Ultrafast transient liquid assisted growth of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \): a new scenario for enhanced vortex pinning

Xavier Obradors

T. Puig\(^1\), J. Banchewski\(^1\), S. Rasi \(^{1,2}\), A. Queralto\(^1\), K. Gupta\(^1\), L. Saltarelli\(^1\), D. Garcia\(^{1,3}\), A. Pacheco\(^1\), R. Vlad\(^1\), L. Soler\(^1\), J. Jareño\(^1\), R. Guzmán\(^1\), N. Chamorro\(^{3,1}\), M. Sieger\(^1\), S. Ricart\(^1\), J. Farjas\(^2\), P. Roura\(^2\), C. Mocuta\(^4\), R. Yanez\(^3\), J. Ros\(^3\)

\(^1\) Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Catalonia, Spain
\(^2\) GRMT, Department of Physics, University of Girona, Girona, Catalonia, Spain
\(^3\) Departament de Química, Univ. Autònoma de Barcelona, Catalonia, Spain
\(^4\) Diffabs beamline, Soleil Synchrotron, Paris, France
Coated Conductors: materials objectives

- CHEAPER
  - Lower capital investment (€)
  - Larger area manufacturing (W, L)
  - Higher throughput
  - Simpler processing
  - Simpler architecture
  - Higher yield

- BETTER
  - Higher performance: $J_c(B, T)$
  - Thicker REBCO films
  - More robust
  - Customized for Applications
  - Thinner substrates ($J_E$)
  - Nanostructure control: APCs
  - Lower ac losses

- CSD - TLAG

- Best combination

- Nanocomposites

\[
\frac{C}{P} = \frac{\€}{G \times L \times W \times J_c}
\]
Chemical Solution Deposition (CSD)

- Supersaturation conditions highly dependent on $P_{HF}$ and $P_{H2O}$
- Growth rate for c-axis growth limited to $\approx 1\text{nm/s}$
- High performances ($I_c=400\text{ A/cm-w}$)
- Complicated R2R gas flow furnaces

Gas-Solid reaction

$\text{Ba(O}_x\text{F}_y\text{)}_2 + 3/2 \text{CuO} + 1/4\text{Y}_2\text{O}_3 + y\text{H}_2\text{O} (g) \rightarrow 1/2 \text{YBa}_2\text{Cu}_3\text{O}_{6.5} + 2y\text{HF} (g)$

First step
- Inks (Trifluoroacetates, low Fluorine)
- Non-vacuum deposition
- Colloidal solutions for nanocomposites
- Industrially scalable: low cost manufacturing

Second step: film growth

Trifluoracetate-route: Low Fluorine TFA metalorganic precursors

Inks

IEEE-CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM (global edition), March 2023. Presentation 3MOr2A-01 was given at Applied Superconductivity Conference, Honolulu, HI, USA, October 26, 2022.
CSD – Transient Liquid Assisted Growth

First step
- Inks (Non-Fluorine)
- Non-vacuum deposition
- Colloidal solutions for nanocomposites
- Industrially scalable: low cost manufacturing

Second step: TLAG film growth

\[ \text{Metalorganic solution propionate based} \]

\[ \text{BaCO}_3(s) + \text{CuO}(s) + \text{Y}_2\text{O}_3(s) \rightarrow (\text{Ba} - \text{Cu}_{I/II-O})_l + \text{Y}_2\text{O}_3(s) \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \]

Coated Conductor manufacturing (1-2 \( \mu \)m)
- Typical growth time TFA: 30-60 min
- Typical growth time TLAG: 5-10 s
- Throughput TFA: 5-10 m/h
- Throughput TLAG: 3,000 - 4,000 m/h

- Non-equilibrium process: kinetic control
- Liquid-solid conversion reaction (high atomic diffusion in liquids)
- Supersaturation degree can be controlled through Ba:Cu ratio
- Ultrafast growth rates >100 – 1,000 nm/s
- Simplified R2R large area reactor for industrial manufacturing
- Environmentally friendly

See T. Puig: 4MOr1C-01 (9:00 am)
Pyrolyzed F-free CSD films

- Propionate precursors + additives
- Optimised solutions of various stoichiometries yield homogeneous nanocrystalline layers

Reduced sizes of the nanocrystalline YBCO precursors favour greatly atomic mobility, enabling *ultrafast growth rates*

- \( \text{BaCO}_3 \) (orthorhombic): 10 - 30 nm
- \( \text{CuO} \): 10 - 25 nm
- \( \text{Y}_2\text{O}_3 \): 5 - 6 nm

Nanoscale homogeneous distribution of the phases throughout the layer

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Multifunctional colloidal ink (Patent EP22382741)

L. Saltarelli et al., ACS Appl Mat Interfaces (2022)
Pyrolyzed F-free CSD films

- **Low porosity** of the layers, decreasing with the increase of the composition’s Cu content

![Image showing pore area vs. composition]

- **Suitability for multideposition** with no loss in homogeneity

![Image showing pore area vs. composition]

L. Saltarelli et al., *ACS Appl Mat Interfaces* (2022)
Transitient Liquid Assisted Growth: TLAG-CSD

Non-equilibrium process kinetically controlled

- Transient liquids (Ba-Cu-O) form much faster than the equilibrium solid phase (YBCO)
- No need of equilibrium liquid phases in the phase diagram

- RE solubility in the liquid controls supersaturation
- Ultrafast growth rates working at high supersaturation

See T. Puig: 4MO1C-01 (9:00 am)
Kinetic process and intermediate phases

In-situ XRD synchrotron exp.
from 100 ms down to 2 ms acquisition time

See T. Puig: 4MOr1C-01 (9:00 am)
Kinetic process and intermediate phases

In-situ XRD synchrotron exp. from 100 ms down to 2 ms acquisition time

See T. Puig: 4MOriC-01 (9:00 am)
TLAG-CSD films: microstructure and properties

Extremely low porosity and highly epitaxial YBCO grown layers

Tunable microstructure: depends a lot on process conditions

High performance demonstrated

L. Soler et al, Nature Communications (2020)
**ss-Nanocomposites:** Not suitable for TLAG

Use of complex solutions for *spontaneous segregation* of nanoparticles (BaZrO$_3$, BaHfO$_3$, Ba$_2$YTaO$_6$, BaCeO$_3$)

- J. Gutierrez et al, Nat Mat (2007);

**pn-Nanocomposites:** Colloidal solutions with *preformed nanoparticles* (N. Chamorro, RSC Adv. (2020))

Suitable for TFA and TLAG

- Spinel (MFe$_2$O$_4$)
- Fluorite (CeO$_2$, ZrO$_2$)
- Perovskite BaMO$_3$ (M= Zr, Hf)
- Bronze Ba(Ta,Nb)$_2$O$_6$

Need to stabilize np in the alcoholic and ionic environment of YBCO precursor solution at high concentrations

- P. Cayado et al, SUST (2015)
- X. Obradors et al, SUST (2018)
- D. Garcia et al., to be published
Nanoparticles for multifunctional colloidal solutions

Requirements

NP solution

- Small-size < 10 nm
- Non-aggregation in alcohol solution
- High concentrations in alcohol solution (≥ 100 mM)

Stabilization in YBCO precursor solution

- NPs compatible and stable in YBCO precursor solution
- Non-aggregation
- No precipitation

Compatibility with CSD-TLAG process

- NP composition non-reactive with YBCO
- High-thermal stability of NP composition

Reactivity:

- ZrO₂ NPs

Pushing effect:

- CeO₂ NPs

Aggregation

Coarsening

Multifunctional colloidal ink (Patent EP22382741)
Nanoparticle synthesis process

Hybrid Hydrolitic-Solvothermal Synthesis (H2S2)
2 steps process for preformed BaMO₃ NP synthesis

1. Hydrolitic (sol-gel) step: nucleation

- **Metal precursor:**
  - Alcoide M(OR)ₓ M=Zr,Hf, Ta or Nb
  - Hydroxide Ba(OH)₂·8H₂O
- **Stabilizer:** TREG
- **Solvent:** Alcohol media

$$\text{Hydrolysis} \quad M(OR)_x + H_2O \rightarrow M - OH$$

$$\text{Polycondensations} \quad M - OH + Ba - OH \rightarrow M - O - Ba$$

2. Solvothermal step: crystallization

- Temperature < 250 ºC
- Reaction Time < 24h

Limiting step: hydrolysis reaction
- Small sized NPs (3-15 nm)
- High NP concentrations (> 100 mM)
- Narrow range of size distribution: FWHM< 3nm
- Stable colloidal solutions (for months)

Multifunctional colloidal ink
(Patent EP22382741)

N. Chamorro et al., RSC Adv. 10, 2020, 28872-28878
BaMO$_3$ (M= Zr and Hf) Nanoparticles

**BaZrO$_3$ NC**

- Stable solutions (size/surface stability) for months
- Tuneable NP size from 4-20 nm

**BaHfO$_3$ NC**

- Frequency (%)
- NP size (nm)

![Graphs and images](image-url)

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Nanocomposite pyrolysis

- Homogenous and reproducible multideposited films (up to 650 nm)
- Thickness of ~450 nm (1 pristine layer +1 layer with 12% mol of NPs)

- Crystalline NPs and no NP coarsening for 10 and 5 nm NPs.
- Same YBCO precursor phases as pristine.

IEEE-CSC & ESAS SUPERCONDUCTIVITY NEWS FORUM [global edition], March 2023. Presentation 3MO02A-01 was given at Applied Superconductivity Conference, Honolulu, HI, USA, October 26, 2022.
**TFA-BHO pn-nanocomposites by Flash Heating**

- Distribution of initial NP: 4-6 nm

- Flash heating (20 °C/s): 20%M BHO (5 nm)

- \( n_{np} \approx 40 \times 10^{22} \text{ m}^{-3} \) (x2.5) (≈ 8 % vol)

- NPs random fraction: 94%

- Flash Heating strongly avoids NP coarsening

- Higher concentration of short stacking faults: higher density of partial dislocations

- NP size very close to the optimal size for vortex pinning (5-8 nm)

- Short SFs are promoted! (20 – 30 nm)

- Vol density partial dislocation: ≈ 2.3 %vol (+ 60 %)

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**References**


J Mat Chem C (2019)
Synergistic combination of Nps and nanostrain: enhanced vortex pinning

CTA: Conventional Thermal Annealing (0.4 °C/s)
FH: Flash heating (20ºC/s) - Enhanced vortex pinning

A leap increase of H* beyond nanostrain NP diameter \(\sim \xi_{ab}\) (coherence length)

Nanostrain & NPs (4-8 nm) Synergistic effect for enhanced vortex pinning

\[ \mu_0 H^* (mT) \]

\[ J_c (MA/cm^2) \]

\[ \xi_{ab} (coherence length) \]

Z. Li et al, J Mat Chem C (2019)
A. Palau et al., SUST (2018)
Nanocomposites growth by TLAG-CSD

$\Delta \phi < 0.8^\circ$

$\Delta \omega < 0.6^\circ$

Epitaxial nanoparticles in TLAG-CSD contrary to TFA-CSD

L. Soler et al, Nat Comm (2020)
Nanoparticles orientation in TLAG-CSD

Measurement: chi: 45º, at BZO (110) most intense reflexion

Low PO₂ route

32% BHO

YBCO (103)

BZO (110)

6% BZO

YBCO (103)

BZO (110)

YBCO (102)

Preformed NPs can rotate within the liquid state to reach epitaxy with YBCO matrix

L. Soler et al, Nat Comm (2020)
J. Banchewski et al, to be published

All NPs percentages:
0-10% random orientation

Example of 80% random orientation NPs (TFA)

Presentation 3MOr2A-01 was given at Applied Superconductivity Conference, Honolulu, HI, USA, October 26, 2022.

Preformed NPs can rotate within the liquid state to reach epitaxy with YBCO matrix

L. Soler et al, Nat Comm (2020)
J. Banchewski et al, to be published
TLAG-CSD superconducting properties

High $J_c$ values with in-field performance of TLAG nanocomposite outperforming pristine films

$H^*$ (T): single vortex regime (a measure of the density of pinning centers)

$J_c^{sf}$ constant up to 24 % mol

$H^*$ increases with nanoparticles percentage, indicating an increase of vortex pinning centers

TLAG-CSD superconducting properties

Isotropic and anisotropic pinning contributions

Effective anisotropy decrease due to nanostrain (SFs) and nanoparticles

*L. Soler et al, Nature Communications (2020)*

J. Banchewski et al, to be published

\[
e_{\text{eff}}(\theta) = \left[ \cos^2\theta + \gamma_{\text{eff}}^2 \sin^2\theta \right]^{1/2}.
\]
Vortex pinning defects in TFA/TLAG - CSD films

- High density of SF
- Small epitaxial NP

Point defects: Cu-O vacancies in the SF

Nanostrain

Broken twin boundaries

J. Gutierrez et al, Nat Mat (2007)
A. Llordés et al, Nat Mat (2012)
A. Palau et al., SUST (2018)
L. Soler et al, Nat Comm (2020)

R. Guzman et al, APLMat (2017)
S.T. Hartman et al, PRMat (2019)
Z. Li et al., Nanoscale Adv (2020)
Vortex pinning defects in TFA/TLAG - CSD films

Defective Stacking Fault is non-superconducting

FH 10 nm

J. Gutierrez et al, Nat Mat (2007)
A. Llordés et al, Nat Mat (2012)
A. Palau et al., SUST (2018)
L. Soler et al, Nat Comm (2020)

R. Guzman et al, APLMat (2017)
S.T. Hartman et al, PRMat (2019)
Z. Li et al., Nanoscale Adv (2020)
Vortex pinning in TLAG-CSD vs TFA-CSD

**TFA-CSD**
- Low density of defects in pristine films
- High density of defects achieved in Nanocomposites (NC)
- Nanocomposites contain random NPs that provide higher density of stacking faults (SFs)
- Flash heating provides less NP coarsening in NC

**TLAG-CSD**
- Pristine TLAG exhibits very high density of defects
- Preformed NPs can rotate within the transient liquid and get embeded epitaxially in YBCO matrix
- Epitaxial NPs in NC do influence little the density of SFs
- Epitaxial small NPs act as core pinning centres, increasing the overall pinning properties

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**Interphase boundary**
- Incoherent (no lattice match.)
- Semi-coherent (partial lattice match.)

**Dislocation**
- BaZrO$_3$
  - 10nm
- YBCO (102)
- YBCO (103)
- BZO (110)
- 6% BZO

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J. Gutierrez et al, Nat Mat (2007)
A. Llordés et al, Nat Mat (2012)
Z. Li et al., Nanoscale Adv (2020)

L. Soler, Nat Comm (2020)

**TLAG-CSD is a very promising process to obtain high vortex pinning films**
Vortex pinning in TLAG-CSD films and nanocomposites

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

Strong increase of H* with nanostrain and very low anisotropy in pristine films

Synergistic effect of nanostrain (partial dislocation) and small NP in TLAG nanocomposites

Outstanding values of H* with low anisotropy in nanocomposite films suggests additional pinning contribution from small NPs which can be included in a higher concentration

J. Banchewski et al, to be published
Pinning contributions of TLAG-CSD

Isotropic-Strong pinning contribution

\[ J_c(T) = J_c^{iso-wk}(T) + J_c^{iso-str}(T) + J_c^{aniso-str}(T) \]

Strong-isotropic pinning contribution of pristine TLAG emulates TFA-nanocomposite

- Enhanced nanostrain in pristine TLAG
- TLAG nanocomposites display high vortex pinning


High field properties of nanocomposites similar for TFA and TLAG
Pinning landscapes in nanocomposite films: very high magnetic fields

\[ J_c(T) = J_c(0)^{\text{iso-wk}} \exp\left(-\frac{T}{T_0}\right) + J_c(0)^{\text{iso-str}} \exp\left(-3\frac{T}{T^*_{\text{iso-str}}}\right)^2 + J_c(0)^{\text{aniso-str}} \exp\left(-3\frac{T}{T^*_{\text{aniso-str}}}\right)^2 \]

D. Abraimov
J. Jaroszynski
D. Larbalestier

F. Vallés et al, Comm Mat 3, 45 (2022)
Optimized pinning landscapes in CSD nanocomposite films

Low and intermediate T - Intermediate and high H (14 years of measurements)

- High density of isotropic defects: Cu-O vacancies, short SF, small NP (better Np than nanorods)
- Large density of strong isotropic and anisotropic defects with long vertical coherence: nanoparticles, nanostrain, long nanorods, long twin boundaries (Nanorods and nanoparticles will add effects)
- High density of anisotropic strong defects with very long vertical coherence: long twin boundaries, elongated nanorods, thick CSD nanocomposites combined with other auxiliary strong or weak isotropic defects to lessen vortex creep excitations (1D-2D mandatory but all defects will help to diminish creep)

D. Abraimov
J. Jaroszynski
D. Larbalestier

F. Valles et al, Comm Mat 3,45 (2022)
Tune charge carrier density by oxygen overdoping

\[ F_p = \sum_i N_p f_{p,i} (B, T) \propto J_c \]

\[ f_p \propto E_c \] condensation energy

\[ J_d^2 \propto n_s E_c \Rightarrow J_c^2 \propto n_H H_0 \] (H₀ from in-plane magnetoresistance)

(three independent experimental parameters)

\[ n_H \text{ and } E_c \text{ increases in the overdoped state, and consequently } J_c \text{ should increase} \]

Carrier concentration effects: oxygen overdoping

YBCO PLD and TFA – CSD thin films

- Carrier concentration determined by Hall effect (100 K)
- Overdoping is achieved by oxygen excess

- Fermi surface reconstruction at the Quantum Critical Point ($p^* > p_{opt}$): large increase of the carrier density $n$ (cylindrical Fermi surface)
- Non-unique relation between the charge carrier density $n$ and doping, $p$.

Strong increase of $J_c$ in the overdoped state

$J_c(p^*) \approx \frac{1}{5} J_d(p^*) = 90 \text{ MA/cm}^2$

$J_d(p^*) \approx 500 \text{ MA/cm}^2$

Overdoping is a robust method to reach ultrahigh $J_c(H)$

$J_c(p^{opt}) \approx \frac{1}{10} J_d(p^{opt})$

$J_d(p^{opt}) \approx 330 \text{ MA/cm}^2$

Strong increase of $J_c$ with $n_H$

(x4 from $p_{opt}$ to $p^*$)

A. Stangl et al, Scientific Reports (2021)

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YBCO TLAG-CSD NANOCOMPOSITE FILMS

Extended to technical substrates in collaboration with

Buffer layers

J_c(5K) = 24 MA/cm^2  J_c(77K) = 2 MA/cm^2

450 nm films
TLAG-CSD Coated Conductors

5 cm test samples of 1 µm thick homogeneous pyrolyzed YBCO deposited on SuNAM substrates

Liquid growth morphology, very high epitaxy and texture quality, with a noticeable improvement of texture of the YBCO layer

\[ T_c = 90 \text{ K} \]
\[ J_c (77K) = 2 \text{ MA/cm}^2 \]
\[ J_c(5 \text{ K}) = 23 \text{ MA/cm}^2 \]

Need to further reduce some secondary phases interrupting current percolation: tuning process conditions

Several different metallic substrates tested successfully
<table>
<thead>
<tr>
<th></th>
<th>TFA-CSD</th>
<th>TLAG-CSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth mechanism</td>
<td>Gas-solid</td>
<td>Liquid-solid</td>
</tr>
<tr>
<td>Growth rate</td>
<td>Slow (~1 nm/s)</td>
<td>Ultrafast (~100-1,000 nm/s)</td>
</tr>
<tr>
<td>Supersaturation control</td>
<td>$P_{H_2O}$, T</td>
<td>[$Y$, Liquid composition, T, $P_{O_2}$]</td>
</tr>
<tr>
<td>C-axis window</td>
<td>narrow</td>
<td>Wide and versatile (T and $P_{O_2}$ routes)</td>
</tr>
<tr>
<td>Nanocomposites</td>
<td>Spont. Segregat., preformed nanoparticles</td>
<td>Preformed nanoparticles</td>
</tr>
<tr>
<td>Nanoparticles orientation</td>
<td>Random</td>
<td>Epitaxial</td>
</tr>
<tr>
<td>Pinning centers</td>
<td>Nanostrain, np</td>
<td>Nanostrain, np, new possible defects</td>
</tr>
<tr>
<td>$H^*$ (single vortex pinning)</td>
<td>100 mT (200 mT in FH-NC)</td>
<td>600 mT in NC</td>
</tr>
<tr>
<td>$J_c$ (77K) / $I_c$(77K)</td>
<td>2 - 5 MA/cm$^2$ (thin film) / 600 A/cm-w</td>
<td>2 - 5 MA/cm$^2$ (thin film) / 150 A/cm-w</td>
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<tr>
<td>Heating rate</td>
<td>Low (coarsening) or Flash Heating</td>
<td>High (no coarsening)</td>
</tr>
<tr>
<td>Cap layer and reactivity</td>
<td>CeO$_2$, weak reactivity</td>
<td>LMO, LSMO, no or weak reactivity</td>
</tr>
<tr>
<td>Thickness</td>
<td>Single deposition : ~ 0.8 - 1 µm</td>
<td>Single deposition : ~ 0.5 µm</td>
</tr>
<tr>
<td></td>
<td>Multideposition: ~ 2.5 µm</td>
<td>Multideposition: ~ 1.5 µm</td>
</tr>
<tr>
<td>Large scale manufacturing</td>
<td>Limited volume / complex furnaces</td>
<td>Higher throughput / simplified furnaces</td>
</tr>
</tbody>
</table>
CONCLUSIONS

- TLAG-CSD is a novel low cost and ultrafast film growth methodology.
- Stable, reproducible multifunctional non-fluorine propionate inks have been developed.
- Knowledge of kinetic phase diagrams is essential: outlined through in-situ synchrotron X-ray diffraction.
- T and PO₂-routes processing paths are based on a fast kinetically-controlled formation of a Ba-Cu-O transient liquid.
- TLAG-CSD nanocomposites with preformed nanoparticles lead to outstanding vortex pinning properties. Epitaxial nanoparticles and a high concentration of intergrowths are generated.
- Several industrially produced CC metallic substrates have been tested successfully.
- TLAG-CSD is foreseen as a game changing high throughput R2R CC manufacturing process.