Conversion of oxy-fluoride based coated conductors

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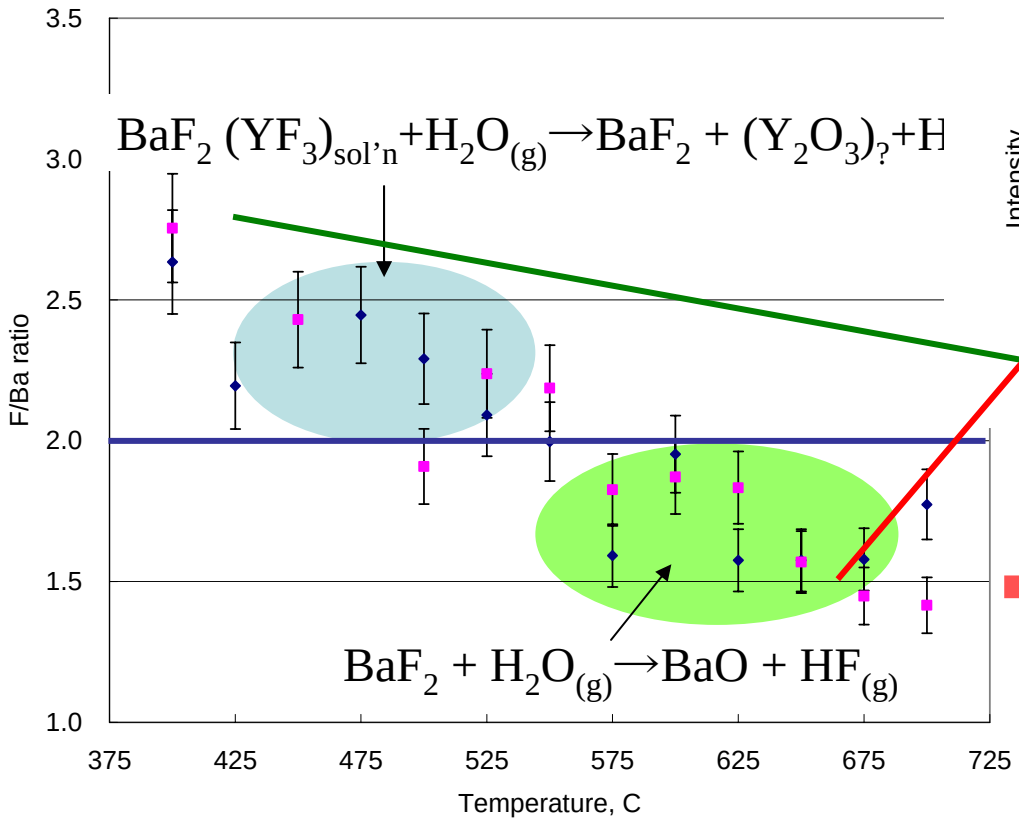
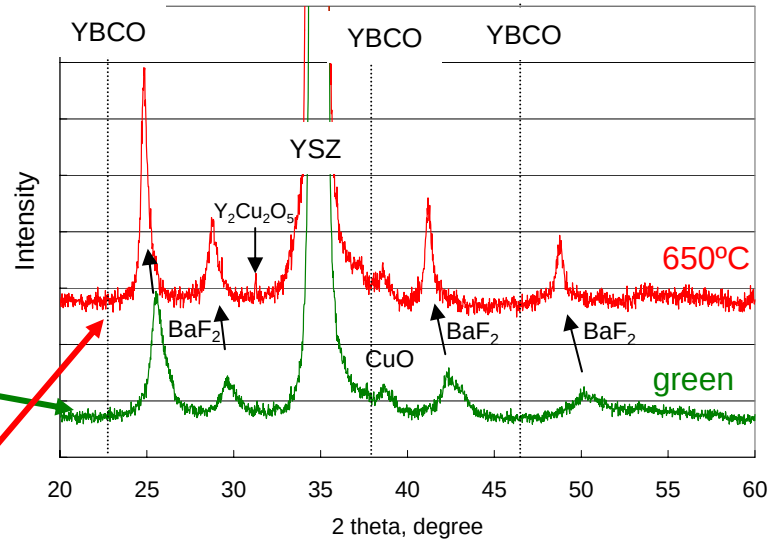
F/Ba Ratio Trajectory of MOD derived film

F/Ba trajectory of MOD-derived YBCO films

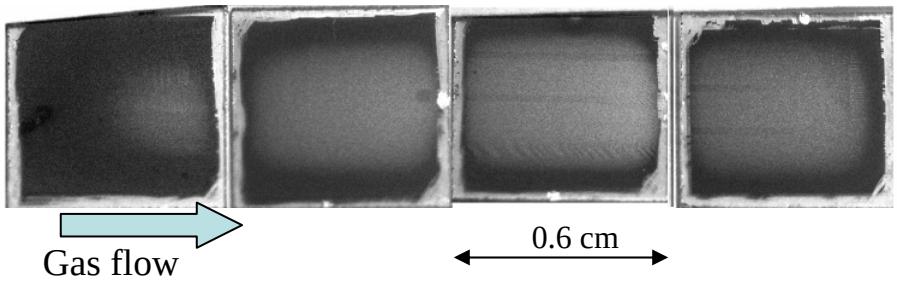


XRD profiles of MOD-derived YBCO films



➡ YBCO formation

- F/Ba trajectory shows fluorine could be released non-uniformly into atmosphere.
- HF gas removal from a film surface has great influence on YBCO growth



I. Seleznev *et. al.*, MRS fall meeting 2001

$$Gr.Rate(nm/\sec) = \frac{1.33 \cdot 10^{12} \cdot \sqrt{P_{H_2O}}}{P_t} \exp\left(\frac{-852000}{4RT}\right)$$

M. Yoshizumi *et. al.*, MRS WS 2002
Solovyov *et. al*, IEEE trans. Appl. Supercond., 2001

- P_{HF} data obtained experimentally is missing

Project goals

- Direct and quantitative measurement of the partial pressure of HF.
- Clarification of relationship between the composition/time trajectory and film performance
- Quantitative measure of the degree of reaction between the YBCO film and the substrate buffer layer.
- Comparison between the results obtained from e-beam derived films with those of MOD derived films
- Understanding/improvement of YBCO coated conductor fabrication processing

FY2004 performance

- Establish modified Knudsen cell technique
  - ✓ Done.
- Make modified Knudsen cell measurements on MOD films
  - ✓ Done.
- Make modified Knudsen cell measurements on pure BaF_2 films to compare with MOD films
  - ✓ Done.
- Publications
  - "Reactions of oxyfluoride precursors for the preparation of barium yttrium cuprate films", Physica C 403 (2004), 191.
  - "Determination of HF partial pressure during *ex situ* YBCO formation", submitted to Physica C.

Project team

MIT

- M. J. Cima, Ph. D, Sumitomo Electric Industries Professor of Engineering
- M. Yoshizumi, Ph. D., Post doctoral researcher and staff scientist at MIT, Thesis finished at Univ. of Tokyo, work experience at ISTEC
- D. Wesolowski, Ph. D. candidate at MIT, work experience at AMSC, Univ. of Wisconsin's Applied Superconductivity Center, and Nexans Superconductor

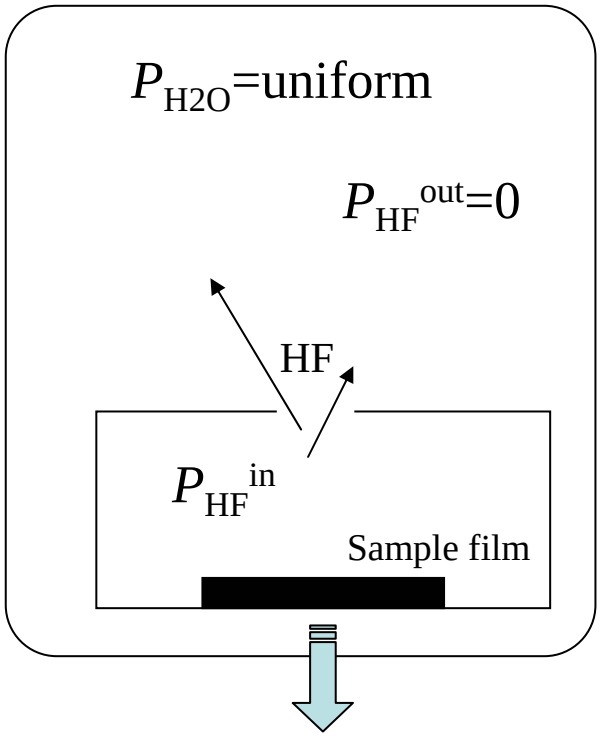
Team responsible for studies on the MOD *ex situ* films and project organization

BNL

- Synthesis and characterization of YBCO thick films (V. Solovyov, H. Wiesmann, and M. Suenaga)
- Theory and modeling of kinetics of epi-YBCO formation and thermo-physical properties (D.O. Welch)

Team responsible for important studies on the conversion of e-beam *ex situ* films.

Calculation to Obtain P_{HF} and ΔG



Fluorine content in the sample films quenched at various times was measured by fluorine ion selective electrode.

Langmuir equation

$$\text{Flux (atoms/time, area)} = \frac{P_{HF}^{in}}{\sqrt{2\pi mkT}}$$

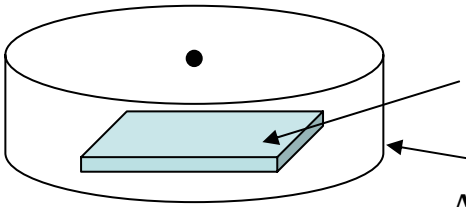
$$P_{HF} = \sqrt{P_{H_2O} \cdot \exp\left(\frac{-\Delta G}{RT}\right)}$$

ΔG for;

$$1/3\ YF3 + \tfrac{1}{2}\ H_2O = 1/6\ Y_2O_3 + HF$$

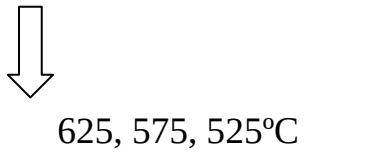
$$\tfrac{1}{2}\ BaF_2 + \tfrac{1}{2}\ H_2O = \tfrac{1}{2}\ BaO + HF$$

Experimental



Green film on LAO (prepared from TFA solution)

Alumina cell with one hole (hole size; 300, 500micron ϕ)



625, 575, 525ºC

Quench

1min. 10~90min

R. T.

Atmosphere; 1 Torr O_2 + 0.3 Torr H_2O

Calculated mean free path ~100μm@1.3 Torr

$$\lambda(mm) = \frac{0.1315}{P(Torr)}$$

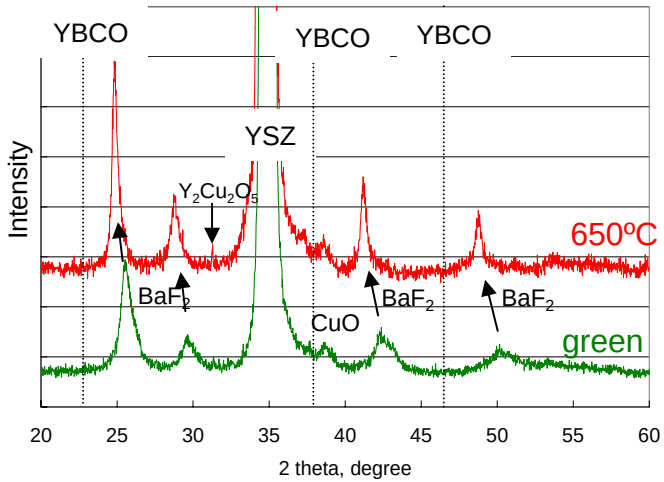
r(HF)~4Å, T=900K

⇨ HF molecule passes into hole with low probability of returning

⇨ Pressure measured will be minimum pressure

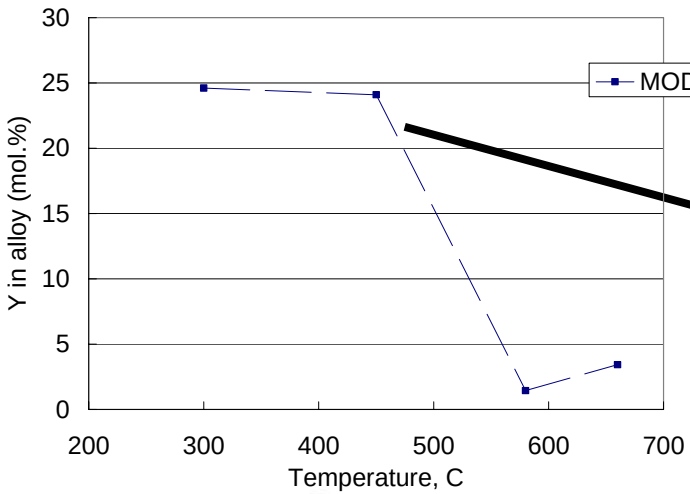
BaF_2-YF_3 alloy

Peak shift due to the formation of BaF_2-YF_3 solid solution



$$\text{Lattice Constant}_{\text{BaF2-YF3}} = -7.6\times10^{-3} C_{at.\%}^{YF3} + 6.2 \quad (\text{Å})$$

B. Sobolev *et. al*. J. Less-Common Metals, (1982)



F/Ba ratio =3 when all Y in BaF_2 (25 at. %) is YF_3
F/Ba ratio of green film is 2.9

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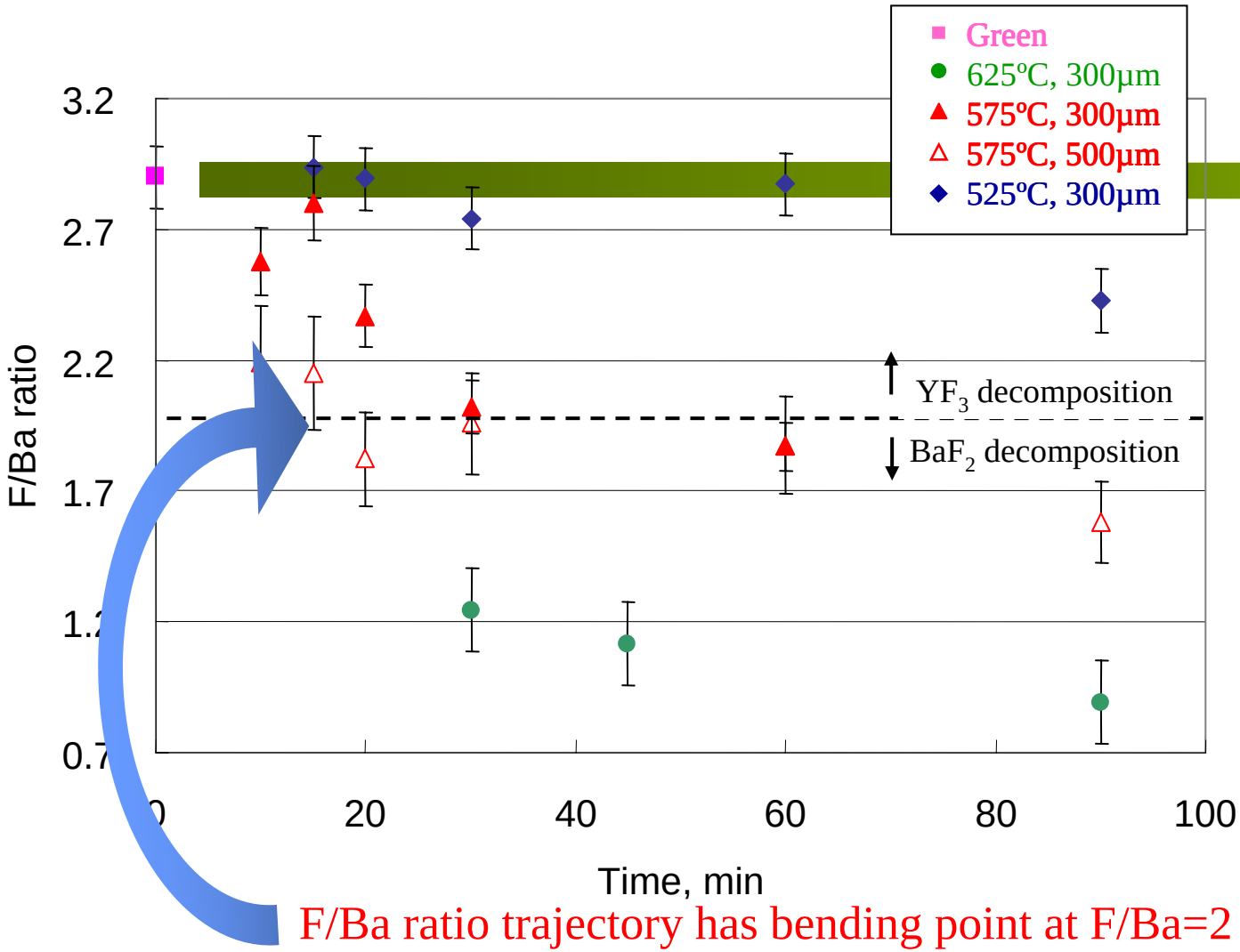
Knudsen cell fluorine loss

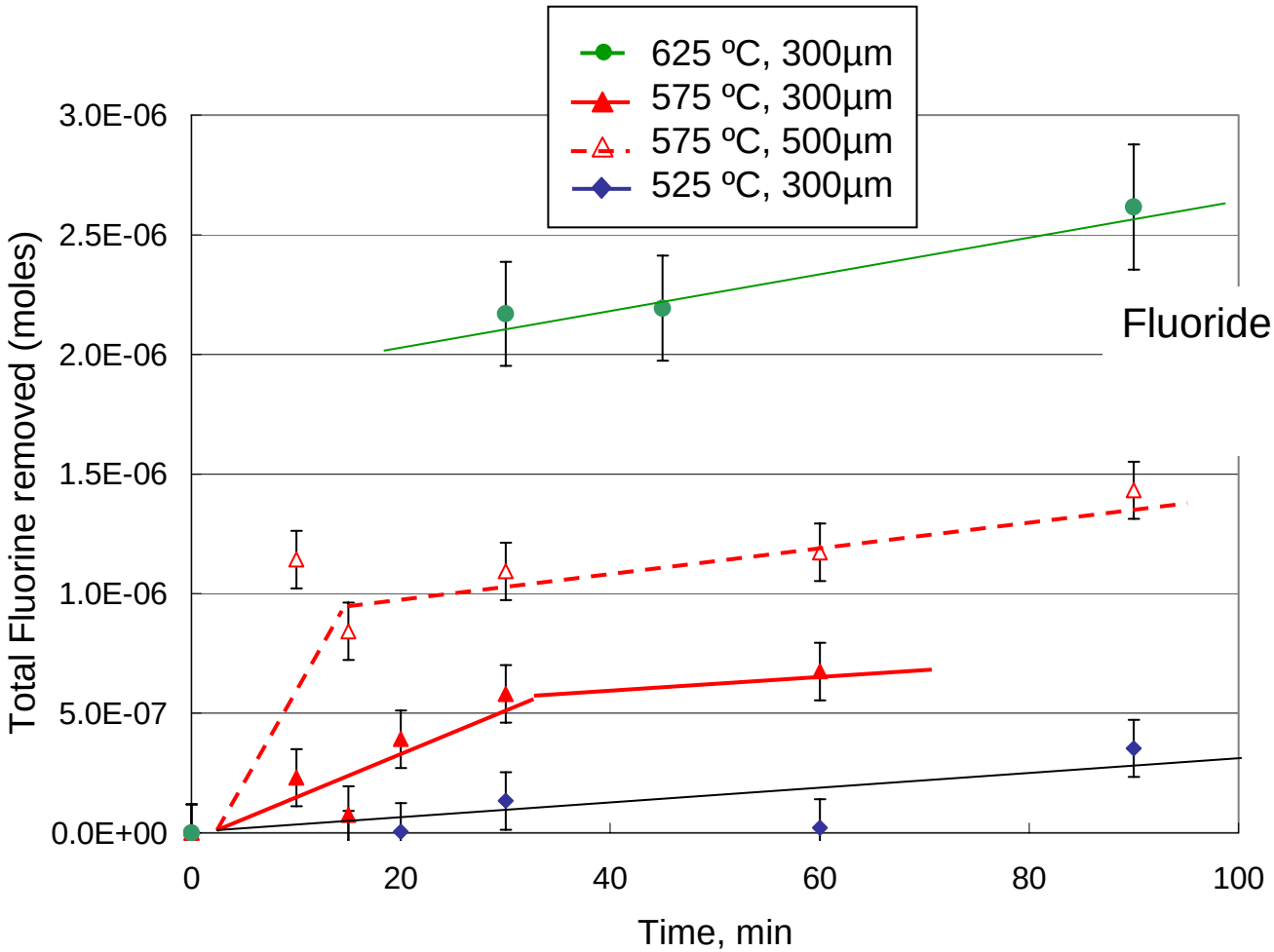


XRD profile

All fluorine is in BaF_2 grains as BaF_2-YF_3 solid solution

F/Ba ratio trajectory has bending point at F/Ba=2

Fluorine Loss Rate from Knudsen cell



Starting F/Ba ratio = 2.9

Fluoride decomposition proceeds;

1st: YF_3 reacts with H_2O

2nd: BaF_2 reacts with H_2O

Thermodynamic Analysis

Measured

Literature

	$1/3(YF_3)_{sol'n}+1/2H_2O_{(g)}=1/6(Y_2O_3)_?+HF_{(g)}$		$1/3YF_3+1/2H_2O_{(g)}=1/6Y_2O_3+HF_{(g)}$	
Temp., ºC	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F
525	2.8±0.3	36.0±0.7	0.29	51.0
575	16±2	26.1±0.7	0.728	47.7

	$1/2BaF_2+1/2H_2O_{(g)}=1/2(BaO)_?+HF_{(g)}$		$1/2BaF_2+1/2H_2O_{(g)}=1/2BaO+HF_{(g)}$	
Temp., ºC	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F
575	2.0±0.2	41±1	1.93×10^{-5}	122.0
625	6.1±0.6	34.7±0.9	7.76×10^{-5}	118.8

Thermodynamic Analysis

Measured **Literature**

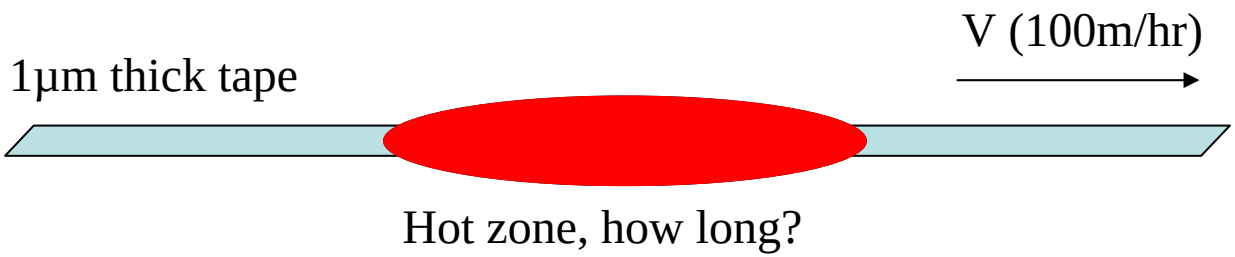
	$1/3(YF_3)_{sol'n}+1/2H_2O_{(g)}=1/6(Y_2O_3)_?+HF_{(g)}$		**$Y_2Cu_2O_5$ formation;** $1/3YF_3+1/3CuO+1/2H_2O_{(g)}=1/6Y_2Cu_2O_5+HF_{(g)}$	
Temp., ºC	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F
525	2.8±0.3	36.0±0.7	0.269-0.308	50.6-51.5
575	16±2	26.1±0.7	0.688-0.77	47.3-48.1

	$1/2BaF_2+1/2H_2O_{(g)}=1/2(BaO)_?+HF_{(g)}$		**YBCO formation;** $1/2BaF_2+1/2CuO+1/8Y_2Cu_2O_5+1/2H_2O_{(g)}=1/4YBCO+HF_{(g)}$	
Temp., ºC	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F	$P_{HF,}\times10^{-2}$Pa	ΔG, kJ/mol-F
575	2.0±0.2	41±1	7.7×10^{-4}-0.114	60.8-96.0
625	6.1±0.6	34.7±0.9	2.49×10^{-3}-0.301	57.1-92.9

So what?

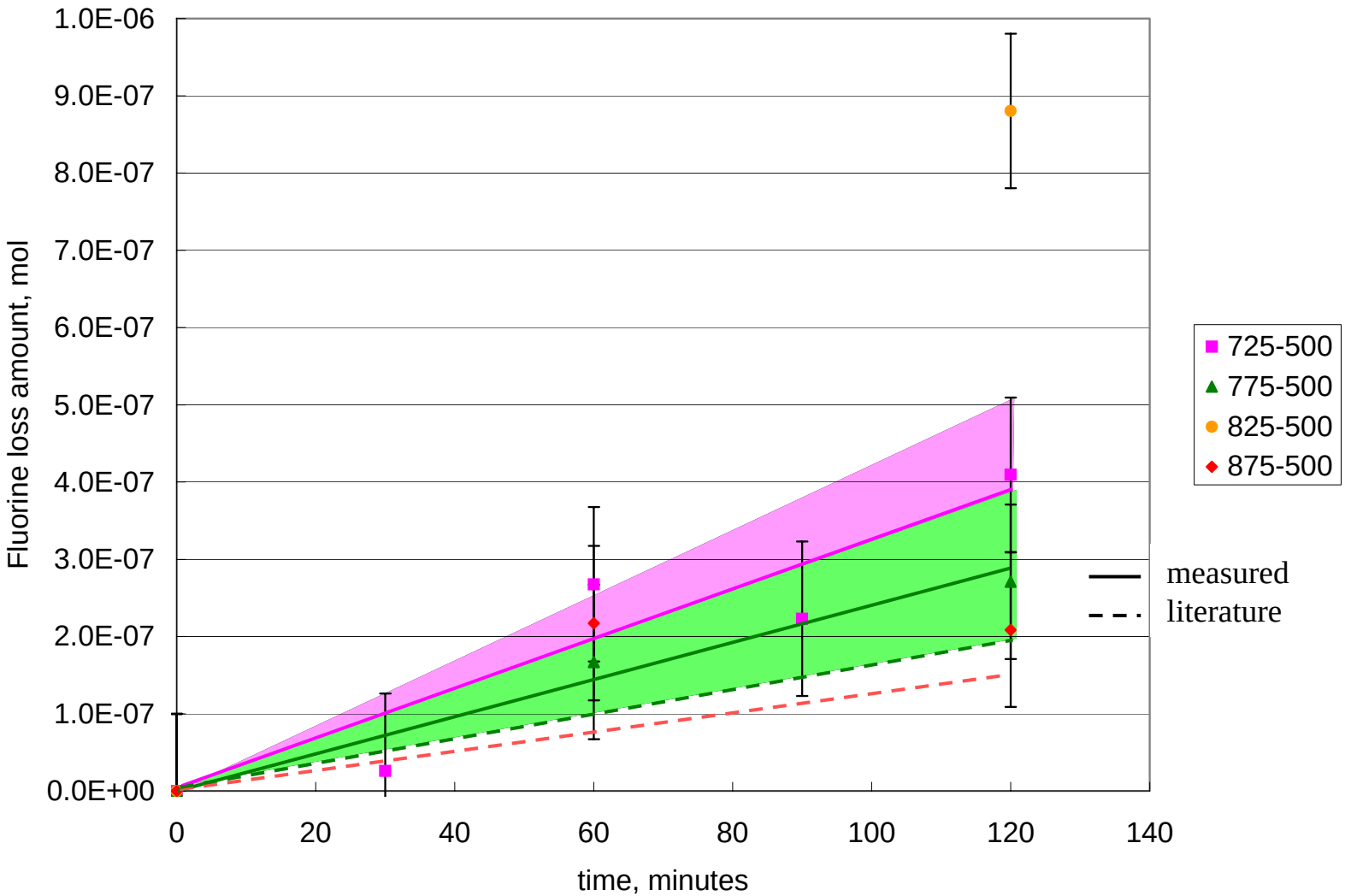
- Proven; formation of YBCO occurs in steps
  - BaF_2-YF_3 solution + CuO + H_2O ⟶ BaF_2 + $Y_2Cu_2O_5$ + HF
  - BaF_2 + H_2O ⟶ BaO + HF
  - BaF_2 + $Y_2Cu_2O_5$ + CuO + H_2O ⟶ YBCO + HF

- Engineering interest on P_{HF}

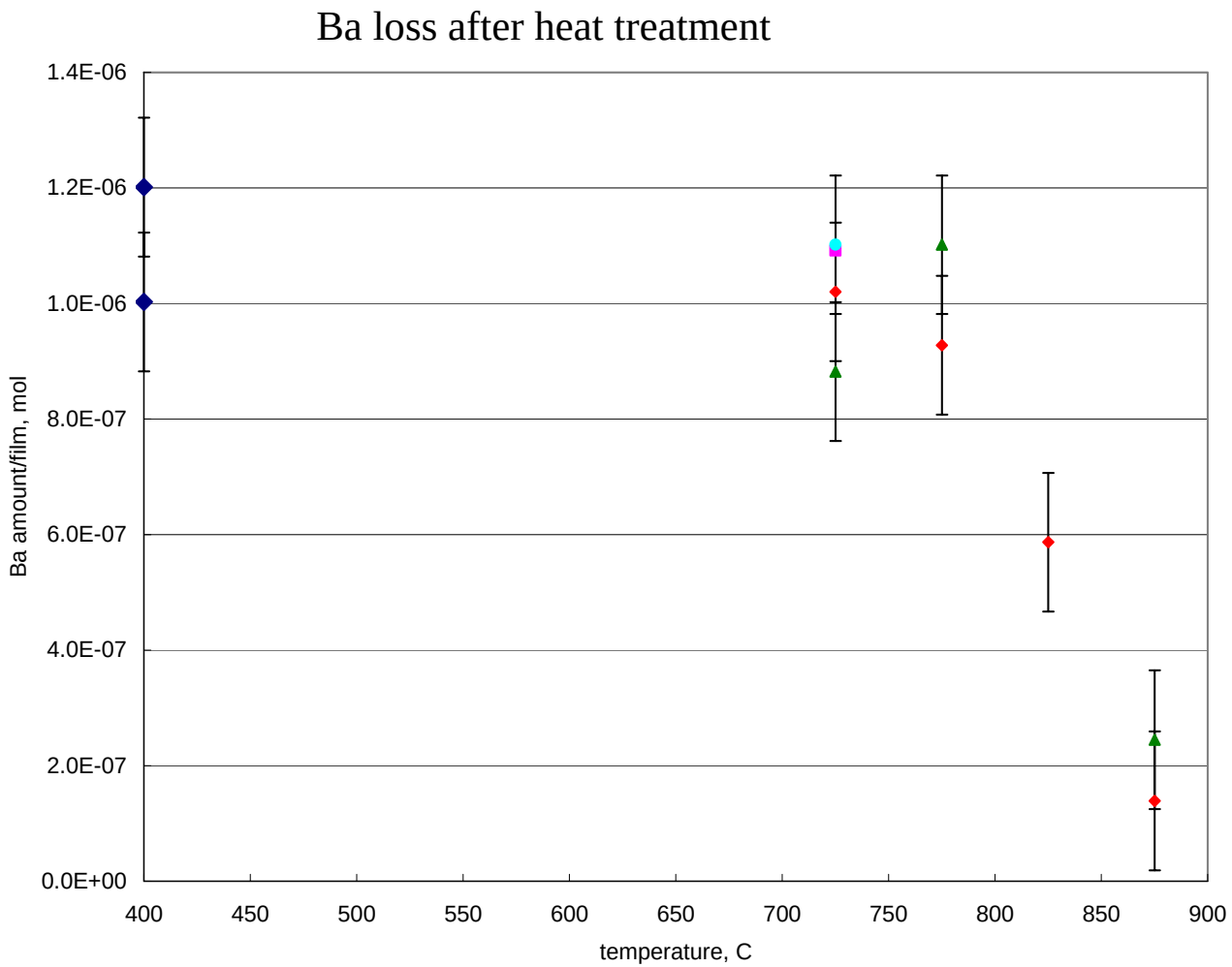


(735C, 1Torr O_2 + 0.3Torr P_{H2O})	This work	Literature
P_{HF}, Torr (Pa)	4.0×10^{-3} (0.525)	1.4×10^{-5} (0.019) - 7.7×10^{-9} (1.0×10^{-6})
Required hot zone length, m	1.5	43 - 7.9×10^{5}

Fluorine loss rate of BaF_2 film



Ba loss of heated BaF_2 film



Ba decreses with heat treatment

Ba may diffuse into substrate

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Short Summary

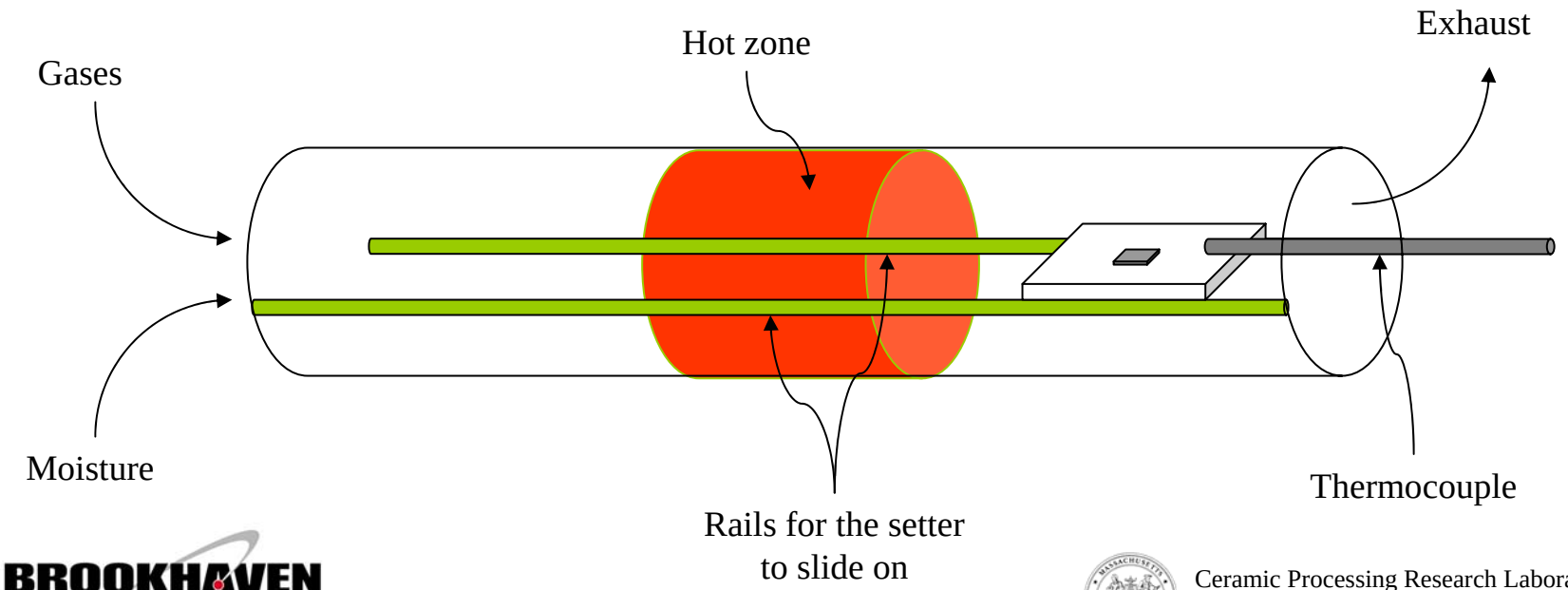
- A technique to measure partial pressure of HF in front of reacting film surface was developed.
- All fluorine in precursor film is in BaF_2 grains as BaF_2-YF_3 solid solution. YF_3 releases fluorine at first and then BaF_2 starts to release.
- Partial pressures of HF at 525, 575 and 625ºC were measured on MOD-YBCO films.
- Experimentally derived ΔG's are substantially different from that calculated from literature values.
- Films containing only BaF_2 show quite low P_{HF} as expected from literature. This and the Ba loss at high temperature make the experiment difficult.

Started FY2005 objectives

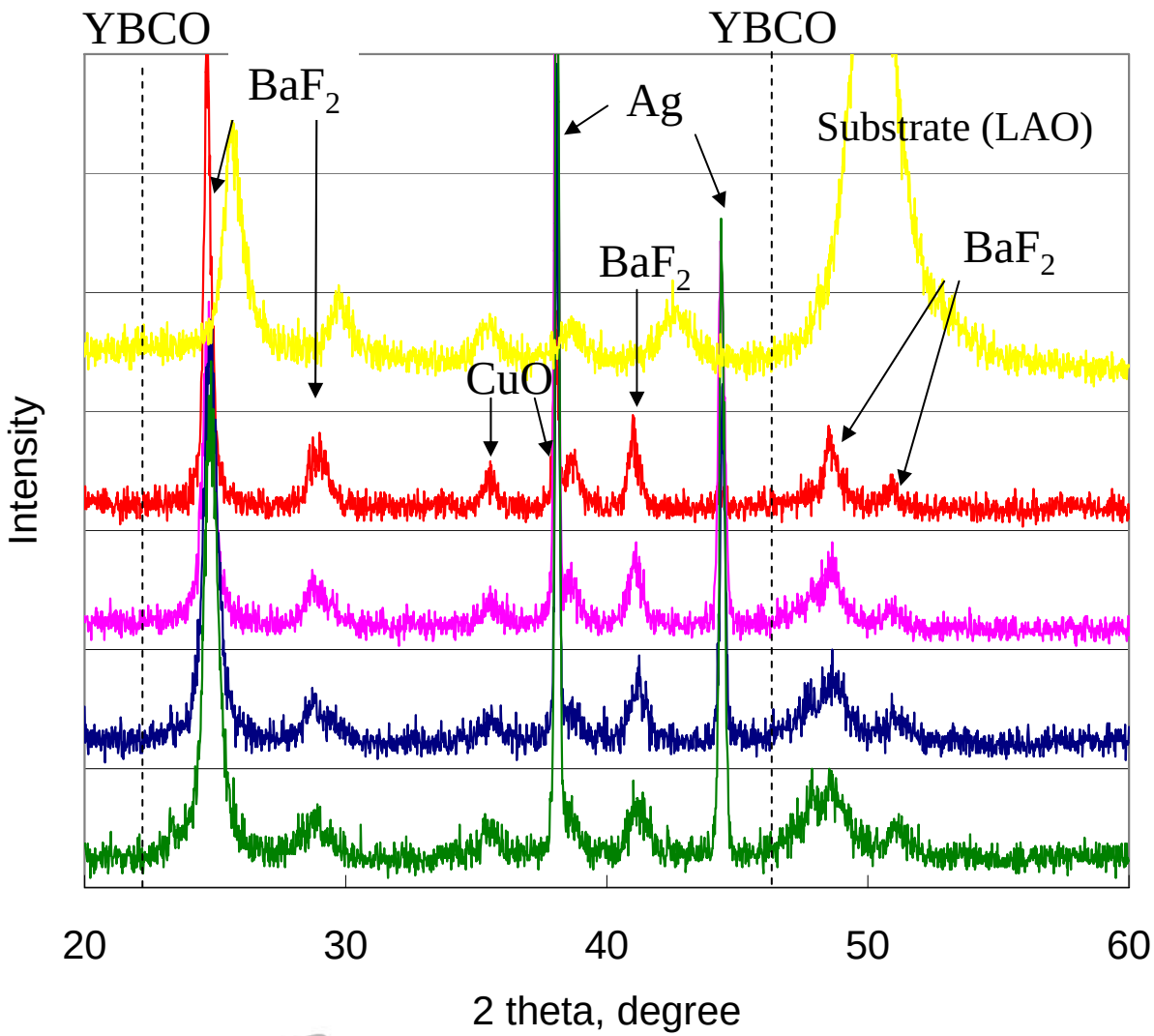
- Knudsen measurement on e-beam films (**FY2005 objective**)
  - ✓ Started. F/Ba trajectory of e-beam film was analyzed. F removal rate was measured and compared with YBCO growth rate.

- Development of reliable procedure for quantifying total $BaCeO_3$ on substrate (**FY2005 objective**)
  - ✓ Started.

- Quench samples to control extent of reaction
  - Specimen with setter is initially as shown in the figure below
  - Setter pushed into hot zone once the desired temperature is reached
    - H_2O on at all times
  - Once sample reaches desired temperature, setter is pushed upstream, to the cold region
    - H_2O turned off just before this step



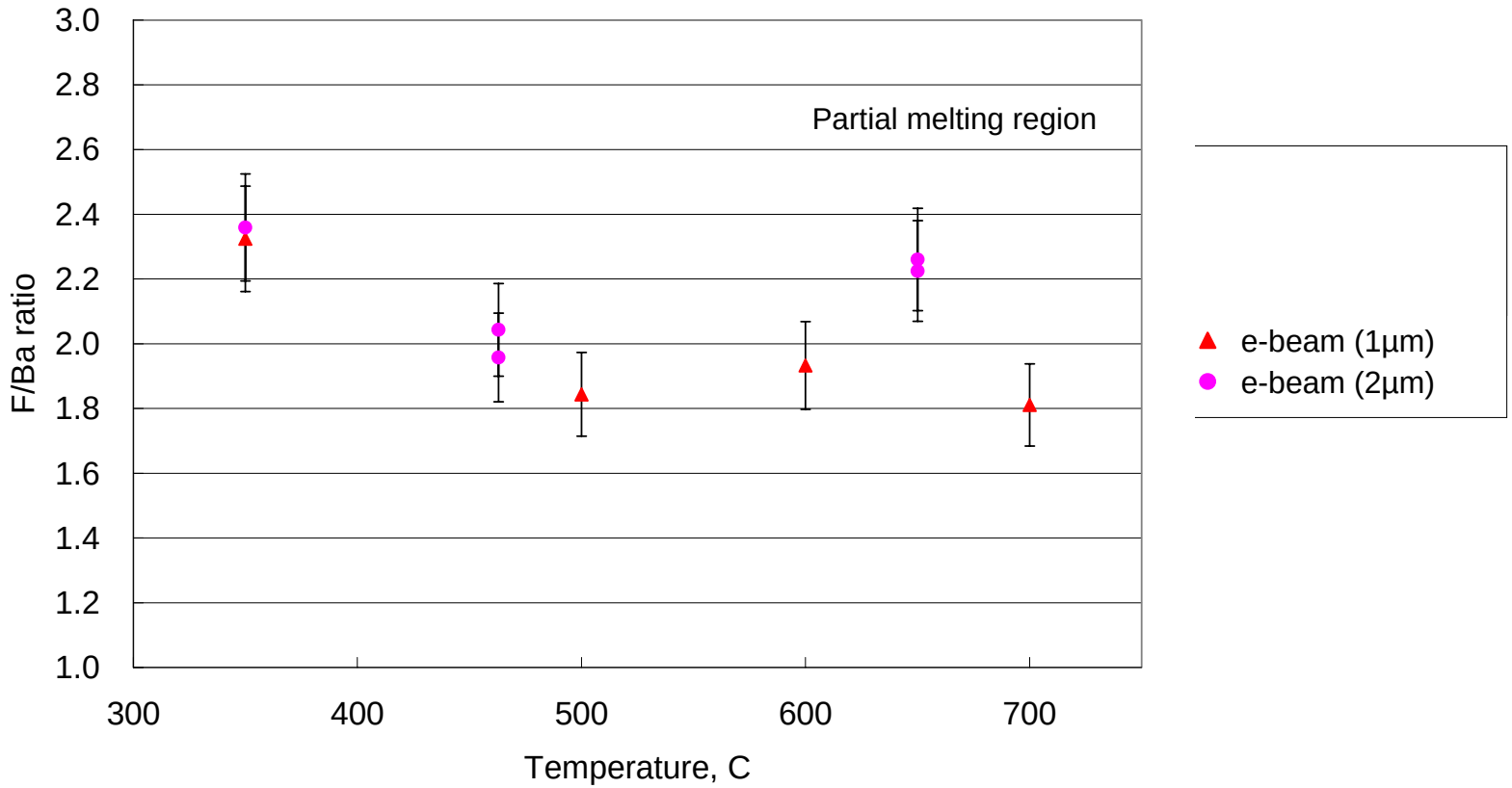
E-beam Derived Films



No peak shift of BaF_2

No YBCO up to 700ºC

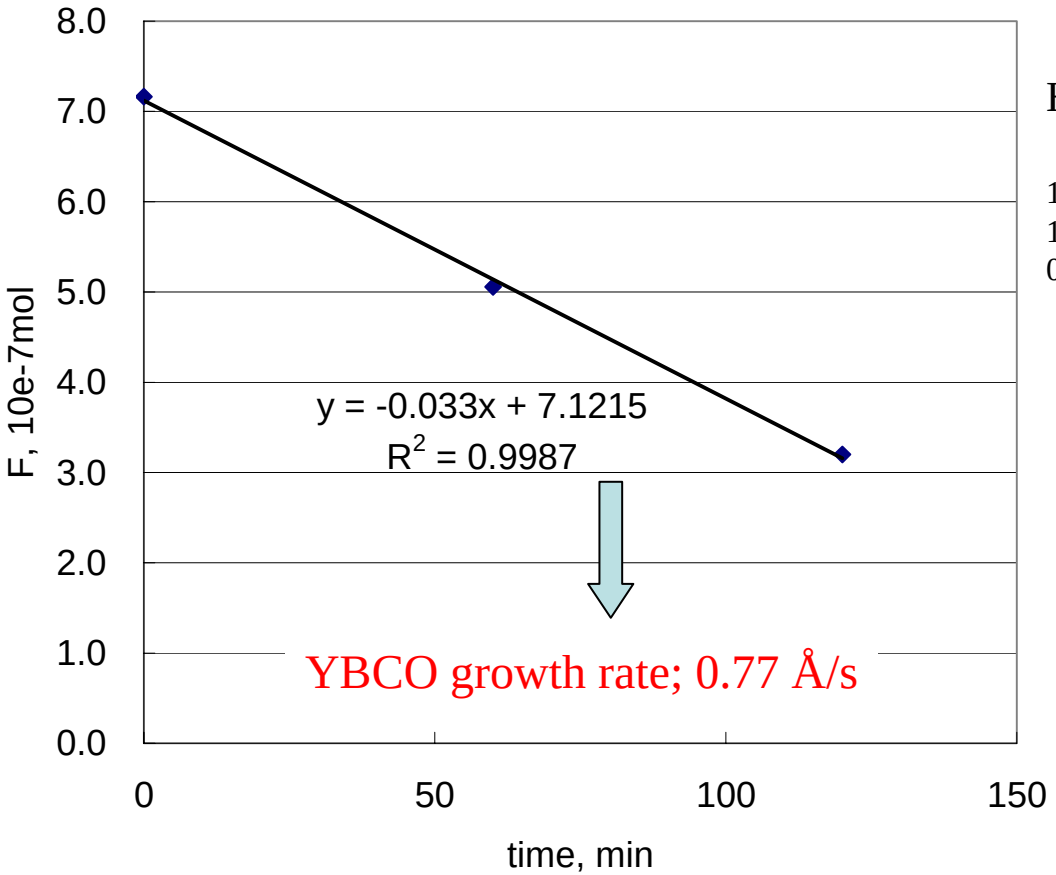
F/Ba Trajectory Comparison



MOD derived films have transient melt during processing
E-beam derived films may have it

Comparison of F removal rate with YBCO growth rate

Fluorine content in e-beam derived YBCO film vs time



Heat treatment

735ºC
100 Torr O_2 + N_2
100%RH
0.2 L/min (gas flow rate)

◆ BNL at 735
— F content

0.7 Å/s BNL measured growth rate (same conditions, measured by conductivity; Solovyov *et. al*. IEEE trans. Appl. Supercond. 1999)

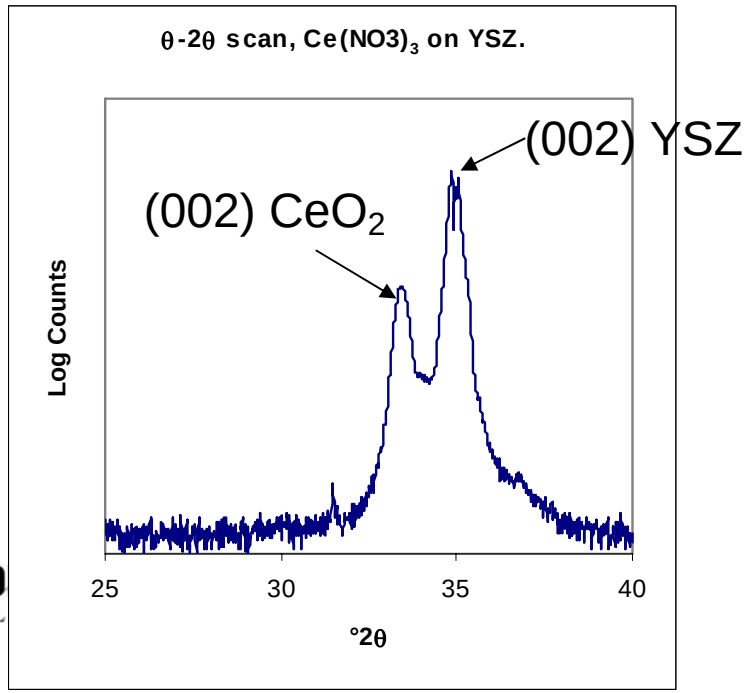
YBCO growth is limited by fluorine removal from a film

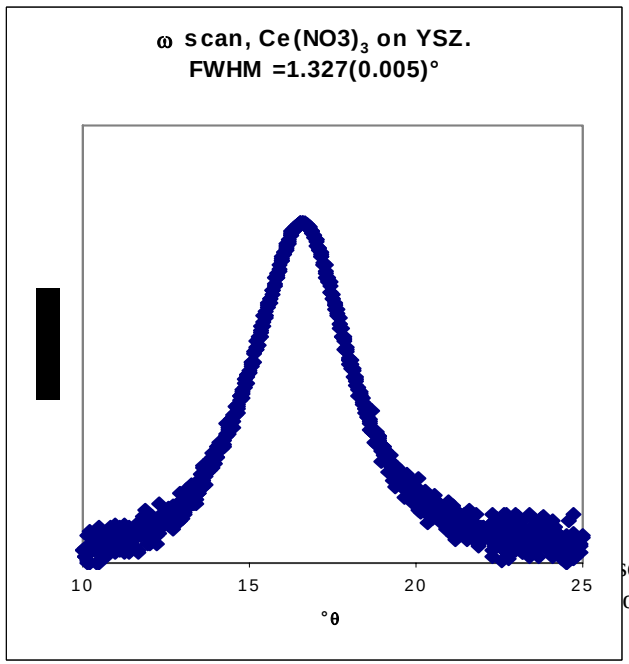
$BaCeO_3$ Quantification

- Problem Definition
  - $BaCeO_3$ forms in CeO_2 cap layer during YBCO conversion
  - All studies to date have examined $BaCeO_3$ using TEM
  - No good measurements of overall film coverage by $BaCeO_3$
  - Unknown J_c response to $BaCeO_3$ formation
- FY 2005 Project Goals
  - Develop reliable procedure for quantifying total $BaCeO_3$ on substrate
  - Relate $BaCeO_3$ to film properties

$BaCeO_3$ Quantification

- Solution Deposition of CeO_2 Cap Layers on YSZ
  - Simple solution: ~0.25M $Ce(NO_3)_2$ in Water
  - 3wt% PVA added to solution to thicken
  - Spin coat YSZ at 4000 RPM, 120s
  - Fast conversion treatment: 5 min at 1100°C in 100% RH 4% H_2/Ar
- Epitaxial CeO_2 forms easily. No Carbonates/Hydroxides
  - Water vapor is necessary to increase pO_2, remove carbon

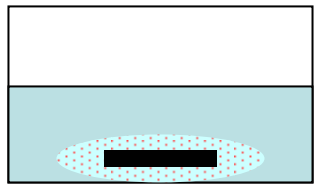




$BaCeO_3$ Quantification

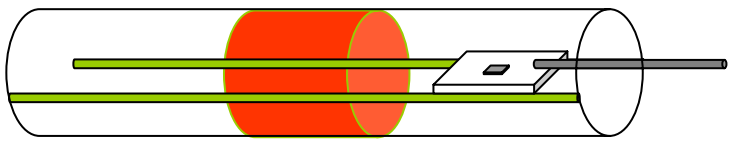
- Technique for Quantifying $BaCeO_3$

Etch



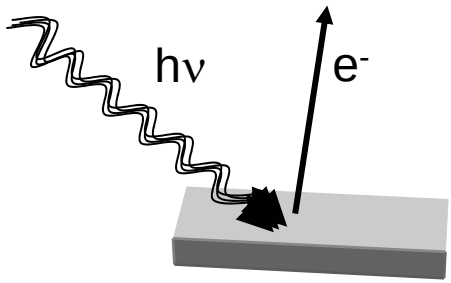
- pH 3 HNO_3 in water
- Removes YBCO, not $BaCeO_3$

React



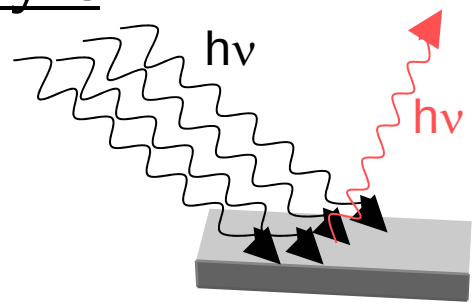
- 1000 ppm O_2 / N_2, 4scfh
- 1 hour annealing
- T_{max}, sample thickness varied

Analyze



XPS

- Small spot size (400-700μm)
- Highly surface sensitive
- Used to check for Ba "islands"



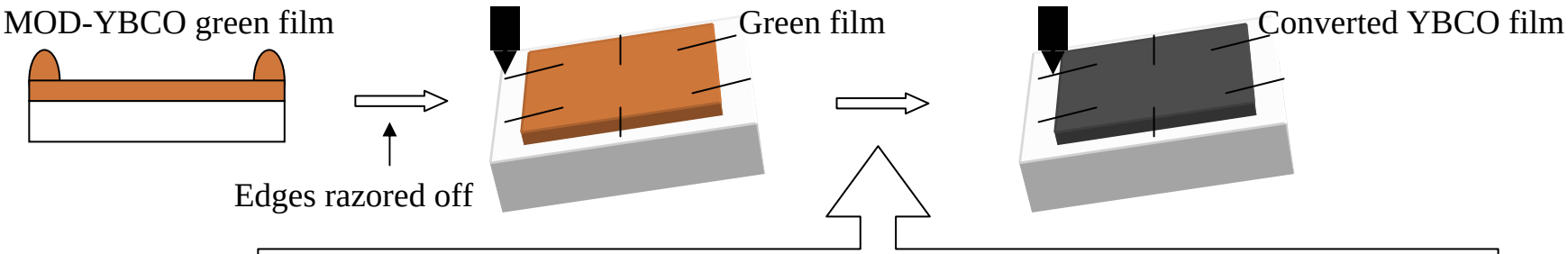
XRF

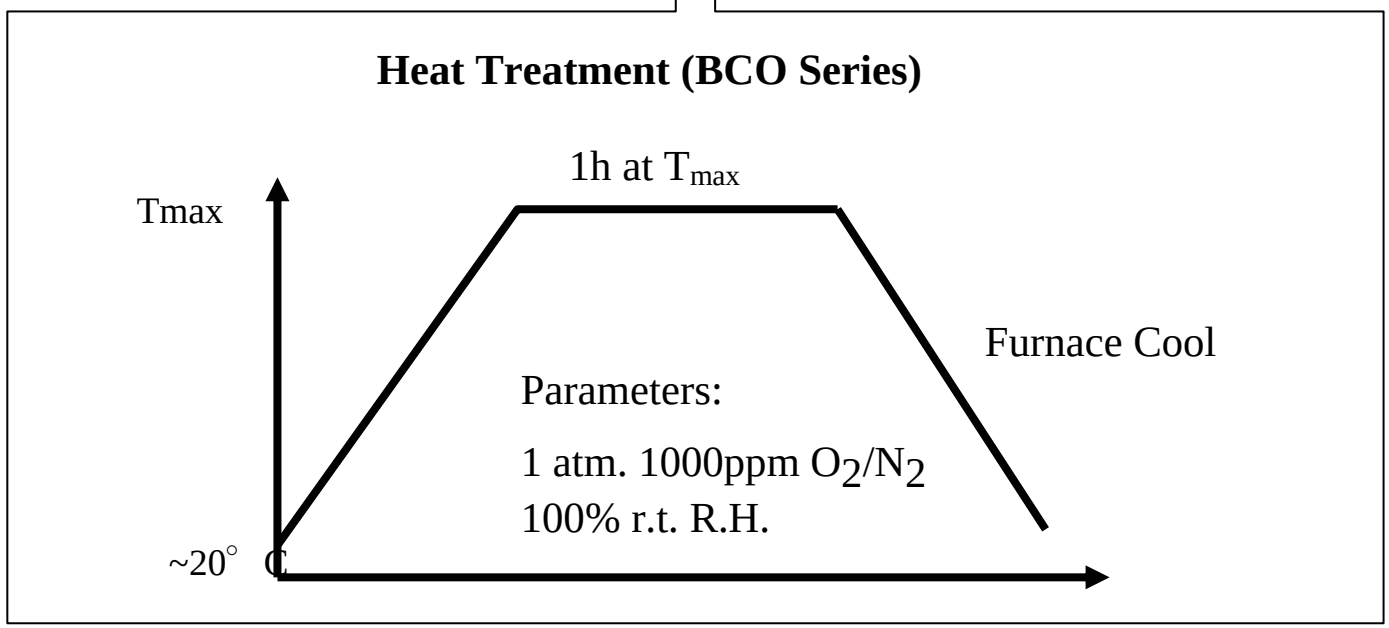
- Large spot size (~5mm)
- Gives surface Ba concentration

Course of reaction via shrinkage measurement

Thickness measurements

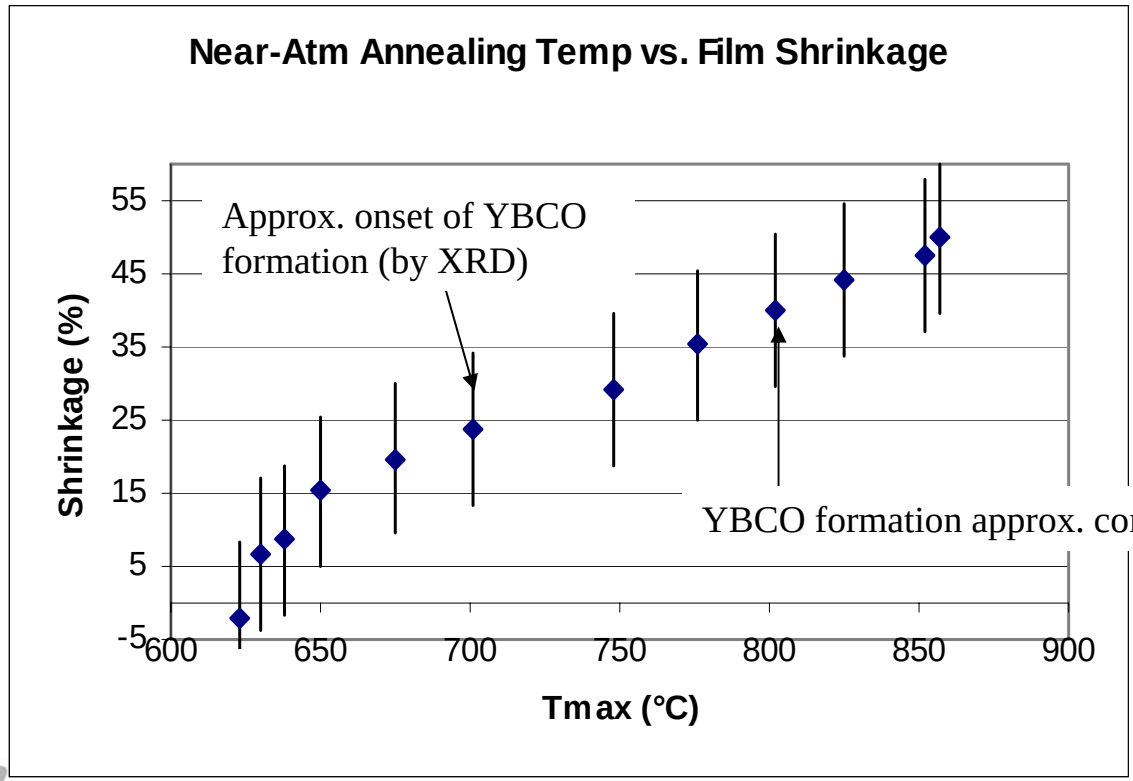
- Tencor P10 Profilometer, 6 step-height scans per sample
- Location of first scan marked on green sample





Course of reaction via shrinkage measurement

- Temperature vs. Shrinkage
  - Very strong trend: density increases with T. Linear above 640°
  - Shrinkage well beyond normal conversion temps
  - Shrinkage begins well before YBCO forms (~700°)



FY2005 objectives

- Knudsen measurement on e-beam derived films
- Trajectory-property relationship
  - MOD derived films
  - E-beam derived films
- Buffer layer
- Degree of reaction