



Italian National Agency for New Technologies,  
Energy and Sustainable Economic Development



# YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> film with Ba<sub>2</sub>Y(Nb,Ta)O<sub>6</sub> nano-inclusions for high field applications

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Glasgow, 2019 September 3rd

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Enabling Research Work Programme  
2015-2017 and 2019-2020



Central Facility for Electron Microscopy



RWTHAACHEN

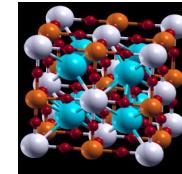


G. Celentano - Glasgow, September 3rd 2019

# OUTLINE

## Introduction

- Interest in high field applications for REBCO;
- Nb- and Ta-based APC for REBCO: state-of-the-art

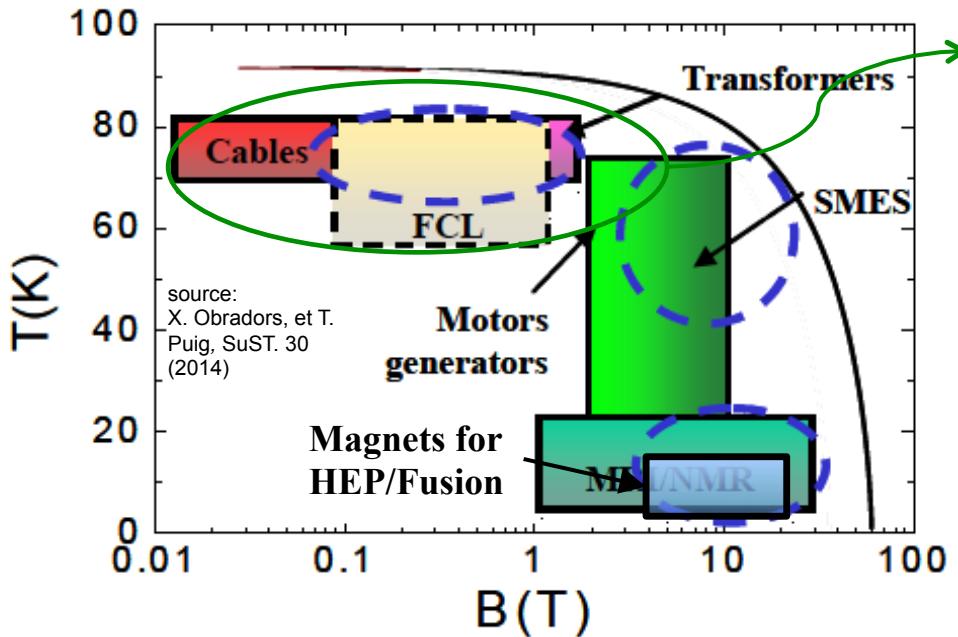


## Mixed doping by $\text{Ba}_2(\text{Y,Ta})\text{O}_6 + \text{Ba}_2(\text{Y,Nb})\text{O}_6$ : 2.5 mol.% + 2.5 mol.%

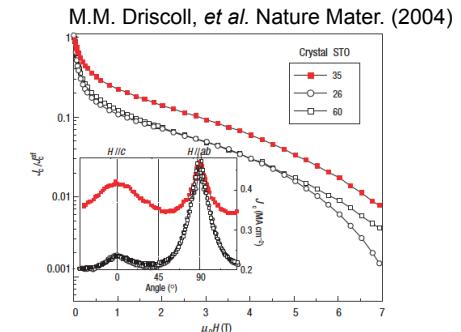
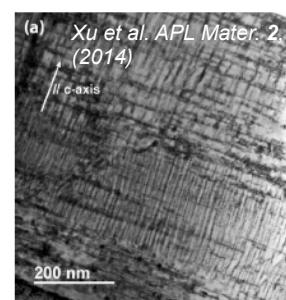
- BYTO single vs mixed BYTO + BYNO doping;
- Defects landscape tunability by growth rate;

## Conclusions & Perspectives

# Intro – High fields: new perspectives of REBCO applications



Effective technology for control of pinning and  $J_c$  optimization @ LN<sub>2</sub> and low/mid field



APC by incorporation of  $\text{BaMO}_3$  (M= Zr, Hf, Sn)  
 Self-assembled columnar structures/ $c$  – axis correlated defects

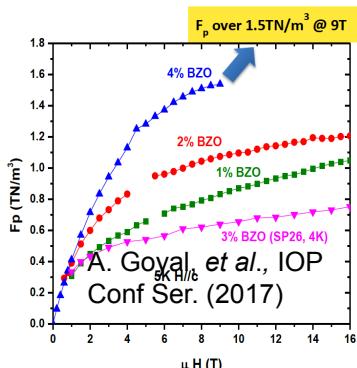
Nuclear fusion and accelerators requests are extremely demanding

Nb<sub>3</sub>Sn technology cannot fulfill these needs

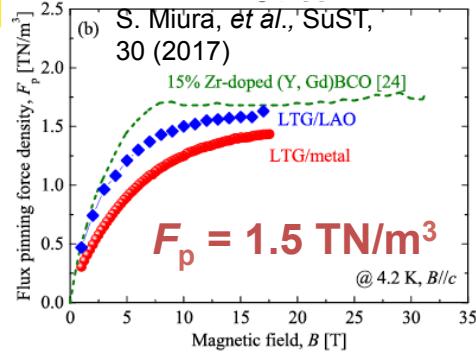
For REBCO this is a unique opportunity to extend its applicability to high field magnets sector

# Intro – What we know @ Low T / High field conditions for REBCO

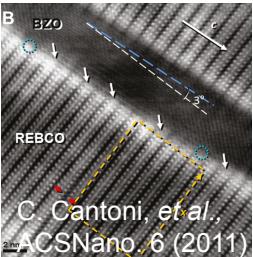
**APC approach is still effective:** APC + additional defects spontaneously generated by APC/YBCO interfacial strain accommodation



PLD-YBCO with BZO

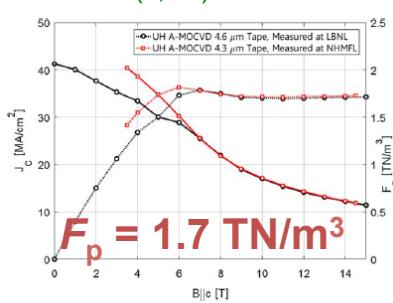


PLD-SmBCO with BHO

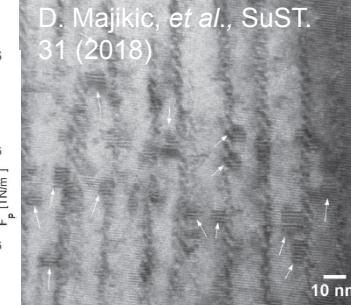


Oxygen disorder in YBCO at interface  
C. Cantoni, et al., ACS Nano 6 (2011)

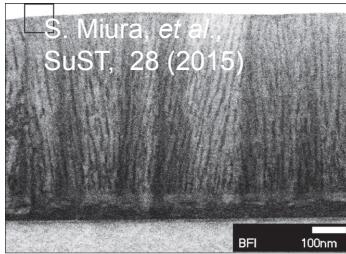
MOCVD-(Y,Gd)BCO with Zr



D. Majikic, et al., SuST. 31 (2018)

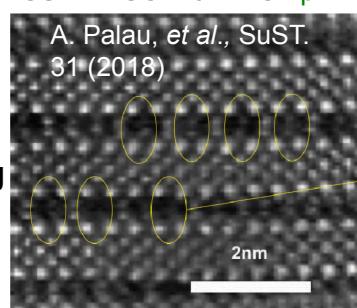


Very thin rods/columns + segregated  $\text{RE}_2\text{O}_3$



Careful control of rods size, density and inclination distribution

Cluster of Cu-O vacancies in stacking faults



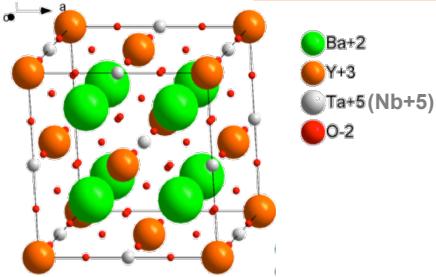
CSD-YBCO with BZO np

Little is known so far:

REBCO poorly investigated in low T/high field conditions

More studies are needed

# Intro: $\text{Ba}_2\text{YTaO}_6$ and $\text{Ba}_2\text{YNbO}_6$ doping: great performances at LN<sub>2</sub>



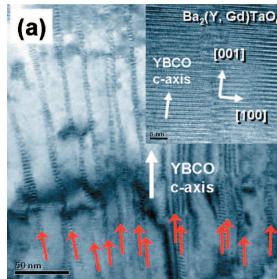
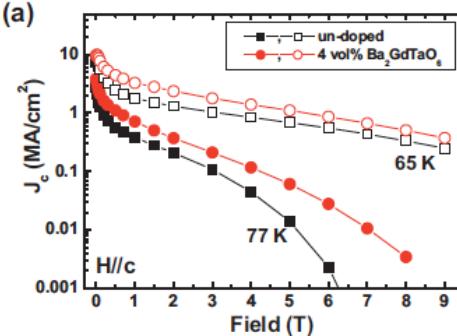
Double perovskite; cubic - Fm3m;  $a = 0.84 \text{ nm}$ ;

- Great phase stability (**chemically inert w.r.t. YBCO**);
- large mismatch w.r.t. YBCO: in plane  $\sim 9.4\%$ ;  $c$ -axis  $\sim 8.3\%$ ;
- $\text{Nb}^{+5} = \text{Ta}^{+5} = 0.78 \text{ \AA}$  ( $\text{Zr}^{+4} = 0.86 \text{ \AA}$ )
- $\text{Ta}_2\text{O}_5$  ( $\text{Nb}_2\text{O}_5$ ) lower melting  $T$  than  $\text{ZrO}_2$ ;
- **larger ion mobility than Zr is expected;**

G. Ercolano et al. SuST 23 (2010)  
 G. Wee et al. PRB 81 (2010)  
 G. Ercolano et al. SuST 24 (2011)

## $\text{Ba}_2\text{RETaO}_6$ (RE=Yb, Er, Gd)

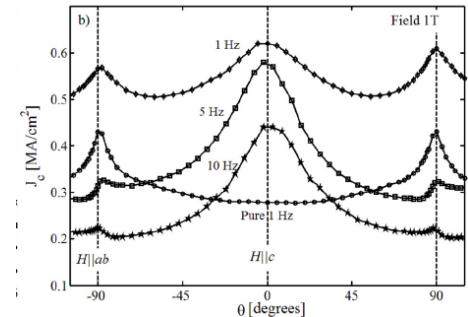
G. Wee et al. PRB 81 (2010)



**Splayed columns,**  
 dense and fine structure  
 $d \approx 6 - 7 \text{ nm}$ ,  
 $B_\phi \approx 5 - 9 \text{ T}$

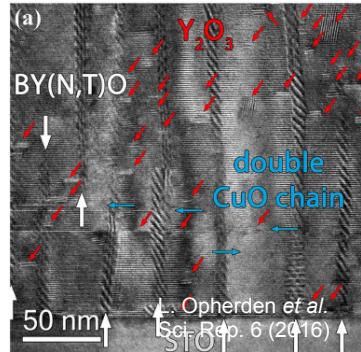
## $\text{Ba}_2\text{YNbO}_6$

G. Ercolano et al. JAP (2014)

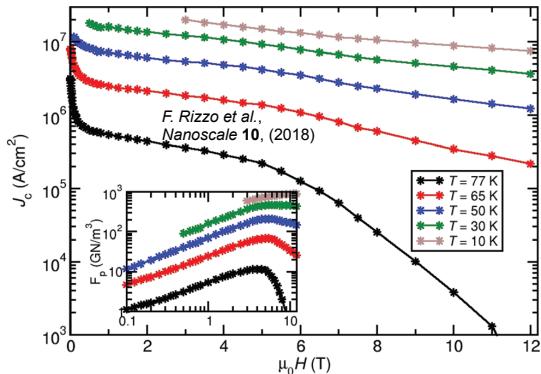


# Intro: Nb and Ta- based double doping

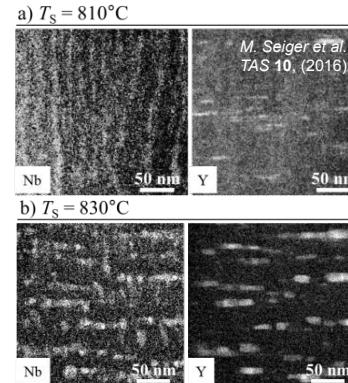
More complex defect landscape    Mixed  $\text{Ba}_2\text{YNbO}_6 + \text{Ba}_2\text{YTaO}_6$  doping



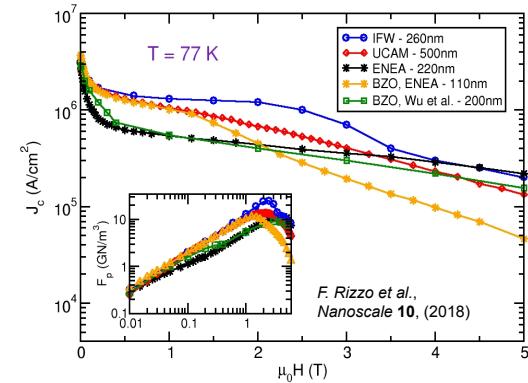
**Complex landscape:**  
 $\text{Ba}_2\text{Y}(\text{Nb},\text{Ta})\text{O}_6$  continuous columns +  $\text{Y}_2\text{O}_3$  nanoparticles



**Tunable:** switch to plate-like defects



**Reproducible:** similar performance for samples grown in different Labs



**Good  $T$  and  $B$  - behavior:  $\text{Ba}_2\text{Y}(\text{Nb},\text{Ta})\text{O}_6$  promising for low  $T$  and high fields regimes**

# OUTLINE

## Mixed doping by $\text{Ba}_2(\text{Y,Ta})\text{O}_6 + \text{Ba}_2(\text{Y,Nb})\text{O}_6$ : 2.5 mol.% + 2.5 mol.%

- BYTO single vs mixed BYTO + BYNO doping;
- Defects landscape tunability by growth rate;

# PLD growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ + tantalate/nobiate based APCs

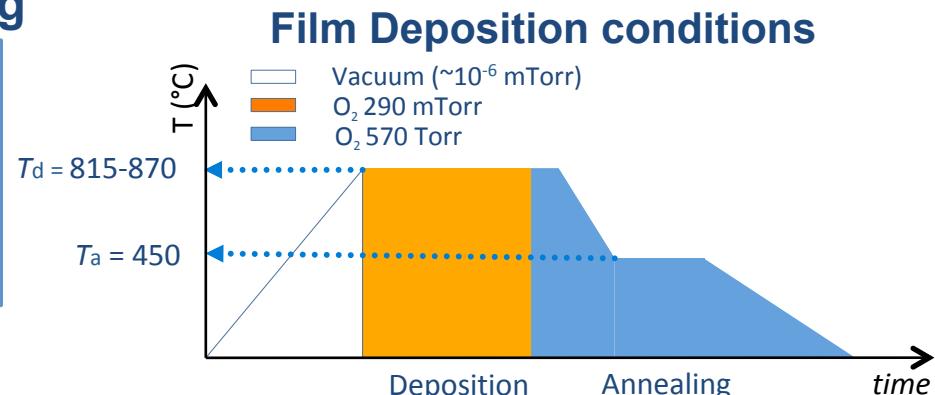
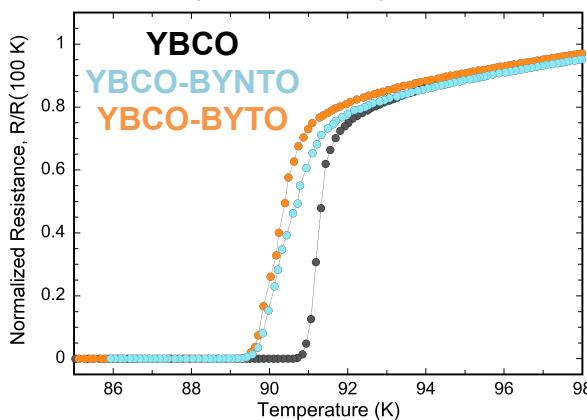
## Single (BYTO) vs balanced mixed doping

### YBCO composite targets

YBCO :  $\text{Ba}_2\text{YTaO}_6$  5 mol. %

YBCO :  $\text{Ba}_2\text{YTaO}_6$  2.5 mol. % +  $\text{Ba}_2\text{YNbO}_6$  2.5 mol.

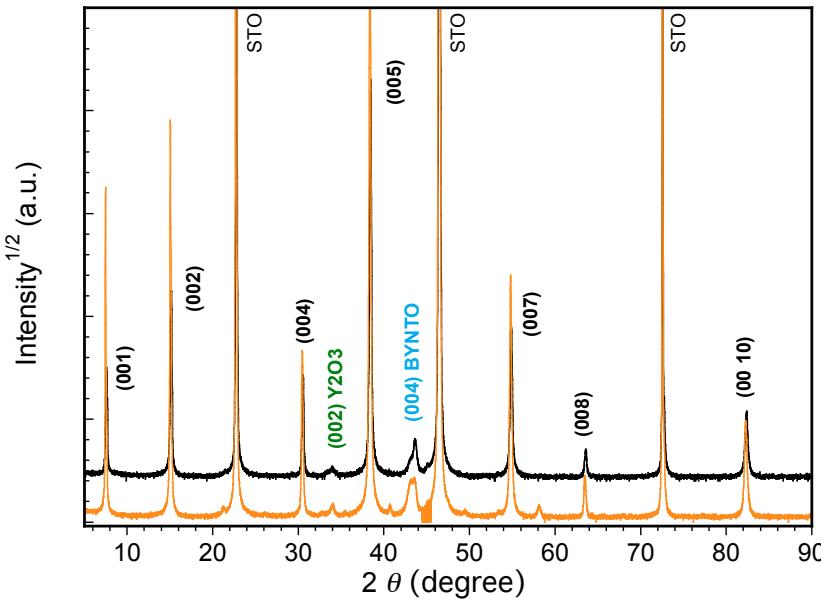
Best  $T_c \approx 89$  K @  $T_d = 840$  °C



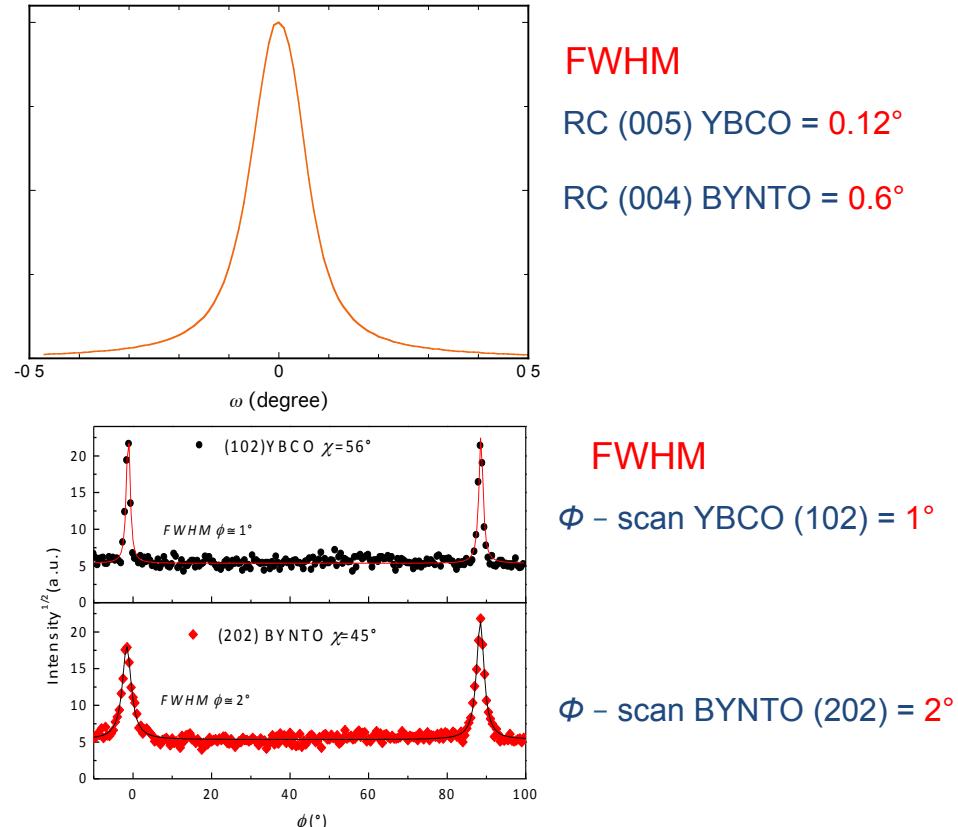
Film thickness  $\approx 200$  nm  
Substrate: (001)  $\text{SrTiO}_3$   
Growth rate,  $\rho \approx 0.3 \text{ nm s}^{-1}$

**PLD setup**  
XeCl Excimer Laser  
 $\lambda = 308 \text{ nm}$   
 $f_L = 10 \text{ Hz}$   
fluence  $\approx 1.5 - 2 \text{ J/cm}^2$

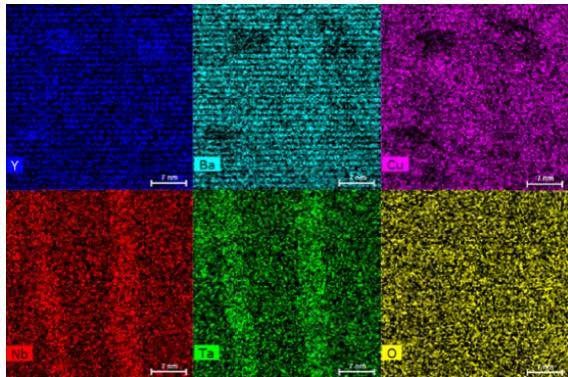
# BYTO 2.5 mol.% + BYNO 2.5 mol.% / BYTO 5 mol.%: structural properties



- good YBCO epitaxial growth
- BYNTO grows cube-on-cube with YBCO
- presence of Y<sub>2</sub>O<sub>3</sub> related peaks



# BYTO 2.5 mol.% + BYNO 2.5 mol.%: TEM/EDX



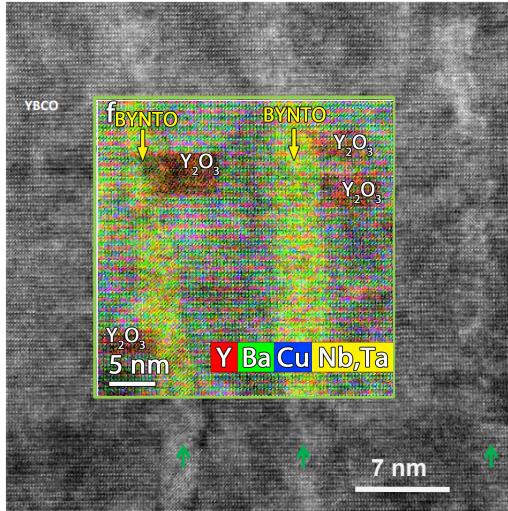
## EDX elemental maps:

Excess of Ta and Nb is present in the columns

- Continue splayed columns are present

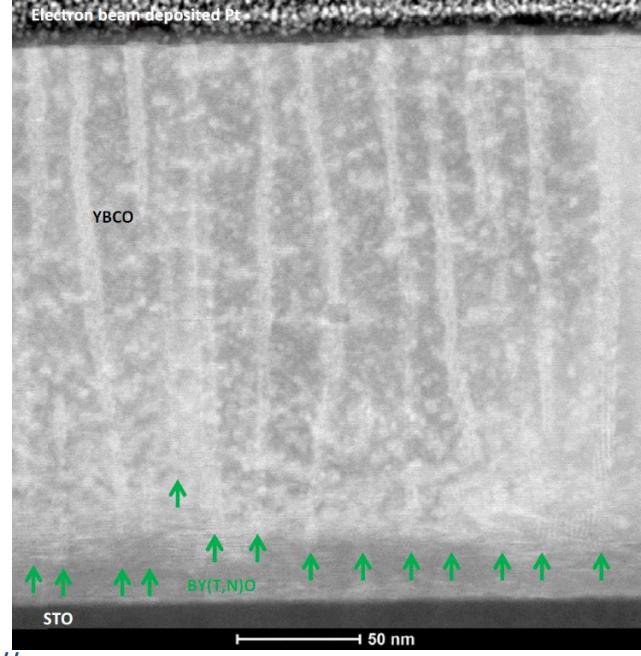
$(0\ 0\ 1)_{\text{BYNTO}} // (0\ 0\ 1)_{\text{YBCO}}$ ,  
 $(100)_{\text{BYNTO}} // (100)_{\text{YBCO}}$

- High density of  $\text{Y}_2\text{O}_3$  nanoparticles is recognized



## $\text{Y}_2\text{O}_3$ nanoparticles

- size  $\leq 10$  nm;
- structural relationship:  $(001)_{\text{Y}_2\text{O}_3} / (001)_{\text{YBCO}}$ ,  $(110)_{\text{Y}_2\text{O}_3} / (100)_{\text{YBCO}}$

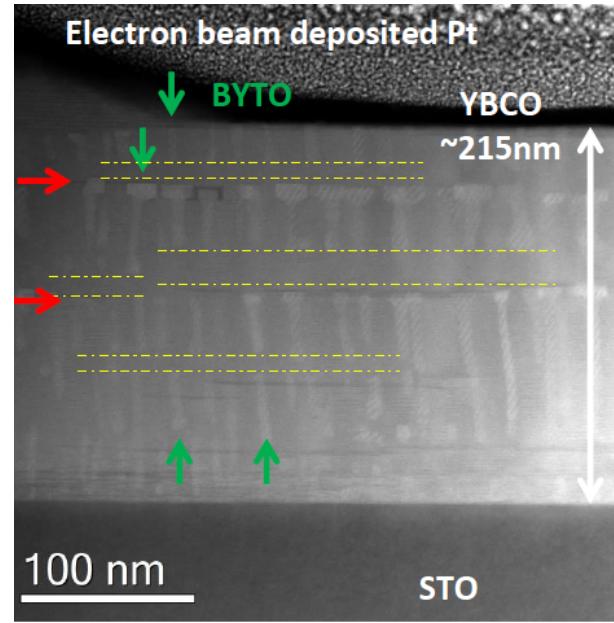
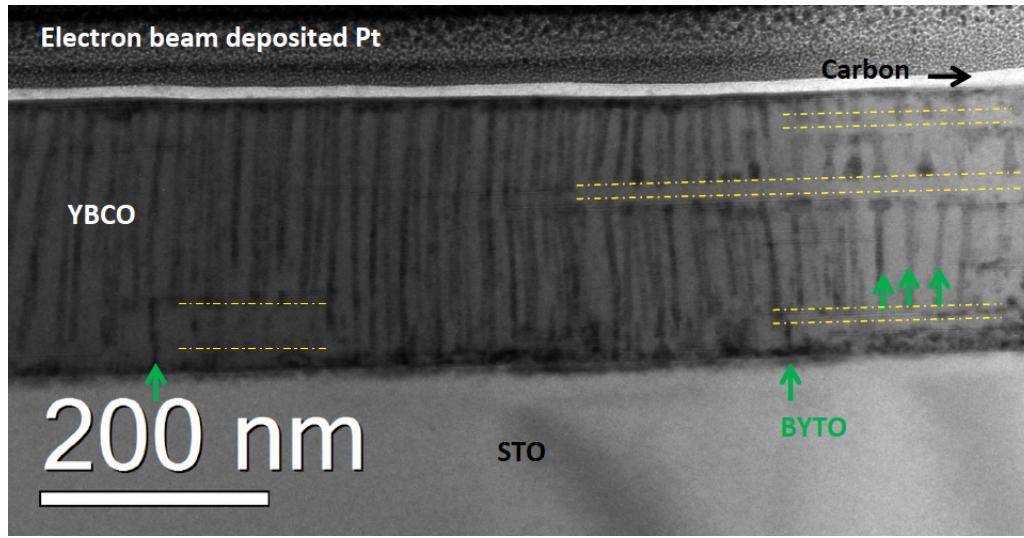


Column size  $d \sim 5$  nm  
 Inter-column distance  $\sim 20$  nm  
 $(n \sim 2500 \mu\text{m}^{-2}, B_\phi \approx 5.2 \text{ T})$

## BYTO 5 mol.%: TEM/EDX

Two type of columnar structures:

- **continuous** through the full YBCO thickness
- and **truncated, some of them with hammerhead**



Column size  $d \sim 5$  nm  
Inter-column distance  $\sim 20$  nm  
( $n \sim 2500 \mu\text{m}^{-2}$ ,  $B_\phi \approx 5.2$  T)

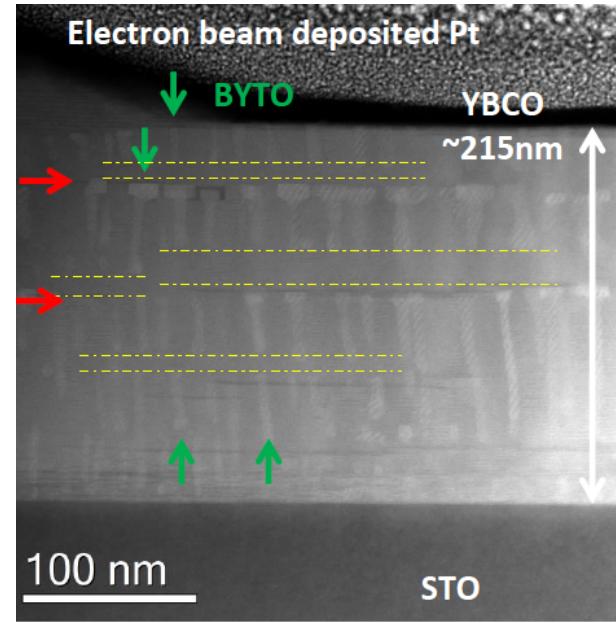
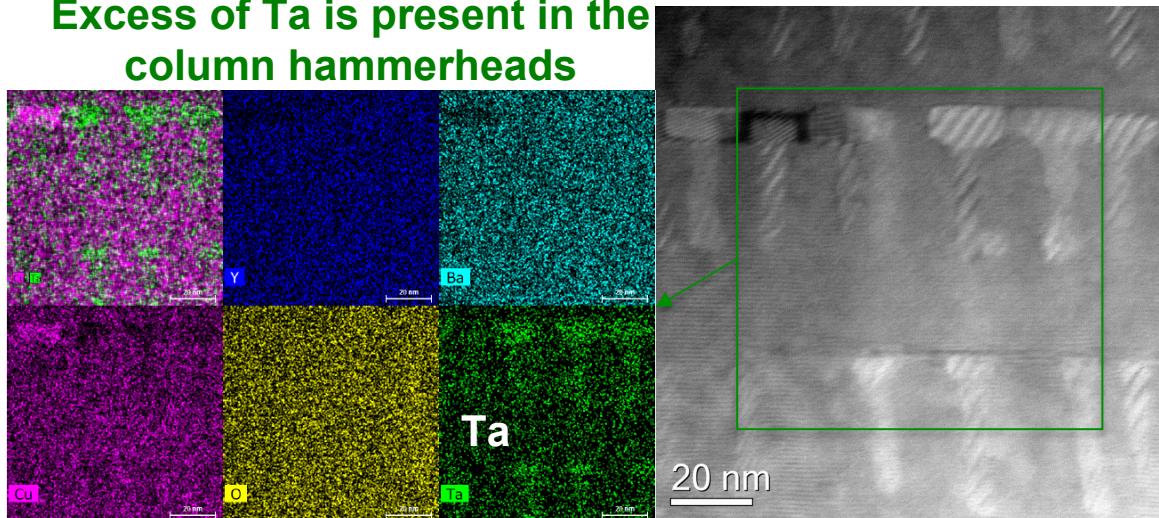
## BYTO 5 mol.%: TEM/EDX

Two type of columnar structures:

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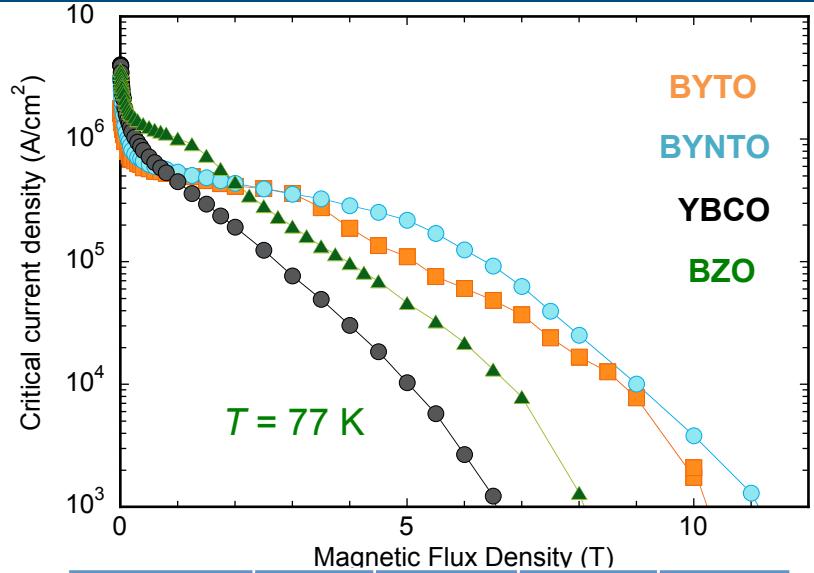
**EDX elemental maps:**

**Excess of Ta is present in the column hammerheads**



Column size  $d \sim 5$  nm  
Inter-column distance  $\sim 20$  nm  
( $n \sim 2500 \mu\text{m}^{-2}$ ,  $B_\phi \approx 5.2$  T)

# BYTO 2.5 mol.% + BYNO 2.5 mol.% / BYTO 5 mol.%: $J_c$ behaviour @ 77 K



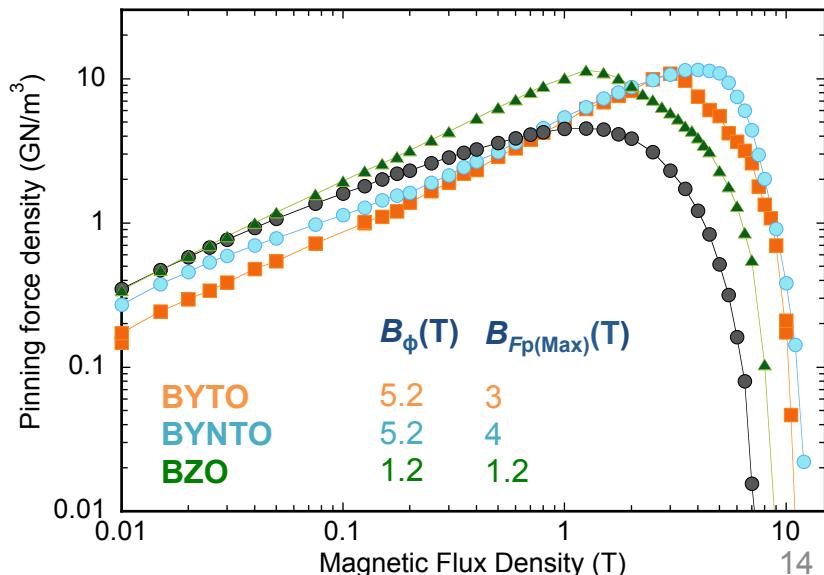
	77 K	BYTO	BYNTO	YBCO	BZO
$J_c(0)$	1.6	3.2	4.0	3.7	
$\alpha, J_c \approx B^{-\alpha}$	0.23	0.28	0.44	0.27	
$B_{irr}$	10.2	11.1	6.7	8	
$F_p(\max)$	10.9	11.5	4.5	11.4	

Comparison with YBCO and YBCO + 5 mol.% BZO  
 deposited by PLD in similar conditions

$d_{BZO} \approx 5 - 7 \text{ nm}, n_{BZO} \approx 600 \mu\text{m}^{-2} (B_\phi \approx 1.2 \text{ T})$

A. Augieri, et al.,  
 JAP. 108 (2010)

BYNTO best mid field  
 performances @ 77 K

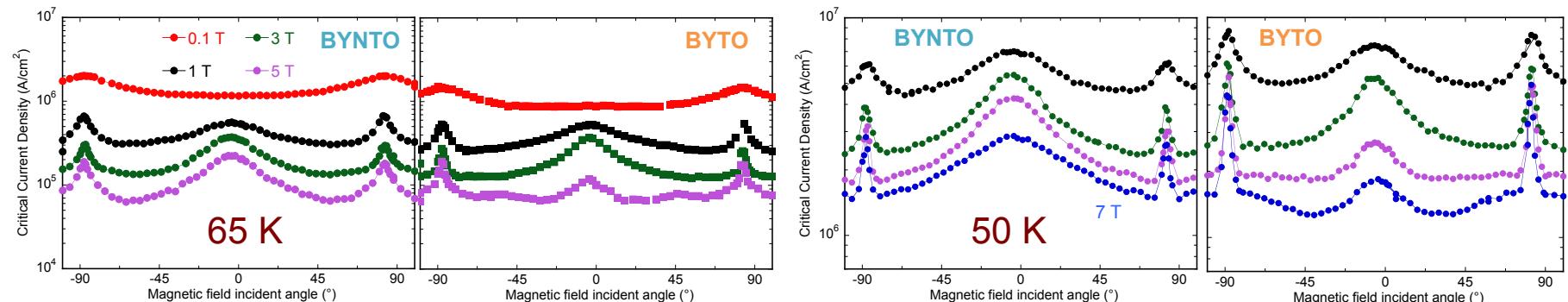
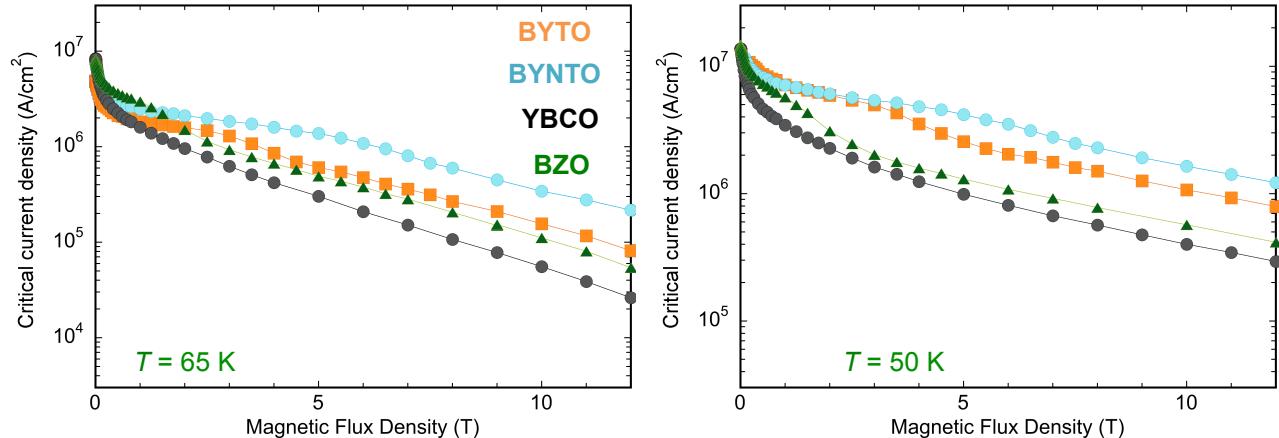


## BYTO 2.5 mol.% + BYNO 2.5 mol.% / BYTO 5 mol.%: $J_c$ behaviour @ intermediate $T$

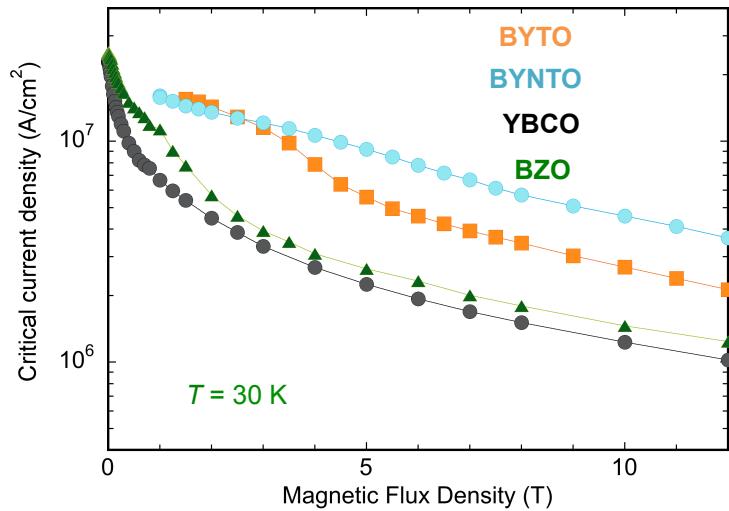
- Both **BYTO** and **BYNTO** improve YBCO
- **BYNTO** shows a stronger  $J_c$  retention in high field

$J_c(\theta)$ : **BYNTO** is more efficient

- Broader peaks and more intense at higher fields

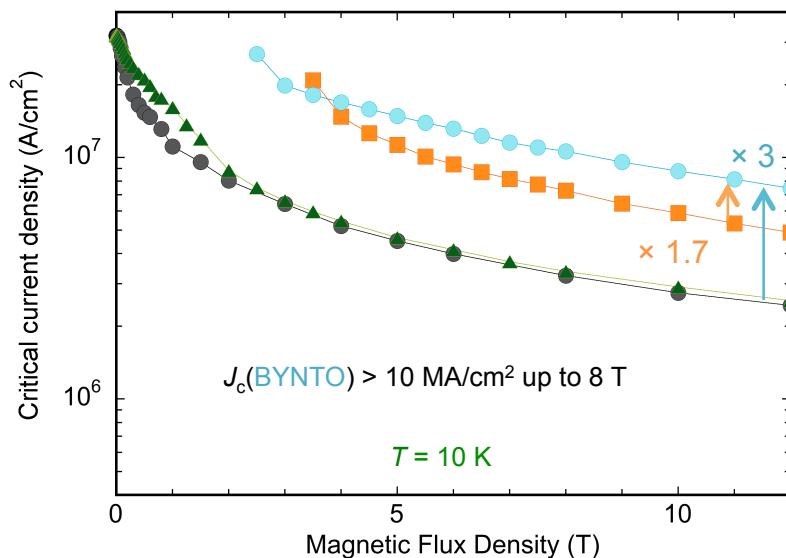


## BYTO 2.5 mol.% + BYNO 2.5 mol.% / BYTO 5 mol.%: $J_c$ behaviour @ low $T$

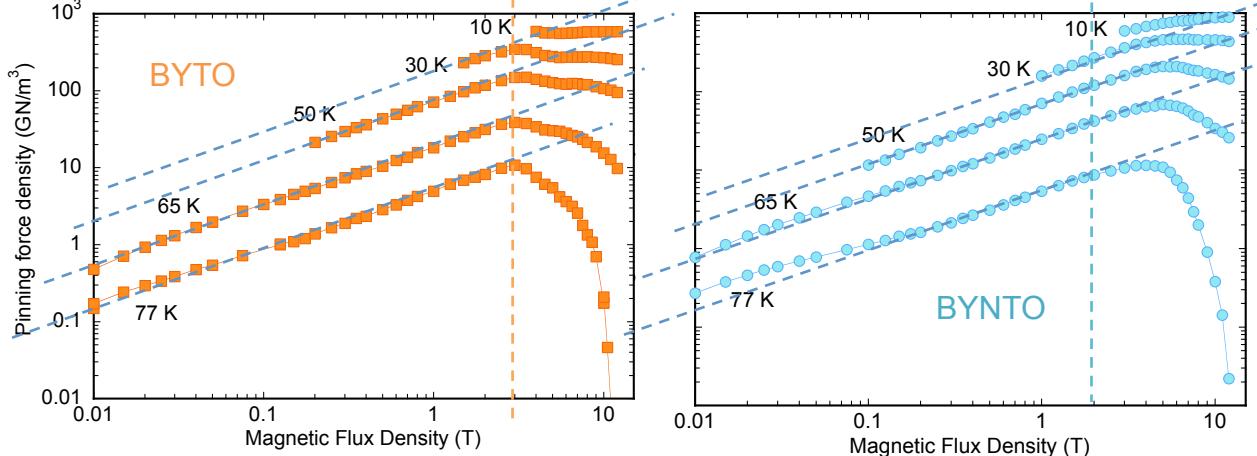


- **BYNTO & BYTO similar low field** behaviour (up to  $B \approx 3 - 4$  T)
- **BYNTO has better high-field behaviour** than **BYTO** (@ 10 K, 12 T  $J_c(\text{BYNTO}) = 1.7 \times J_c(\text{BYTO})$ )

Both **BYTO** and **BYNTO** largely improve YBCO performances in whole  $T$ - and  $B$ - range  
 (@ 10 K, 12 T  $J_c(\text{BYNTO}) = 3 \times J_c(\text{YBCO})$ )



# BYTO 2.5 mol.% + BYNO 2.5 mol.% / BYTO 5 mol%: Pinning Force Density, $F_p$



power law exponents  
are  $T$ -independent

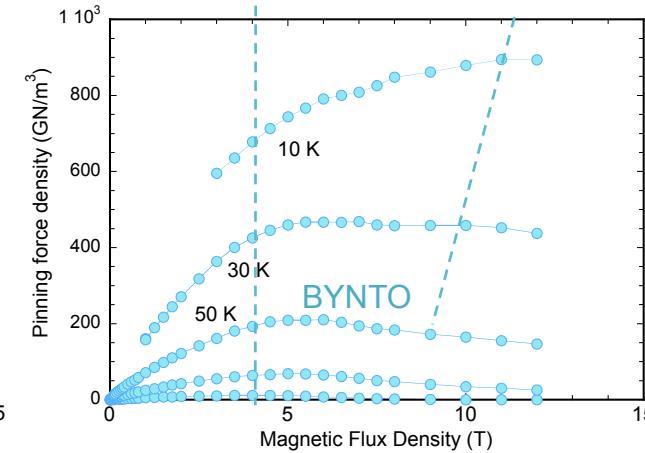
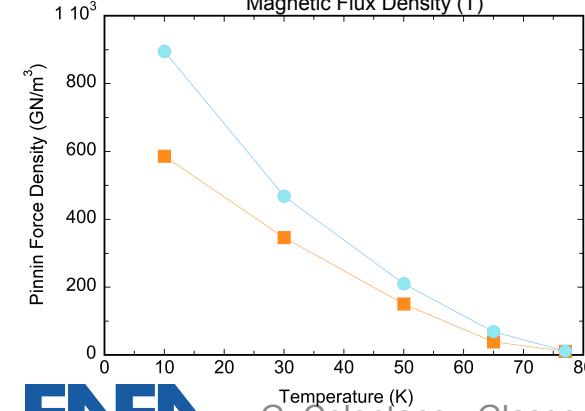
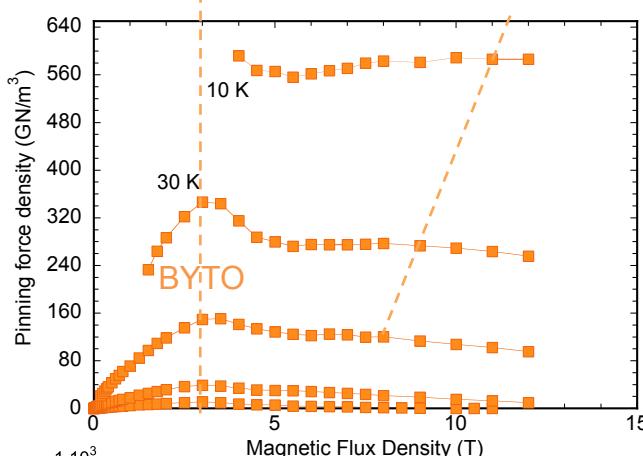
Matching field effect

BYTO/BYNTO  
columnar  
systems is  
effective in the  
whole  $T$ -range  
and dominate for  
 $B [0 - B_\Phi]$

BYTO	77 K	65 K	50 K	30 K	10 K
$\alpha, J_c \approx B^{-\alpha}$	0.23	0.26	0.22	0.26	---

BYNTO	77 K	65 K	50 K	30 K	10 K
$\alpha, J_c \approx B^{-\alpha}$	0.28	0.24	0.21	0.26	---

# BYTO 2.5 mol.% + BYNO 2.5 mol.% / BYTO 5 mol%: $F_p$ behaviour @ low T



BYNTO	77 K	65 K	50 K	30 K	10 K
$F_p(\max)$ (GN/m <sup>3</sup> )	12	69	210	469	895
$B @ F_p(\max)$	4	5	6	7	11

BYNTO/BYTO  
presence of a  
second high field  
 $F_p$  component  
emerging at low  $T$

BYNTO has a  
second high field  
 $F_p$  component  
which makes it more  
performing wrt  
to BYTO at low  $T$

# Conclusions 1/2

Mixed doping by  $\text{Ba}_2(\text{Y,Ta})\text{O}_6 + \text{Ba}_2(\text{Y,Nb})\text{O}_6$ : 2.5 mol.% + 2.5 mol.%

- BYTO single vs mixed BYTO + BYNO doping;

**BYNTO exhibits the best  $J_c$  in extended  $T$  and  $B$  ranges**

This results from a **synergetic combination** of:

- **density** of columns;

- **size** of columns;

- **continuity**;

- **splay**;

-  **$\text{Y}_2\text{O}_3$  nanoparticles** decorating BYNTO columns;

- **CuO intergrowth** density;

**key factors** (by comparison with BYTO)

This landscape provide an **effective contribution to vortex pinning at low  $T < 30$  K**

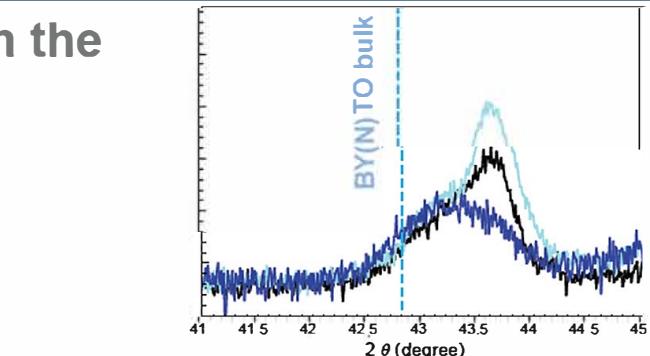
**Can the defect landscape be tuned?**

## Mixed doping BYTO 2.5% + BYNO 2.5%: analysis of the film growth rate

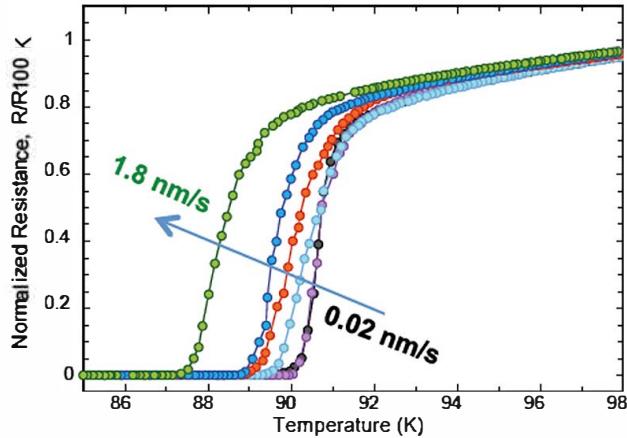
Film growth rate ( $\rho$ ) tuned in the range  $\rho \approx 0.02 - 1.8 \text{ nm s}^{-1}$   
 by:  
 - laser repetition rate;  
 - laser wavelength;  
 rate per pulse @248 nm  $\approx 3 \times$  @308 nm

**PLD setup**  
 XeCl/KrF Excimer Laser  
 $\lambda = 308 \text{ nm}$   
 $\lambda = 248 \text{ nm}$   
 $f_L = 1 - 15 \text{ Hz}$   
 fluence  $\approx 1.5 - 2 \text{ J/cm}^2$

Film thickness  $\approx 200 \text{ nm}$

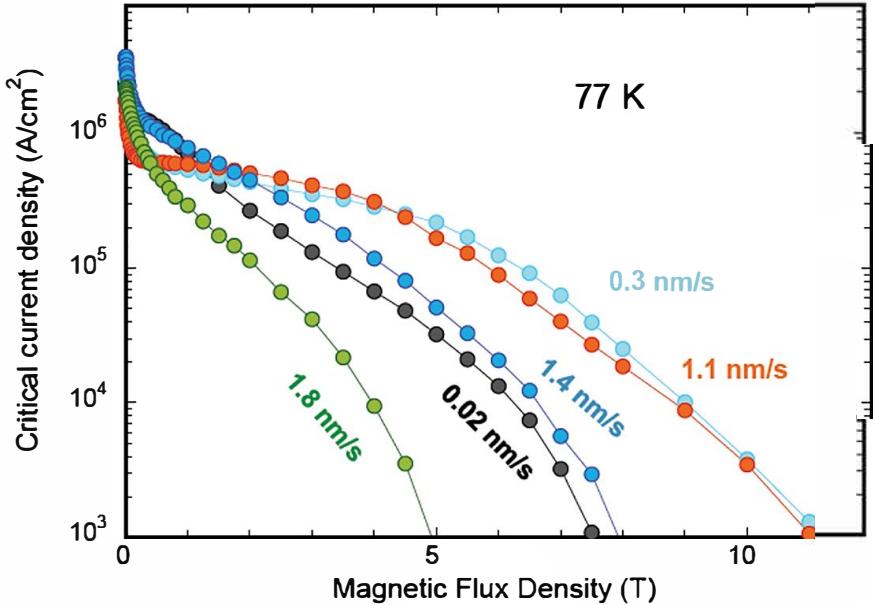


Growth rate (nm/s)	0.02	0.3	1.4
$c_{\text{YBCO}} (\text{\AA} \pm 0.007)$	11.696	11.692	11.714
$a_{\text{BY(N)TO}} (\text{\AA} \pm 0.01)$	8.31	8.30	8.36
FWHM (005)	0.12	0.13	0.13

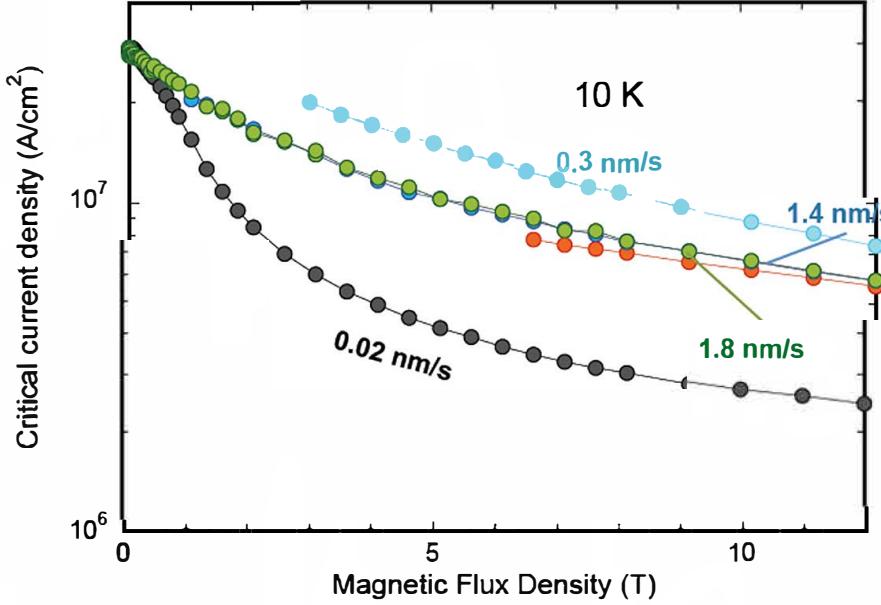


With higher rates:  
 - higher strain in YBCO;  
 - change in BYNTO;  
 - lower  $T_c$ ;

more details will be provided by F. Rizzo in his talk, today



@ 77 K, best  $J_c$  in field behaviour for rates within 0.3 – 1.1 nm/s with extended plateau and highest  $H_{\text{irr}}$



@ 10 K,  $J_c(B)$  for high rates very similar (1.4 nm/s and 1.8 nm/s fully overlap!)

$$J_c(12 \text{ T}) = 7.4, 5.8, 6.0, 6.0 \text{ MA/cm}^2$$

## Conclusions 2/2

Mixed doping by  $\text{Ba}_2(\text{Y,Ta})\text{O}_6 + \text{Ba}_2(\text{Y,Nb})\text{O}_6$ : 2.5 mol.% + 2.5 mol.%

- BYTO single vs mixed BYTO + BYNO doping;

**BYNTO** exhibits the best in extended angular,  $T$  and  $B$  ranges

The landscape provides an **effective contribution to vortex pinning at low  $T < 30$  K**

- Defects landscape tunability by growth rate;

**Very low rate (0.02 nm/s  $\leftarrow$ )**: continuous columns with reduced density and increased diameter +  $\text{Y}_2\text{O}_3$  nanoparticles

**high rate ( $\rightarrow 1.8$  nm/s)**: ab-plane platelets + c-axis rods

**crossing 0.3 - 1.1 nm/s**

**high performances in the whole T-range**

Growth rates (nm/s)	High T	low T
<i>low rates</i>		
<i>intermediate (0.3-1.1)</i>		
<i>high rates</i>		

Thank you for your attention

