Development of a fluorine-free polymer-assisted-deposition route for $YBa_2Cu_3O_{7-x}$ superconducting films

[a]**M. Nasui**, [a]R.B. Mos, [a]A. Tomolea, [a]T. Petrisor Jr., E. Ware[b], [a]A. Mesaros, [a]M.S. Gabor, [a]L. Ciontea, [a]T. Petrisor

[a]Technical University of Cluj-Napoca, Memorandumului street No. 28, RO-400114 Cluj-Napoca, Romania
[b]Imperial College London, Exhibition Road, South Kensington, London, SW 7 2AZ, United Kingdom

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Talk Outline

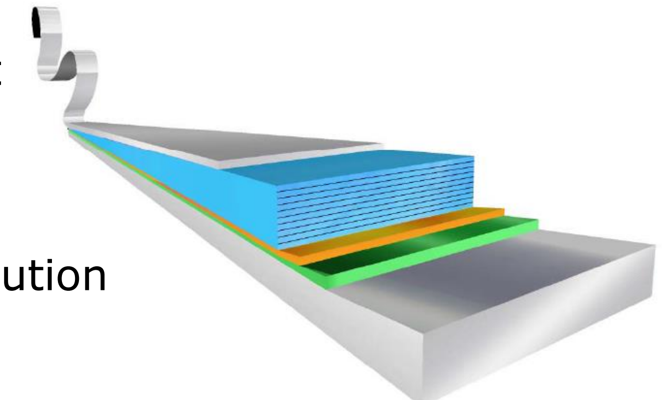
Goal: Polymer-Assisted Deposition (PAD) of YBCO thin films for coated conductor fabrication

Content

- Advantages of using PAD technique for deposition of YBCO films
- PAD - precursor chemistry
- Precursor characterization
- Phase evolution of YBCO-PAD - Single step thermal treatment
- Influence of pyrolysis temperature on the crystallized films
- Conclusions

Introduction

Coated conductors fabrications by chemical solution deposition



- High performance, low investment and running cost
- Non-vacuum technique
- High production rate and large area
- Molecular scale homogeneity
- Trace elements can easily be introduced into the solution
- Water sensitive organic salts and flourine solution

Novelty — Polymer-Assisted Deposition Method, PAD

The idea is to combine solutions of metal precursors with a soluble polymer

- **ENCAPSULATE** the metal to prevent chemical reaction
- **MAINTAIN HOMOGENEOUS DISTRIBUTION** of the metal in solution

✓ **Eco-friendly process – non fluorine solution (nitrate, acetate, etc.)**

Q. X. Jia et al. Nature Materials | VOL 3 | AUGUST 2004
G. F. Zou et al. Chem. Soc. Rev., 2013, 42, 439

Polymer-Assisted Deposition (PAD) technique

PEI – polyethyleneimine
EDTA –ethylenediaminetetraacetic acid

Select metal salts — Nitrate, acetate

↓ + H_2O

Mix with polymer (pH) — (PEI:EDTA)

↓

Ultrafiltration– remove all unbounded cantion/anions

↓

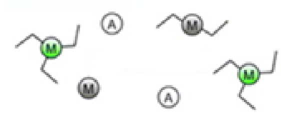
Mix metal-polymer solutions

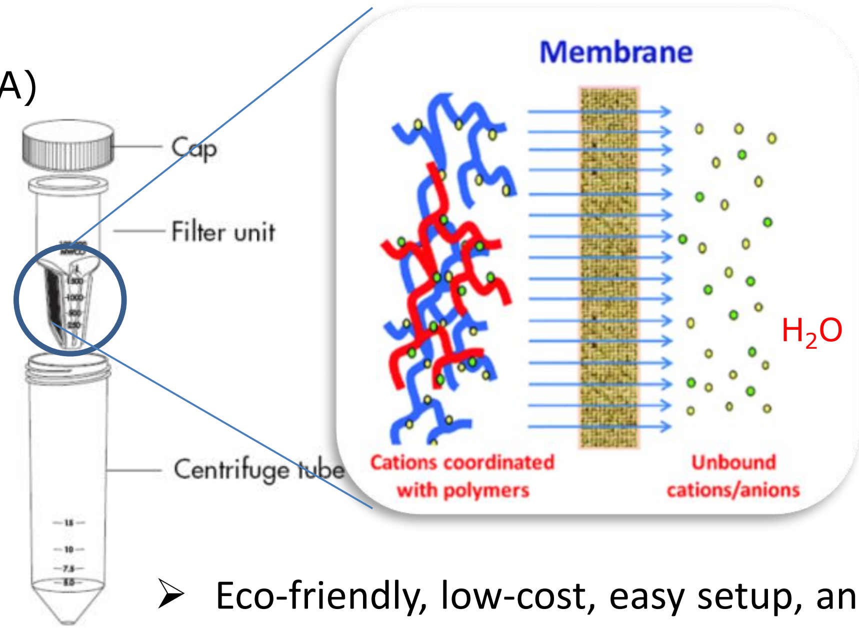
↓

Deposition method (spin-coating, …)

↓

Thermal treatment (Decomposition)





- Eco-friendly, low-cost, easy setup, and ability to coat irregular surfaces

Versatility of the PAD method:
- Nanostructures
- Thin Films
- Thick Films

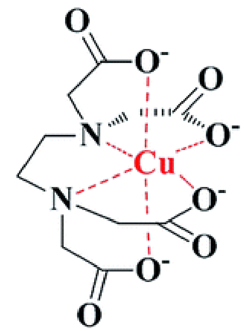
- Long shelf life of the PAD precursor solution (years)

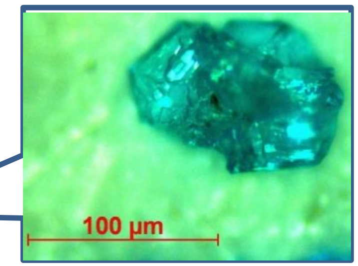
PAD - precursor chemistry

PEI – polyethyleneimine
EDTA –ethylenediaminetetraacetic acid

Reaction of $M^{+n}(NO_3)_3$ with EDTA (M: Y-, Ba-, Cu-)

$$M^{+n} + EDTA^{-4} \longrightarrow MEDTA^{n-4}$$

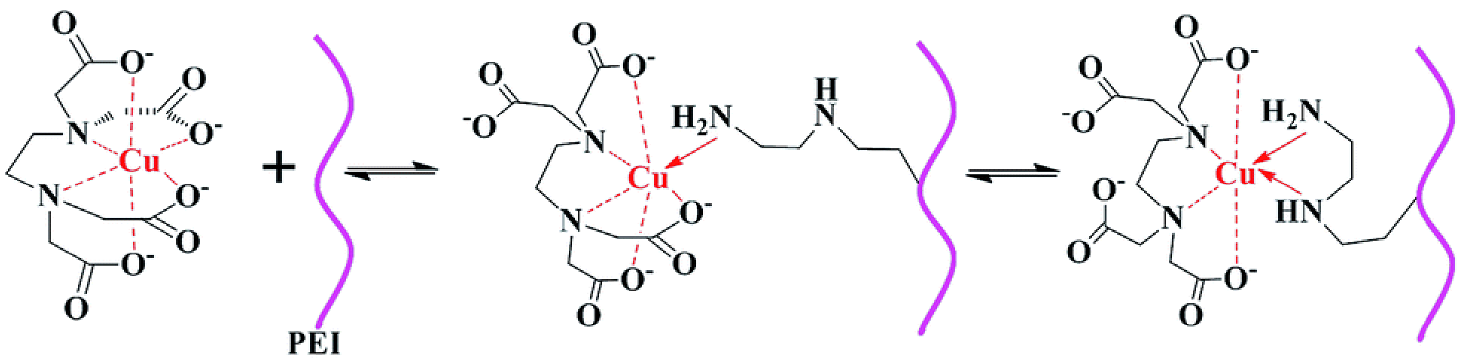




Single-crystal under study

Metal–EDTA complex- hexadentate (chelating) ligand

Reaction of $M^{+n}(EDTA)^{-}$ with PEI



The possible bonding mode of PEI with Cu–EDTA

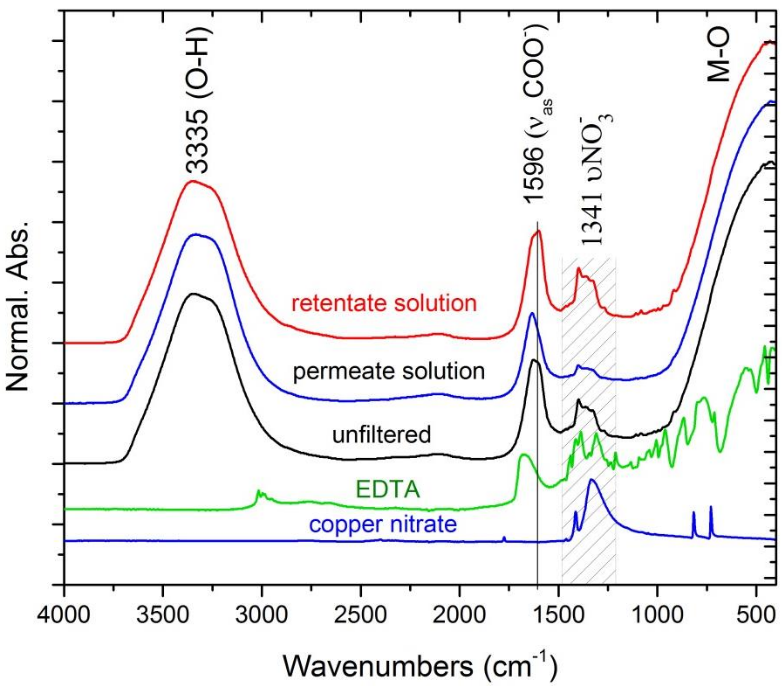
- EDTA complexes bind to the PEI *via* a combination of **hydrogen bonding** and **electrostatic attraction;**

Precursor characterization

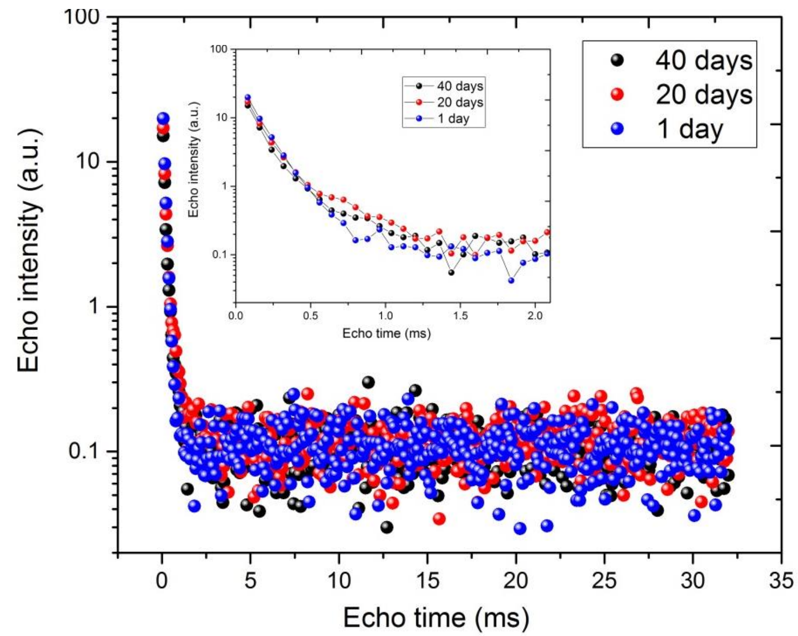
Y-, Ba-, Cu-nitrate+H_2O+EDTA+PEI

Solution	Y^{3+}	Ba^{2+}	Cu^{2+}
Initial solution concentration	0.28 M	0.47 M	1.07 M
Final solution concentration (after centrifugation) -ICP	0.12 M	0.15 M	0.36 M
pH	**5**	**5**	**5**
M^{+n}:EDTA	1:1	1:1	1:1
Efficiency (%)	**59**	**40**	**52.6**

Cu-precursor - FTIR



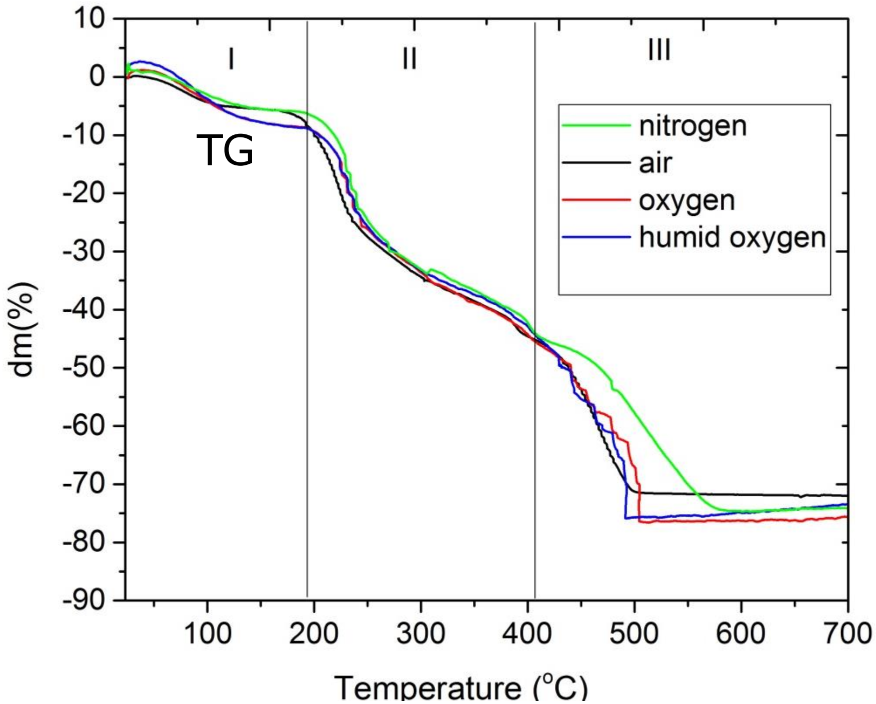
AGING EFFECT- NMR Relaxometry



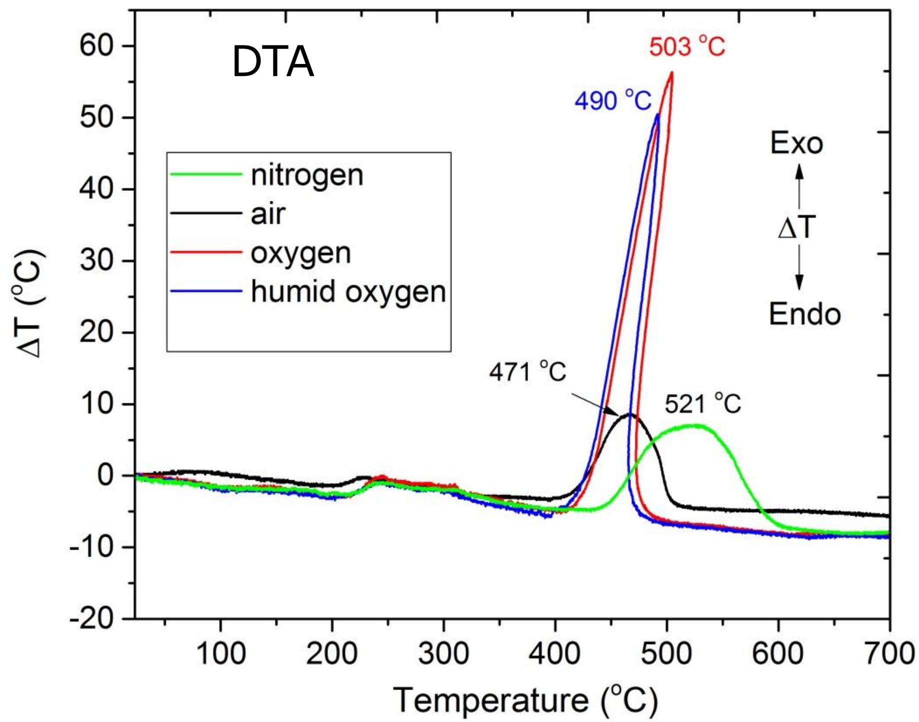
- Long stability of the precursor solution

Precursor characterization

Thermal decomposition of the (Y-, Ba-, Cu-) precursor powder



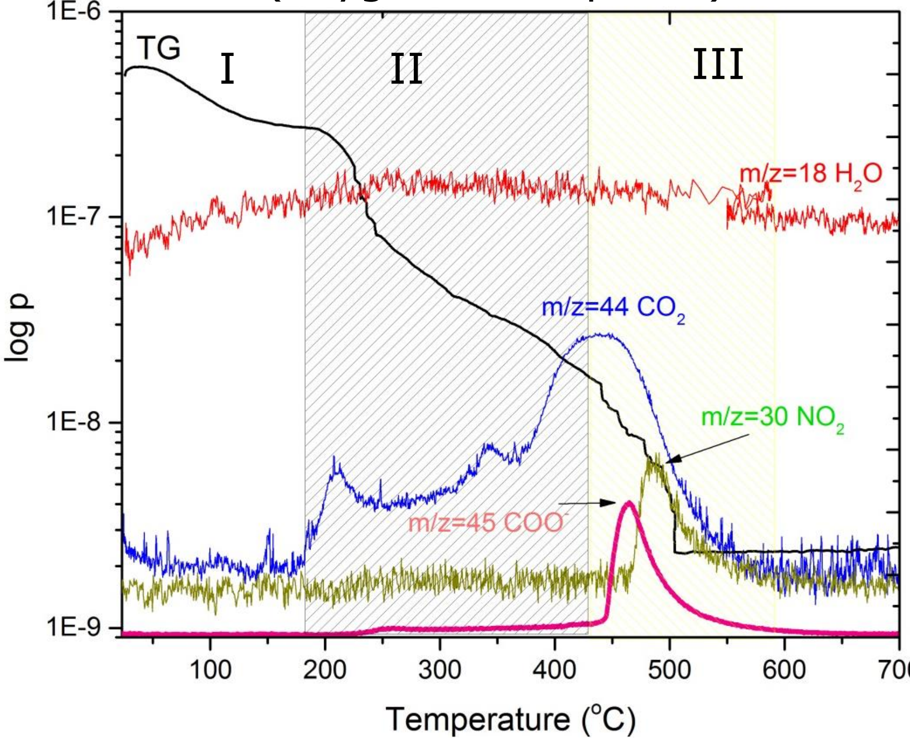
- 23-200 °C - evaporation of water
- 200-400 °C - decomposition of polymer
- 400-550 °C - decomposition of metal complex



- DTA analysis demonstrate that the reaction is exothermic in any of these atmospheres
- Enthalpy of the reaction is higher in O_2

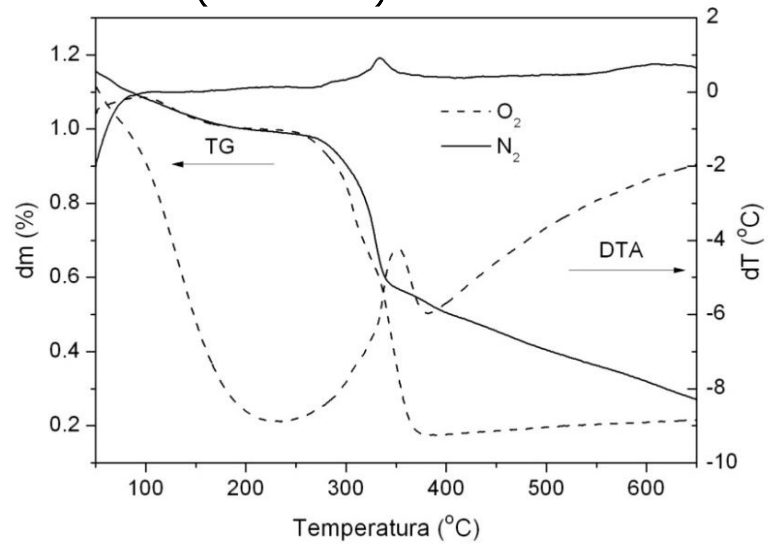
Precursor characterization

TG- MS (oxygen atmosphere)

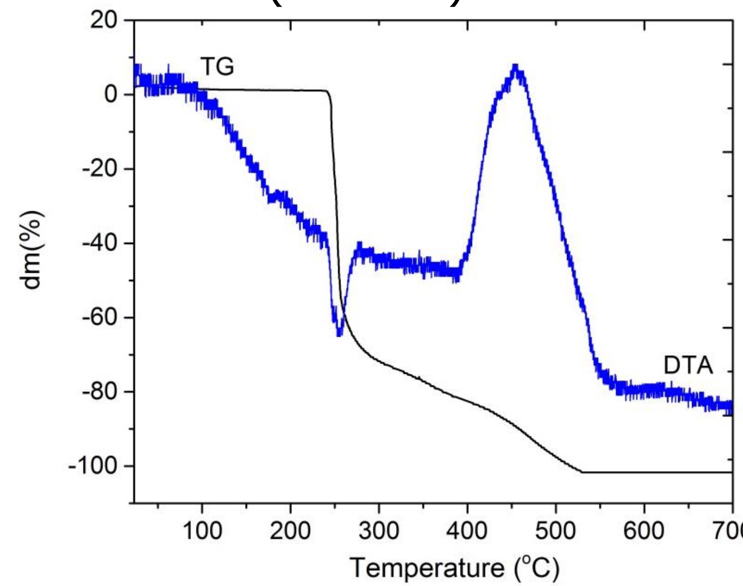


Stage	Mass fragment
I - evaporation of solvent	m/z = 18 (H_2O)
II - decomposition of PEI	m/z = 18 (H_2O) m/z = 44 (CO_2)
III - decomposition of EDTA complex	m/z = 44 (CO_2) m/z = 30 (NO_2) m/z = 45 (COO^-)

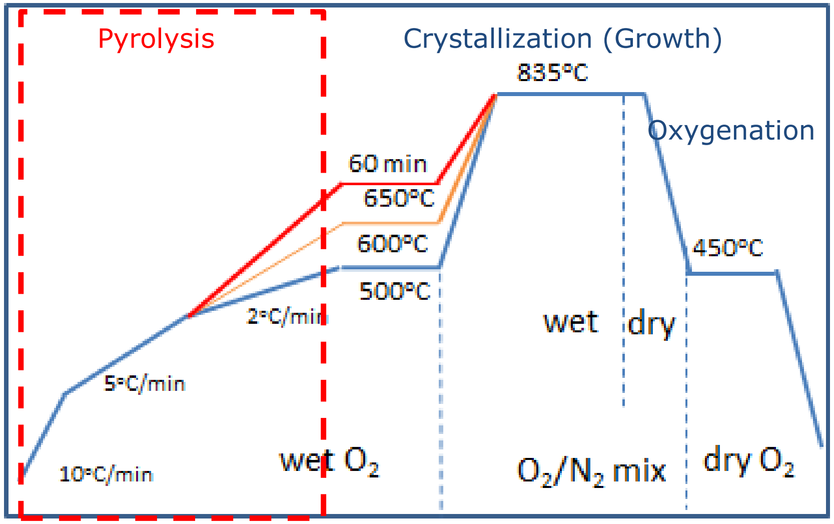
PEI (TG-DTA)



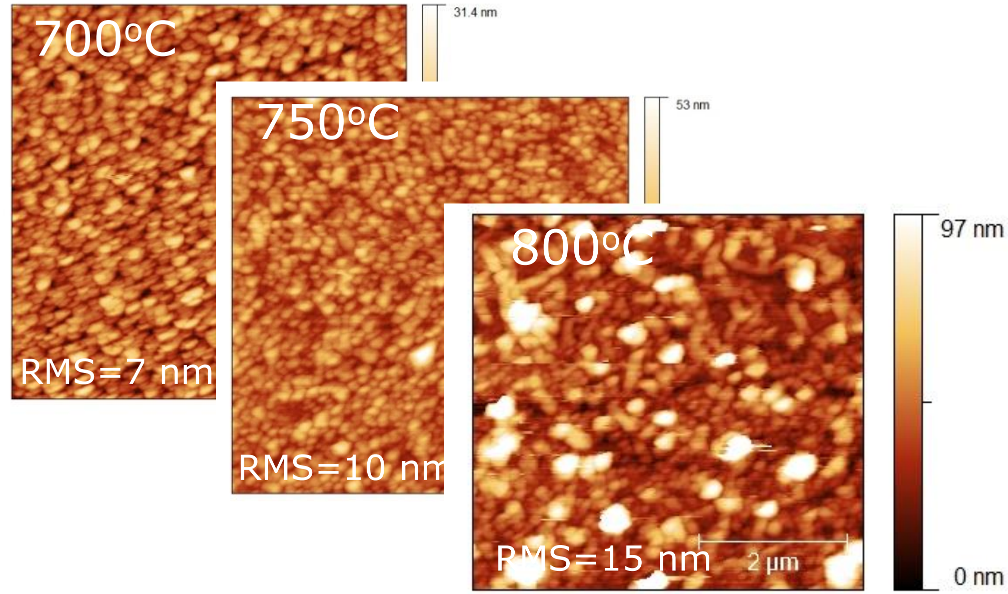
EDTA (TG-DTA)



Single step thermal treatment

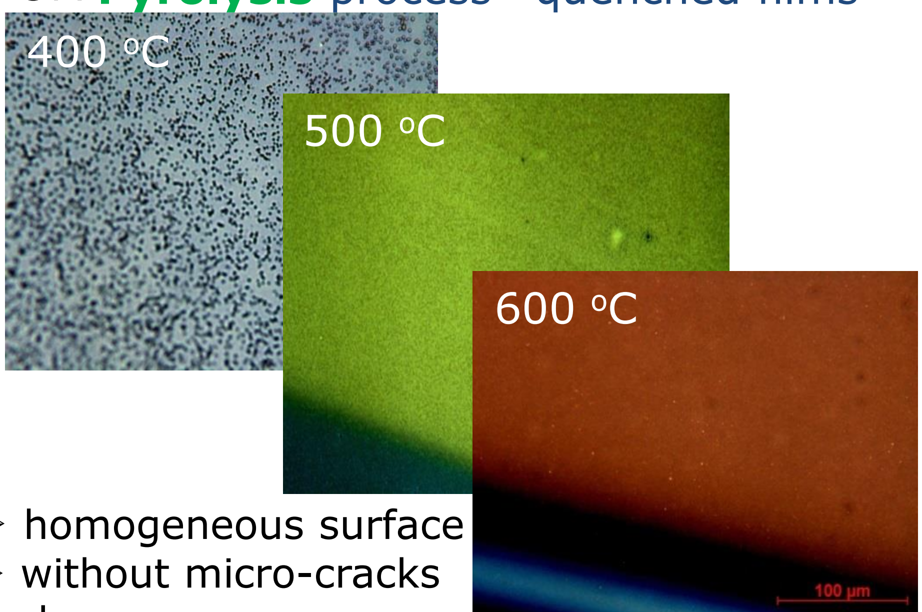


AFM **Crystallization** (Growth)



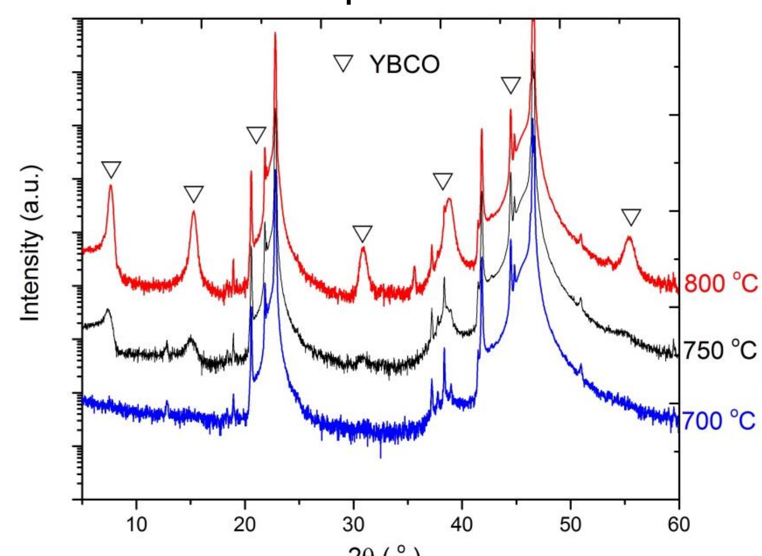
- grains size increase with the increasing crystallization temperature

OM **Pyrolysis** process –quenched films



- homogeneous surface
- without micro-cracks and pores

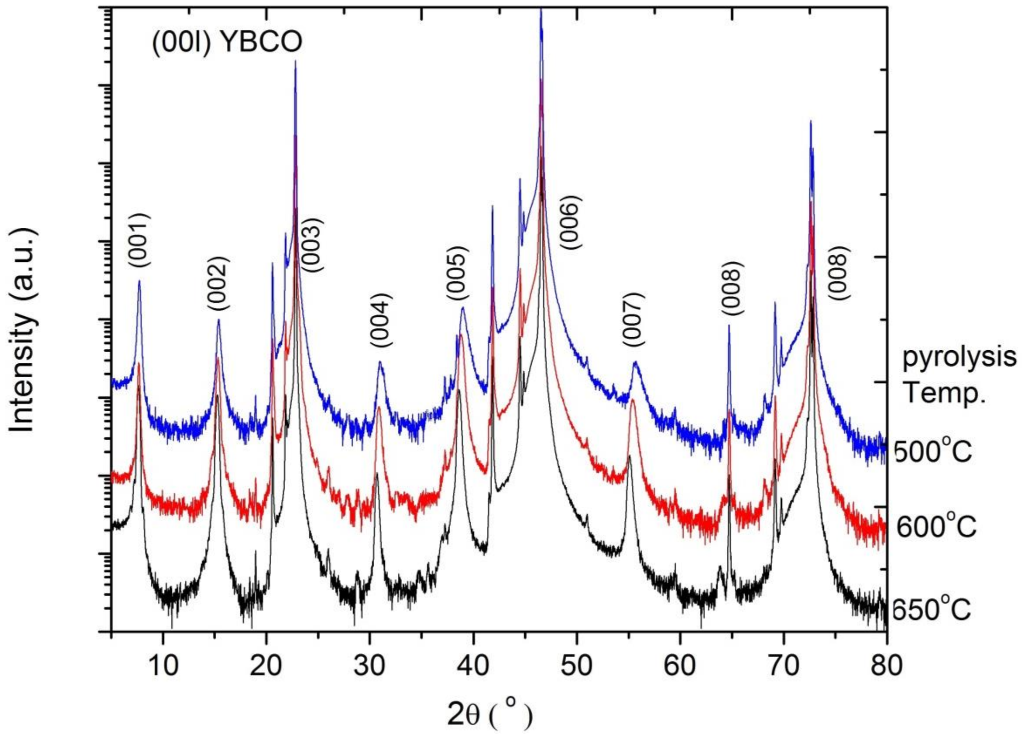
XRD of the quenched films



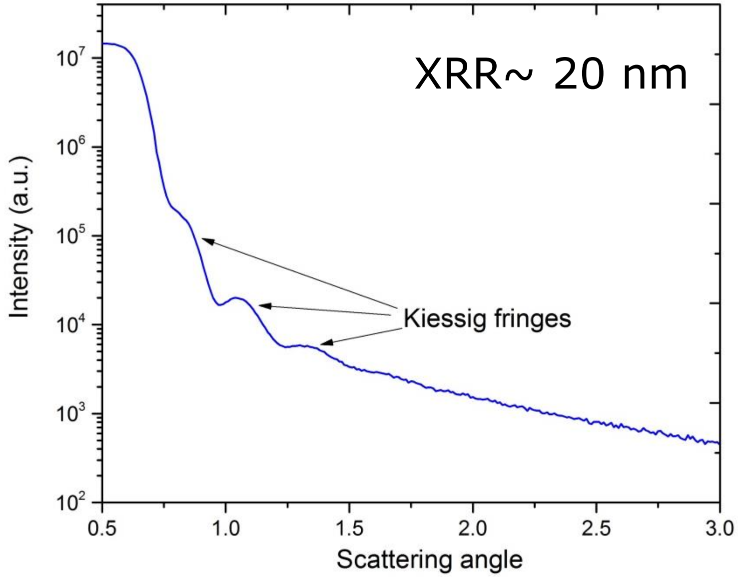
Structural properties of the YBCO thin films

Influence of pyrolysis temperature

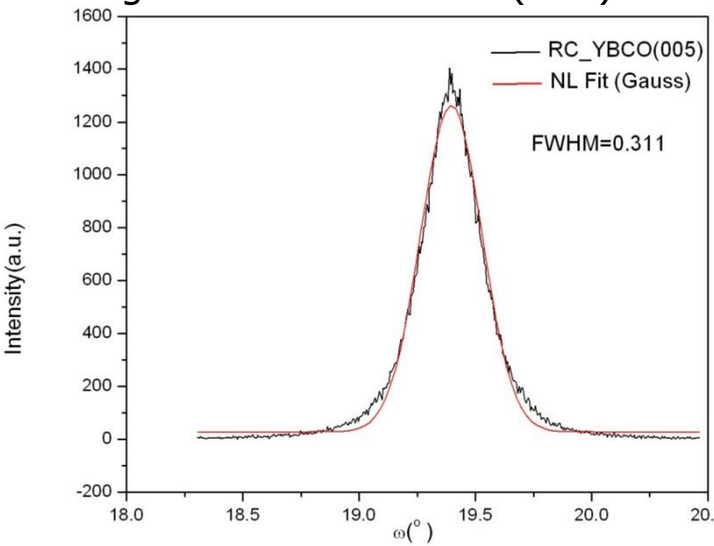
XRD– after crystallization 835 °C



Py- 650°C



Rocking curves around the (005) reflection



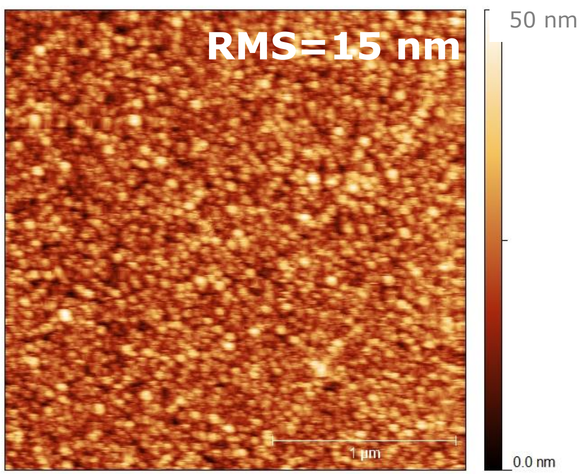
- HR-XRD θ-2θ scans for the thin films exhibit only (00l) type reflections, indicating that the films are **c - axis oriented**
- No secondary phases

- FWHM = 0.31°, indicates a **low mosaicity**

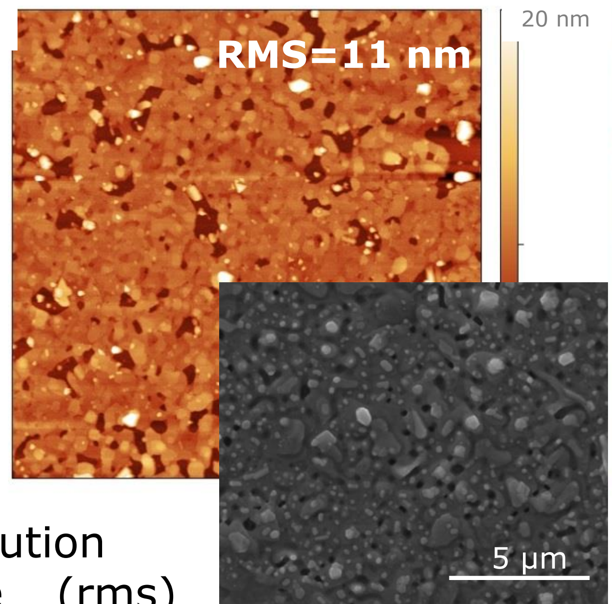
Morphological properties

AFM – after crystallization 835 °C

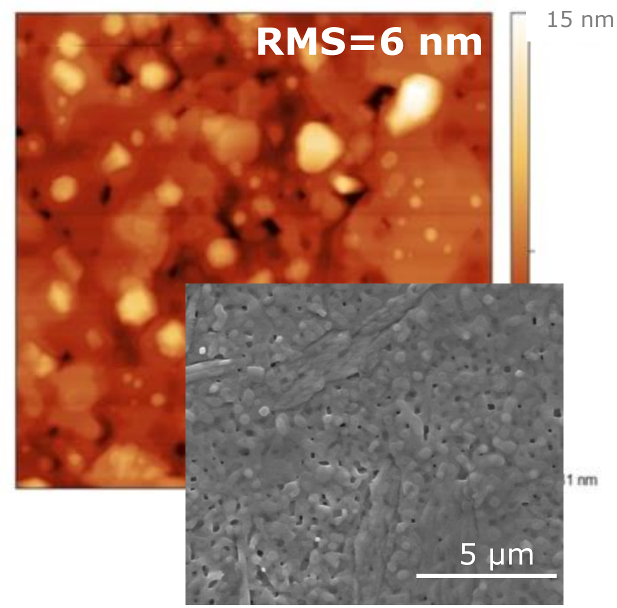
Py-500°C



Py-600°C



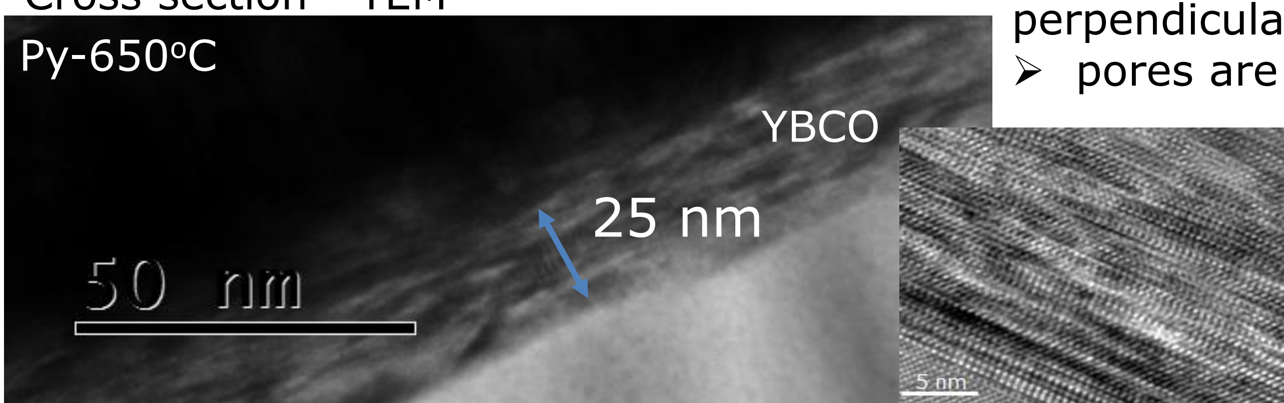
Py-650°C



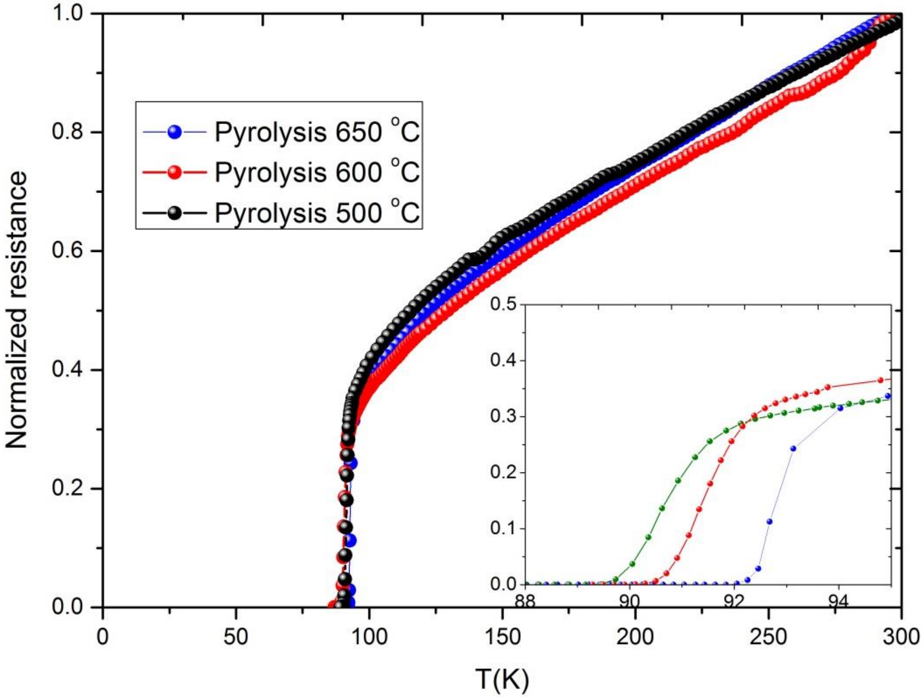
- homogeneous grain distribution
- the root mean square (rms) roughness value of the YBCO thin films is about 6 nm

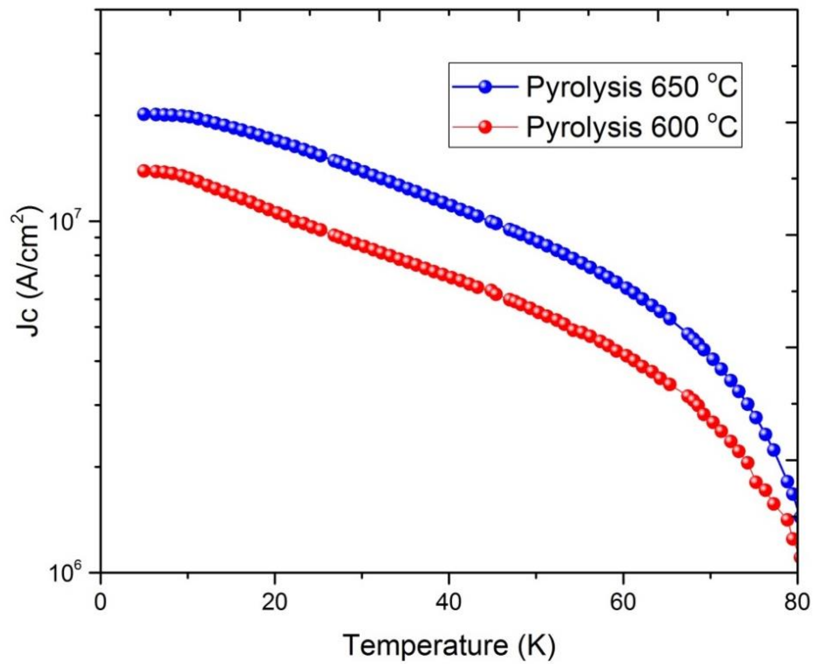
- coalescence of the film is quite good
- no grains with the a-axis oriented perpendicular to the substrate
- pores are observed

Cross section - TEM



Electrical properties of the YBCO-PAD thin films





Magnetization measurements – J_c values at different temperature

Pyrolysis temp.	T_c (K)	J_C (MA/cm^2)
500 °C	88	0.45
600 °C	90	1.5
650 °C	**91**	**2**

Conclusions

- It has been demonstrated the possibility of obtaining epitaxial YBCO thin films by Polymer-Assisted-Deposition using nitrates as starting reactants;

- The precursor chemistry were studied by TG, DTA, MS and NMR-relaxometry analyses in order to optimized thermal treatment

- The influence of the pyrolysis temperature (500, 600 and 650 ^{o}C) on the final YBCO films was studied

- Crystalline and epitaxially oriented YBCO layers (20 nm) with smooth surfaces and small surface roughness of about 6-10 nm were obtained on (100)LAO single-crystalline substrates;

- The electrical characterization have indicated that the YBCO thin films have the T_c=90 K (R=0), J_c (77K)=0.45 -2 MA/cm^2

Future work

- Variation of the pH values in order to increase the efficiency after ultrafiltration

- Increasing the thickness of the YBCO-PAD films (conc., multiple deposition)

- Test over metallic tapes

Acknowledgments

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Thank you for your attention