Ex Situ Processing of YBCO Precursors

Oak Ridge National Laboratory

T. Aytug, H.M. Christen, S.W. Cook, R. Feenstra, A.A. Gapud, A. Goyal, L. Heatherly, H. Hsu, S. Kang, D.F. Lee, K.J. Leonard, F.A. List, P.M. Martin, M. Paranthaman, S. Sathyamurthy, E.D. Specht, Y. Xu, J. Yoo

Presented at the
2004 DOE Superconductivity Program Annual Peer Review
Washington DC, July 28, 2004

Funding: $900,000

<u>Project goal:</u>
To understand and explore means to fabricate high performance YBCO using <u>alternative ex-situ techniques</u>.

Activities in support of the Coated Conductor Development Roadmaps:

<u>Faster YBCO Deposition Rates Strategies</u>

- R&D Needs for BaF_2 type precursor:
  - **What are the limits to the conversion rate and thickness?**
- Recommended Activities:
  - ➢ **Determine process parameter space for YBCO,**
  - ➢ **Develop *ex situ* conversion technology,**
  - ➢ **Develop methods to increase YBCO production rates, increase area.**

<u>RE-123 Nucleation, growth, and flux pinning Strategies</u>

"Processing Understanding (How to grow films fast)":
one of the "Top 5 highest rated R&D activities to achieve 2010 vision"

Approach

To perform <u>*ex situ* conversion</u> of YBCO using two classes of precursors:

- PVD precursors -
  - E-beam deposited "BaF_2" precursor,
  - Pulsed Electron Deposition (PED) of "BaF_2-YF_3" type precursor,
- Solution precursors -
  - Non-fluorine, hybrid, TFA

at <u>various pressures</u>.

- **<u>Focus is on deposition and conversion methods, short lengths.</u>**

FY2004 Objectives

1. Investigate using reel-to-reel (R2R) Pulsed Electron-Beam Deposition (PED) for YBCO precursors.
2. Develop a R2R slot-die coater for solution precursors.
3. Explore YBCO conversion characteristics and performance of various types of ex-situ precursors.
4. Investigate differences in solution and PVD precursors responsible for different reaction rates, and increase the reaction rate of PVD precursors.
5. Add and develop both reduced- and low-pressure R2R capabilities for precursor conversion.
6. Identify pinning centers and processing parameters responsible for different field dependencies in samples converted in different systems.
7. Process double-sided precursors.
8. Continue to collaborate with ANL to study conversion of precursors with R2R XRD and R2R Raman.

With reduction in funding (loss of 2 staff, 1 post-doc, 1 consultant), we were forced to limit some tasks to exploratory level or defer to later date!

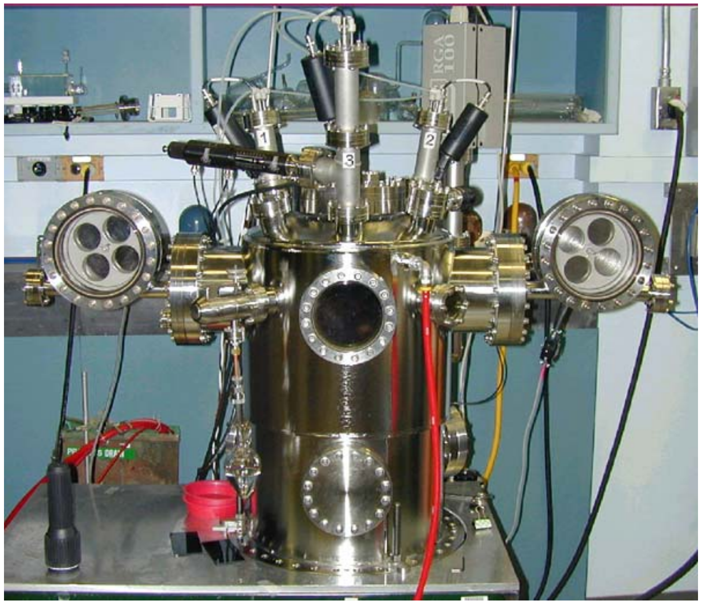
Outline

- "Standard" low-rate conversion (1 Å/s):
  - ➢ R2R PED precursor development
  - ➢ Solution precursor development
- "High-rate" conversion (10 Å/s):
  - ➢ PED precursor
  - ➢ E-beam precursors
- FY2004 Performance
- FY2005 Plans
- Technology Integration

Reasons for exploring an additional precursor deposition system

Problems with our laboratory-scale e-beam evaporation system:

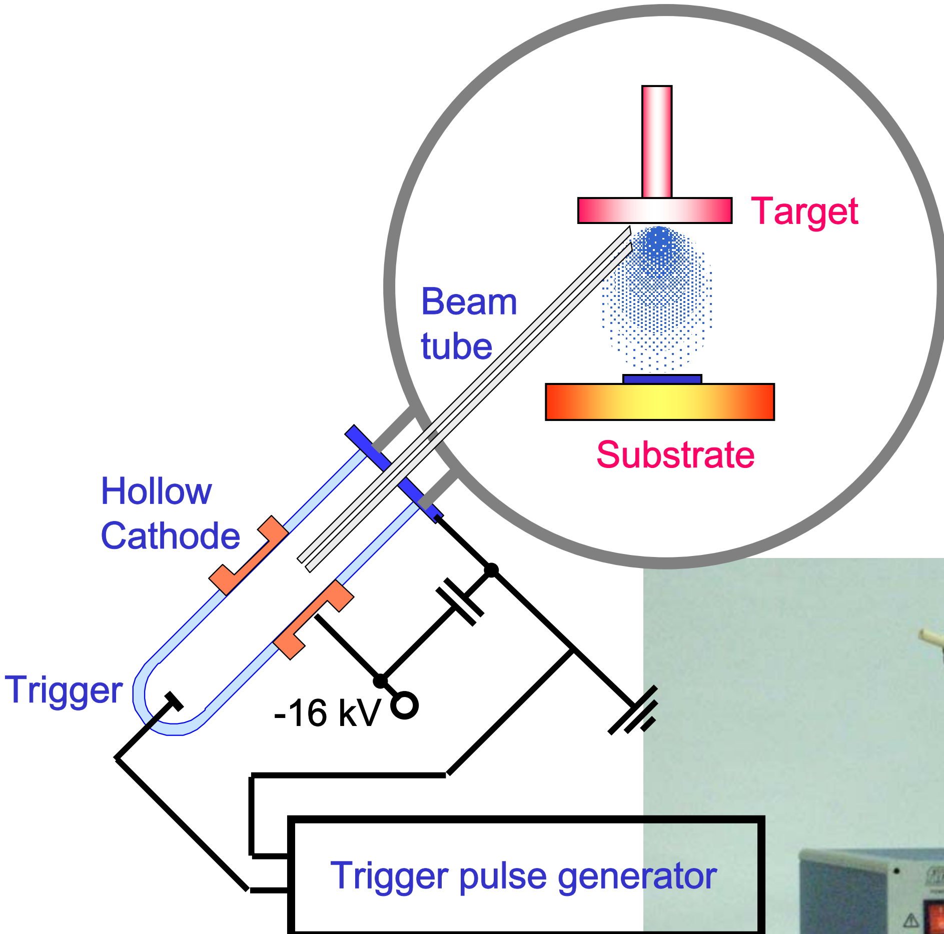
- Stoichiometry depends on precise control of individual fluxes
  - BUT: cross-talk between quartz thickness monitors
  - Limited life of monitors
- Tape heating: crystallization of BaF_2 (111) during precursor deposition
- Observed change in CeO_2 lattice parameter:
  - Reduction due to metallic Y? – need to deposit in oxygen background
- Materials usage



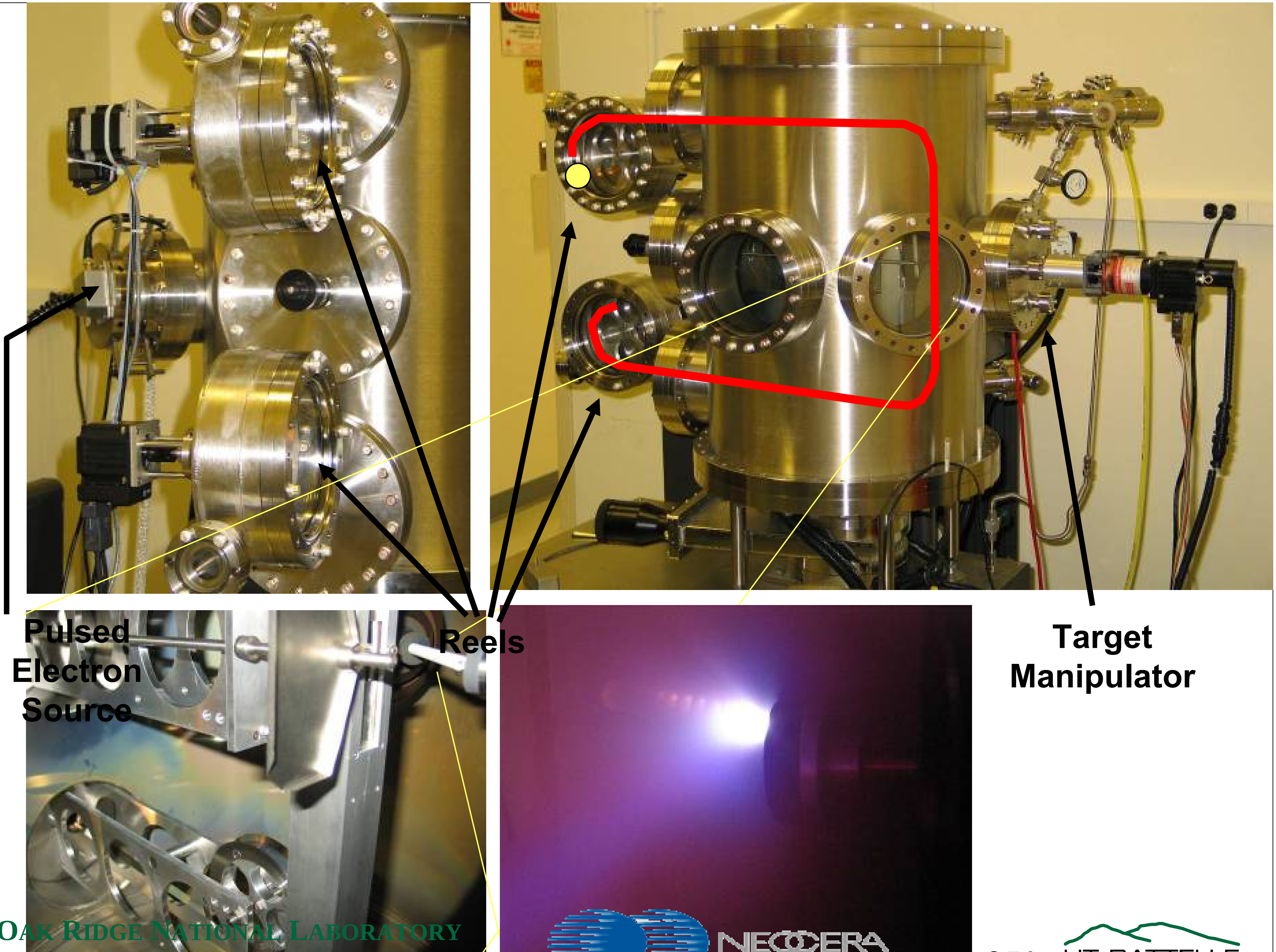
PED offers significant potential advantages for precursor deposition

- Run-to-run stoichiometry control (single source)
- Potential for thick precursors
- Material utilization; instrument cost
- Scalability (multiple-source system demonstrated elsewhere)
- Flexibility (e.g. for doping/alloying/substitution/vary fluorine content)
  - 1" targets suffice
- True room-temperature deposition (no change in CeO_2 lattice parameter, no crystalline BaF_2)

PED: Collaboration with Neocera, Inc.



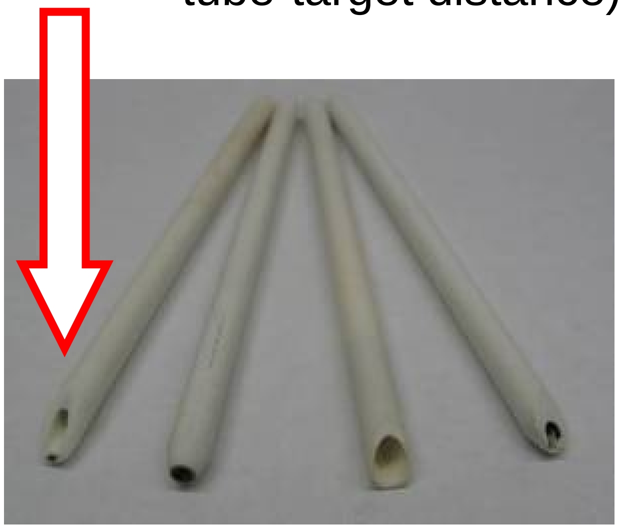
- Small
- Scalable
- Affordable


Pulsed Electron Source
Reels
Target Manipulator

The key deposition parameters had to be determined

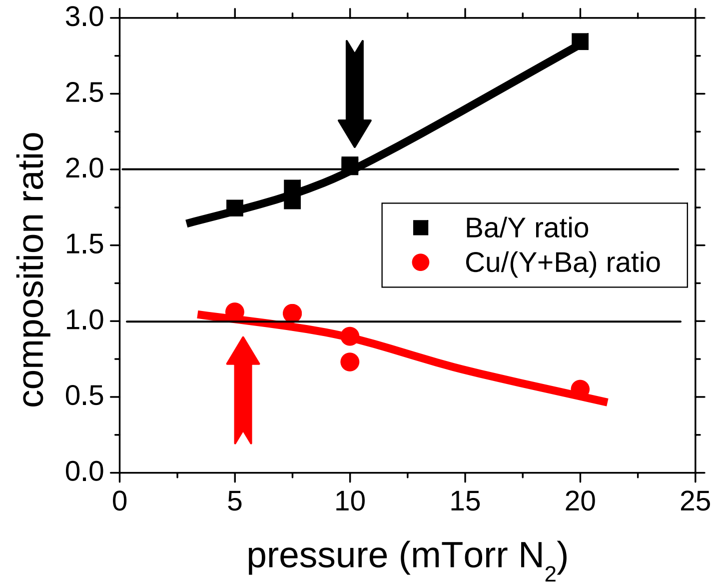
PED specific:

- Voltage (10-18 kV)
  →growth rate, target wear
- Beam delivery
  (tube diameter, shape,
  tube-target distance)



Deposition

- Target-substrate distance
- Target fluorine content
- Background pressure



Major problems remained:

- Stoichiometry control (film composition different from target composition)
- Long-term source stability and reliability initially poor
- Decrease of growth rate during long runs

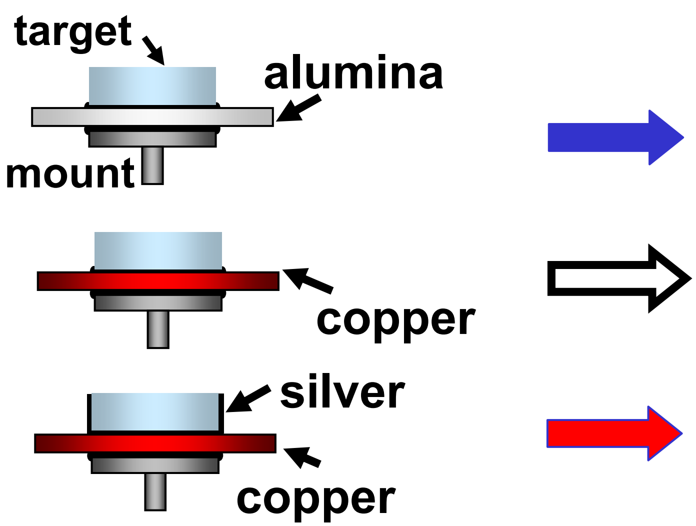
Main issues (cleared hurdles)

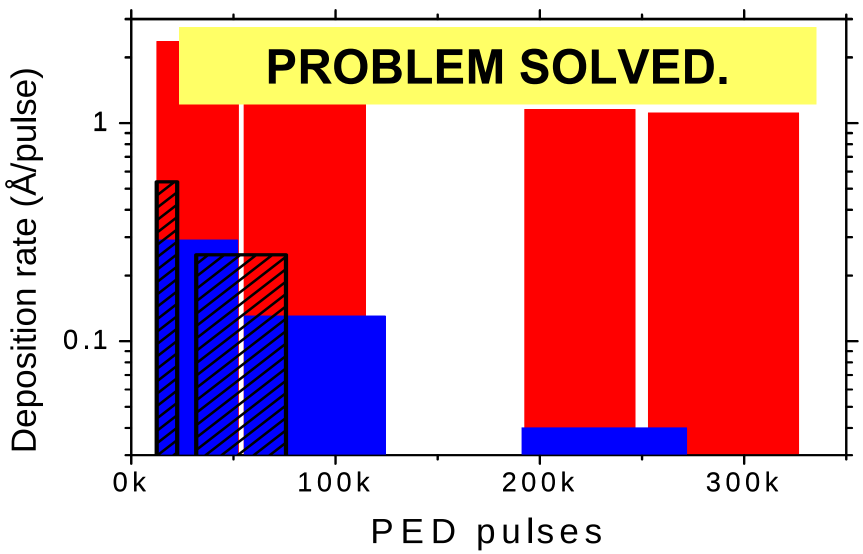
Source stability

- Initially satisfactory, but source missed pulses after prolonged use in oxygen
- Change to nitrogen
- More than 7 million pulses fired perfectly

PROBLEM SOLVED.

Reduction in deposition rate: related to electrical grounding of target





Main issues (cleared hurdles) (continued)

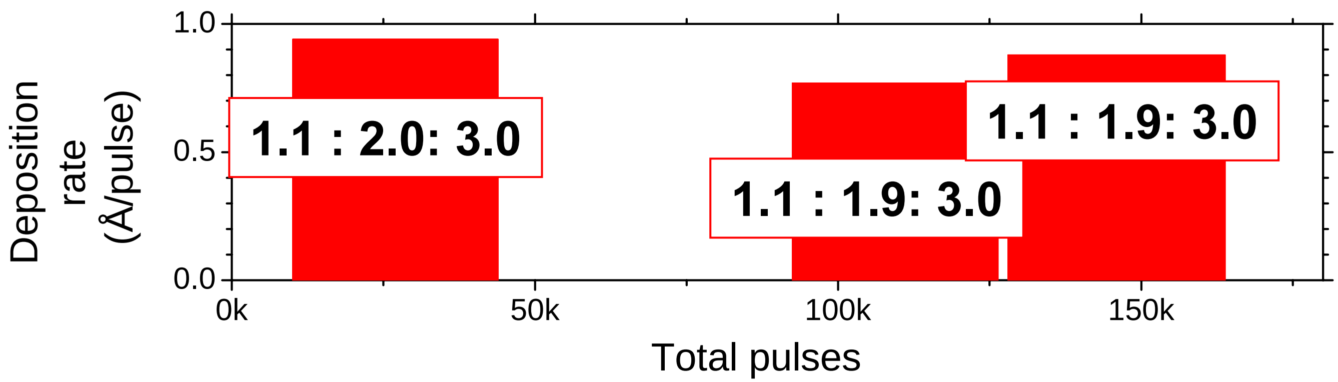
Stoichiometry control

- Film composition is different from target composition
  → choose appropriate target composition

PROBLEM SOLVED.

- Long-term stability of composition demonstrated

Y:Ba:Cu ratio in target: 1.0 : 1.8 : 3.0



Pulsed Electron Deposition

- cost-effective (materials, equipment)
- scalable
- flexible
- single-source, easy-to-control

Deposition of precursors onto moving tape

Conversion under various conditions

- J_c > 1.6 MA/cm^2 (0.72 µm thick)
- I_c = 159 A / cm-width (1.3 µm)

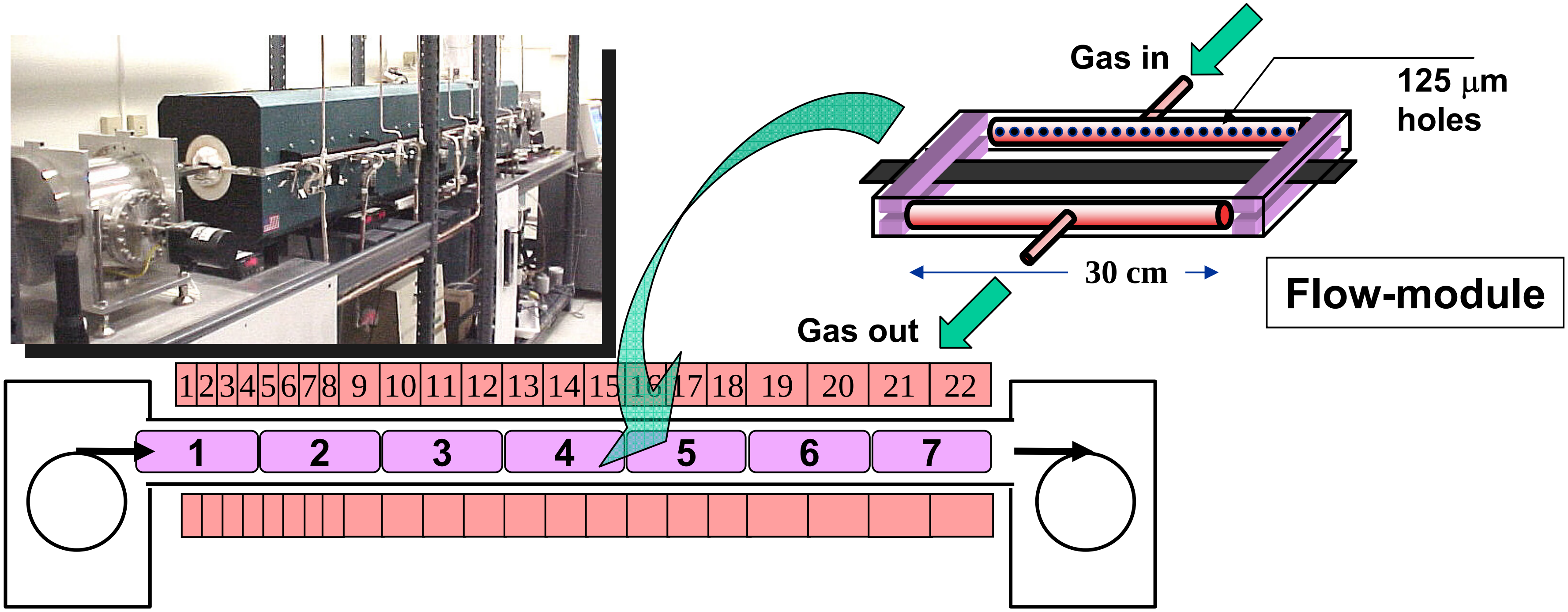
(77 K, self-field)

American Superconductor

AMSC production-grade RABiTS were used for all conversion experiments

Objective 3: Convert different precursors

Initial trials of PED precursor were performed in R2R system based on standard low-rate process developed for e-beam BaF_2



R2R system can process long tapes in moving configuration,

BUT is flow limited (HF accumulation, boundary layer) and operates at 1.5 atm (pressure buildup limits aggressiveness).

Objective 3: Convert different precursors

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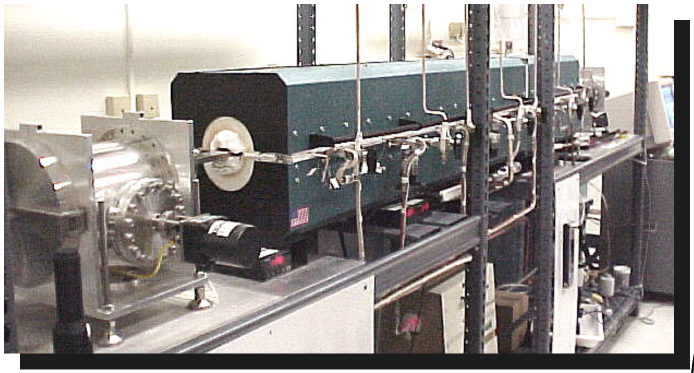
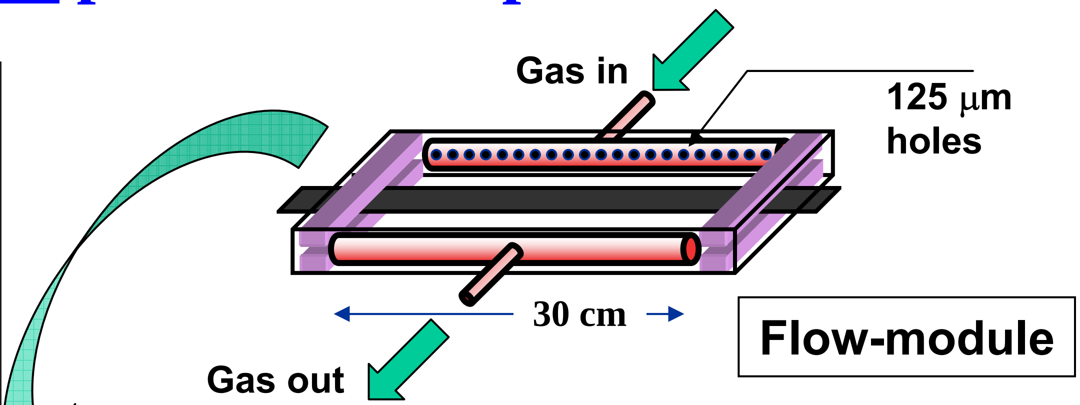
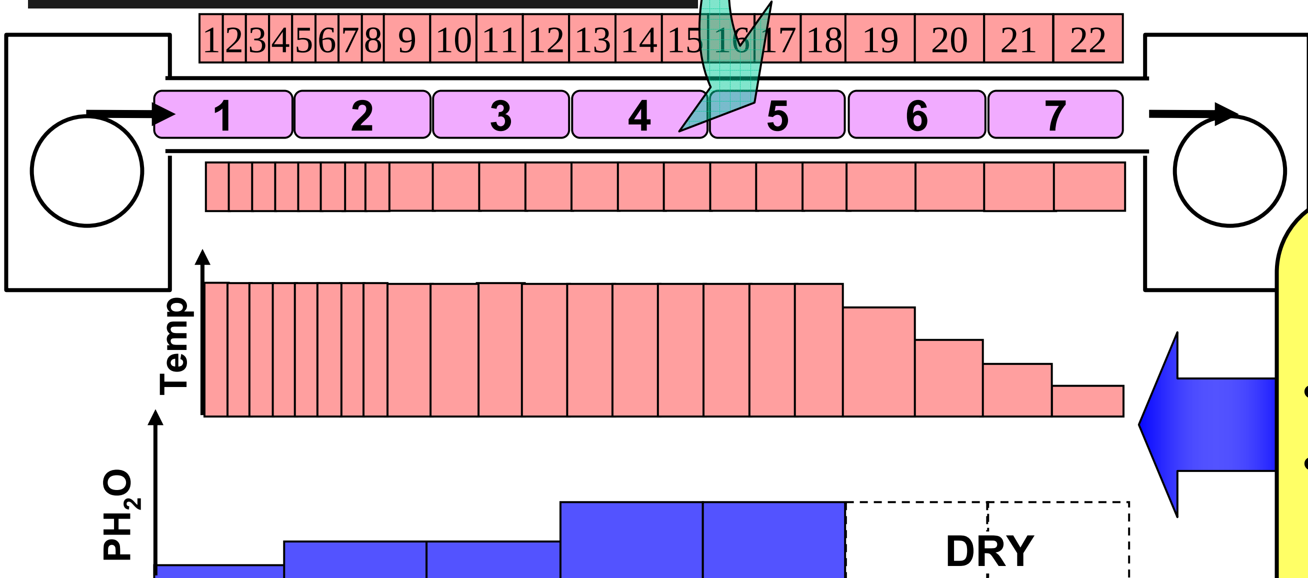




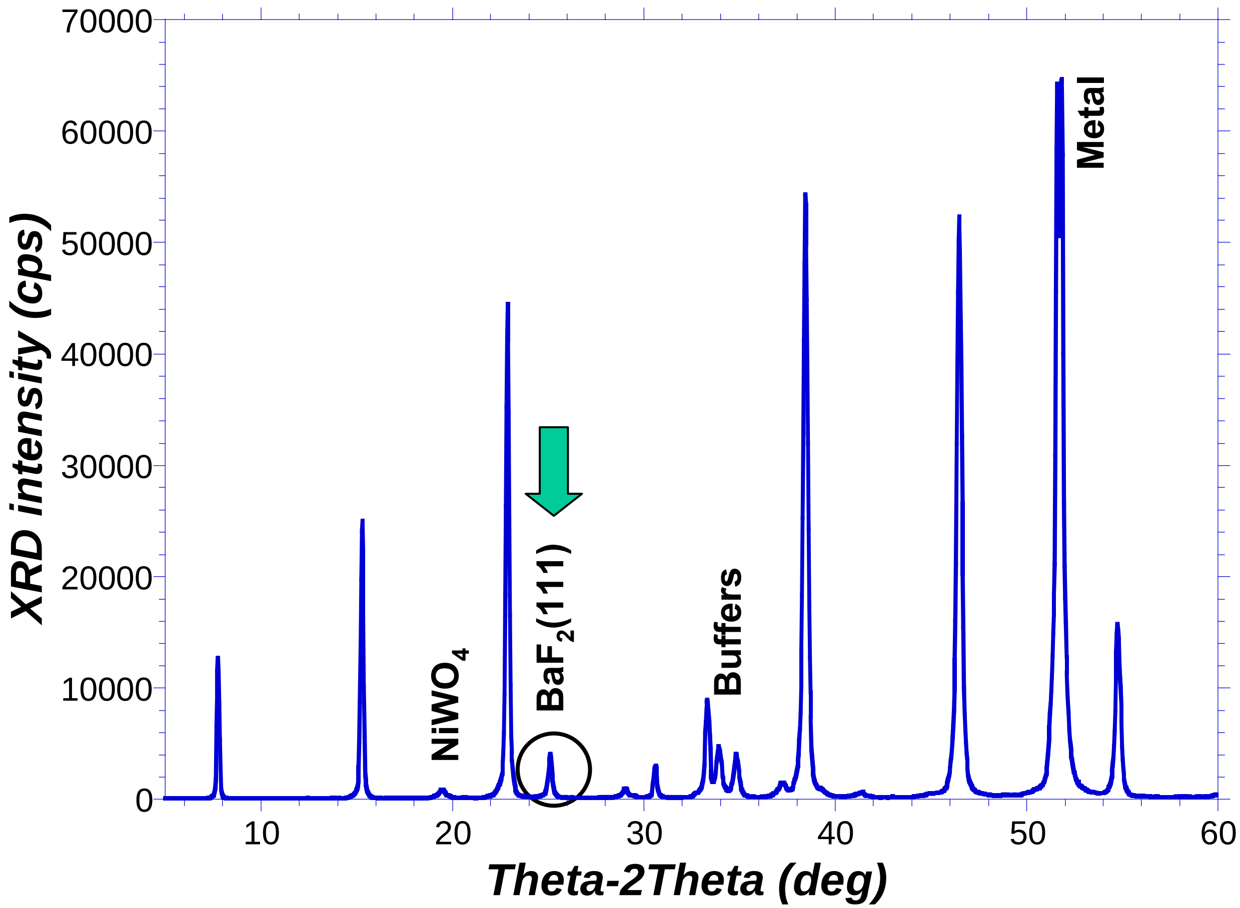


Standard low rate (G_p ~ 1 Å/s)

- Moderate temperature
- Increase from non-aggressive to aggressive (increase PH_2O)

Good J_c was obtained immediately → PED precursor conversion behavior is substantially <u>similar</u> to standard e-beam at low conversion rates (G_p)

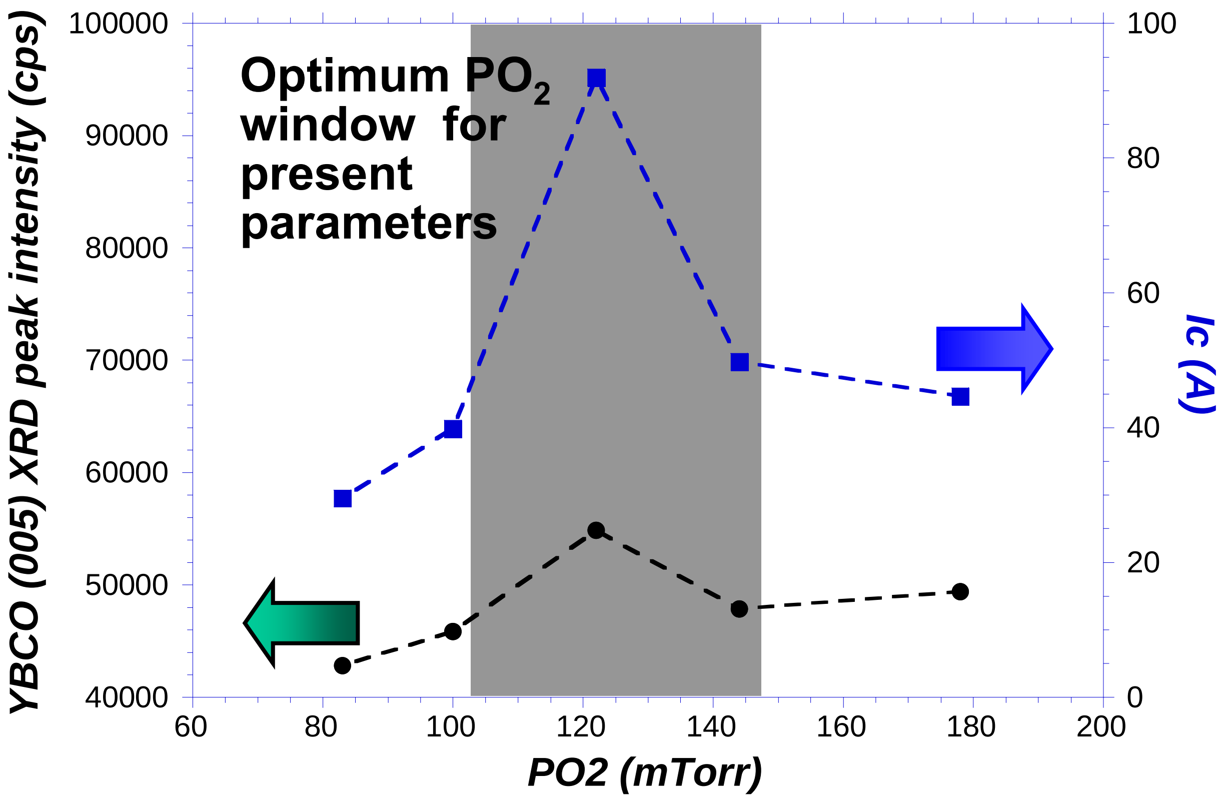
- 1X3 cm samples cut from R2R PED, stoichiometric precursor.
- Conversion time = 100 min.



- 1.2 μm precursor → **0.86 μm YBCO** ~ 30% shrinkage.
- G_p < 1.4 Å/s.
- I_c = 85 A.
- J_c = 1 MA/cm^2.

PED precursor has similar PO_2 dependency as our standard e-beam precursor under low G_p condition

- **1.2 μm precursor → 0.86 μm YBCO**
- **Rate = 0.7 to 1.0 Å/s**



- **Variation in PO_2 leads to changes in YBCO intensity AND I_c.**
- **Full width I_c ranges from 30 A to 92 A**

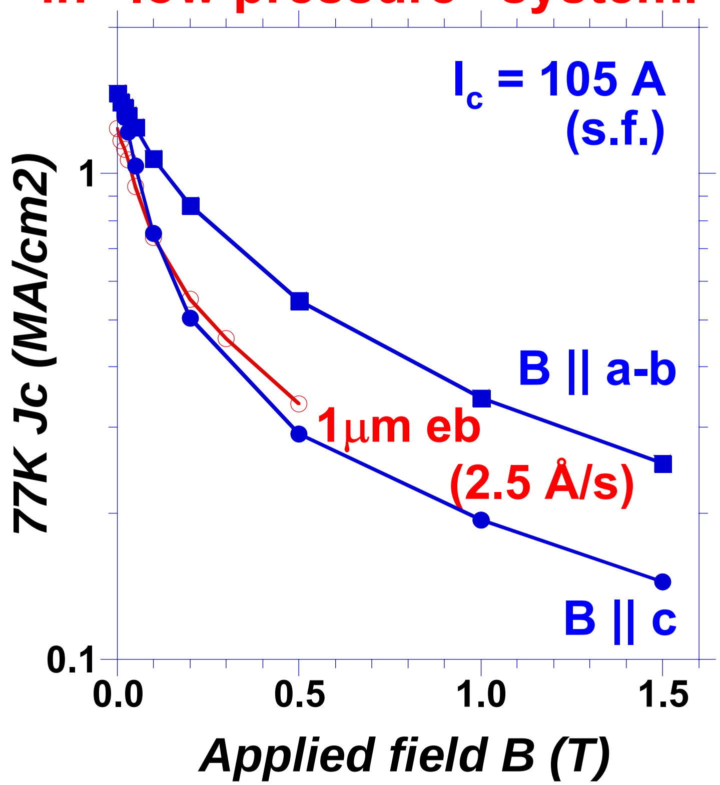
  J_c from 0.34 to 1.1 MA/cm²

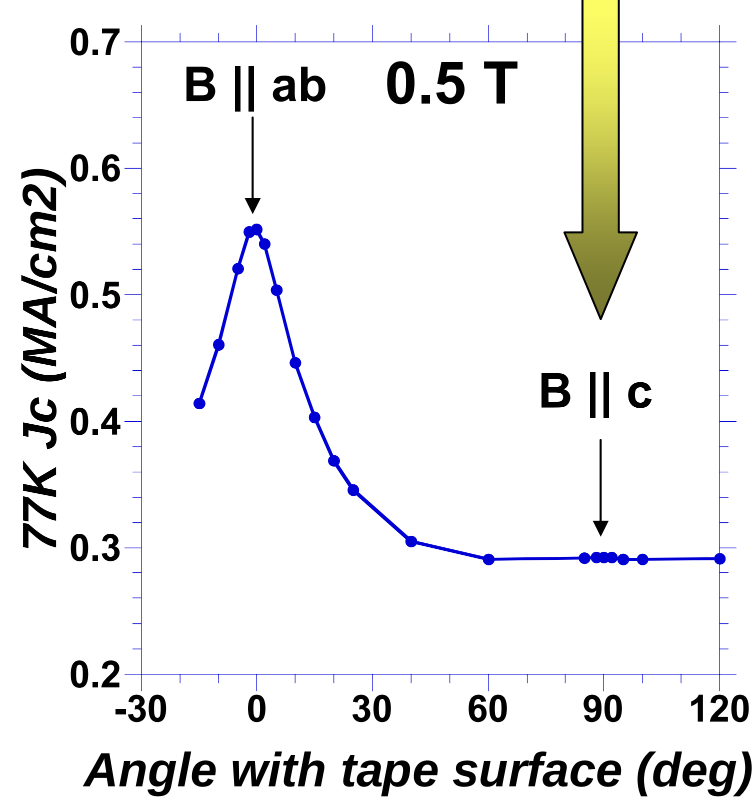
High I_c/J_c have been obtained on R2R PED precursors

- 1 μm precursor → <u>0.72 μm YBCO</u>.
- Rate = 0.6 to 0.8 Å/s.
- <u>Highest I_c = 117 A (J_c = 1.6 MA/cm^2).</u>

  *Similar result of 125 A/cm (J_c = 1.7 MA/cm^2) obtained on SAME precursor in "low pressure" system.

No pinning contribution from correlated defects along c-axis



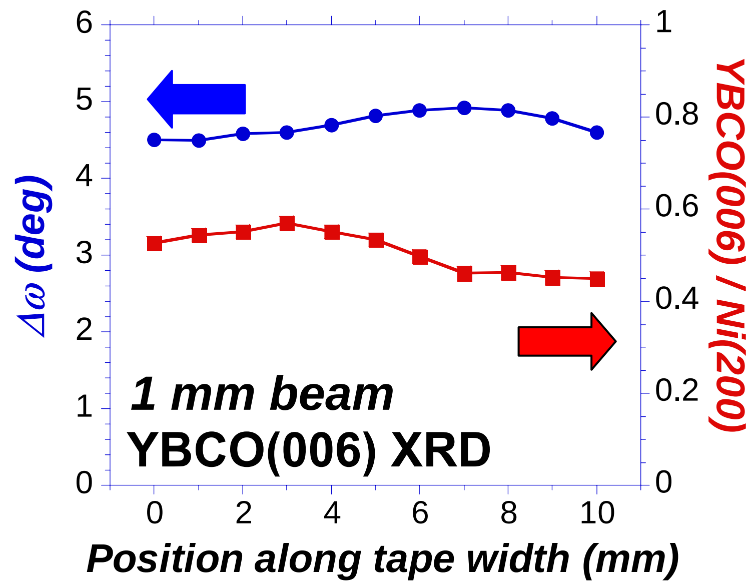


Converted YBCO films possess good texture resulting in high current performance

- 0.72 μm YBCO @ 0.6 Å/s: I_c = 117 A (J_c = 1.6 MA/cm^2).
- 0.86 μm YBCO @ 0.8 Å/s: I_c = 92 A (J_c = 1.1 MA/cm^2).
- 0.94 μm YBCO @ 0.7 Å/s: I_c = 100 A (J_c = 1.1 MA/cm^2).
- 1.30 μm YBCO @ 0.7 Å/s: I_c = 159 A (J_c = 1.2 MA/cm^2).

Early target

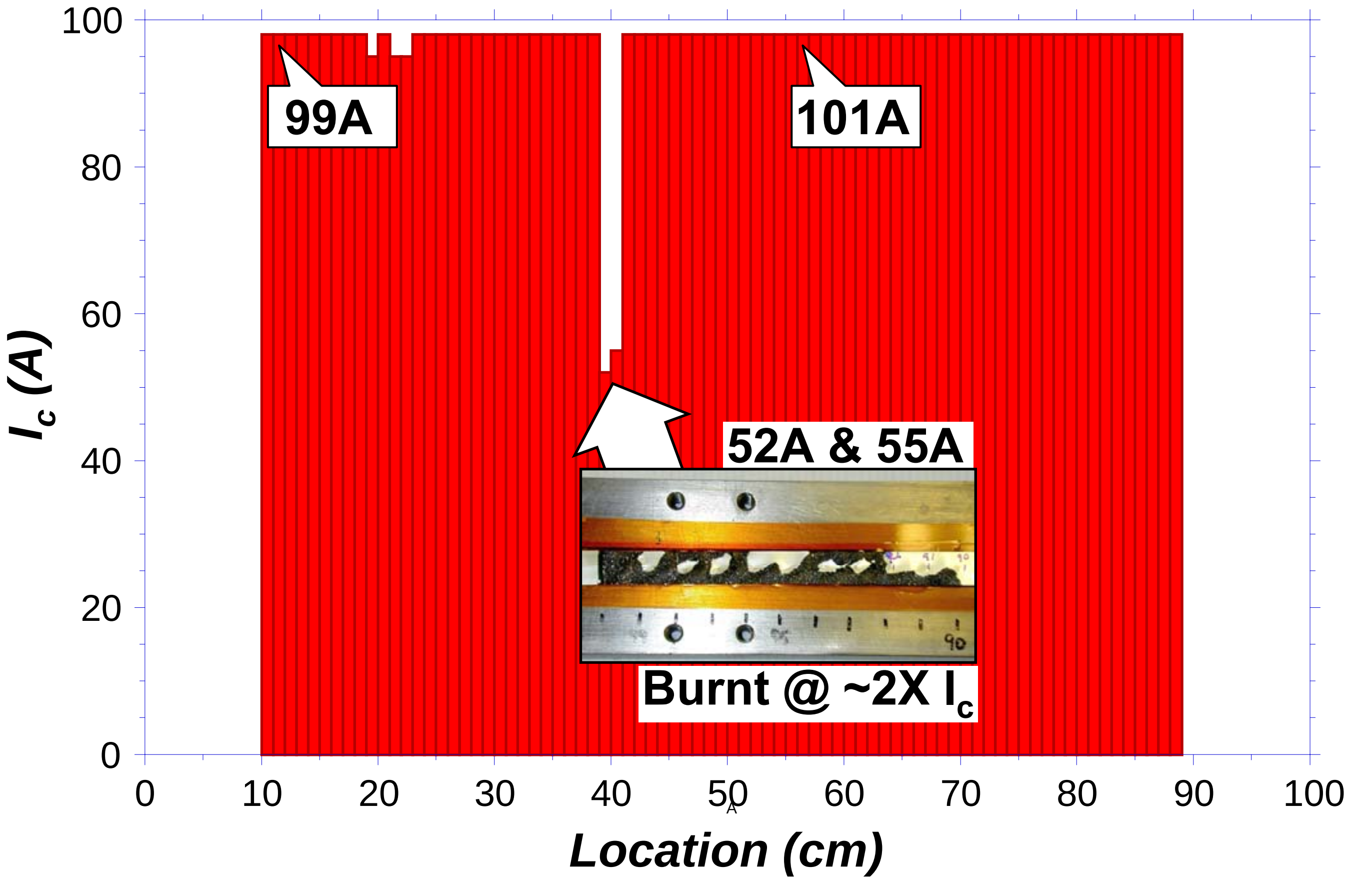
2 mm beam	Δω FWHM R / T	Δϕ FWHM
YBCO	5.6° / 7.1°	6.8°
CeO_2	5.7° / 8.0°	6.6°
YSZ	5.6° / 7.7°	6.5°
Ni-W	5.9° / 9.4°	7.0°



Relatively homogeneous edge-to-edge

Attempt to characterize a meter-length tape resulted in catastrophic failure at I = 98 Amps

- 1.5 μm PED precursor → 1.08 μm YBCO.
- G_p = 0.8 Å/s.



- Good I_c but with low performance sections.
- Much work remains for PED to become a routine deposition tool.

Objective 2: Develop R2R slot-die coater
Objective 3: Convert different precursors

Epi-YBCO film on RABiTS via a hybrid solution approach

Motivation: To study influence of stoichiometry, doping and substitution on pinning of REBCO.

Collaboration with Sandia National Lab to develop their solution precursor in length.

Why hybrid? Initial solutions from SNL had wetting issues with the slot-die coater (working with SNL to address this issue).

Previous work on non-fluorine MOD precursor on RABiTS resulted in J_c upper-limit of 1 MA/cm^2 (1.6 MA/cm^2 on X'stal), BUT difficult to reproduce.

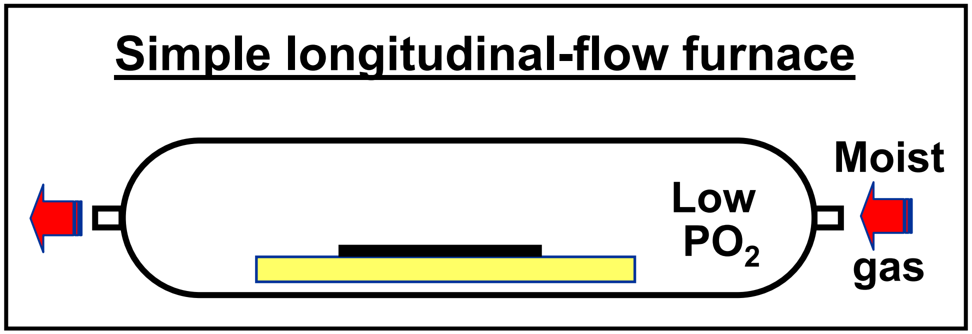
Lower fluorine content (compared to TFA) may reduce HF build-up and affect the conversion rate.

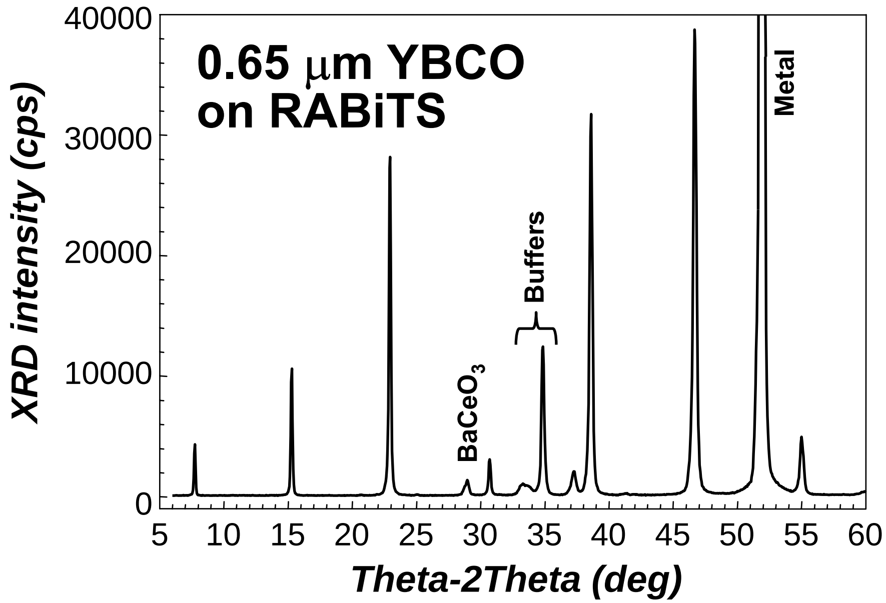
Better wetting characteristics with slot-die coater.

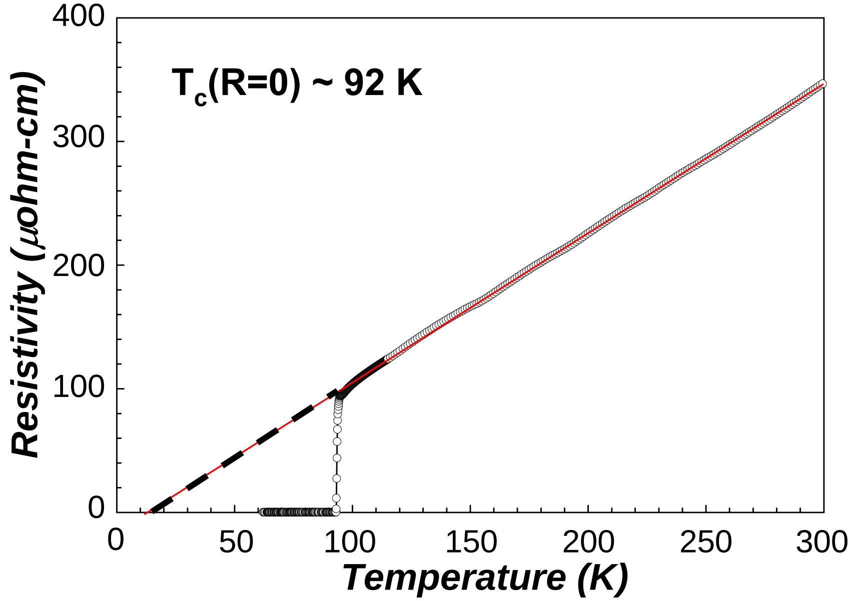
Hybrid MOD: Solution contains dissolved Y-TMA, Ba-TFA and Cu-TMA. Ba content varies from 2 to 1.5

Hybrid solution precursor films processed at low G_p exhibit good XRD and superconducting characteristics

- **Small 0.4 X 2 cm samples.**
- **0.65 μm YBCO film by single spin coat.**
- **Converted at 0.6 Å/s under non-aggressive condition in simple longitudinal-flow furnace.**



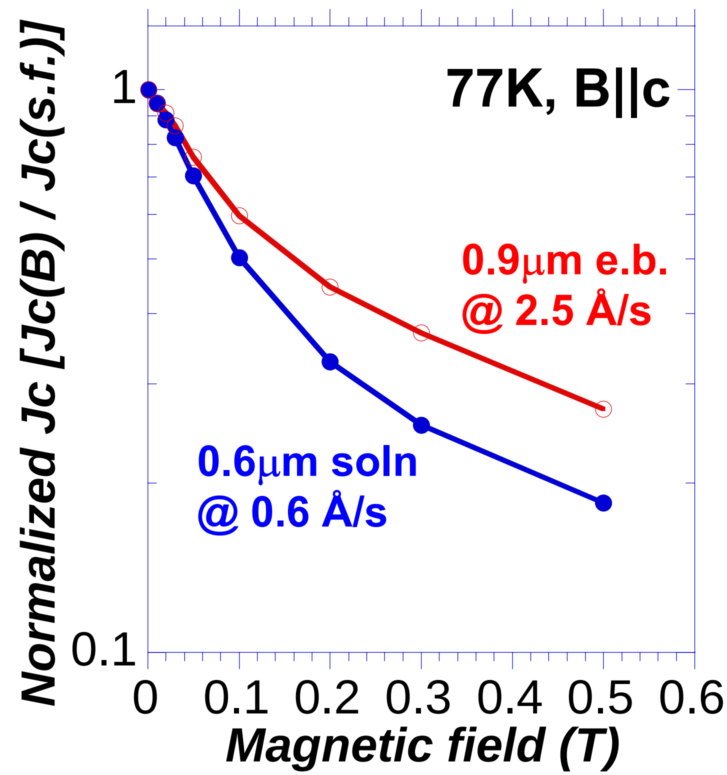




High J_c's have been obtained on RABiTS using the hybrid MOD precursor

- YBCO = 0.65 μm.
- G_p = 0.6 Å/s.
- I_c consistently > 1 MA/cm².

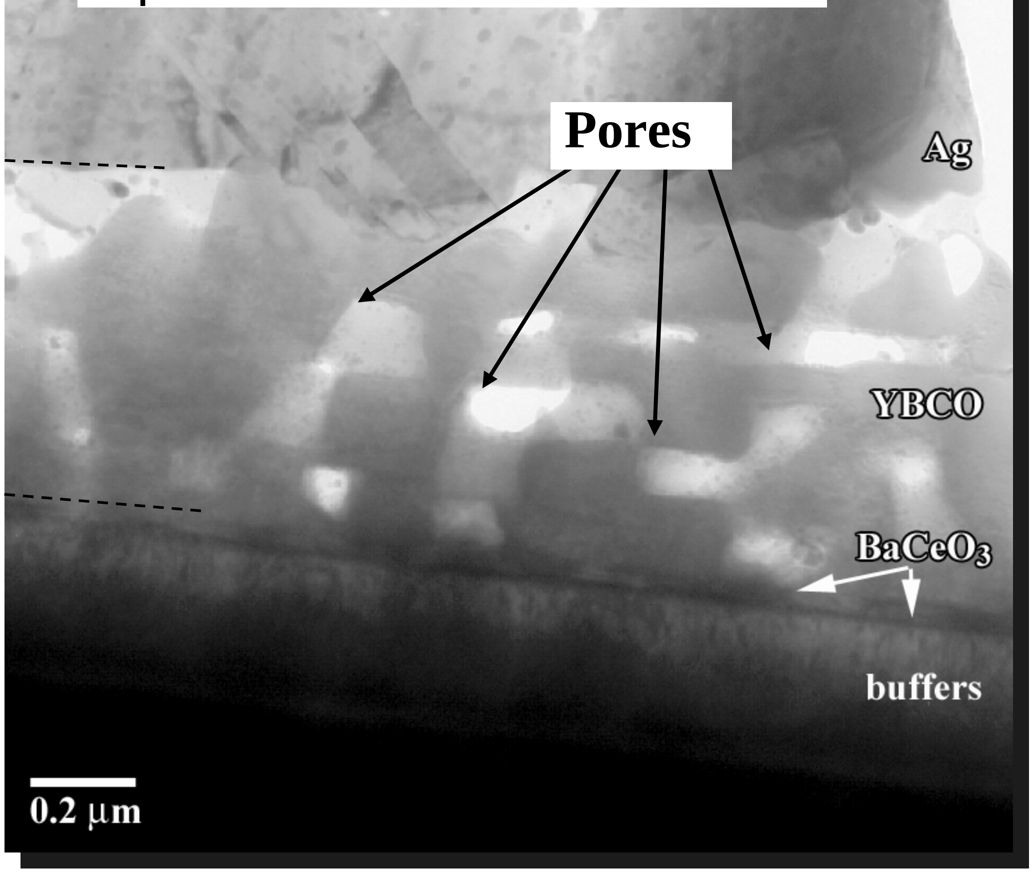
Samples *(Ba=1.5)*	*Δω(R) / Δω(T) (°)*	*Δφ (°)*	*I_c (A)*	*Width (mm)*	*J_c (MA/cm²)*
YL725	5.2 / 6.0	6.3	51.5	≤ 4	1.98
YL728			47.4	≤ 4	1.82
YL722	5.3 / 6.2	8.0	44.7	≤ 4	1.72
YL729	5.3 / 6.4	7.8	56.4	≤ 4	2.20



Sample exhibits a strong magnetic field dependency

TEM imaging revealed that these high J_c films contain large second-phase particles and are porous

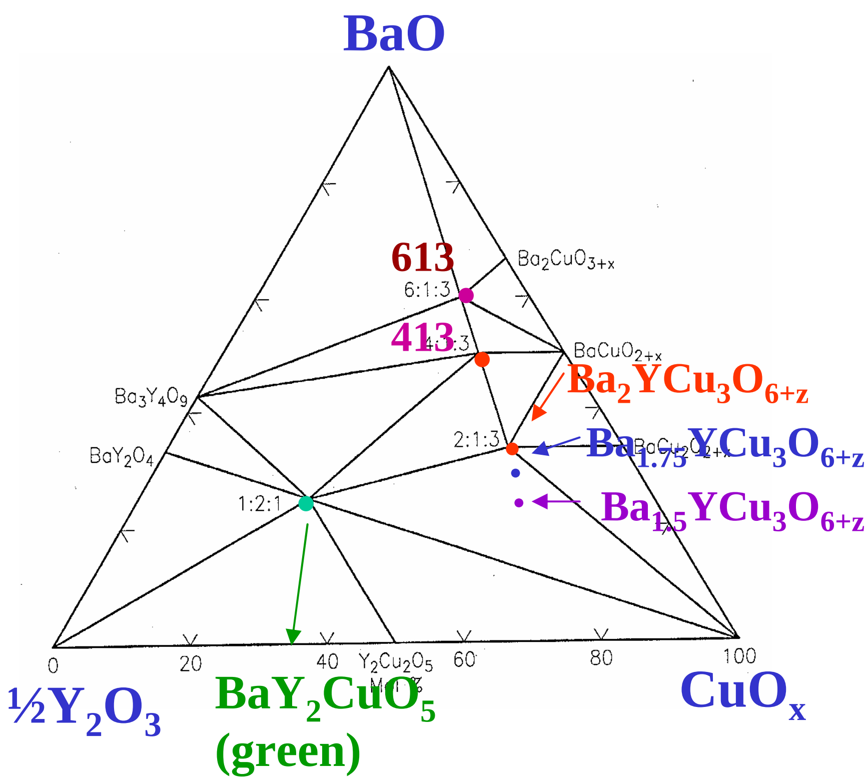
d = 0.65 μm, J_c = 1.8 MA/cm^2
G_p = 0.6 Å/s



- **Porous microstructure is typical of solution-based YBCO.**
- **High J_c's observed in MOD & PVD ex-situ films converted at high G_p with this microstructure,**

may facilitate gas exchange and high conversion rates?

We are studying phase development in hybrid solution precursors with NIST



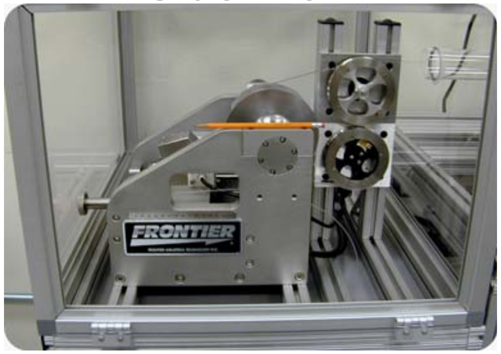
Wong-Ng, J. Suh and L.P. Cook, Physica C, 377 107-113 (2002).

- $Ba_{1.75}YCu_3O_{6+z}$ and $Ba_{1.5}YCu_3O_{6+z}$ fall on the three-phase region ($Ba_2YCu_3O_{6+z}$ – BaY_2CuO_5 – CuO)
- Improved superconductivity property of $Ba_{1.75}$ and $Ba_{1.5}$ over Ba_2 stoichiometry probably due to the presence of second phases acting as flux pinning sites

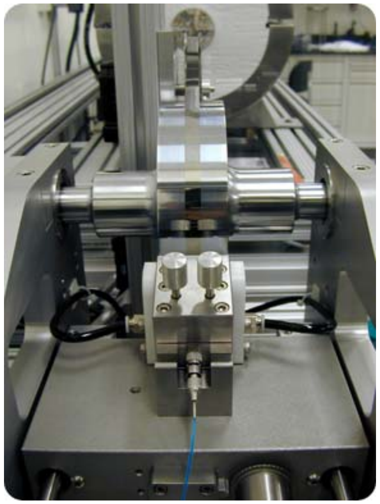
Continuous solution precursor deposition is being developed using our R2R slot-die coater

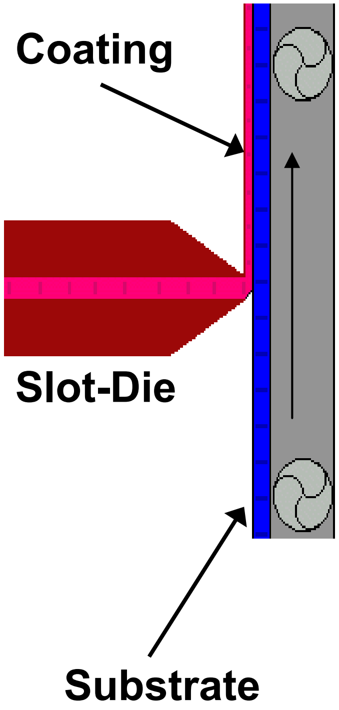
Why continuous length? **Necessary to provide uniform stock for systematic pinning study (avoid batch variation during spin coating)**

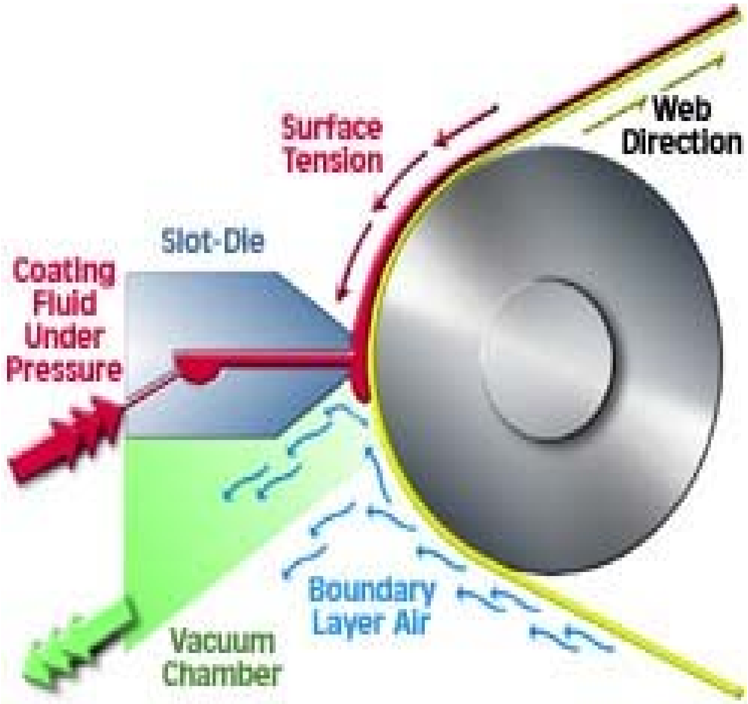
Side View



End View

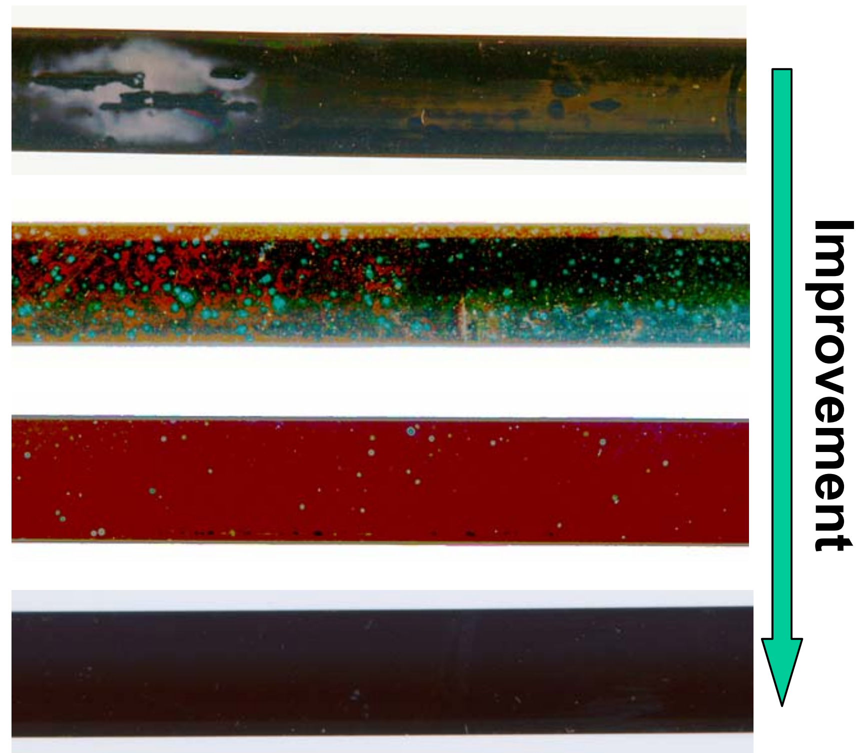






We have produced continuous lengths (~0.5m) of crack-free hybrid MOD precursors thicker than 1 μm

- **Quality of coating depends on:**
  - Solution molarity/viscosity
  - Surface tension
  - Tape speed
  - Solution delivery rate
  - Die gap
- **Greater than 1 μm coatings obtained by multiple passes.**
- **Soln injection rate: 5 μL/min**
  Tape speed: 10 cm/min

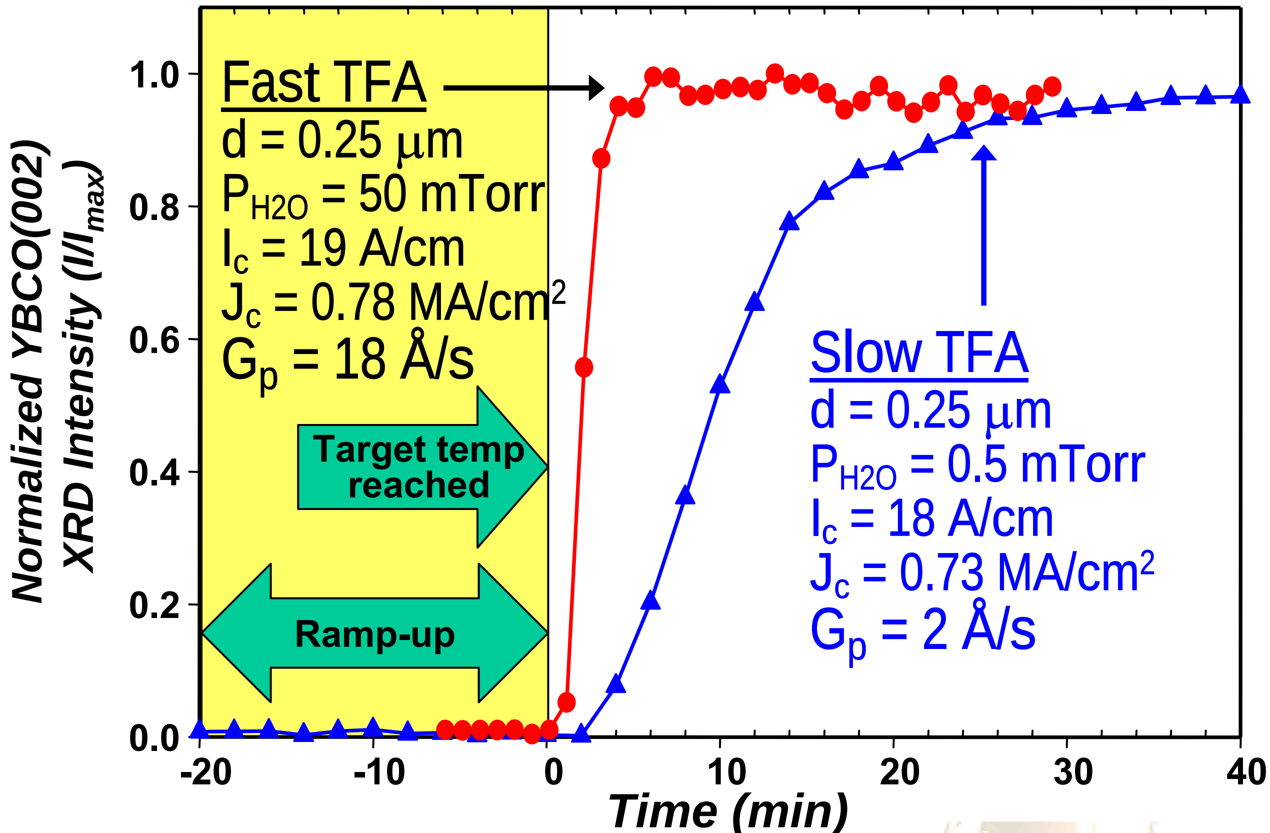


- **FY04 effort has been concentrated on developing uniform crack-free coating on RABiTS.**
-
- **Initial conversion results yielded J_c ~ 0.45 MA/cm^2.**

Objective 4: Increase G_p of PVD precursor(s)

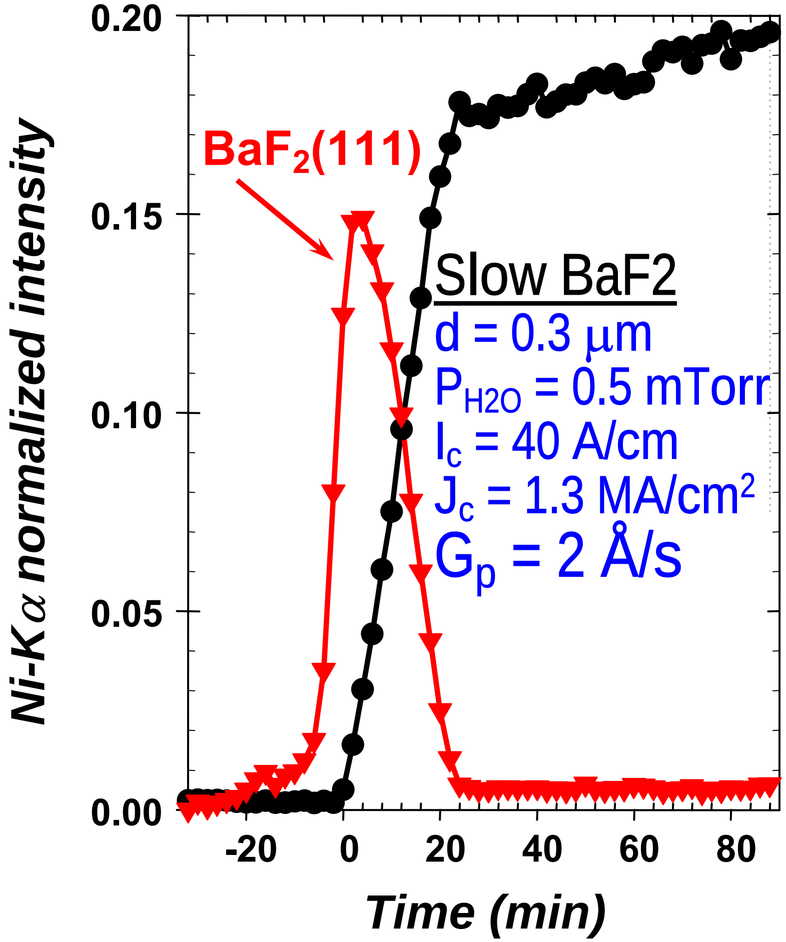
For fast YBCO growth, a precursor has to tolerate "aggressive" condition where epi-YBCO can nucleate and grow at the earliest stage of reaction

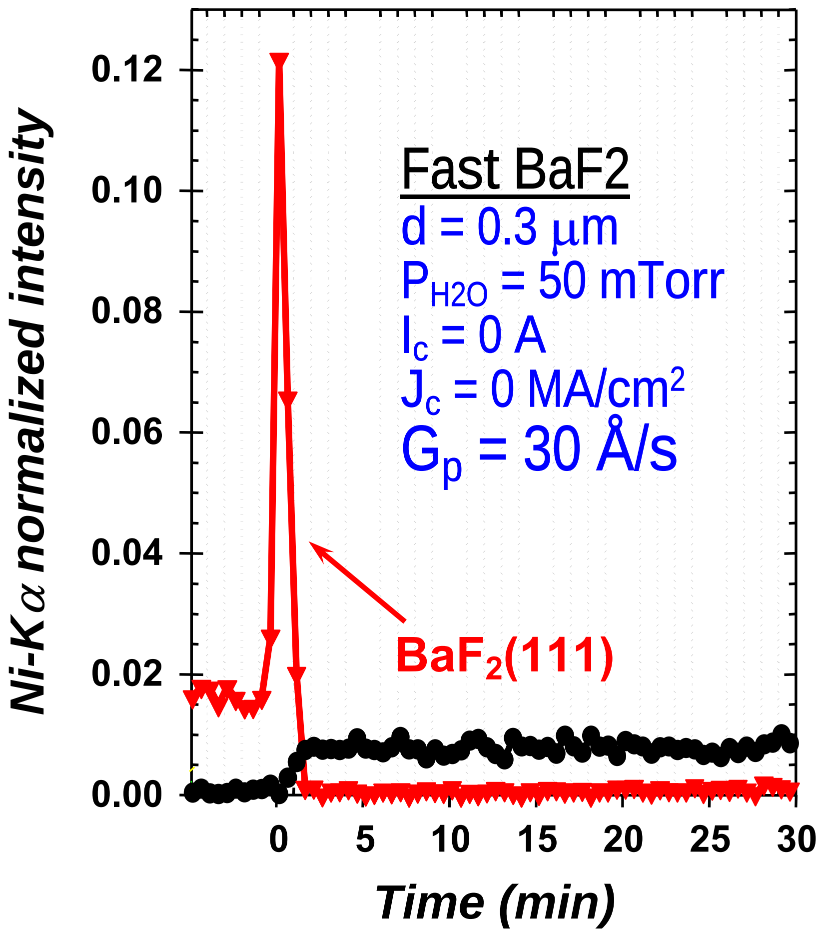
- **Solution precursors appear to be this type of material.**
- **In FY03, we demonstrated that good J_c at high G_p can be obtained in thin TFA precursor.**



However, not all precursors can be converted at high rates AND retain good J_c's

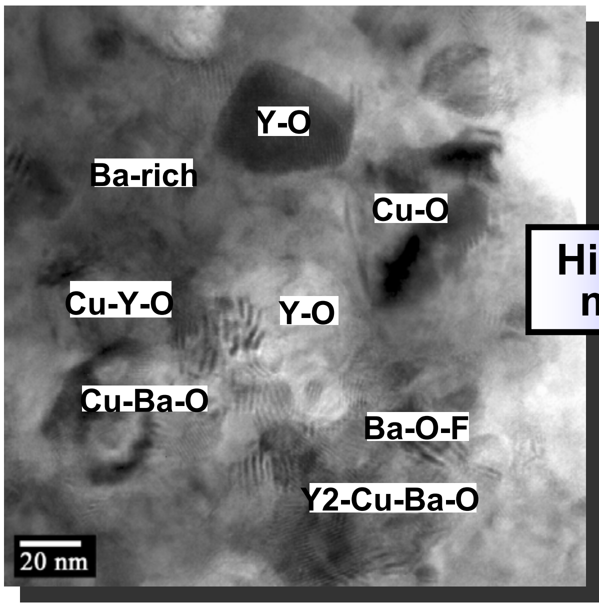
- **<u>In FY03</u>, we demonstrated that YBCO development is very sluggish in our <u>standard</u> e-beam BaF_2 precursor.**



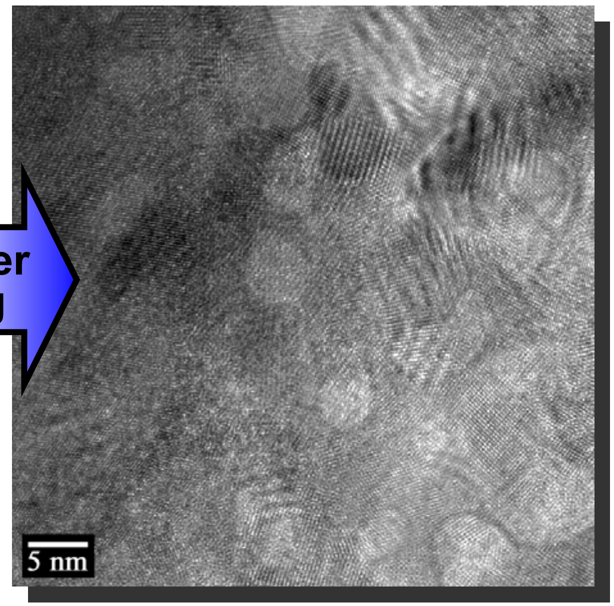


Questions: What about PED precursor? Is PED precursor similar to <u>standard</u> e-beam BaF_2?

- **TEM:** PED precursor was converted for 1 min, and quenched to room temp in 15 sec.



Higher mag

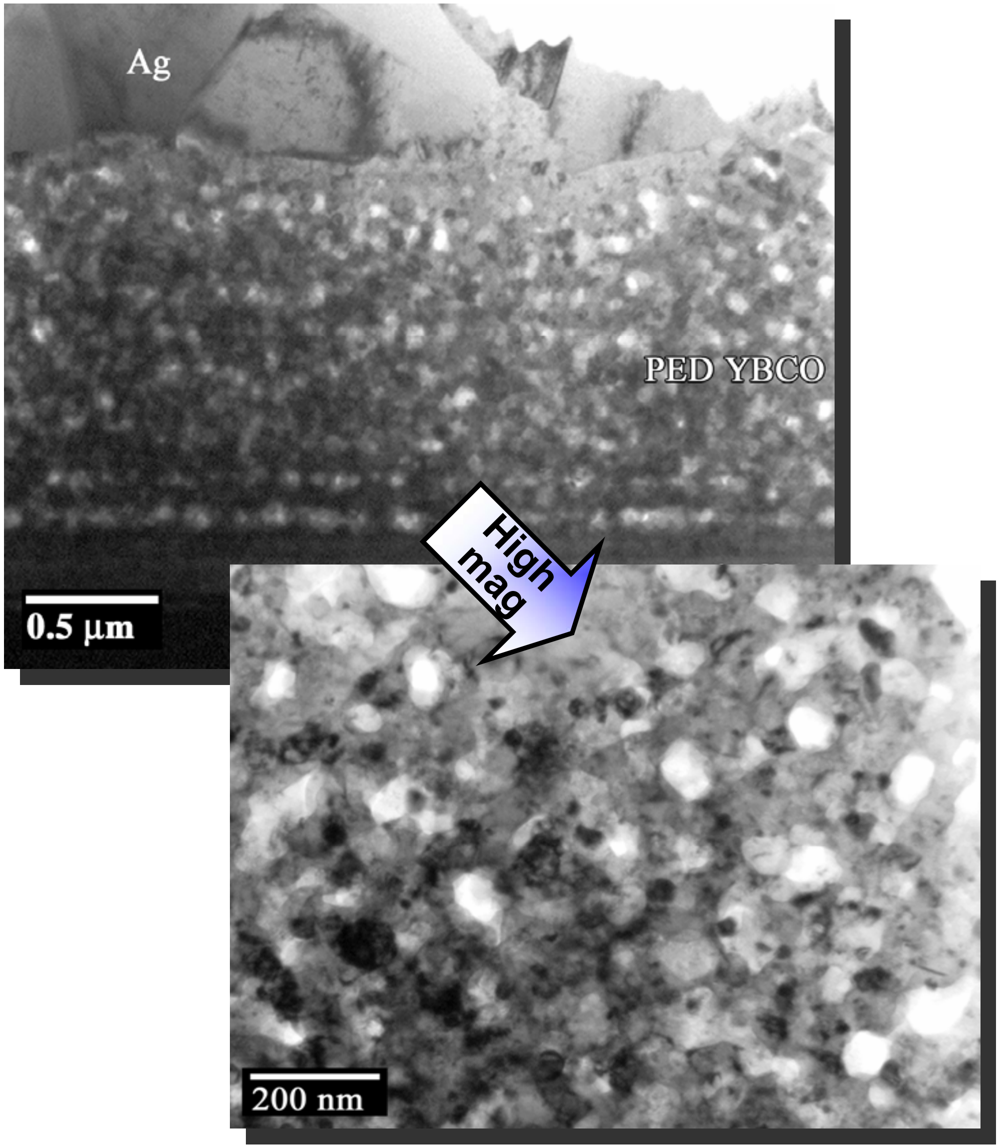


- SAD and EDS show a wide variety of phases before YBCO nucleation and growth.

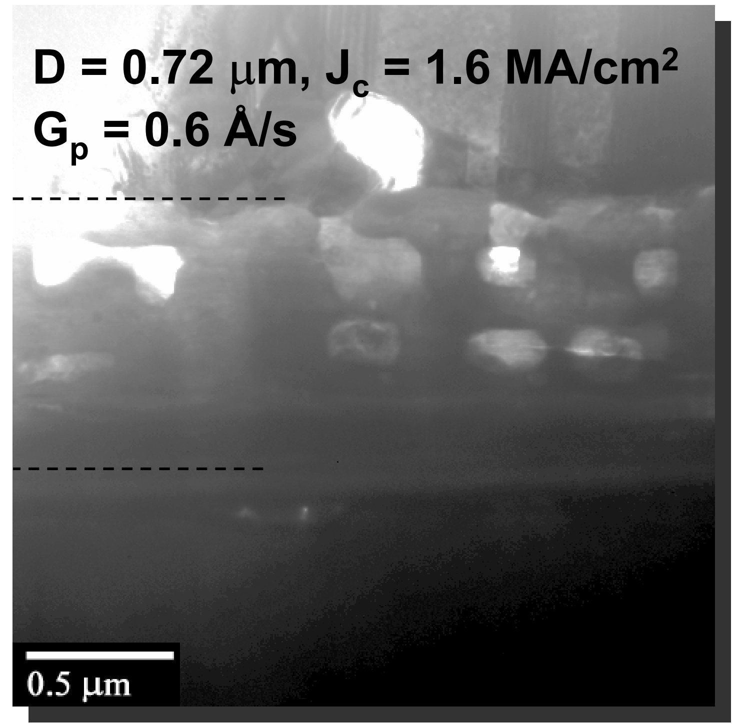
- Area consists on agglomeration of nano-scale grains

Precursor phase assemblage and grain scale are <u>Indistinguishable</u> from our standard e-beam precursor

PED precursor film is found to be porous, in contrast to e-beam precursors

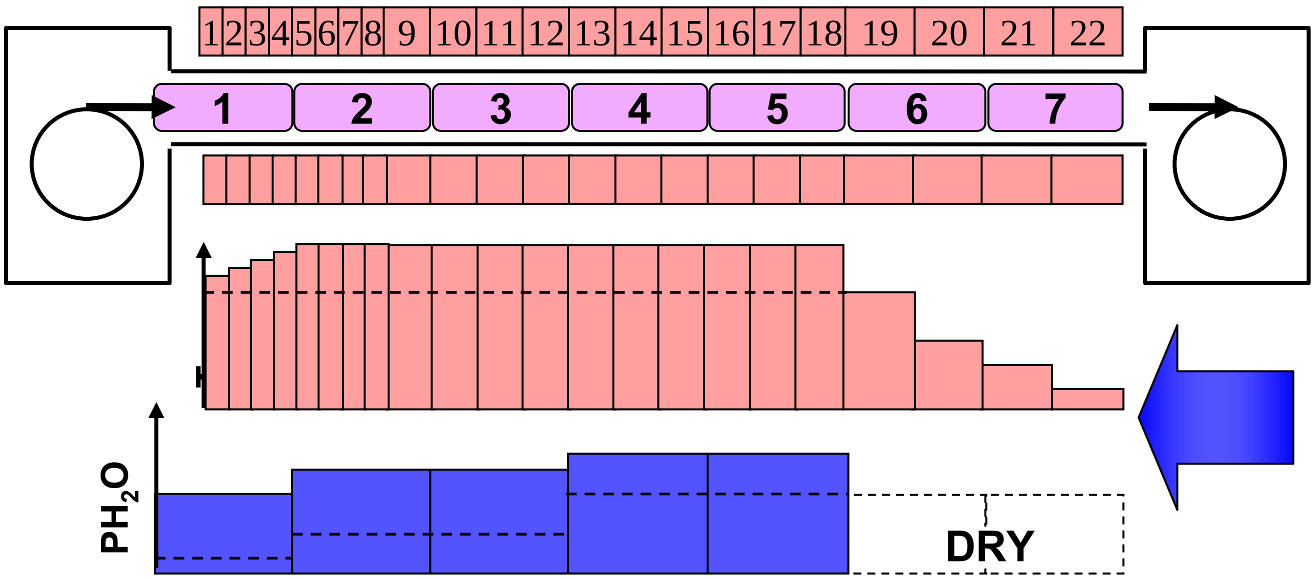


- Porosity remains in YBCO after conversion.



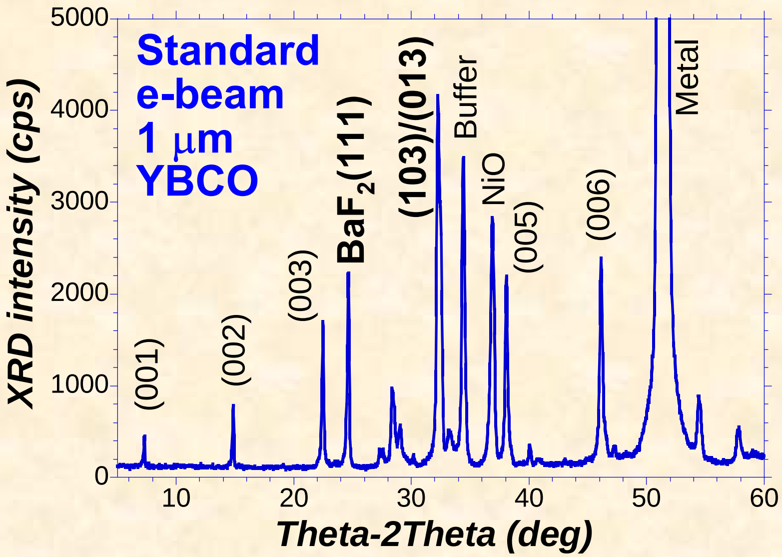
Can this porous precursor microstructure aid in gas exchange and enable faster conversion?

For the R2R furnace, G_p is increased by subjecting the precursor to aggressive conditions at the earliest stage



Higher G_p:

- High temperature
- Increase PH_2O

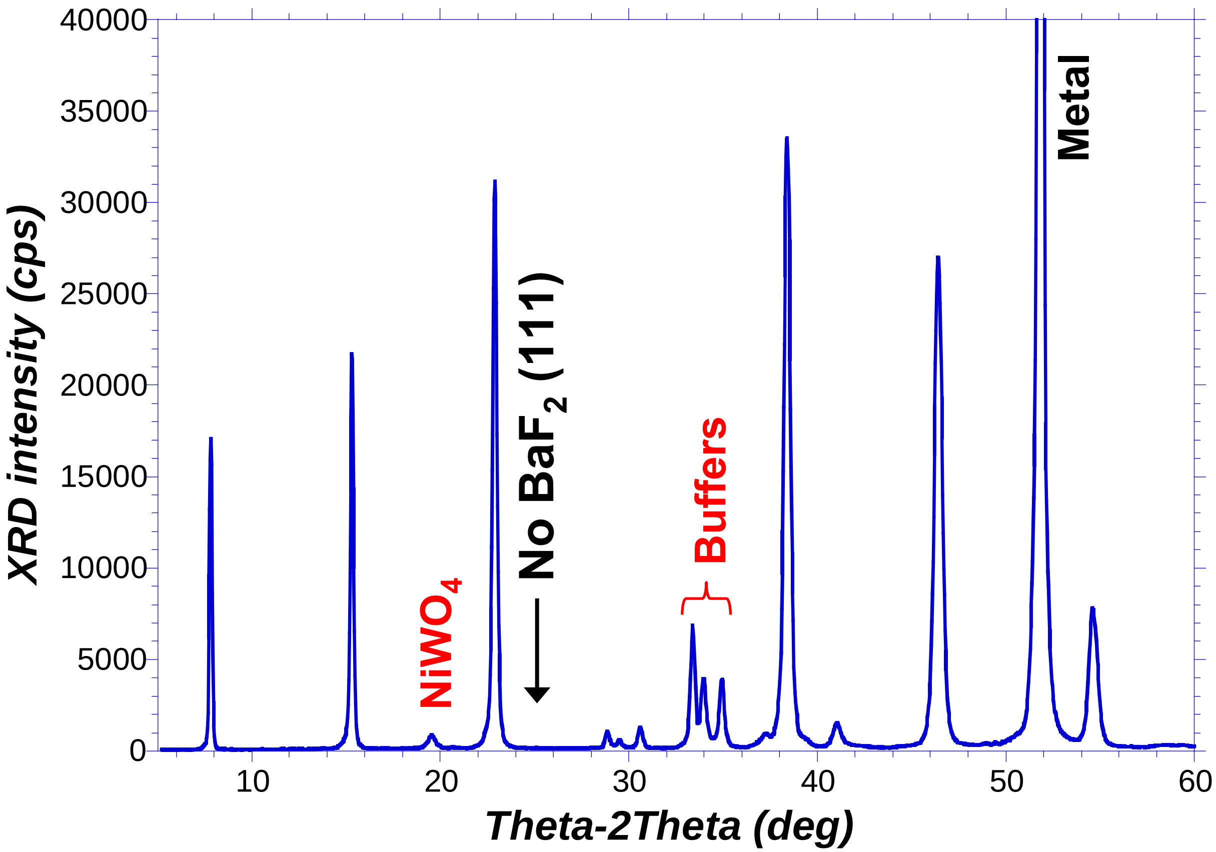


Standard e-beam precursor

- Process under aggressive condition → < 3.3 A/s.
- Retained BaF_2.
- LOW YBCO (00L) peaks
- Large random YBCO (high (103)/(013) and other peaks.

In contrast, PED precursor can be fully converted into Epi-YBCO even under aggressive conditions at the onset of conversion

- **1 μm precursor → 0.72 μm YBCO**
- **$G_p \geq 2.2$ Å/s**



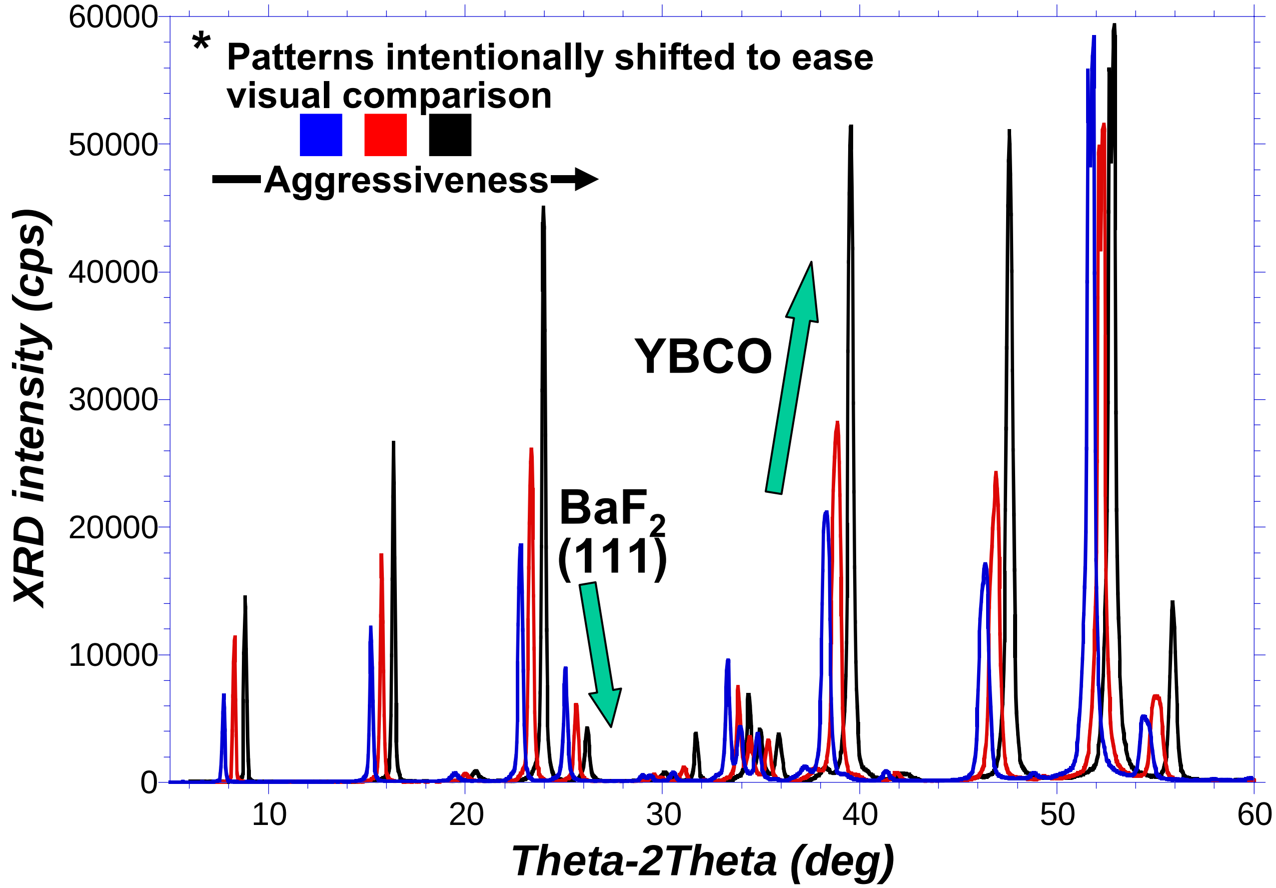
I_c = 67 A
J_c = 0.93 MA/cm^2

(compared to J_c of 1.46 MA/cm^2 at G_p = 0.8 Å/s for SAME precursor)

G_p of PED can be increased even in a system where HF buildup and gas flow are of concern.

Further attempts in increasing the G_p led to incomplete conversion

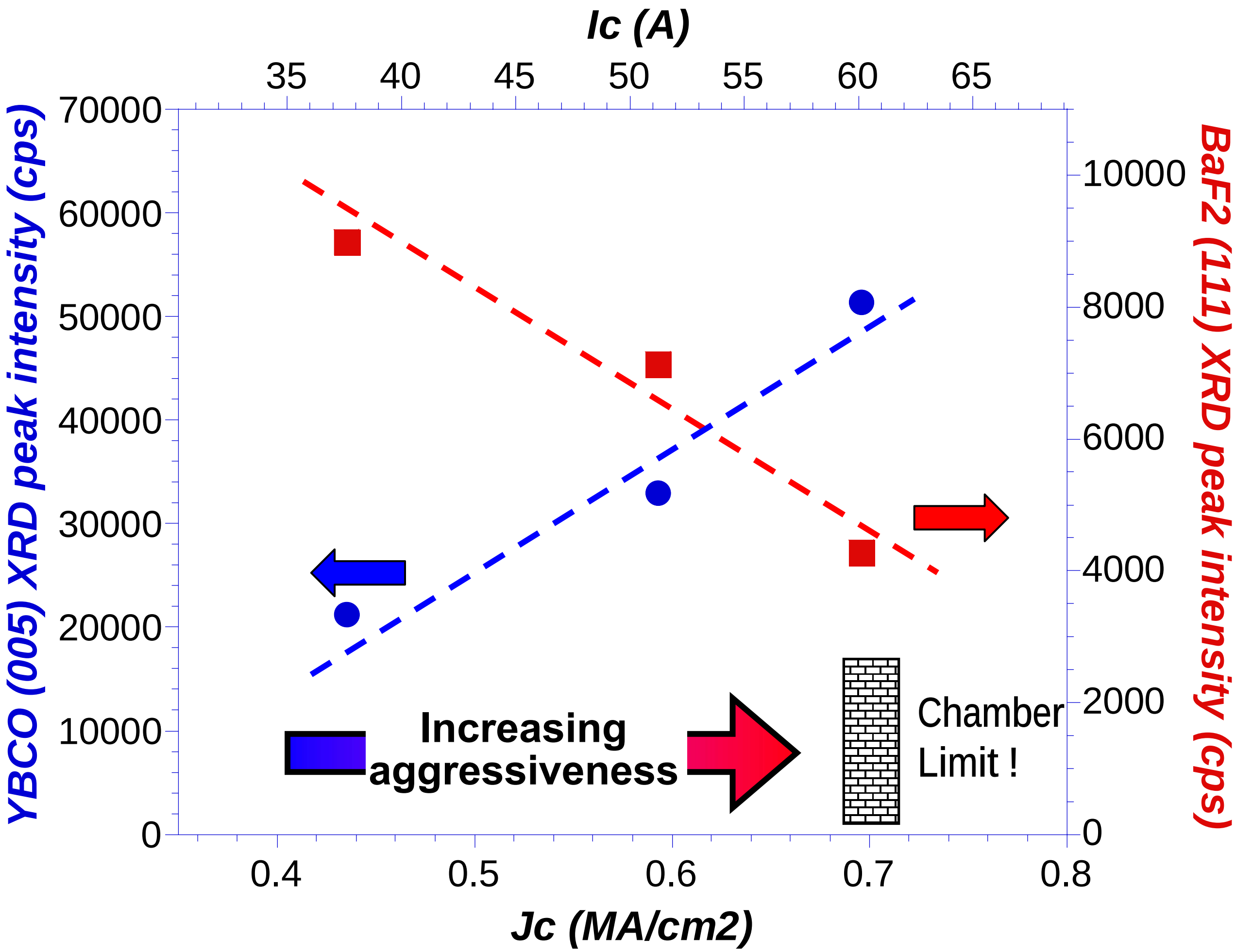
- **Samples cut from a 1.2 μm precursor tape**
  → <u>0.86 μm YBCO</u>
- **Conversion time = 45 min → $G_p \leq 3.2$ Å/s**



Significant improvement in YBCO growth and crystallinity with conversion aggressiveness

However, conversion <u>did not</u> go to completion.

Partially converted sample processed under the most aggressive condition possesses good J_c



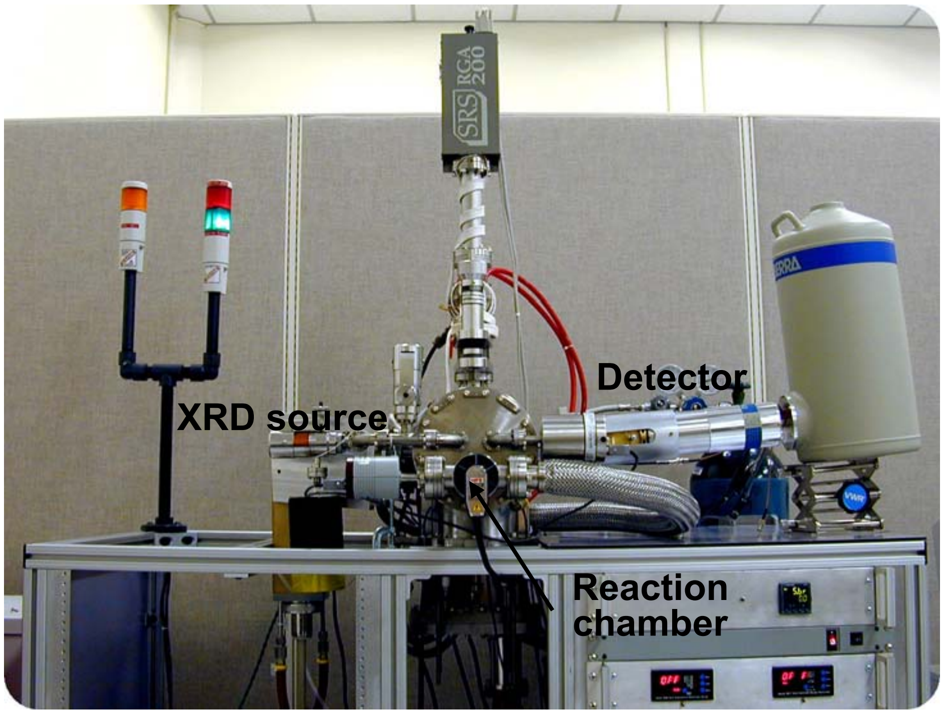
J_c of 0.7 MA/cm^2 was obtained under the most aggressive condition → Pressure within chamber > 2 atm.

I_c(s.f.) / I_c(0.5T) = 4.3

Highest J_c achieved with this precursor at slow rate = 1 MA/cm^2.

Need to study precursor capability in a system which is not limited by high pressure, gas flow and HF accumulation.

Our "low pressure" conversion system with in-situ XRD is ideally suited for rate studies



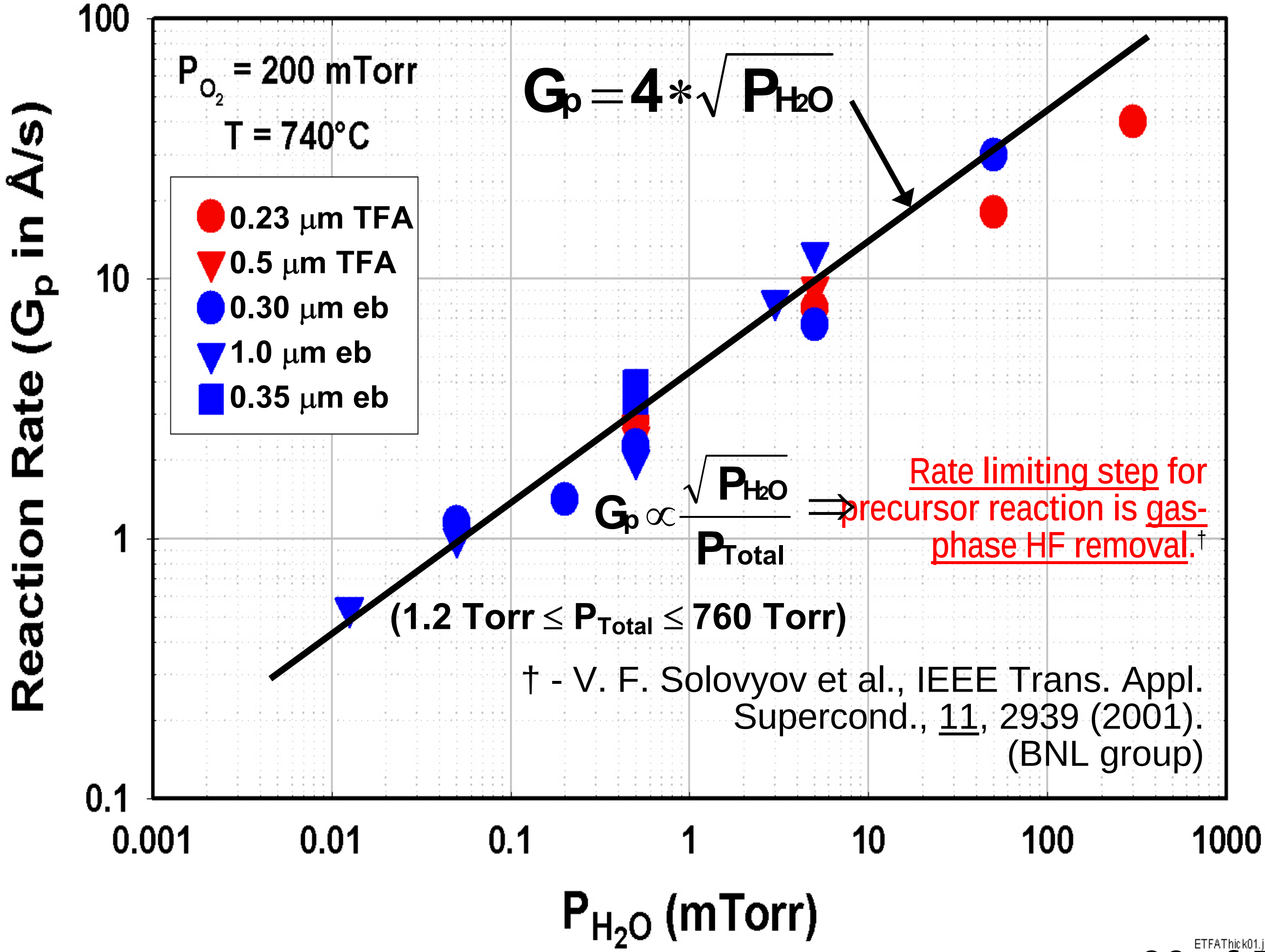
- Base pressure = $5x10^{-8}$ Torr.
- Sample is resistively heated with spot-welded thermocouple

Aggressiveness increased by:

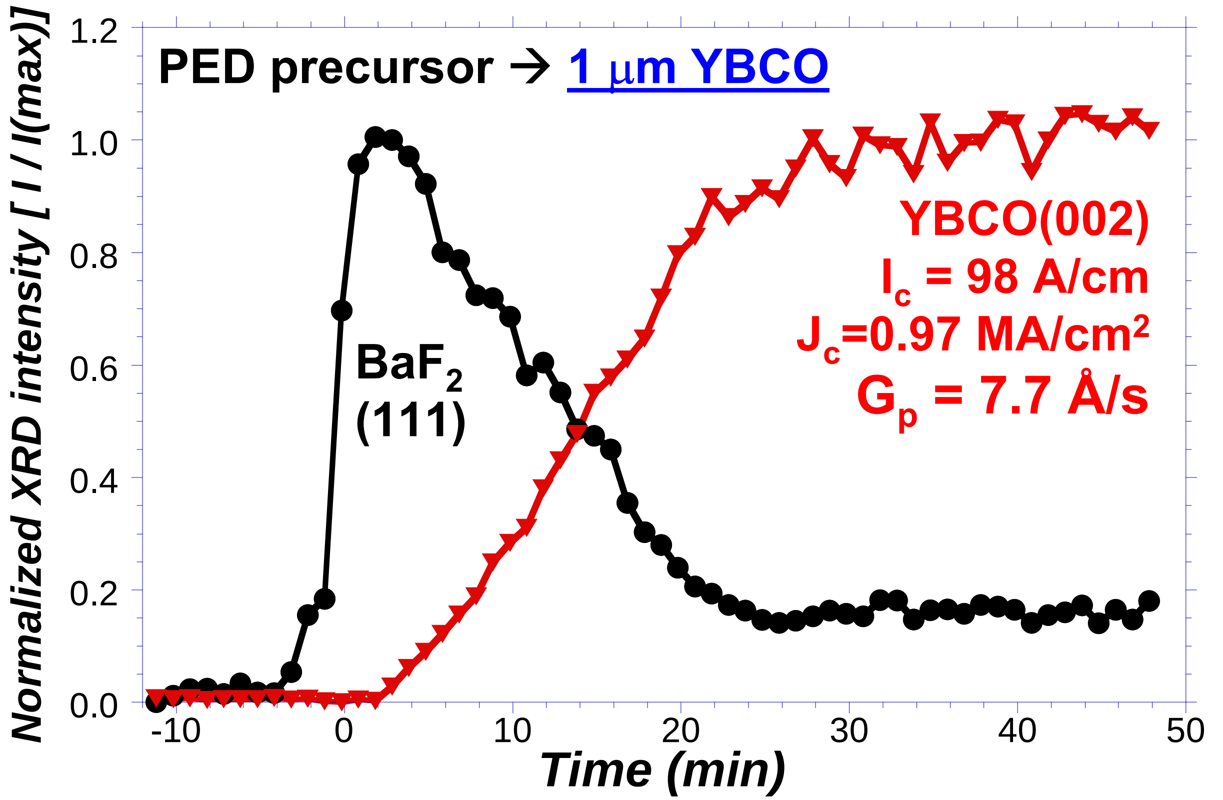
- Higher temperature
- Higher PH_2O
- Lower P_{Total}

This low pressure system can probe the G_p capability of a precursor

We showed in FY03 that $G_p \propto \sqrt{P_{H_2O}}$ for samples processed in this furnace → P_{H_2O} can be used to control precisely high G_p and probe the capability of a precursor.

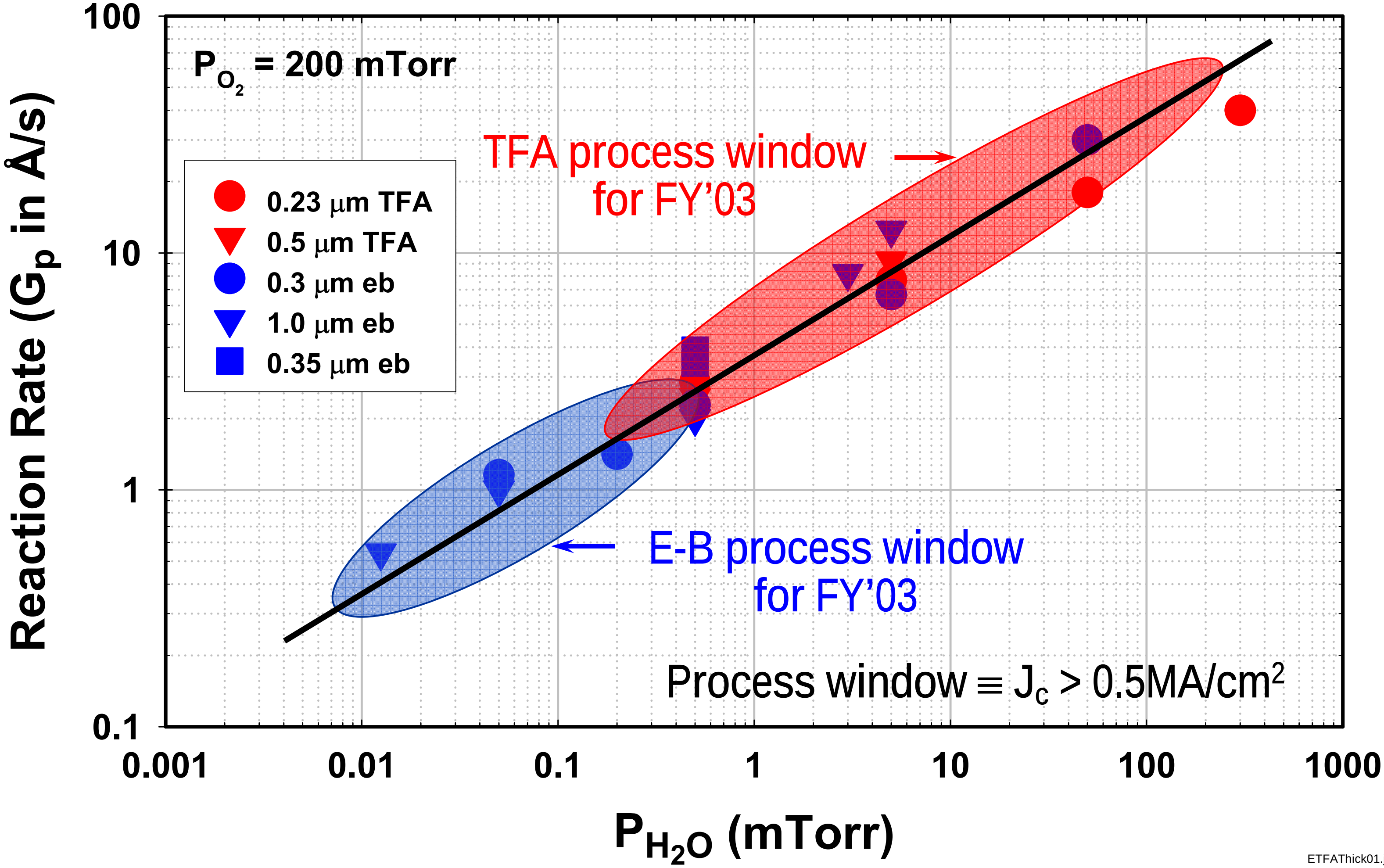


Initial trials showed that as-deposited PED precursor can be converted at high G_p with good J_c



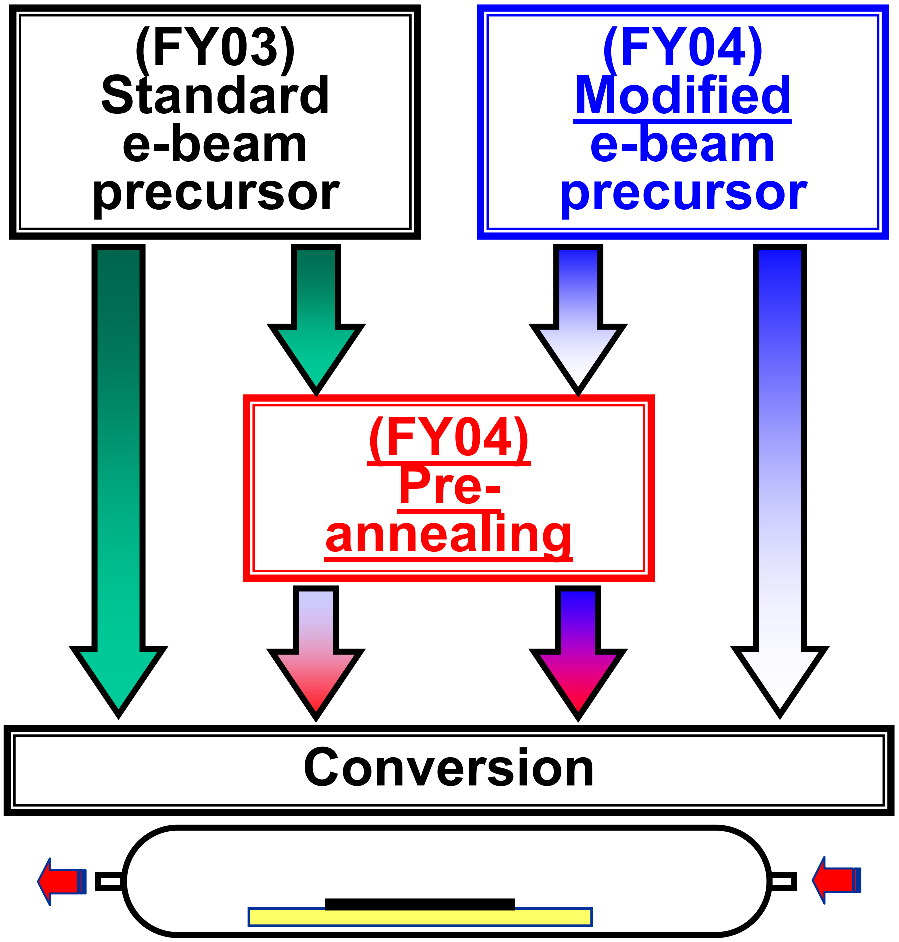
- **We should be able to increase J_c and G_p through:**
  - **Process optimization**
  - **Precursor modification**

We showed in FY03 that conversion rate of standard e-beam precursor with good J_c (>0.5 MA/cm^2) is limited to ~ 2.5 Å/s



ETFAThick01.jnb

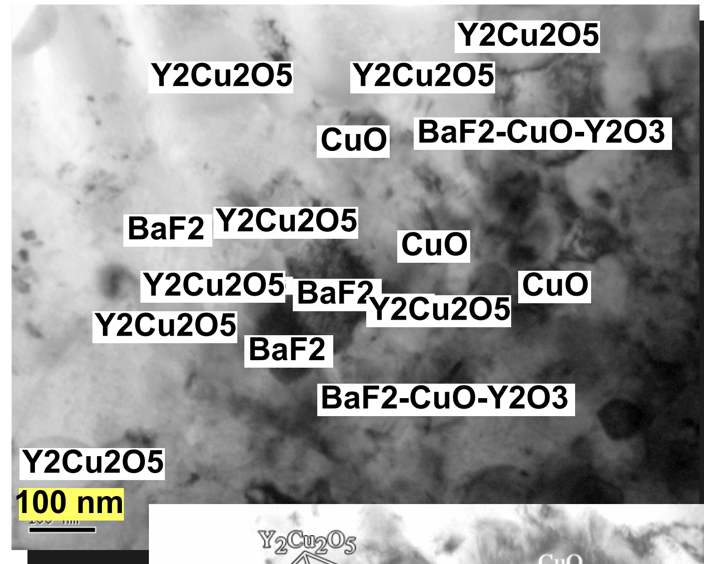
In FY04, we have developed a <u>modified</u> e-beam BaF_2 precursor with a <u>pre-annealing</u> procedure that can be converted at high rates (>10 Å/s) with high J_c

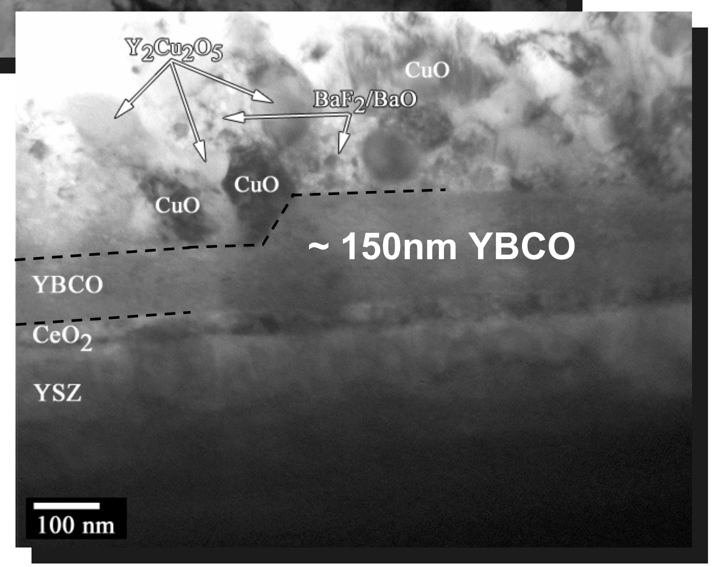


- **Modified e-beam precursor deposited using our small co-evaporator.**
- **Samples ≤0.5 cm wide X 1.5 cm were initially converted in a longitudinal-flow furnace:**
  - **<u>I_c > 300 A/cm (extrapolated)</u> has been obtained on 1.25 μm film.**

TEM of quenched precursor shows that epi-YBCO nucleation and growth is <u>rapid</u>

- Sample quenched in 5 sec after 1 min of conversion:
  - ➢Precursor is <u>dense</u>.
  - ➢Phase assemblage <u>indistinguishable</u> from standard precursors.
  - ➢YBCO nucleates and grows <u>readily</u> at the earliest stage of conversion under aggressive condition.

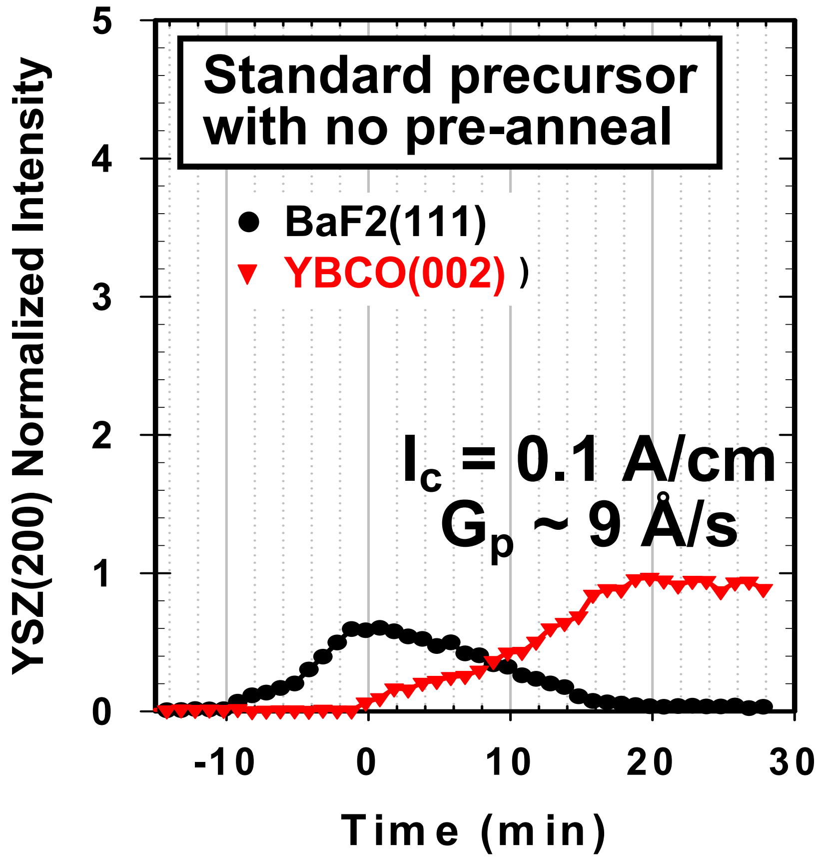


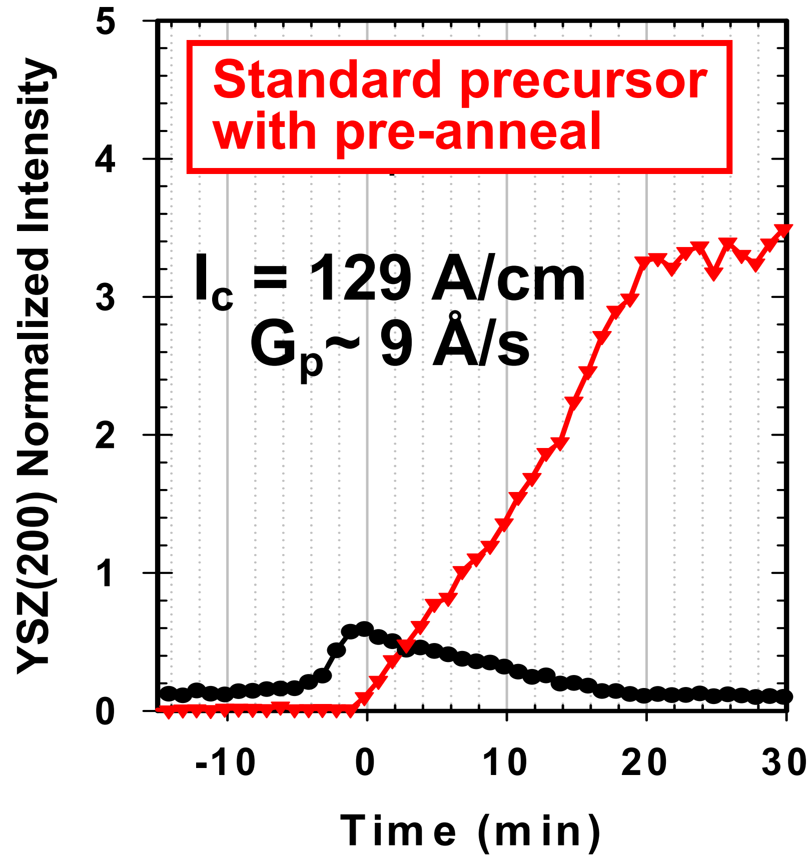


- 1 cm <u>full-width samples</u> are then converted in low pressure system to:
  - Ensure higher G_p with high J_c is transferable to wider samples
  - Maximize G_p while maintaining high J_c.

Effect of pre-annealing on conversion behavior is clearly seen in the low pressure system

- 1 μm YBCO's:

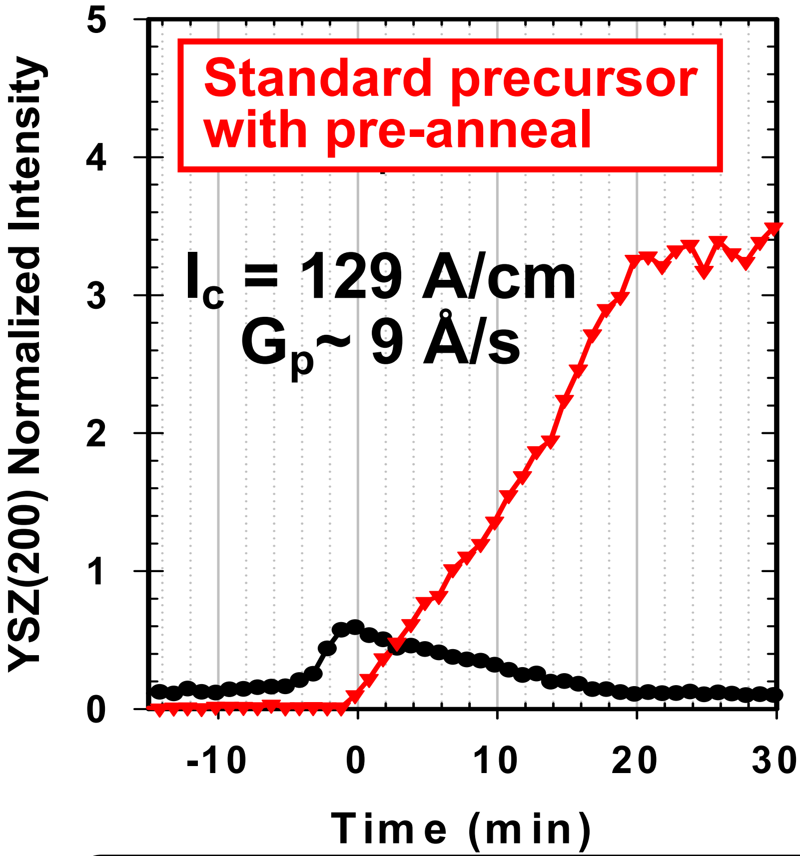


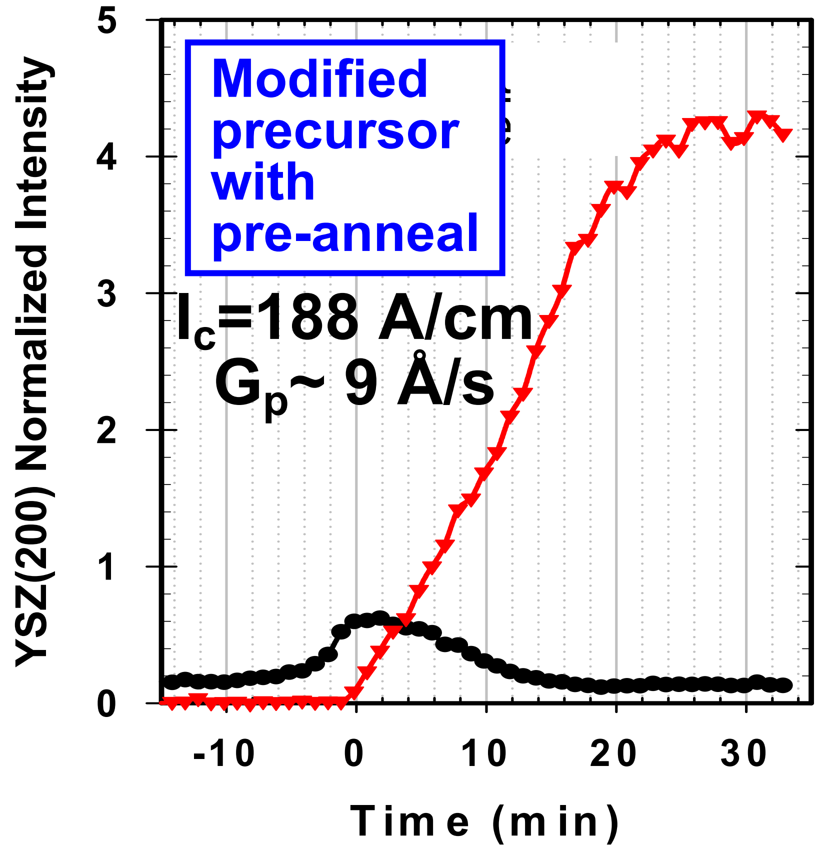


Much higher YBCO(00L) for pre-annealed precursor under identical consition → high I_c and J_c

Modified conditions for e-beam precursor deposition have led to further enhancements of I_c

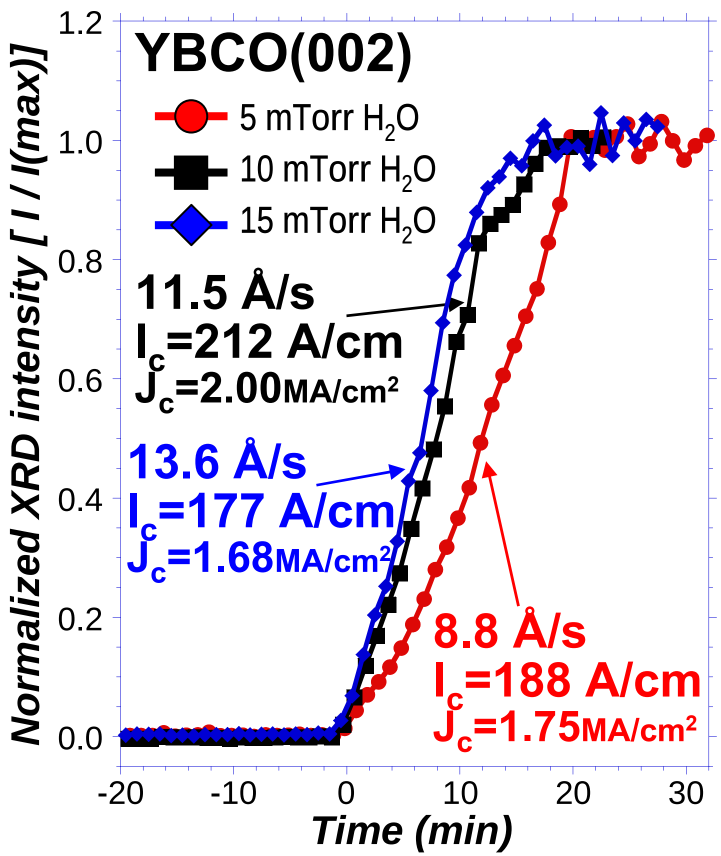
- 1 μm YBCO's:

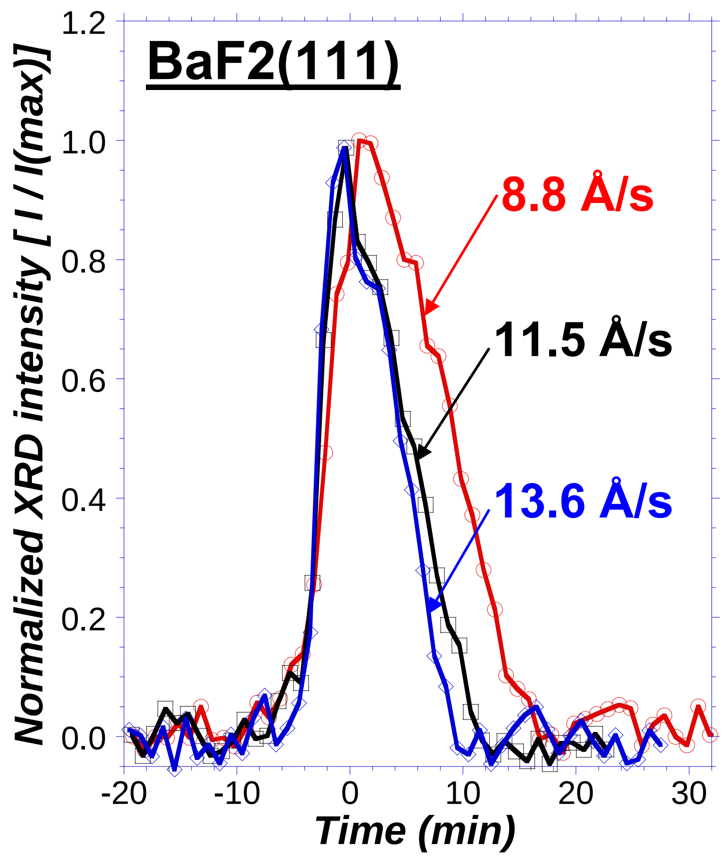




Even higher YBCO(00L) for pre-annealed modified precursor → J_c = 1.74 MA/cm^2.

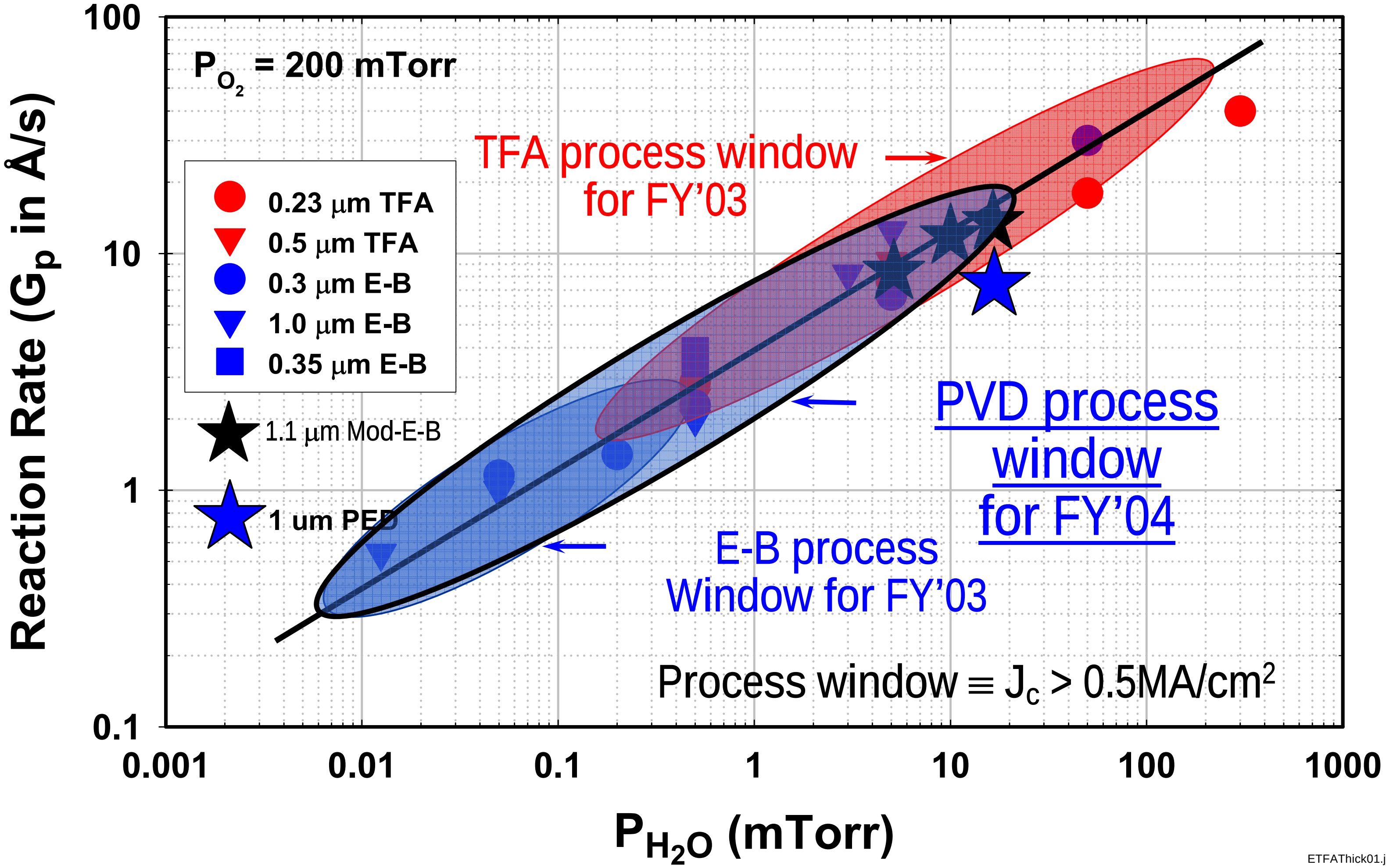
High I_c tapes have been demonstrated for conversion rates as high as 13.6 Å/sec





Highest I_c = 212 A/cm → J_c = 2 MA/cm^2 at G_p > 11.5 Å/s.

For FY'04, the processing window for e-beam precursors has been extended to higher rates.



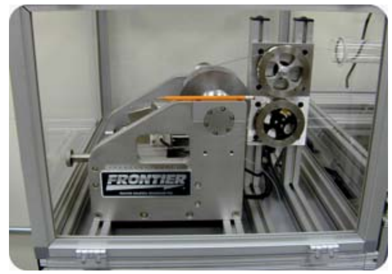
FY2004 Performance (Scoring Criteria)

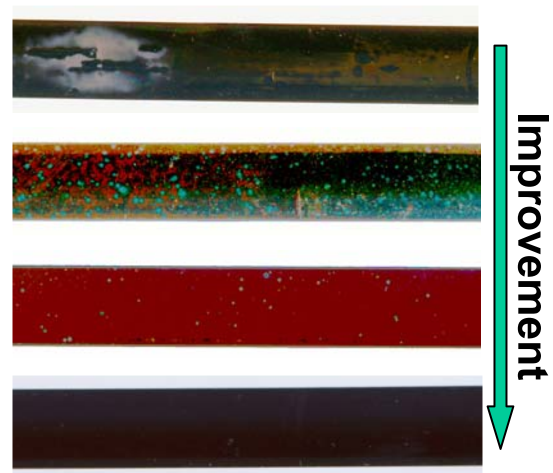
Precursor Deposition

1. Investigate using reel-to-reel (R2R) Pulsed Electron-Beam Deposition (PED) for YBCO precursors. ☑

- **Reels installed & samples up to 1 m-long deposited.**
- **Multiple system & operation related issues solved.**
- **Converted PED precursor into YBCO.**

2. Develop a R2R slot die coater for solution precursors. ☑





- **R2R slot-die coater in operation in May 04.**
- **Methodology developed to deposit crack-free >1μm precursor in lengths.**
- **Short sample J_c = 0.45 MA/cm^2.**

FY2004 Performance (Scoring Criteria)

Slow Conversion

3. ☑ Explore YBCO conversion characteristics and performance of various types of ex-situ precursors.

PED

- PED precursors can be converted under similar slow condition as standard e-beam precursors,
- At slow conversion rates (~ 1 Å/s):
  - J_c = 1.6 MA/cm^2 for 0.72 μm YBCO (R2R & low pressure chambers).
  - I_c = 159 A for 1.3 μm YBCO (R2R).
  - Non-uniform I_c for 1 meter tape: I_c > 98 A for most sections.

Solution precursor

- Developed a hybrid solution precursor: TMA and TFA.
- 0.65 μm converted YBCO by one spin coat.
- Porous YBCO films.
- At slow conversion rate (0.6 Å/s):
  - J_c as high as 2.2 MA/cm^2 for Ba=1.5 films (simple longitudinal-flow chamber).

FY2004 Performance (Scoring Criteria)

Fast Conversion

4. ☑ Investigate differences in solution and PVD precursors responsible for different reaction rates, and increase the reaction rate of PVD precursors.

PED

- PED precursors & converted YBCO films are porous.
- Can be converted in R2R at G_p ~ 3 A/s (limited by chamber),
  - Tolerates aggressive condition at the onset.
  - J_c = 0.7 MA/cm^2 (0.86 μm).
- Converted in low pressure at G_p = 7.7 Å/s:
  - J_c = 0.95 MA/cm^2 for 1 μm YBCO.

e-beam

- Developing a modified e-beam precursor and pre-anneal step.
- Combination resulted in high G_p with high J_c.
- Dense precursor and YBCO films.
- I_c > 300 A/cm at ~ 10 Å/s (small sample, longitudinal-flow chamber).
- I_c = 212 A/cm at 11.5 Å/s → J_c = 2 MA/cm^2 (1-cm full width sample, low pressure chamber).

FY2004 Performance (Scoring Criteria)

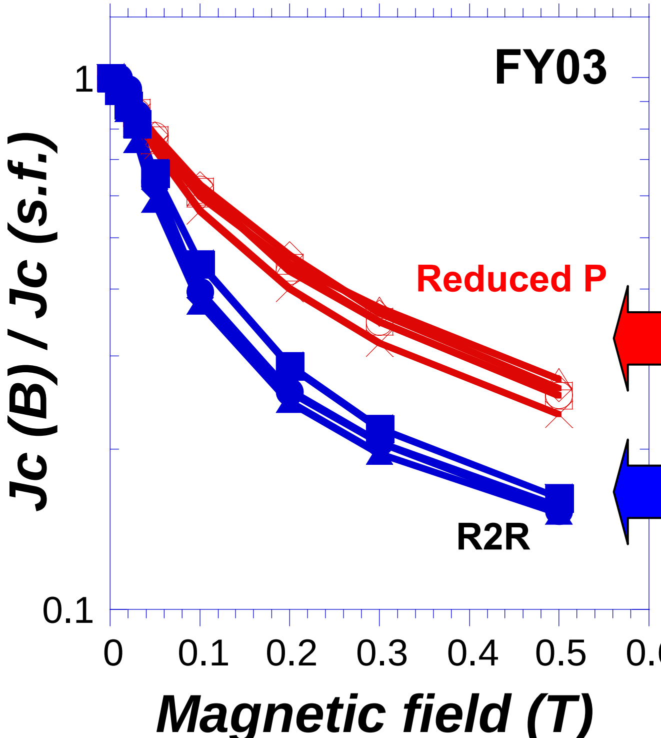
Limited or deferred plans

5. *Add and develop both reduced- and low-pressure R2R capabilities for precursor conversion.*

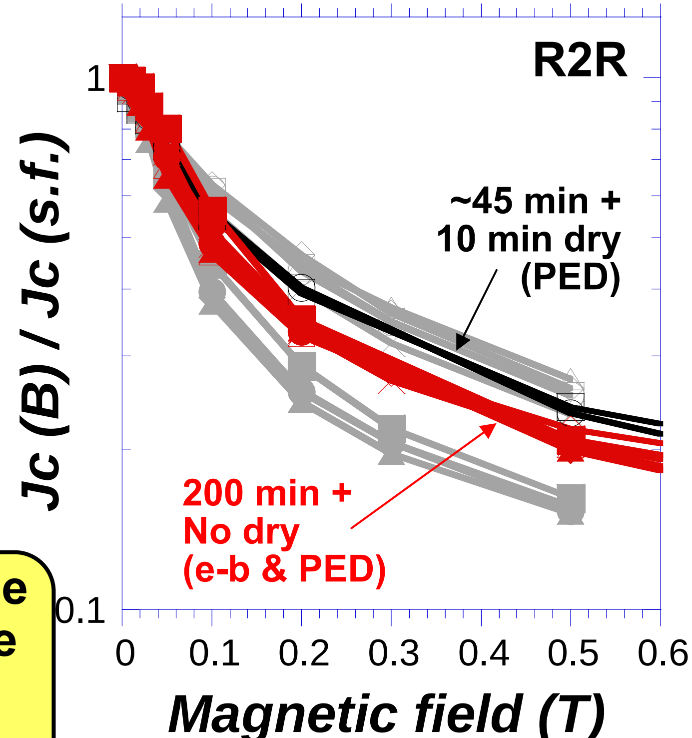
☒ Deferred due to lack of funds.

6. *Identify pinning centers and processing parameters responsible for different field dependencies in samples converted in different systems.*

☑



- 50% increase in I_c(s.f.) needed for R2R to compensate.
- 1 μm YBCO:
- G_p = 2.5 A/s 60 min+10 min dry.
- G_p = 0.8 A/s 200 min+60 min dry.



Extended resident time at high temp may have led to reduction in pinning defects

FY2004 Performance (Scoring Criteria)

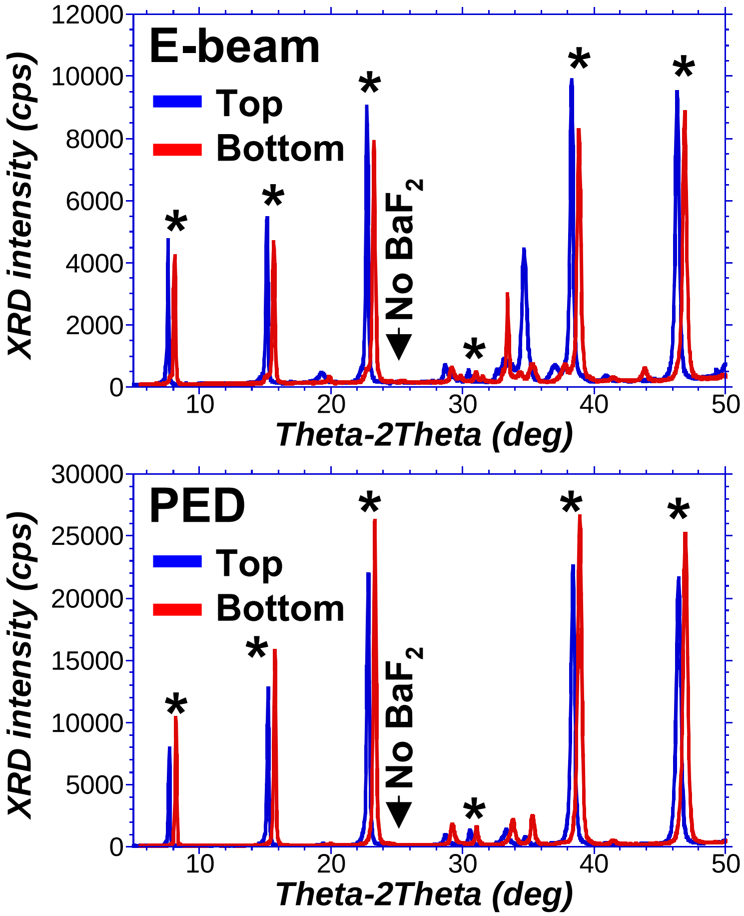
Limited or deferred plans

7. ✗ Process double-sided precursors.

- **Insufficient funds to procure non-contact heating for R2R buffer deposition.**
- **Performed stationary sequential 2-sided buffer deposition on short samples → non-uniform thin buffers.**

Slow conversion →

Low J_c believed to be due to inadequacy of thin non-uniform buffers.



8. ✗ Continue to collaborate with ANL to study conversion of precursors with R2R XRD and R2R Raman.

Deferred due to lack of funds.

FY2005 Plans (Scoring Criteria)

PED

1. Further develop R2R PED as a routine precursor deposition tool.
2. Optimize precursor to enable fast G_p with high J_c to the performance level of modified e-beam precursor.
3. Increase intra-granular J_c and pinning thru modifications such as composition variation , RE substitution or doping.
4. Jointly with Neocera, develop a high repetition rate PED source (>50Hz).

E-beam

5. Continue precursor modification to increase G_p and I_c/cm.
6. Increase I_c performance of 1 cm-wide precursor to that of small samples.
7. Transfer the deposition conditions to R2R evaporation system.

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8. Develop R2R low pressure system.
9. Collaborate with NIST and ANL on the phase development of ex-situ precursors.
10. Collaborate with SNL to develop solution precursor suitable for R2R slot-die coater.

Technology Integration (Scoring Criteria)

AMSC:
- AMSC RABiTS used in most ex-situ conversion studies in FY04.
- Discussions and assistances from AMSC on slot-die operation.
- AMSC conversion of ORNL PED precursors.
- Participation in WDG on e-beam precursor conversion (R.F.).

MetOx:
- On-site visits to ORNL & MetOx to discuss collaboration and CRADA.

Neocera:
- Regular contacts and visits to discuss PED operation.
- Tech transfer to Neocera concerning operation stability.

NIST-G:
- In-situ XRD of hybrid solution precursors.

SNL:
- R2R deposition of SNL solution precursor and buffer.

ANL:
- Analysis of R2R XRD and Raman data resulting in talks and publication.

U. Cincinnati:
- Work on non-fluorine precursor. Degree conferred to Ph.D. student now at UES.

U. Houston:
- Ph.D. student at ORNL on buffer & ex-situ conversion of YBCO.

Publications:
- 9 published. Many presentations.