Reel-to-Reel Characterization of Time-Based Phase Evolution in YBCO Coated Conductors: The BaF_2 Precursor*

Oak Ridge National Laboratory

D.F. Lee, K. Leonard, L. Heatherly, S. Cook, M. Paranthaman

Argonne National Laboratory

V.A. Maroni, K. Venkataraman, M. Mika

ORNL: $75,000 0.2 FTE and 0.25 Post-Doc
ANL: $125,000 0.2 FTE and 1.0 Post-Doc

***Research sponsored by the U.S. Department of Energy, Energy Efficiency and Renewable Energy as part of a DOE program to develop electric power technology**

Pioneering Science and Technology

ornl

U.S. Department of Energy
Energy Efficiency and Renewable Energy

Project Goals

- **Develop/demonstrate effective diagnostic methods to facilitate the optimization of *ex situ* processed YBCO.**

- **Evaluate XRD and Raman Spectroscopy as means to study precursor phase evolution and *ex situ* YBCO formation.**

- **Determine the feasibility and efficacy of XRD and Raman Spectroscopy as on-line monitoring/control tools for both *ex situ* and *in situ* YBCO processes.**

These activities are in support of the Coated Conductor Development Roadmap

Process Monitoring & Control Strategies / Methods

- **Recommended Activities:**
  - **Experiments to determine what can be detected & influences of changed parameters to correct.**
  - **Develop *in situ* processing monitoring and diagnostic capability.**
  - ***In situ* study of buffer and superconductor layer growth … XRD.**
  - ***In situ* Raman.**

- **2005 Performance Targets:**
  - **Lab technology to manufacturing environment.**

FY2003 Objectives

- Conduct coordinated reel-to-reel (R2R) XRD and Raman microscopy analyses to elucidate the Y-BaF_2-Cu precursor transformation mechanism on long-length textured substrates.

- Establish a basis for the study of YBCO precursor reaction mechanism under conditions that relate directly to long-length coated conductor (CC) fabrication.

Approach

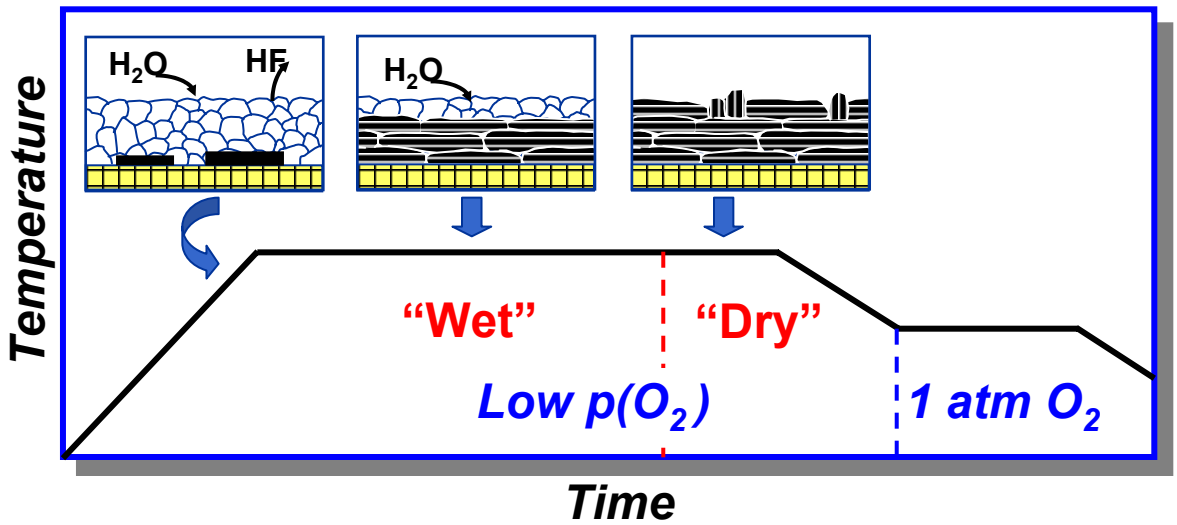
- Process a length of YBCO CC that encompasses a wide range of conversion time with identical processing history.

- Examine sample with R2R XRD and Raman.

FY2003 Results Outline

- **Procedure** used in the processing of a long-length CC with graded-YBCO from e-beam (PVD) "BaF_2" precursor.
- **R2R XRD:**
  - Time-based YBCO formation of 0.3 μm & 1 μm-thick CC,
  - Relate R2R-XRD-extracted "optimum" time domain with transport I_c,
  - Inability of R2R XRD in distinguishing intermediate phases.
- **R2R Raman Microscopy:**
  - Background on observable Raman active phonons of YBCO,
  - Measurement configuration,
  - Results on ORNL graded-composition tapes,
  - Hypothetical remarks about the reaction mechanism.
- **FY2003 Performance.**
- **FY2004 Plans.**
- **Research Integration.**

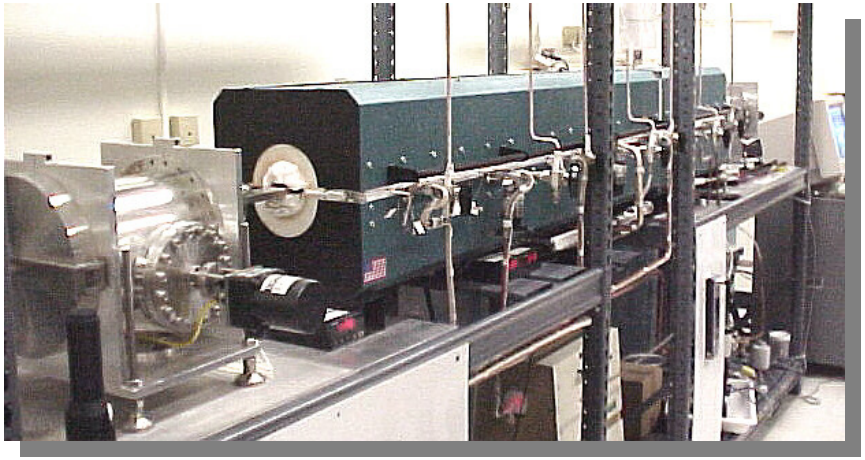
A significant number of processing parameters are involved in the conversion of *ex situ* YBCO

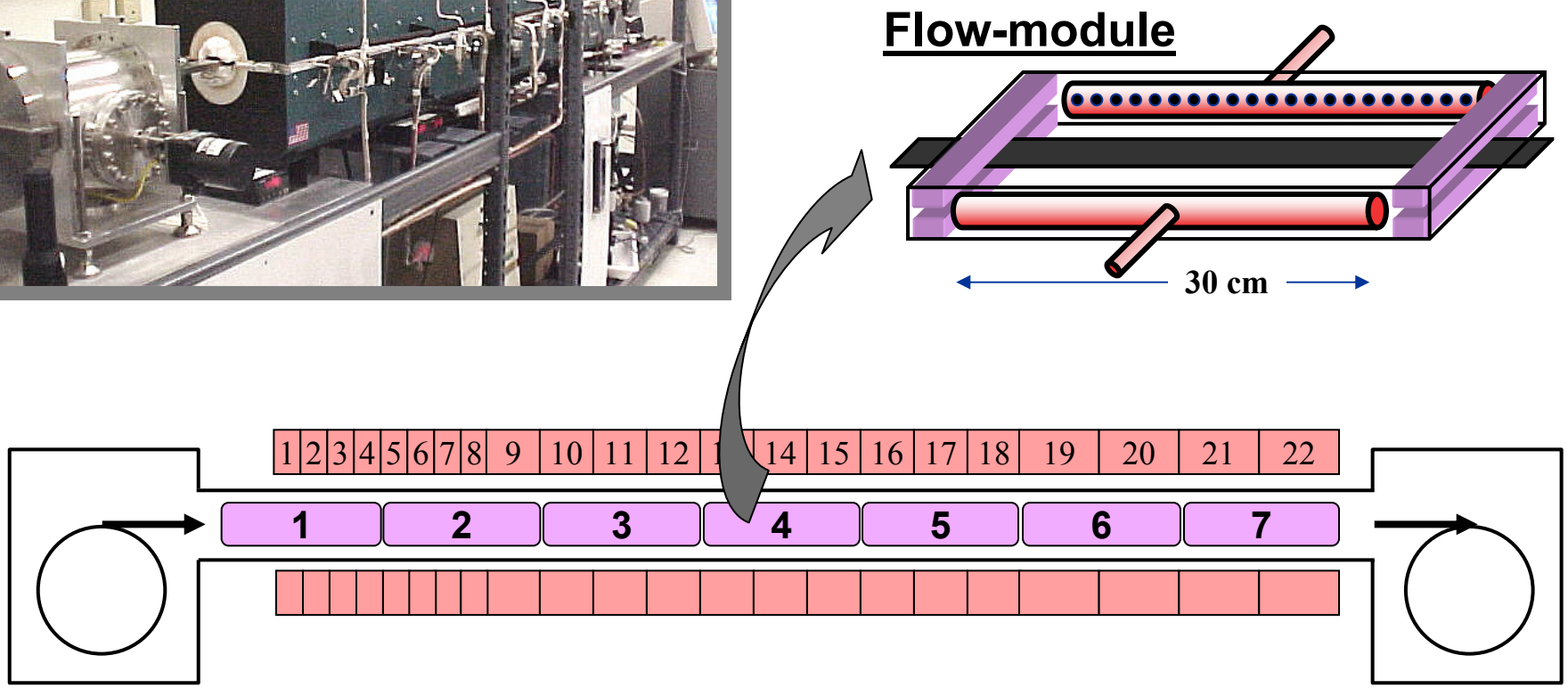


- **Some processing parameters are:**
  - Processing temp
  - Processing time
  - Ramp-up rate
  - Flow rate
  - $P(O_2)$
  - $P(H_2O)$
  - P(chamber)
  - Etc.

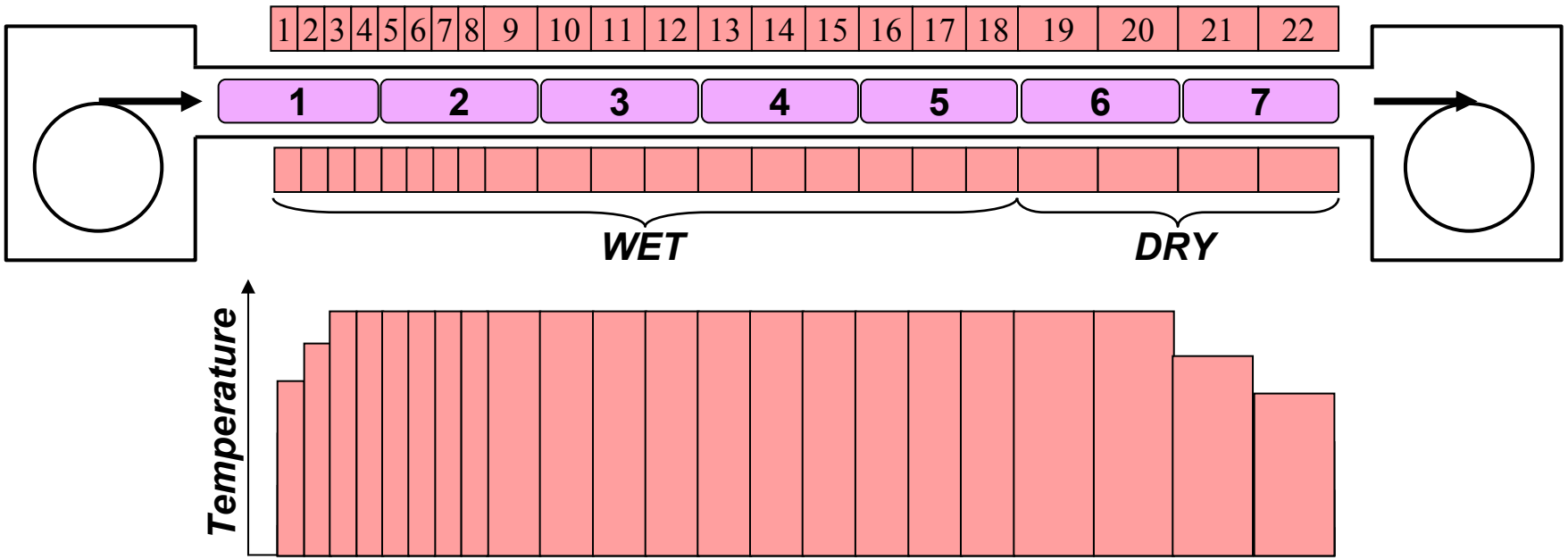
- **Difficult and time consuming to process multiple samples for every set of parameters while ensuring the parameters are kept identical.**

We used our R2R conversion chamber to process a single length of sample with graded YBCO phase assemblage





"Quenching" of YBCO



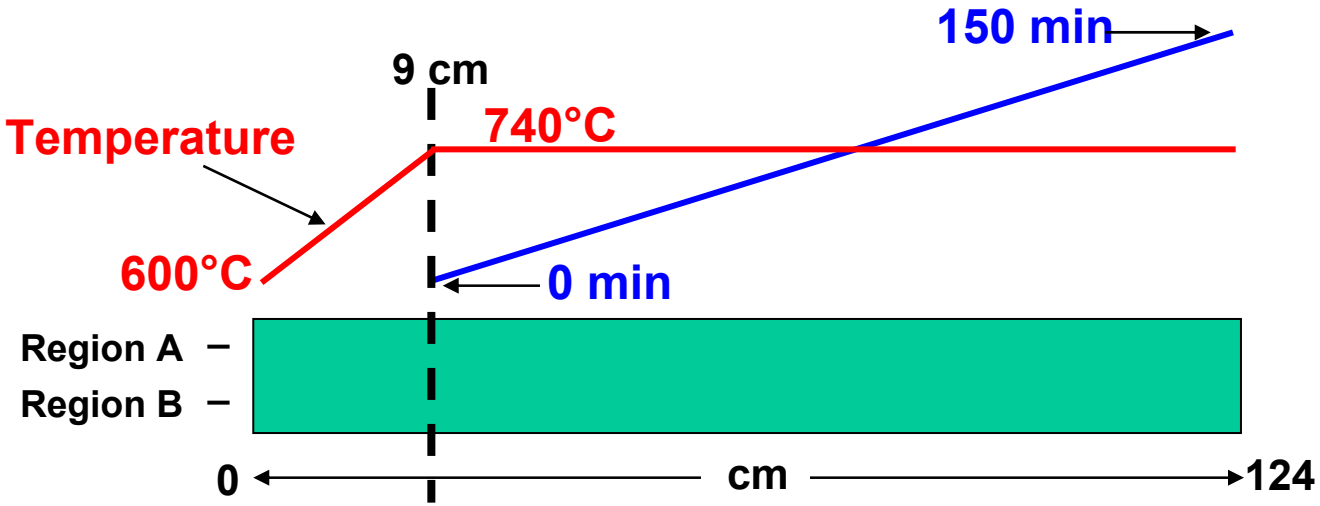
Quench Speed = 2 m/min

$T<T_{conv}$ t=0 t>0

- **YBCO converted for various amounts of time under fixed processing conditions AND history:**
  - **1) precursor material during ramp-up,**
  - **2) initial formation of YBCO,**
  - **3) time domain of optimally converted YBCO, and**
  - **4) time domains past the optimum.**

A 1.2 meter-long RABiTS with ~300 nm of PVD "BaF_2" precursor was processed

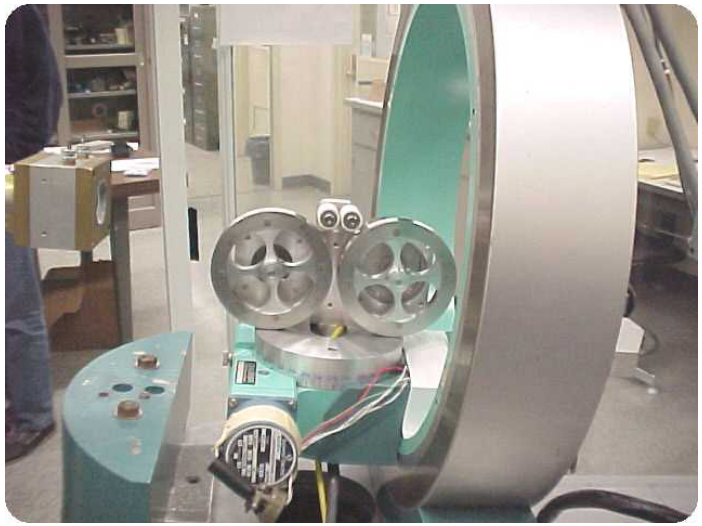
- Ramp-up gradient ~ 16°C/cm
- Processing temp = 740°C
- $P(O_2)$ = 135 mTorr
- $P(H_2O)$ = 35 Torr
- Travel speed = 46 cm/h

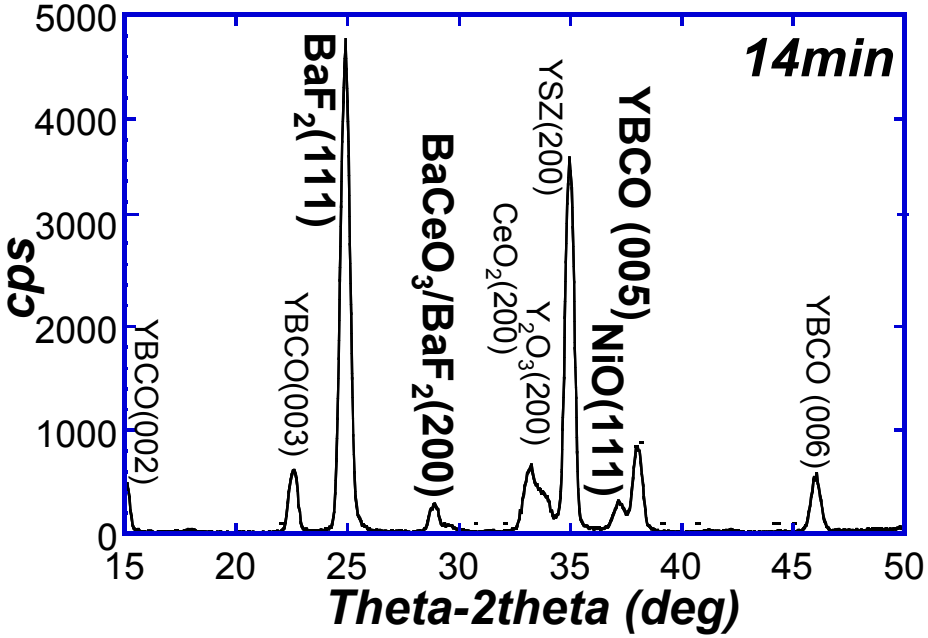


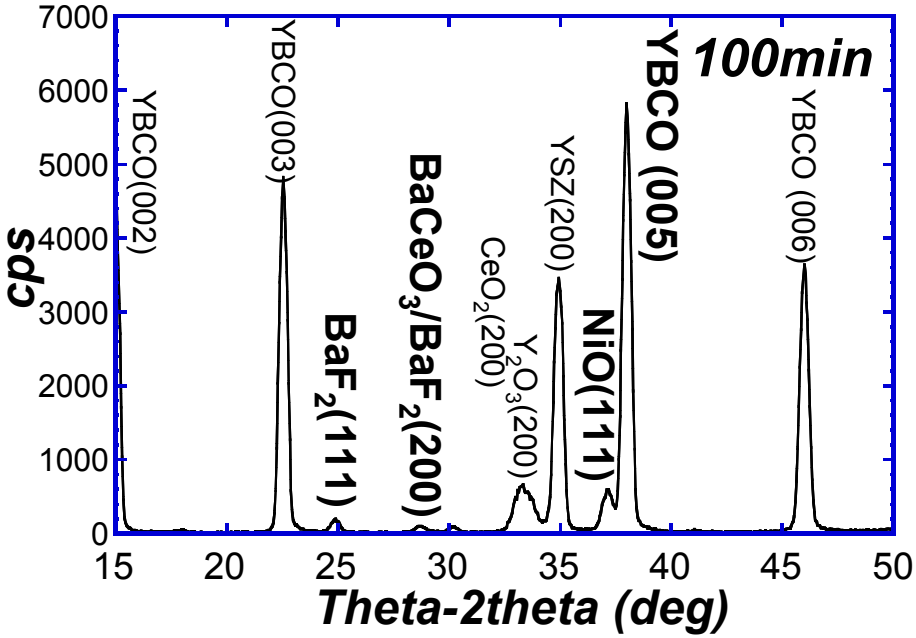
- Knowing the traveling speed and tape location, we can relate position on tape to conversion time and temperature.

Quenched tape was analyzed off-line with ORNL's R2R XRD unit

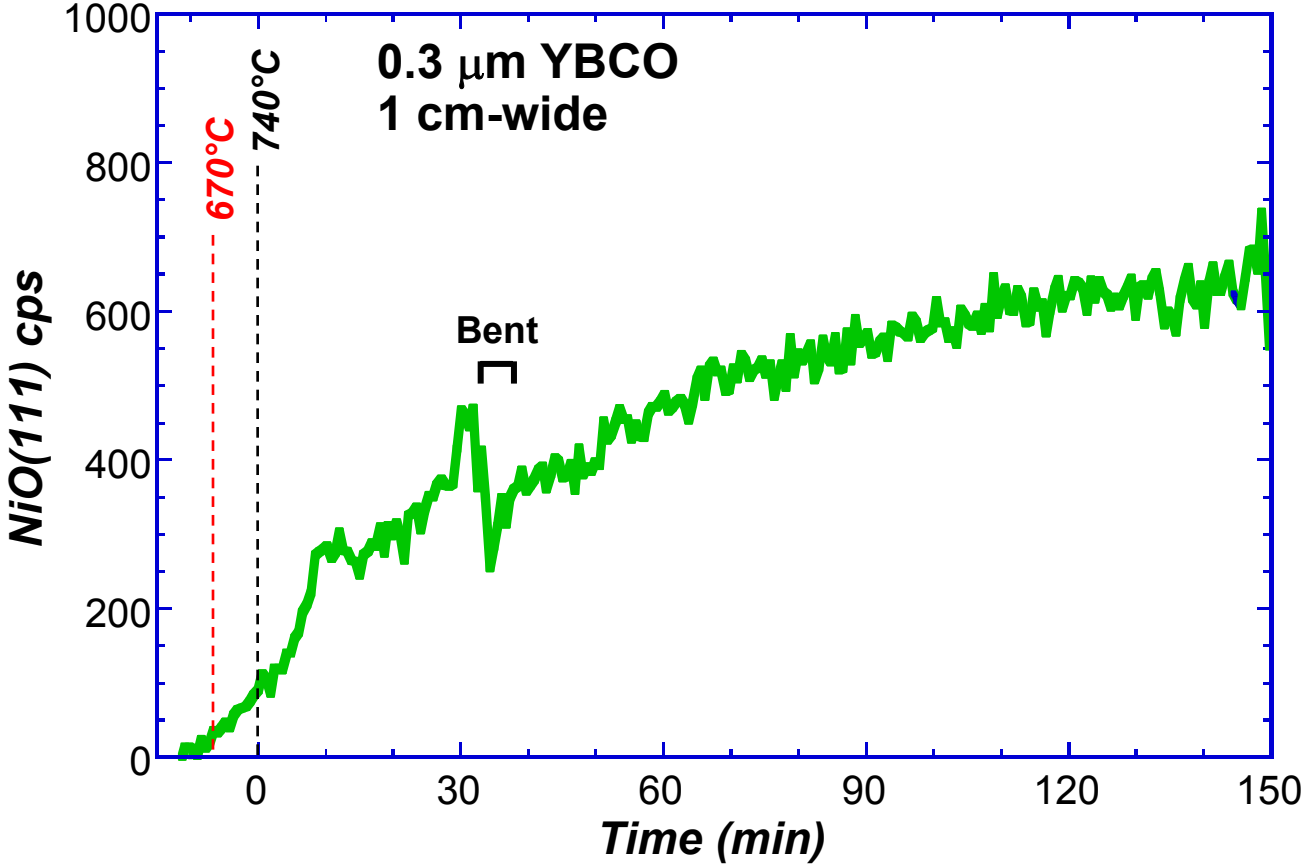
- θ-2θ scans were performed at different locations to determine the peak position of various phases.





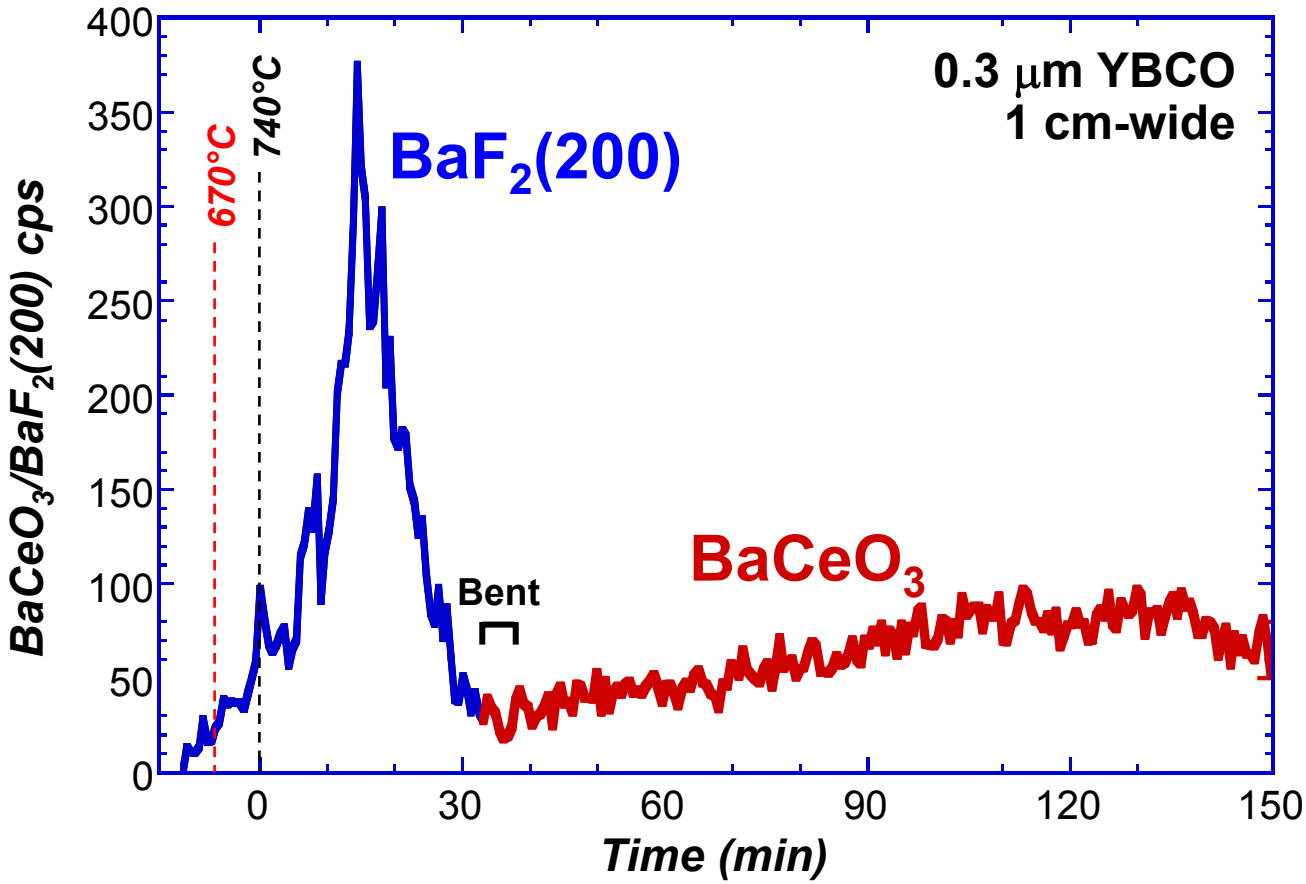


Ni(111) scan can be performed to determine the oxidation of metal substrate and possible delamination



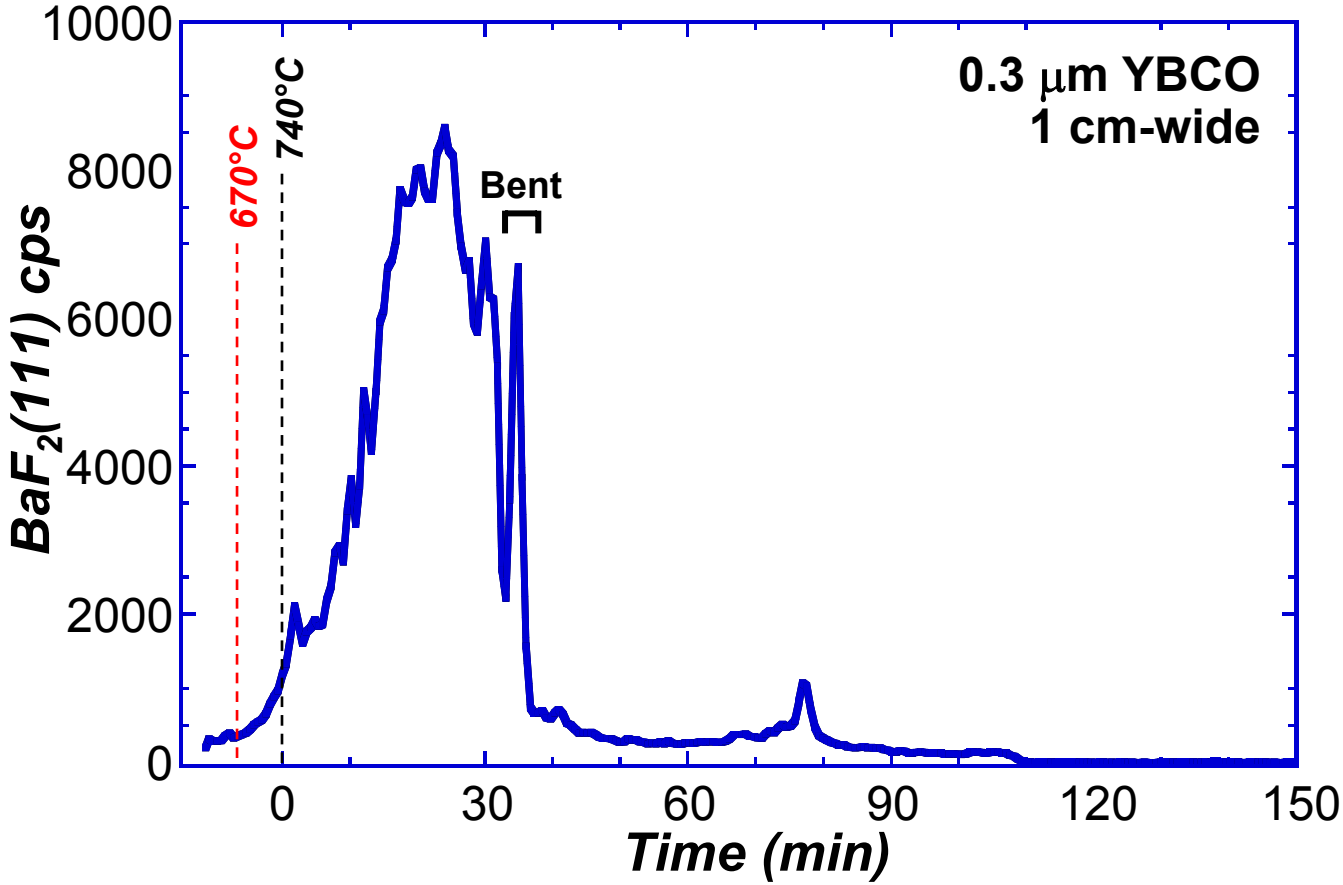
- Oxidation rate of Ni typically levels off after processing temperature has been reached.

Intensity of $BaCeO_3$ indicates the reactivity of CeO_2 cap layer



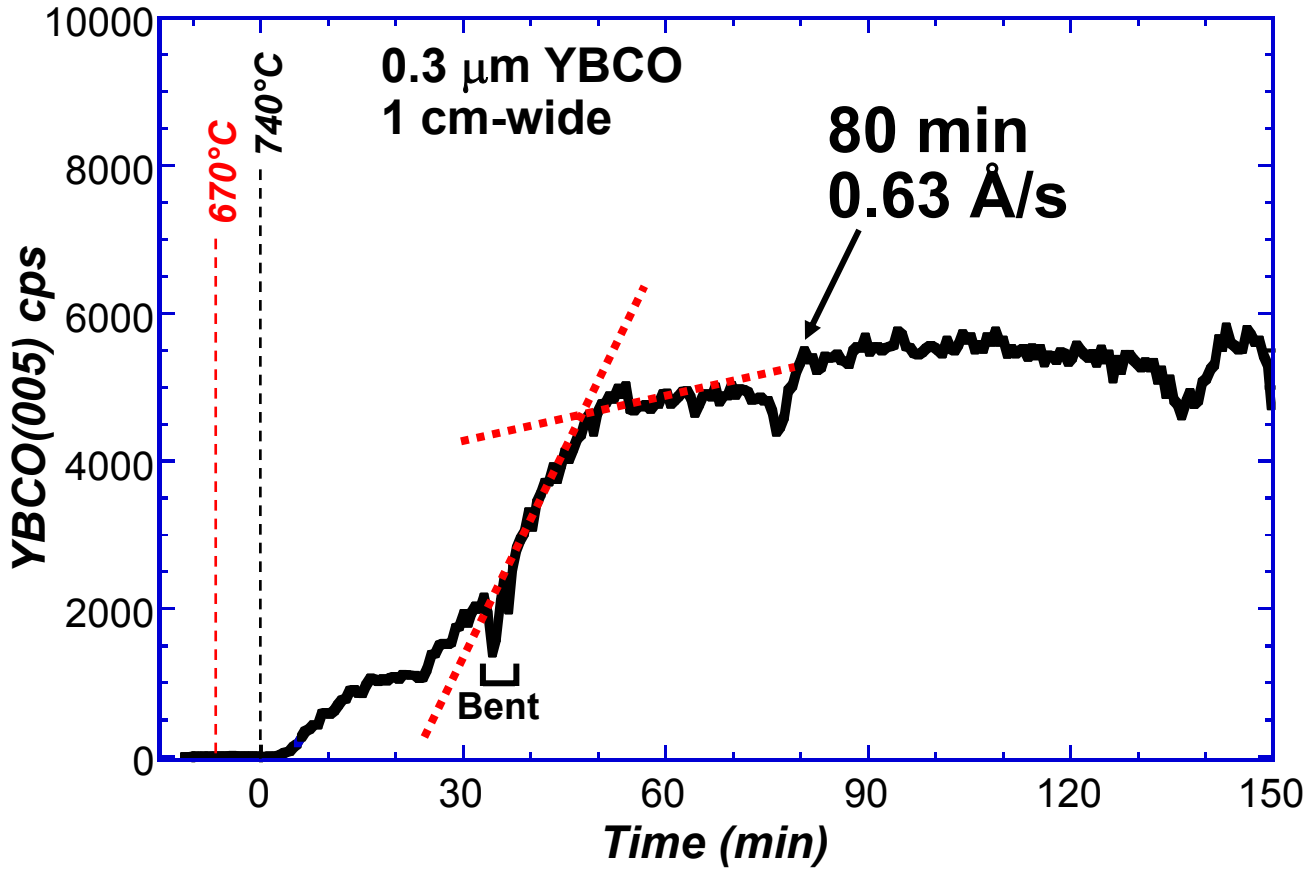
- $BaF_2(200)$ is occasionally seen.

The rate of $BaF_2(111)$ crystallization and decomposition depends on the processing conditions



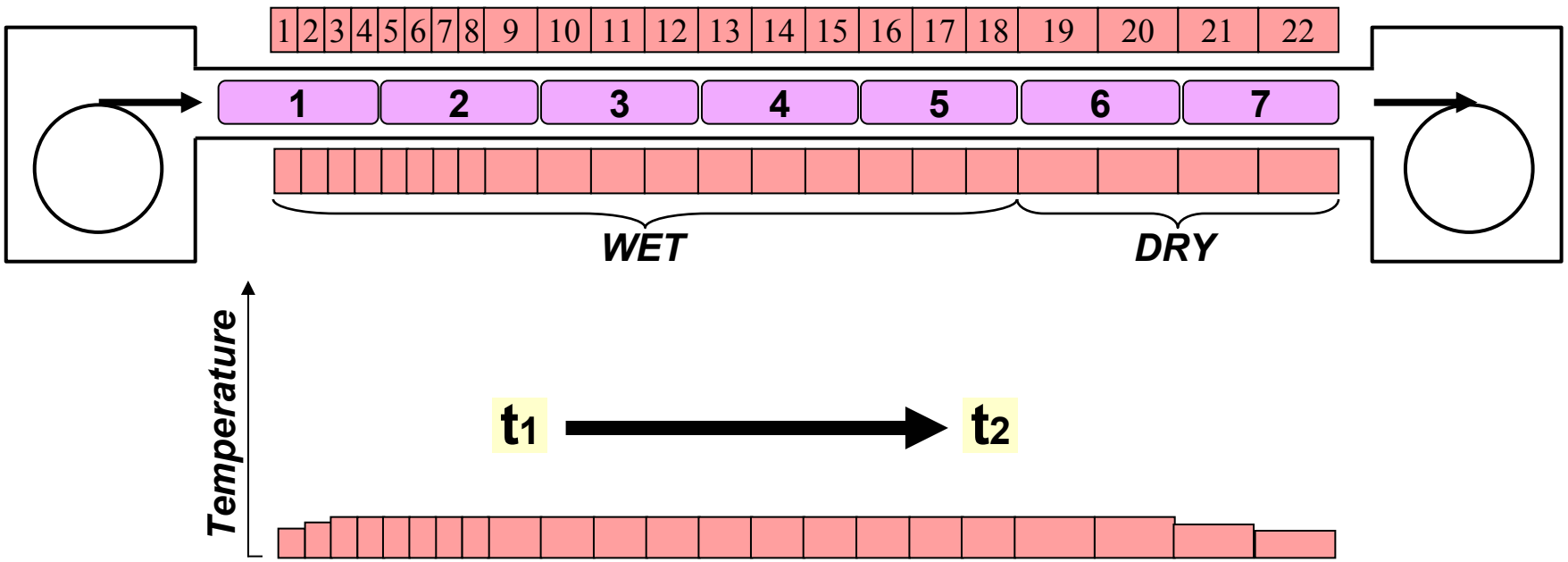
- Frequently, a small amount of BaF_2 remains after YBCO has been fully converted.
- A "saddle" point is frequently seen.

Under the present processing conditions, YBCO intensity levels off after ~ 80 min



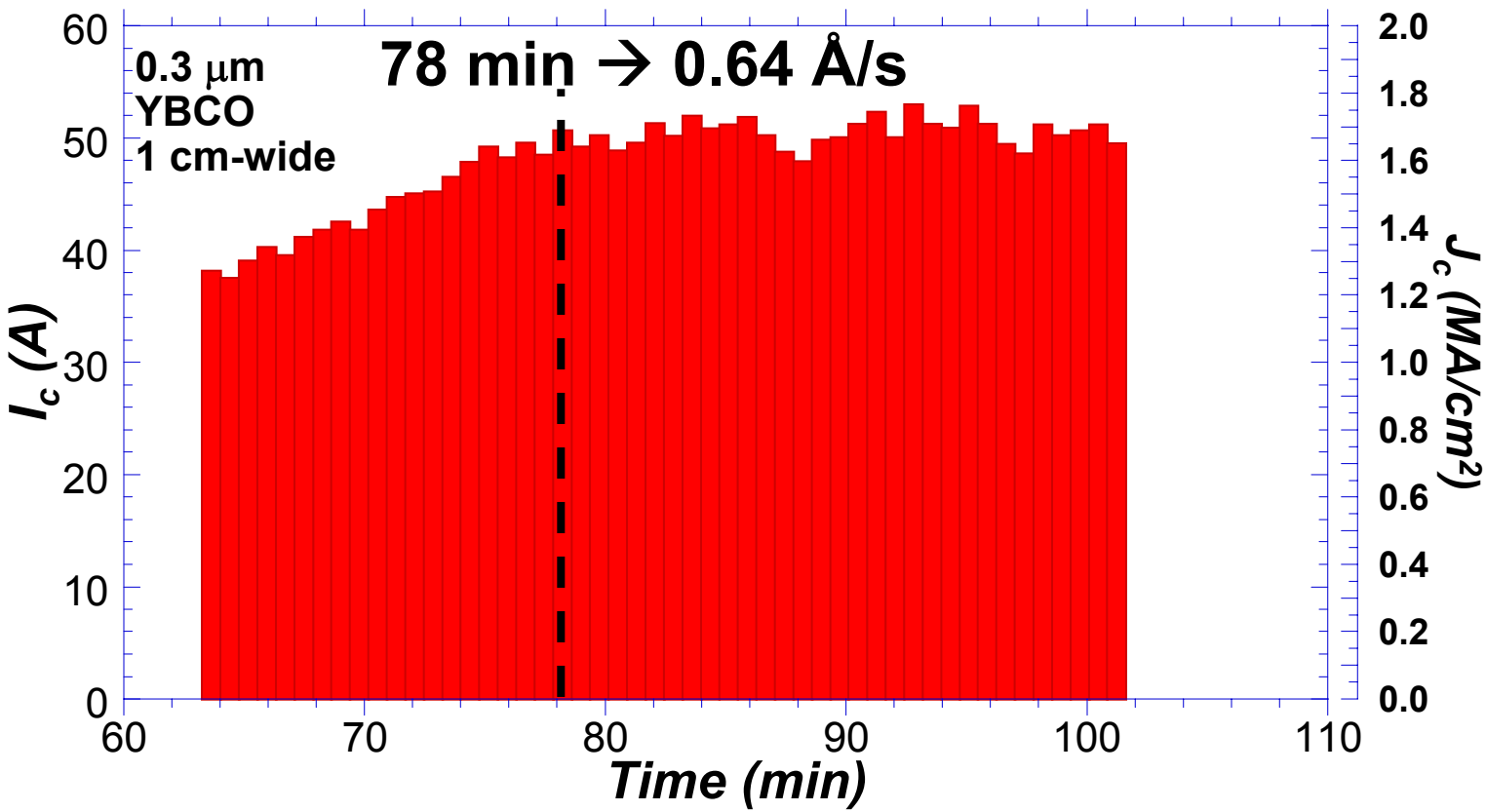
- **Result suggests that more "aggressive" conditions may be used to increase the conversion rate at the latter stage of processing.**

Similar sample was processed using a "Variable Conversion" procedure to correlate the XRD results with CC performance

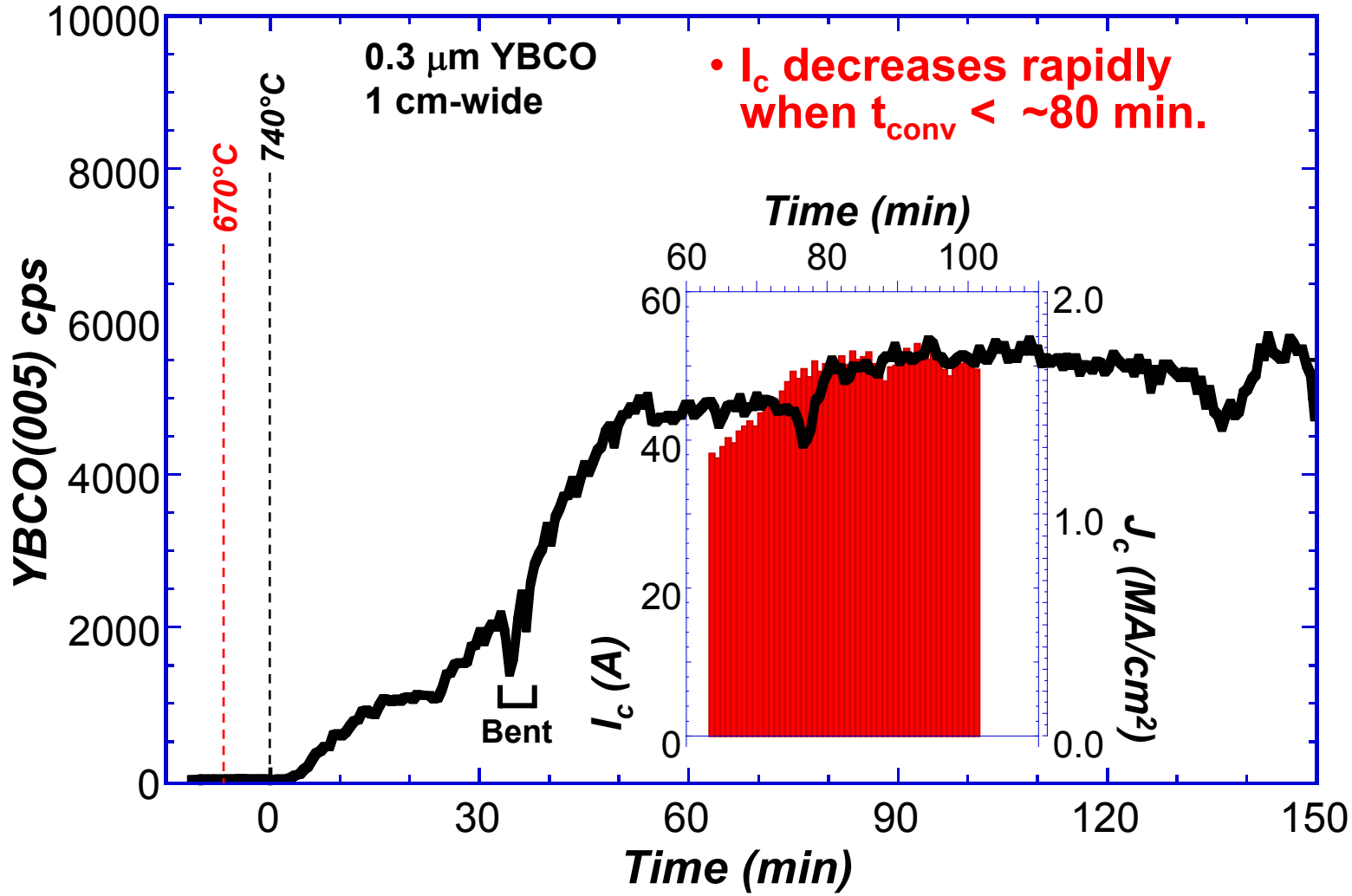


- YBCO converted for various amounts of time under fixed processing conditions AND history.
- Enables study of variation in conversion time with phase content and properties.

I_c measurement confirms the optimum time domain indicated by XRD (~ 80 min)

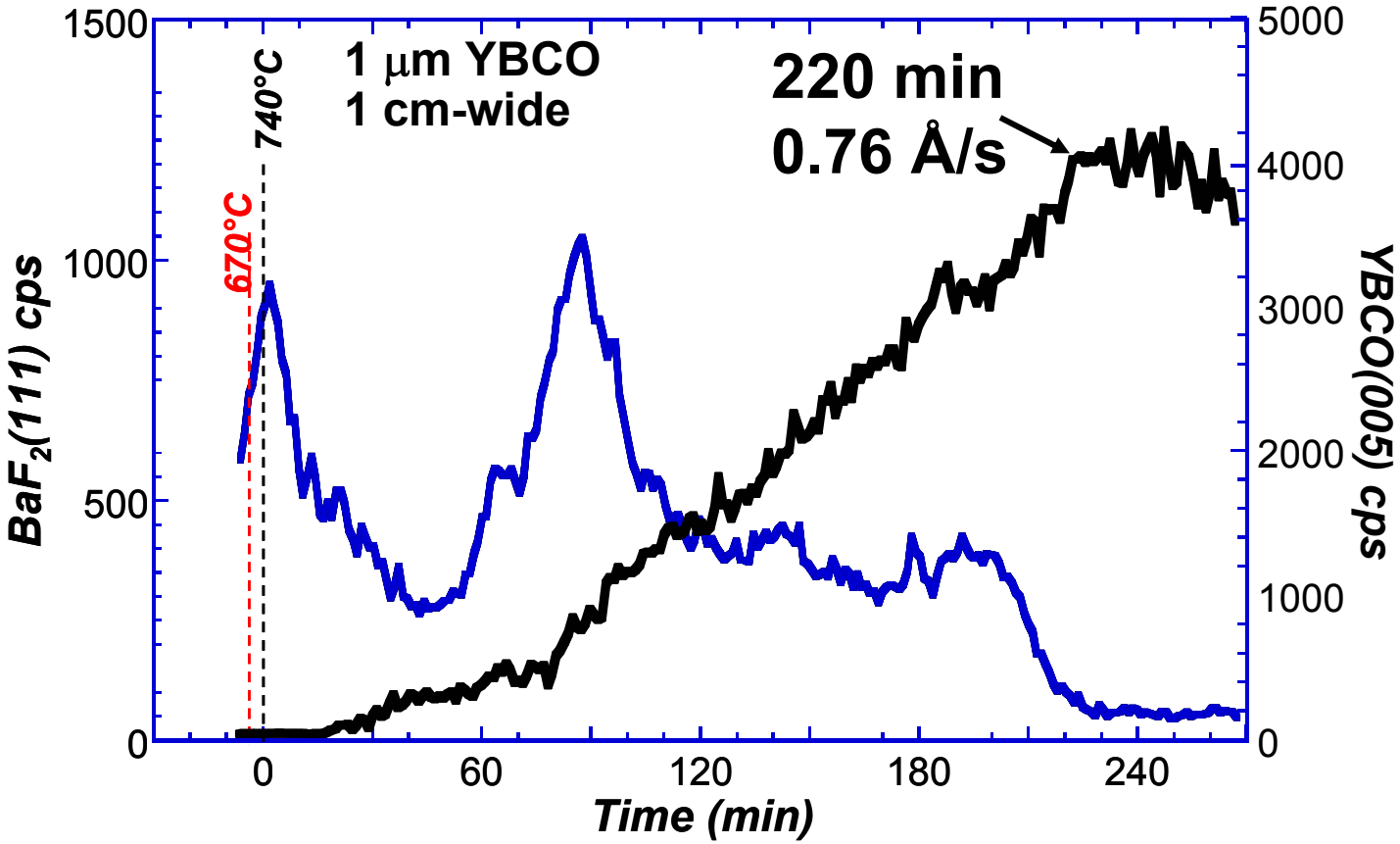


I_c measurement confirms the optimum time domain indicated by XRD (~ 80 min)

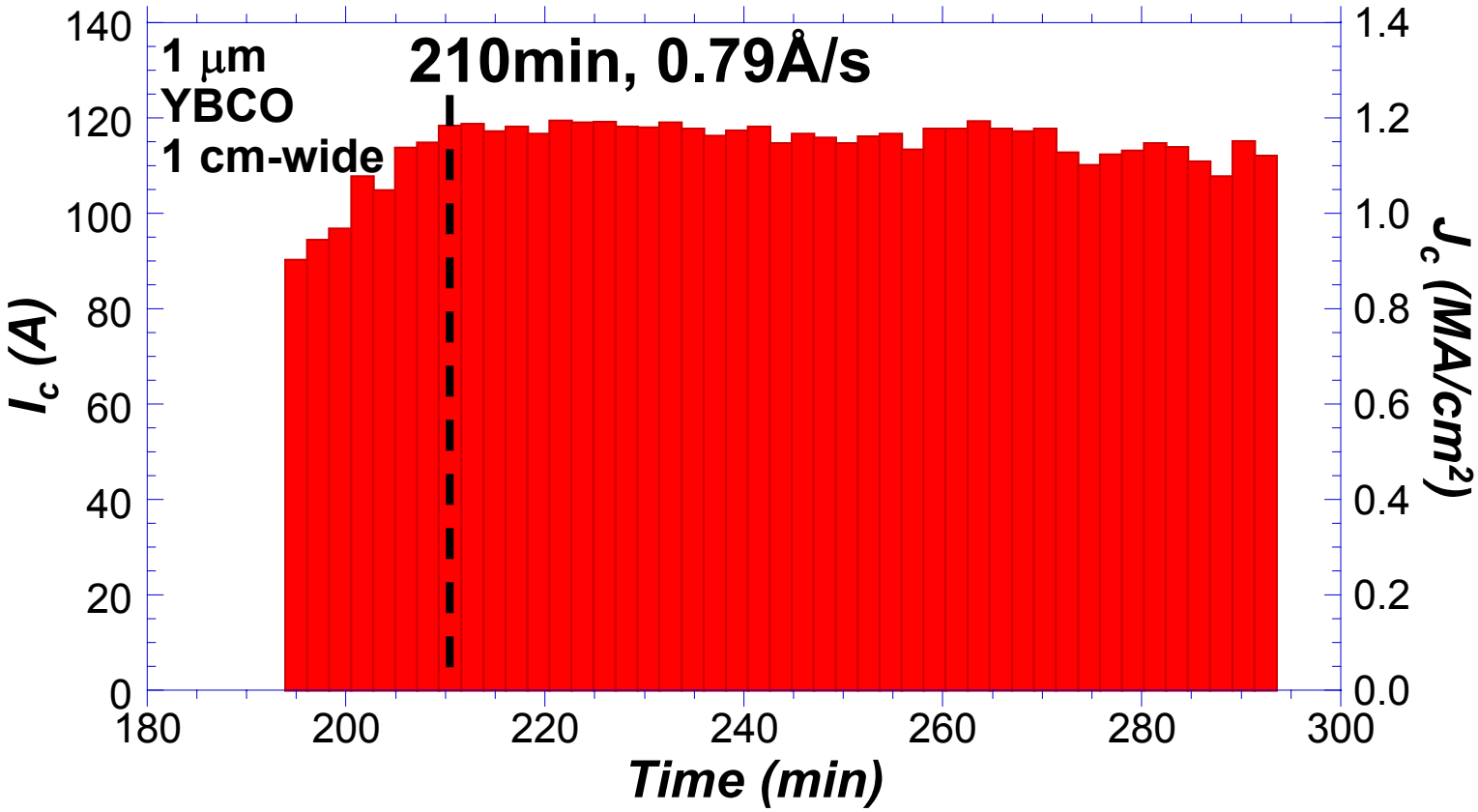


Another 1.1 meter-long RABiTS with 1000 nm of PVD "BaF_2" precursor was quenched

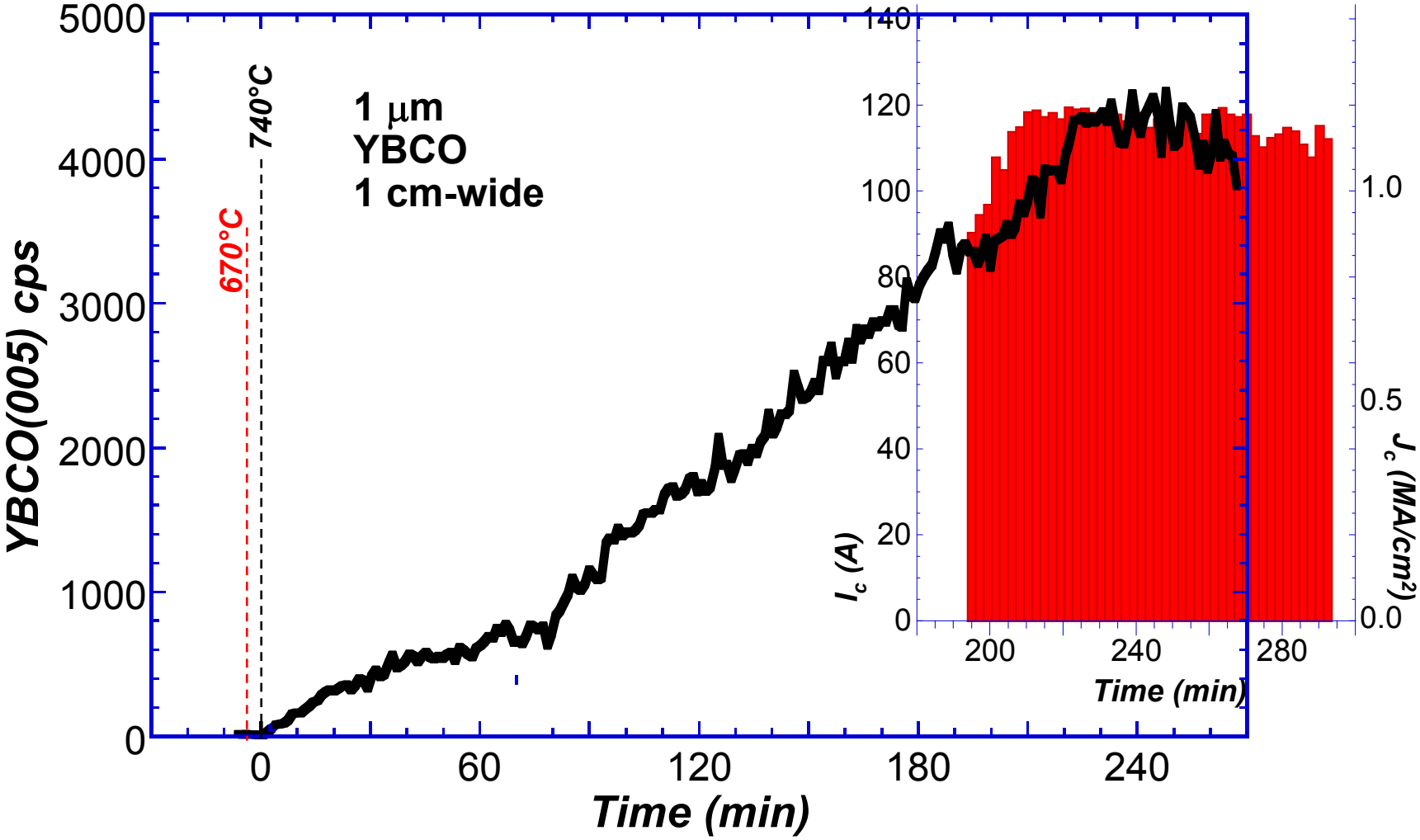
- Ramp-up gradient ~ 32°C/cm
- Processing temp = 740°C
- $P(O_2)$ = 135 mTorr
- $P(H_2O)$ = 4 to 35 Torr
- Travel speed = 24.7 cm/h



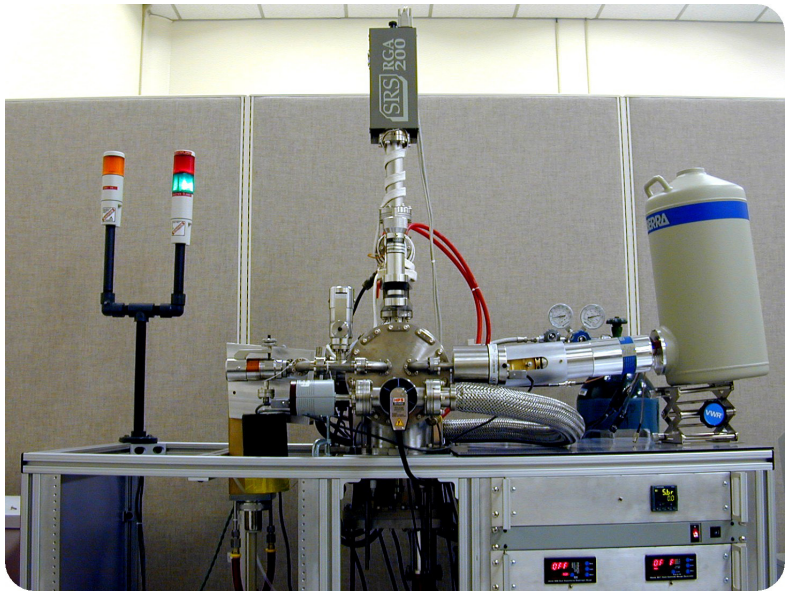
Optimum time domain of similarly processed "variable conversion" sample is in excellent agreement with XRD result (~ 220 min)

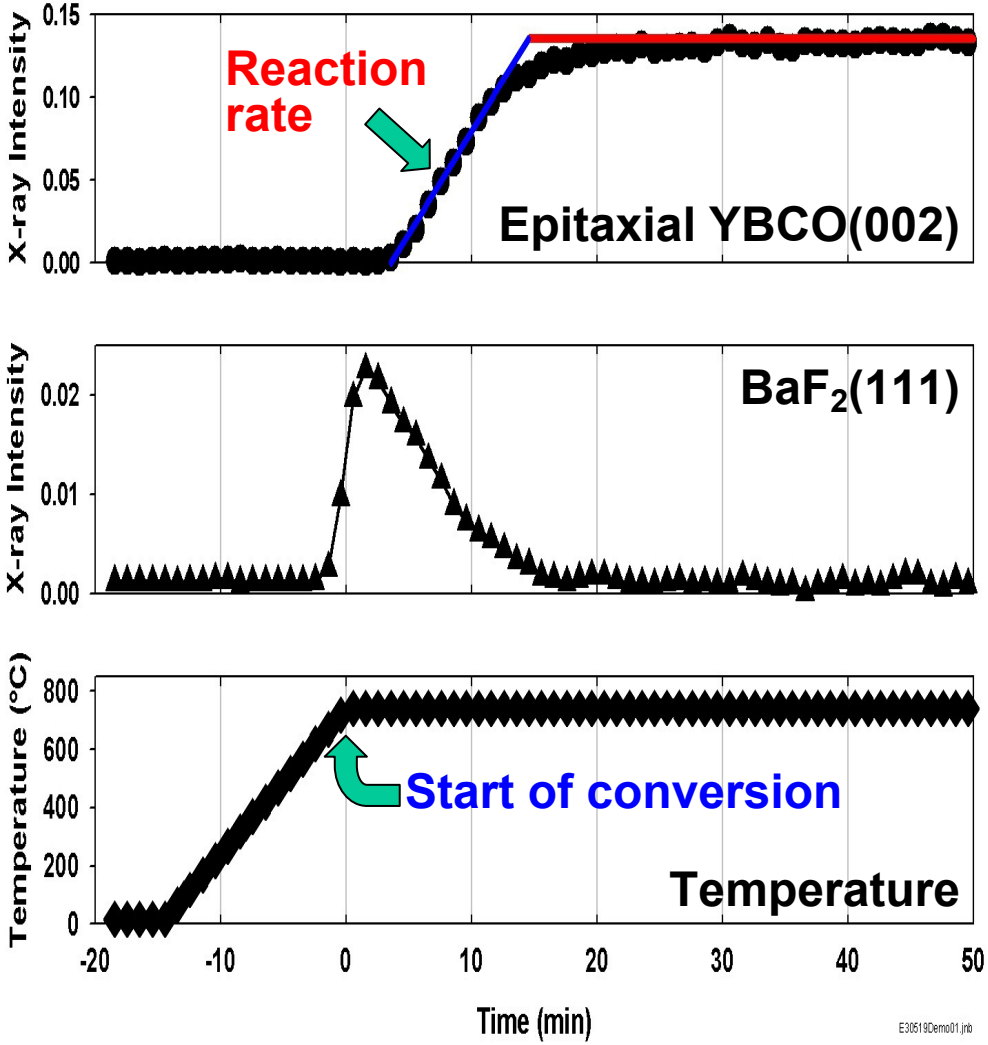


Optimum time domain of similarly processed "variable conversion" sample is in excellent agreement with XRD result (~ 220 min)

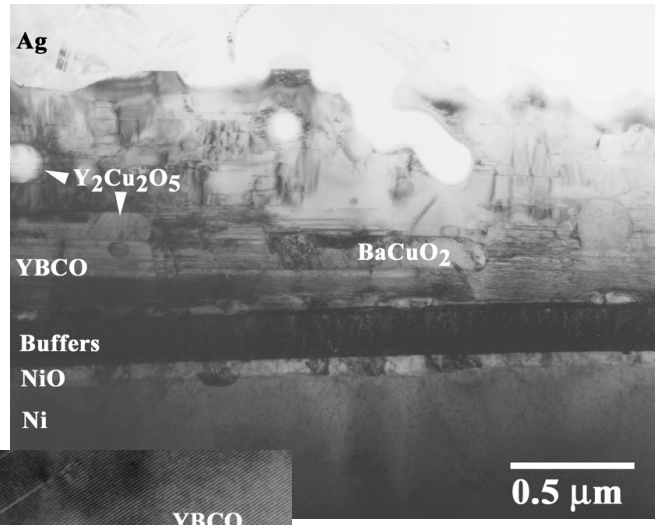


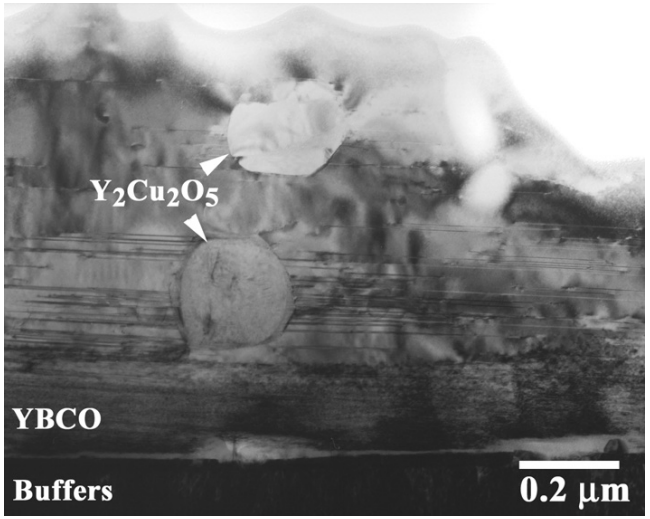
The value of an *in situ* XRD is being demonstrated in our short sample system
(Lee-List, 2003 Review)

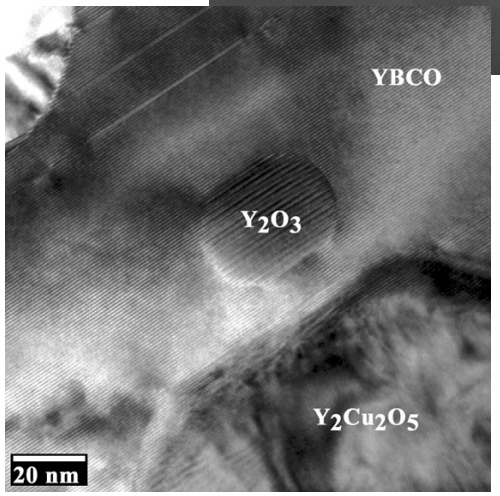


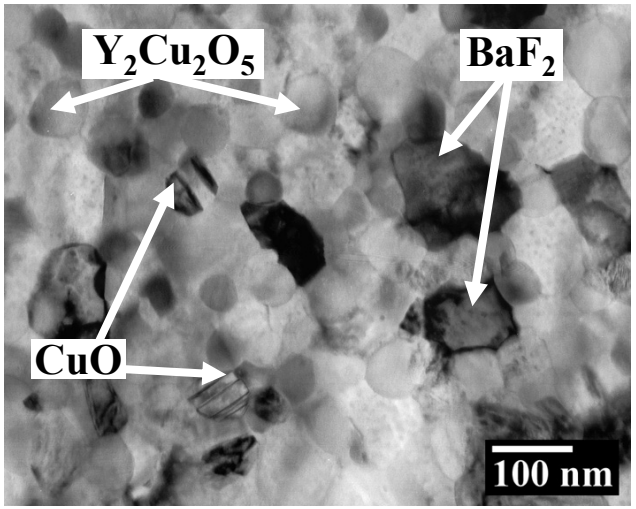


TEM analyses show various intermediate phases in the unreacted precursor



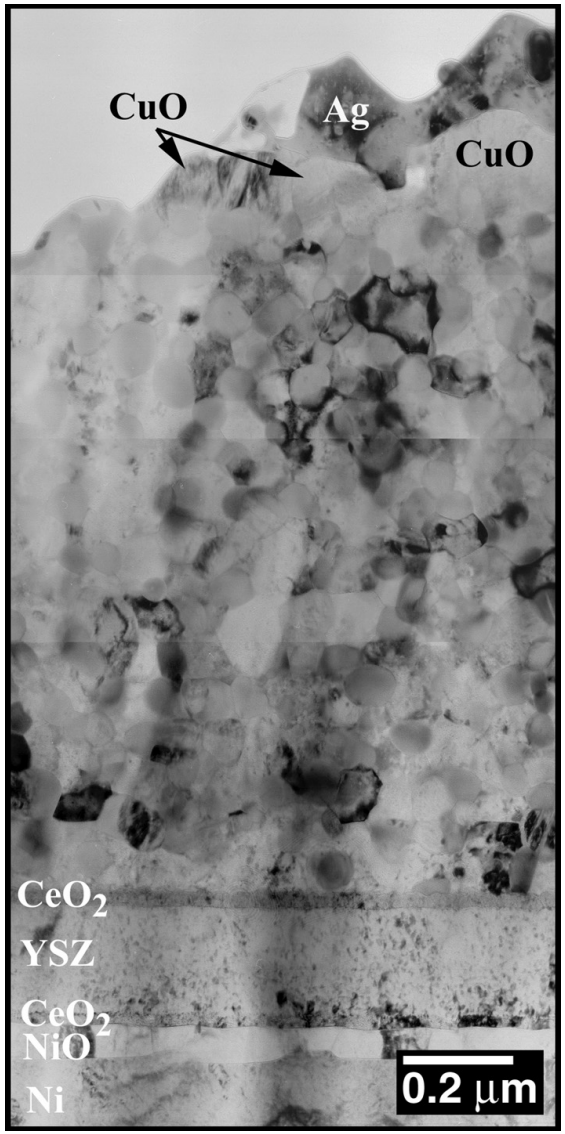


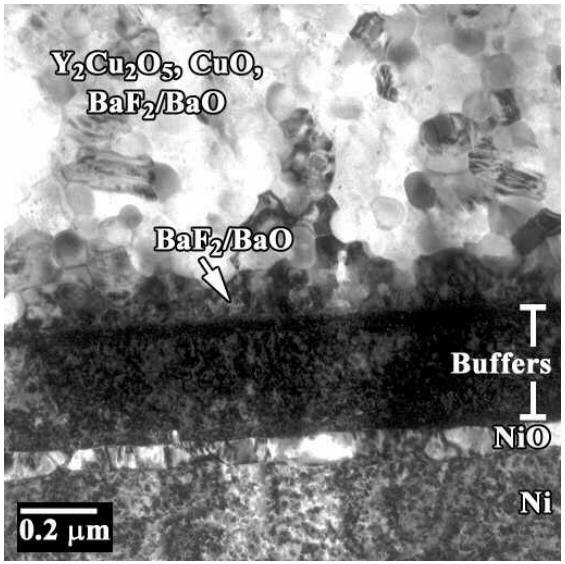


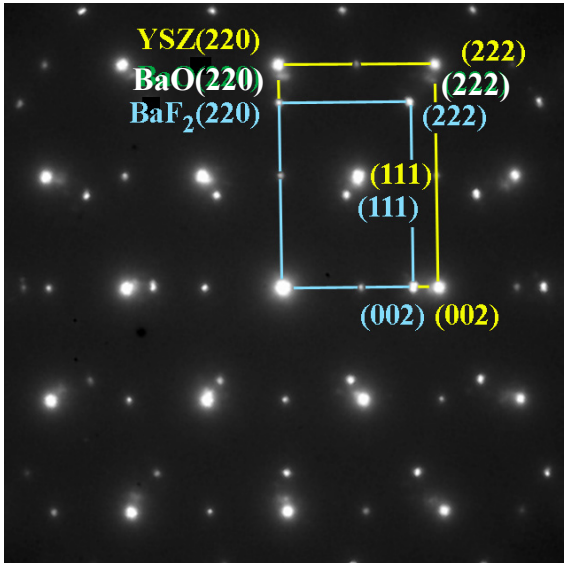


- These include $Y_2Cu_2O_5$ (202), Y_2O_3, CuO, $BaCuO_2$, BaF_2 …

Orientation relationship has been seen between BaF_2, BaO and RABiTS

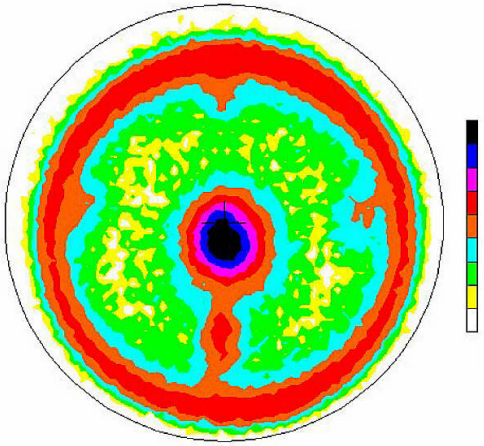




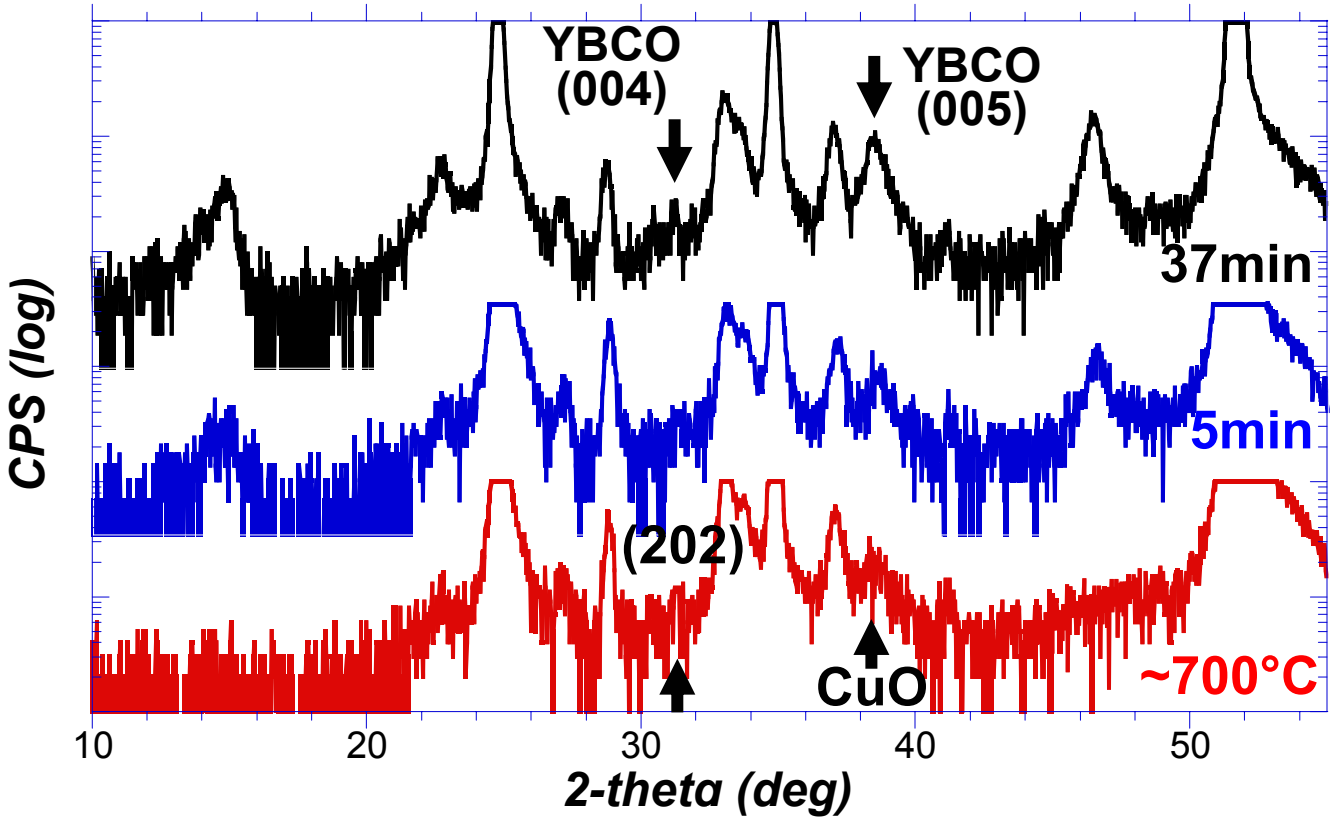


- BaF_2 and BaO at CeO_2 boundary holds orientation relation.
- Image taken on Ni[100]//YSZ[110]//CeO_2 [110]// BaF_2[110] zone axis.

BaF_2 (111) pole fig



These intermediate phases are obscured by other peaks in the developing XRD pattern



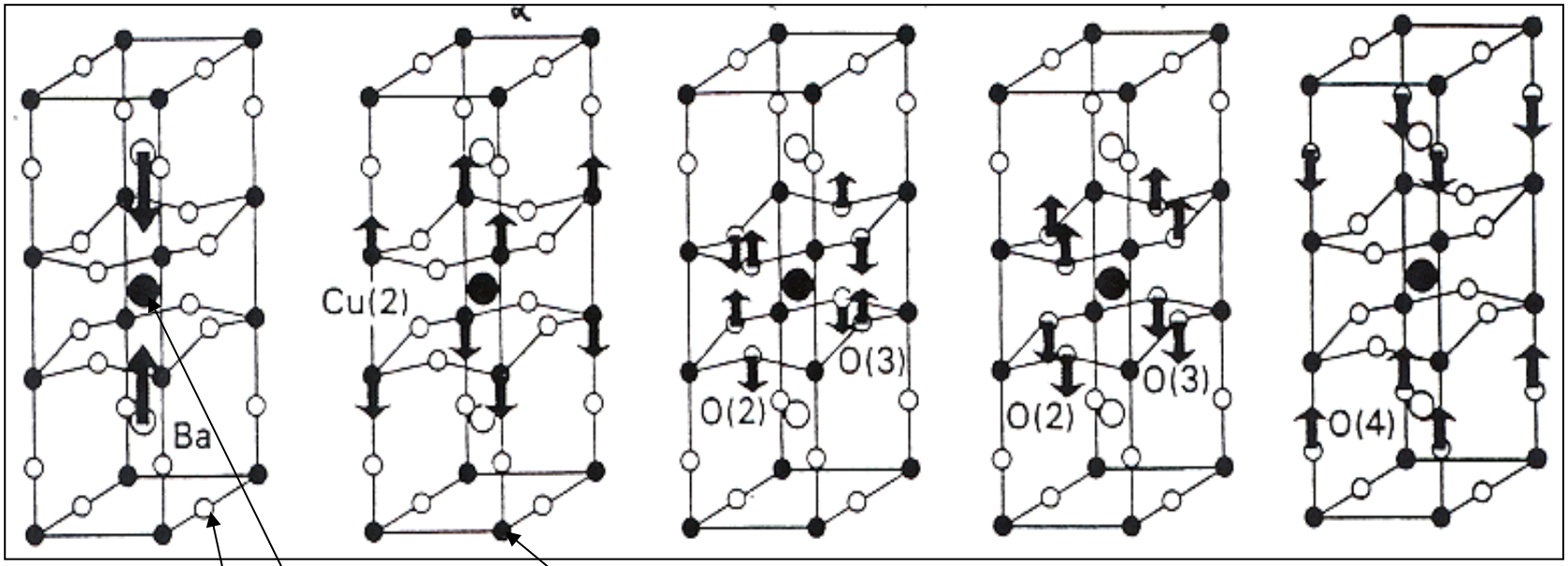
- A <u>more effective method</u> is necessary for study of intermediate phases.

Coupling of Raman Microscopy with XRD Results to Identify/Investigate Intermediate Phases During Y-BaF_2-Cu Precursor Transformation

- Some words about the observable Raman active phonons of YBCO
- Measurement configuration for reel-to-reel (R2R) Raman microscopy
- Raman results for ORNL's graded-composition tapes
- Some hypothetical remarks about the reaction mechanism
- Performance Summary:
  - FY 2003 Performance/Results
  - FY 2004 Plans
  - Research Integration

Raman Active c-axis Phonons of Orthorhombic and Tetragonal $YBa_2Cu_3O_{7-x}$ (YBCO/O and YBCO/T)

YBCO/O	118 cm^{-1}	149 cm^{-1}	335 cm^{-1}	433 cm^{-1}	502 cm^{-1}
YBCO/T	116 cm^{-1}	142 cm^{-1}	340 cm^{-1}	450 cm^{-1}	475 cm^{-1}
	Ba mode	Cu2 mode	O2+/O3- mode	O2+/O3+ mode	O4 mode



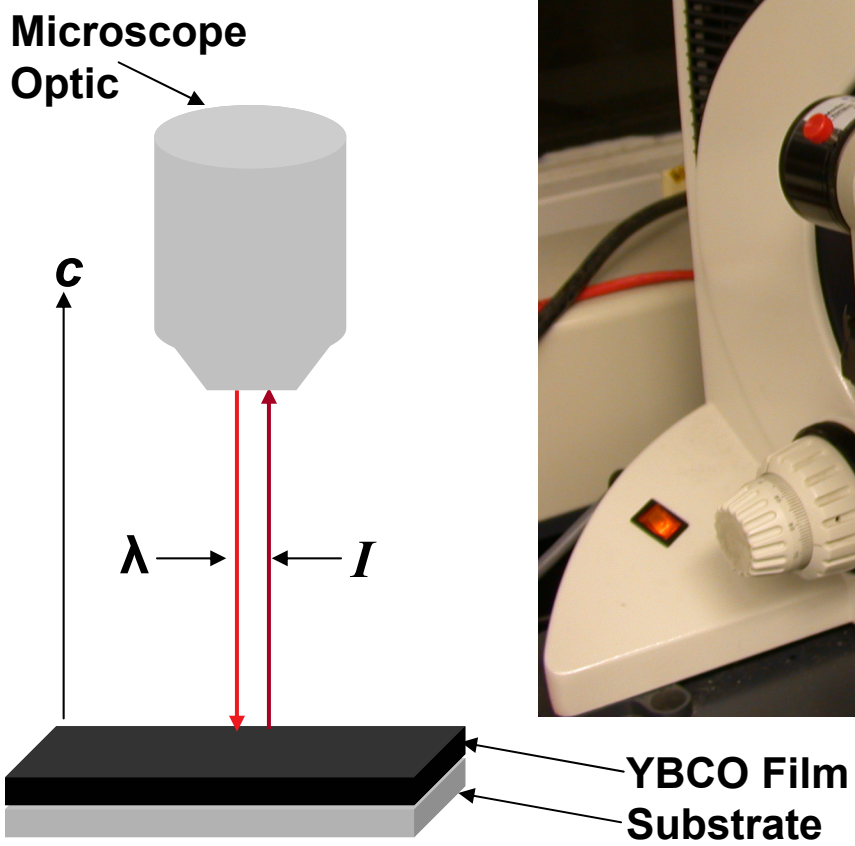
Y

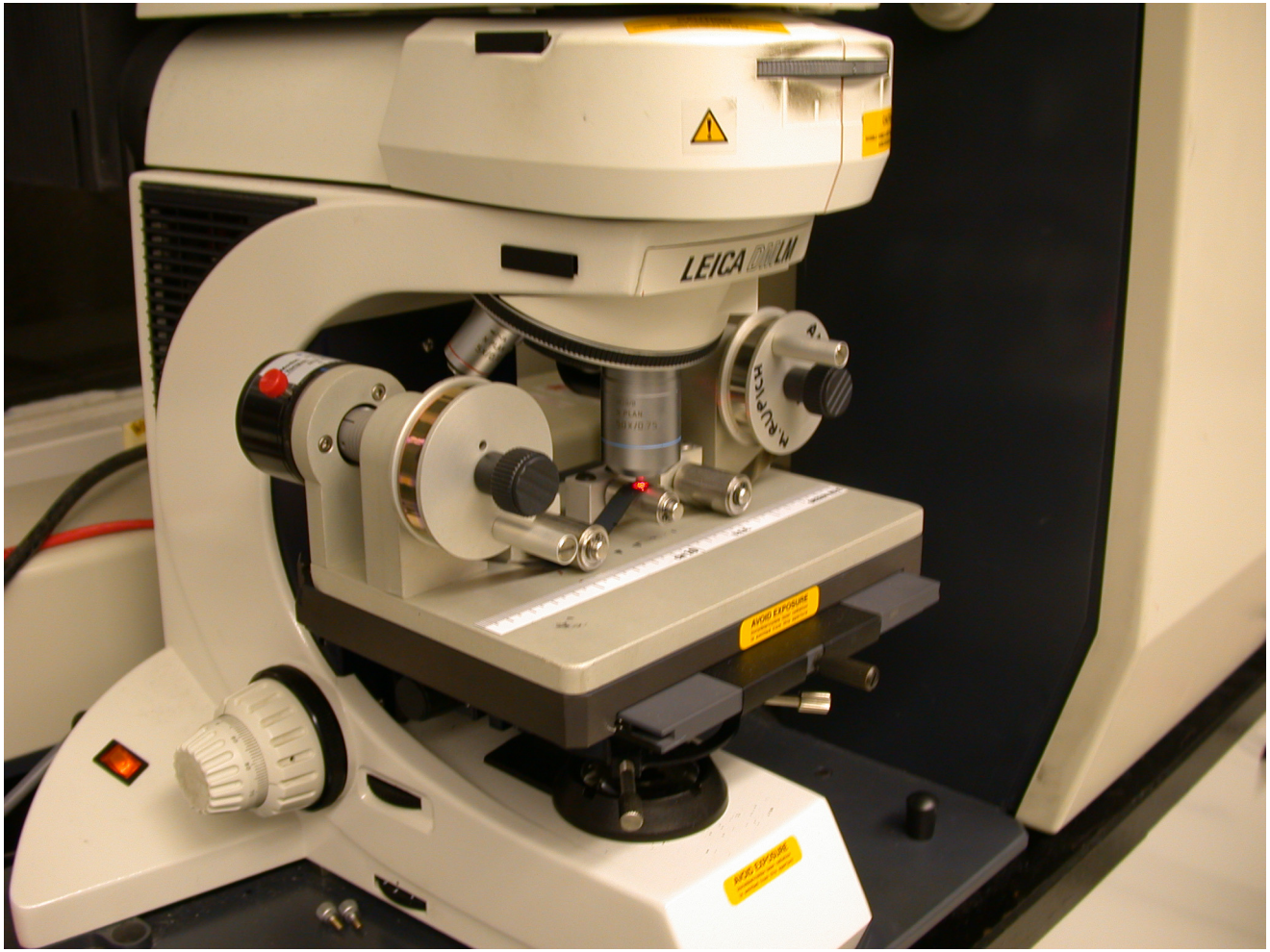
O(1)

Cu(1)

R2R Raman Microscopy: Measurement Configuration

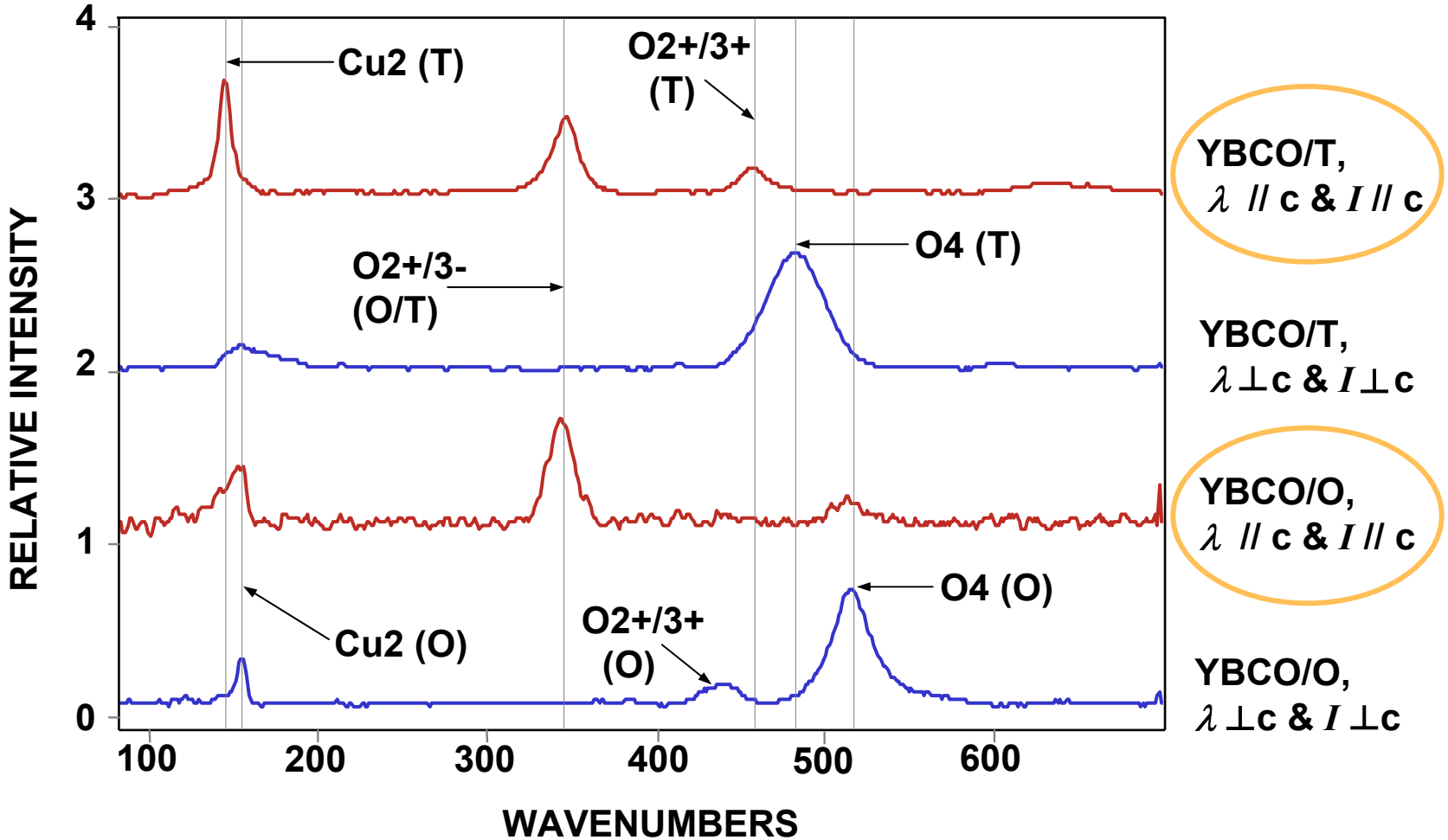
λ = laser direction
I = Raman observation direction





Raman Scattering from "Single Crystal" YBCO/O and YBCO/T

- scattering intensity of each phonon is a function of incident laser direction (λ) and direction of observation of the Raman scattering (I)

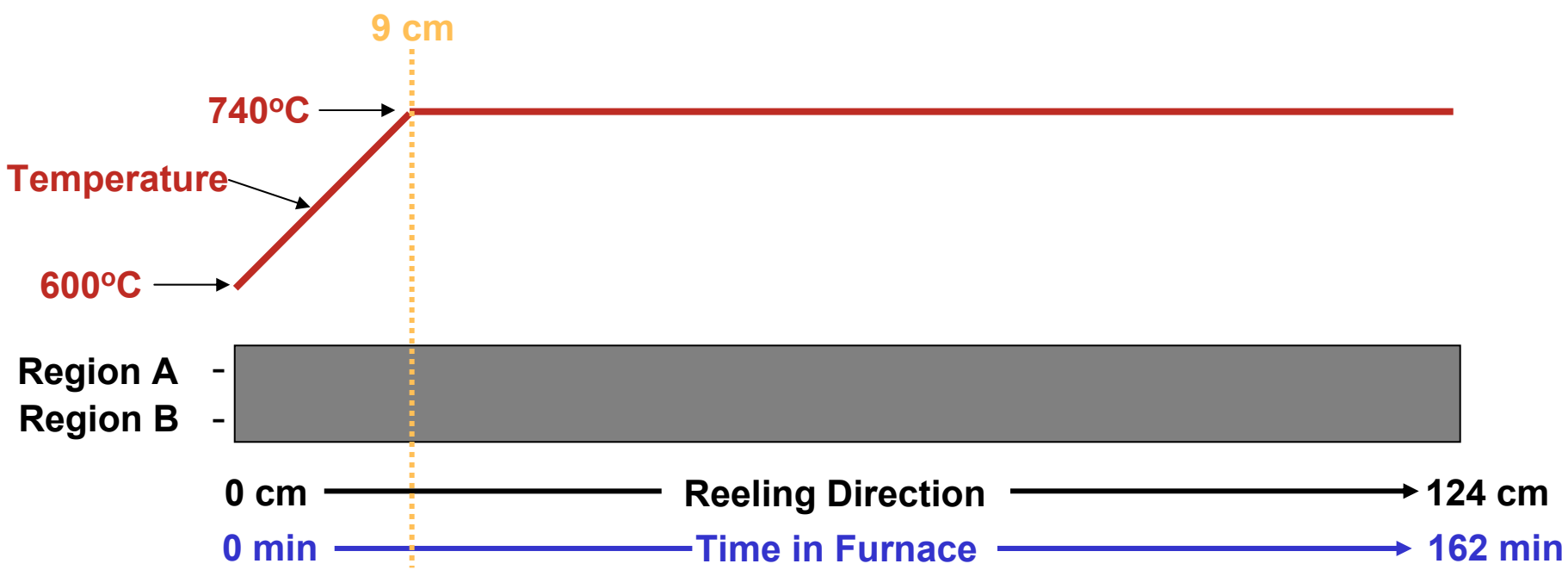


Reel-to-Reel Raman Examination of the 1.25 m Coated Conductor Tape Differentially Heat Treated by Dominic Lee (ORNL)

- **Tape Embodiment:**

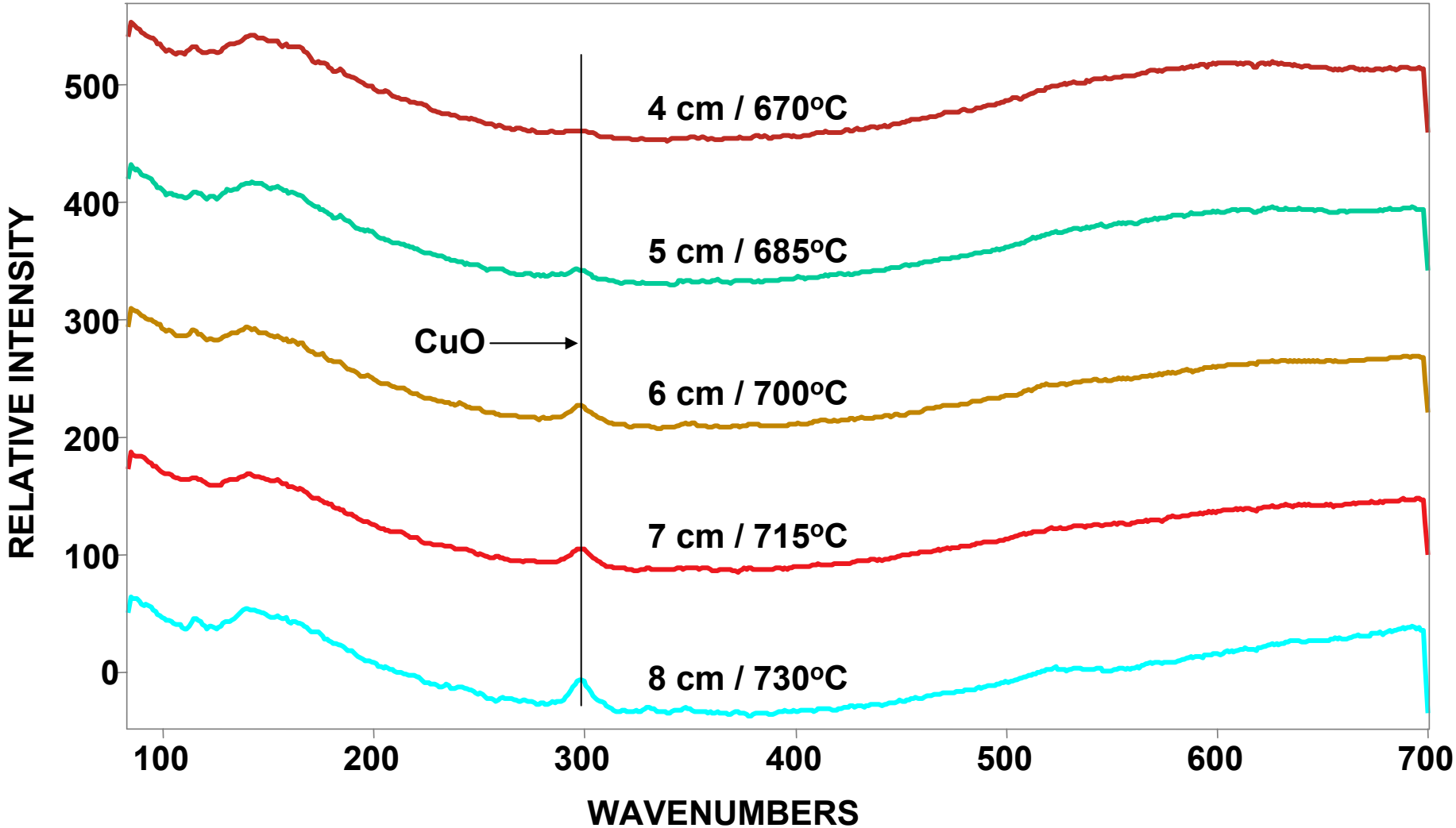
YBCO (300 nm) / CeO_2 (15 nm) / YSZ (200 nm) / Y_2O_3 (15 nm) / Ni (1 μm) / Ni-W (50 μm)

- **YBCO Precursor Deposition by e-beam evaporation of Y, BaF_2, and Cu**
- **Nature of Treatment: Impose time-at-temperature gradient and back-reel "quench"**



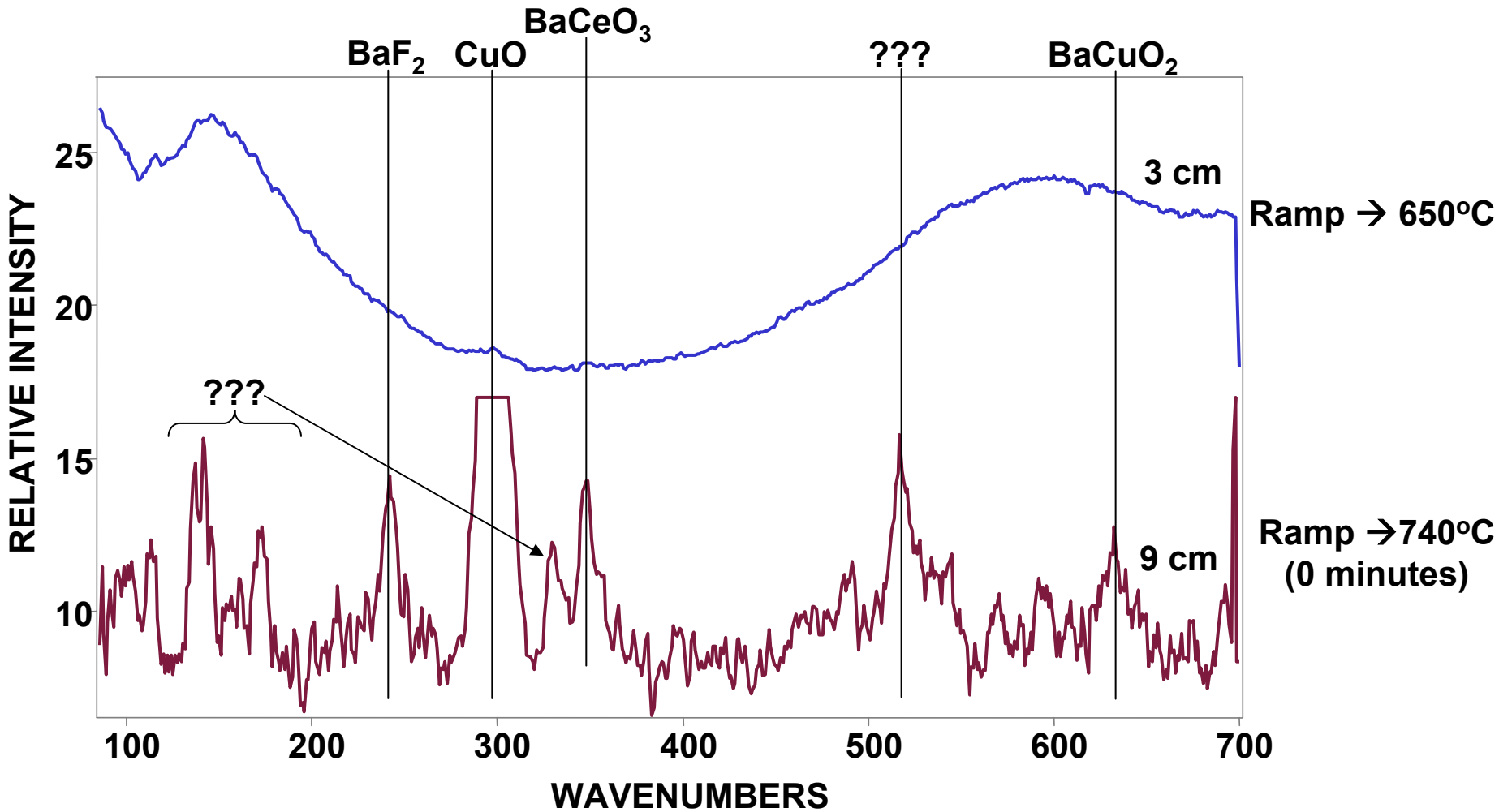
Raman Spectra from 1.25 m Tape DL01: 4 → 8 cm in 1 cm intervals

• incipient crystallization of CuO from a "primordial mush"



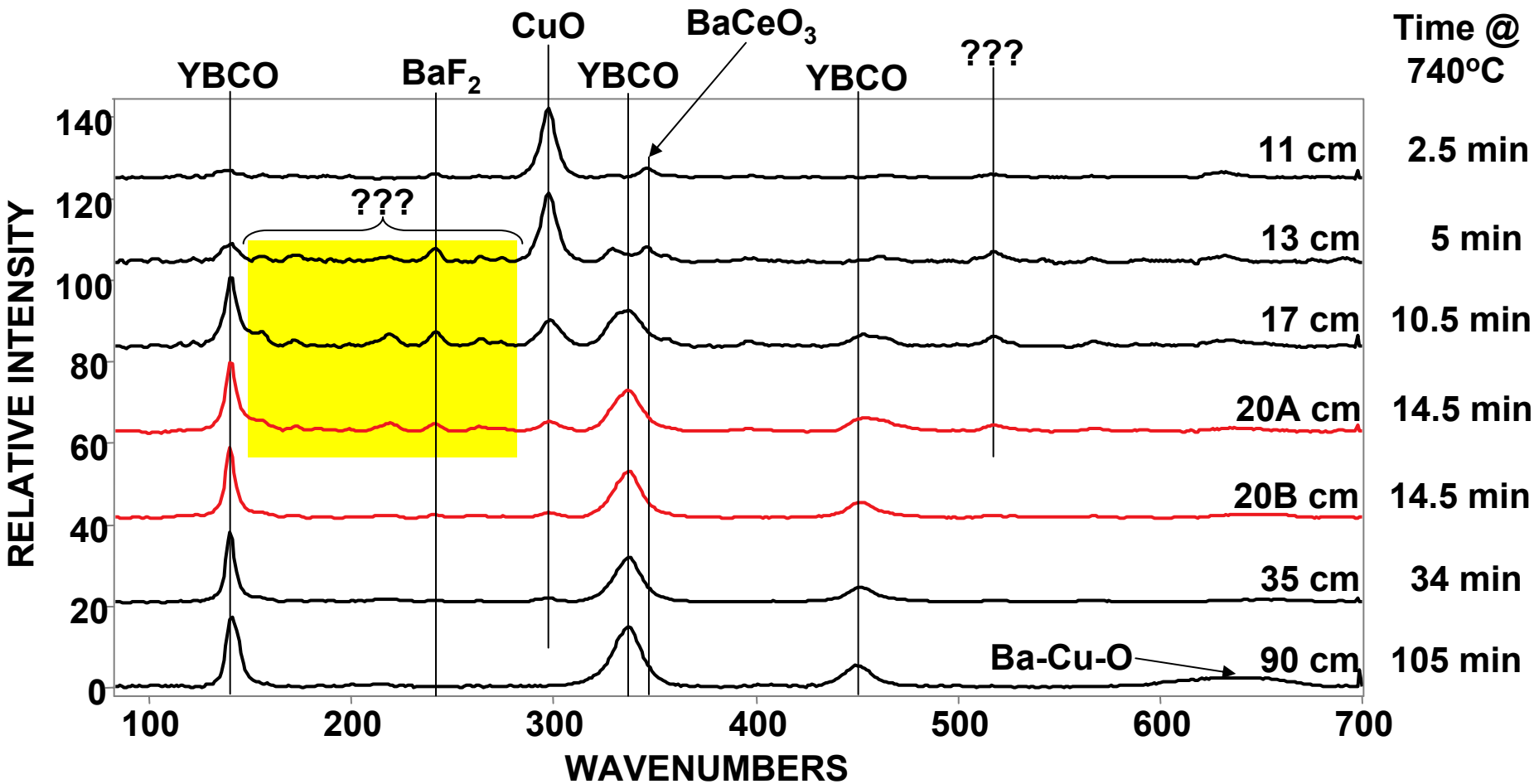
Raman Spectra from 1.25 m Tape DL01: 3 and 9 cm points on tape

- as the precursor reaches 740°C, other phases crystallize from the "primordial mush"

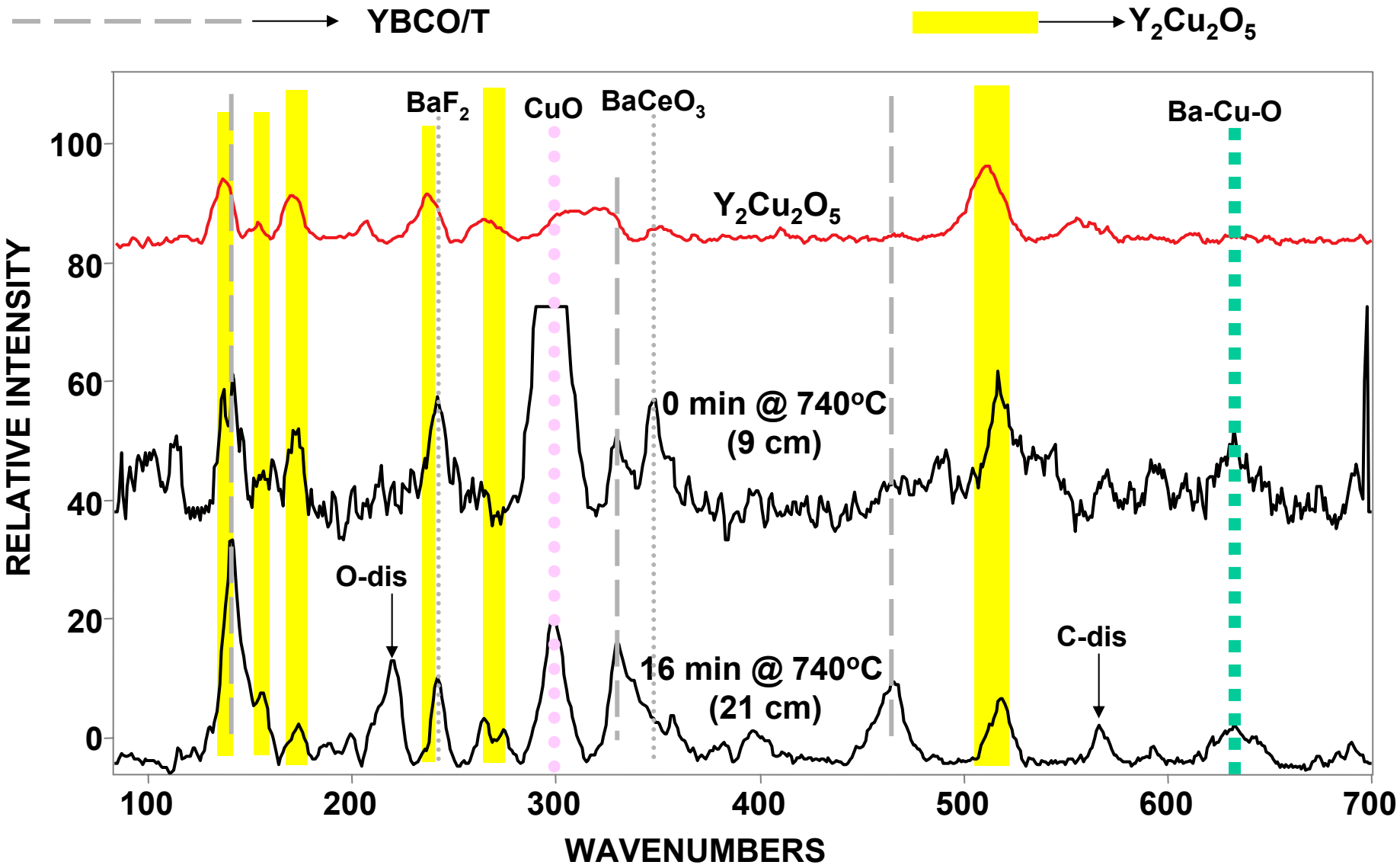


Raman Spectra from 1.25 m Tape DL01: Overview of the 740°C Plateau

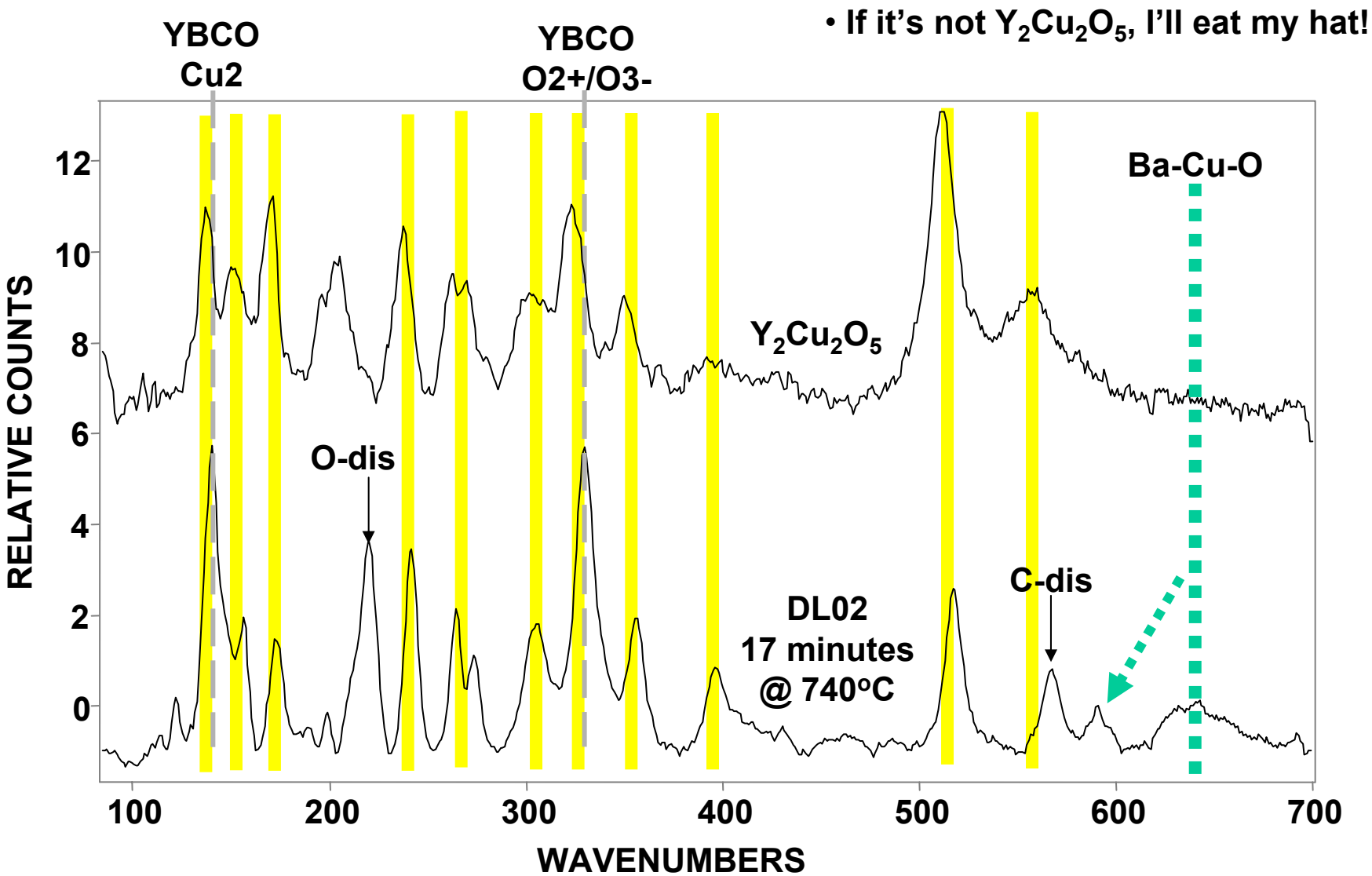
- in less than 40 minutes at 740°C most of the precursor is converted to YBCO/T



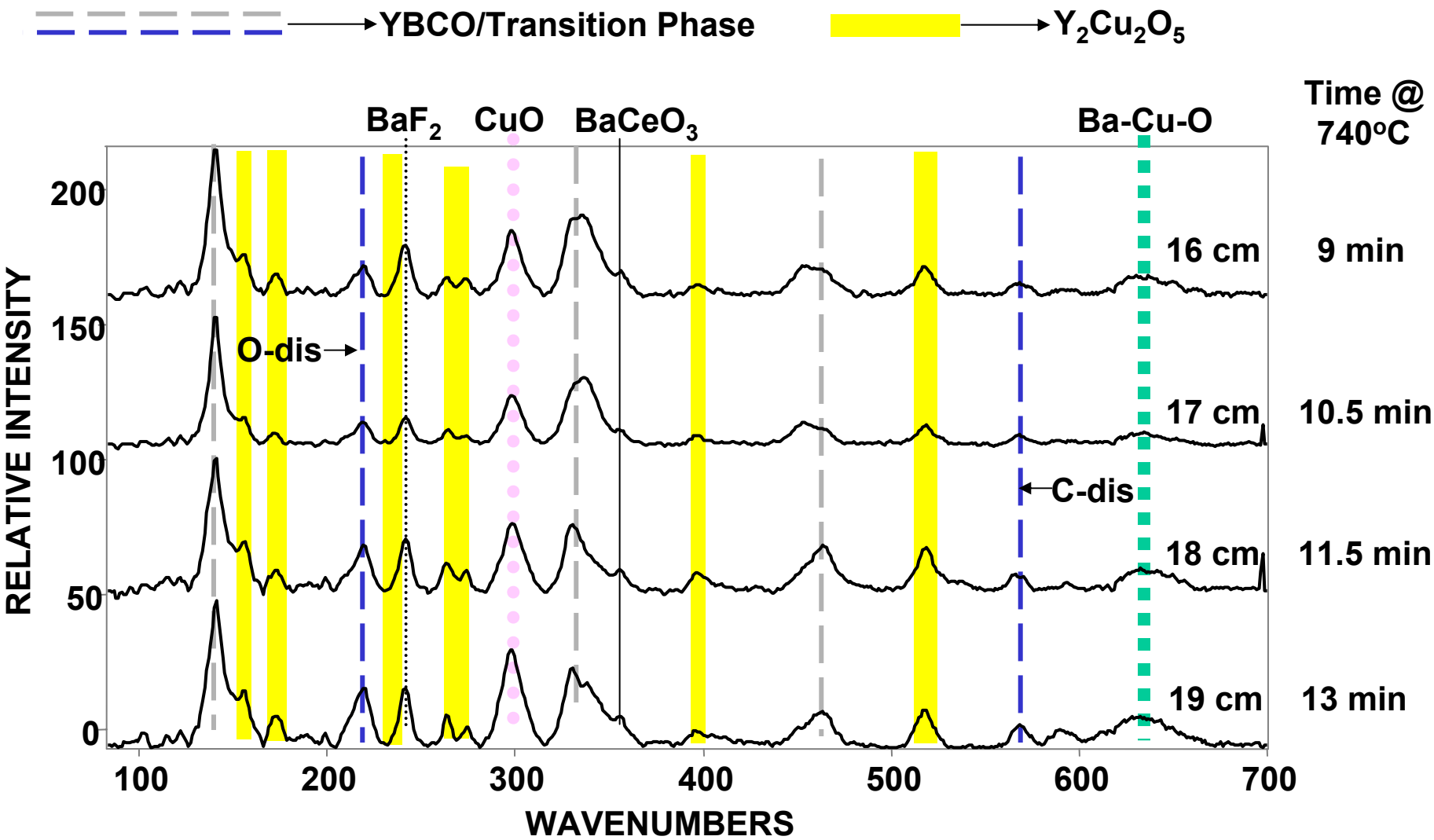
Raman Spectra from 1.25 m Tape DL01: What's the "???" stuff?



Raman Spectra from 1.14 m Tape DL02: The 1000 nm YBCO precursor

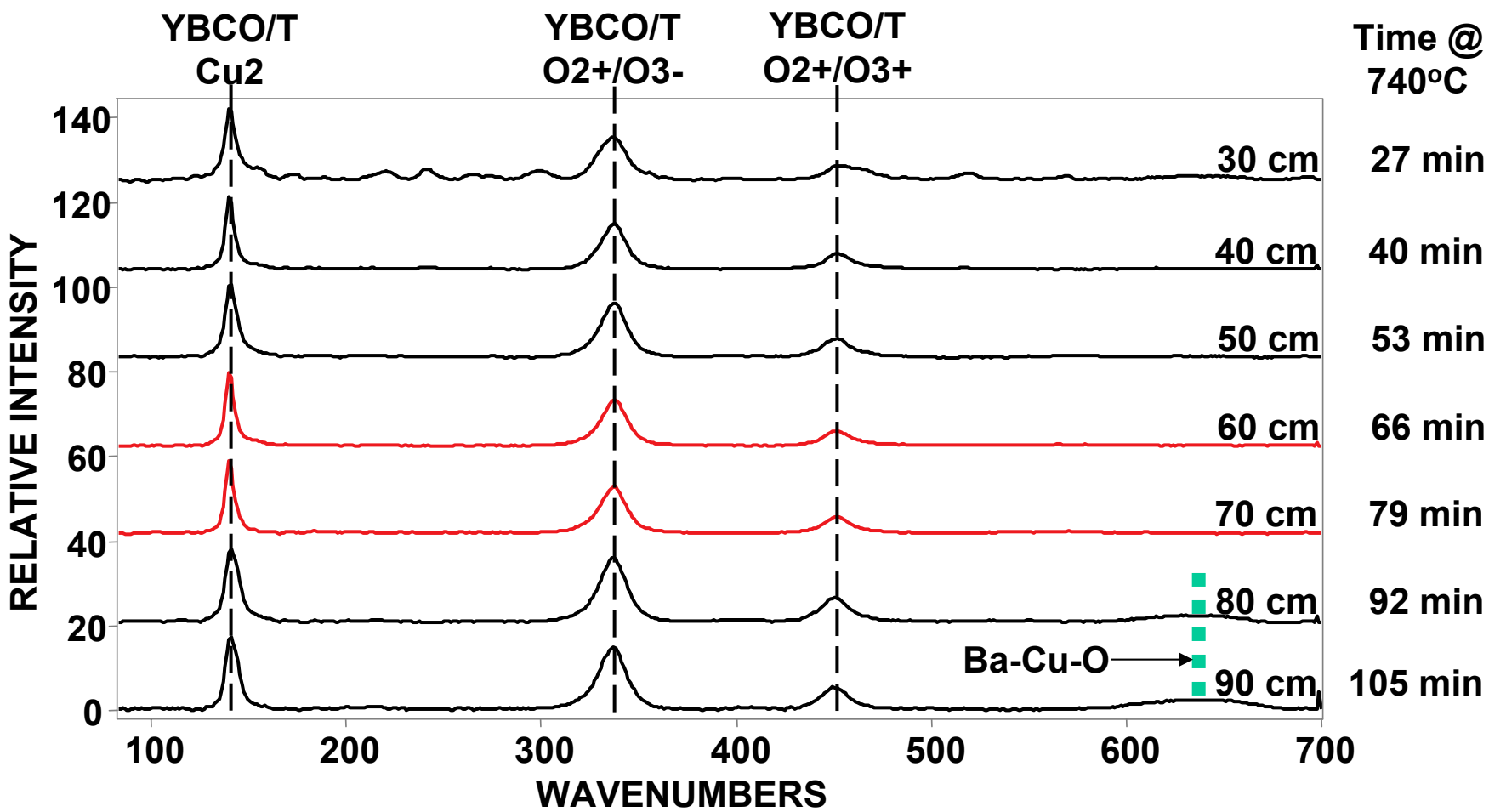


Raman Spectra from 1.25 m Tape DL01: Tracking the reaction front

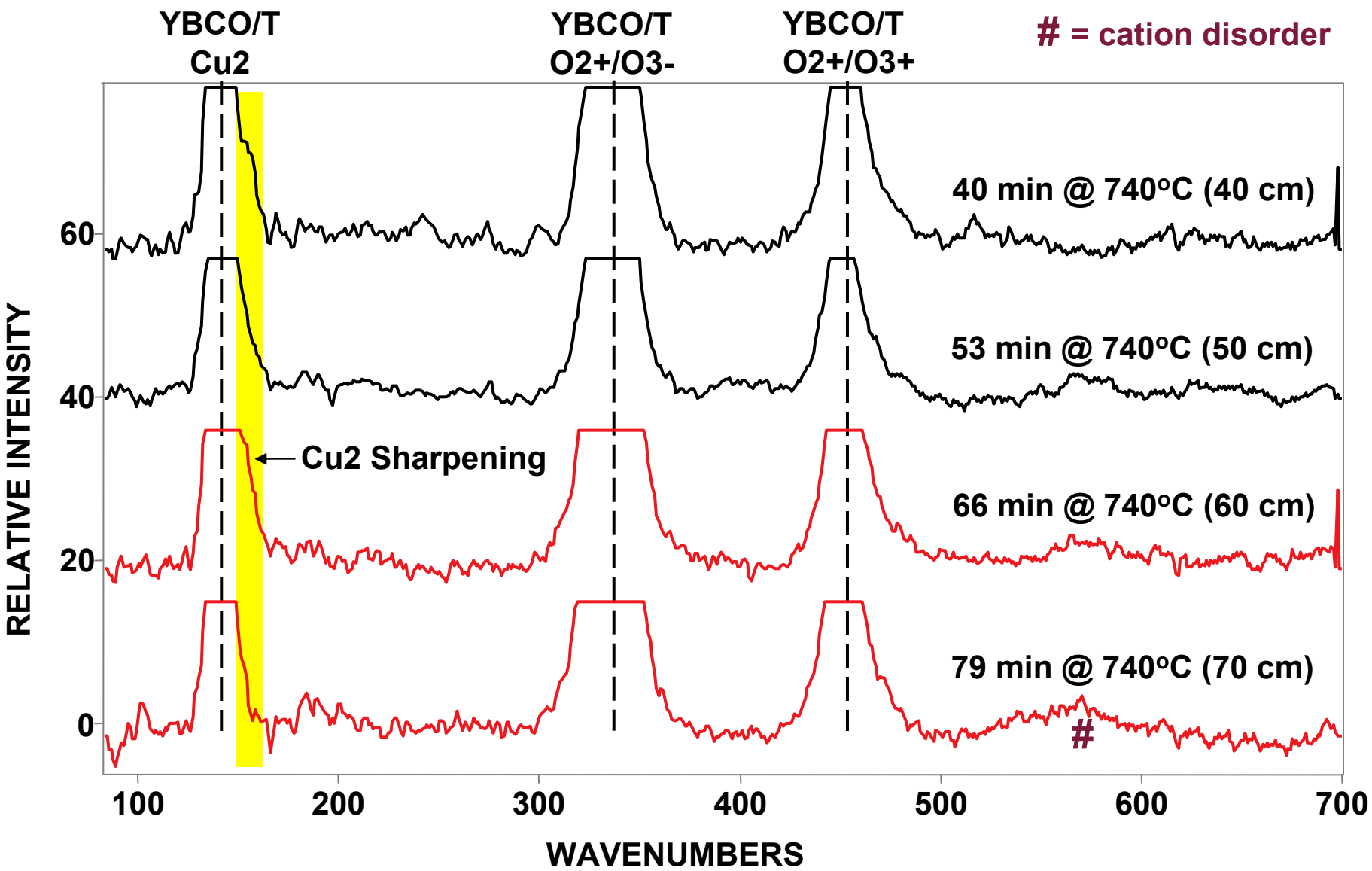


Raman Spectra from 1.25 m Tape DL01: Finding the YBCO "sweet spot"

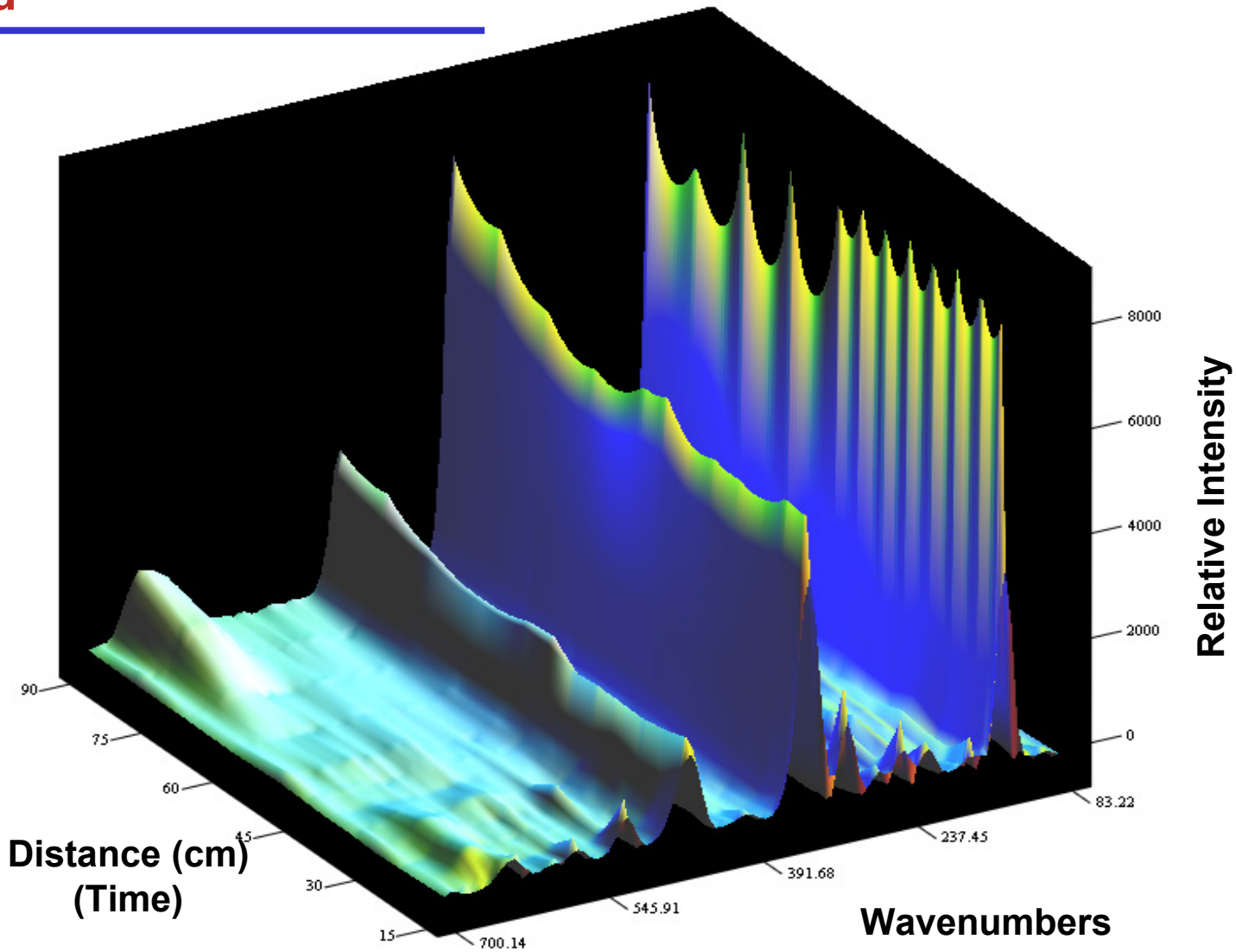
- the Raman-based phase purity "sweet spot" appears to occur at 75 ± 5 minutes for the 300 nm YBCO film; it occurs at 220 ± 10 minutes for the 1000 nm YBCO film

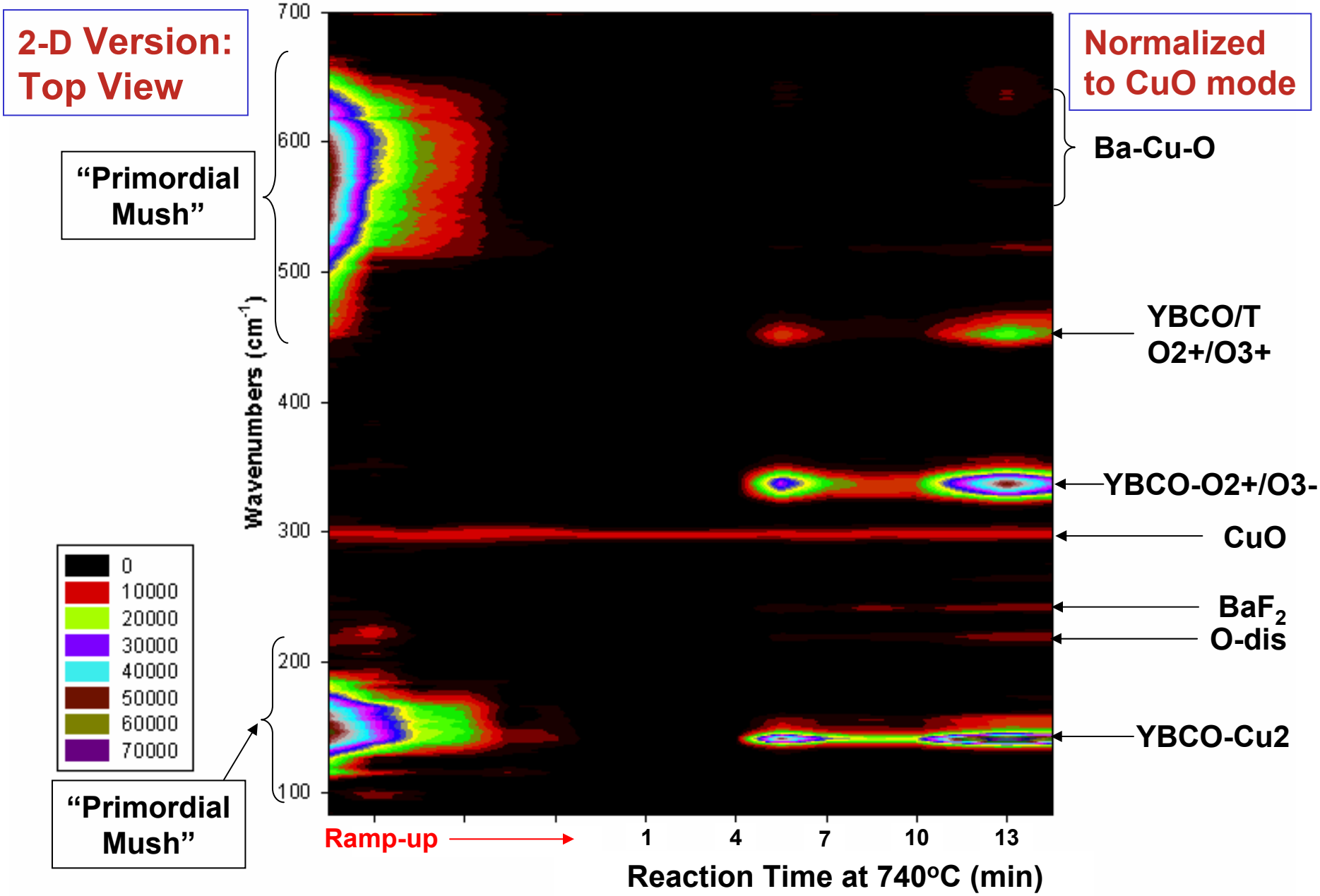


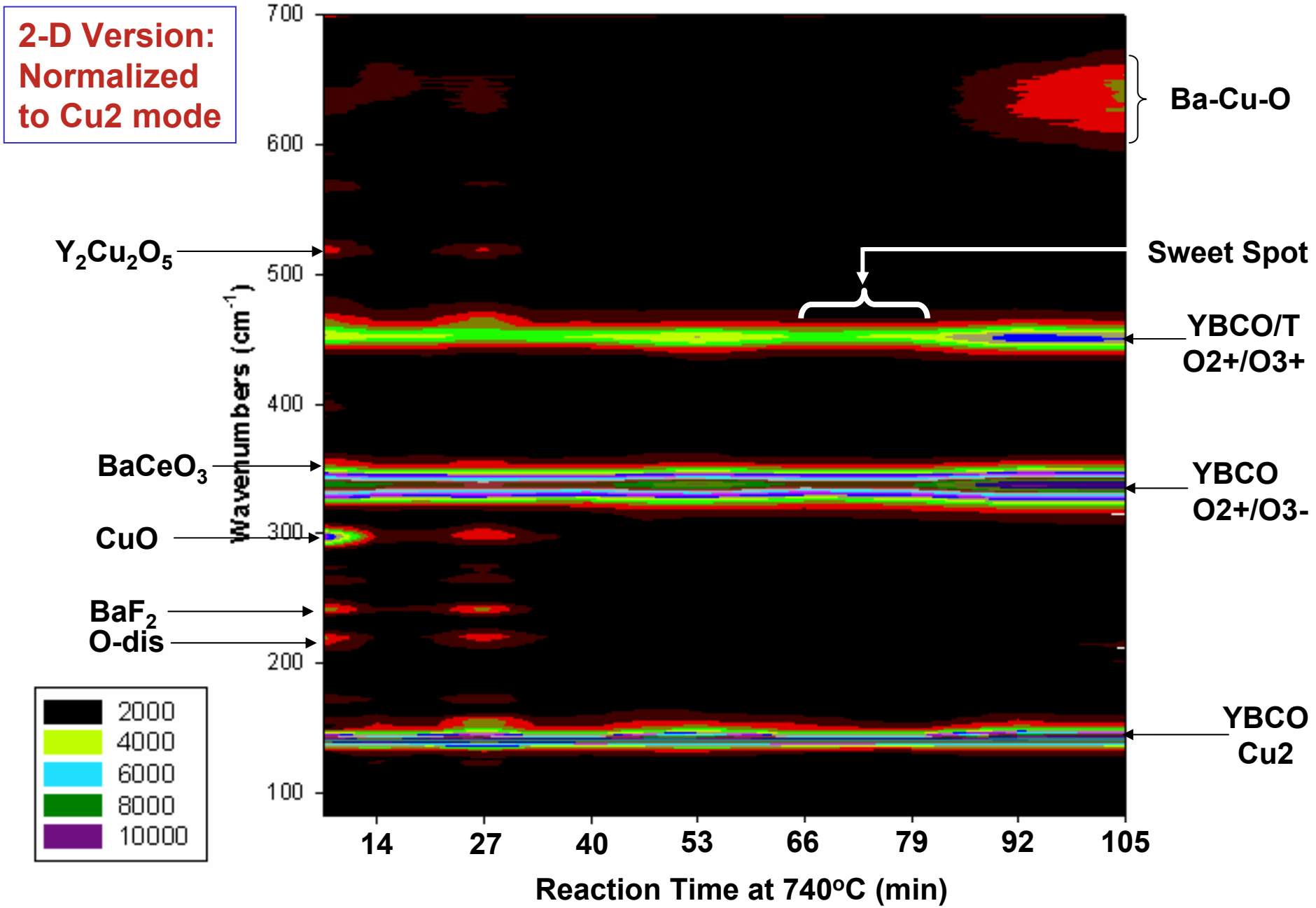
Raman Spectra from 1.25 m Tape DL01: A closer look at the "sweet spot"



Raman Spectra from 1.25 m Tape DL01: 3-D plot of reaction contour along the 740°C plateau




2-D Version: Top View
Normalized to CuO mode
"Primordial Mush"
Ba-Cu-O
YBCO/T
O2+/O3+
YBCO-O2+/O3-
CuO
BaF2
O-dis
YBCO-Cu2
"Primordial Mush"
Wavenumbers (cm-1)
700
600
500
400
300
200
100
0
10000
20000
30000
40000
50000
60000
70000
Ramp-up
1
4
7
10
13
Reaction Time at 740°C (min)



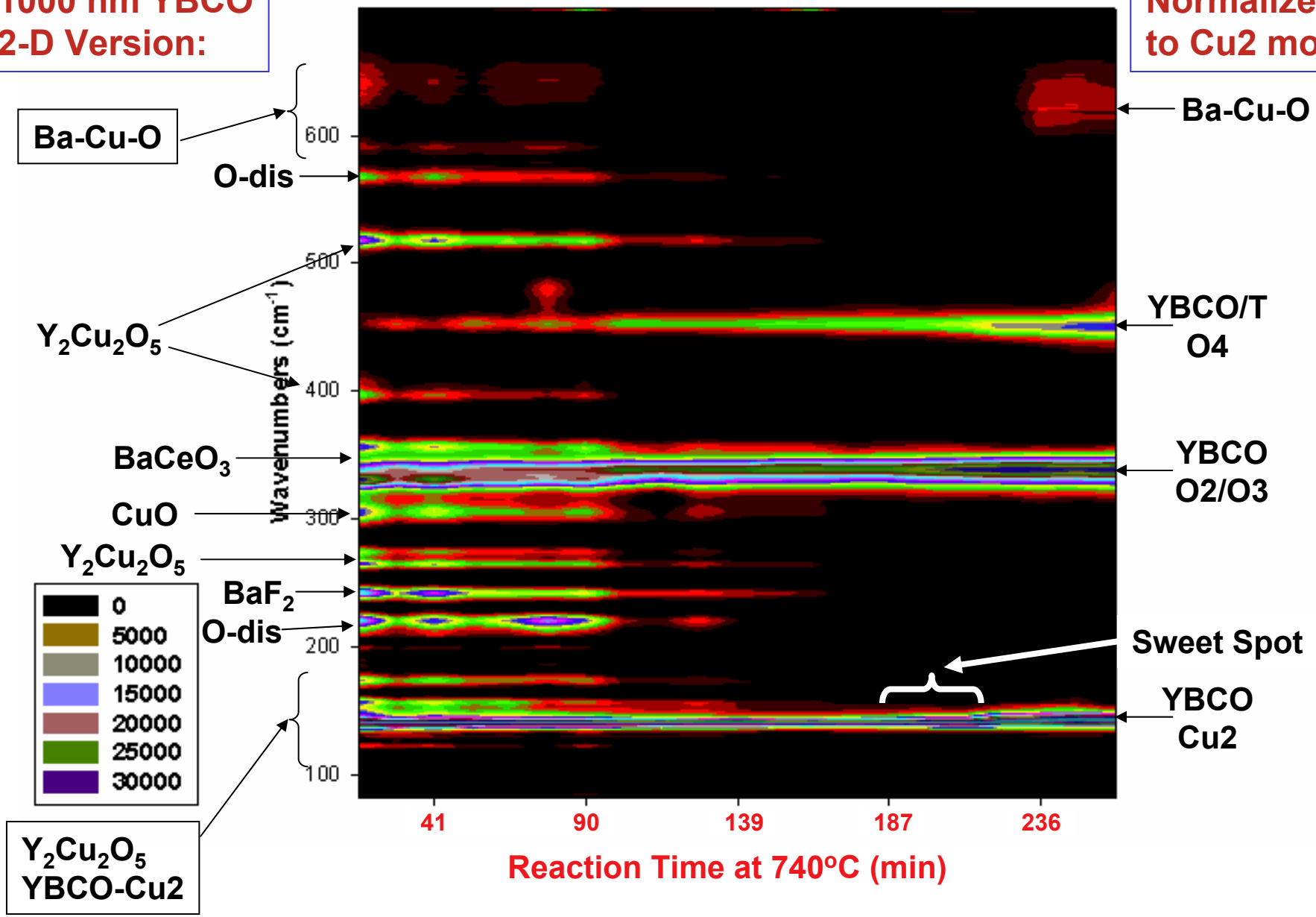
Pioneering Science and Technology

ornl

U.S. Department of Energy
Energy Efficiency and Renewable Energy

1000 nm YBCO 2-D Version:

Normalized to Cu2 mode



Pioneering Science and Technology

ornl

U.S. Department of Energy
Energy Efficiency and Renewable Energy

Bridging FY 2003 Results to FY 2004 Plans: What next for Y-BaF_2-Cu?

- **ORNL's graded composition approach effectively creates staged increments of transformed precursor states in long-length coated conductor segments:**
  - -we observed the incipient crystallization of the precursor
  - -we identified intermediate phases in the Y-BaF_2-Cu → YBCO transformation
  - -we located a purity/performance "sweet spot" in the time-at-temperature relationship
  - -we found evidence that the YBCO growth rate is linear with YBCO thickness
- **The results provide a basis for elucidating the Y-BaF_2-Cu → YBCO transformation reaction mechanism—but questions remain:**
  - -how does BaF_2 get activated, e.g., by H_2O?
  - -where does $Y_2Cu_2O_5$ come from?
  - -what's the rate limiting reaction step?

What forms when BaF_2 is in contact with H_2O at 740°C: Can we learn anything from studies of $Ba(OH)_2$ –BaF_2 mixtures?

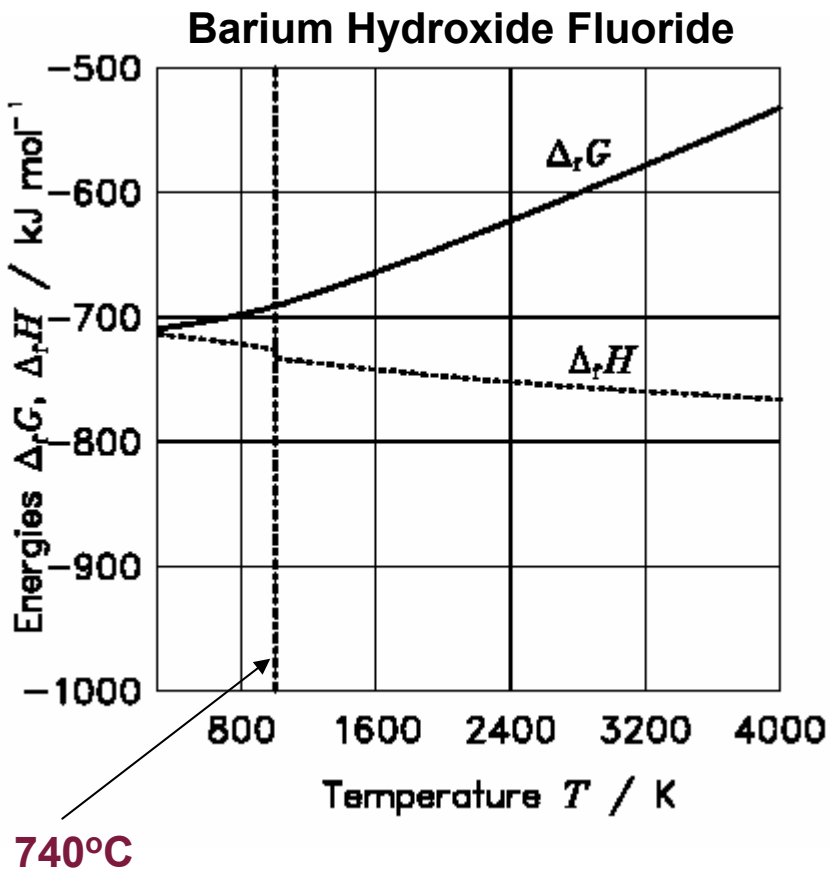
- **What does the literature tell us?:**
  - **$Ba(OH)_2$ undergoes gradual thermal dehydration to BaO upon heating**
  - **BaF_2 melts at 1280°C; BaO melts at ca. 1900°C**
  - **BaO-BaF_2 used as a flux (?? phase diagram ??--should be like CaO-CaF_2)**
  - ***Ba(OH)F observed in gas phase (ΔG, ΔH); equilibrium favors BaO and HF***

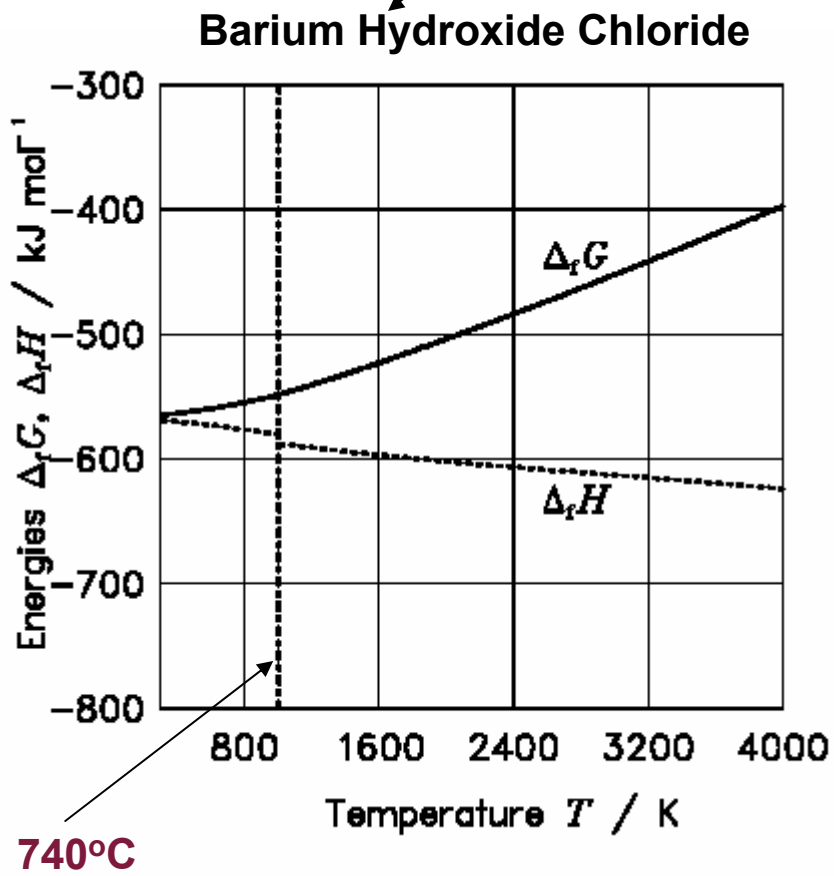
- **$Ba(OH)_2$-BaF_2 mixtures heated to 740°C in flowing air:**
  - **TGA indicates minimal weight loss (what loss there is starts at ca. 450°C)**
  - **DTA indicates no significant exo- or endothermic events up to 1000°C**
  - ***O-H Raman peaks diminish in intensity with time***
  - **XRD indicates mainly cubic BaF_2 (plus other weak diffraction lines)**

- **What other experiments make sense for understanding the BaF_2 / H_2O reaction?:**
  - ***steam BaF_2 in H_2O at 400°C → 740°C***

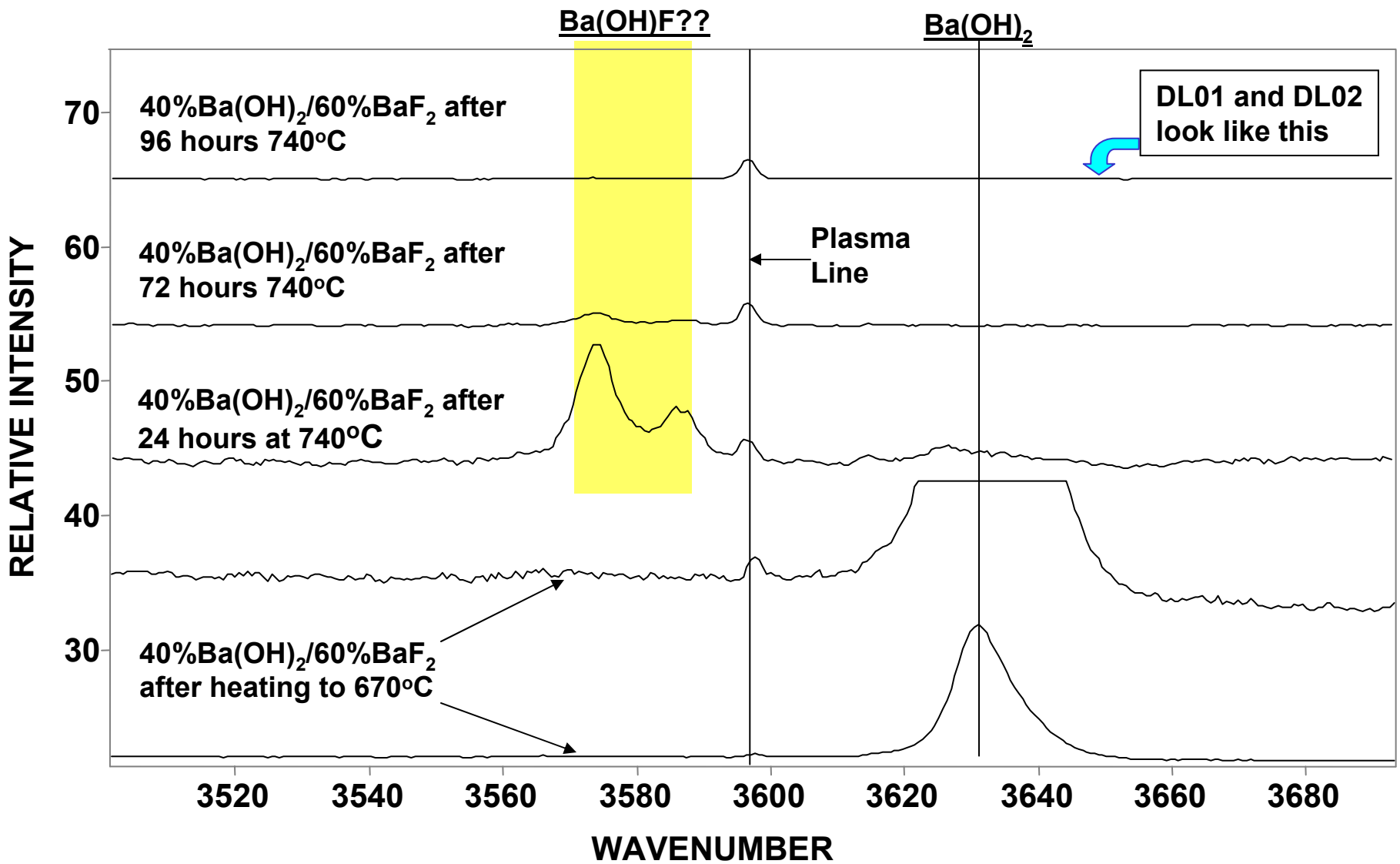
Landolt-Börnstein Reports Existence of Ba(OH)Cl as well as Ba(OH)F

A well-studied proton conductor

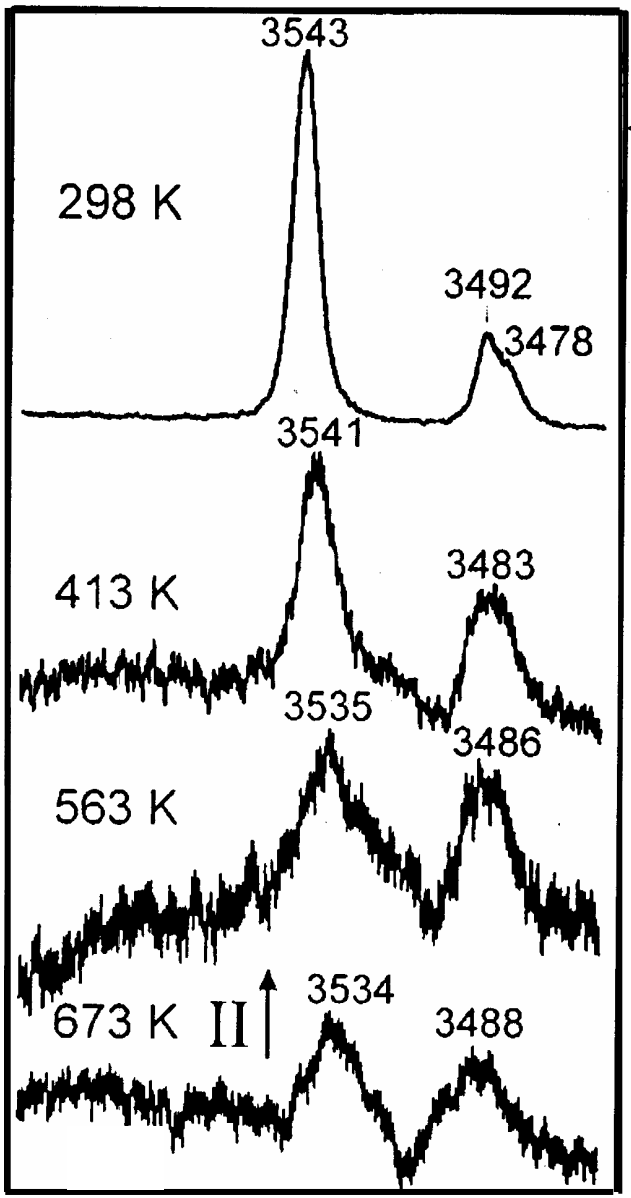




What Happens When We Cook a BaF_2 / $Ba(OH)_2$ mixture?

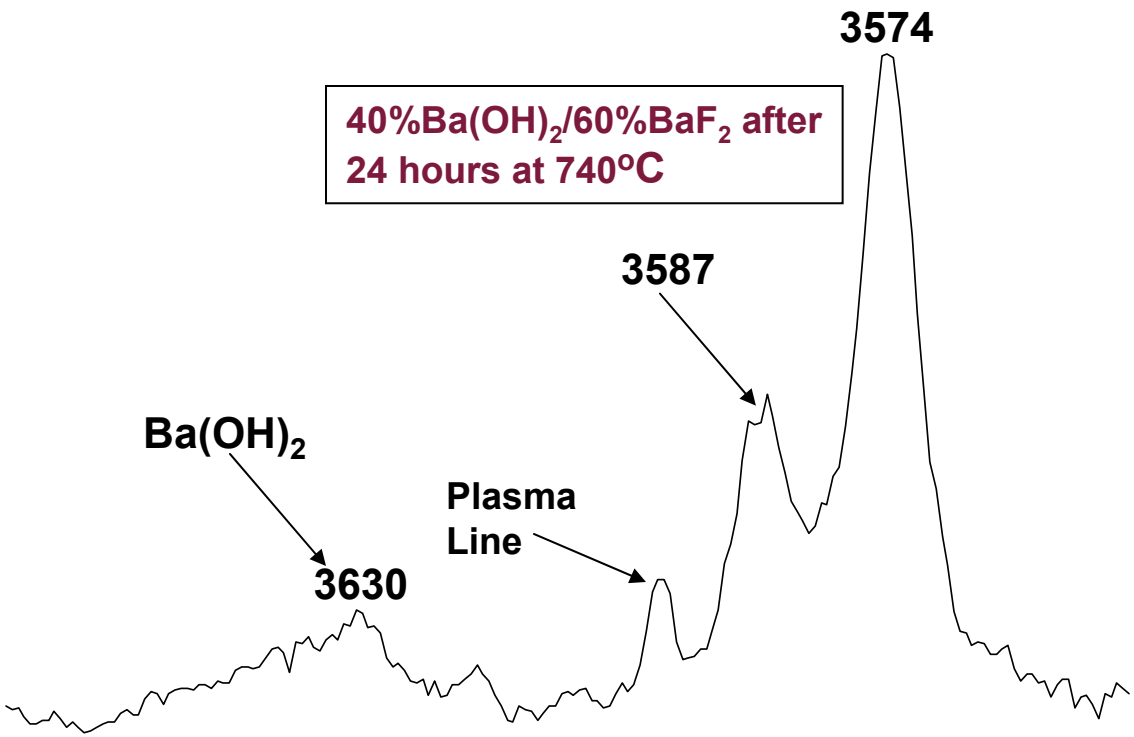


Results of a Raman Spectrum Comparison



Peter et al. J. Solid State Chem. 151, 267 (2000)

Both Sr(OH)Br and hypothetical Ba(OH)F exhibit a pair of O-H Raman bands. Frequency and intensity differences can be attributed to cation and halide induced shifts.



Reported O-H Phonon Frequencies of the Alkaline Earth Hydroxy-Halides

- most alkaline earth hydroxy-halides [M(OH)X] crystallize in the Laurionite [Pb(OH)Cl] structure (Pnma) and exhibit one intense O-H phonon
- Sr(OH)Br crystallizes in a distorted Laurionite structure ($P2_13$) and exhibits two O-H phonons

M(OH)X	O-H Bands (cm^{-1})	Reference
Sr(OH)Br	3543, 3485	S. Peter et al., J. Solid State Chem. 151, 267 (2000)
Sr(OH)I	3596	H.D. Lutz et al., Spectrochim. Acta 51A, 755 (1995)
"Ba(OH)F"	*3587, 3574*	Maroni et al.
Ba(OH)Cl	3594	H.D. Lutz et al., Spectrochim. Acta 51A, 755 (1995)
Ba(OH)Br	3605	H.D. Lutz et al., Spectrochim. Acta 51A, 755 (1995)
Ba(OH)I	3590	H.D. Lutz et al., Spectrochim. Acta 51A, 755 (1995)
$Ba(OH)_2$	3630	Maroni et al.; well established in literature

Does the information we have support a plausible reaction mechanism?

Try to interpret overall reaction (1) in terms of a series of "two component" reactions—some faster than others—forming a single condensed phase or a single condensed phase and an escaping gas.

From Raman and/or XRD we detect CuO, Y_2O_3, $Y_2Cu_2O_5$, BaF_2, Ba-Cu-O, $YBa_2Cu_3O_{6.5}$.

$$Y_2Cu_2O_5 + 4BaF_2 + 4CuO + 4H_2O \rightarrow 2YBa_2Cu_3O_{6.5} + 8HF(\uparrow) \qquad (1)$$

$$Y_2O_3 + 2CuO \longrightarrow Y_2Cu_2O_5$$

$$BaF_2(\text{excess}) + H_2O \longrightarrow Ba(OH)F + HF(\uparrow)$$

$$Ba(OH)F + CuO(\text{excess}) \xrightarrow{\text{FAST?}} BaCuO_2 + HF(\uparrow)$$

$$Y_2Cu_2O_5(\text{excess}) + 4BaCuO_2 \xrightarrow{\text{FAST?}} 2YBa_2Cu_3O_{6.5}$$

FY2003 Performance

- Developed a broadly useful procedure to process CCs with graded YBCO phase assemblages.
- Built and put in operation a tape handling device for R2R Raman micro-spectroscopy → detected key intermediate phases.
- Coupled reel-to-reel (R2R) x-ray diffraction with R2R Raman microscopy to establish a coordinated/complementary capability for interrogating long-length YBCO coated conductor.
- Demonstrated close correlation of YBCO XRD intensity and Raman-deduced phase purity with tape segment I_c in CCs having two different YBCO thicknesses.
- Initiated studies of a plausible model for YBCO formation mechanism.
- Demonstrated the functionality of an *in situ* XRD unit.
- *Conducted a design analysis, cost estimate, and concept test for an on-line Raman probe (Gray-Maroni-Miller, FY 2003 Review).*
- *Strengthened the case to employ R2R x-ray diffraction and R2R Raman microscopy for on-line coated conductor process monitoring.*

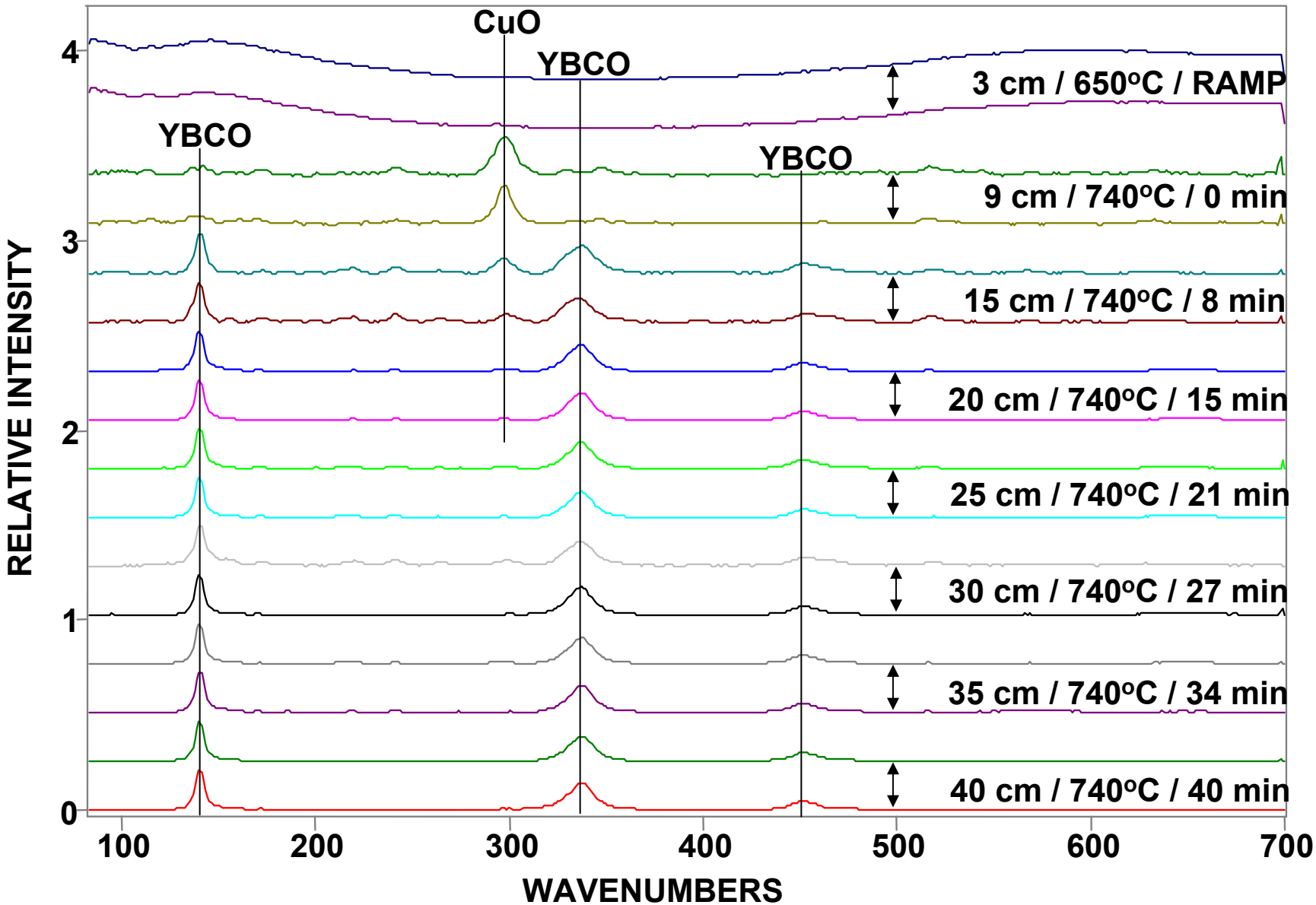
FY2004 Plans

- **Extend graded composition methodology to examine phase transformation and YBCO reaction rate to other promising *ex situ* precursors:**
  - e-beam PVD "BaF_2" at reduced pressures (Lee-List, 2003 Review)
  - "modified" BaF_2 precursor with different phase assemblage (in light of results from this work)
  - pulsed-electron-deposited "BaF_2-YF_3" precursor, TFA, non-fluorine, etc.
- **Orchestrate research activities to provide guidance and support to process optimization efforts at, e.g., AMSC, ORNL, and SuperPower:**
  - determine rate controlling reaction steps
  - investigate thickness dependence issues
  - probe J_c of "sweet spot" and adjacent segments after YBCO/T → YBCO/O treatment
- **Assemble and test a transportable Raman microprobe instrument suitable for on-line interrogation of coated conductors; initiate field verifications at, e.g., AMSC, LANL, ORNL, SuperPower**

Research Integration

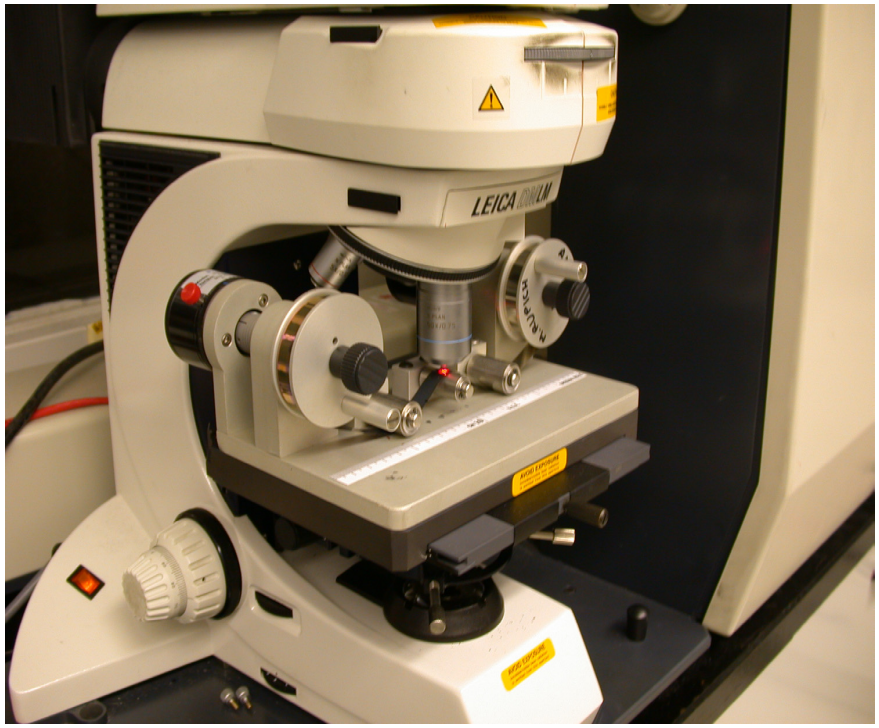
- **American Superconductor: :**
  - adopted the graded composition approach to test their precursor conversion (R2R Raman microscopy done by ANL)
  - performed YBCO and substrate experiments using ORNL's R2R XRD
  - conducted experiments using ORNL's *in situ* XRD
- **SuperPower, Inc:**
  - ANL performed R2R Raman microscopy on a 12 meter CC tape from SuperPower
- **Oxford and MCT:**
  - conducted experiments on ORNL's R2R XRD
- **Kaiser Optical Systems and SBI Analytical:**
  - worked with ANL to complete design analysis, cost estimate, and concept test of *in situ* Raman probe
- **Manuscript in preparation**

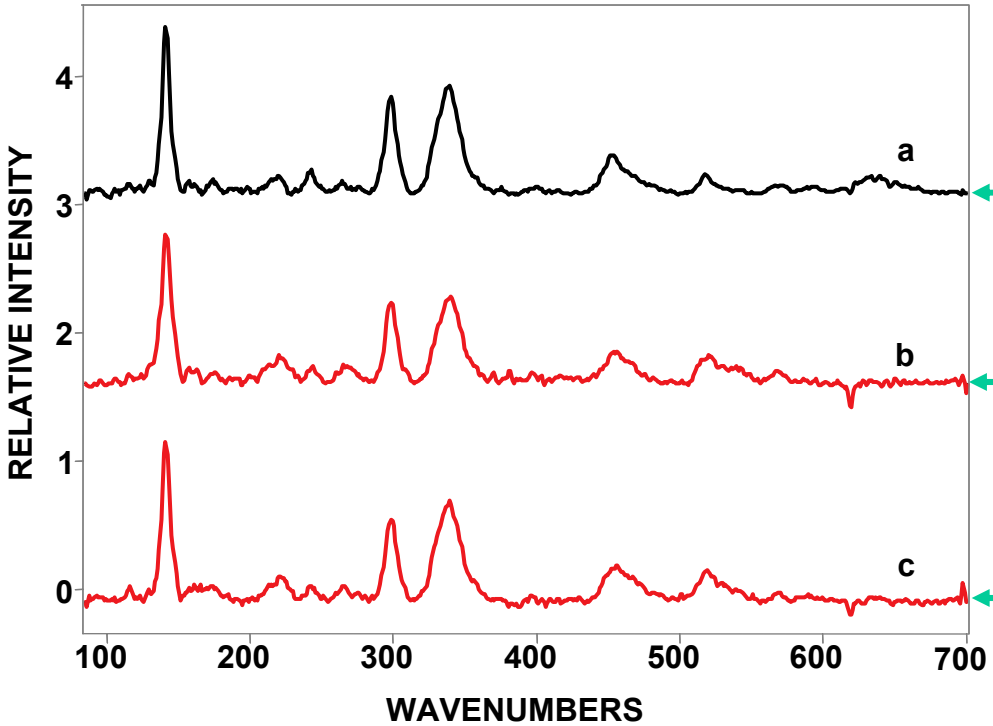
A and B RAMAN SPECTRA OF 1.25 METER TAPE DL01: 3 to 40 cm in ca. 5 cm INTERVALS



Using Raman Microscopy to Examine Long-Length Conductor Specimens

- easily adapted to reel-to-reel movement
- useful for studying quenched tapes and other types of partially processed samples
- can be applied to moving samples (requires dynamic focusing to accommodate vertical motion)





(a) Still sample: avg. of eleven 10 s scans over a 10 cm segment

(b) Moving sample: 0.1 cm/s, 100 s scan over a 10 cm segment (static grating mode)

(c) Moving sample: same as (b) but moving in opposite direction