ORNL-AMSC Strategic Research

American Superconductor Corporation

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FY 2006 Funding: $800 K - DOE-OE
$180 K -Funds-in from AMSC
Matching funds at AMSC

CRADA Objectives

Carry out R&D required for achieving the cost/performance necessary for commercial HTS applications

Provide technical assistance to scale up of AMSC's Pilot operation

Provide advanced measurements and characterizations to assist AMSC's development of a commercial 2G HTS wire based on the MOD/RABiTS™ technology

FY 2006 CRADA Goals (1)

- **Assist AMSC personnel in manufacturing alloy substrates (4 cm wide by 100 m long) using the ORNL rolling mill facility with clean room.**
  - ✓ Over 4 km of 4 cm wide NiW substrate was produced in the ORNL rolling mill facility
- **Improve the RABiTS™ template manufacturing reliability through fundamental characterization of buffer layer properties and uniformity along length and width.**
  - ✓ Improved quality and reduced variability in AMSC's RABiTS template production
- **Development of improved buffers or buffer architectures leading to improved performance and/or reduced manufacturing cost**
  - ✓ Increased deposition rate; improved seed texture
- **Optimization of self-field Ic and pinning mechanisms in 0.8 – 2.0 µm thick YBCO films produced in AMSC's Pilot manufacturing line**
  - ✓ Qualified RE-nanodot insertion into AMSC baseline production
  - ✓ Optimized performance of 1.4 µm YBCO R&D demo

FY 2006 CRADA Goals (2)

- **Demonstration of solution deposited buffer layers in a continuous process with performance comparable to AMSC's standard CeO_2/YSZ/Y_2O_3 buffer architecture produced by physical vapor deposition**
  - ✓ Demonstrated *Ic* on continuously deposited LZO buffer
- **Development of a reel-to-reel direct printing technology for striated YBCO films.**
  - ✓ Moved to ORNL Conductor Design for HTS Applications Talk (F.A. List)
- **Characterization and testing of 2G HTS wires and wire products**
  - ✓ Deferred until FY07

How the ORNL CRADA Operates

- **FY2006 Funding**
  - $800 K at ORNL (funding from DOE-OETD and matching funds at AMSC)
  - $180 K funds-in from AMSC
- **Proprietary Information Agreement protects confidential ideas, enabling free exchange during meetings**
  - 2 CRADA related patents filed in FY2006
- **Program activity reviews, weekly teleconferences, sample exchange, AMSC scientist/engineers work at ORNL facilities**
  - Over 130 samples exchanged/studied in FY2006
  - AMSC scientists/engineers worked for 12 weeks at ORNL
- **AMSC supplies high quality RABiTS template for ORNL core program work**

Inter-related Collaborations Support Rapid Development of 2G Technology

AMSC
Baseline Production

WDG
Fundamental Studies and Characterization

R&D Samples
(4 cm x 2 m)

ORNL CRADA
Long Length Baseline Development

(4 cm x 20 – 100 meter)

- Process Optimization
- Process Qualification
- Failure Analysis
- Cost Reduction

Special capabilities:
4 cm Ic measurements (LANL)
X-ray characterization (ORNL)

AMSC-ORNL CRADA Presentation

- **FY 2006 Results**

  ORNL-AMSC CRADA Goals **(Wei)**
  2G Development (YBCO/RABiTS) at AMSC
  2G wire manufacturing at AMSC: ORNL contributions

  Scale-up of MOD HTS: Optimization of Pilot production to fabricate high performance conductors **(Amit)**
  Scale-up of MOD LZO solution buffers on RABiTS

  Fundamental development of solution buffer layers **(Parans)**

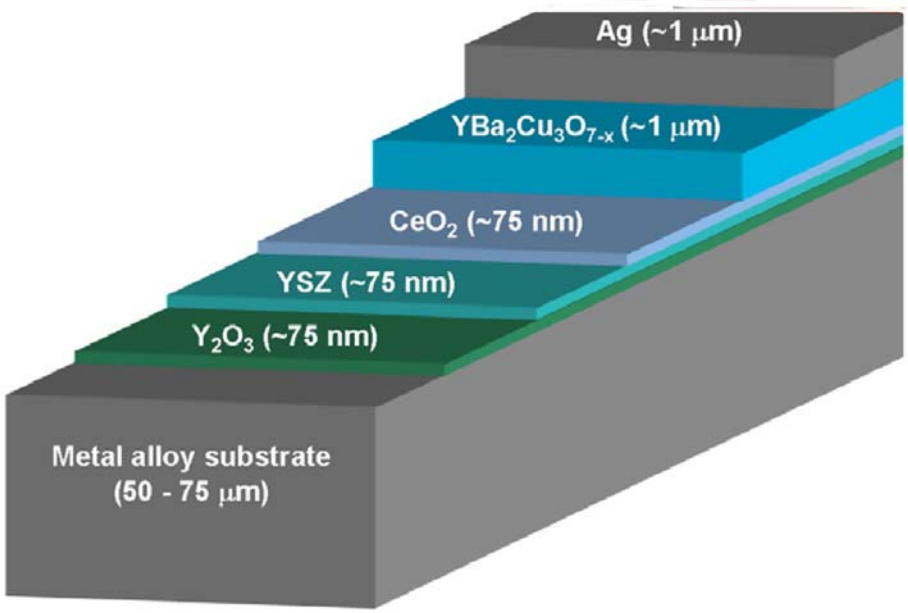
- **FY 2006 Performance and FY 2007 Plans** **(Parans)**
- **Research Integration**

AMSC's 2G HTS Wide Strip Technology

RABiTS / MOD 2G Strip Architecture

Width Evolution
1 cm → 4 cm → 10 cm

- **Substrate: Ni-5at%W alloy**
  - Deformation texturing
- **Buffer stack: Y_2O_3/YSZ/CeO_2**
  - High rate reactive sputtering
- **YBCO**
  - Metal Organic Deposition of TFA
- **Ag**
  - DC sputtering



- Not to scale -

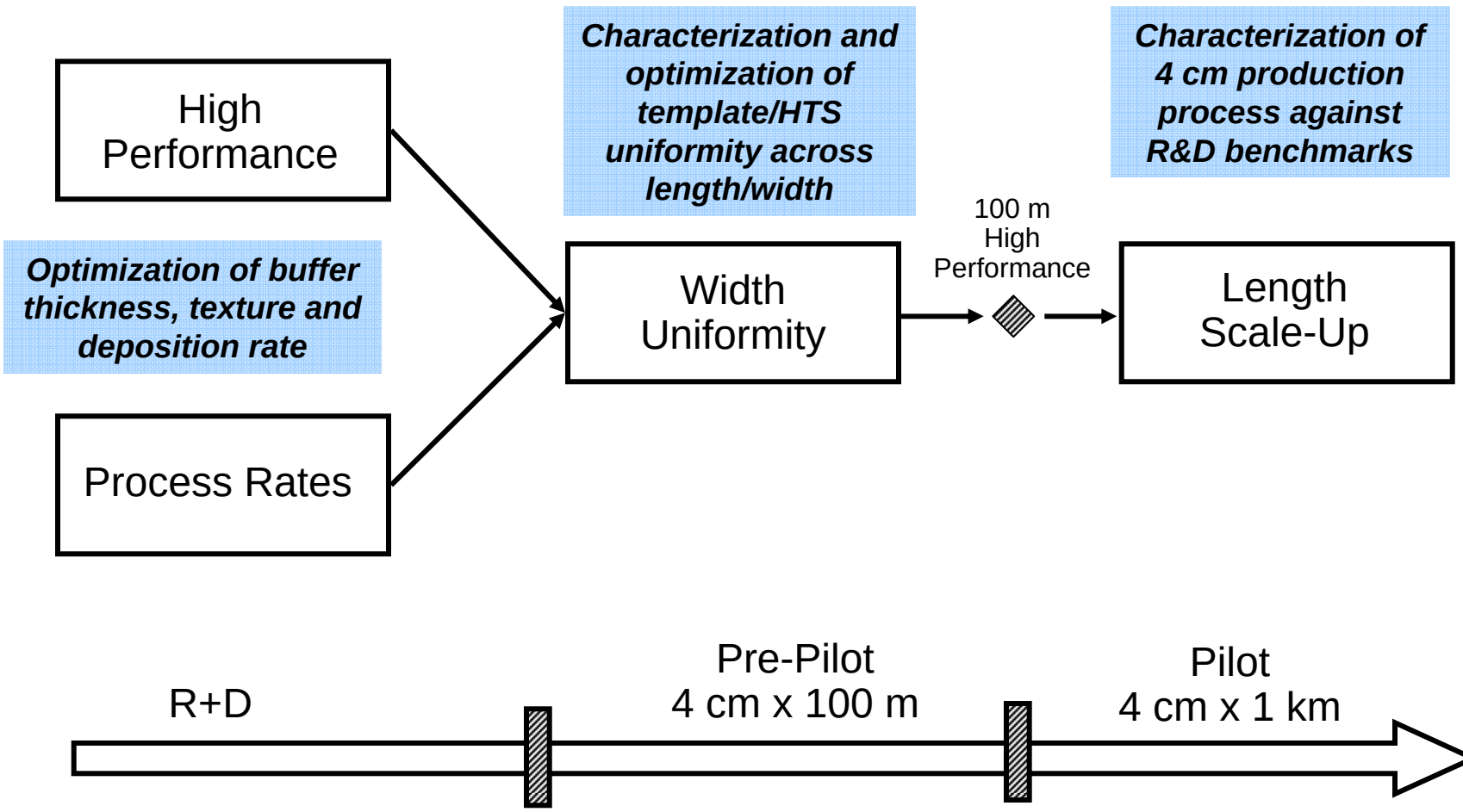
Wider strips facilitate high throughput manufacturing and reduce cost

FY2006 AMSC Focus

- **2G Scale-Up**
  - 4 cm pilot operation
    - 4 cm equipment development/installation
    - Improve process rate
  - Routine production runs (~100 meter)
- **Supporting R&D**
  - Nanodot insertion for improved pinning increased I_c
  - Thick film demonstration for high I_c
  - Low-cost process development
    - Solution buffers
  - Substrate improvement (strength and thickness)

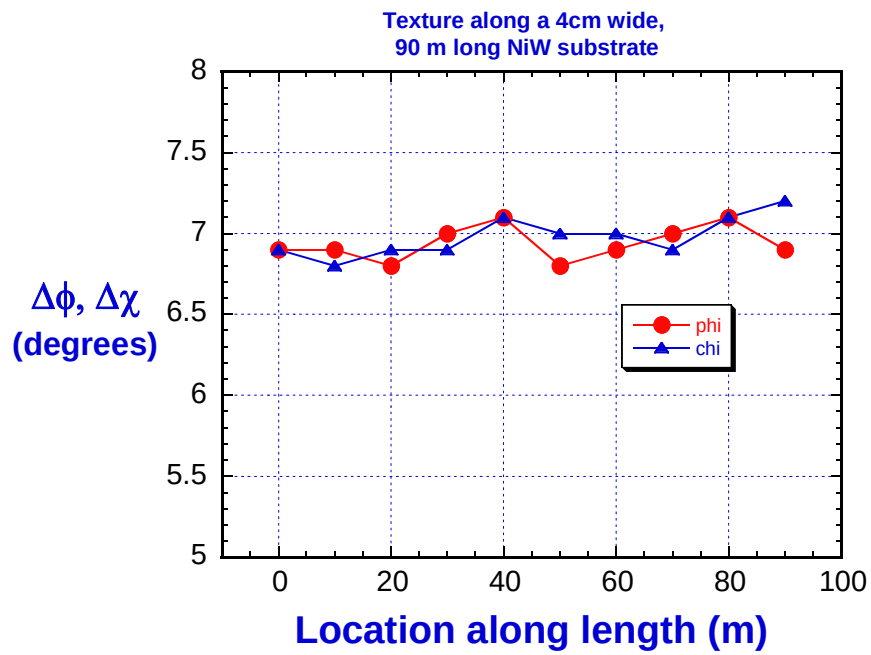
ORNL team provided critical R&D and characterizations for implementing 4 cm process

ORNL CRADA Supports Development of Continuous Processing



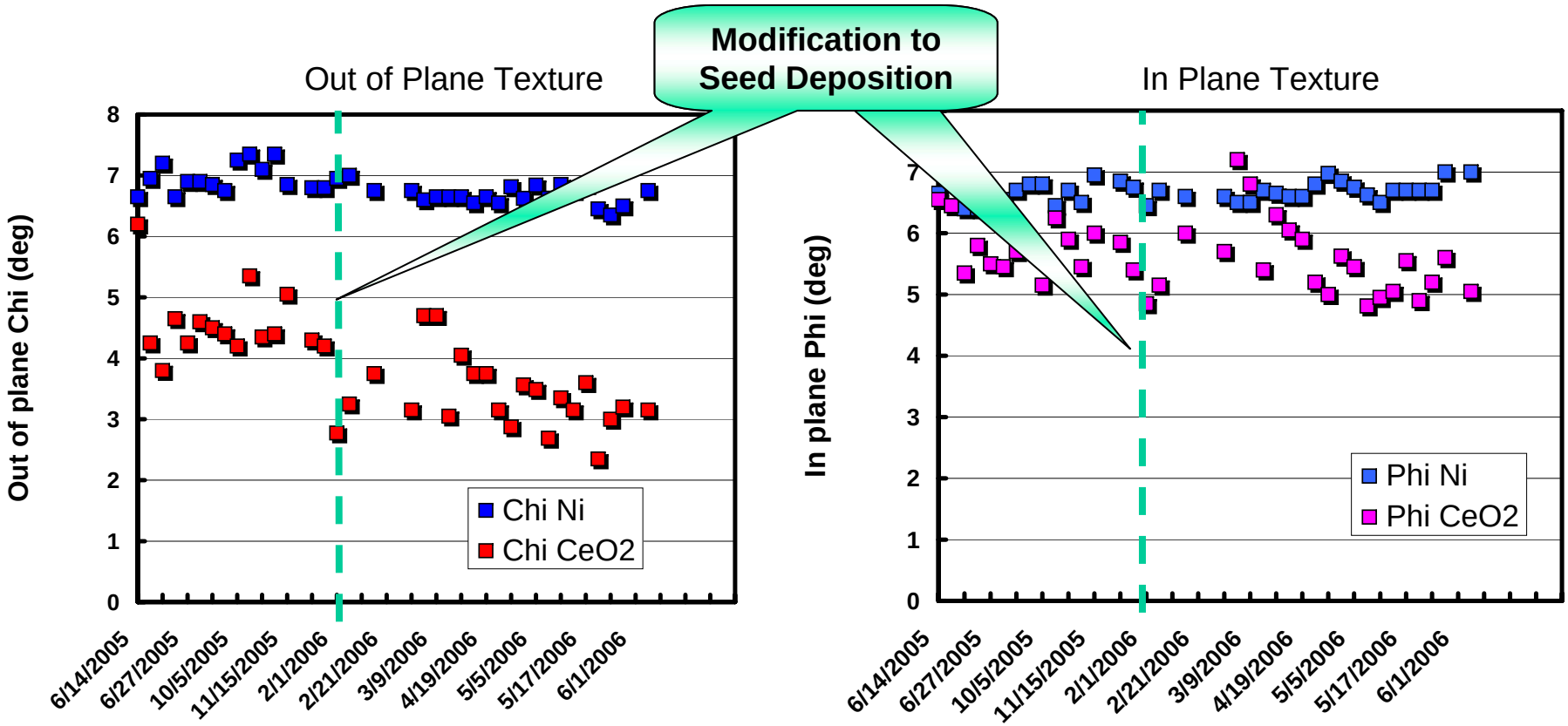
Substrate Production

- AMSC's Pilot substrate facility is functional
  - Rolling Mill
  - Degreaser
  - Texture Anneal Furnace
- Pilot rolling mill produces substrate in 100 m length
  - In-plane texture $\phi = 6.9°$
  - Out-of-plane texture $\chi = 7.0°$
- ORNL rolling facility was used throughout FY2006 to supplement AMSC 2G production



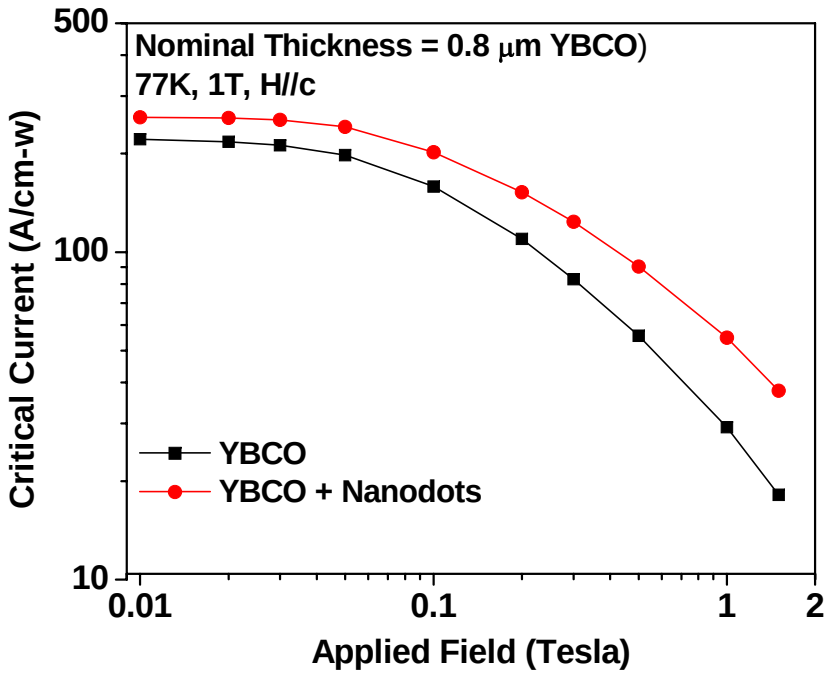
Excellent progress in bringing front-end Pilot equipment on-line

RABiTS™ Template 100m Production

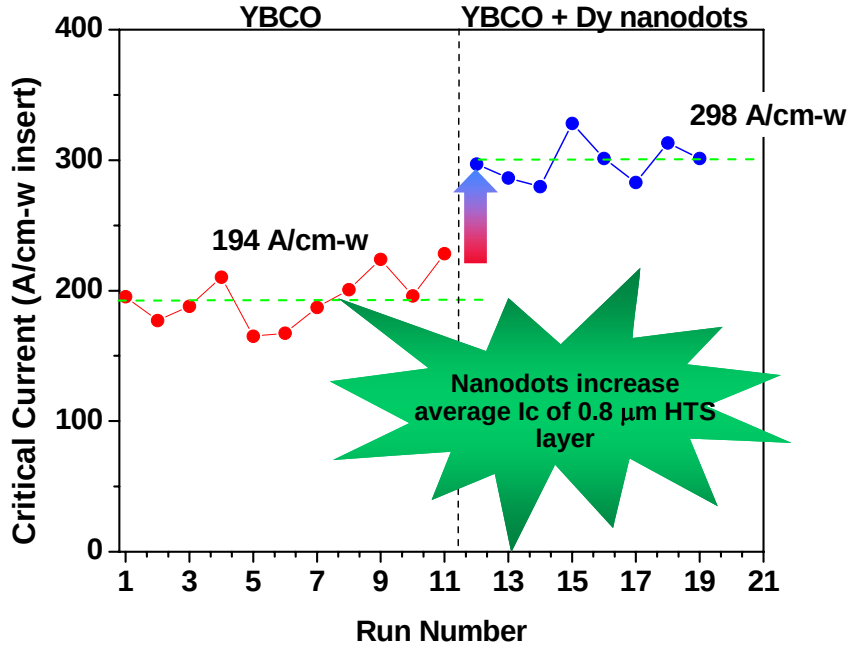


Seed deposition improves texture relative to substrate

YBCO+Nanodot Insertion into Production



Production Runs of 4 cm Strips

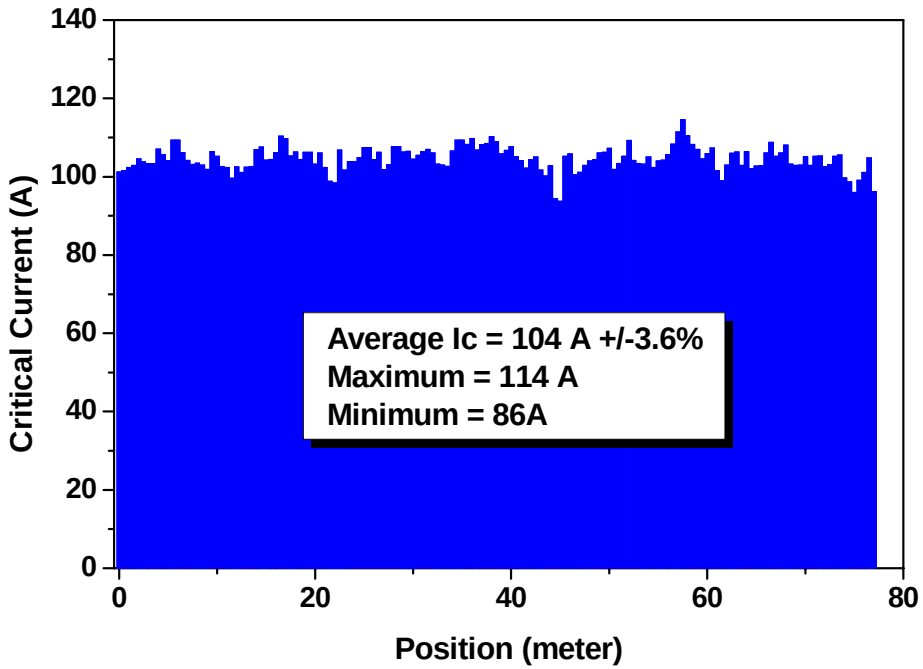


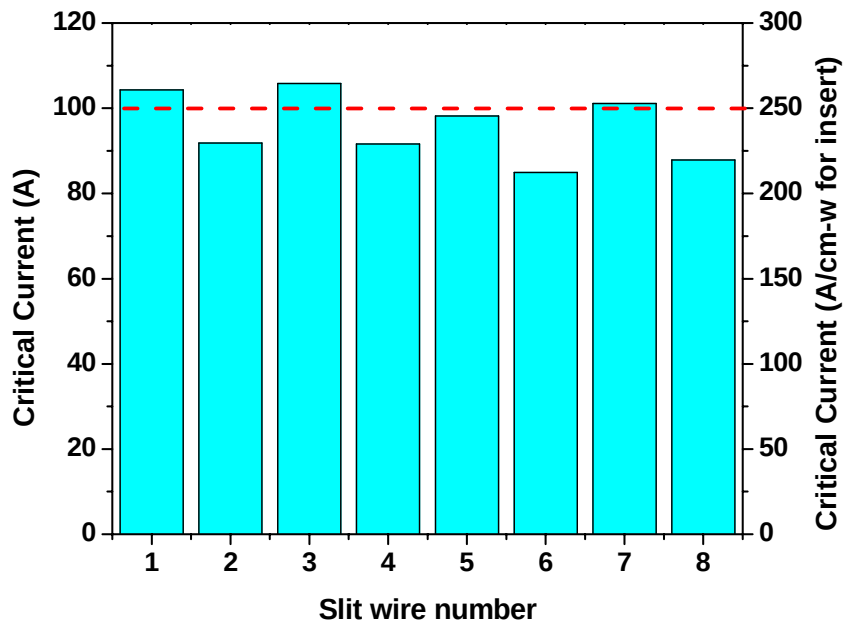
Goyal-ORNL

YBCO+nanodot improves both c-axis pinning and self field performance

344 Superconductors (Final Slit and Laminated Wire) Achieve 100 A Performance

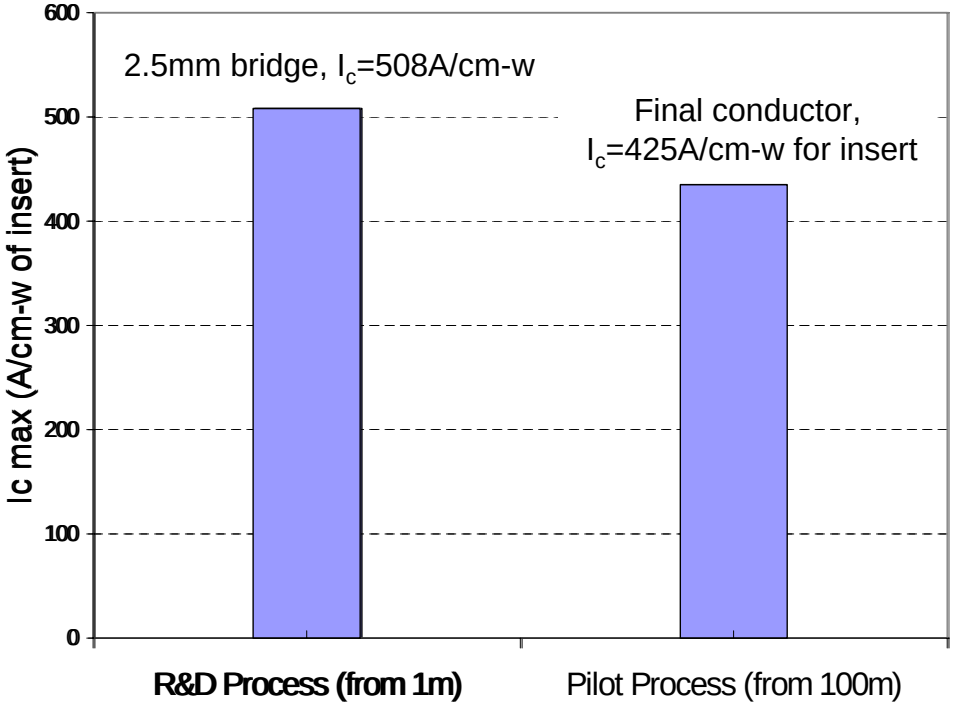
YBCO with Dy-nanodots
Single Coat (0.8 μm)

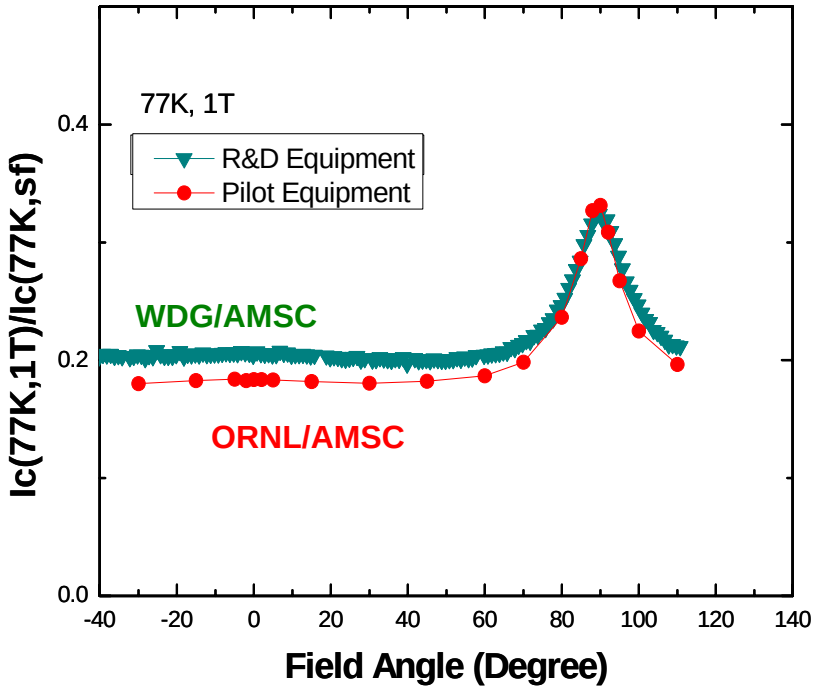




100 A performance in 344 superconductor achieved with single coat

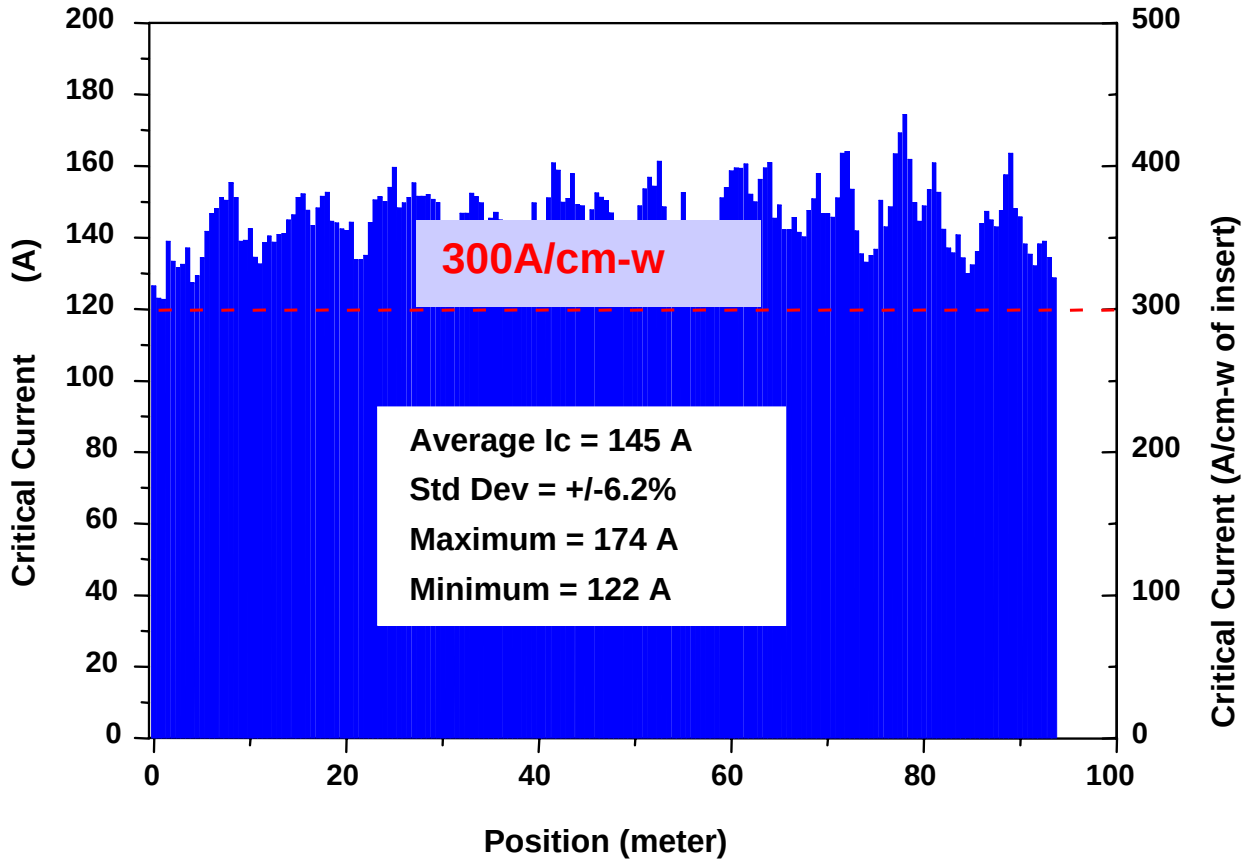
Demonstrate 1.4 µm Process in Pilot Operation





Successfully transferred R&D knowledge to long length process

344 Superconductors Achieve 77 K I_c of 141A (350 A/cm-width of insert) over 94m



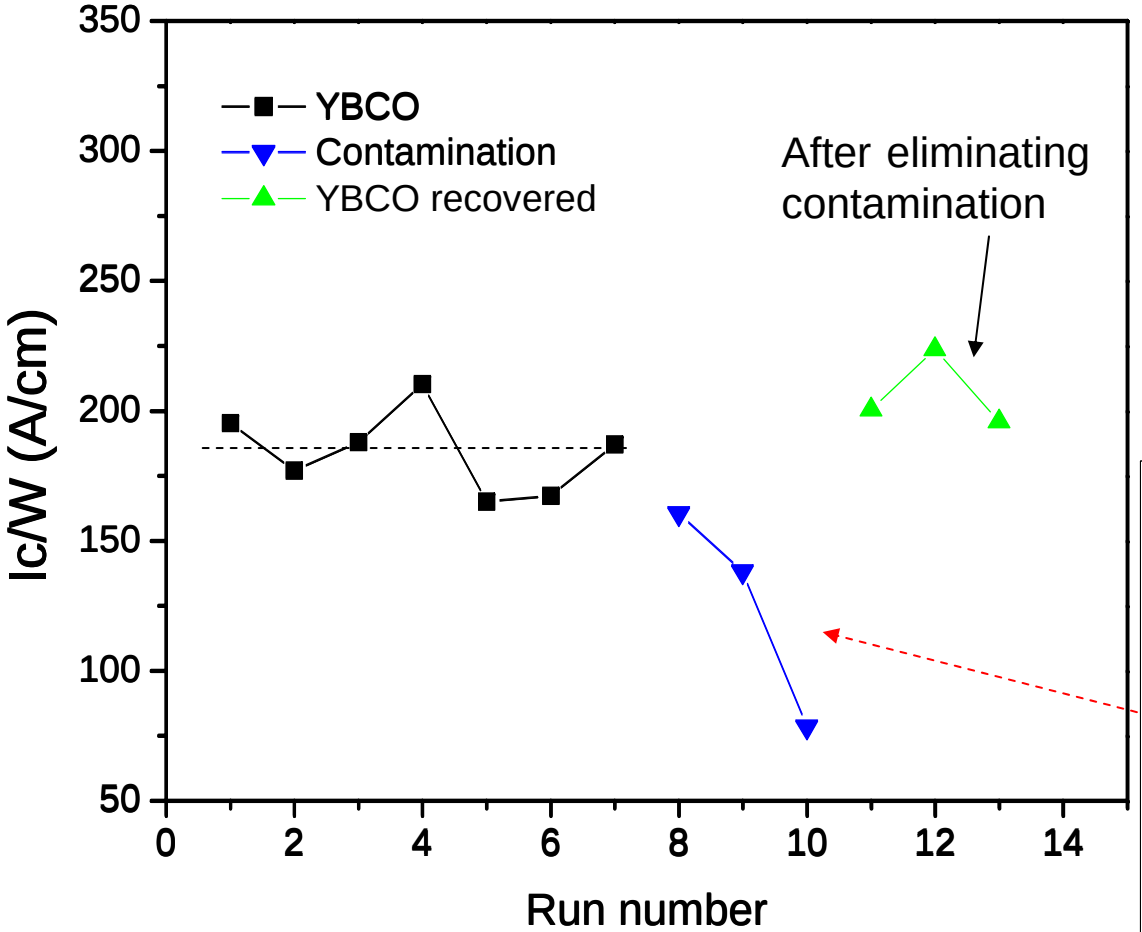
344 superconductors achieve DoE FY2006 Goal of 300 A over 100 m

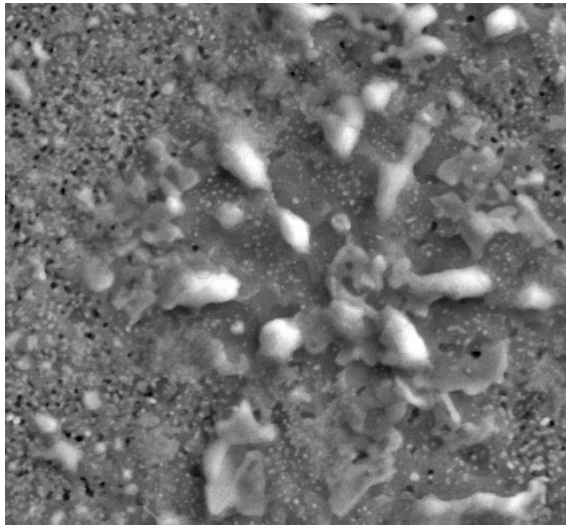
ORNL Scientists Also Played Critical Role in Trouble Shooting Unexpected Issues in Pilot Operation

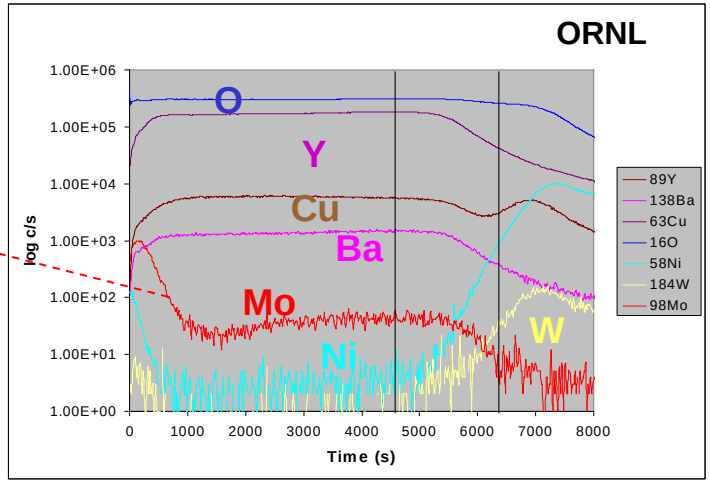
- **Contamination in YBCO processing**
- **Stacking faults reduction**
- **Contamination in rolling lube**

Rapid response by ORNL group essential to maintaining schedule for bringing pilot operation on-line

ORNL Scientists Play Key Role in Identifying Contamination Issue in 2G Manufacturing

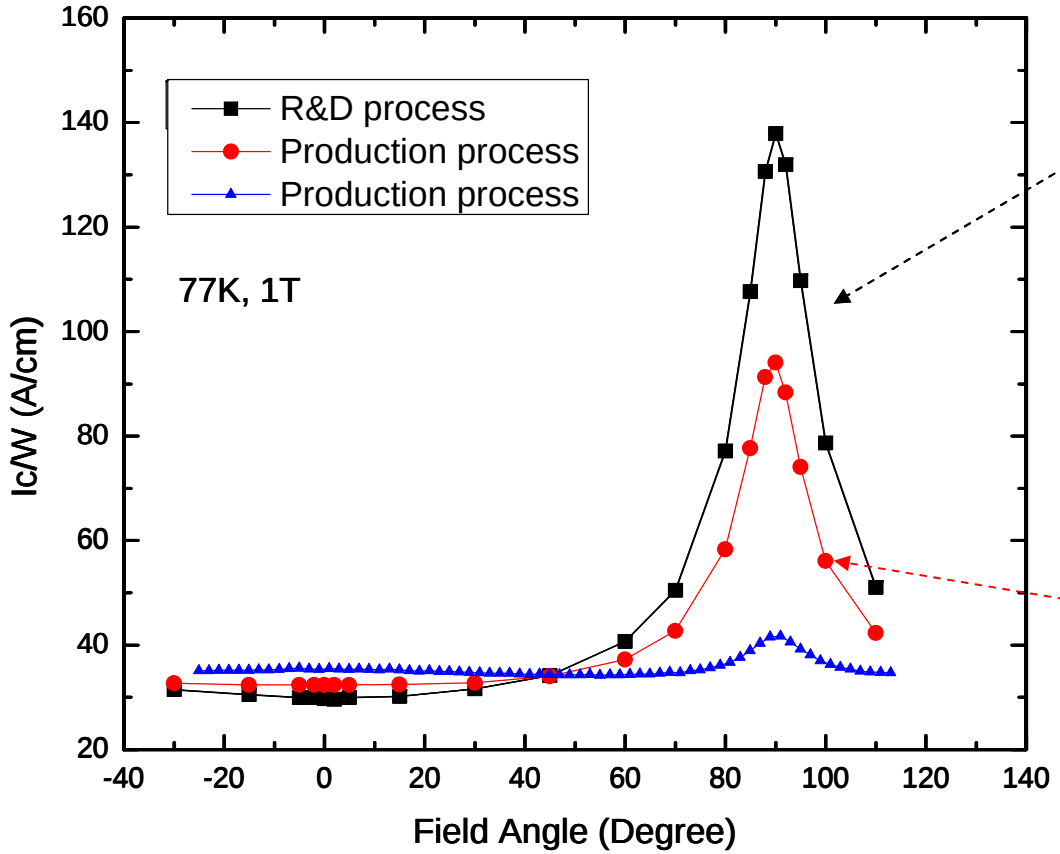


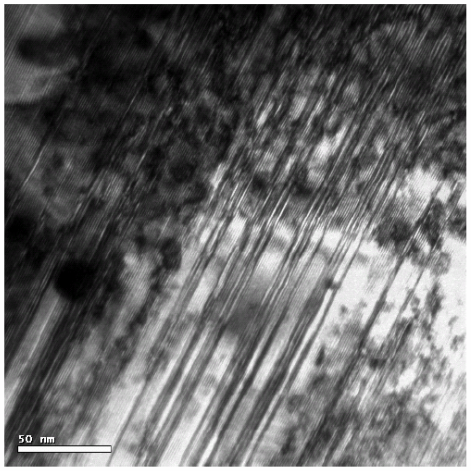


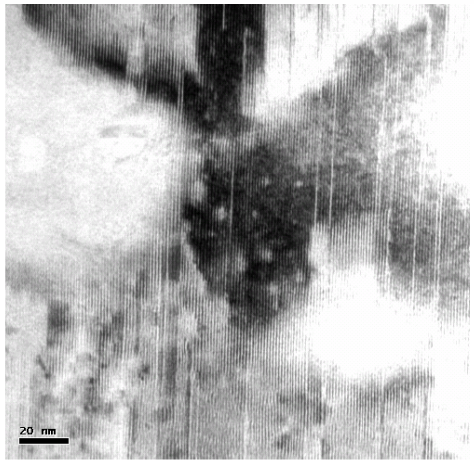


Problem rapidly identified and resolved

Problem: ab-plane I_c Suppressed in Pilot Process







Civale – LANL/WDG **Goyal – ORNL**

Goyal – ORNL

ORNL helped identify the processes responsible for the reduction of H//ab pinning

AMSC-ORNL CRADA Presentation

- **FY 2006 Results**

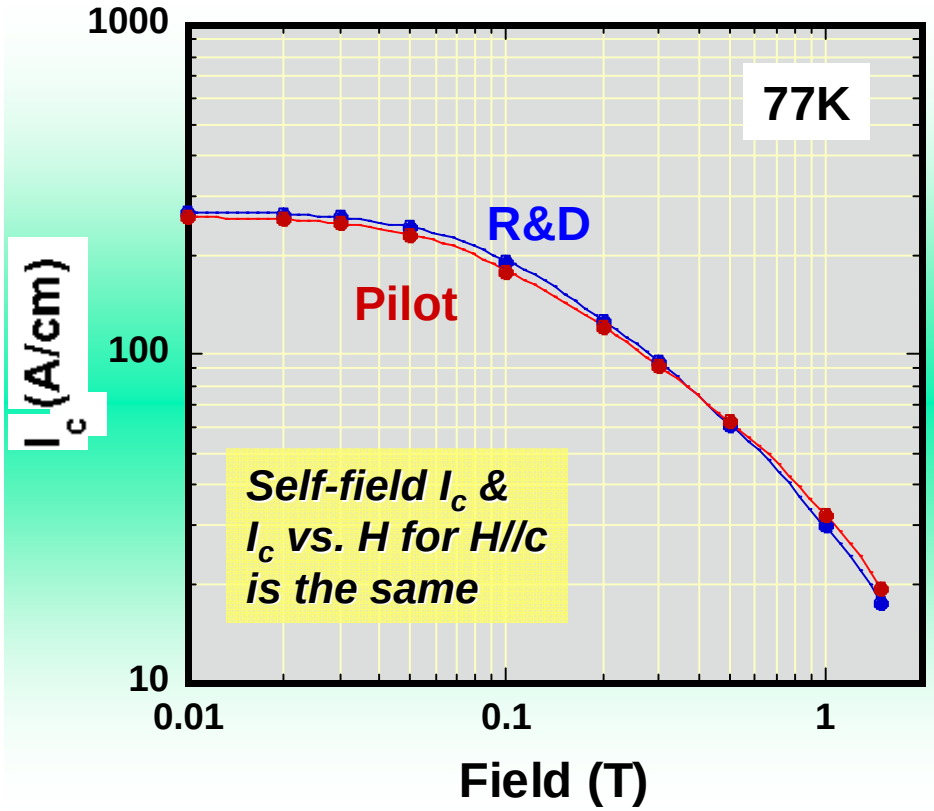
  ORNL-AMSC CRADA Goals **(Wei)**
  2G Development (YBCO/RABiTS) at AMSC
  2G wire manufacturing at AMSC: ORNL contributions

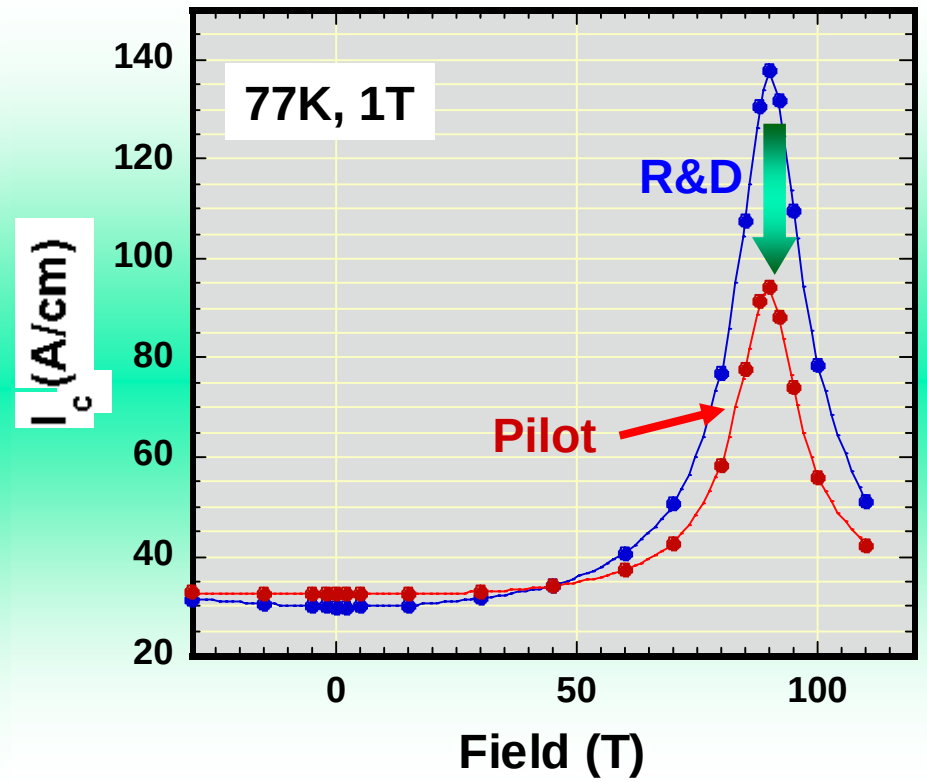
  Scale-up of MOD HTS: Optimization of Pilot production **(Amit)**
  to fabricate high performance conductors
  Scale-up of MOD LZO solution buffers on RABiTS

  Fundamental development of solution buffer layers **(Parans)**

- **FY 2006 Performance and FY 2007 Plans** **(Parans)**
- **Research Integration**

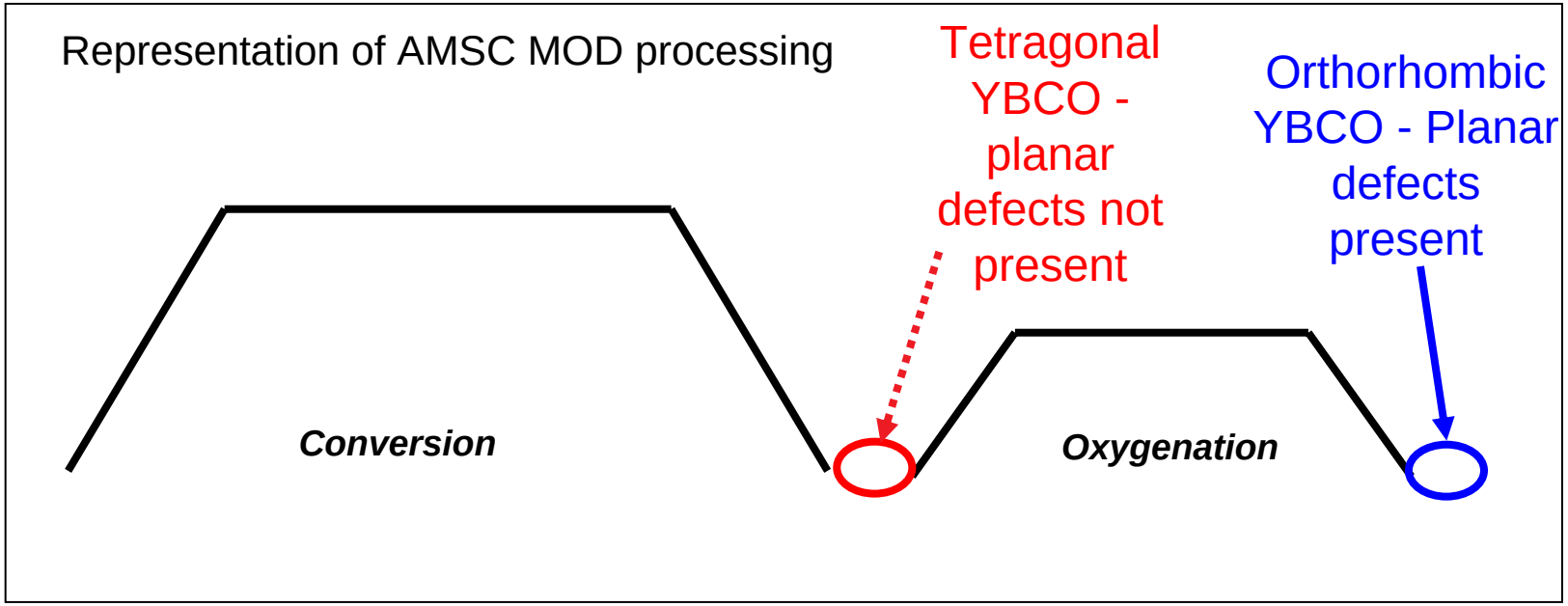
Problem: Angular Dependence of I_c of 344 Superconductors Produced in AMSC's Pilot Operation Differed from R&D Samples



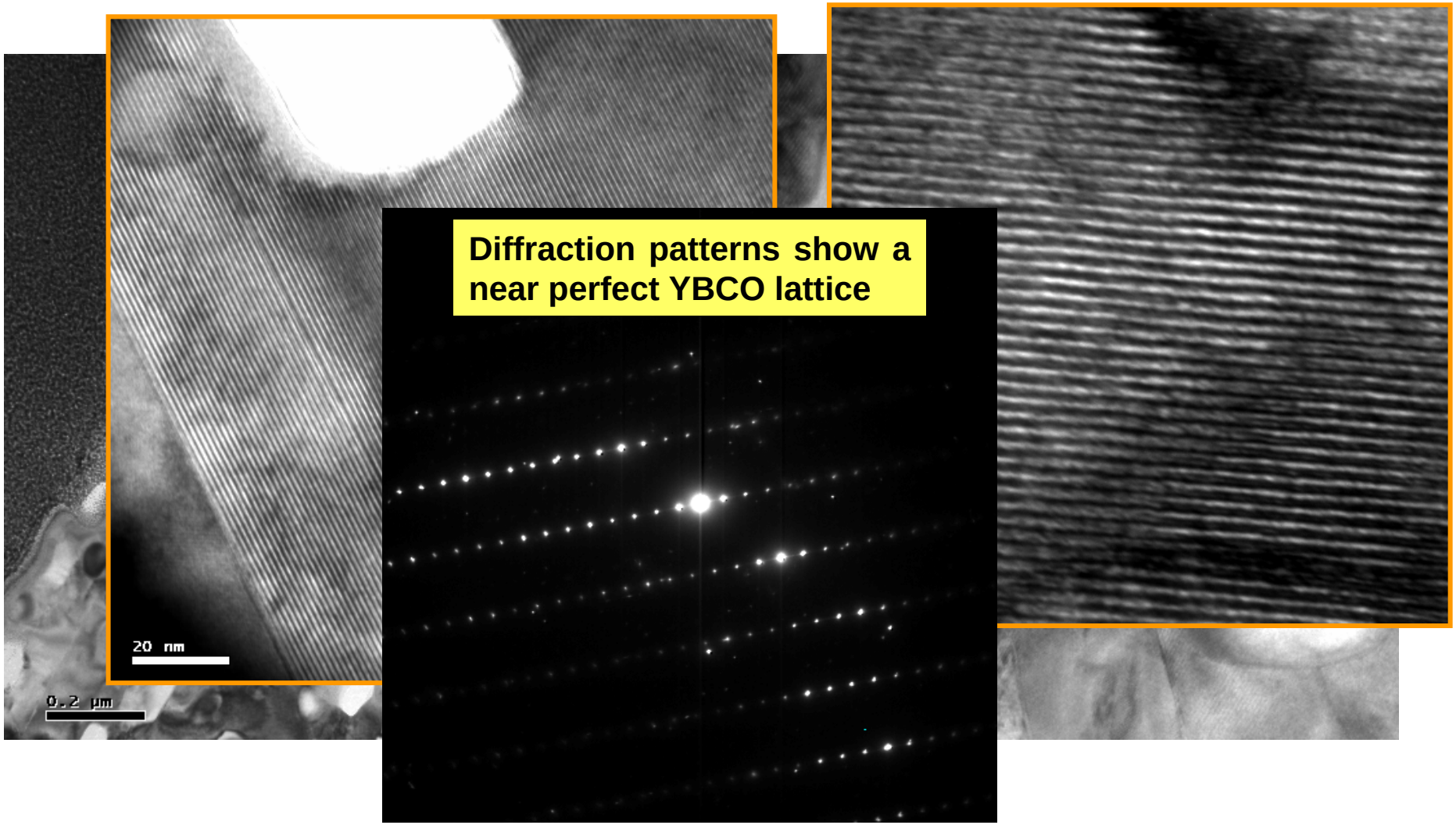


Angular dependence of I_c of pilot produced samples is significantly lower!

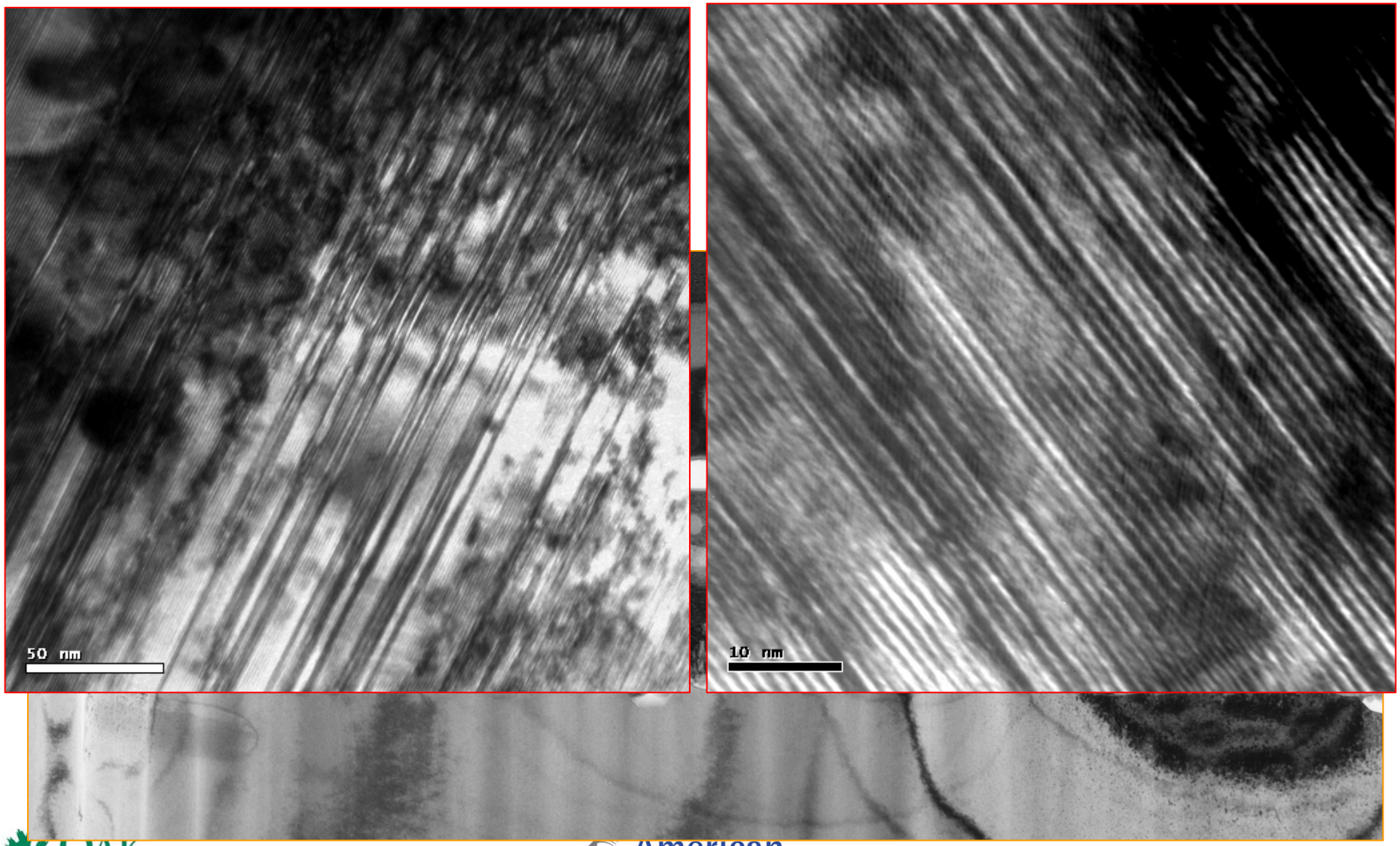
Origin of Planar Defects in AMSC MOD-YBCO Process



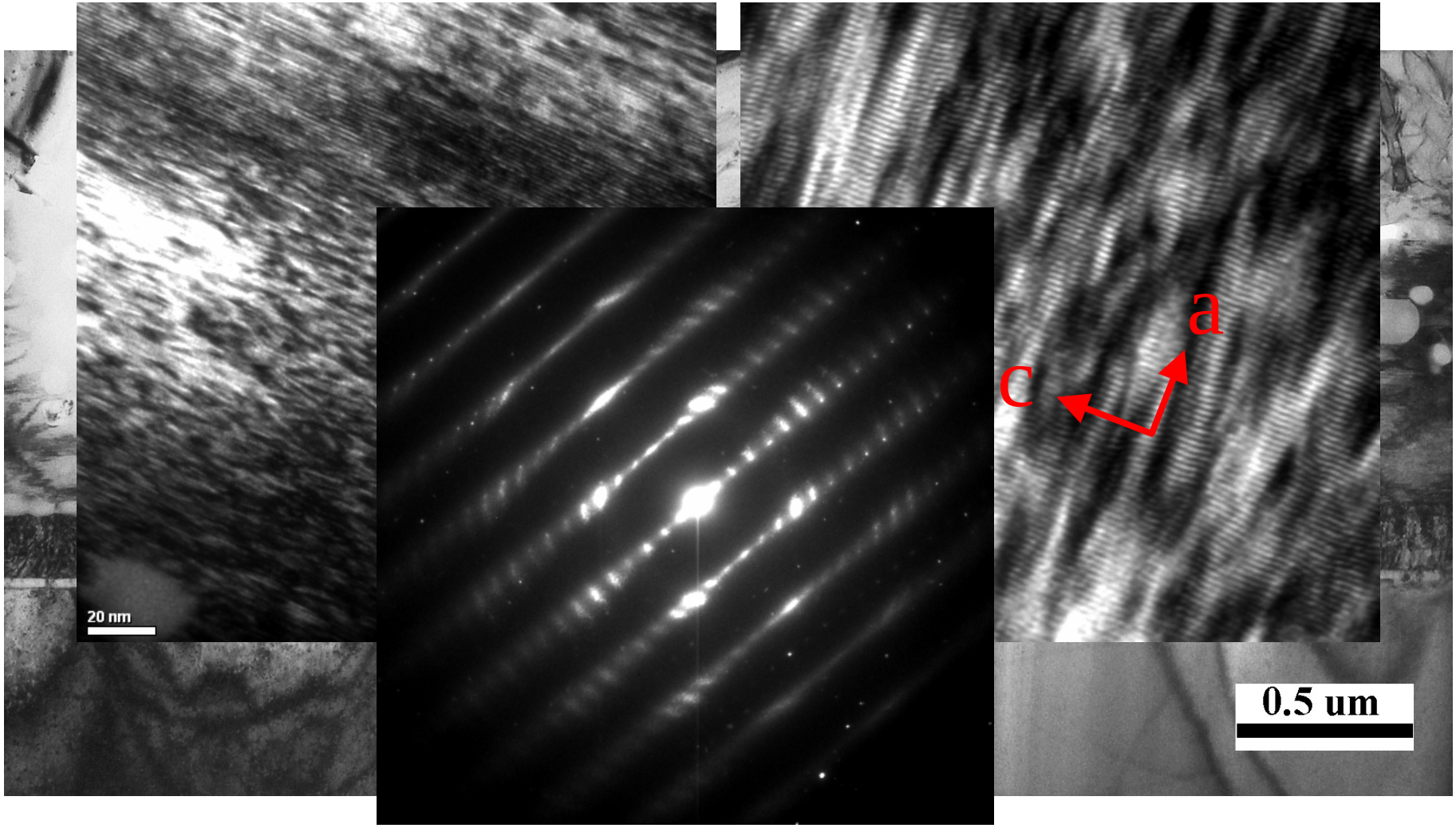
Before Oxygenation, R&D YBCO Films Reveal a Well Defined Lattice



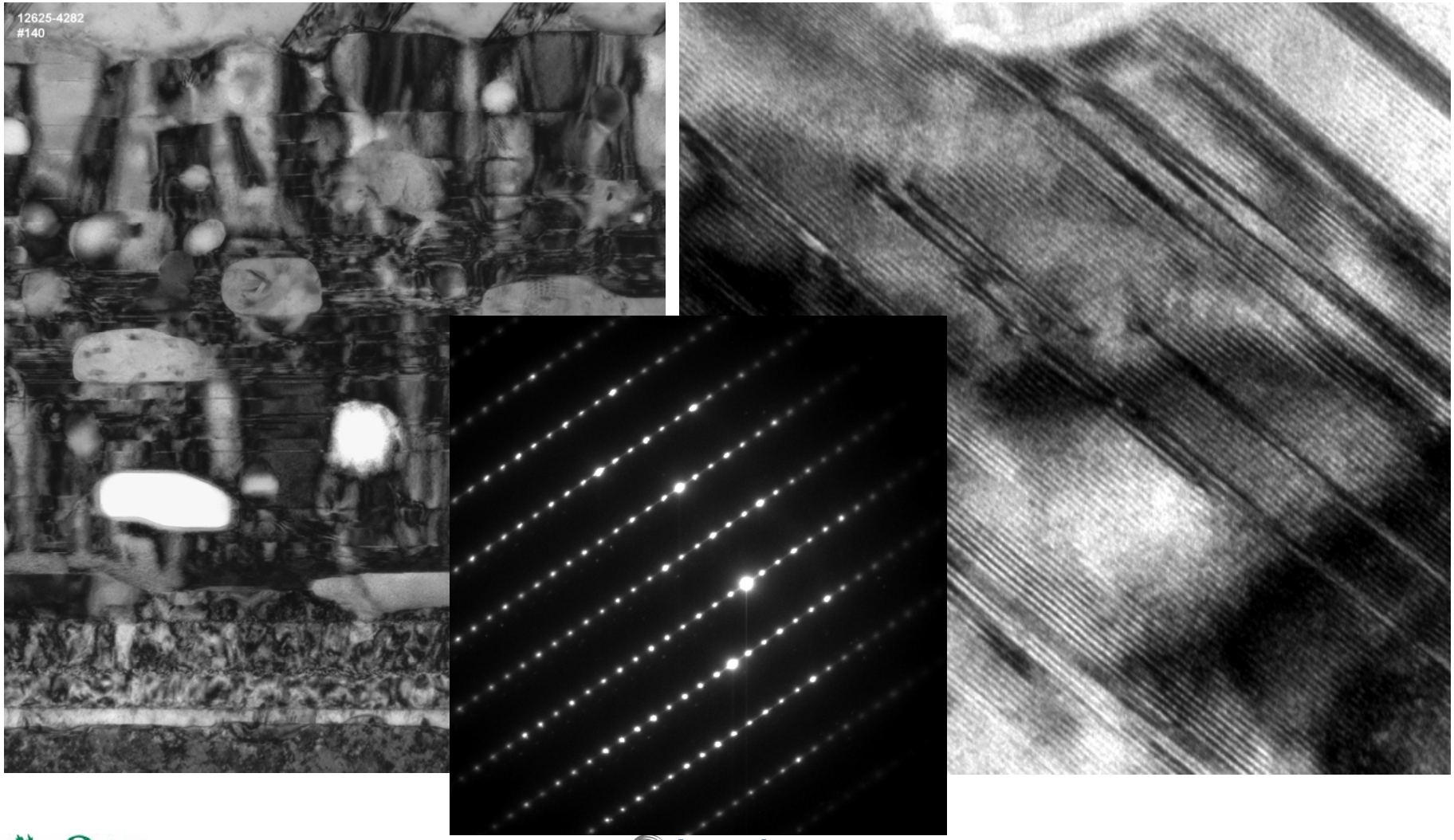
High Density of 124-type Stacking Faults Form during Oxygenation Step in R&D Process



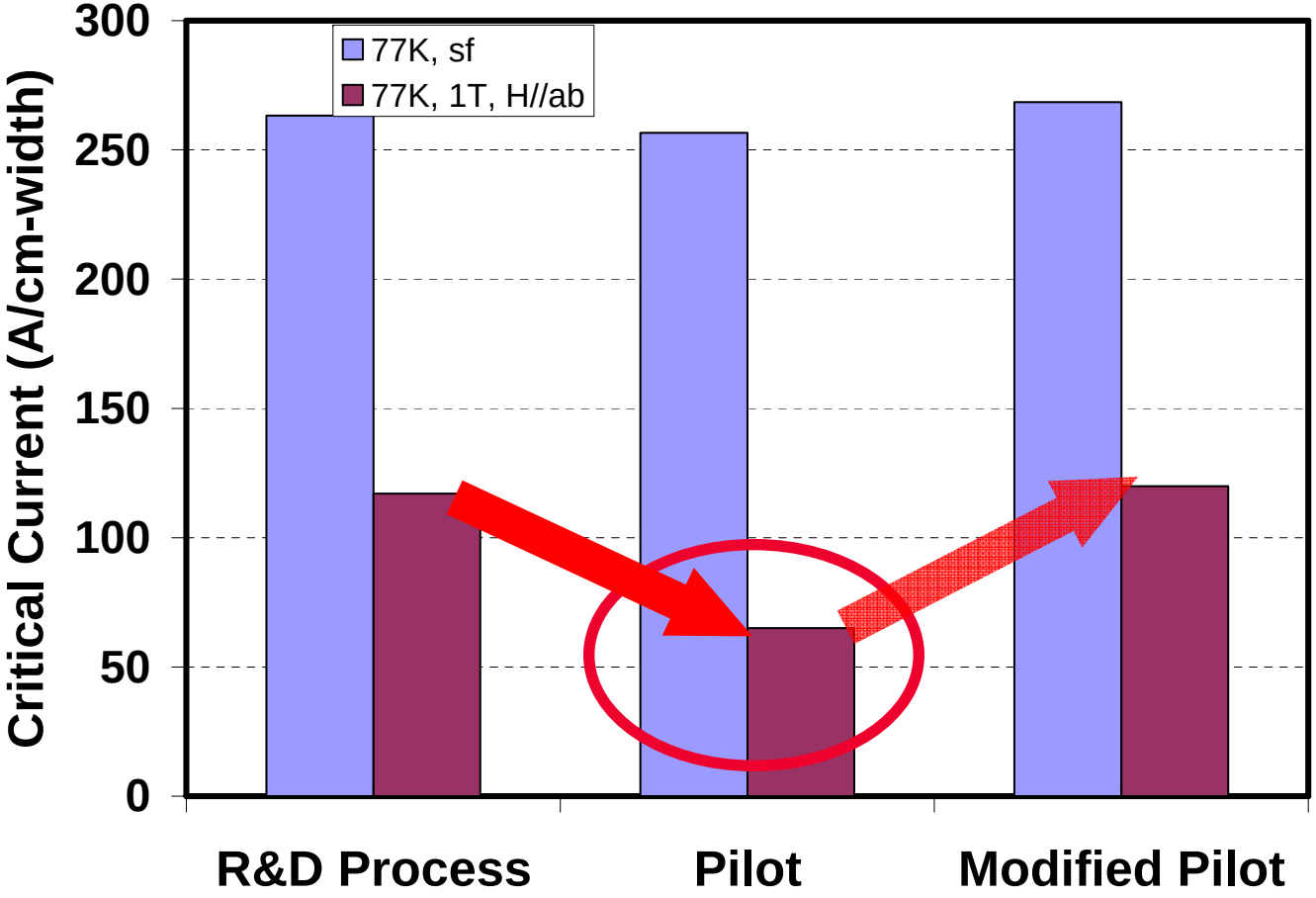
Reel-to-Reel Process Used in AMSC Pilot Operation Disrupts YBCO Lattice



Subsequent Oxygenation Step Restores YBCO Lattice, but Density of 124-type Stacking Faults is Reduced

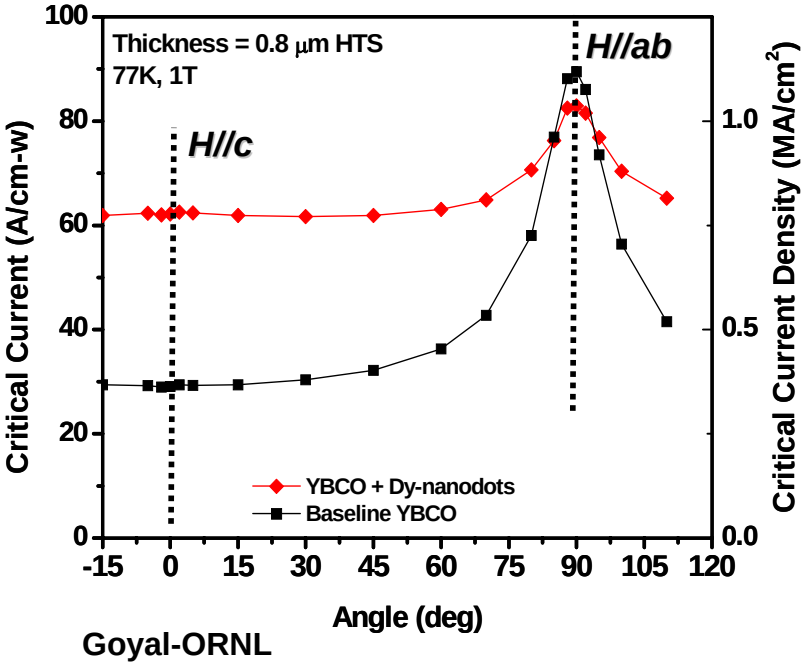


Pilot Equipment Modified to Prevent Disruption of YBCO Lattice – Performance now Matches that of R&D Samples



High I_c obtained for H//ab by modified pilot process!

Characterization of YBCO + Dy-nanodots (0.8 μm) Films Produced in Pilot Operation Aided Insertion into AMSC's Baseline Production



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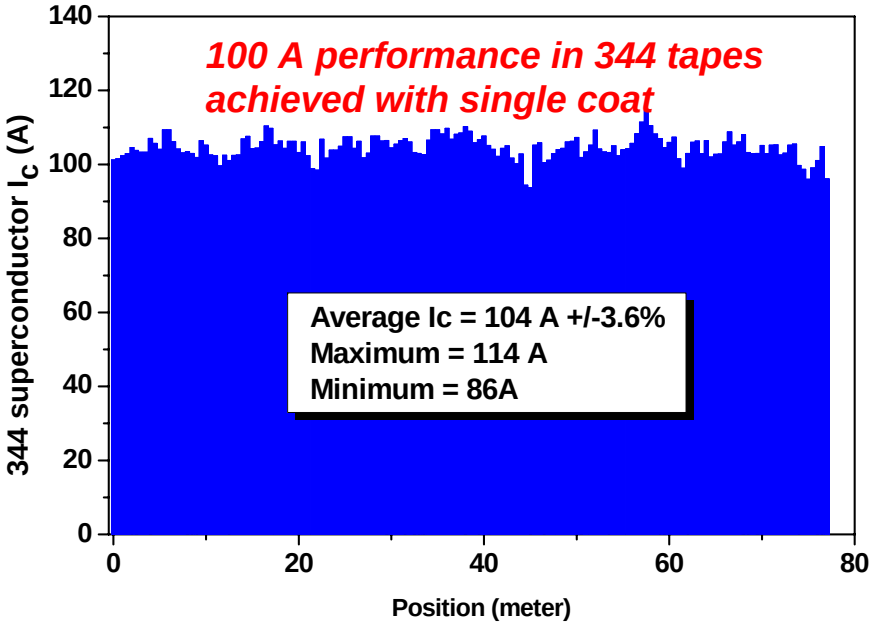
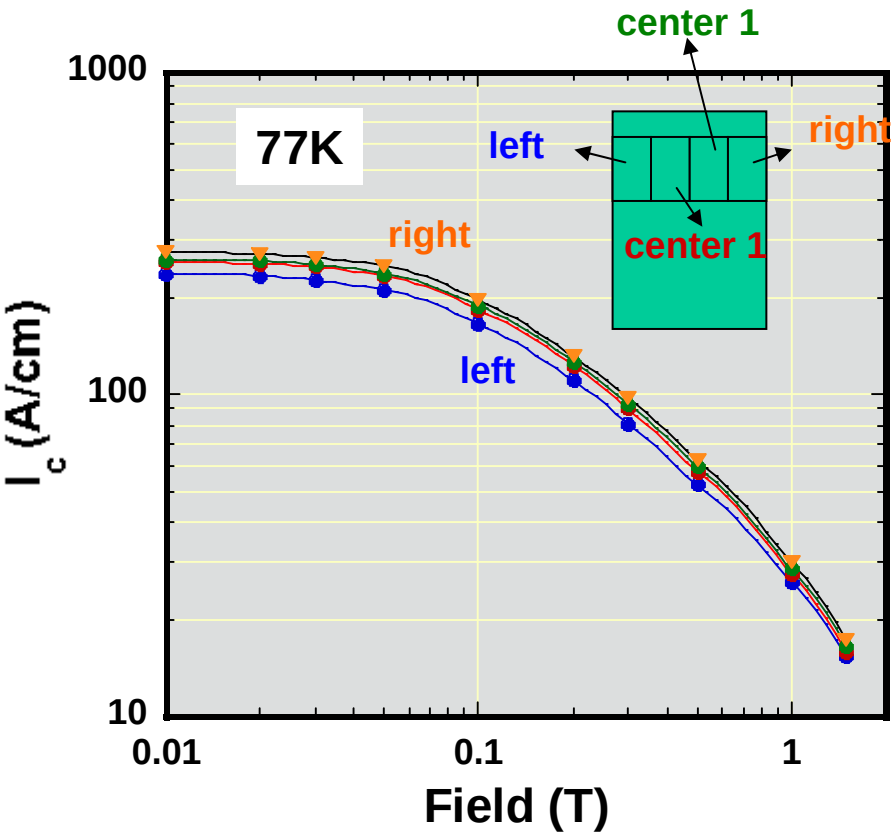
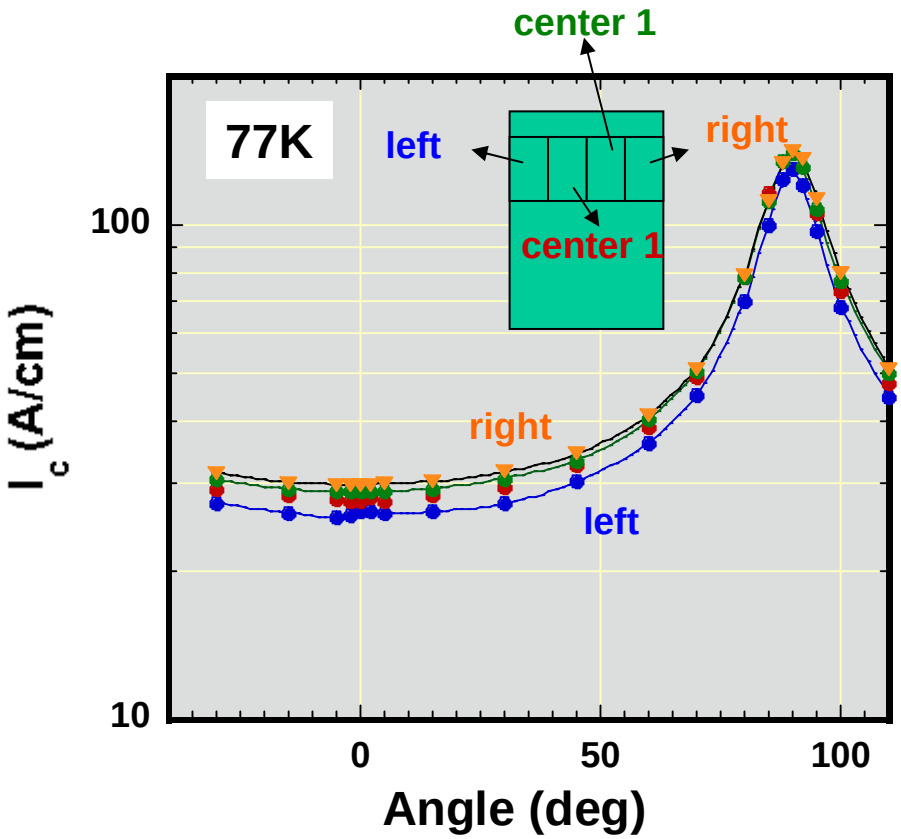


YBCO with Dy-nanodots demonstrated in R&D in FY2005

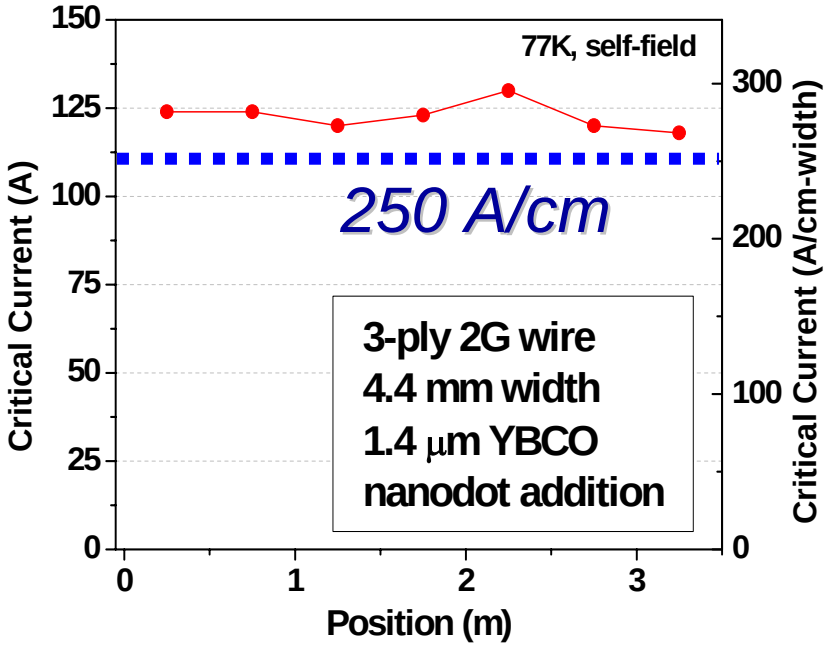
YBCO with Dy-nanodots inserted into AMSC Baseline production in FY2006

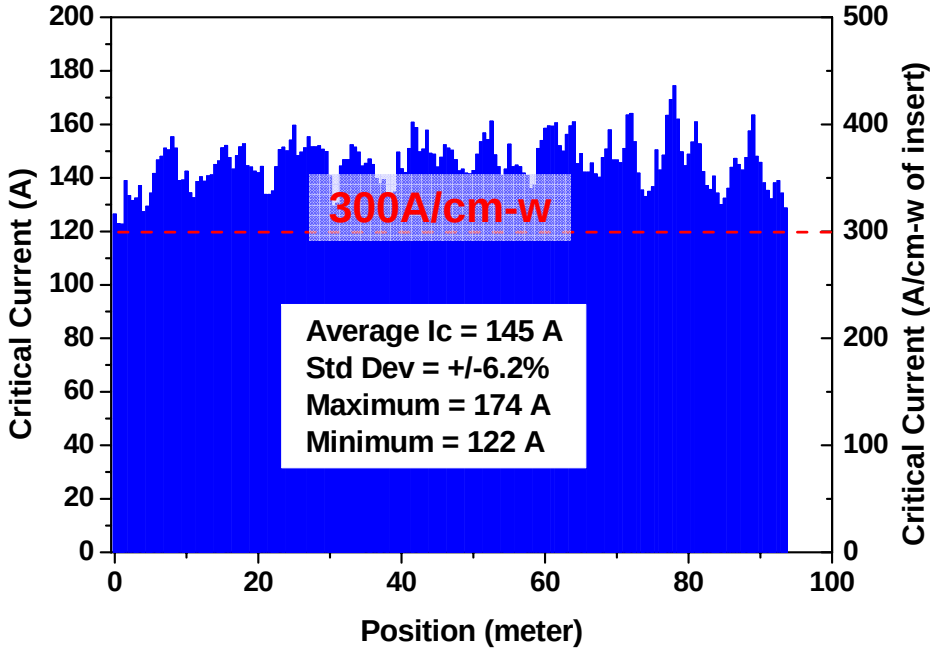
Homogeneity in Performance across the Width of the 4cm Wide Tape Confirmed in Pilot Operation





Characterization of 1.4 μm (YBCO/Dy-nanodots + YBCO) Films Produced in Pilot Operation 100 Meter Process

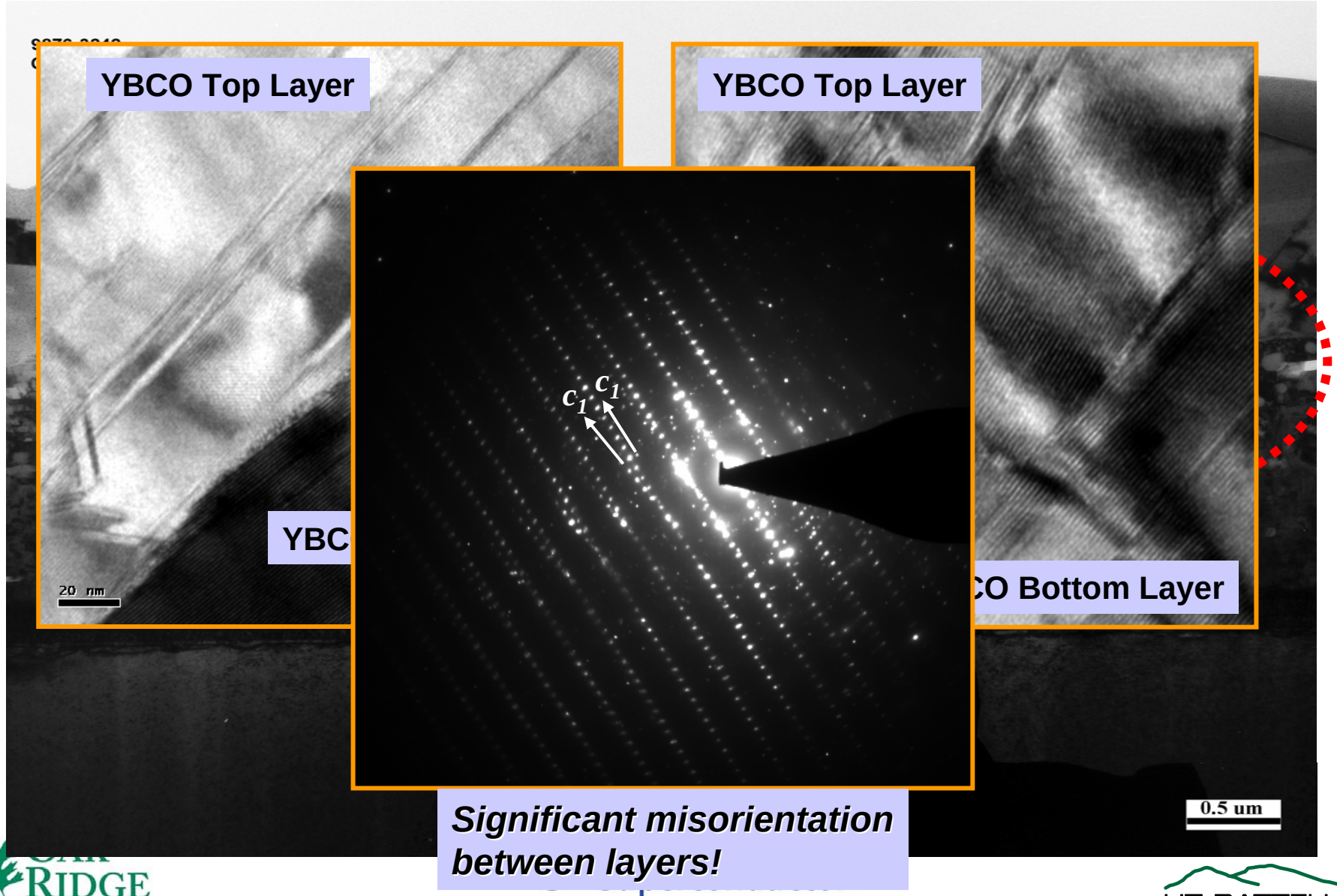




1.4 μm Hybrid HTS (0.8 μm YBCO/ Dy nanodots + 0.6 μm YBCO) demonstrated in R&D in FY2005

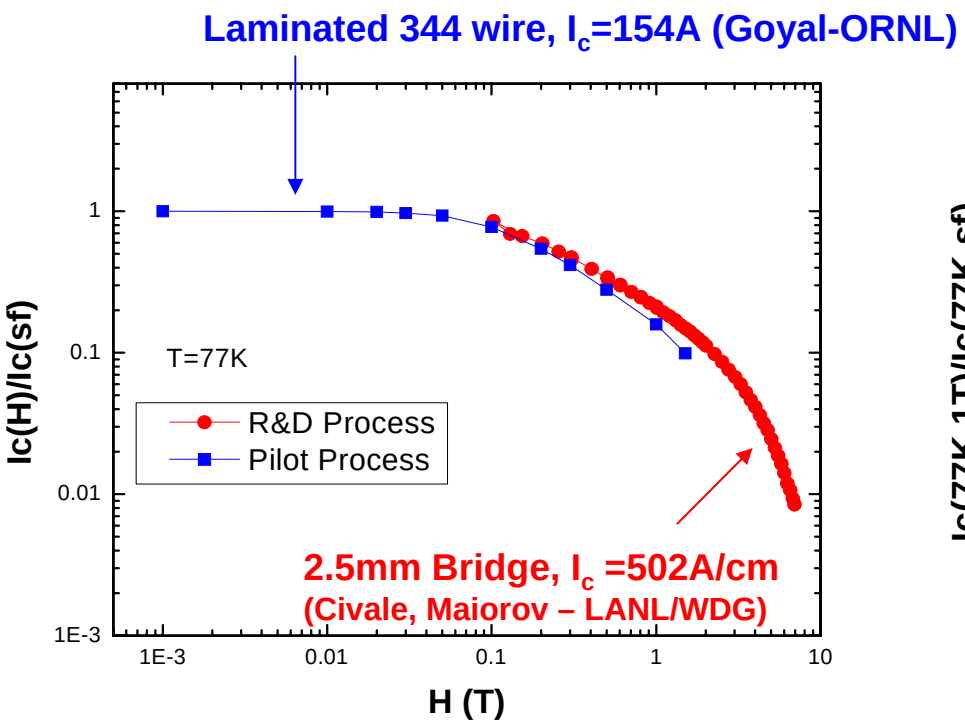
1.4 μm Hybrid HTS (0.8 μm YBCO/Dy nanodots + 0.6 μm YBCO) demonstrated in Pilot facility in FY2006

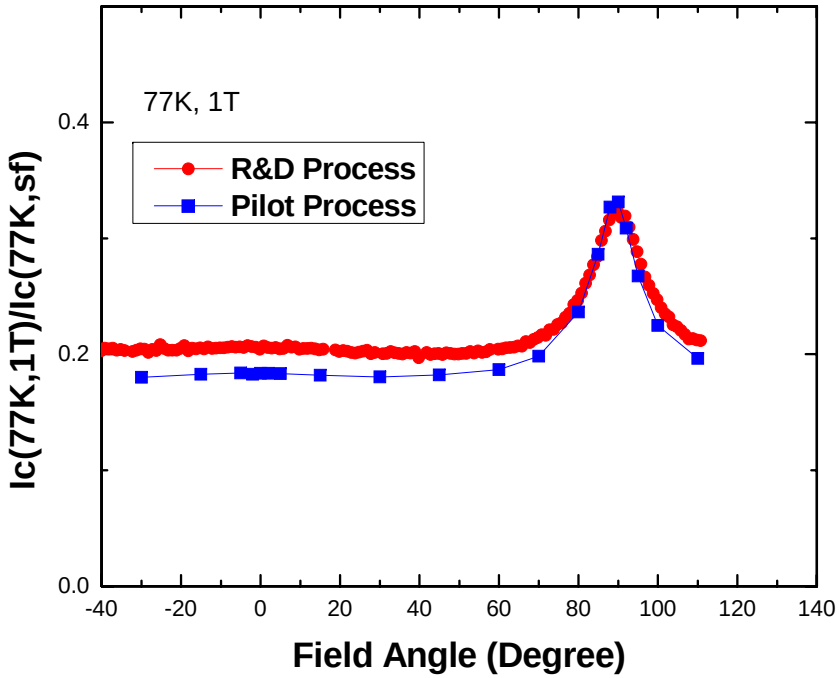
In FY2006, We Examined the Microstructure of this Two-Layer 1.4 μm Film on RABiTS



Significant misorientation between layers!

344 Superconductors with 1.4 μm HTS Layer Produced in Pilot Operation Benchmarked against R&D Performance

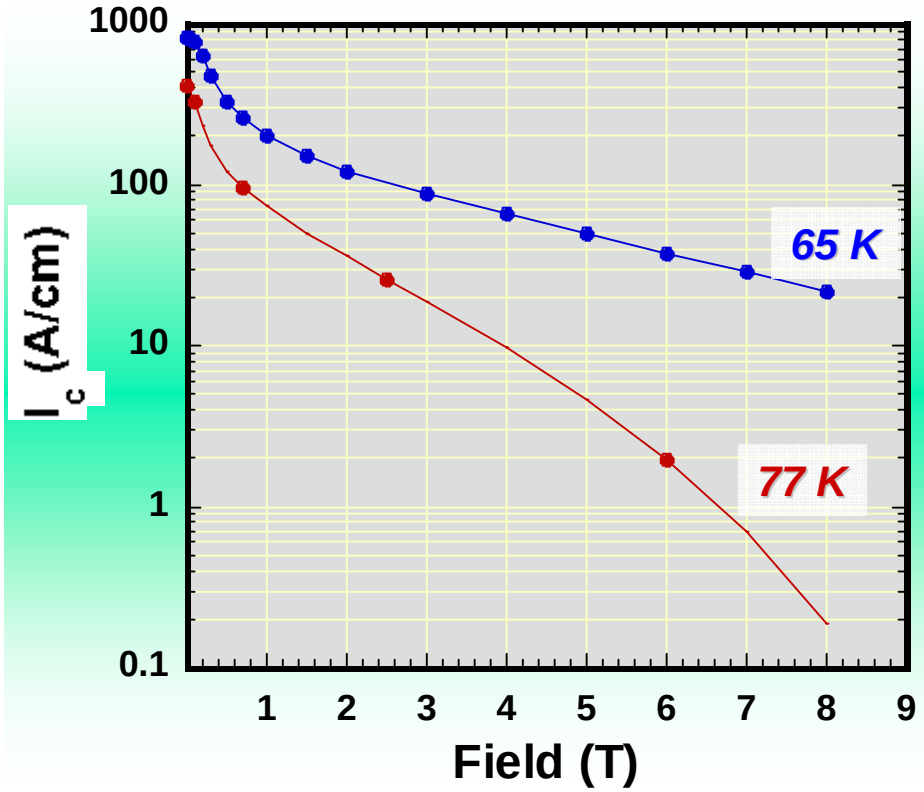


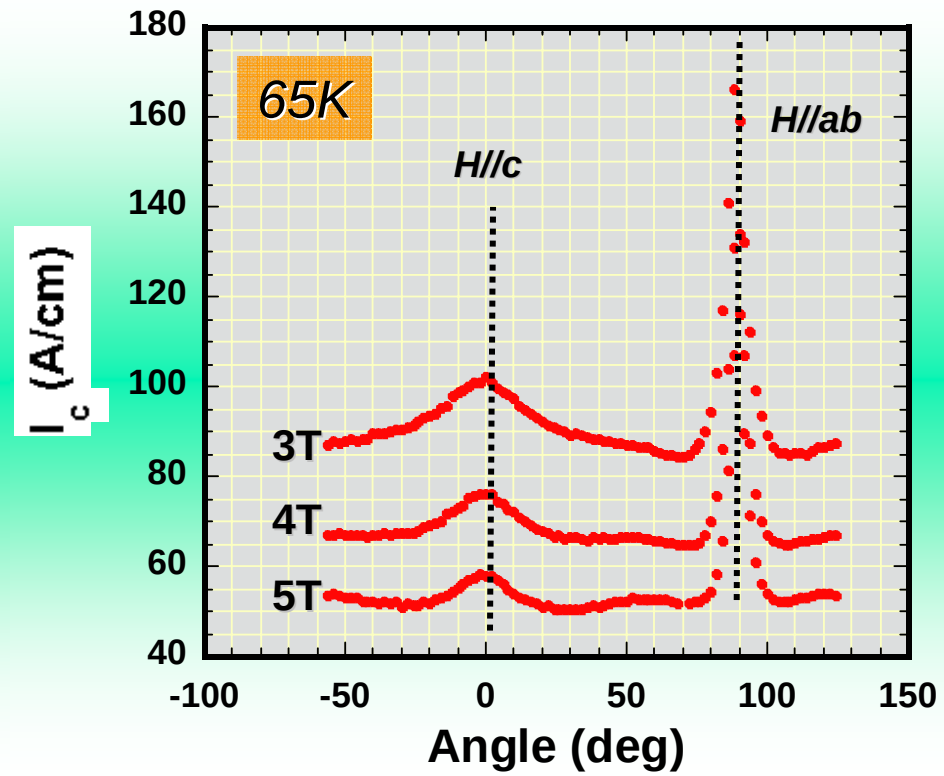


In-field performance benchmarked with R&D process

High Performance is Also Obtained at Lower Temperatures and Higher Fields

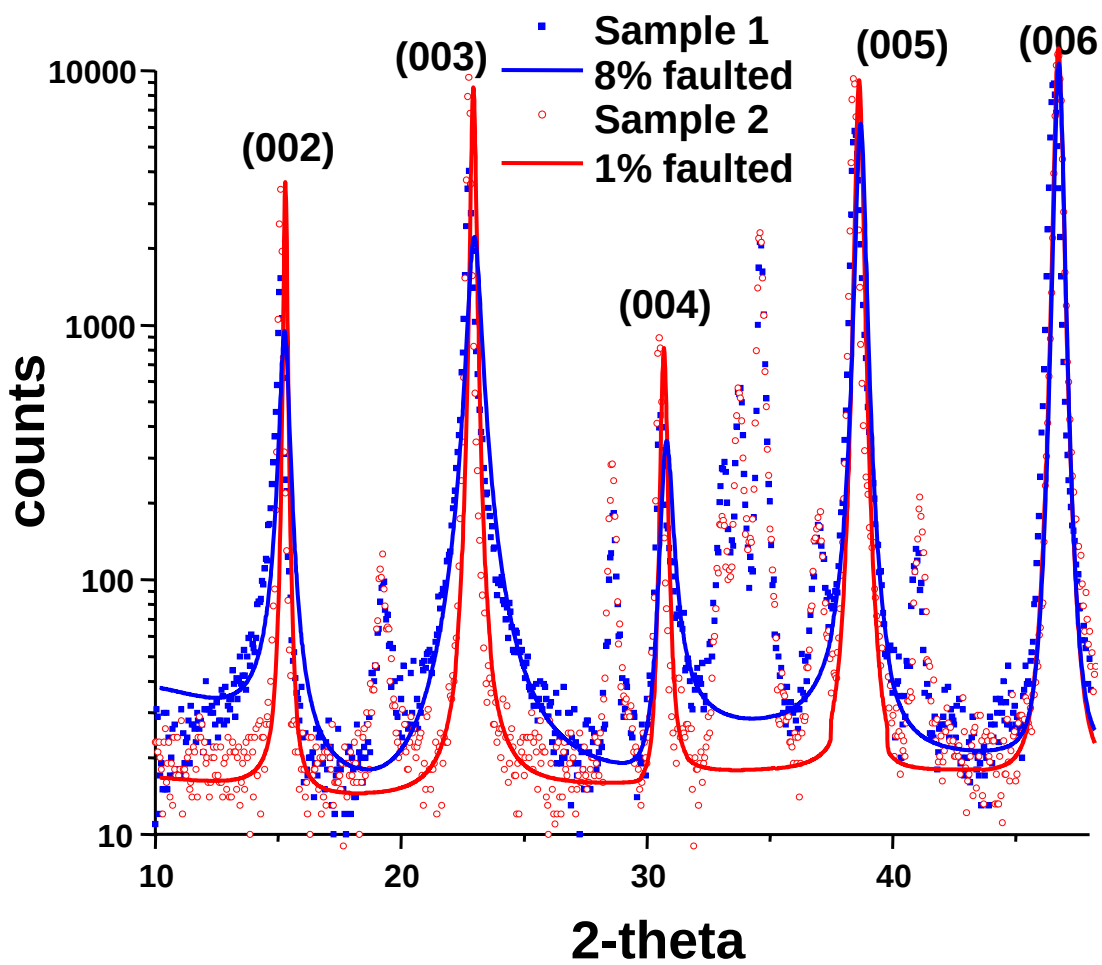
I_c/W (77K) = 416 A/cm	I_c/W (65K) = 811 A/cm
J_c (77K) ~ 2.9 MA/cm^2	J_c (65K) ~ 5.8 MA/cm^2

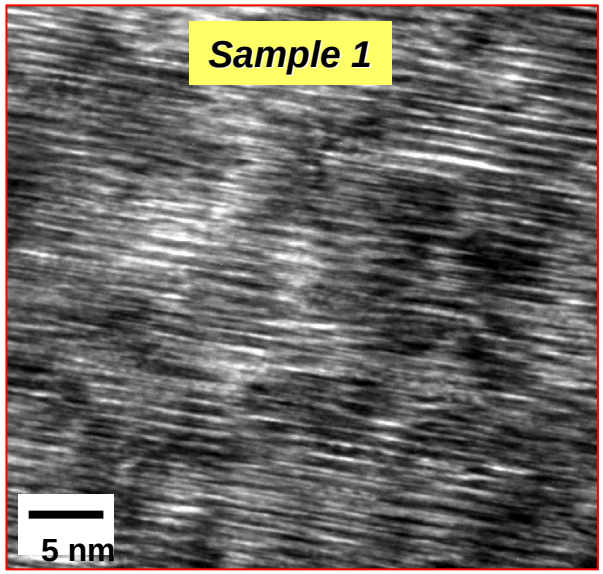


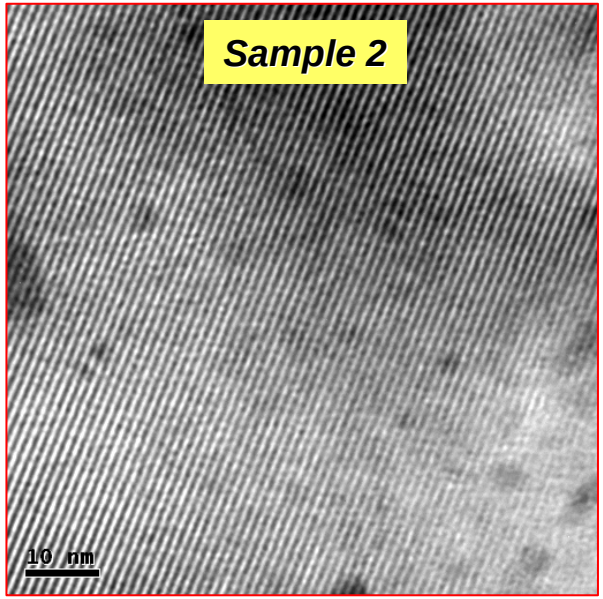


ORNL Measurements

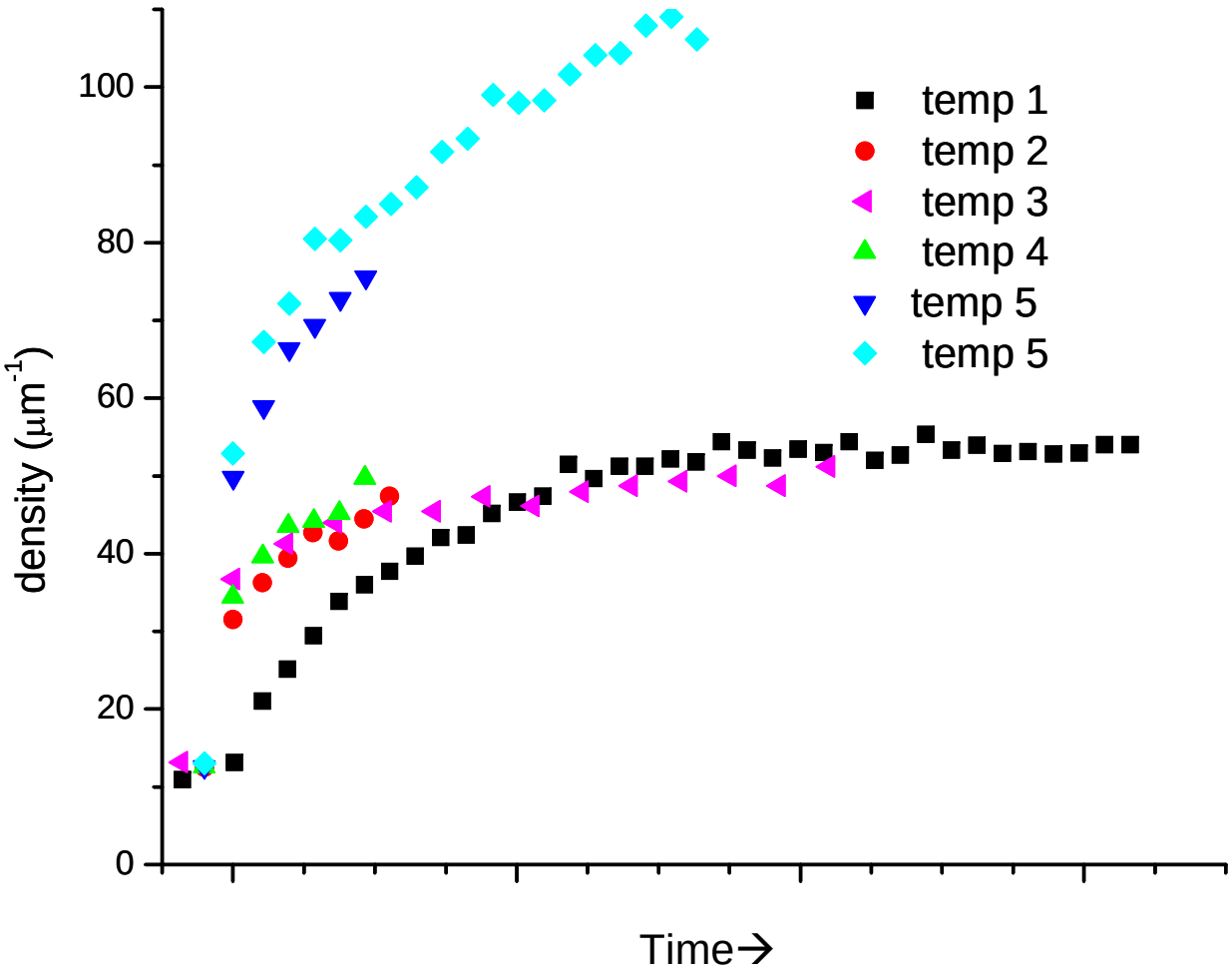
Formation of Stacking Faults Studied in-situ with High Temperature X-ray diffraction using Model Developed in FY05







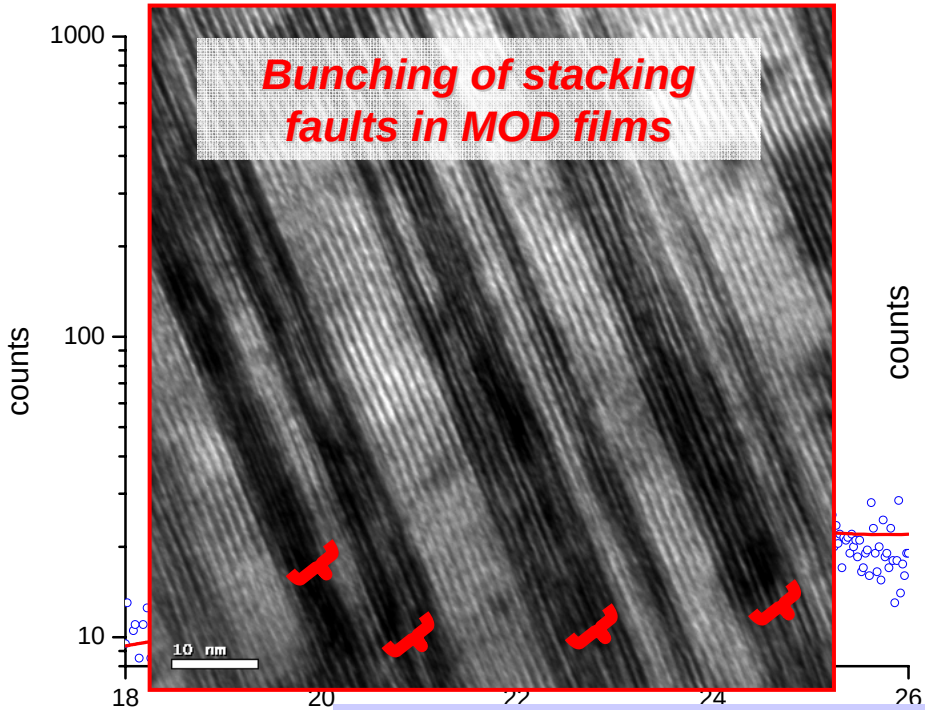
Formation of Stacking Faults Studied in-situ with High Temperature X-ray Diffraction

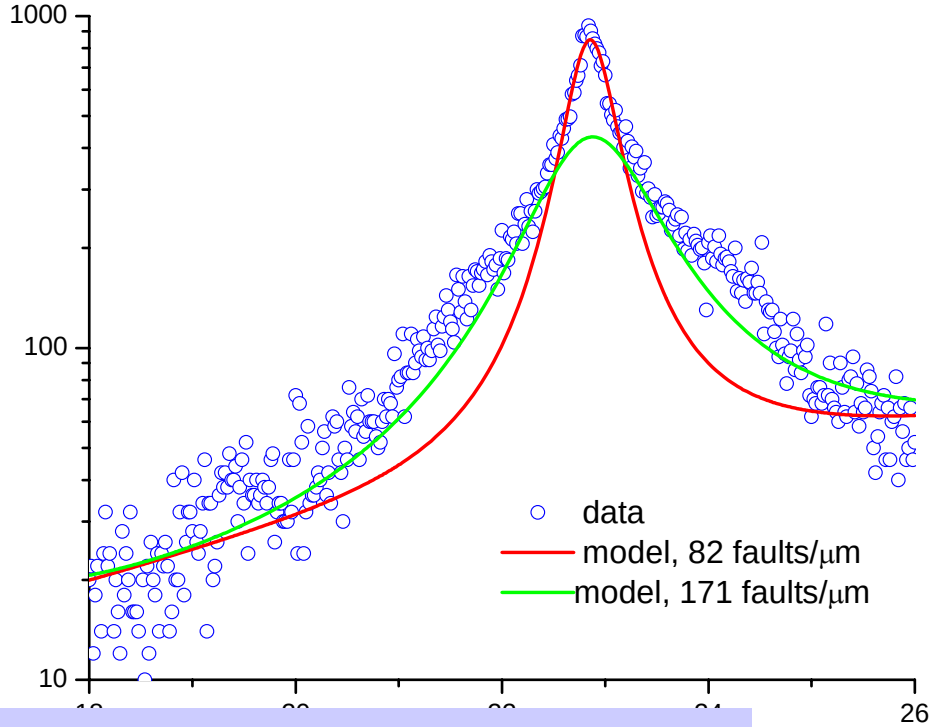


X-ray Peak Profile Details Reveal More about Nature of Stacking Faults in the Superconductor

At lower temperatures, stacking faults are well described by a random mixture Of 124 type defects

At higher temperatures, diffraction peaks do not fit a random-fault model. TEM suggests bunching of faults





Ongoing experiments and TEM from various stages of stacking fault formation in i*n-situ* experiments will reveal more about mechanisms of fault formation!

Significant Work Done as Part of the CRADA to Accomplish Scale-up of High Performance 2G Wire

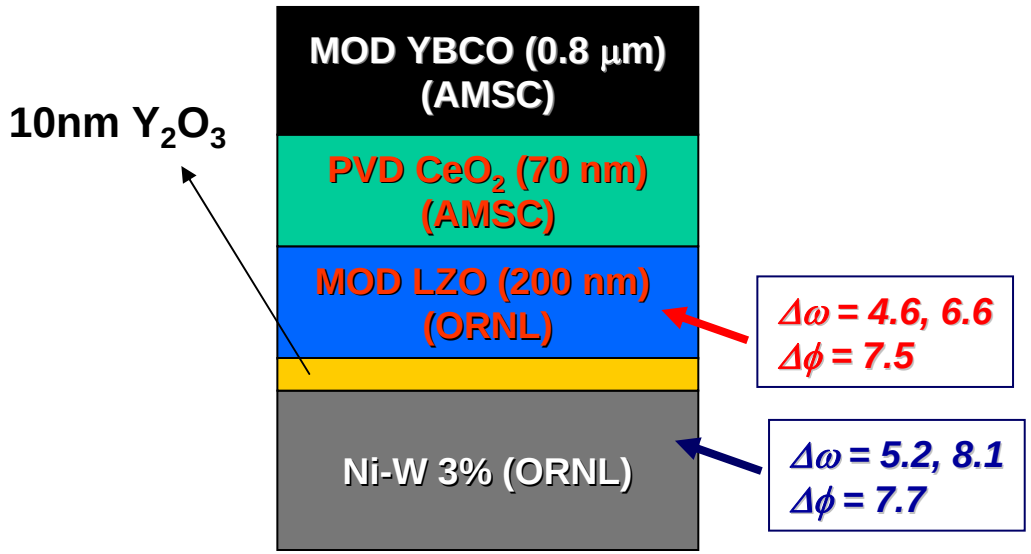
Over a 100 samples were characterized w.r.t. transport properties (I_c vs. H and I_c vs. Angle) and over 1000 TEM images were obtained in support of AMSC 2G Pilot scale up!

The "Speed" of doing the analysis – transport, X-ray and TEM has been another cornerstone of this CRADA

Scale-up of Solution Buffers via a High-Speed Continuous Deposition Process

FY05: Short samples of spin-coated MOD LZO sustained high-J_c MOD YBCO and were as good as PVD buffers

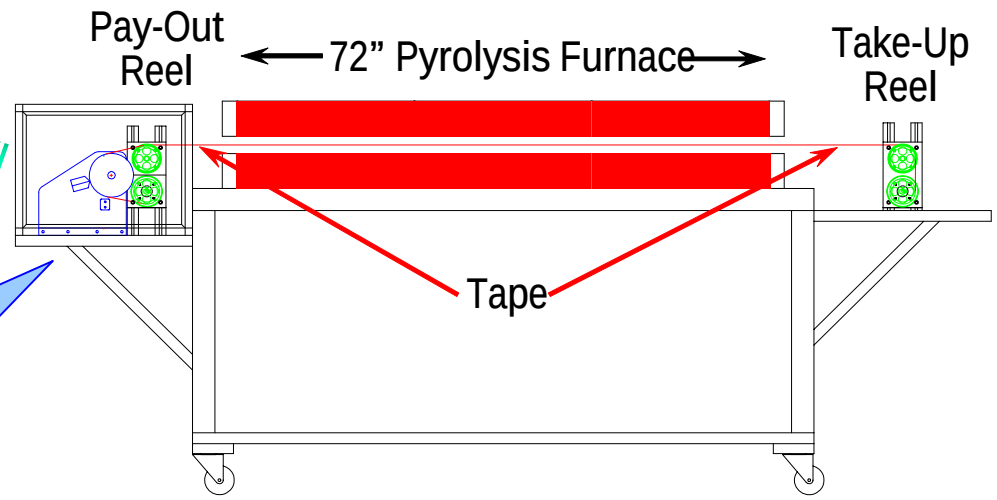
I_c = 255 A/cm-width
J_c = 3.1 MA/cm^2

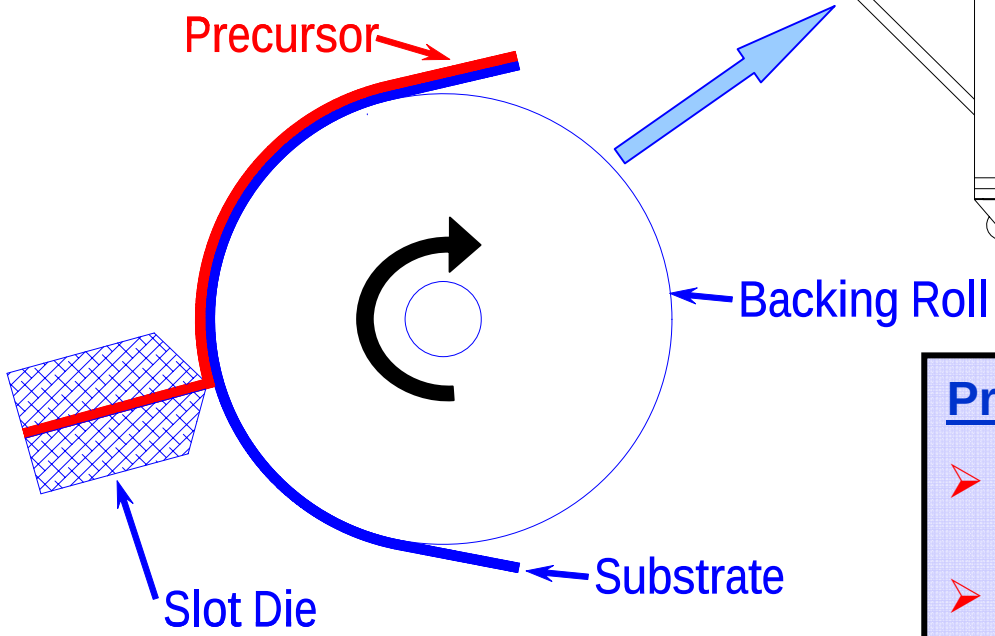


FY06 Objective:
To demonstrate the feasibility to reproducibly fabricate at high-speeds, homogeneous, solution $La_2Zr_2O_7$ layers on RABiTS

Approach: Develop slot-die coating of LZO.
- **AMSC is already using this technique for YBCO**
- ***Offers possibility for high speeds and excellent control***

Slot-Die Coating of LZO



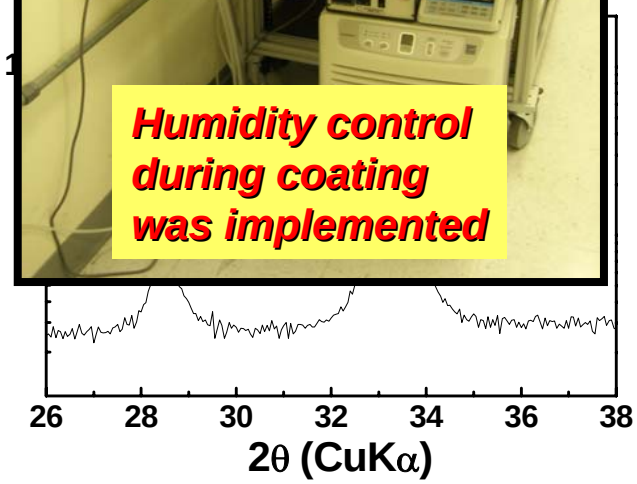


Problems addressed this FY:

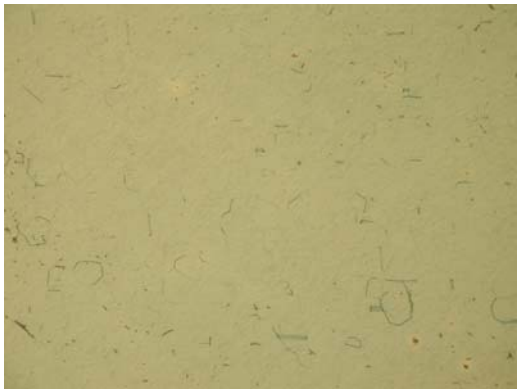
- **Cracking during slot-die coating**
- **Cracking during conversion**
- **Avoiding formation of undesirable texture components**
- **Reduction of porosity in films**

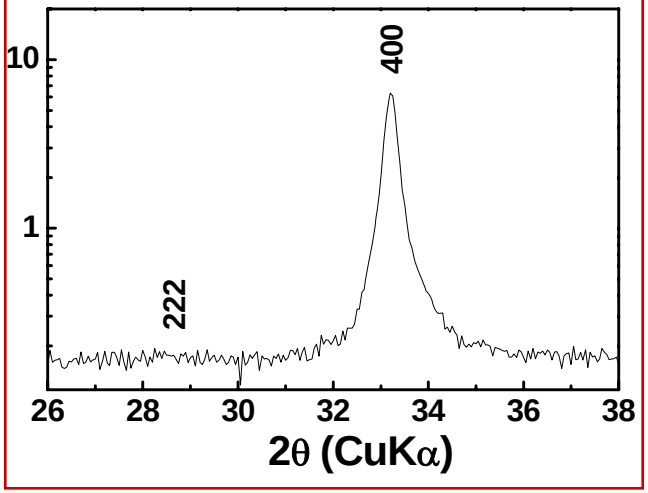
Control of Humidity During Slot-die Coating and during Subsequent is Essential for Obtaining Good LZO Layers

Low Humidity

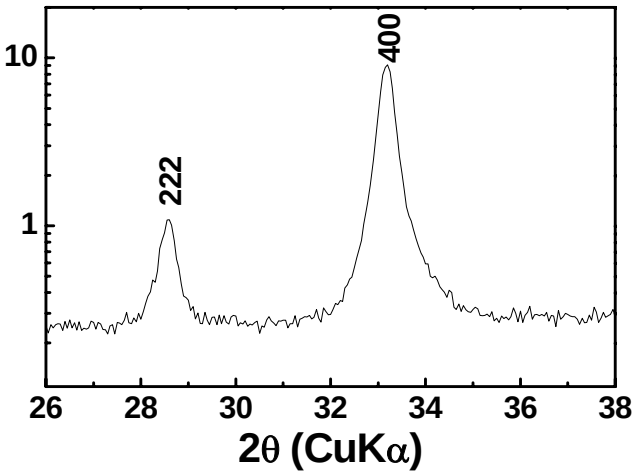


Correct Humidity Range





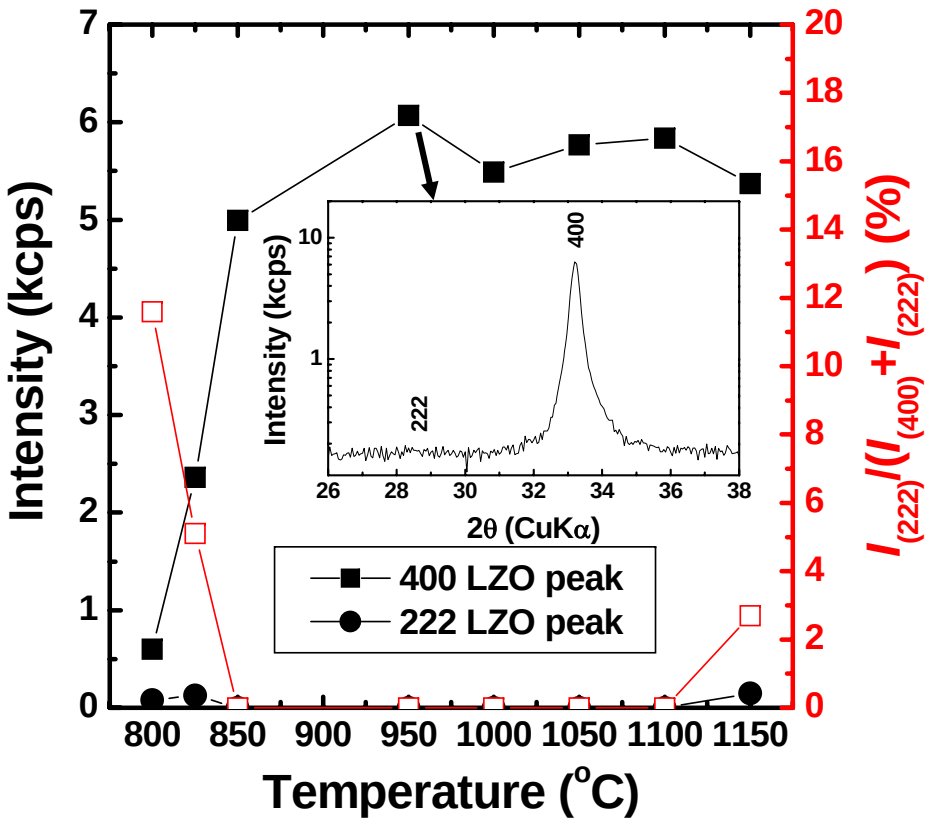
High Humidity



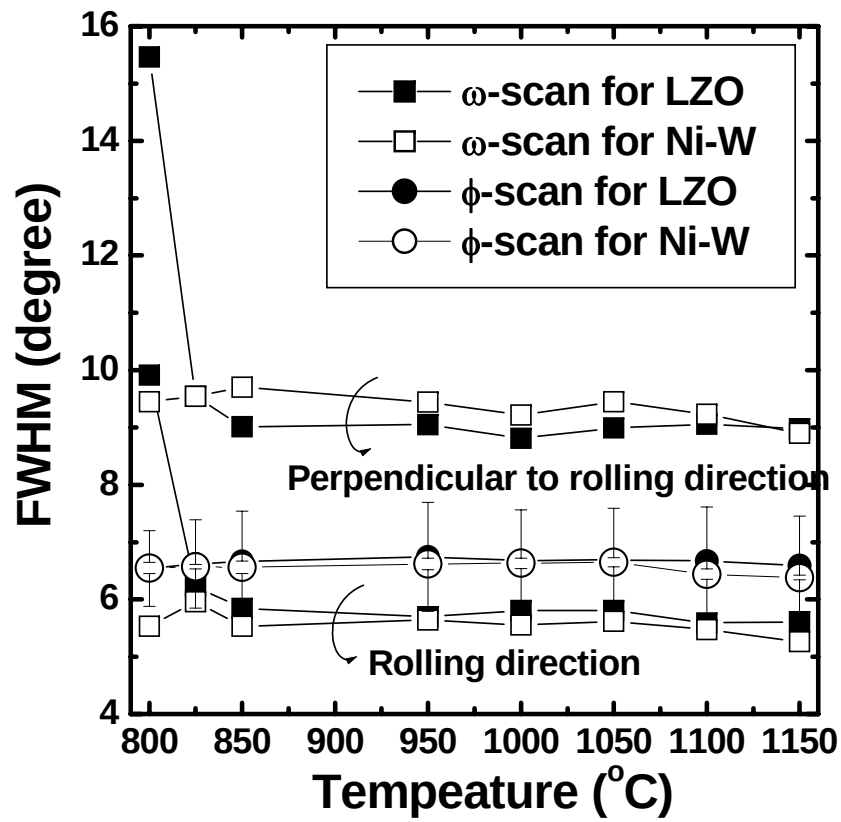
Optimal Conditions for Conversion Were Developed: Temperature, Time, Humidity, Heating Rate, etc.

X-ray diffraction shows that LZO films of single phase and epitaxy can be obtained

Intensity of (400) and (222) LZO peak

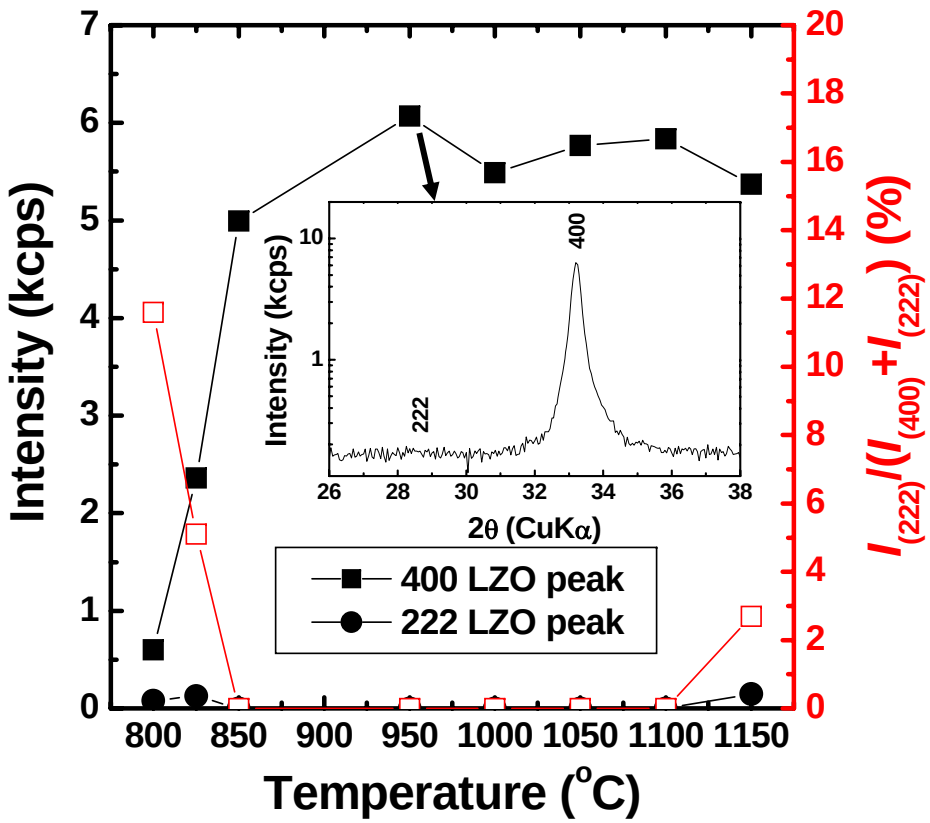


FWHM of ω-scan and φ-scan

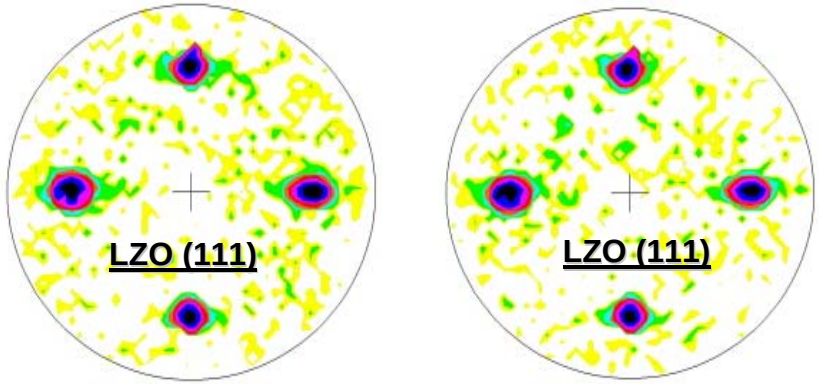


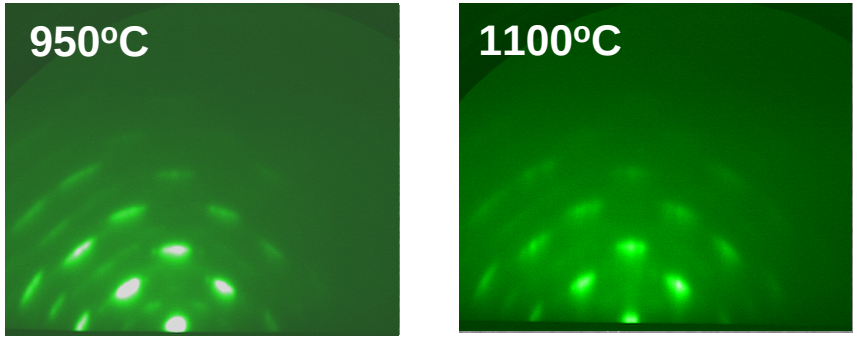
Texture, Roughness and Cleaniness Of Surface as a Function of Annealing Temperature for Slot-die Coated LZO

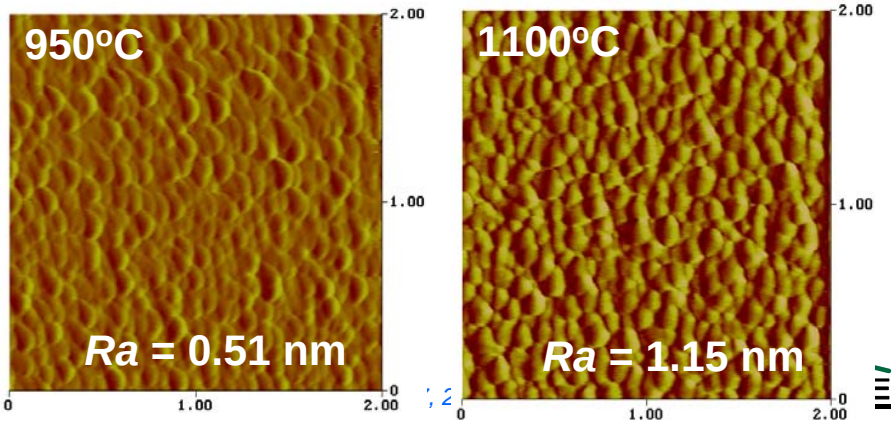
X-ray intensity of (400) and (222) LZO peak



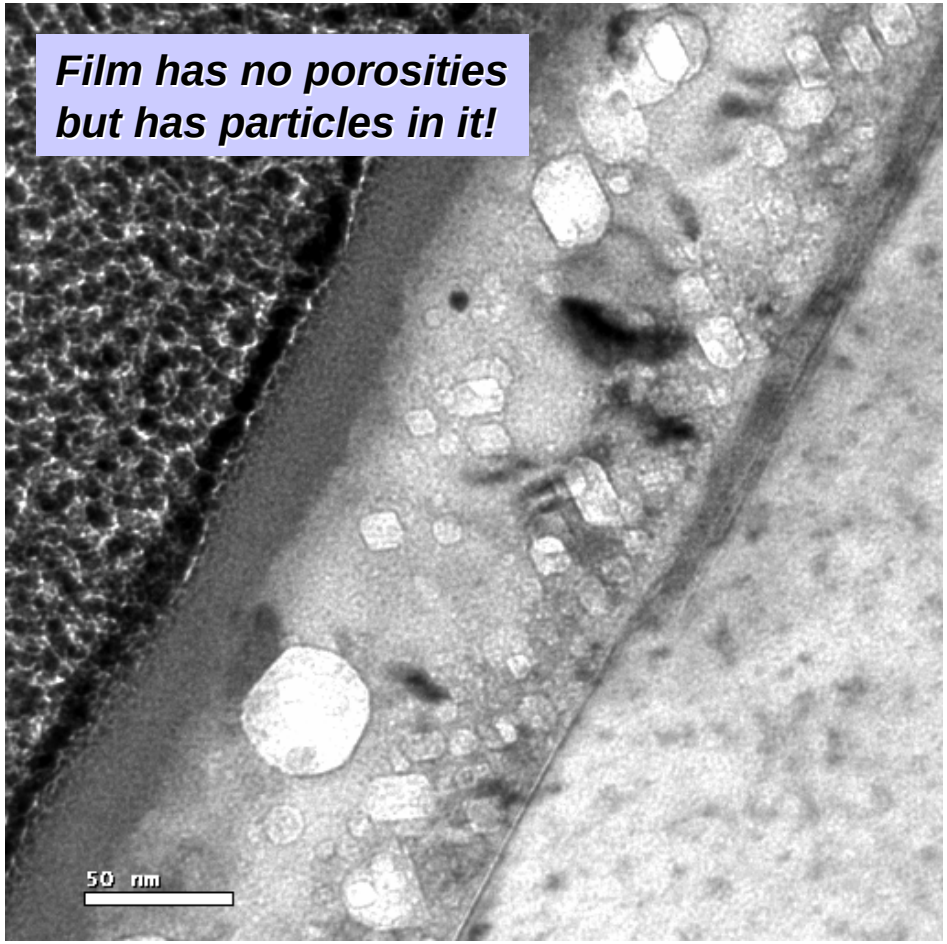
950°C **1100°C**



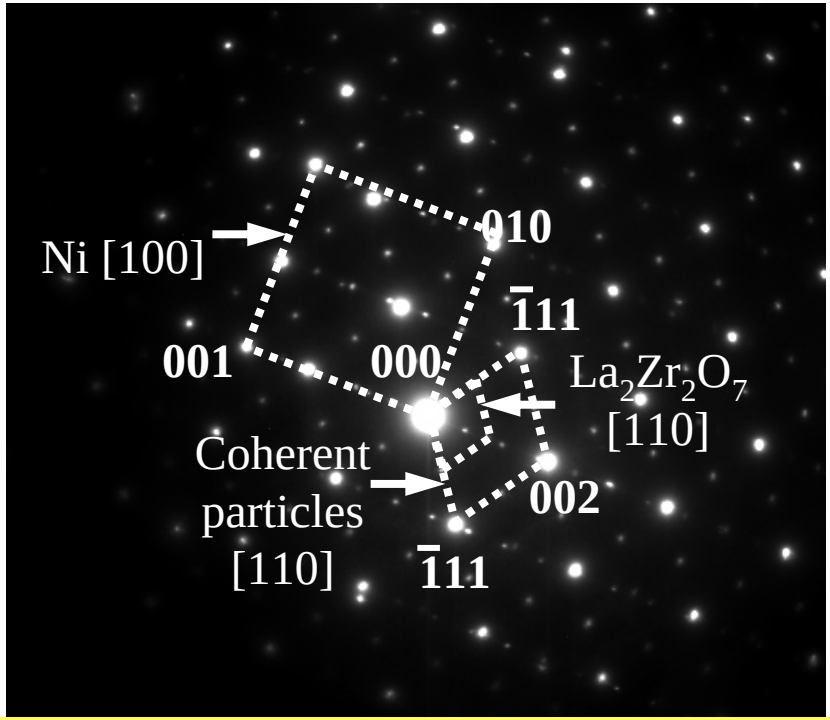




Microstructure of LZO is Complicated: X-ray Diffraction Shows Single Phase Film but Film is a Composite!



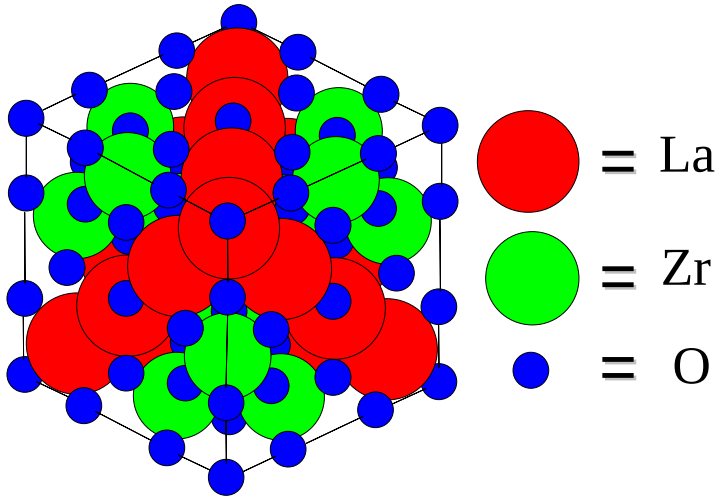
Electron diffraction shows a combination of three patterns!



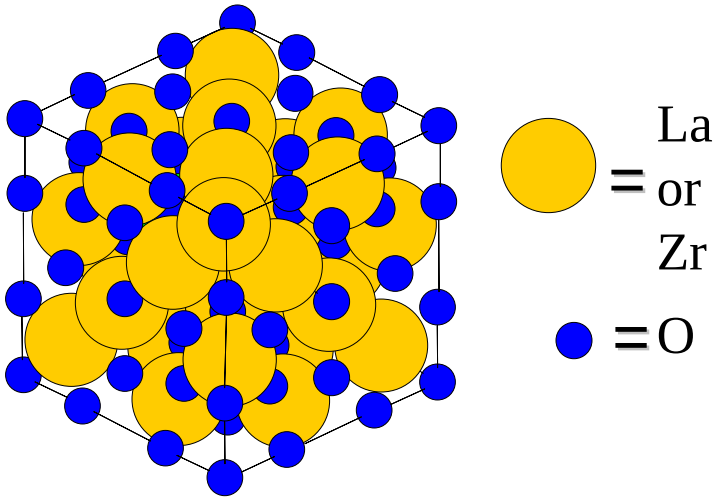
Coherent particle: **Fluorite structure**
Matrix: **Pyrochlore structure**

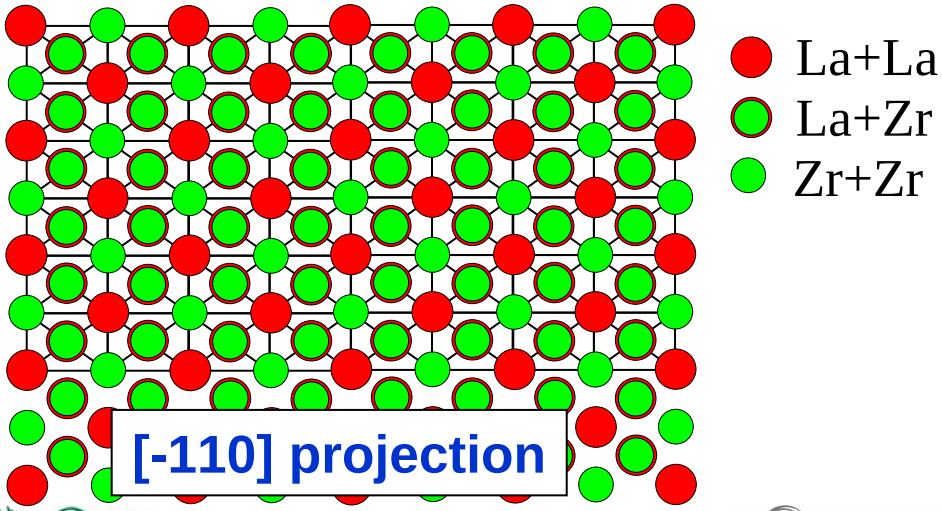
Crystal Structure Models of Possible Structures in Film

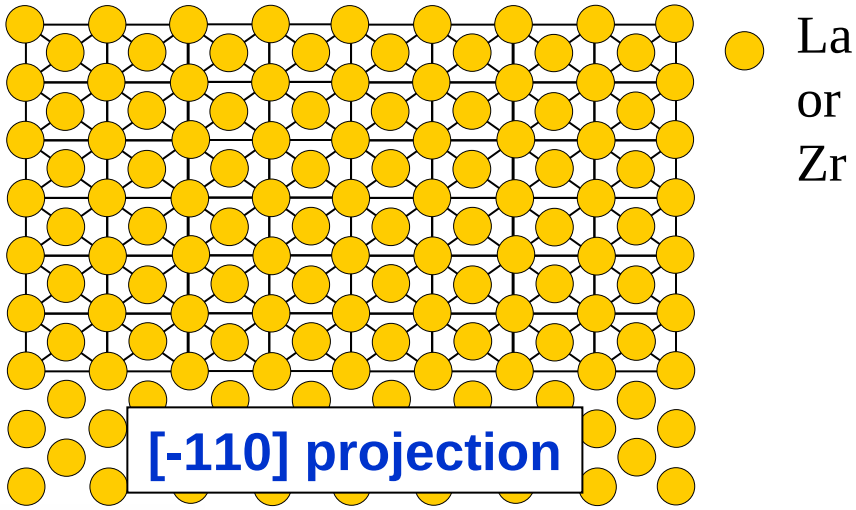
Pyrochlore $La_2Zr_2O_7$



"Fluorite" $La_2Zr_2O_7$

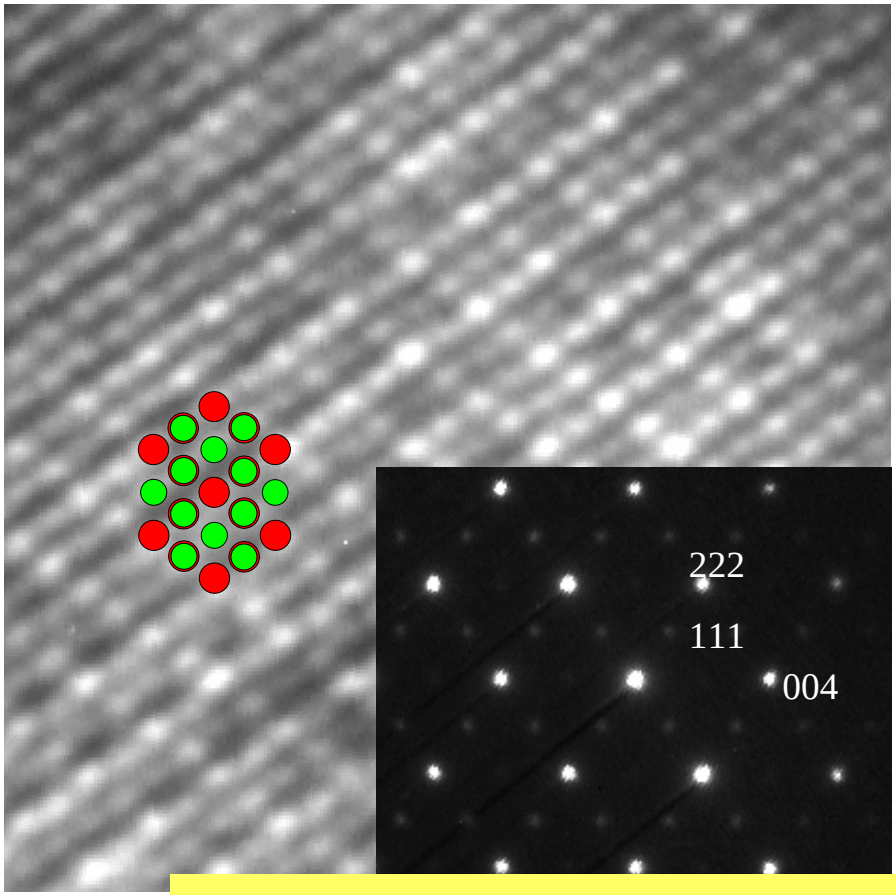




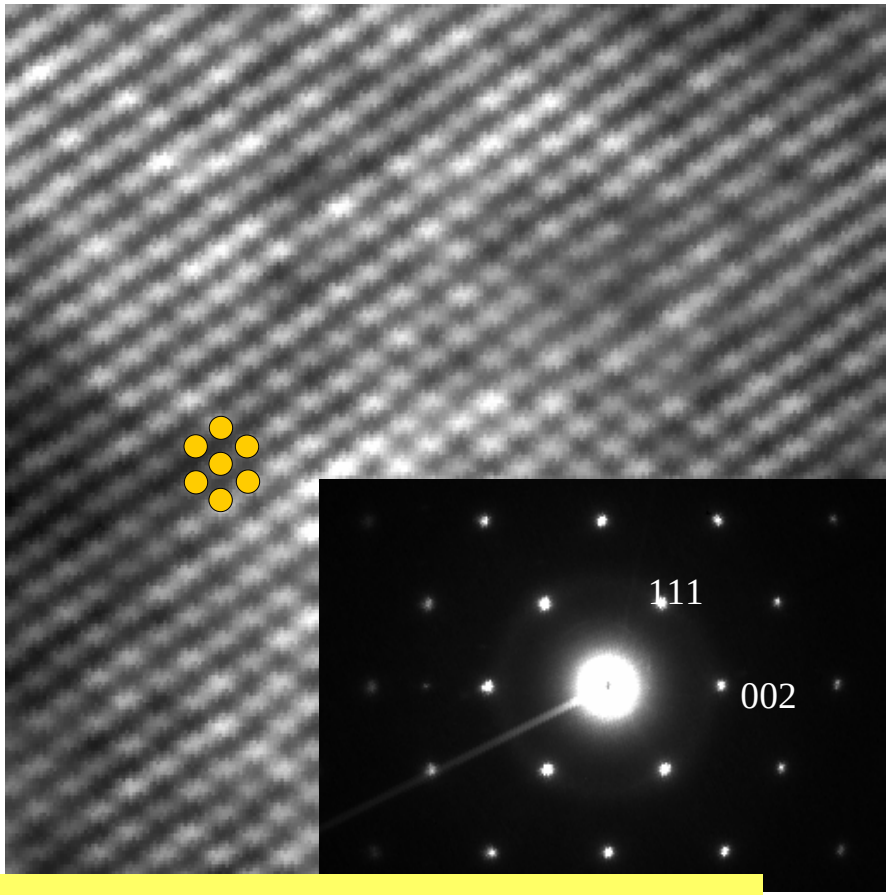


HREM, Electron Diffraction and FFT Consistent with Crystal Structures Suggested in Previous Slide

Pyrochlore $La_2Zr_2O_7$



Fluorite $La_2Zr_2O_7$



It is not at all clear if this phase separation is detrimental!

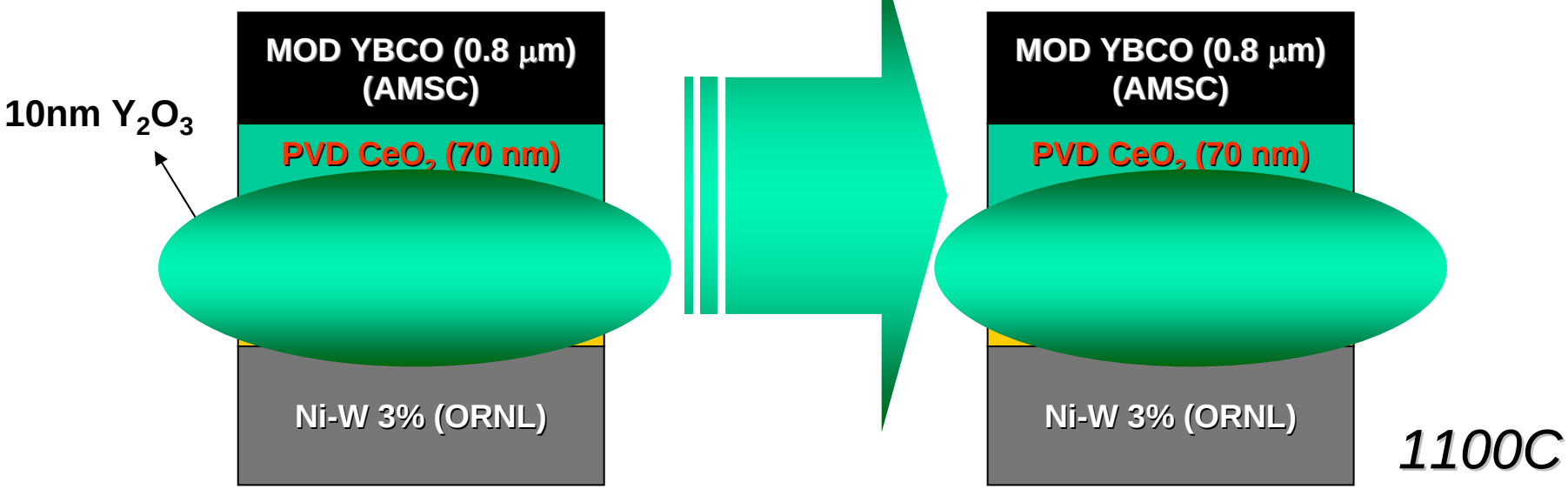
Understanding and Optimization of Process Issues Resulted in High Performance Coatings at High Speeds

FY2005: LZO via Spin coating - static

FY2006: LZO via high-speed Slot-die coating – continuous process

I_c = 255 A/cm-width
J_c = 3.1 MA/cm^2

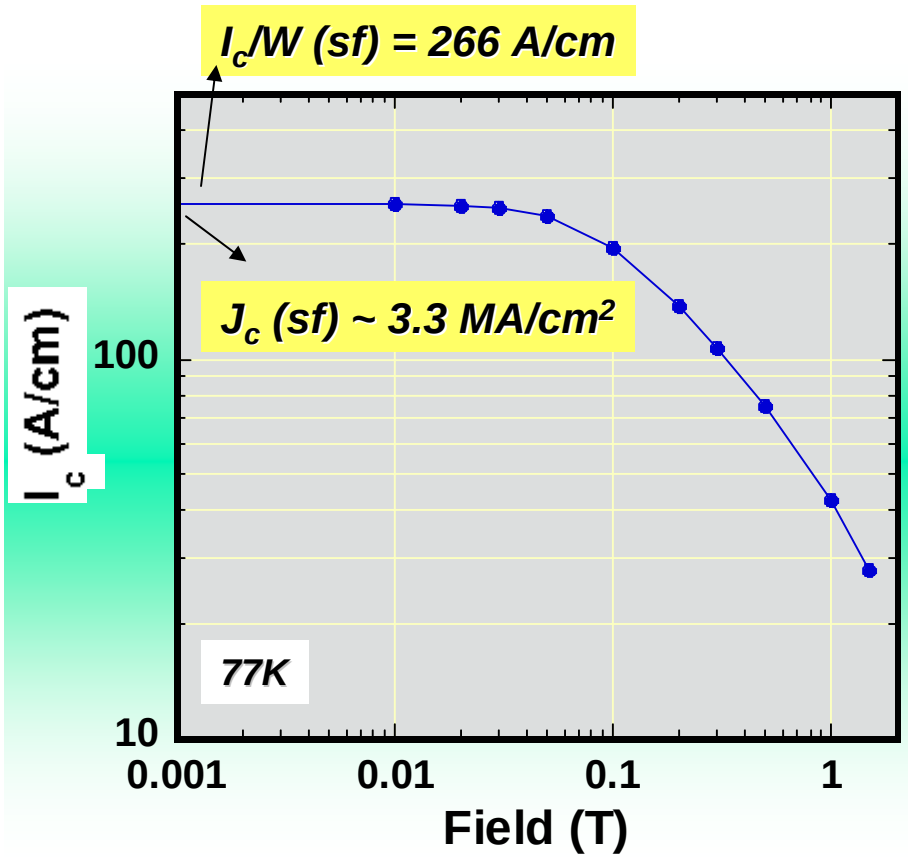
I_c = 266 A/cm-width
J_c = 3.3 MA/cm^2

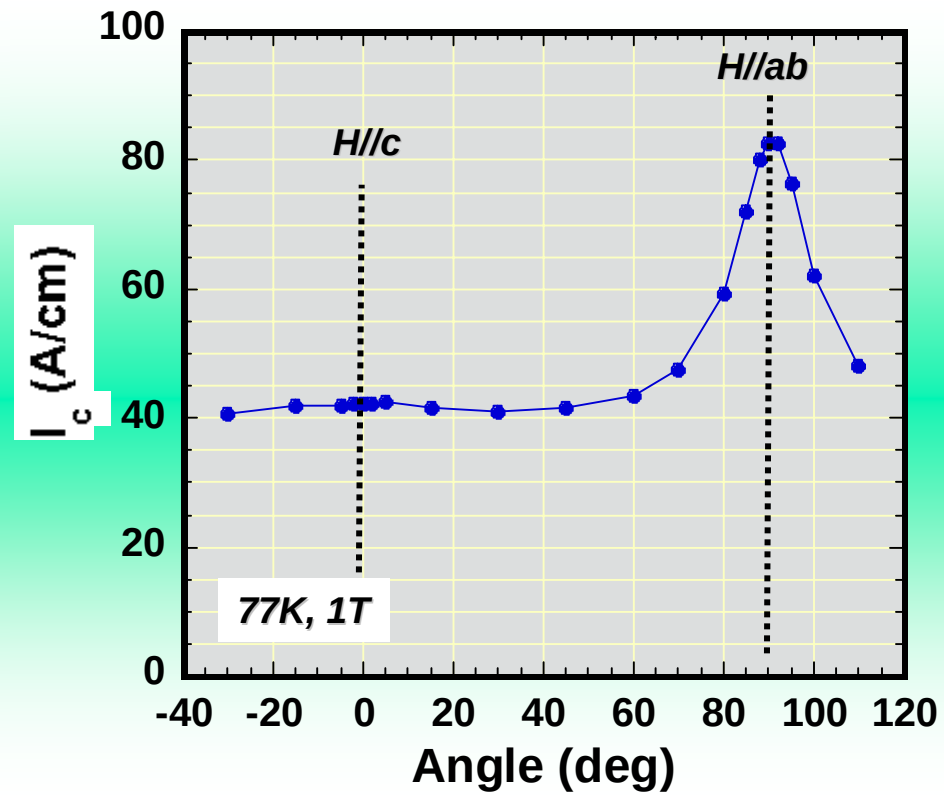


1100C

Highest J_c reported so far on a solution buffer

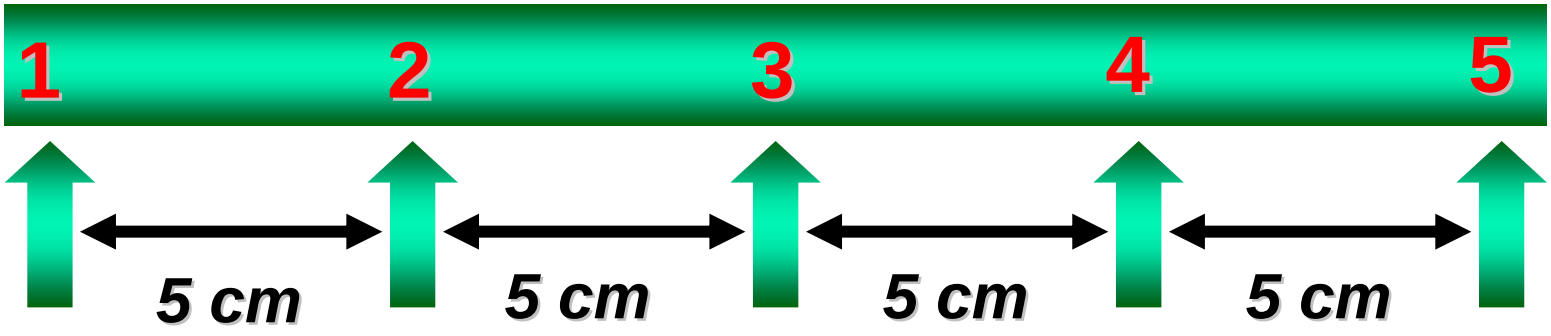
In-field and Angular Dependence of J_c is as Expected for a Standard High-J_c MOD YBCO Film on RABiTS





MOD-YBCO/PVD-CeO_2/MOD-LZO/PVD-Y_2O_3/NiW

J_c along the Length of a Continuously Processed (at All Steps), 20cm Long Tape with MOD LZO on RABiTS



Position	I_c
1	231
2	269
3	264
4	266
5	269

SLOT-DIE COATING: Advantages

- Coating speeds in excess of 2 meters/min have been demonstrated
- Time to conversion: ~ 5 min
- Very wide webs possible

AMSC-ORNL CRADA Presentation

- **FY 2006 Results**

  ORNL-AMSC CRADA Goals **(Wei)**
  2G Development (YBCO/RABiTS) at AMSC
  2G wire manufacturing at AMSC: ORNL contributions

  Scale-up of MOD HTS: Optimization of Pilot production **(Amit)**
  to fabricate high performance conductors
  Scale-up of MOD LZO solution buffers on RABiTS

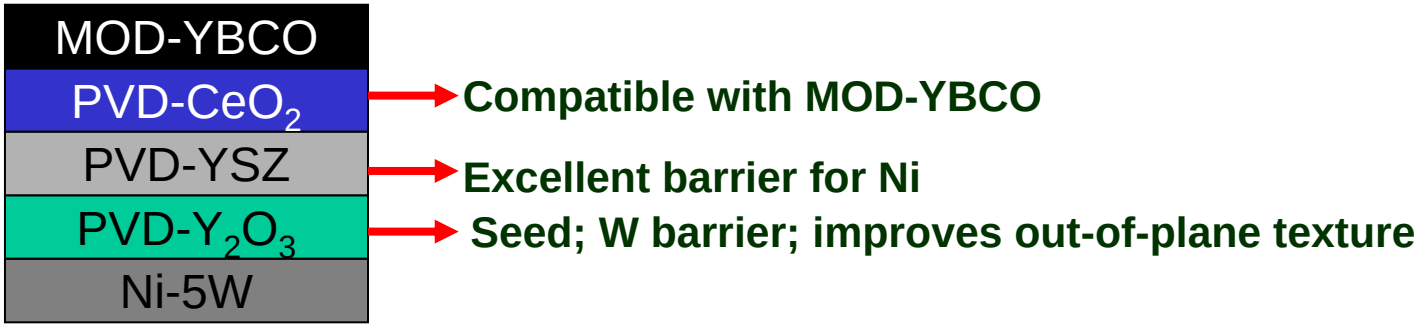
  Fundamental development of solution buffer layers **(Parans)**

- **FY 2006 Performance and FY 2007 Plans** **(Parans)**
- **Research Integration**

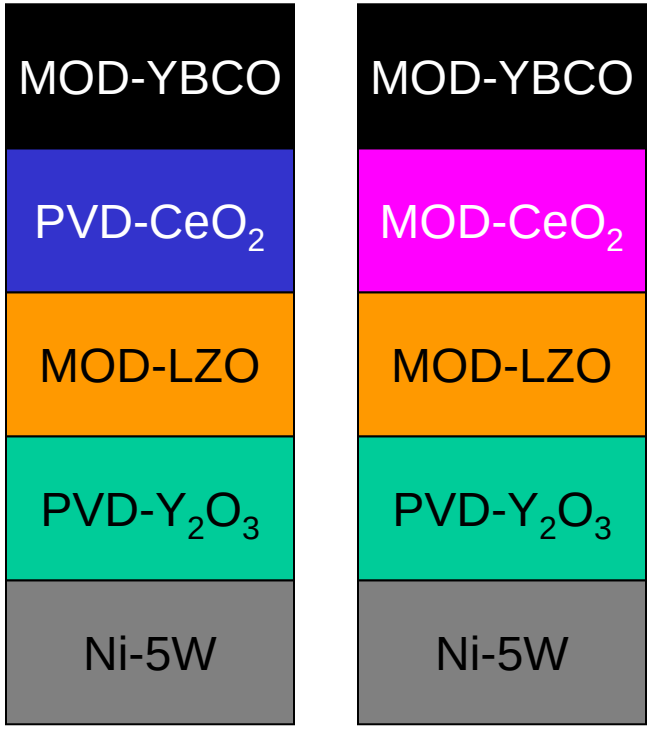
Fundamental Development Of Solution Buffer Layers

- **MOD CeO_2 cap development**
  Need to reduce the formation of $BaCeO_3$ with MOD-YBCO to match the performance of all-PVD buffers

- **Is $La_2Zr_2O_7$ (LZO) the best MOD barrier layer to scale up?**
  I_c of 266 A/cm achieved on slot-die coated LZO

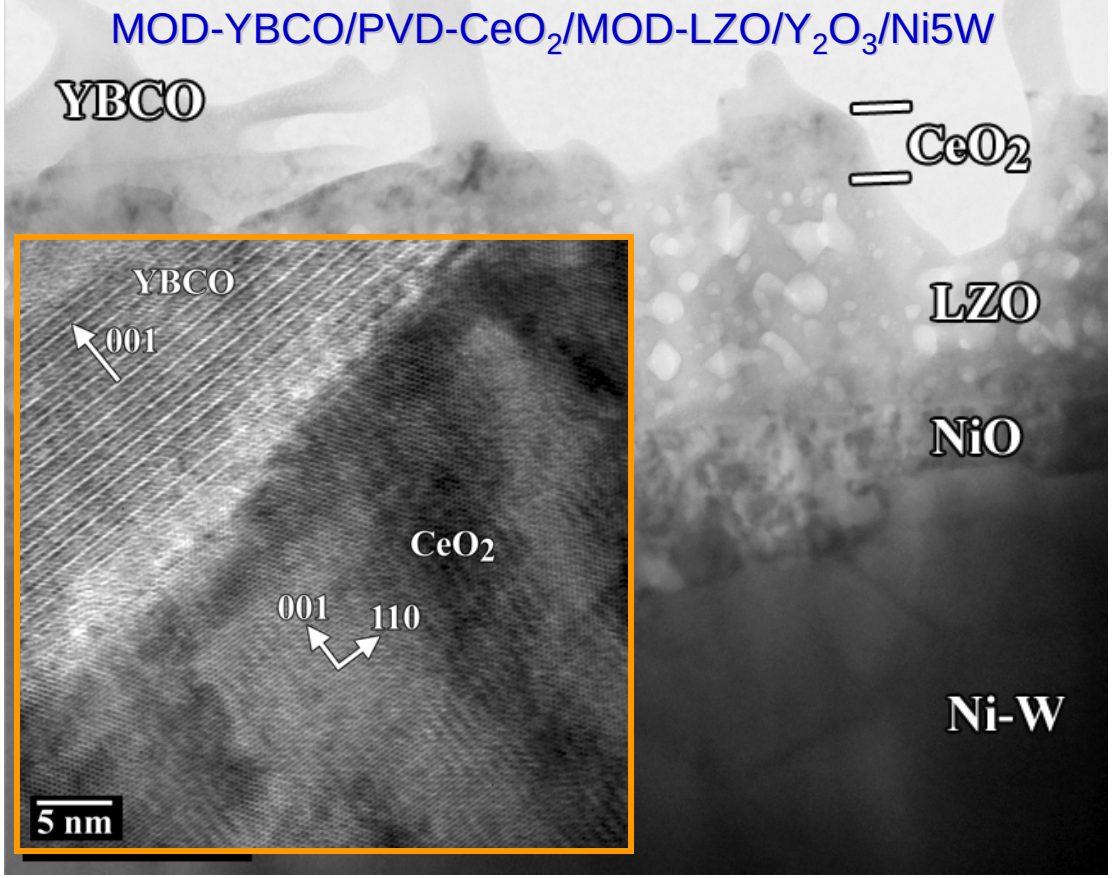


What is Limiting the Performance of MOD CeO_2 Cap Layers?

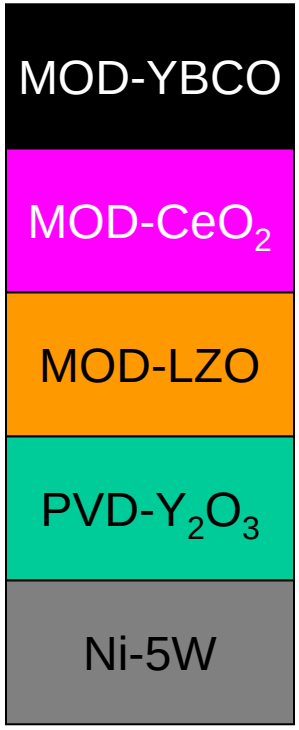


FY05: 255 A
FY06: 266 A

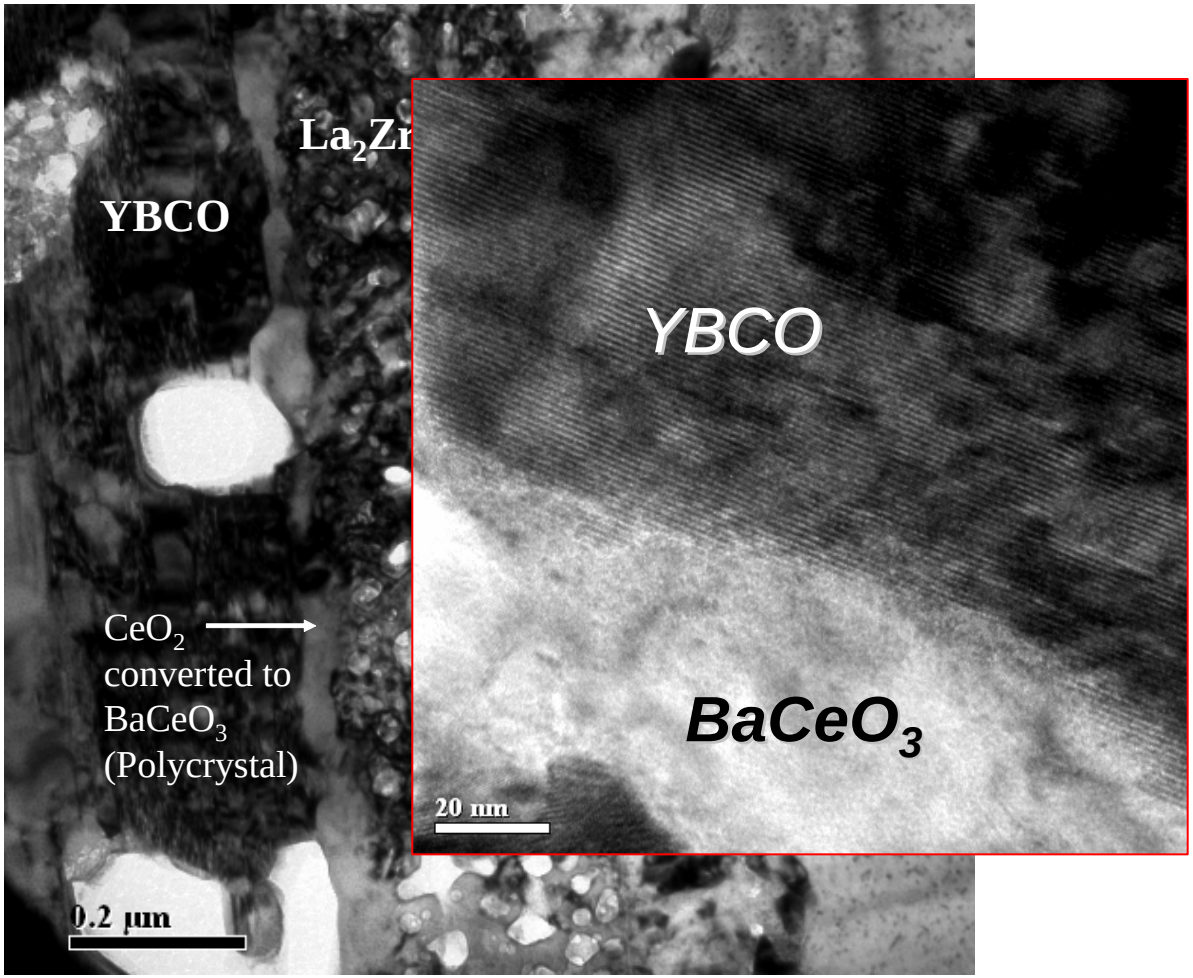
FY05: 200 A



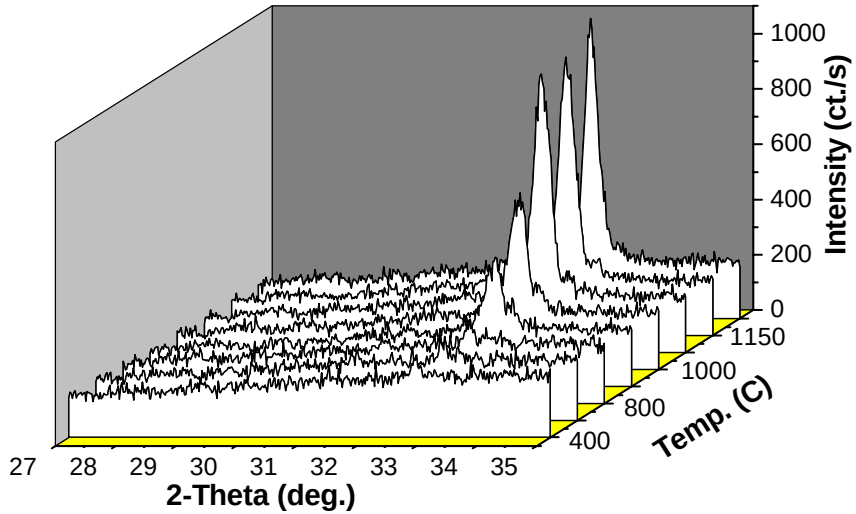
MOD CeO_2 Cap Layers on MOD LZO React Completely to Form $BaCeO_3$

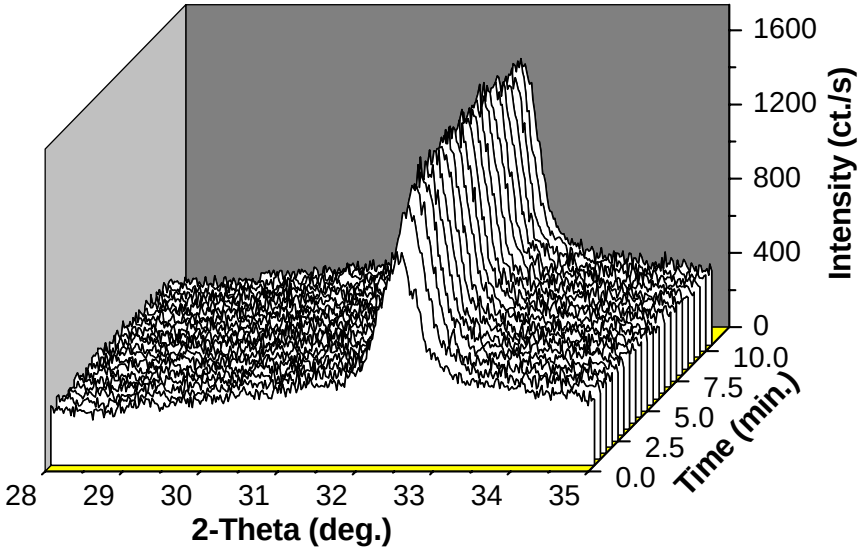


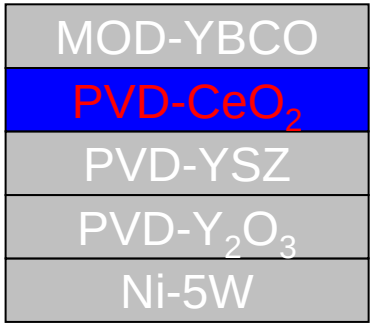
FY05: 200 A



High Temp. in-situ XRD Analysis of MOD CeO_2







- **CeO_2 (004) starts to nucleate at 600°C**
- **No (222) peaks**

Crystallization is completed in 5 min at 1000°C

Is LZO the Best MOD Barrier Layer to Scale Up?

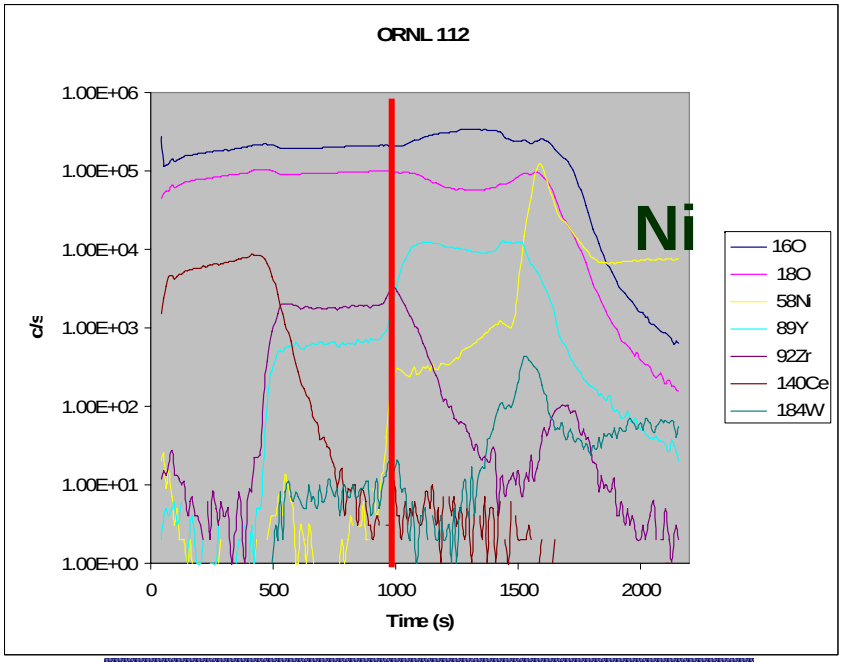
<u>MOD layers on RABiTS considered</u>: $La_2Zr_2O_7$ (LZO); $Gd_2Zr_2O_7$ (GZO); $La_{1.6}Gd_{0.4}Zr_2O_7$ (LGZO); Gd_3NbO_7 (GNO); YSZ.

<u>Methodology</u>:
- All MOD layers were grown epitaxially on Y_2O_3/NiW substrates
- Samples were then subjected to a simulated anneal under YBCO processing conditions
- SIMS depth profiling was used to study metal and oxygen diffusion

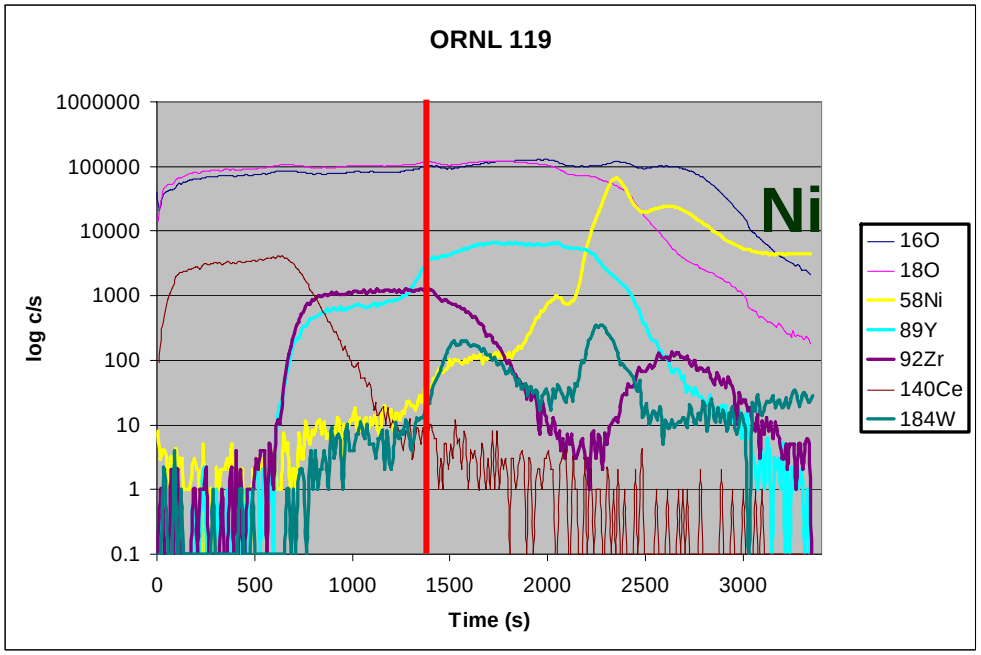
MOD-YBCO
PVD-CeO_2
PVD-YSZ
PVD-Y_2O_3
Ni-5W

PVD YSZ vs. MOD YSZ (Material vs. Processing Tech.?)

SIMS Depth Profile Studies



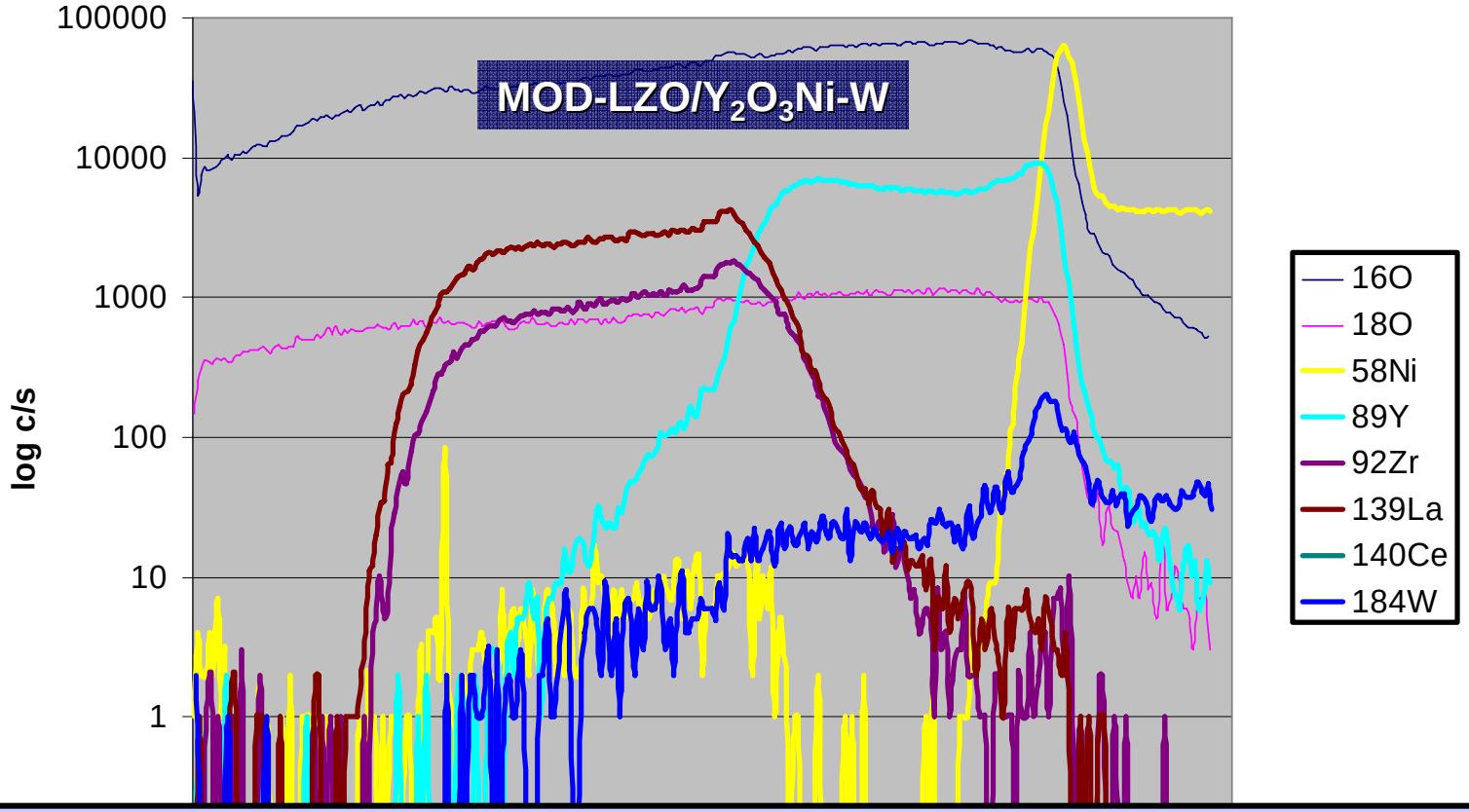
PVD-CeO_2/PVD-YSZ/PVD-Y_2O_3



PVD-CeO_2/MOD-YSZ/PVD-Y_2O_3

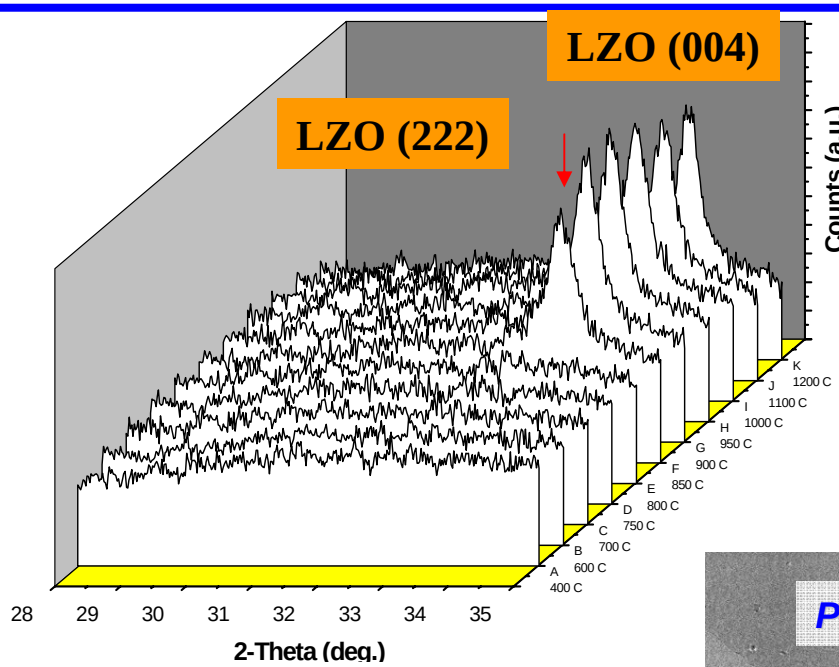
SIMS depth profiling shows that Ni is contained at the Y_2O_3/PVD-YSZ interface. However, Ni diffuses into MOD-YSZ.

Ni Diffusion is Contained within 75 nm Thick LZO



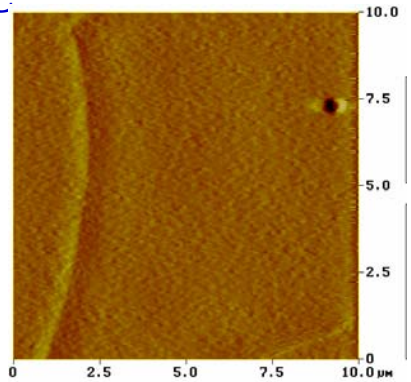
SIMS depth profiling showed that LZO was the best Ni and W diffusion barrier compared to other layers. However, a minimum of 75 nm of LZO to contain Ni.

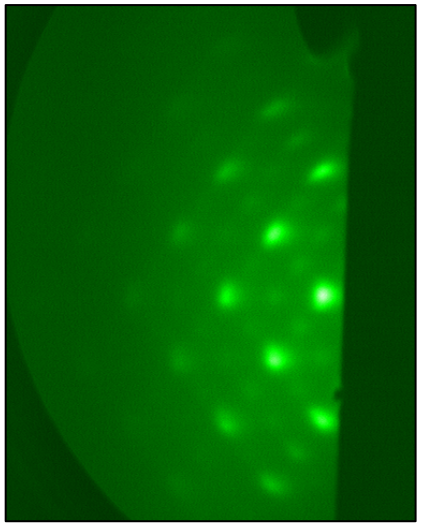
By Controlling the Humidity During Coating, LZO Process Temperature Has Been Reduced by 200 °C



- **HTXRD @ various T**
- **LZO *(00l)* nucleate at 850°C**
- **LZO crystallization complete at 900°C in 15 min.**

MOD-LZO @900° C/Y_2O_3/NiW





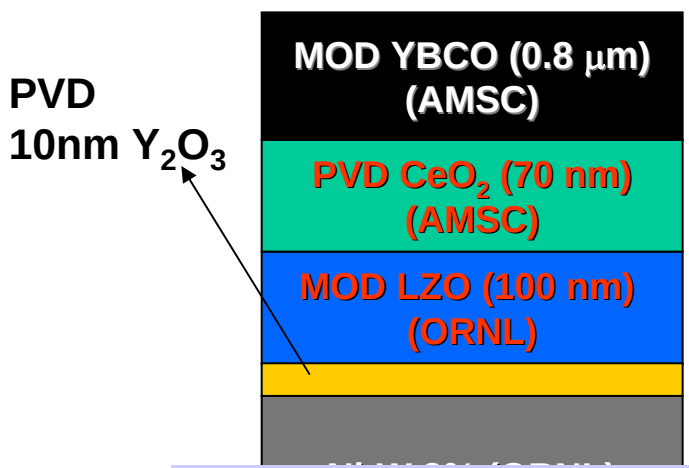
Temp./time (°C/min)	Surface roughness
900 (15)	Ra 0.5 nm
950 (30)	Ra 1.5 nm
1000 (20)	Ra 1.9 nm
1050 (15)	Ra 1.9 nm
1100 (10)	Ra 2.0 nm

We will now follow-up with MOD CeO_2/MOD YBCO

LZO Processing Temperature Reduction Raises J_c

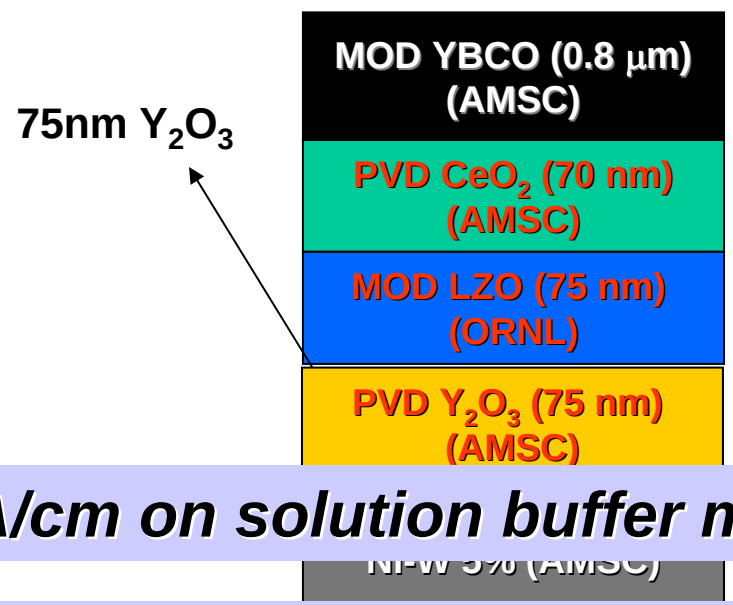
FY2006: LZO via high-speed Slot-die coating – continuous process. Annealing conditions: 1100 ºC, 15 min.

I_c = 266 A/cm-width
J_c = 3.3 MA/cm^2



FY2006: Short spin-coated sample. Annealing conditions: 900 ºC, 15 min.

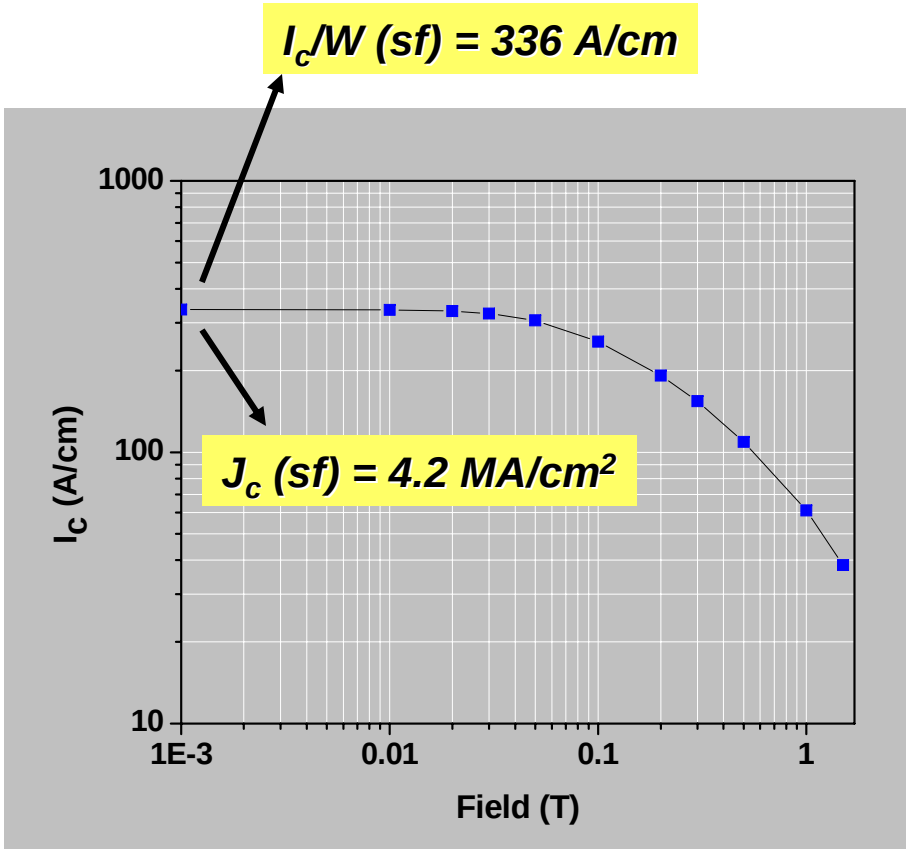
I_c = 336 A/cm-width
J_c = 4.2 MA/cm^2

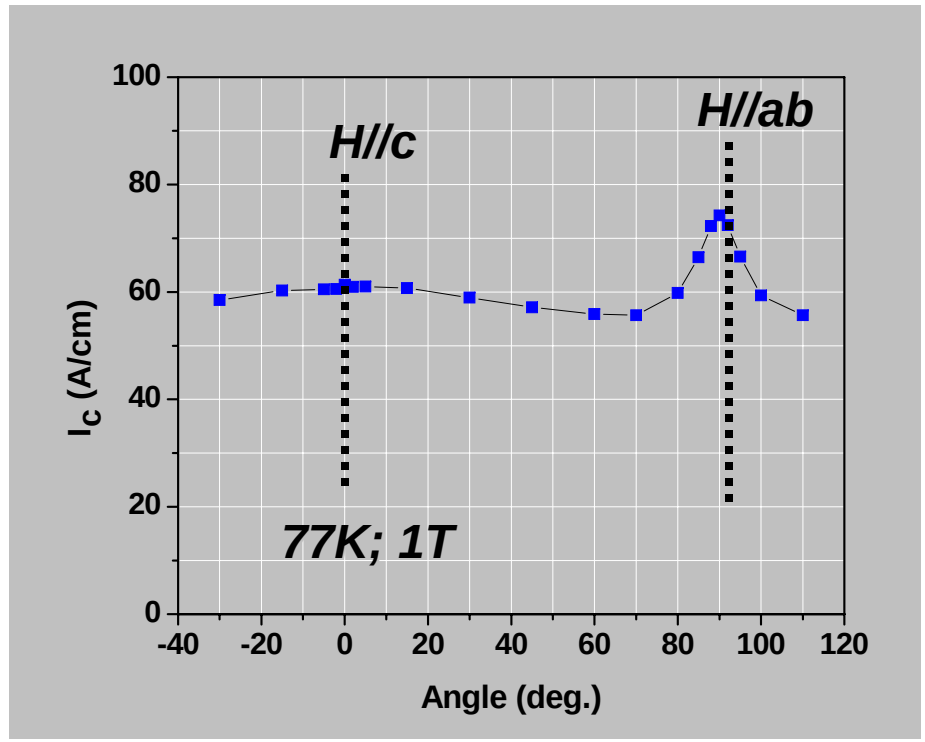


DOE Milestone of 300 A/cm on solution buffer met!

Solution buffer yields similar performance as PVD buffers

336 A/cm Achieved on MOD-LZO Barrier Processed at 900℃





MOD-YBCO/PVD-CeO_2/MOD-LZO/PVD-Y_2O_3/Ni5W

FY 2006 Plans and Performance

FY2006 Plans

- Assist AMSC personnel in manufacturing alloy substrates (4 cm wide by 100 m long) using the ORNL rolling mill facility with clean room

FY2006 Performance

✓ ORNL rolling mill facility was used to produce over 4 km of 4 cm wide substrates in support of AMSC's 2G production

✓ AMSC's Pilot substrate facility is functional including rolling mill, degreaser, and texture anneal furnace

FY 2006 Plans and Performance

FY2006 Plans (cont'd)

- Improve the RABiTS™ template manufacturing reliability through fundamental characterization of buffer layer properties and uniformity along length and width
- Development of improved buffers or buffer architectures leading to improved performance and/or reduced manufacturing cost

FY2006 Performance

✓ Texture of buffer layers improved relative to substrate

✓ Uniform texture demonstrated in pilot production of 4 cm wide RABiTS templates at 100 meter length

✓ Increased deposition rate demonstrated for standard RABiTS architecture (Y_2O_3 / YSZ / CeO_2) on 4 cm wide substrates

FY 2006 Plans and Performance

FY2006 Plans (cont'd)

- **Optimization of self-field I_c and pinning mechanisms in 0.8-2.0 µm thick YBCO films produced in AMSC's Pilot manufacturing line**

FY2006 Performance

- ✓ **2G HTS wire achieves DOE FY06 goal of over 300 A over ~100 meters**
- ✓ **YBCO with RE nanodots inserted into AMSC Pilot process**
- ✓ **Stacking fault formation was studied in-situ using high temperature XRD**

FY 2006 Plans and Performance

FY2006 Plans (cont'd)

- Demonstration of solution deposited buffer layers in a continuous process with performance comparable to AMSC's standard $CeO_2/YSZ/Y_2O_3$ buffer architecture produced by physical vapor deposition

FY2006 Performance

- ✓ LZO buffers deposited over multi-meter length using slot die coating approach
- ✓ 266 A/cm-width (J_c of 3.3 MA/cm^2) demonstrated on slot-die coated LZO buffer using a fully continuous process
- ✓ 336 A/cm-width (J_c of 4.2 MA/cm^2) demonstrated on a short spin-coated LZO buffer. Matches performance of PVD deposited YSZ buffers

FY 2007 Plans

- **Demonstration of 10 meters of slot-die coated, MOD YBCO and MOD LZO on NiW substrates with a performance of 250 A/cm with a standard deviation of less than 5%.**
- **Develop slot-die coated, MOD CeO_2 comparable to PVD CeO_2 layer, which can support 100A class 344 superconductor.**
- **Develop methods to improve mechanical properties of Ni-alloy substrates for 2G HTS wire (increased strength, reduced magnetism, enhanced texture, etc.) and development of thermo-mechanical processing parameters.**
- **Continue to support AMSC's production of alloy substrates (4 cm wide by 100 m long) using the ORNL rolling mill facility with clean room.**
- **Optimization of pinning in 4cm wide thick (0.8-2 μm) MOD YBCO films produced in AMSC's pilot operation.**
- **Characterization and testing of 2G wires and wire products.**

Research Integration

- Regular weekly conference calls
- Frequent sample exchanges
- CRADA meetings
- Personnel exchange
  - AMSC staff used of ORNL rolling mill facilities (once a month)
  - AMSC staff worked on ORNL slot die and inkjet printing facilities
- Joint development of substrate/buffers, joint materials evaluation and testing
- Collaborative research with WDG to explore fundamental pinning mechanisms
- Collaborated with Albany Nanotech for MOD buffer characterization
- Several joint publications and joint presentations
  - 10 presentations at national/international meetings
  - 11 publications (9 published; 2 submitted)
- Joint patent applications filed (2)

A key to the success of the CRADA interaction is the ability to rapidly address critical manufacturing issues, identify solutions and transfer the improvements into AMSC's production process

Papers published joint (ORNL-AMSC; 2005-2006)

1. Title: Solution-processed lanthanum zirconium oxide as a barrier layer for high I-c-coated conductors
Author(s): Sathyamurthy S, **Paranthaman M**, Heatherly L, Martin PA, Specht ED, Goyal A, Kodenkandath T, Li XP, Rupich MW
Source: JOURNAL OF MATERIALS RESEARCH 21 (4): 910-914 APR 2006
2. **Title: Assessment of chemical solution synthesis and properties of Gd2Zr2O7 thin films as buffer layers for second-generation high-temperature superconductor wires**
Author(s): Aytug T, **Paranthaman M**, Leonard KJ, Zhai HY, Bhuiyan MS, Payzant EA, Goyal A, Sathyamurthy S, Beach DB, Martin PM, Christen DK, Li X, Kodenkandath T, Schoop U, Rupich MW, Smith HE, Haugan T, Barnes PN
Source: JOURNAL OF MATERIALS RESEARCH 20 (11): 2988-2996 NOV 2005
3. **Title: Second generation HTS wire based on RABiTS substrates and MOD YBCO**
Author(s): Schoop U, Rupich MW, Thieme C, Verebelyi DT, Zhang W, Li X, Kodenkandath T, Nguyen N, Siegal E, Civale L, Holesinger T, Maiorov B, Goyal A, **Paranthaman M**
Source: IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY 15 (2): 2611-2616 Part 3, JUN 2005
4. **Title: Improved YBCO coated conductors using alternate buffer architectures**
Author(s): **Paranthaman MP**, Sathyamurthy S, Bhuiyan MS, Goyal A, Kodenkandath T, Li X, Zhang W, Thieme CLH, Schoop U, Verebelyi DT, Rupich MW
Source: IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY 15 (2): 2632-2634 Part 3, JUN 2005
5. **Title: Solution deposition approach to high J(c) coated conductor fabrication**
Author(s): Sathyamurthy S, **Paranthaman M**, Bhuiyan MS, Payzant EA, Lee DF, Goyal A, Li X, Kodenkandath T, Schoop U, Rupich M
Source: IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY 15 (2): 2974-2976 Part 3, JUN 2005
6. **Title: Investigation of TiN seed layers for RABiTS architectures with a single-crystal-like out-of-plane texture**
Author(s): Cantoni C, Goyal A, Schoop U, Li X, Rupich MW, Thieme C, Gapud AA, Kodenkandath T, Aytug T, **Paranthaman M**, Kim K, Budai JD, Christen DK
Source: IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY 15 (2): 2981-2984 Part 3, JUN 2005
9. **Title: Mechanical properties of pure Ni and Ni-alloy substrate materials for Y-Ba-Cu-O coated superconductors**
Author(s): Clickner CC, Ekin JW, Cheggour N, Thieme CLH, Qiao Y, Xie YY, **Goyal A**
Source: CRYOGENICS 46 (6): 432-438 JUN 2006
10. **Title: Measurement of stacking fault density in YBa2Cu3O-*x*- using x-ray diffraction and correlation with transport properties**
Author(s): E. D. Specht, A. Goyal, J. Li, P. M. martin, X. Li and M. Rupich
Source: To be submitted to Applied Physics Letters.