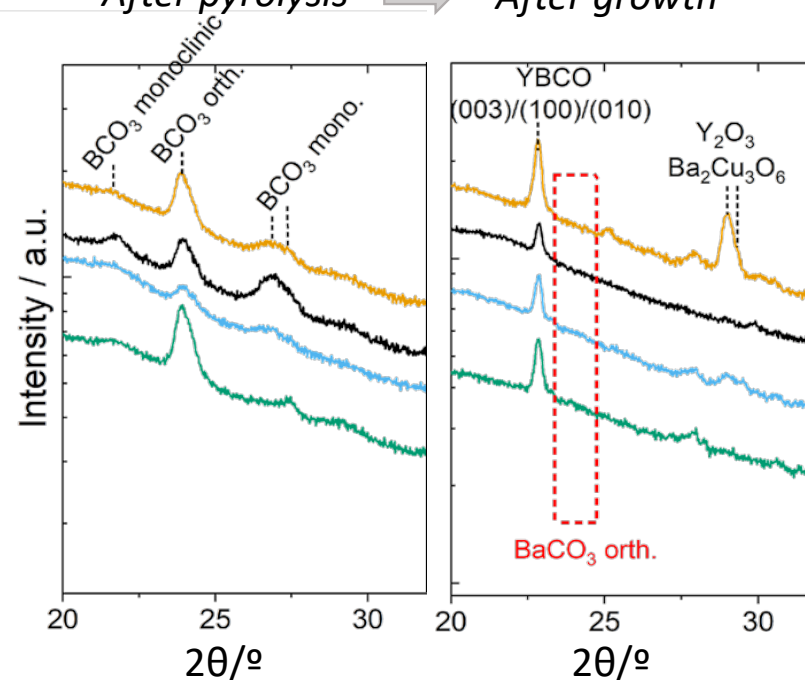
In-situ XRD at Soleil sync.



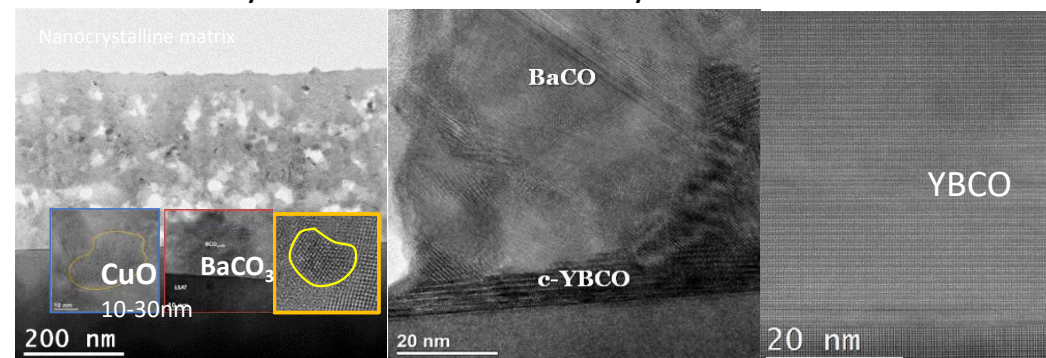
Decomposition in seconds at high heating rates

See 3-MO-CU-02S (J. Bancheswki), 3-MO-CU-04S (S. Rasi)

After pyrolysis → After growth



1 μm thick epitaxial layers





Transient Liquid Assisted Growth: TLAG-CSD



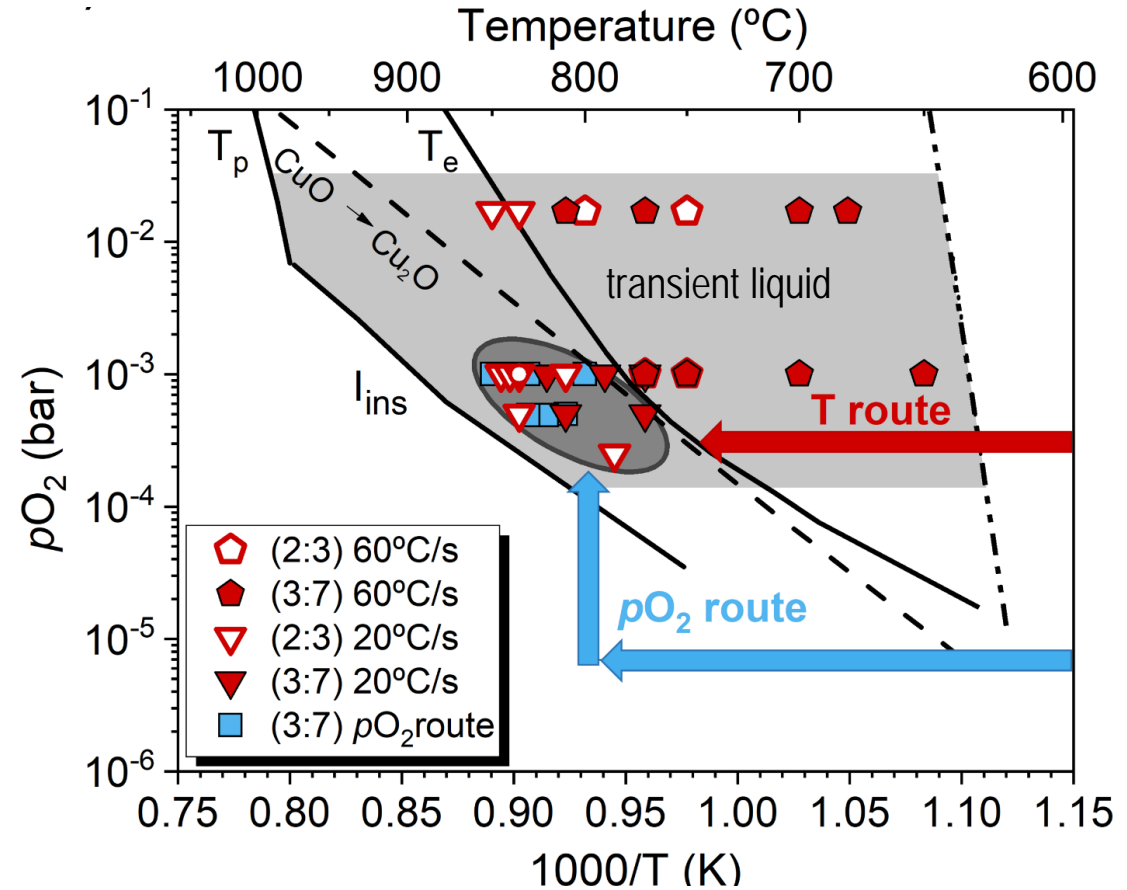
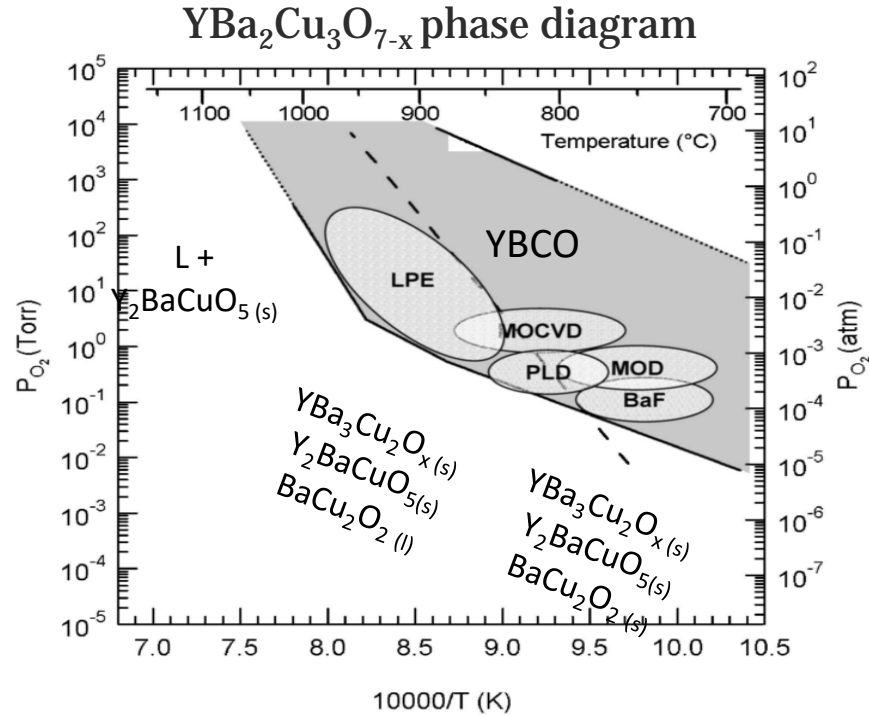
CSIC



CMAB



UdG

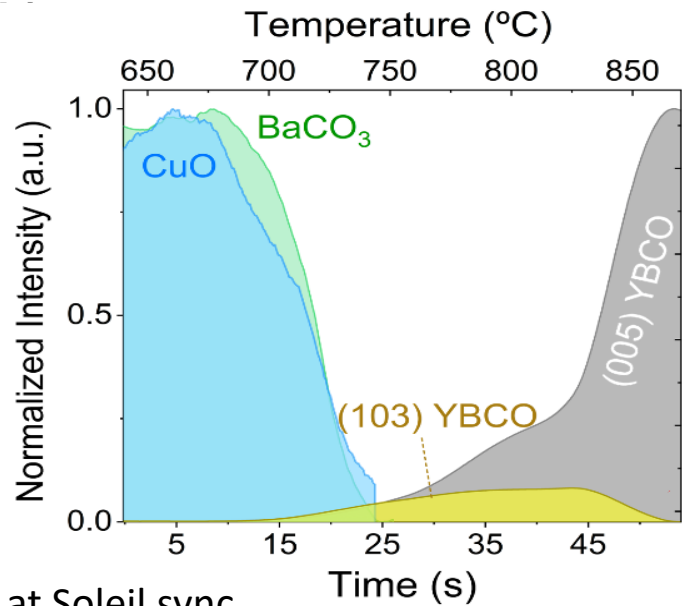
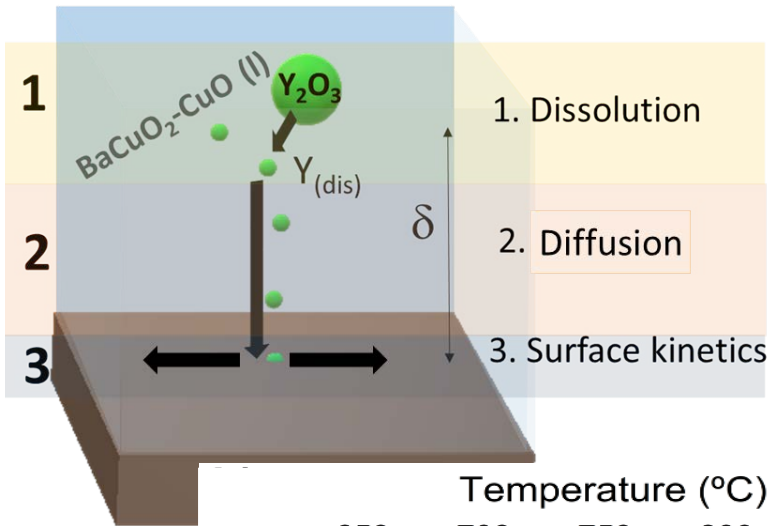


- Transient liquids (BaCuO₂-CuO) form much faster than the equilibrium solid phase (YBCO)
- No need of equilibrium liquid phases in the phase diagram
- Kinetically driven growth process

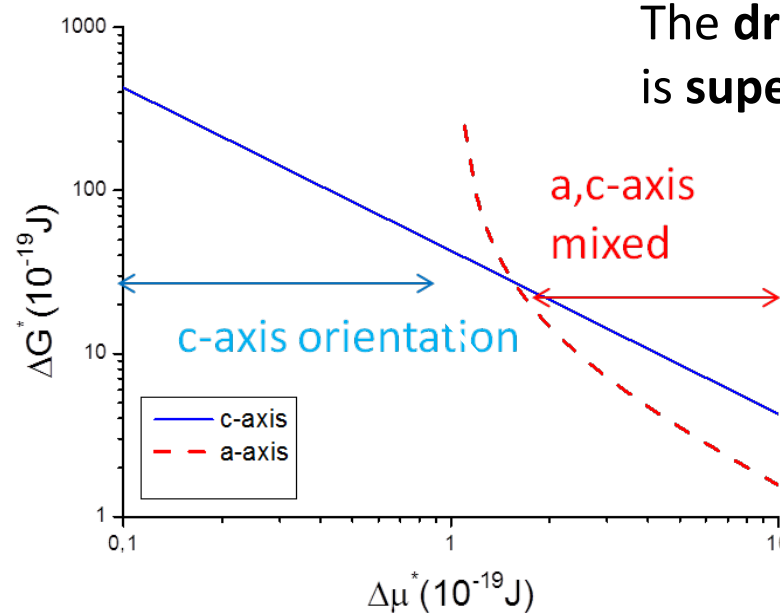
Very wide area of YBCO c-axis nucleation if heating rates > 20°C/s (RTA furnaces)

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TLAG-CSD: $[2\text{BaCuO}_2 + \text{CuO}](\text{l}) + 1/2\text{Y}_2\text{O}_3 + 2\text{CO}_2(\text{g}) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6.5} + \text{yO}_2(\text{g})$

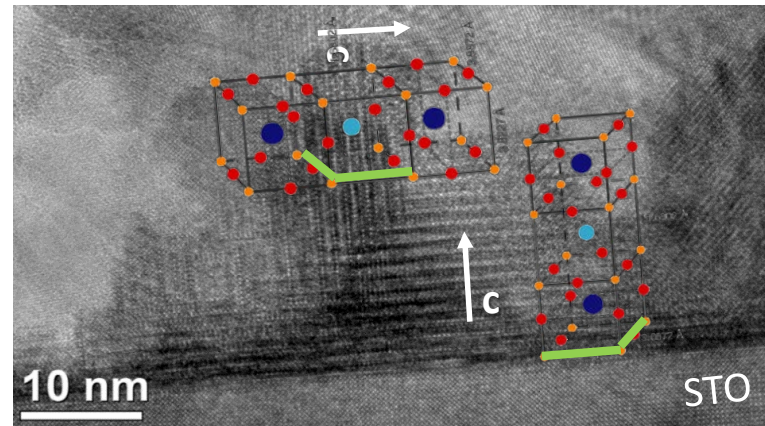


In-situ XRD at Soleil sync.



The driving force for nucleation is supersaturation:

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



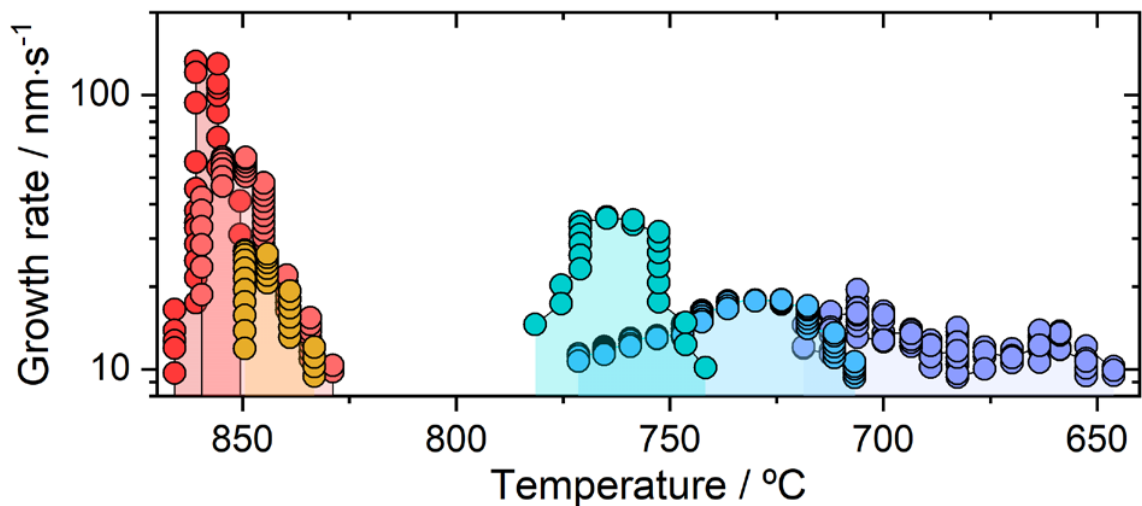
For YBCO c-axis growth, low supersaturation is needed

(Y (RE) concentration & solubility, liquid composition)

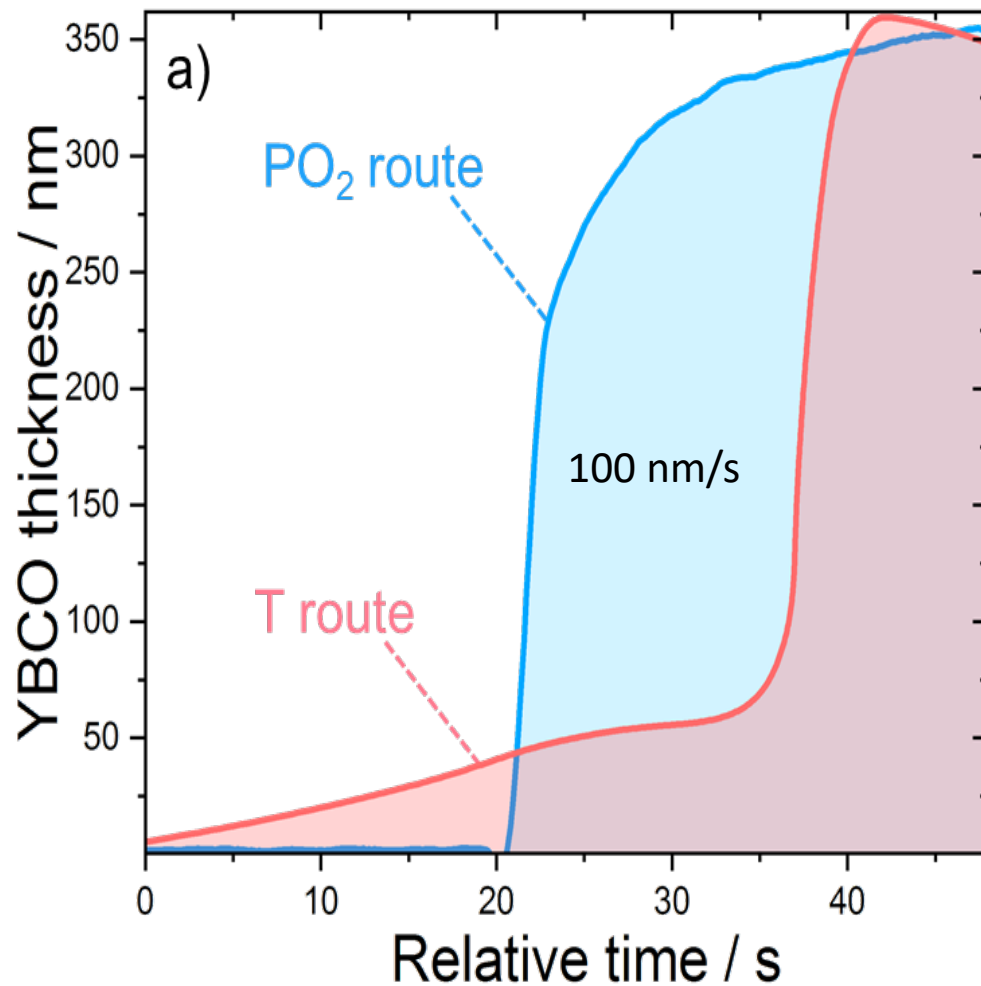


Ultrafast growth by TLAG-CSD

In-situ XRD at Diffabs
(*col. C. Mocuta*)
100 ms acquisition time



See 3-MO-CU-02S (J. Bancheswki)



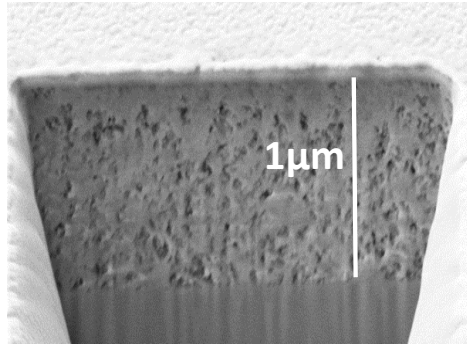
L. Soler et al, submitted

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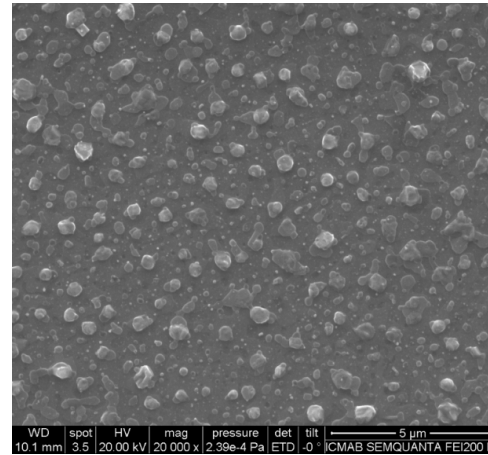




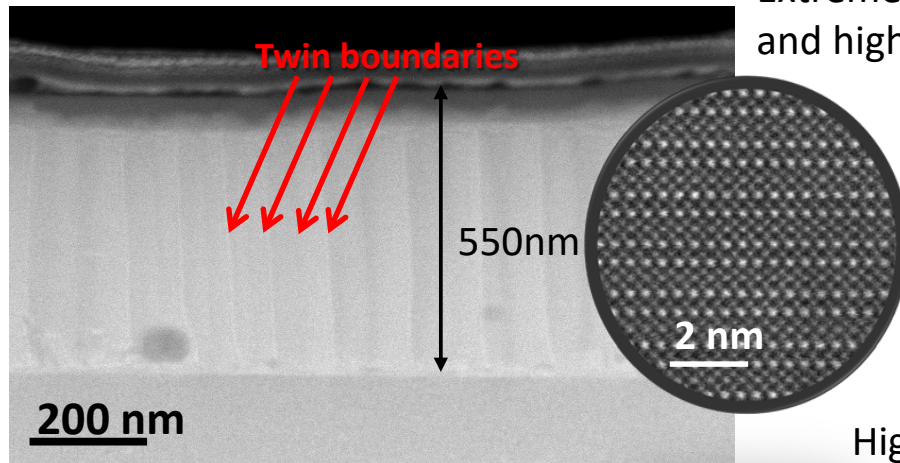
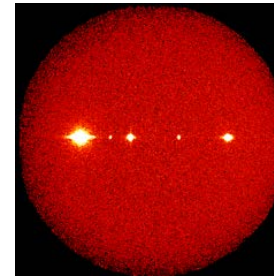
Transient Liquid Assisted Growth (TLAG-CSD) films



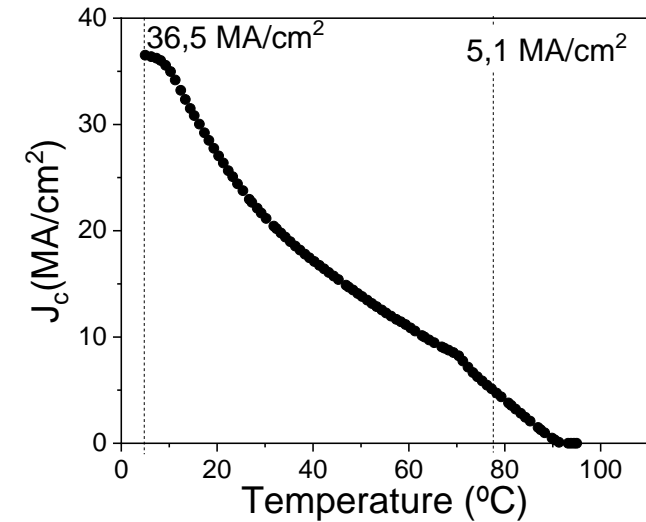
Homogeneous pyrolysis and compatible with IJP



Extremely low porosity and highly epitaxial



High quality growth

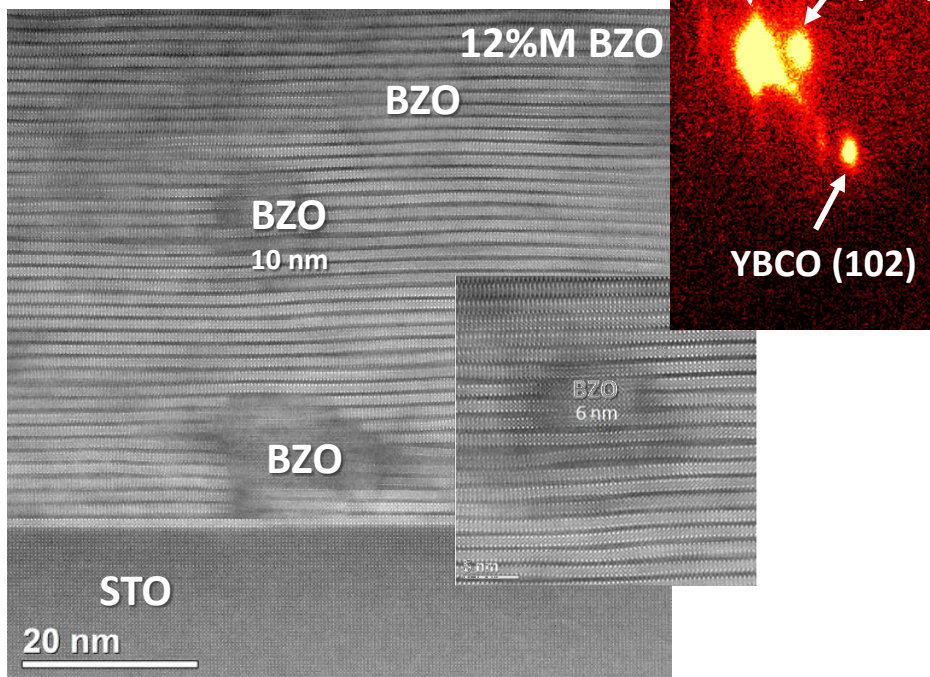
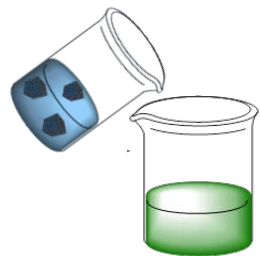


High performance demonstrated
 $J_c(77K) \sim 5 \text{ MA/cm}^2$
 $T_c \sim 90 \text{ K}$

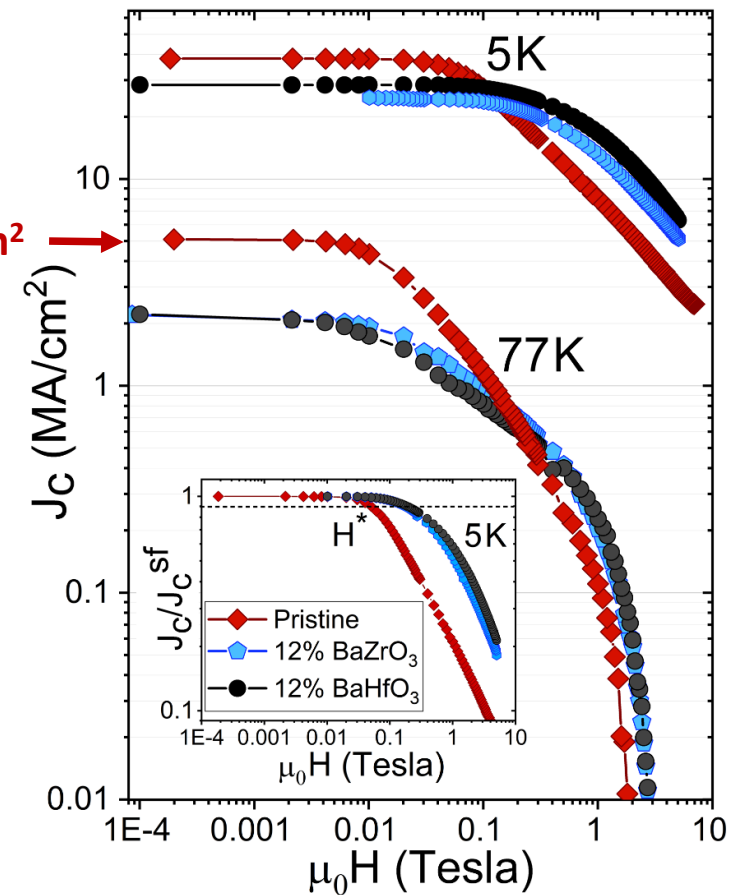
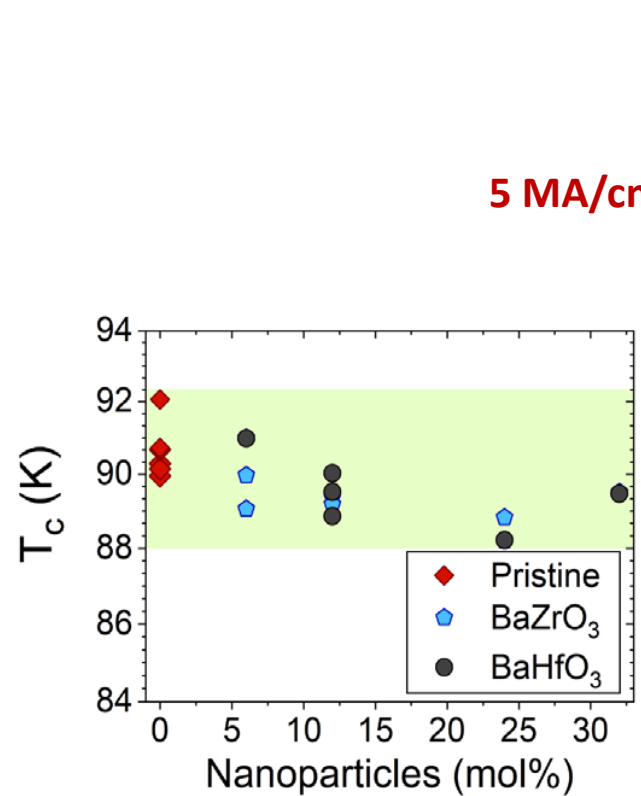
L. Soler et al, to be published

T. Puig -EUCAS 2019

Nanocomposites by TLAG-CSD



Very high density of defects and small epitaxial nanoparticles in nanocomposites



In-field performances of TLAG nanocomposite outperform pristine films

L. Soler et al, submitted

See 2-MO-FP1-05S (X. Obradors) and 1-MPCC1-102 (A. Queralto) for opportunities with Ink Jet Printing

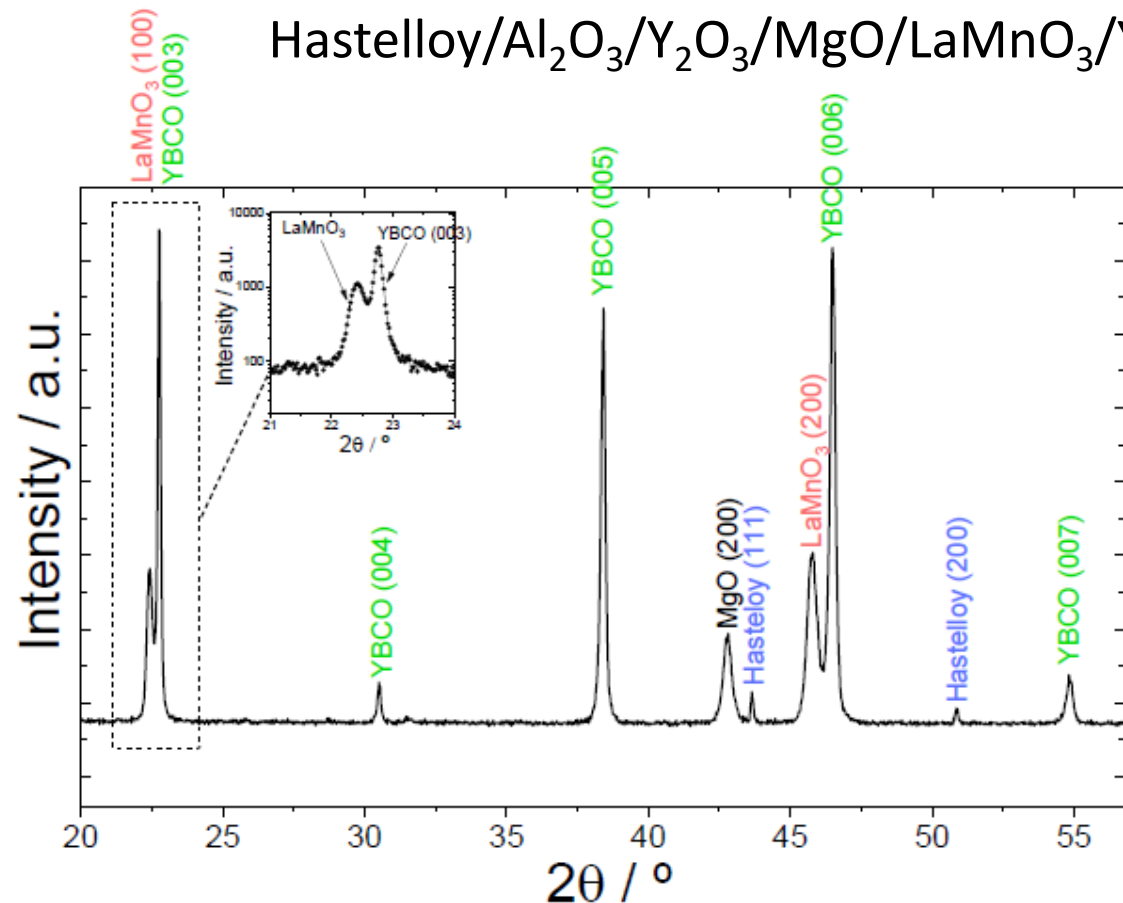
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TLAG-CSD Coated Conductors

SUNAM IBAD substrates:

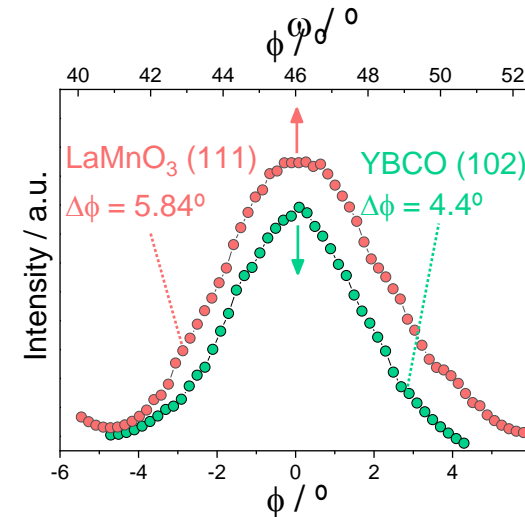
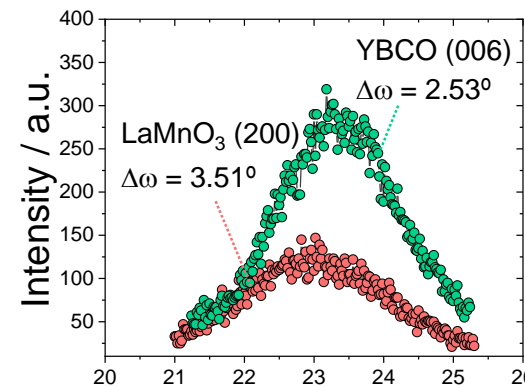
Hastelloy/Al₂O₃/Y₂O₃/MgO/LaMnO₃/YBCO



CSIC



ICMAB



High texture quality , no interfacial reaction

Colab. between SuNAM, OXOLUTIA and ICMAB within

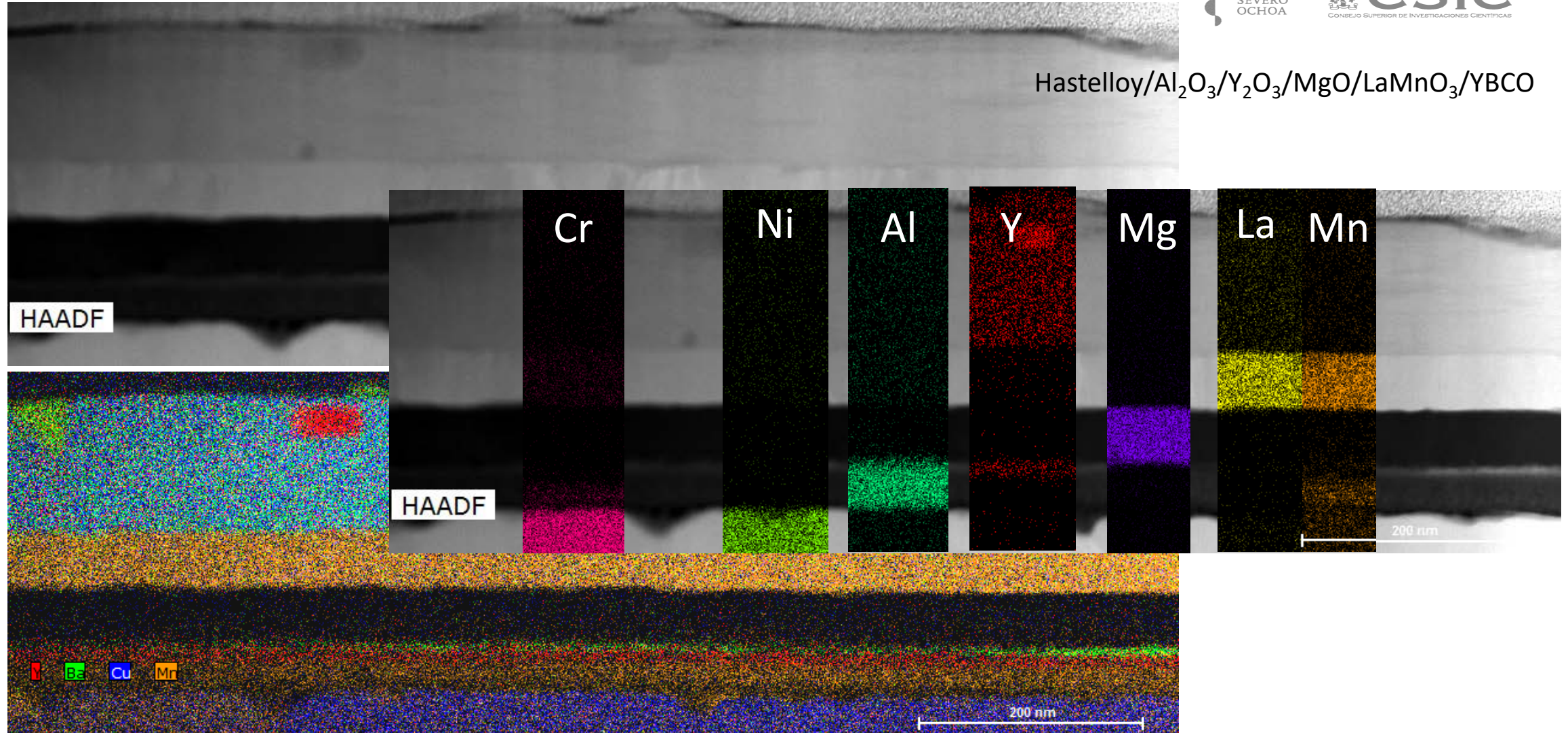


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TLAG YBCO coated conductor

TEM-EDX analysis: Homogeneous layers and clean interfaces without reactivity



Conclusions and prospectives



- ❑ HTS coated conductors have reached impressive performances also at high magnetic fields
- ❑ Strategies are being followed to decrease cost/performance ratio. In particular by:
 1. Increasing manufacturing rates
 2. Using high growth rate processes like those assisted by liquids
- ❑ Very good prospectives are envisaged for PLD, RCE-DR and TLAG-CSD concerning fast fabrication rates
- ❑ TLAG-CSD is a new opportunity combining very high growth rates of 100 nm/s with CSD methods and nanocomposites growth